MODERN GLASS CHARACTERIZATION

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CONTENTS

PREFACE
LIST OF CONTRIBUTORS

1 DENSITY, THERMAL PROPERTIES, AND THE GLASS TRANSITION TEMPERATURE OF GLASSES
   Part I: Introduction to Physical Properties and Their Uses
   Part II: Density
      1.1 DENSITY: EXPERIMENTAL BACKGROUND AND THEORY
   Part III: Thermal Effects with a Focus on the Glass Transition Temperature
      1.2 OVERVIEW
      1.3 EXPERIMENTAL METHODS AND THEORY
      1.4 INSTRUMENTATION USED FOR DETERMINING $T_g$ AND RELATED THERMAL EVENTS
      1.5 ANALYSIS OF DATA AND EXTRACTION OF USEFUL INFORMATION
      1.6 CASE STUDIES FROM GLASS SYSTEMS
      1.7 CONCLUSION TO THERMAL PROPERTIES

ACKNOWLEDGMENTS
REFERENCES

2 INFRARED SPECTROSCOPY OF GLASSES
   2.1 INTRODUCTION
   2.2 BACKGROUND AND THEORY
   2.3 INSTRUMENTATION
   2.4 ANALYSIS OF INFRARED DATA
   2.5 CASE STUDIES
   2.6 CONCLUSIONS

ACKNOWLEDGMENTS
REFERENCES

3 RAMAN SPECTROSCOPY OF GLASSES
   3.1 INTRODUCTION
   3.2 BACKGROUND
   3.3 INSTRUMENTATION AND DATA ANALYSIS
   3.4 CASE STUDIES
   3.5 CONCLUSIONS
List of Tables

Chapter 1
   Table 1.1
   Table 1.2
   Table 1.3
   Table 1.4
   Table 1.5

Chapter 2
   Table 2.1

Chapter 4
   Table 4.1

Chapter 5
   Table 5.1
   Table 5.2
   Table 5.3
   Table 5.4
   Table 5.5

Chapter 6
   Table 6.1

Chapter 7
   Table 7.1

Chapter 8
   Table 8.1

Chapter 10
   Table 10.1
   Table 10.2
List of Illustrations

Chapter 1

**Figure 1.1** Schematic of a pycnometer's operation.

**Figure 1.2** A Quantachrome® manual pycnometer.

**Figure 1.3** Molar volumes of the alkali and alkaline-earth borate glass system [5]. R is the molar ratio of metal oxide to boron oxide. The error is smaller than the symbols used.

**Figure 1.4** Molar volumes per mole glass former in the lithium borate, lithium silicate, and lithium germanate glass systems [6]. R is the molar ratio of lithia to silica, germania, or bora.

**Figure 1.5** Packing fractions from a series of alkali and alkaline-earth borate glasses. R is the molar ratio of alkali oxide to boron oxide [8].

**Figure 1.6** The density of alkali and alkaline-earth borates as a function of R, the molar ratio of modifying oxide to boron oxide [5]. The error is smaller than the symbols.

**Figure 1.7** Density of lithium silicate glasses by the sink-float method from Peters et al. [10] and a comparison of literature values compiled by Bansal and Doremus [11]. J is the molar ratio of lithium oxide to silicon dioxide.

**Figure 1.8** The $Q^j$ structural units found in alkali silicate glasses, from left to right they advance from $Q^4$ to $Q^0$ where the superscript denotes the numbers of bridging oxygens per Si. $A^\pm$ represents an alkali ion.

**Figure 1.9** The lever rule for lithium silicate glasses.

**Figure 1.10** Volume per mol silica from a series of lithium silicate glasses, $JLi_2O.SiO_2$. The data are taken from Bansal and Doremus [11]. J is the molar ratio of lithium oxide to silica.

**Figure 1.11** Density of lithium borate glasses as a function of R, the molar ratio of lithium oxide to boron oxide [12]. Also shown in the figure is the fraction, $f_2$, of tetrahedral borons [13].

**Figure 1.12** Volumes per mole $B_2O_3$ of the cesium borate glass system from Kodama [3] The error is less than the symbol size.

**Figure 1.13** The triborate and diborate superstructural groups.

**Figure 1.14** Molar volumes of the alkali borates using Kodama's data as a function of R, the molar ratio of alkali oxide to boron oxide [3].

**Figure 1.15** Stiffness as a function of composition, R [3].

**Figure 1.16** Stiffness as a function of molar volumes for the cesium borate case [3].
Figure 1.17 The DSC head uncovered for sample insertion (from Wikipedia).

Figure 1.18 Representative thermogram from a DSC.

Figure 1.19 A schematic of the operation of a DTA.

Figure 1.20 A TA® modulated DSC.

Figure 1.21 A Netzsch® DTA.

Figure 1.22 A Typical DSC thermogram [17]. It is from a lithium borate glass with $R = 1.5$, where $R$ is the molar ratio of alkali oxide to boron oxide. Note that endothermic/exothermic directions are reversed from what was given earlier in the chapter.

Figure 1.23 The $T_g$s of barium borosilicate glasses of the form $\text{RBaO.B}_2\text{O}_3\cdot\text{KSiO}_2$ [18].

Figure 1.24 The fraction of four-coordinated borons, $N_4$, of barium borosilicate glasses of the form $\text{RBaO.B}_2\text{O}_3\cdot\text{KSiO}_2$ [19].

Figure 1.25 The $T_g$s of calcium borosilicate glasses of the form $\text{RCaO.B}_2\text{O}_3\cdot\text{KSiO}_2$ [18].

Figure 1.26 The $T_g$s of lithium borosilicate glasses of the form $\text{RLiO.B}_2\text{O}_3\cdot\text{KSiO}_2$ [20].

Figure 1.27 (a), Critical cooling rate versus the glass stability parameter $K_{LL}$ for several glasses [GeO2 (G), PbO.SiO2 (PS),Na2O.2SiO2 (NS2), 2MgO.2Al2O3.5SiO2 (M2A2S5), Li2O.2SiO2 (LS2), CaO.MgO.2SiO2 (CMS2),CaO.Al2O3.2SiO2 (CAS2), Li2O.2B2O3 (LB2)]. (b), the same $K_{LL}$ versus composition in the Li2O–B2O3 system [17].

Figure 1.28 (a), Critical cooling rate versus the glass stability parameter $K_2$ for several glasses [GeO2 (G), PbO.SiO2 (PS),Na2O.2SiO2 (NS2), 2MgO.2Al2O3.5SiO2 (M2A2S5), Li2O.2SiO2 (LS2), CaO.MgO.2SiO2 (CMS2),CaO.Al2O3.2SiO2 (CAS2), Li2O.2B2O3 (LB2)]. (b), Glass stability parameter $K_2 = \frac{T_h}{T_m}$ versus composition [17].

Chapter 2

Figure 2.1 Infrared response of a two-Lorentzian-oscillator model; reflectance spectrum $R(\nu)$ (a), real $\epsilon_1(\nu)$ and imaginary $\epsilon_2(\nu)$ part of the dielectric function (b), and real $n(\nu)$ and imaginary $k(\nu)$ part of the refractive index (c). The dielectric function $\epsilon^*(\nu)$ is modeled according to Eq. 2.19 using the parameters: $\nu_1 = 1080 \text{ cm}^{-1}$, $\Gamma_1 = 55 \text{ cm}^{-1}$, $\Delta \epsilon_1 = 0.65$, and $\nu_2 = 460 \text{ cm}^{-1}$, $\Gamma_2 = 40 \text{ cm}^{-1}$, $\Delta \epsilon_2 = 0.90$. The high frequency dielectric constant is $\epsilon_{\infty} = 2.15$.

Figure 2.2 Comparison of the reflectance spectrum $R(\nu)$ (a) with the imaginary part
\[ \varepsilon_2(\nu) \] (b) and the energy-loss function \( \text{Im}(-1/\varepsilon^*(\nu)) \) (c) of the dielectric function \( \varepsilon^*(\nu) \), for the two-Lorentzian-oscillator model used in Figure 2.1.

**Figure 2.3** Optical layout of the Fourier-transform Bruker Vertex 80v spectrometer. Infrared radiation from a mid-infrared (MIR) or far-infrared (FIR) source passes through the variable aperture (APT) to the beam splitter (BMS) of the Michelson-type interferometer and then directed to the sample and detector (D1, D2) compartments. (Reprinted with permission from Bruker Optics)

**Figure 2.4** (a) Interferograms \( F(s) \) (arb. units) measured in specular reflectance at 11° off-normal from a gold mirror (reference) and a polished slab of vitreous \( \text{SiO}_2 \) (sample); (b) Single-beam spectra \( I(\tilde{\nu}) \) (arb. units) obtained by Fourier-transformation of interferograms \( F(s) \) shown in (a); and (c) Reflectance spectrum \( R(\tilde{\nu}) \) of silica glass in the far- and mid-IR range calculated by \( R(\tilde{\nu}) = I(\tilde{\nu})_{\text{sample}} / I(\tilde{\nu})_{\text{reference}} \) (for details see text).

**Figure 2.5** Comparison of results by Kramers–Krönig transformation (KK), Eq. 2.18, and reflectance fitting by classical dispersion theory (fit), Eq. 2.19, employed for the analysis of the infrared reflectance spectrum of glass \( \text{K}_2\text{O}-2\text{B}_2\text{O}_3 \). The experimental reflectance spectrum (solid line) and the best fit spectrum (circles) are shown in (a). The results of KK analysis (full lines) and curve-fitting (circles) for the \( n(\nu) \), \( k(\nu) \), \( \varepsilon_1(\nu) \) and \( \varepsilon_2(\nu) \) spectra are shown in (b), (c), (d), and (e), respectively.

**Figure 2.6** (a) Deconvolution of the \( \alpha(\nu) \) spectrum of glass 0.67\text{CuI}-0.33[\text{Cu}_2\text{MoO}_4-\text{Cu}_2\text{PO}_4] \) (solid black line) into Gaussian component bands according to Eq. 2.41) solid grey lines). The simulated spectrum is shown by open circles. Inset, (b) shows the measured infrared reflectance spectrum (solid line) compared to the best fitting with Eq. 2.19) open circles).

**Figure 2.7** Refractive index \( n(\nu) \) and extinction coefficient \( k(\nu) \) spectra of the bulk glass 0.2\text{AgI}-0.8[\text{Ag}_2\text{O}-2\text{B}_2\text{O}_3] \) obtained by Kramers–Krönig transformation of the measured reflectance spectrum.

**Figure 2.8** Effect of film thickness on the calculated absorbance spectra of free-standing glass films with composition 0.2\text{AgI}-0.8[\text{Ag}_2\text{O}-2\text{B}_2\text{O}_3].

**Figure 2.9** Comparison of infrared absorption coefficient spectra of alkaline-earth borate glasses \( x\text{MO}-(1-x)\text{B}_2\text{O}_3 \) with metal oxide contents \( x = 0.33 \) (a) and \( x = 0.45 \) (b). The spectra were obtained by KK transformation of the measured reflectance spectra.

**Figure 2.10** Relative integrated absorption \( A_1 = A_4 / A_3 \) as a function of metal oxide content in alkaline-earth borate glasses \( x\text{MO}-(1-x)\text{B}_2\text{O}_3 \). Integrated absorptions \( A_2 \) and \( A_3 \) correspond to tetrahedral and triangular borate units, respectively. Lines through data points are drawn to guide the eye.
Figure 2.11 Fraction of four-coordinated boron atoms, $N_4$, as function of MO mole fraction in alkaline-earth borate glasses $x$MO-(1−$x$)B$_2$O$_3$. The $N_4$ values obtained by infrared analysis (IR) are compared to those of NMR spectroscopy [88, 89], neutron diffraction, and molecular dynamics studies [90] and the theoretical curve $N_4 = x/(1−x)$. The $N_4$ curve is obtained when one mole of added MO converts two moles of neutral BØ$_3$ triangular units into two moles of charged borate tetrahedral BØ$_4^-$ (Ø = bridging oxygen atom). Lines through IR data points are drawn to guide the eye.

Figure 2.12 Far-infrared absorption coefficient spectra of glasses 0.45MO-0.55B$_2$O$_3$ (M = Mg, Ca, Sr, Ba), deconvoluted into Gaussian component bands. The experimental spectrum (solid black line) is compared with the simulated spectrum (open circles).

Figure 2.13 Metal ion-site vibration frequencies versus the square root of the inverse metal ion mass $M^{-1/2}$ for glasses $M_2$O-3B$_2$O$_3$ (M = Li, Na, K, Rb and Cs) and 0.45MO-0.55B$_2$O$_3$ (M = Mg, Ca, Sr, and Ba) glasses. Frequencies denoted by $\nu_{M-O(H)}$ (a) and $\nu_{M-O(L)}$ (b) correspond to peak maxima of bands H and L, respectively, and were obtained from fitting the far-infrared spectra (Figure. 2.12). Frequency data for the alkali borate glasses $M_2$O-3B$_2$O$_3$ were obtained from Reference 93. Error bars are of the size of symbols. Lines are least-square fits to the data.

Figure 2.14 Dependence of glass transition temperature, $T_g$, on the effective force constant, $F_{M-O}$, of the metal ion-oxygen (M–O) bond in alkaline-earth and alkali borate glasses of the diborate composition 0.33MO-0.67B$_2$O$_3$ (note that glass with this composition is not formed in the Mg-borate system). Lines are least-square fits to data.

Figure 2.15 Infrared spectra of thin films deposited by sputtering from a Li-borate target with composition Li$_2$O-2B$_2$O$_3$. The spectra of films on Si and Au substrates were measured by transmission, T, and reflection-absorption, R-A, respectively. Comparison is made with the transmittance spectrum of a free-standing Li$_2$O-2B$_2$O$_3$ film of 1 μm thickness, as calculated from the optical response of the Li$_2$O-2B$_2$O$_3$ bulk glass. For details see text.

Figure 2.16 Comparison of infrared experimental and calculated reflection-absorption, R-A, spectra of thin films on Au having nominal composition Li$_2$O-2B$_2$O$_3$. For details see text.

Figure 2.17 Low resolution experimental transmittance spectrum, $T_{\text{exp}}$, of a Li-borate thin film deposited by rf sputtering on Si substrate (0.6 mm) from a Li$_2$O-2B$_2$O$_3$ target. The measured spectrum is compared with spectra calculated using the $n(\nu)$ and $k(\nu)$ infrared responses of bulk glasses $x$Li$_2$O-(1−$x$)B$_2$O$_3$ with $x = 0.33$, 0.275, and 0.25. For details see text.

Chapter 3
Figure 3.1 Mechanisms of normal (spontaneous) Raman scattering: S, Stokes; AS, anti-Stokes. Also in the figure: R, Rayleigh scattering; IR, infrared absorption; \( v = 0 \) or \( 1 \)—quantum number defining the vibrational level. The dashed lines represent the virtual state.

Figure 3.2 Schematic diagram of a micro-Raman spectrometer.

Figure 3.3 (a) Polarized (HH and HV) Raman spectra of the 50 SiO\(_2\)-50 Na\(_2\)O glass composition (50SiNa); (b) depolarization ratio \( (I_{HV}/I_{HH}) \) of the 50SiNa composition.

Figure 3.4 Polarized (HH) Raman spectra of \((100 - x)\)SiO\(_2\) - \(x\) Na\(_2\)O glasses. (a) Raw data; (b) normalized data.

Figure 3.5 Peak-fitting of metasilicate Raman spectrum in the region between 800–1200 cm\(^{-1}\) with: (a) three Gaussian peaks; (b) four Gaussian peaks; (c) four Lorentz peaks, and (d) four Voigt peaks.

Figure 3.6 Polarized (HH) Raman spectra of v-SiO\(_2\) and 80 SiO\(_2\)-20 R\(_2\)O glasses, with R = Li, Na, K. (Reprinted from Reference 33.)

Figure 3.7 Optical micrographs of the initial stages of devitrification of LTCP glass, treated at 760°C for 2 and 3 minutes. (Magnification: 40×).

Figure 3.8 Micro-Raman spectra of LTCP glass in the different regions indicated in Figure 3.7 and (d) after 12 hours of heat treatment at 760°C.

Figure 3.9 Ceramic/LNCP glass interface for both 2 and 5 minutes of heat treatment at 830°C (top); Raman spectra taken in the regions indicated (bottom).

Figure 3.10 Polarized (HH) Raman spectra of \((50 - x)\)GeO\(_2\) - \(x\) SiO\(_2\) - 25 Na\(_2\)O - 25 K\(_2\)O glasses. (Reprinted from Reference 58.)

Figure 3.11 Germanosilicate glass structure, based on Raman spectroscopy data.

Figure 3.12 Raman spectra of the 40GeO\(_2\)-10SiO\(_2\)-25Nb\(_2\)O\(_3\)-25K\(_2\)O glass composition before and after heat treatments, plus the K\(_3.0\)Nb\(_2\)Ge\(_2\)O\(_{20.4}\) crystalline phase.

Figure 3.13 (a) HH and (b) HV polarized Raman spectra of \((100 - x)\)GeS\(_2\) - \(x\) Sb\(_2\)S\(_3\) glasses \((0 \leq x \leq 100)\) and c-Sb\(_2\)S\(_3\) crystallites. The inset of (a) represents the HH and HV spectra of GeS\(_2\) (0% Sb) glass. (Reprinted with permission from Reference 76. Copyright 2012 American Chemical Society.)

Figure 3.14 (a) DSC curves for the \((100 - x)\)GeS\(_2\) - \(x\) Sb\(_2\)S\(_3\) glasses \((0 \leq x \leq 100)\) at a heating rate of 10 K/min. (b) Glass \( T_g \) as a function of the Sb\(_2\)S\(_3\) content. The lines are only guides to the eye.

Figure 3.15 Schematic representation of the IRO structure of \((100 - x)\)GeS\(_2\) - \(x\) Sb\(_2\)S\(_3\)
glasses with different mol% Sb$_2$S$_3$. (Reprinted with permission from Reference 76. Copyright 2012 American Chemical Society.)

Chapter 4

**Figure 4.1** Schematic of how the wavelength and propagation direction of the phonon being probed in the Brillouin scattering process is controlled by the scattering angle. Density changes associated with the phonon are depicted as varying gray scale levels. The momentum vector balance diagram reflects the diffraction condition, which is that the light scattered from equivalent phase points along the sound wave superimposes at a path difference equal to an integral number of wavelengths.

**Figure 4.2** Illustration of the transmission orders across a Fabry–Pérot cavity for different mirror reflectivity. The higher the reflectivity, the better the filtering quality.

**Figure 4.3** Principle of the spectral filtering using a tandem Fabry–Pérot interferometer. Because of the differential in the scanning amplitude between the two cavities, $d_2 = \zeta d_1$, where $\zeta$ is a fractional number close to but not equal to unity, simultaneous transmission through both cavities occurs only when the orders interference are $l = \zeta m$, which given that $l$ and $m$ are integers, increases the free spectral range by a factor $n$, such that $n\zeta$ is an integer. Within that free spectral range all intermediate orders are suppressed and the assignment of Brillouin peaks is unambiguous.

**Figure 4.4** Schematic of the tandem Fabry–Pérot interferometer design by J.R. Sandercock.

**Figure 4.5** Common scattering geometries used for bulk samples: (a) backscattering and (b) 90° scattering. $k_i$ and $k_s$ designate the wavevectors of the incident and scattered light inside the sample, respectively; the additional subscript $e$ designates the light propagation directions external to the sample. $q$ designates the phonon probed.

**Figure 4.6** Platelet scattering geometry used for studying layered structures with parallel surfaces or thin films: (a) light enters and exits on opposite sides of the sample at an angle that is bisected by the film plane; phonons probed propagate in the film plane. (b) if the transmitted beam is collimated and reflected on itself, a second peak appears in the Brillouin spectrum in addition to the one discussed for (a), which corresponds to phonons that propagate perpendicular to the film plane. (c) when the film is supported on a reflective substrate, light entering from the free surface gives rise to backscattering, while the light reflected from the substrate gives rise to platelet geometry scattering, similar to the case depicted in (a). For thin films, this geometry also produces two peaks in the Brillouin spectrum, one probing phonons propagating nearly perpendicular to and the other one propagating parallel to the film plane. $k_i$ and $k_s$ designate the wavevectors of the incident and scattered light inside the sample, respectively; the additional subscript $e$ designates the light propagation directions external to the sample. $q$ designates the phonon probed.
**Figure 4.7** Typical Brillouin scattering spectrum from a molten alkali borate system. Circles represent the experimental data, and the lines represent the best fits of these data using Eq. 4.22. The contributions from the different terms of Eq. 4.22 are shown as labeled in the legend.

**Figure 4.8** Schematic showing the viscosity attributed to a single relaxation mechanism as a function of temperature according to Eq. 4.40, probed at different frequencies. Inset: comparison of the viscosity of a polyolefin standard as determined by Brillouin scattering at $\sim 10^{10}$ Hz (squares) and rotating cylinder viscometry at 0 Hz (circles).

**Figure 4.9** Typical Brillouin scattering spectrum of fused silica: triangles are measured in the HV polarization directions, resolving the shear peaks, and circles are measure using the VV directions, resolving the longitudinal peaks.

**Figure 4.10** Elastic longitudinal ($M'$), Young's (E), bulk (K), and shear ($G'$) moduli of a tempered borosilicate glass plate as a function of the distance from the surface. The decrease of the moduli near the surface reflect the compressive state of the glass.

**Figure 4.11** Longitudinal elastic moduli of sodium borate glasses and melts as a function of the Na$_2$O concentration. Small open circles represent data measured using ultrasound propagation at room temperature, solid circles and solid squares represent data measured using Brillouin scattering at room temperature and 1000°C, respectively.

**Figure 4.12** Longitudinal and shear elastic moduli of three major glass formers, SiO$_2$, GeO$_2$, and B$_2$O$_3$, measured as a function of temperature using Brillouin scattering. Note the anomalous increase in stiffness with temperature for all three compounds. Also note the abrupt change in slope for GeO$_2$ and B$_2$O$_3$ at their glass transition temperature.

**Figure 4.13** Longitudinal elastic moduli of (a) potassium silicates; (b) potassium germates; and (c) sodium borates, as a function of temperature and for various alkali oxide concentrations, measured using Brillouin scattering. Discontinuities in slope indicate the glass transition temperature.

**Figure 4.14** (a) Specific loss modulus for B$_2$O$_3$ as a function of the temperature, revealing three energy-dissipating mechanisms: the dissolution of boroxol rings, the network disintegration, and the diffusion of impurities; (b) comparison of the viscosity of B$_2$O$_3$ measured using rotating cylinder viscometry and Brillouin light scattering, the latter being converted to zero-frequency quantities (contributions of all three dissipation are shown as lines, but the overall viscosity is dominated by network disintegration); (c) superposition of bulk, shear, and longitudinal viscosities of B$_2$O$_3$ measured using Brillouin scattering; (d) real and imaginary components of the Poisson ratio as a function of temperature. Note the positive values of Im($\nu^*$) in the temperature range in which the bulk viscosity dominates.

**Figure 4.15** Storage and loss moduli of (a) 38Na$_2$O·62B$_2$O$_3$ and (b) 20K$_2$O·80TeO$_2$ as a function of temperature. Symbols represent the data measured using Brillouin
scattering and the lines represent best fits of Eq. 4.54. Note that the borate system exhibits two relaxation mechanisms, whereas the tellurite system has only one. The areas shaded in color represent the energy stored and dissipated in respective mechanisms. Underlying to the storage modulus is the change in static modulus due to structural changes associated with the glass transition.

**Figure 4.16** Longitudinal elastic moduli of layer-by-layer deposited polymer-cellulose nanofiber thin-film composite, as a function of the cellulose fiber volume fraction. $c_{11}$ refers to the in-plane and $c_{33}$ to the out-of-plane modulus.

**Figure 4.17** Schematic of a diamond anvil pressure cell and the laser beam pass through it.

**Figure 4.18** Longitudinal sound velocity of B$_2$O$_3$ glass as a function of pressure, measured using Brillouin scattering. Filled symbols represent data upon compression and open symbols upon decompression. Data for different maximum pressures are shown. While the change in sound velocity is continuous upon compression, all decompression data exhibit a discontinuity at around 3 GPa, regardless of the maximum pressure reached during the compression-decompression cycle.

**Figure 4.19** Longitudinal storage and loss moduli of two silica hydrogels, one aged and not the other before they were dried, as a function of the silica volume fraction.

**Figure 4.20** Longitudinal, shear, Young's, and bulk moduli, as well as the Poisson ratio of an epoxy system as a function of time while it was curing, measured using in situ Brillouin scattering.

**Chapter 5**

**Figure 5.1** The geometry for a neutron diffraction experiment.

**Figure 5.2** The neutron flux distribution for three different moderators at the ILL reactor (left-hand scale) and for the liquid methane moderator at the ISIS accelerator (right-hand scale).

**Figure 5.3** Schematic of a neutron diffractometer for a continuous source.

**Figure 5.4** The D4c liquids and amorphous diffractometer at the Institut Laue Langevin [1].

**Figure 5.5** Schematic of a time-of-flight neutron diffractometer for a pulsed source.

**Figure 5.6** The GEneral Materials diffractometer, GEM, at the ISIS Facility [2].

**Figure 5.7** The scattering geometry for a single atom, $j$, at a position $R_j$ relative to an arbitrary origin $O$. For the wave scattered from the atom, there is a path length difference $\Delta_i - \Delta_f = R_j (\hat{k}_i - \hat{k}_f)$ relative to the origin.

**Figure 5.8** The lower $Q$ region of the corrected differential cross-section, $I^N(Q)$, for liquid CCl$_4$, showing how it can be separated into either self and distinct contributions.
or into coherent and incoherent contributions.

**Figure 5.9** The bound atom coherent neutron scattering length of the natural elements (and deuterium) as a function of atomic number [32]. Elements with a negative scattering length (and deuterium) are indicated by the element symbol.

**Figure 5.10** Key stages in the analysis of (corrected and normalized) neutron diffraction data from a glass: subtraction of self scattering, Fourier transformation, addition of \( T^0(r) \).

**Figure 5.11** The differential cross-section of \( \text{B}_2\text{O}_3 \) glass, \( I^N(Q) \) (corrected and normalized), measured on the D4 diffractometer, together with the calculated self scattering [12].

**Figure 5.12** (a) The calculated self scattering, \( I^S(Q) \), for \( \text{B}_2\text{O}_3 \) glass on the GEM diffractometer. (b) The (corrected and normalized) differential cross-section of \( \text{B}_2\text{O}_3 \) glass, \( I^N(Q) \), measured on the GEM diffractometer (continuous line), together with the calculated self scattering (dashed line) [13]. The curves for the different detector banks are shown with vertical offsets for clarity.

**Figure 5.13** The distinct scattering, \( i^N(Q) \), for \( \text{SiO}_2 \) glass (dashed line), together with a Debye equation simulation for an ideal \( \text{SiO}_4 \) tetrahedron with realistic thermal displacement factors (continuous line). The Si–O and O–O contributions to the simulation are shown (together with the experimental result shown again as a dashed line) with vertical offsets. The inset shows the corresponding correlation function, \( T^N(r) \), for the simulation, and a \( \text{SiO}_4 \) tetrahedron.

**Figure 5.14** The neutron correlation function, \( T^N(r) \), for \( \text{B}_2\text{O}_3 \) glass [13], together with a fragment of a two-dimensional \( \text{B}_2\text{O}_3 \)-like network, showing how the peaks in the correlation function arise from the interatomic distances.

**Figure 5.15** Neutron correlation functions for \( \text{GeO}_2 \) glass [16]: (a) the total correlation function, \( T^N(r) \); (b) the differential correlation function, \( D^N(r) \); (c) the pair correlation function, \( g^N(r) \); and (d) the radial distribution function \( n^N(r) \). In each case the experimental result is shown as a continuous line, whilst the relevant average density term is shown as a dashed line.

**Figure 5.16** The distinct scattering, \( i^N(Q) \) (left-hand side), and the neutron correlation function, \( T^N(r) \) (right-hand side), for liquid carbon tetrachloride, \( \text{GeO}_2 \) glass, and \( \text{GeO}_2 \) in its quartz crystalline form [16].

**Figure 5.17** Time-of-flight spectra for (a) vanadium; (b) polycrystalline silicon; and (c) \( \text{GeO}_2 \) glass. Also shown are the normalized spectra for (d) polycrystalline silicon and (e) \( \text{GeO}_2 \) glass.
**Figure 5.18** Neutron diffraction results for 2CaO·Na₂O·3P₂O₅ glass [2, 42]. (a) The distinct scattering, ²N(Q), with the high Q region shown in an inset. (b) The step and Lorch modification functions [37] for Q_{max} = 55 Å⁻¹. (c) The total neutron correlation function, T²N(r), obtained using the two modification functions shown in part (b) with the first peak region shown in an inset.

**Figure 5.19** Simulation of the total neutron correlation function, T²N(r) (as obtained using the Lorch modification function [37]), for an ideal GeO₄ tetrahedron, showing the effect of maximum momentum transfer, Q_{max}, on real-space resolution and termination ripples. (a) Q_{max} = 24 Å⁻¹, (b) Q_{max} = 40 Å⁻¹.

**Figure 5.20** The first peak region of the total neutron correlation function, T²N(r), for (a) GeO₂ glass [16] (thick grey line is experiment, thin black line is fit, dashed line is residual); (b) 18Cs₂O·88GeO₂ glass [16]; and (c) 2CaO·Na₂O·3P₂O₅ glass (thick grey line is experiment, thin line is fit, dashed line is fitted P-NBO component, dotted line is fitted P-BO component, dot-dashed line is residual (offset)) [2, 42].

**Figure 5.21** The low r region of the correlation function for crystalline Y₂O₃, showing (a) D_{meas}(r) prior to renormalization (thick grey line), together with −T⁰₁(r) (dashed line) and a fit to the first peak in D_{meas}(r) (thin black line) and (b) T²N(r) after renormalization (thick grey line), together with a simulation (thin black line).

**Figure 5.22** (a) The predicted distinct scattering for an isolated sphere of radius 20 Å, with I₀ = 1000. The inset shows a Guinier plot of the prediction, together with the corresponding Guinier approximation. (b) The measured nuclear SANS for amorphous Dy₇Ni₃. The inset shows a Porod plot of the experimental data, together with a Porod fit to the data.

**Figure 5.23** The (corrected and normalized) differential cross-section of 10K₂O·90TeO₂ glass, ²N(Q), measured on the former LAD diffractometer [65]. The curves for the different detector banks are shown with vertical offsets for clarity.

**Figure 5.24** (a) The differential cross-section measured by Bank5 (93°) of the GEM diffractometer [2] for amorphous zeolite precursor LTA₅ [68], together with a smooth cubic spline fit. (b) The estimate of the distinct scattering which is obtained from a difference of the two curves in (a).

**Figure 5.25** The distinct scattering, ²N(Q), for a tin borate glass sample with nominal composition 70SnO·30B₂O₃ before and after removal of Bragg peaks (see text) [13]. Also shown is a simulation of the diffraction pattern for crystalline SnO₂ and vertical tick marks indicate the positions of the Bragg peaks.

**Figure 5.26** The differential cross-section, ²N(Q), of amorphous Dy₇Ni₃ for three different isotopic compositions (superscripts Nat and 0 indicate the natural isotopic
composition and the null isotopic composition), shown as a continuous line [58]. The dashed line indicates the sum of the magnetic scattering, $I^M(Q)$, and the calculated nuclear self scattering, $I^S(Q)$, for each sample.

**Figure 5.27** The three measured partial correlation functions for amorphous Dy$_7$Ni$_3$ [58], together with the partial correlation functions for a Percus–Yevick calculation of the partial correlation functions for a binary hard sphere liquid. The inset in the figure shows how a similar Ni–Ni distance arises in crystalline Dy$_7$Ni$_3$ [79] (large, translucent spheres are Dy, smaller, solid spheres are Ni).

**Figure 5.28** The differential cross-section for 24.6Tb$_2$O$_3$·72.2P$_2$O$_5$·3.2Al$_2$O$_3$ glass at 4 K, showing (a) the diffraction pattern with and without the application of the 4 T magnetic field; and (b) the field-on minus field-off difference, $\Delta I^N(Q)$. [90].

**Figure 5.29** The differential correlation functions for 24.6Tb$_2$O$_3$·72.2P$_2$O$_5$·3.2Al$_2$O$_3$ glass at 4 K [90], showing (a) the differential correlation function with and without the application of the 4 T magnetic field; (b) the field-on minus field-off difference, $\Delta D^N(r)$ (together with the simulation of the contribution from the first two distances described in the text); and (c) a reverse Monte Carlo simulation of the partial Er–Er differential correlation function for erbium metaphosphate glass [91] (together with an arbitrary scaling of $\Delta D^N(r)$).

**Figure 5.30** The measured distinct scattering (thick grey lines), $i^N(Q)$, for anhydrous PdO (vertically offset) and for hydrous PdO [100]. Also shown (thin black line) is a simulation of $i^N(Q)$ for a spherical particle of PdO of diameter 18 Å (inset) embedded in a homogenous medium.

**Figure 5.31** The measured differential neutron correlation function (thick grey lines), $D^N(r)$, for anhydrous PdO (vertically offset) and for hydrous PdO [100]. Also shown are simulated (see text) differential neutron correlation functions (thin black lines).

**Figure 5.32** Important examples of coordination polyhedra for glasses. (a) AX$_3$ triangle; (b) AX$_3$ trigonal pyramid; (c) AX$_4$ tetrahedron; (d) AX$_4$ disphenoid; (e) AX$_5$ trigonal bipyramid; (f) AX$_5$ square pyramid-based unit; (g) AX$_6$ octahedron; (h) AX$_6$ trigonal prism; (i) AX$_{10}$ Archimedean antiprism; (j) AX$_{12}$ icosahedron.

**Figure 5.33** The total neutron correlation function, $T^N(r)$, of crystalline U$_4$O$_9$. (a) The experimental correlation function, $T^\text{exp}(r)$, compared with the U–O and U–U contributions, $T^\text{Contrib}(r)$, as determined by EXAFS [163]. (b) The experimental correlation function, compared with the total neutron correlation function, $T^\text{XTAL}(r)$, simulated from the crystallographically determined structure of U$_4$O$_9$ [160]. (c) The experimental correlation function, compared with the partial components of $T^\text{XTAL}(r)$ [160].


**Figure 6.1** Zachariasen–Wright [4] network model of a glass in which the structure is “random” within the steric packing constraints of the local units. The dashed lines of periodicity $Q_1$ arise from correlations between rings, which comprise the glassy network. $Q_2$ represents the length scale of the bulk connectivity of the network. The black circles represent the modifier atoms which break up the connectivity of the network, often in clusters for oxide glasses [5], and the shaded regions represent different ring sizes.

**Figure 6.2** Shows three ranges of order, from the local short range unit, to the packing of adjacent tetrahedra and associated torsion angles, to the intermediate range structures over longer distances (see text).

**Figure 6.3** The free atom form factors for the elements H, O, Ge and Pb normalized to their number of electrons at $Q = 0$ [18]. The insert shows a zoomed in region of the atomic form factor for H using the independent atom approximation (solid line) compared to the modified atomic form factor for H obtained using Eq. 6.2 with $z_\alpha = 0.5$ corresponding to the electron residing halfway along the bond and $\delta = 2.0$ obtained from fitting to the quantum mechanical calculations of Wang et al. for $H_2O$ [19].

**Figure 6.4** Measured X-ray intensity for GeSe$_2$ glass normalized to the sum of the constituent atomic form factors squared plus the Compton scattering (dashed line) at high $Q$. The insert shows the normalization in the high-$Q$ region.

**Figure 6.5** The measured X-ray structure factor for GeSe$_2$ glass, multiplied by $Q$, to illustrate the extent of the oscillations at high momentum transfers.

**Figure 6.6** Different representations of the X-ray pair distribution function for GeSe$_2$ glass: $G_X(r)$ oscillating about unity at high $r$ and zero at low $r$, $T_X(r)$ oscillating about zero at low $r$ and $4\pi pr$ at high $r$, $D_X(r)$ oscillating about $-4\pi pr$ at low $r$ and zero at high $r$, and $N_X(r)$ oscillating about zero at low $r$ and $4\pi pr^2$ at high $r$.

**Figure 6.7** Photon scattering cross-sections for SiO$_2$ as a function of incident energy [34]. The photoelectric absorption cross-section (dash-dot line) dominates for energies below ~50 keV, above which the incoherent Compton scattering dominates (dotted line). The K-edge absorption from Si occurs at 0.14 keV.

**Figure 6.8** $Q$-dependent X-ray weighting factors for the three partial structure factors of glassy SiO$_2$ [18].

**Figure 6.9** Bragg–Brentano reflection geometry (top) versus high energy transmission (direct) geometry [13,16].

**Figure 6.10** Weighted X-ray structure factors, $Q[S_X(Q)−1]$, for two diffraction experiments on glassy $P_2O_5$ made with Ag $K\alpha$ X-rays $\lambda = 0.561$ Å (open symbols) and
X-ray synchrotron radiation $\lambda = 0.088 \text{ Å (filed circles).}$ Digitized from Hoppe et al. [51]).

**Figure 6.11** The X-ray structure factor for glassy SiO$_2$ measured at the Advanced Photon Source synchrotron (circles). The line represents a fit to the first three peaks in $G_X(r)$, Si–O, O–O and Si–Si using Eq. 6.12 with the parameters in Table 6.1.

**Figure 6.12** The X-ray and neutron pair distribution functions are shown for glassy SiO$_2$ (lines). Also shown is the fit to the first three peaks in $G_X(r)$ corresponding to, Si–O, O–O, and Si–Si, respectively, obtained using Eq. 6.12 with the parameters in Table 6.1 (circles). Inset shows a comparison of the direct and Lorch Fourier transforms of the fit to the Si-O peak.

**Figure 6.13** The Si–O–Si bond angle ($\beta$) determined from combined high-energy X-ray and neutron data by Neufefind and Liss [53] (solid line) compared to that from the early X-ray data of Mozzi and Warren [54] (circles).

**Figure 6.14** The X-ray pair distribution functions for glassy and liquid SiO$_2$ obtained from experiment (circles), compared to classical MD simulations (dashed line) [56] and *ab initio* MD simulations (solid line) [45].

**Figure 6.15** The measured partial distribution functions Si–Si, Si–O and O–O obtained with a combination of X-ray diffraction and neutron diffraction data (circles) [52] compared to the results of an earlier RMC simulation of Kohara et al. (line) [57].

**Figure 6.16** The partial pair distribution functions $T_{ij}(r)$ for glassy SiO$_2$ corresponding to the measured circles in Figure 6.15 shown together with schematics of the atom–atom interactions within the bulk structure of the glass.

**Figure 6.17** The ring size distribution for SiO$_2$ glass calculated from the RMC model of Kohara et al. (white bars) [58] and the classical MD simulation by Rino et al. (black bars) [58].

**Figure 6.18** The behavior of the height of the first sharp diffraction peak (FSDP) versus concentration of network forming cations, for a series of selenium binary glasses, Bychkov et al. [64].

**Figure 6.19** The low $Q$ dependence of the X-ray structure factor of glassy GeSe$_2$ as a function of increasing pressure [66].

**Figure 6.20** The energy dependence of the X-ray form factor for lead. The inset highlights the small absorption edge at 88 keV. (Taken from [78]).

**Chapter 7**

**Figure 7.1** XAFS origins from the electronic transitions excited by X-ray photons from core levels to unoccupied levels just below of the conduction band (excitation) or to the continuum of free states (ionization).
**Figure 7.2** K-edges of As and Se in As$_2$Se$_3$. The XANES and EXAFS regions are indicated at the Se K-edge.

**Figure 7.3** Schematic synchrotron beamline for XAFS measurements.

**Figure 7.4** XAFS detection modes.

**Figure 7.5** Apparatus for transmission XAFS experiments. The beam intensities $I_0$ and $I$, measured by ionization chambers, are enough for recording the XAFS spectra; sometimes a third chamber is used to accurately calibrate the energy scale by recording the XAFS spectrum of a standard such as, for instance, a metal foil. The X-ray beam crosses the chambers through thin low absorbing windows. The electrodes collecting the electrons and ions generated by the ionization of the gas contained in the ion chambers are shown in figure. The measured currents are proportional to X-ray fluxes crossing the chambers.

**Figure 7.6** Energy Dispersive XAFS. Sub-second data collection set-up. The optical elements are static. It is usable only in transmission mode; energy range and resolution are more limited than scanning techniques.

**Figure 7.7** Schematic set-up of a fluorescence detection mode: $I_0$ is the X-ray beam intensity impinging onto the sample and $I_F$ the X-ray fluorescence intensity emitted from the selected atomic species of interest. A metallic filter and a Soller slit absorbs the unwanted radiation. Often the incoming X-ray flux is monitored by collecting the total electron yield $I_0$ excited by the X-ray beam in a polyethylene foil covered by a metallic thin film.

**Figure 7.8** (a) Single scattering of the photoelectron wave outgoing from the absorbing atoms, $A$, from parts of it back-scattered from the neighboring atoms, $B$. (b) Some possible multiple scattering paths followed by the photoelectron.

**Figure 7.9** XAFS spectra at the K-edge of Ge in crystalline Ge at 10 K and 300 K are reported for comparison with the XAFS of an amorphous Ge. The effect of disorder (thermal and structural) is evident comparing the spectra (vertically and horizontally, respectively).

**Figure 7.10** Fourier transforms of the spectra in Figure 7.9. The peak positions are related to the coordination shells around the absorbing atoms. In amorphous Ge the dramatic effect of structural disorder cause the disappearance of the shells beyond the first one.

**Figure 7.11** (a) Rough XAFS spectrum of Ge at 10K, (b) pre-edge background removal, (c) removal of the atomic absorption contribution $\mu_0(E)$, and (d) $k$-weighted XAFS signal.

**Figure 7.12** Fourier transform of the XAFS signal reported in Figure 7.11d.

**Figure 7.13** Fourier filtering: the XAFS signals of the first three coordination shells of
Ge obtained by reverse Fourier transforming the peaks reported in Figure 7.12.

**Figure 7.14** Beyond the two-body correlation functions: $\chi_i(k)$ represent the SS and MS contribution to the EXAFS signal, $g_j$ represent a pair and multi-body correlation functions (Reference 30).

**Figure 7.15** Normalized EXAFS spectra above the Na K-edge (11.94 Å) in disilicate glass and soda-lime silica glass (left panel) and their atomic distribution $F(r)$ about sodium in sodium disilicate glass and soda-lime-silica glass (right panel); the dotted curves are calculations using Lee and Pendry's spherical wave theory. The two panels have been extracted from the Figure 7.2 and 7.4 reported in Reference 88.

**Figure 7.16** XANES spectrum at the K–Si edge in silica: comparison between the experimental spectrum and two theoretical spectra corresponding to two samples generated by classical MD and *ab initio* MD calculations each averaged over two clusters [101].

**Figure 7.17** Room temperature Si K-edge XANES spectra for SiO$_2$ polymorph [103].

**Figure 7.18** Si K-edge XANES spectra for SiO$_2$ α-quartz brought to high temperature. Phases were assigned from calculated spectra. The liquid was assigned from the thermodynamic stability field [103].

**Figure 7.19** Evidence of the coexistence of two different sites in *q*-GeO$_2$ in the pressure range of the phase transitions. XANES spectrum of c (7.4 GPa) is well reproduced in d by a weighted addition of XANES spectra in the low and high pressure phase (a and b, respectively) [110].

**Figure 7.20** Experimental Ge K-Edge XANES spectra of LiO$_2$–4GeO$_2$ glass (*g*-GeO$_2$) together with the XANES of the reference compound of GeO$_2$ in rutile and quartz (*q*-GeO$_2$) forms. The arrows indicate the two shoulders characteristic of sixfold coordination of Ge [111].

**Figure 7.21** Moduli of the EXAFS Fourier transforms at the K-edge of Ge in crystalline and amorphous GeO$_2$; the peak positions are backward shifted with respect to the actual interatomic distances as the transforms were performed without phase shift correction [112].

**Figure 7.22** Ge–O first coordination distance in crystalline and amorphous GeO$_2$ versus pressure [112].

**Figure 7.23** Modulus of Ag K-Edge EXAFS at 10 K for ion exchanged glass containing particles of 1.5 nm. The dashed line represents the result of fitting [116].

**Figure 7.24** Ag–Ag bond lengths of nanoparticles compared with XRD data of single-crystalline Ag [116].

**Figure 7.25** Experimental data of Debye–Waller factor. The theoretical fit function
yields a static part and a dynamic part [116].

Figure 7.26 The static Debye–Waller factor of all the samples with different average particle size [116].

Figure 7.27 (a) Er L3-edge EXAFS spectra of Er$^{3+}$-doped SiO$_2$-HfO$_2$ waveguides at different concentrations of HfO$_2$ (see Table 7.1 for details). Spectra are vertically shifted for clarity. EXAFS signals $k \chi(k)$, (b) Fourier transforms moduli of the EXAFS signals $k^2 \chi(k)$ [121].

Figure 7.28 Modeling results of Er L3-edge EXAFS signals $k^2 \chi(k)$ of different waveguides. Spectra are vertically shifted for clarity. (a) Comparison between experimental data and calculated spectra of the waveguides containing the lowest molar concentration of HfO$_2$ (W1: 10%), and the largest (W5: 50%): calculated Er-O and Er-Hf EXAFS contributions are shown with their summation and the residual signal, and compared with the experimental EXAFS data (empty circles). The residual (black curve) EXAFS signals $k^2 \chi(k)$. (b) Experimental and best-fit calculated Fourier transforms of the $k^2 \chi(k)$ EXAFS signals for different waveguides (see Table 7.1). The calculated Modulus and the imaginary parts lie over the respective experimental data (dashed lines).

Figure 7.29 EXAFS at the I-K-edge and the corresponding Fourier transforms for the reference compound β-AgI at 300 K (panel a) and three glasses AgI$_{0.50}$ (Ag$_2$O:4 B$_2$O$_3$)$_{0.50}$ (panel b), AgI$_{0.50}$ (AgPO$_3$)$_{0.50}$ (panel c) and AgI$_{0.30}$ (Ag$_2$WO$_4$)$_{0.70}$ (panel d) at liquid nitrogen temperature. Dashed and continuous lines in the Fourier transform are the imaginary part and the modulus, respectively.

Figure 7.30 Mean I–Ag distance measured by EXAFS in different families of AgI-based glasses at liquid nitrogen temperature, plotted against their activation energy for dc ionic conductivity. The symbols refer to the glass family: ⊗ = AgI – Ag$_2$O – 2 · B$_2$O$_3$, ⊕ = AgI – Ag$_2$O – 3 · B$_2$O$_3$, • = AgI – Ag$_2$O – 4 · B$_2$O$_3$, ● = 1/4AgI – AgPO$_3$, ◆ = AgI – Ag$_2$MoO$_4$, ♦ = AgI – Ag$_2$WO$_4$. Dashed line is the reference value of crystalline β-AgI at liquid nitrogen temperature.

Chapter 8

Figure 8.1 Generalized energy-level diagram for an $S = 3/2$ nuclide as a function of applied magnetic field. Arrows indicate energies for the central (CT) and satellite (ST) transitions.

Figure 8.2 Spin description of an NMR experiment: (a) precession of a nuclear spin about the magnetic field vector, representing an ensemble of precessing spins with the bulk magnetization aligned with $\vec{B}_0$; (b) after rotation by a $B_1$ field directed along the $y$-axis, the bulk magnetization lies in the observable $x$–$y$ plane.

Figure 8.3 Schematic anisotropically broadened chemical shielding powder pattern
under conditions of: (a) non-spinning (static), (b) slow MAS, and (c) fast MAS.

**Figure 8.4** $^{21}$Ga MAS NMR spectra of a lead galloborate glass under various experimental conditions: (a) $B_0 = 14.1$ T, $\nu_{rot} = 38$ kHz; (b) $B_0 = 21.1$ T, $\nu_{rot} = 32$ kHz; (c) $B_0 = 21.1$ T, $\nu_{rot} = 62.5$ kHz. Four-, five-, and six-coordinate gallium peaks are modeled using a Czjzek distribution. Spinning sidebands are marked by grey dots.

**Figure 8.5** Schematic depictions of half-integer quadrupolar central-transition NMR lineshapes: (a) crystalline environment under non-spinning conditions, (b) crystalline environment under MAS, and (c) glassy material under MAS. All three spectra are based on the same NMR parameters.

**Figure 8.6** Typical single-pulse (a.k.a. Bloch decay) pulse sequence for the acquisition of an NMR signal: a 90° rf pulse followed by detection of the free-induction decay. Fourier transformation (FT) of this time-domain signal produces a frequency-domain spectrum.

**Figure 8.7** Variation of bulk magnetization for a spin-3/2 nucleus as a function of excitation pulse duration for small-$C_Q$ (solution-like) and larger-$C_Q$ (solid) sites. Shaded portion indicates regime of linear excitation.

**Figure 8.8** $^{31}$P MAS NMR spectra of $(Na_2O)_{0.4}[(B_2O_3)_x(P_2O_5)_{1-x}]_{0.6}$ glasses. Signals from phosphates with 0, 1, 2, and 3 bridging oxygens are labeled. Asterisks denote spinning sidebands. (Adapted from Reference [29].)

**Figure 8.9** $^{11}$B MAS NMR spectra of $(Na_2O)_{0.4}[(B_2O_3)_x(P_2O_5)_{1-x}]_{0.6}$ glasses. Signals from three- and four-coordinated borons are labeled. (Adapted from Reference [29].)

**Figure 8.10** $^{27}$Al NMR spectra ($B_0 = 17.6$ T) of a calcium aluminosilicate glass (16 wt% CaO, 42 wt% $Al_2O_3$, 42 wt% $SiO_2$): (a) MAS spectrum with modeling based on four-, five-, and six-coordinate Al using a Czjzek distribution; (b) MQMAS spectrum depicting four- and five-coordinate Al. (Adapted from Reference [49].)

**Figure 8.11** $^{17}$O NMR spectra ($B_0 = 14.1$ T) of borosilicate glasses: (a) triple-quantum 2D MQMAS of lithium borosilicate glass ($K = SiO_2/B_2O_3 = 0.2; R = M_2O/B_2O_3 = 0.75$) with non-bridging and three types of bridging oxygens labeled; (b) isotropic 1D projections of MQMAS spectra of sodium borosilicate glasses ($K = 0.2$) with bridging oxygens labeled. (Adapted from Reference [50].)

**Figure 8.12** Isotropic projections of $^{11}$B MQMAS NMR spectra ($B_0 = 14.1$ T) of sodium borosilicate glasses with peak assignments for three- and four-coordinate borons; compositions listed according to $K = SiO_2/B_2O_3$ and $R = M_2O/B_2O_3$. (Adapted from Reference [50].)

**Figure 8.13** MAS NMR spectra of alkali borate glasses. (a) $^{133}$Cs MAS NMR ($B_0 = 14.1$ T) spectra of cesium borate glasses; (b) $^{39}$K MAS NMR ($B_0 = 21.1$ T) of
potassium borate glasses. The lines are added as guide for the eye. Crystalline impurities are marked by asterisks. (Adapted from Reference [26].)

**Figure 8.14** Chemical shifts of alkali modifiers in binary alkali borate glasses as a function of alkali content, normalized to the known chemical shift ranges of each nuclide (%) and referenced to the shift of the 16.7 mol% composition. (Adapted from Reference [26].)

Chapter 9

**Figure 9.1** Spatial correlations in network glasses.

**Figure 9.2** Measurement of the $^7\text{Li}[^6\text{Li}]$ dipolar second moment in isotopically enriched lithium carbonate (95% $^6\text{Li}$), using the SEDOR sequence. Filled squares, $F(2t_1)/F(0)$; open triangles, $I(2t_1)/I(0)$. The dashed curve is a fit to Eq. 9.7, while the solid curve was calculated with this expression using the $M_2$ value calculated with Eq. 9.5 from the known internuclear distances in lithium carbonate.

**Figure 9.3** Top: Timing of a REDOR pulse sequence, showing the evolution of the dipolar coupling Hamiltonian during the rotor cycle [21]. Bottom: Experimental and calculated $^{11}\text{B}[^{31}\text{P}]$ REDOR curve of crystalline BPO$_4$. The dotted curve shows the parabolic approximation.

**Figure 9.4** Constant time (CT-REDOR). Top: pulse sequences, in (a) the pulse position $t_{PP}$ of the I-spin dephasing pulses are stepped from 0 to $T_R$ (CT-VPP-REDOR; variable pulse position); in (b) the pulse widths $t_{PP}$ of the I-spin dephasing pulses are stepped from 0 to 2p (CT-VPD-REDOR; variable pulse duration). Bottom: $^{11}\text{B}[^{31}\text{P}]$-CT-VPP-REDOR results for BPO$_4$ for $N = 2$ (filled black circles); $N = 4$ (open black circles); $N = 6$ (filled red circles); and $N = 8$ (open red circles). Dotted curves show results of a two-spin calculation employing the theoretical $M_2$-value of $1.87 \times 10^7$ rad$^2$/s$^2$; solid curves show results of a two spin calculation assuming $M_2$-values of $1.77 \times 10^7$ rad$^2$/s$^2$ ($N = 2$); $1.60 \times 10^7$ rad$^2$/s$^2$ ($N = 4$), $1.57 \times 10^7$ rad$^2$/s$^2$ ($N = 6$), and $1.34 \times 10^7$ rad$^2$/s$^2$ ($N = 8$).

**Figure 9.5** Timing diagram of the rotational echo adiabatic passage double resonance (REAPDOR) pulse sequence.

**Figure 9.6** Top: Pulse sequence used for cross-polarization. The rf field applied to the I nuclei during the contact time is phase shifted by 90° relative to the corresponding preparation pulse. Bottom: Relaxation processes and corresponding time constants involved in the cross-polarization experiment.

**Figure 9.7** $^{19}\text{F}\{^{11}\text{B}\}$ heteronuclear correlation experiment of a lead fluoroborate glass. Top: Contact time 200 μs; preferential detection of the B-bonded F species. Bottom: Contact time 5 minutes, proportional detection of both B-bonded and non-B-bonded F species.
Figure 9.8 Heteronuclear DQ filtering experiment based on J-coupling. Top: Pulse sequence timing diagram. Bottom: Results of the \( ^{113}\text{Cd}^{31}\text{P} \) DQ filtering experiment on \( \text{Zn}_{0.875}\text{Cd}_{0.125}\text{GeP}_2 \). (a) Single-pulse \( ^{31}\text{P} \) spectrum, (b) selective detection of the signal component attributed to \( ^{113}\text{Cd}-\text{bonded P atoms (originating from the PCdZnGe}_2 \text{ site).} \\

Figure 9.9 Timing diagram of the spin echo decay method. The spin echo amplitude is measured as a function of total dipolar evolution time \( 2t_1 \). \\

Figure 9.10 Top: The RFDR sequence with two \( \pi/2 \)-pulses sandwiching the \( t_1 \) evolution period. The mixing period is comprised of rotor-synchronized \( \pi \)-pulses. The third \( \pi/2 \)-pulse produces transverse magnetization. Bottom: \( ^{31}\text{P} \) RFDR spectrum of the ion conductor \( \text{Ag}_7\text{P}_3\text{S}_{11} \). The two crystallographically distinct phosphorus sites B and C belonging to the \( \text{P}_2\text{S}_7^{\pm} \) group give rise to a cross-peak indicating the presence of homonuclear magnetic dipole–dipole coupling between them. The weaker dipolar couplings between more distant P atoms are not observed under the experimental conditions used. \\

Figure 9.11 \( ^{31}\text{P} \) Homonuclear single quantum (SQ)/ double quantum (DQ) NMR correlation spectrum of the ion conductor \( \text{Ag}_7\text{P}_3\text{S}_{11} \). The two crystallographically distinct phosphorus sites B and C belonging to the \( \text{P}_2\text{S}_7^{\pm} \) group give rise to the strongest cross-peak owing to the strongest homonuclear magnetic dipole–dipole coupling between them. Weaker couplings are also observed and give rise to the correlation peaks A–A, A–B, A–C, B–B, and C–C. \\

Figure 9.12 DQ-DRENAR pulse sequence [74], based on the excitation of DQ coherences by POST-C7 blocks. In the \( C \) block, the phases of all pulses are shifted by 90° relative to those in the C block. Implicit in the C7 scheme, the \( ^{31}\text{P} \) nutation frequency is seven times as high as the spinning rate. \\

Figure 9.13 Top left: DQ-DRENAR results on \( \text{Ag}_7\text{P}_3\text{S}_{11} \) [74]. Top right: Results on some phosphate glasses: squares and circles, data for \( \text{Q}^2 \) and \( \text{Q}^1 \) units in \( (\text{Na}_2\text{O})_{0.6}(\text{P}_2\text{O}_5)_{0.4} \) glass (inset, spectra for measurement of \( S_0 \) and \( S' \) at \( NT_1 = 0.89 \text{ ms} \)). Up-triangles, \( \text{Q}^0 \) units in gel-prepared \( \text{AIPO}_4 \); down-triangles, \( \text{Q}^0 \) units in \( 0.5\text{AlPO}_4-0.5\text{SiO}_2 \) glass [73]. Solid curves represent parabolic fits to the initial data range. Bottom left: Experimental results on \( (\text{Ag}_3\text{PO}_4)_{2-2x}(\text{AgI})_{x} \) glasses \( (0 \leq x \leq 1) \) and crystalline \( \text{Ag}_3\text{PO}_4 \). Right: Linear dependence of the average mean squared dipolar coupling constant on phosphate concentration as expected from a random spatial distribution of the phosphate ions [77]. \\

Figure 9.14 Top: Two-dimensional homonuclear J-resolved spectroscopy. Following the preparation by a \( \pi/2 \) pulse, evolution takes place under the influence of homonuclear J-coupling during the evolution time \( t_1 \). Chemical shift and heteronuclear J-coupling evolution are refocused by the central \( \pi \) pulse, and direct dipolar couplings
are averaged out by MAS. The evolution is stopped by the second \( \pi/2 \) pulse, while the third \( \pi/2 \) pulse is used for detection. During the acquisition period \( t_2 \) the regular MAS Hamiltonian is effective. Bottom: Two-dimensional-J-resolved spectroscopy of \( \text{Ag}_7\text{P}_3\text{S}_{11} \).

**Figure 9.15** Top: Timing and coherence level diagrams of the INADEQUATE pulse sequence. Bottom: Two-dimensional single-quantum/double-quantum correlation spectrum recorded by the INADEQUATE sequence on \( \text{Ag}_7\text{P}_3\text{S}_{11} \). Note the complete suppression of the \( ^{31}\text{P} \) resonance of the monomeric \( \text{PS}_4^{2-} \) group at 103 ppm. See Figure 9.14 for comparison.

**Figure 9.16** Dipolar second moment values \( M_2^{(23}\text{Na}--^{23}\text{Na}) \) measured via the \( ^{23}\text{Na} \) spin echo decay method, for sodium silicate and sodium borate glasses as a function of cation number density.

**Figure 9.17** Top: \( ^{7}\text{Li}\{^{6}\text{Li}\} \) SEDOR measured on (\( \text{Li}_2\text{O}\))\(_{0.1}\)-(\( \text{SiO}_2\))\(_{0.9}\) glass (top) and (\( \text{Li}_2\text{O}\))\(_{0.1}\)-(\( \text{B}_2\text{O}_3\))\(_{0.9}\) glass (middle). Both glasses have a \( ^{6}\text{Li}/^{7}\text{Li} \) isotope ratio of 9:1. The Hahn spin echo amplitude of the residual \( ^{7}\text{Li} \) nuclei is measured as a function of dipolar evolution time \( 2t_1 \) in the absence (solid symbols) and the presence (open symbols) of the \( ^{6}\text{Li} \) recoupling pulses. The dotted curves are fits to the experimental data using Eq. 9.7. Bottom: Dipolar second moment \( M_2^{(6}\text{Li}--^{7}\text{Li}) \) measured via \( ^{7}\text{Li}\{^{6}\text{Li}\} \) SEDOR in lithium silicate and lithium borate glasses as a function of cation number density.

**Figure 9.18** Top: Site-resolved \( ^{29}\text{Si}\{^{7}\text{Li}\} \) REDOR data on a lithium silicate glass containing 15 mole\% \( \text{Li}_2\text{O} \). Middle: Dependence of \( M_2^{(29}\text{Si}--^{7}\text{Li}) \) for the \( \text{Q}^{(3)} \) and \( \text{Q}^{(4)} \) units on lithium oxide content \( x \) in the (\( \text{Li}_2\text{O}\))\(_{x}\)-(\( \text{SiO}_2\))\(_{1-x}\) glass system. Bottom: Schematic illustrating lithium clustering in lithium silicate glasses, bringing multiple Li ions into proximity of multiple \( \text{Q}^{(3)} \) units.

**Figure 9.19** \( ^{11}\text{B}\{^{23}\text{Na}\} \) REDOR results on sodium borate glasses. Top: Site-resolved REDOR data on trigonal and tetrahedral boron species. Bottom: Site-selective \( M_2^{\text{B-Na}} \) values extracted from these data as a function of sodium oxide content. (From Reference 95).

**Figure 9.20** Static \( ^{31}\text{P} \) NMR spectra (top) and spin echo decay (bottom) of glasses in the system 70\( \text{SiO}_2\)-30 \( [(\text{Al}_2\text{O}_3)_x(\text{P}_2\text{O}_5)_{1-x}]_x \). (From Reference 96).

**Figure 9.21** Top and middle: \( ^{31}\text{P}\{^{27}\text{Al}\} \) REAPDOR curves for the \( \text{Al}_2\text{O}_3\):(30-x)\( \text{P}_2\text{O}_5\):70\( \text{SiO}_2 \) glasses. The experimental data are compared with simulations based on \( \text{P} \) interacting with one, two, and three \( ^{27}\text{Al} \) neighbors (two-spin, three-spin, and four-spin system, respectively). Experimental data for glassy sol-gel-prepared \( \text{AlPO}_4 \) glass are also included. Bottom: Total number of \( \text{P}--\text{O)--Al} \) linkages \( n_{\text{P-O-Al}} \) as extracted from
27Al{ 31P} REDOR (circles) and 31P{ 27Al} REAPDOR analysis (open triangles). Solid curves illustrate the prediction from the extreme aluminum phosphate cluster scenario. See plate section for a color version of this figure. (From Reference 96).

Figure 9.22 One-dimensional 31P refocused INADEQUATE (right) and 31P single-pulse MAS-NMR spectra (left) of glasses in the system [K2O]1/3[(B2O3)x(P2O5)1-x]2/3, measured at 7.1 T and MAS-rotor frequencies of 14.0 kHz. Spinning sidebands have been omitted. Experimental spectra are displayed in black, their total fits in red, and the individual fitting components are shown as dashed lines [110].

Figure 9.23 Network former unit species concentrations (normalized to 100 %) obtained via 11B MAS-NMR for the B^n species and deduced for the P^n species on the basis of charge balance (solid) and obtained independently via deconvolution of the 31P MAS-NMR spectra (dashed), for glasses of the system [K2O]1/3[(B2O3)x(P2O5)1-x]2/3 [110]. Lines are guides to the eye.

Figure 9.24 (a) 11B{ 31P} REDOR curve of [K2O]1/3[(B2O3)x(P2O5)1-x]2/3-glass (x = 0.6). Red curves correspond to parabolic fits to Eq. 9.8. Measurements were done at 9.4 T and MAS-rotor frequencies of 8, 10, and 12 kHz. (b) M^2 values as a function of x for glasses of the systems [M2O]1/3[(B2O3)x(P2O5)1-x]2/3 (M = Li, K, Cs). (c) Values of m determined by REDOR versus values of m determined from the 11B isotropic chemical shifts for glasses of the systems [M2O]1/3[(B2O3)x(P2O5)1-x]2/3 (M = Li, K, Cs) [110]. The solid line represents the identity case.

Figure 9.25 Connectivity distribution of the bridging oxygen atoms in [K2O]1/3[(B2O3)x(P2O5)1-x]2/3 glasses derived from NMR data and comparison with different linkage scenarios. Dashed curves, random linkage scenario; solid curves, scenario corresponding to the maximum possible number of B^4-O-P linkages excluding the formation of B^3-O-P linkages [110].

Figure 9.26 31P MAS-NMR spectra of [Na2S]2/3[(B2S3)x(P2S5)1-x]1/3 glasses [128]. Black curves show experimental spectra and red curves display simulations, with individual deconvolution components shown as dashed curves.

Figure 9.27 31P J-resolved spectrum of [Na2S]2/3[(B2S3)0.1(P2S5)0.9]1/3 glass with x = 0.1 (left) and 1-D 31P refocused INADEQUATE spectrum of [Na2S]2/3[(B2S3)0.3(P2S5)0.7]1/3 glass (bottom) [128].

Figure 9.28 Top: 11B{ 31P} REDOR curves for B^3 and B^4 units of a [Na2S]2/3[(B2S3)x(P2S5)1-x]1/3 glass with x = 0.5 and parabolic fits of the ΔS/S_0 < 0.2 region [128].
ionization of atoms from a sample surface. In zero-field, an atom sits on the specimen surface at an equilibrium position \( x_0 \) and must reach the sublimation energy \( \Lambda \) to escape. In contrast, the energy barrier for an ion to escape the specimen surface in the presence of an electric field \( Q(F) \) is substantially decreased, allowing ionized atoms to escape at a critical separation distance \( x_c \). (Adapted from Reference [13]).

**Figure 10.2** Schematic plot depicting a line of constant ionization rate and the role of temperature and electric field strength. Between pulses, the APT specimen is maintained below the ionization threshold at \( V_0, T_0 \). Voltage pulsing raises the effective electric field by \( \Delta V \) to the ionization threshold, while laser pulsing raises the effective temperature by \( \Delta T \) to the ionization threshold.

**Figure 10.3** Schematic illustration of the primary components of a modern local-electrode atom probe system (not to scale).

**Figure 10.4** Schematic illustration of a position-sensitive APT detector depicting a microchannel plate with single-atom sensitivity backed by a stack of crossed delay line detectors for both time of flight measurement and spatial positioning of the detected ion.

**Figure 10.5** Generalized FIB-based APT specimen preparation. (a) Schematic cross-section of the lift out sample geometry. (b) SEM image of an undercut lift-out bar ready for extraction. (c) Extraction of the lift-out bar using an *in situ* micromanipulator. (d) Low magnification SEM image of a pre-manufactured Si micropost array used for mounting FIB-prepared APT specimens. This particular array can hold 36 individual APT specimens. (e) Approach of the lift-out bar to an individual Si micropost. (f) Mounting a small piece of the lift-out bar onto an individual micropost.

**Figure 10.6** SEM images of the sharpening of a thin-film APT specimen. (a) Mounted specimen prior to annular milling. (b) Same specimen after coarse milling at 30 kV. (c) Same tip at higher magnification. (d) Same tip after low kV cleanup and positioning in the thin-film region of interest.

**Figure 10.7** Representative mass spectra from two binary materials systems: MgO (a) and Ni-5Cr (b). Each data set contains ~1.5 M detected ions. The metallic spectrum is composed primarily of so-called “elemental” single-atom peaks, while the spectrum for MgO is comprised of both single-atom peaks and several multi-atom complex ions. Note the significant peak overlap at 32 a.m.u. between \( ^{16}\text{O}_2^{1+} \) and \( ^{24}\text{Mg}^{16}\text{O}^{2+} \) which must be deconvoluted for proper oxide stoichiometry measurement. (MgO mass spectrum courtesy of Dr. Arun Devaraj, PNNL.)

**Figure 10.8** Schematic illustration of ion trajectories and geometric considerations for data reconstruction. (not to scale.)

**Figure 10.9** Representative analysis of a B-rich oxide precipitate (dark dots—outlined by a 2.5 at. % B isoconcentration surface) within a Ni-Fe oxide using a one-dimensional concentration profile (left) and a proximity histogram (right). The resulting
concentration profiles across the interface are depicted below each image. The red region schematically depicts the area from which an individual concentration measurement is calculated in each case. The one-dimensional concentration profile proceeds linearly along the length of the analysis cylinder, while the proximity histogram follows the contours defined by the isoconcentration surface. The error bars represent one standard deviation (σ) as defined by Eq. 1.8

**Figure 10.10** APT reconstruction of a Ni-Fe spinel oxide that exhibits ordered atomic planes, demonstrating the sub-nm spatial resolution of APT in ordered oxide structures. While the atomic planes are only apparent along the crystallographic pole, crystalline planar faults that incorporate hydrogen (OH) are apparent across the entire tip diameter.

**Figure 10.11** Schematic illustrating local magnification artifacts associated with field evaporation of heterogeneous materials. (a) A high field material exhibits local magnification (trajectory spreading) resulting in an apparent lower atomic density at the detector than the surrounding matrix. (b) A low field material exhibits local demagnification (trajectory overlap) resulting in an apparent higher atomic density than the surrounding matrix.

**Figure 10.12** Representative mass spectra from SON68 glass in (a) pristine glass of Sample 2 (loaded isotopes); (b) pristine glass of Sample 1 (natural isotopes); and (c) hydrated glass of Sample 1. Peaks unique to (a) and (c) are denoted by different font styles, with bold corresponding to intentionally enriched isotopes in Sample 2, and bold italics denoting peaks absent in the hydrated glass, and non-bold italics denoting peaks found only in the hydrated glass. The vertical axis has been normalized in each spectrum to the maximum of the 16 a.m.u. (\(^{16}\text{O}^+\)) peak for more direct comparisons.

**Figure 10.13** A small region of the TOF mass spectra comparing the various samples highlighting the peak overlap for Cr\(^{2+}\), BO\(^+\) and Al\(^+\). The colored vertical lines indicate the precise atomic mass of each species, which gives a slight asymmetry to the peak shape for overlapping species.

**Figure 10.14** (a) Element-specific ion maps of the pristine glass / hydrated glass interface from Sample 1 (20 nm image depth). (b) Proximity histogram extracted across the same interface. The interfacial width seems quite different for different species, with H and Li being much broader (10–15 nm) than B and Na (3–5 nm).

**Figure 10.15** (a) Element specific atom maps and (b) corresponding concentration profiles of the corrosion layer in the 1-year corroded SON68 specimen (Sample 2). The regions labeled I-IV in (a) correspond to the gel layer, hydrated corroded layer, hydrated pristine glass, and pristine glass, respectively. The B profile is again extremely sharp (1.5 nm) while the other elemental profiles are substantially broader.
PREFACE

It is a fair statement to say that the study of glass has relied heavily on the development of new and improved experimental techniques. The amorphous nature of the material has always presented a particular challenge to researchers, and insights had to wait until technology was able to provide a clearer picture of its structure and behavior. And although our understanding of the basic properties and atomic arrangement is far better than it was when Zachariasen wrote his landmark paper, the essential role of state-of-the-art experimental techniques remains true.

This book provides a snapshot of the state of several spectroscopic techniques, and it is to be considered a follow-up to the wonderful tome edited by C.J. Simmons and O.H. El-Bayoumi, *Experimental Techniques of Glass Science*, published in 1993. Indeed, some of the chapters cover the same techniques, though technology has progressed significantly in the intervening 22 years. Thus, nuclear magnetic resonance (NMR) counts on a plethora of pulse sequences and multidimensional measurements that were nonexistent back then. Other chapters, like the one covering Atom Probe Tomography, represent completely new advances. In all cases, the chapters have been designed to serve a pedagogical purpose, presenting background and details for the graduate student and researcher beginning to explore the capabilities of each technique. To enhance this purpose, chapters include case studies and common mistakes, and the theoretical background has been kept, where possible, short.

All edited books are exposed to the preferences of the editor, and to the availability of authors. This one is no different. Nuclear Magnetic Resonance has two chapters devoted to it, a decision I made based on its current importance in the field. This division also allows for readers to explore NMR based on their background and interest. Another example of editorial choice is the first chapter, on density and calorimetry, two techniques that are affordable by beginning researchers. Finally, other common techniques such as Raman, Brillouin, and infrared spectroscopy provide an overview of vibrational, light-based techniques, a coherence I found important.

It is of course quite obvious that the book would not be possible without the chapter authors. Their work and patience are much appreciated. I made a special effort to gather true experts in the field, researchers who combined expertise in the particular technique with broad knowledge of the field of glass science. This combination, critical in my eyes, will provide readers with a very special look at the use of current, state-of-the-art techniques on these challenging materials, with all of the nuances it entails. It is my sincerest hope that it will prove useful to our scientific community.

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1

DENSITY, THERMAL PROPERTIES, AND THE GLASS TRANSITION TEMPERATURE OF GLASSES

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Part I: Introduction to Physical Properties and Their Uses

Any computer-generated or spectroscopic determination of the atomic structure of glass is tempered by the necessity that the resulting structural model be consonant with physical property measurements. As a result, the basic physical properties play a key role in the acceptance of any model of atomic arrangements. In this chapter, two of the most fundamental properties are examined: density ($\rho$) and thermal properties with a focus on the glass transition temperature ($T_g$). How these measurements are made and interpreted will be discussed. Also, some comparisons between the resulting properties and models of glass structure are given.

First, however, a note of caution is provided. It is not possible to go from direct measurements of the physical properties to a unique model of atomic arrangement. This multiplicity of paths is an example of an *ill-posed problem*. What can be done is to use experimental property data to provide a consistency check on models. That is significant.

Density is perhaps the single-most fundamental and important measure of a glass. Its value is needed in manifold experimental techniques such as neutron, electron, and x-ray scattering. It is also an essential value in molecular dynamics simulations. In addition, density stands on its own as an intrinsic property capable of casting light on various ranges of order within glasses [1].

Furthermore, density can be used to extract a variety of useful volumes including the molar volume, the volume per mole glass former, and for a given model of atomic structure, the volumes of the individual atomic-level structural units themselves. Another useful parameter directly derived from density is the dimensionless packing fraction, the ratio of filled space to total volume within a glass [2]. Additionally, as these property data have become available from a wide variety of glass systems over extended compositional regimes, it has become possible to gain greater insight into atomic arrangement comparisons between systems. What has emerged from this work is a comprehensive set of data which has been quantitatively linked to models of both the short range and intermediate order.

The glass transition temperature is a defining universal condition for a material to be a glass. It is an independent and useful parameter in its own right but the experimental thermogram can also be used to determine other temperatures as well (recrystallization temperature, melting points, pre-glass transition temperature exothermic rearrangements, and more) and to extract the fictive temperature. It will be shown in this chapter that the atomic structure of glass gives rise to systematic changes in $T_g$ with composition. For example, it will be shown that in borate glasses the presence of tetrahedral borons increases $T_g$. 
Part II: Density

1.1 DENSITY: EXPERIMENTAL BACKGROUND AND THEORY

1.1.1 Overview

In this section, methods of how density is determined in a number of ways will be discussed at some length. Density, \( \rho \), is defined by

\[
\rho = \text{mass}/\text{volume}.
\]  

(1.1)

Density is a function of a number of experimental variables including ambient temperature, chemical purity of the sample, the presence of bubbles, thermal history (fictive temperature), and more. Thus, the conditions under which the samples were prepared and the density measured need to be specified in any reporting of such experimental data. In the following it is assumed that a sample of high quality has been prepared without bubbles, with a known thermal history, and whose composition is well characterized.

In summary, in this section of this chapter several of the various methods by which density is determined are described. Later in the chapter some illustrative examples of density trends in glass forming systems are examined.

1.1.2 Experimental Methods and Theory

1.1.2.1 Direct Determination of Mass and Volume

In principle, the most straightforward way of determining density is the direct determination of the mass and volume of the object. For example, a high quality cylinder may have its volume determined by measuring its diameter \( D \), and length \( L \), and using a precision mass scale for mass \( M \). Then the density would be simply

\[
\rho = M/V = M/(\pi D^2 L/4) = (4M/\pi D^2 L)
\]  

(1.2)

This method is not often used for glasses due to the need for such highly symmetric shapes. The most important source of error in this method will likely be in the determination of volume since mass may be routinely determined to high accuracy in a modern laboratory.

1.1.2.2 Archimedes' Principle: Wet/Dry Weighing

This beautiful method relies on weighing the glass sample in both a liquid \( W_{\text{sample in liquid}} \) and in air \( W_{\text{sample in air}} \). Separate measurements of mass and volume are not needed. Rather, Archimedes' principle states that the buoyant force, \( B \), exerted on a solid immersed in a liquid is given by the weight of the displaced fluid, \( W_{\text{displaced fluid}} \):
\[ B = W_{\text{displaced fluid}} = \rho_{\text{liquid}} V_{\text{sample}} g \]  

where \( \rho_{\text{liquid}} \) is the density of the liquid, \( V_{\text{sample}} \) is the sample volume, and \( g \) is the acceleration due to gravity. Ignoring the small buoyant force of air makes, \( W_{\text{sample in air}} = W_{\text{sample}} \), and allows \( W_{\text{sample in liquid}} \) to be expressed by

\[ W_{\text{sample in liquid}} = W_{\text{sample in air}} - B \]  

Noting that \( V_{\text{sample}} \) is \( M_{\text{sample}}/\rho_{\text{sample}} \) produces

\[ W_{\text{sample in liquid}} = W_{\text{sample in air}} - B = W_{\text{sample in air}} - \rho_{\text{liquid}} V_{\text{sample}} g \]

This leads to the working equation

\[ \rho_{\text{sample}} = \rho_{\text{liquid}} \left( \frac{W_{\text{sample in air}}}{W_{\text{sample in air}} - W_{\text{sample in liquid}}} \right) \]  

The density is then determined using Eq. 1.6 after having measured \( W_{\text{sample in liquid}} \) and \( W_{\text{sample in air}} \), and with knowledge of \( \rho_{\text{liquid}} \). This method is commonly used and has several advantages.

- There is no limitation on the density of the sample.
- It is inexpensive to perform.
- Sample shape does not matter.
- Pure water can often be used as the working fluid if the density is not very high and if the sample is not hygroscopic.

There are some disadvantages that make it difficult to exceed 1% accuracy in the final density.

- The density of the working fluid tends to be more temperature dependent than the sample leading to the need for good temperature control of the fluid.
- It is not easy to perform the wet weighing and one must be extremely careful for precision results. Be on the lookout for fluid adhering to the fine thread that holds the sample.
- Bubbles would lead to an underreporting of the density.

### 1.1.2.3 Archimedes' Principle: Sink-Float Method

The sink-float method also relies on Archimedes' Principle [1]. In this technique, the sample is initially sunk in a solution of two miscible fluids such as acetone (\( \rho_{\text{ace}} = 0.78 \, \text{g/cc} \)) and diiodomethane (\( \rho_{\text{dii}} = 3.32 \, \text{g/cc} \)). The acetone-diiodomethane solution that is prepared is chosen to have a slightly smaller density than that approximated for the sample. Drops of diiodomethane are added until the sample floats (usually done in duplicate to ensure reliability and to provide a better estimate of error). A magnetic stirrer stirs the solution to ensure homogeneity.
It has been determined experimentally that this additive solution is fully miscible for these fluids. Thus, the volumes of the two fluids very nearly satisfy

$$V_{\text{liquid}} = V_{\text{ace}} + V_{\text{dii}} \tag{1.7}$$

Under these conditions, at the point where the sample just floats

$$\rho_{\text{sample}} = \frac{\rho_{\text{liquid}}}{\rho_{\text{sample}}} = \frac{M_{\text{liquid}}}{V_{\text{liquid}}} = \frac{(M_{\text{ace}} + M_{\text{dii}})}{(V_{\text{ace}} + V_{\text{dii}})}$$

$$= \frac{(1 + M_{\text{dii}}/M_{\text{ace}})/((V_{\text{ace}} + V_{\text{dii}})/M_{\text{ace}})}$$

or

$$\rho_{\text{sample}} = \rho_{\text{ace}}(1 + Q)/(1 + Q) \frac{\rho_{\text{ace}}/\rho_{\text{dii}}) \tag{1.8}$$

where $Q$ is the mass ratio, $M_{\text{dii}}/M_{\text{ace}}$.

Equation 1.8 is the working equation for density for the sink-float method. Note that in the limit of $Q$ going to zero, the density becomes that of acetone whereas as $Q$ becomes large the equation predicts a density near that of diiodomethane. The range of observed glass densities is therefore, $0.78 \text{ g/cc} < \rho_{\text{glass}} < 3.32 \text{ g/cc}$. 

If the densities of the two fluids are well known then the sink-float method has the advantage of needing just the masses of the two fluids (easy to measure) to determine the density of a glass flake as small as a few tens of milligrams. Furthermore, the sample may be of an irregular shape. The method has the disadvantage of being limited to the range of the densities of the working fluids, as mentioned above.

In some cases the fluids may react with the samples. In such circumstances the sample density may be found by bracketing the glass densities with mixtures of closely varying densities.

### 1.1.2.4 Pycnometry

Gas pycnometry is an experimental method that determines volume. It involves the use of the ideal gas law to convert pressure changes to volume determination.

In the following discussion, we assume the use of helium, the least reactive, most penetrating, and most ideal of all gases, although other gases may be used such as nitrogen. Two volumes, the reference volume and the sample volume are used as shown below in Figure 1.1.
Previous to using the device it is assumed that the reference and sample chamber volumes have been calibrated. Standard metal spheres are typically used for this step. The reference and sample volumes are denoted $V_1$ and $V_2$ as shown in Figure 1.1.

A sample of unknown volume, $V_s$, is inserted into the sample chamber (in the photograph of the instrument in Figure 1.2, this is done by opening the black screw top lid and inserting the sample in a sample cup). Initially $V_1$ is filled with He when valve 1 is opened and valve 2 is left closed. Pressure $P_1$ is measured. Valve 2 is opened and Pressure $P_2$ is observed. For fixed temperature and cancelling out a common atmospheric pressure term the ideal gas law becomes

$$P_1 V_1 = P_2(V_1 + V_2 - V_s)$$

(1.9)
This equation can be rearranged to find the working equation for $V_s$.

$$V_s = V_1(1 - P_1/P_2) + V_2$$  \hspace{1cm} (1.10)

Use of a high quality electronic balance to find the sample mass then completes the measurement for density.

This method has several advantages.

- There is no bound on what the density of the sample is.
- After the initial purchase of the pycnometer and balance (both may sum to $10,000 or more in 2015 dollars) it is inexpensive to perform measurements. A tank of helium may last years.
- Shape does not matter. Powders can be measured readily.
- It is easy to perform multiple volume determinations on the same sample and determine

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{quantachrome.png}
\caption{A Quantachrome® manual pycnometer.}
\end{figure}
high precision statistical measures of accuracy.

There are some disadvantages as well.

- There is a fairly strong temperature dependence on the pressure leading to the need for good temperature control of the instrument.
- Outgassing of the sample can be an issue.
- Be wary of bubbles. The presence of bubbles will give an artificially low density result.
- Sample size is limited by the sample cell. Typically, it is difficult to measure accurately sample volumes below 0.5 cc or so.

1.1.2.5 The Gradient Density Column—the ASTM D1505 Method for Determining Density

In this method a long tube is filled with a fluid whose density changes with height. If the temperature is controlled, this method may be accurate to within 0.05 %. Where accuracy of 0.05 % or better is desired, the gradient tube is made so that vertical distances of 1 mm represent density differences no greater than 0.0001 g/cm$^3$. The sensitivity of the column is then 0.0001 g/cm$^3$·mm. For further details, including instrumentation needed, the reader is referred to the American Society for Testing and Materials (ASTM) method which is found at [http://www.astm.org/Standards/D1505.htm](http://www.astm.org/Standards/D1505.htm). Furthermore, there are additional ASTM methods for determining density such as ASTM D792-08 Standard Test Methods for Density and Specific Gravity (Relative Density) of Plastics by Displacement.

1.1.3 Instrumentation Used for Determining Density

1.1.3.1 Direct Determination of Mass and Volume

*Instrumentation Needed:* Digital micrometer, typically accurate to ±0.00001m or better, and a precision digital balance. A modern digital balance needs to be precise to ±0.0001 g. This would result in density being determined to better than ±0.1%. For example, Masao Kodama found [3] the density of well-characterized boron oxide glass from this method to be 1.839 ±0.001 g/cm$^3$.

1.1.3.2 Archimedes' Principle: Wet/Dry Weighing

*Instrumentation Needed:* Precision digital balance designed to do both dry and wet massings, a suitable and high purity fluid such as mineral oil, distilled water, or reagent grade diiodomethane, a beaker to hold the fluid, and a small container with fine thread to hold the sample for weighing. It is difficult to determine density by this technique to better than 1%. To do better precise temperature control of the fluid and knowledge of the fluid density would be essential. The greater the fluid density, the greater will be the difference in the weighings and hence the more precise the density measurement.

1.1.3.3 Archimedes' Principle: Sink-Float Method
**Instrumentation Needed**: Glass cylinder, perhaps 20 cc in capacity or less with a ground glass stopper; suitable, miscible fluids such as reagent grade acetone and diiodomethane; magnetic stirrers with an external stirring apparatus, a microburette to dispense the denser fluid, and a quality balance. The density maybe readily found to an accuracy of 1%. Relative densities may be found to be better than 0.1%.

### 1.1.3.4 Pycnometry

**Instrumentation Needed**: a pycnometer, a mass balance, a tank of gas, preferably helium, although nitrogen may be used as well. With temperature control or correction density may be found to 0.1% for a sample volume of 1 cc.

### 1.1.3.5 General Considerations

There are several common considerations that make density difficult to determine absolutely. The sample preparation is one such limitation. For example, once again considering boron oxide, there is a variation in density of a few percent in going from a rapidly quenched sample to a well annealed glass [4]. It is best to study samples with similar thermal histories. Relaxation may play a role as the density may slightly vary over time as the sample relieves stress. Also, some techniques exhibit a sample size consideration in terms of precision. This is true for pycnometry and the Archimedes' wet/dry dual weighing methods.

### 1.1.4 Analysis of Data, Extraction of Useful Information, and Other Ways to Express Density

While density is useful in its own right there are several different ways to present these data in useful forms. Three alternatives will be discussed including molar volume, volume per mole glass former, and packing fraction. This will be followed by a brief discussion of the extraction of atomic level volumes directly from the density.

#### 1.1.4.1 Molar Volume

The molar volume, $V_M$, is defined by

$$V_M = \frac{\text{Mass of a mole of glass}}{\rho} \quad (1.11)$$

For a borate glass of composition $RM_2O.B_2O_3$ the molar volume can be rewritten by

$$V_M = \frac{\text{Mass}(RM_2O.B_2O_3)}{((1 + R)\rho)} \quad (1.12)$$

where the factor 1+R comes about because there are R moles of $M_2O$ and one mole of $B_2O_3$.

Molar volume may also be written in terms of molar fractions by

$$V_M = \frac{\text{Mass}(XM_2O.(1 - X)B_2O_3)}{\rho} \quad (1.13)$$

where $X$ is the molar fraction of alkali oxide and $1 - X$ is the molar fraction of $B_2O_3$. The units
of $V_M$ are cm$^3$/mol for densities expressed in g/cm$^3$ and mass in g/mol. The practical benefit of molar volume is the elimination of mass from the density making structural comparisons easier to observe.

As an example, Figure 1.3 shows the molar volumes of the alkali and alkaline-earth borate glass systems as a function of R [5].

![Figure 1.3 Molar volumes of the alkali and alkaline-earth borate glass system [5]. R is the molar ratio of metal oxide to boron oxide. The error is smaller than the symbols used.](image)

Note, for example, in Figure 1.3, that the same trend is observed for molar volumes in the lithium, sodium, magnesium, and calcium borate glasses systems. This presumably implies that in borate systems in which the modifying ion is smaller than oxygen, the molar volume trend is dominated by the boron oxide network.

1.1.4.2 Volume per Mole Glass Former

The volume per mole glass former, $V_{\text{mole former}}$, is defined by
For the alkali borate system the volume per mol boron oxide is

\[ V_{\text{mole former}} = \frac{\text{Mass of a mol of glass former}}{\rho} \] (1.14)

This may linearize the volume trend (see discussion below of lithium silicates).

A comparison of the volume per mole of glass former three binary glass systems is shown in Figure 1.4 [6]. There is clear evidence in the figure for coordination changes in the borates (3 to 4) and germanates (4 to 5 or 6) by the presence of the minima in the volume per mole of glass former as a function of modifier content. No minimum is seen for the silicates, see Figure 1.4.

![Graph showing molar volumes per mole glass former](image)

**Figure 1.4** Molar volumes per mole glass former in the lithium borate, lithium silicate, and lithium germanate glass systems [6]. R is the molar ratio of lithia to silica, germania, or bora.

1.1.4.3 Packing Fraction

The packing fraction, pf, is a dimensionless measure of density and is determined by the ratio of the filled space in a glass to the total volume available

\[ pf = \frac{\text{Volume of all ions in a mole of glass}}{V_M} = \sum N_A (4/3) \pi r_i^3 / V_M \] (1.16)
Here $r_i$ is the ionic radius of the $i^{th}$ atom in the chemical formula for the glass and $N_A$ is Avogadro’s number. Ionic radii are typically determined by diffraction and Shannon provides a good source for such numerical information [7]; see Table 1.1.

**Table 1.1** Ion coordination and size [7, 8].

<table>
<thead>
<tr>
<th></th>
<th>Be</th>
<th>Mg</th>
<th>Ca</th>
<th>Sr</th>
<th>Ba</th>
<th>Li</th>
<th>Na</th>
<th>K</th>
<th>Rb</th>
<th>Cs</th>
<th>O</th>
<th>Si</th>
<th>III B</th>
<th>IV</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Coordination</strong></td>
<td>4</td>
<td>6</td>
<td>7–8</td>
<td>8</td>
<td>9</td>
<td>4</td>
<td>6</td>
<td>8</td>
<td>9</td>
<td>10</td>
<td>2</td>
<td>4</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td><strong>Radius (Å)</strong></td>
<td>0.41</td>
<td>0.86</td>
<td>1.23</td>
<td>1.4</td>
<td>1.61</td>
<td>0.73</td>
<td>1.16</td>
<td>1.65</td>
<td>1.77</td>
<td>1.95</td>
<td>1.21</td>
<td>0.4</td>
<td>0.15</td>
<td>0</td>
</tr>
<tr>
<td><strong>Radial uncertainty (Å)</strong></td>
<td>0.1</td>
<td>0.06</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
<td>0.03</td>
<td>0.02</td>
<td>0.02</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td><strong>Volume (Å³)</strong></td>
<td>0.29</td>
<td>1.50</td>
<td>7.80</td>
<td>11.49</td>
<td>17.48</td>
<td>1.63</td>
<td>6.54</td>
<td>14.71</td>
<td>19.16</td>
<td>31.06</td>
<td>7.42</td>
<td>0.25</td>
<td>0.01</td>
<td>0</td>
</tr>
<tr>
<td><strong>Volume uncertainty (Å³)</strong></td>
<td>0.22</td>
<td>0.56</td>
<td>0.95</td>
<td>1.23</td>
<td>1.63</td>
<td>0.34</td>
<td>0.51</td>
<td>0.6</td>
<td>0.8</td>
<td>1</td>
<td>0.37</td>
<td>0.02</td>
<td>0.003</td>
<td>0</td>
</tr>
<tr>
<td><strong>Fractional volume uncertainty</strong></td>
<td>0.76</td>
<td>0.37</td>
<td>0.12</td>
<td>0.107</td>
<td>0.09</td>
<td>0.21</td>
<td>0.08</td>
<td>0.04</td>
<td>0.04</td>
<td>0.03</td>
<td>0.05</td>
<td>0.08</td>
<td>0.3</td>
<td>0</td>
</tr>
</tbody>
</table>

**Figure 1.5** depicts the packing fractions of the alkali and alkaline-earth borates [8].

**Figure 1.5** Packing fractions from a series of alkali and alkaline-earth borate glasses. R is the molar ratio of alkali oxide to boron oxide [8].
The packing trends reveal much about the structure. The lithium and magnesium systems have very similar pf values presumably because these ions are much smaller than oxygen. The result is a common compositional trend for the filling of space by the borate network as the glass is modified.

### 1.1.4.4 Atomic Volumes from the Alkali and Alkaline-Earth Borate Glass Systems

Figure 1.6 depicts the density of the alkali and alkaline-earth borates as function of R, the molar ratio of modifying oxide to boron oxide [5]. It is evident that all systems follow a rapid increase in density followed by either a decrease or a milder increase in the density. Further analysis of the density itself is possible through knowledge of the atomic arrangements. For example, it is possible to determine the volumes of the short-range structural groups through knowledge of the density and the nuclear magnetic resonance (NMR)-determined fractions of the short-range units by

\[
\rho(R) = \frac{\text{Mass of the glass structural groups}}{\left(\sum (f_i V_i)\right)}
\]  

(1.17)

Figure 1.6 The density of alkali and alkaline-earth borates as a function of R, the molar ratio of modifying oxide to boron oxide [5]. The error is smaller than the symbols.

where \(f_i\) and \(V_i\) are the fractions and volumes of the \(i^{\text{th}}\) structural group. These structural
volumes of the atomic-level units, relative to that of the three-coordinated borons in boron oxide glass are given for the alkali borates in Table 1.2. The structural units in this table are reported as $Q^{ni}$ where the integer $n$ refers to the boron coordination and $i$ denotes the number of bridging oxygens per boron.

**Table 1.2** Volumes of the alkali borate short-range order groups [5].

<table>
<thead>
<tr>
<th>System</th>
<th>Unit</th>
<th>Least squares derived volumes of the structural groups</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>$Q^{33}$</td>
<td>0.98</td>
</tr>
<tr>
<td></td>
<td>$Q^{44}$</td>
<td>0.94</td>
</tr>
<tr>
<td></td>
<td>$Q^{32}$</td>
<td>1.28</td>
</tr>
<tr>
<td></td>
<td>$Q^{31}$</td>
<td>1.61</td>
</tr>
<tr>
<td>Na</td>
<td>$Q^{33}$</td>
<td>0.95</td>
</tr>
<tr>
<td></td>
<td>$Q^{44}$</td>
<td>1.24</td>
</tr>
<tr>
<td></td>
<td>$Q^{32}$</td>
<td>1.58</td>
</tr>
<tr>
<td></td>
<td>$Q^{31}$</td>
<td>2.12</td>
</tr>
<tr>
<td>K</td>
<td>$Q^{33}$</td>
<td>0.95</td>
</tr>
<tr>
<td></td>
<td>$Q^{44}$</td>
<td>1.66</td>
</tr>
<tr>
<td></td>
<td>$Q^{32}$</td>
<td>1.99</td>
</tr>
<tr>
<td></td>
<td>$Q^{31}$</td>
<td>2.95</td>
</tr>
<tr>
<td>Rb</td>
<td>$Q^{33}$</td>
<td>0.98</td>
</tr>
<tr>
<td></td>
<td>$Q^{44}$</td>
<td>1.92</td>
</tr>
<tr>
<td></td>
<td>$Q^{32}$</td>
<td>2.27</td>
</tr>
<tr>
<td></td>
<td>$Q^{31}$</td>
<td>3.41</td>
</tr>
<tr>
<td>Cs</td>
<td>$Q^{33}$</td>
<td>0.97</td>
</tr>
<tr>
<td></td>
<td>$Q^{44}$</td>
<td>2.28</td>
</tr>
<tr>
<td></td>
<td>$Q^{32}$</td>
<td>2.62</td>
</tr>
<tr>
<td></td>
<td>$Q^{31}$</td>
<td>4.13</td>
</tr>
</tbody>
</table>

Note: The volumes are reported relative to the volume of the BO$_{1.5}$ unit in B$_2$O$_3$ glass. The units are reported as $Q^{ni}$ where the integer $n$ refers to the boron coordination and $i$ denotes the number of bridging oxygens per boron.

The reader is referred to an extensive literature on this topic [5, 8, 9, 10].

In general one sees that the volumes are strong functions of the alkali. The $Q^{33}$ units are independent of alkali and hence are of similar size in each system (the reported values are
best-fit values for all compositions at which the unit is present). The other units show an expected increase with increasing non-bridging oxygen (NBO) content and increasing alkali content. In some cases involving potassium, rubidium, and cesium the volumes of the structural units are dominated by the alkali's ionic volume.

### 1.1.5 Case Studies from Some Glass Systems

#### 1.1.5.1 Lithium Silicates

Among the most basic glass systems are the lithium silicates. Figure 1.7 presents the densities of this system determined by Peters et al. [10] using the sink-float method as a function of J, the molar ratio of lithia to silica. The figure also depicts a literature compilation of densities from Bansal and Doremus [11].

![Figure 1.7](image)

**Figure 1.7** Density of lithium silicate glasses by the sink-float method from Peters et al. [10] and a comparison of literature values compiled by Bansal and Doremus [11]. J is the molar ratio of lithium oxide to silicon dioxide.

The sink-float method agrees well with the literature compilation by Bansal and Doremus [10, 11] except that the scatter is larger since the error in this one study is one percent versus the compiled data of 16 independent studies, whose error is far less.

The changing atomic structures in this system are closely approximated by $Q^i$ units shown in Figure 1.8.
Figure 1.8 The $Q^i$ structural units found in alkali silicate glasses, from left to right they advance from $Q^4$ to $Q^0$ where the superscript denotes the numbers of bridging oxygens per Si. $A^+$ represents an alkali ion.

The abundances of these units closely follow a simplified lever rule model [10] as shown below and in Figure 1.9:

\[
Q^4 = 1 - 2J \quad Q^3 = 2J \quad 0.0 \leq J \leq 0.5 \tag{1.18a}
\]
\[
Q^3 = 2 - 2J \quad Q^2 = 2J - 1 \quad 0.5 \leq J \leq 1.0 \tag{1.18b}
\]
\[
Q^2 = 3 - 2J \quad Q^1 = 2J - 2 \quad 1.0 \leq J \leq 1.5 \tag{1.18c}
\]
\[
Q^1 = 4 - 2J \quad Q^0 = 2J - 3 \quad 1.5 \leq J \leq 2.0 \tag{1.18d}
\]

Figure 1.9 The lever rule for lithium silicate glasses.
Notice in Figure 1.7 the sharp transition in density near $J = 0.5$. This is the composition at which there is a significant structural rearrangement in the silicates as it is the $Q^3$ composition that lies at the boundary between $Q^4$ changing to $Q^3$ and the consequent compositional region where $Q^3$ adds an NBO to form $Q^2$ units. This may also be seen in the volume per mole silica as shown in Figure 1.10.

![Volume per mol silica from a series of lithium silicate glasses, JLi$_2$O.SiO$_2$. The data are taken from Bansal and Doremus [11]. J is the molar ratio of lithium oxide to silica.](image)

Figure 1.10 Volume per mol silica from a series of lithium silicate glasses, JLi$_2$O.SiO$_2$. The data are taken from Bansal and Doremus [11]. J is the molar ratio of lithium oxide to silica.

Note that using the volume per mole silica linearizes the molar volume results. This results in the slope of each linear region representing the volume change for the silicate structural units as follows:

\[ Q^4 \rightarrow Q^3 \text{ for } J < 0.5 \text{ and } \]
\[ Q^3 \rightarrow Q^2 \text{ for } 0.5 < J < 1.0 \]

Equations (1.18) a–d) and the density may be linked together to find the volumes of the lithium silicate structural groups by insertion in Eq. 1.17 and the use of a least squares analysis. This yields the volumes given in Table 1.3[10].
Table 1.3 Relative volumes of the silicate units in Li$_2$O.SiO$_2$ glasses. All volumes are relative to the volume of the SiO$_2$ tetrahedron in silica glass.

<table>
<thead>
<tr>
<th>Unit</th>
<th>Least squares derived volumes of the structural groups</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Q^4$</td>
<td>1.00</td>
</tr>
<tr>
<td>$Q^3$</td>
<td>1.17</td>
</tr>
<tr>
<td>$Q^2$</td>
<td>1.41</td>
</tr>
<tr>
<td>$Q^1$</td>
<td>1.69</td>
</tr>
<tr>
<td>$Q^0$</td>
<td>1.95</td>
</tr>
</tbody>
</table>

1.1.5.2 Alkali Borates

Shown in Figure 1.11 is the density of the lithium borate glass system as a function of R, the molar ratio of lithia to bora. These data are from the paper by Shibata et al. [12]. Also shown in the figure is the tetrahedral fraction of borons, f$_2$, as found in Jellison, Feller, and Bray's 1978 paper [13]. The two quantities track each other well indicating a strong connection between atomic arrangement and physical property.
Figure 1.11 Density of lithium borate glasses as a function of R, the molar ratio of lithium oxide to boron oxide [12]. Also shown in the figure is the fraction, $f_2$, of tetrahedral borons [13].

Shown in Figure 1.12 are the precise density data of Kodama [3] from the cesium borate system. These data, presented as the volume per mole boron oxide, from very homogeneous glasses prepared for velocity of sound measurements are accurate to better than 0.1 %. The undulations appearing in the density trend are real and represent subtle density fluctuations that have been correlated to intermediate range structures such as triborate and diborate rings [3], see Figure 1.13.
Figure 1.12 Volumes per mole $\text{B}_2\text{O}_3$ of the cesium borate glass system from Kodama [3] The error is less than the symbol size.

Figure 1.13 The triborate and diborate superstructural groups.
A further example of the utility of density data is found in a comparison of elastic properties with molar volumes. Using Kodama's density data, the molar volumes of the alkali borates are shown in Figure 1.14. The reader may see further evidence for intermediate range order in the systematic variations of the molar volume as alkali content, R, increases.

**Figure 1.14** Molar volumes of the alkali borates using Kodama's data as a function of R, the molar ratio of alkali oxide to boron oxide [3].

Kodama also found the elastic constants for the system using velocity of sound measurements. A representative example, stiffness, is shown below in Figure 1.15 as R is changed [3].
Next, we examine the stiffness as a function of molar volumes for the representative cesium borate case [3], see Figure 1.16.
The trend of stiffness versus molar volume maybe understood in terms of simultaneous volume and stiffness changes [3]. The values for B$_2$O$_3$ may be found in the lower left part of the figure (molar volume just under 38 cc/mol and stiffness of just under 7 GPa). From there the amount of cesium modifier increases as one traces the data first to lower molar volumes then to higher ones. Initially, the glass shrinks as tetrahedral borons form; this results in a stiffer glass as the stiffness surpasses 9 GPa. Then the glass expands as the stiffness remains approximately constant. This maybe attributed to the formation of open triborate rings. Then, near 40 cc/mol, the glass ceases to expand but stiffens instead; this behavior is likely due to the formation of tight and compact diborate groups. Further addition of cesium oxide causes the formation of non-bridging oxygens on the borons, destroying the superstructural groups and opening up the structure. The molar volume increases as the glass becomes less stiff.

1.1.6 Conclusion to Density Measurements

Density is of fundamental importance in glass physics. It is measured using a wide variety of techniques depending on the sample and the desired precision.

Knowledge of the density is crucial in the various scattering experiments employing x-rays, electrons, and neutrons. Also, any structural model for atomic arrangements must pass the density test: does the model predict the correct density?

Density is used to determine a variety of volumes such as molar volume, volume per mole glass former, and atomic level structural volumes. Furthermore, density is used to determine
packing fractions that, in effect, represent density in a dimensionless way.
Part III: Thermal Effects with a Focus on the Glass Transition Temperature

1.2 OVERVIEW

In this part of the chapter we will go through how thermal events and particularly the glass transition temperature, \( T_g \), are determined in a number of ways. As with density it is impossible to uniquely go from experimental \( T_g \)s to the true representation of atomic arrangements. \( T_g \) is affected by many factors but the principal one of interest in this chapter will be atomic arrangements in a manner analogous to the density discussed in Part II of this chapter. \( T_g \) data have become available from a wide variety of glass systems over extended compositional regimes [14]. Hence, it has become possible to gain greater insights into atomic arrangement variations between systems. As stated before, what has emerged from this work is a comprehensive set of data which has been linked to models of the short and intermediate range order.

1.3 EXPERIMENTAL METHODS AND THEORY

1.3.1 Calorimetry

1.3.1.1 Differential Scanning Calorimetry

A differential scanning calorimeter (DSC) is composed of two matched electrical heating elements that are programmed to simultaneously heat two sample holders with encapsulated pans in them. This occurs in such a way as to raise the temperature of both pans at the same heating rate [15]. A well-known method to accomplish this is to “power compensate” for the presence of a sample in a pan (usually aluminum) on one side and a blank pan on the other. The result of the experiment is a thermogram as shown in Figure 1.17. The vertical scale is given in differential power, typically in mW. In this figure, vertically downward displays endothermic events in which heat enters the system. whereas vertically upward shows exothermic reactions in which heat leaves the system.
Figure 1.17 The DSC head uncovered for sample insertion (from Wikipedia).
Figure 1.18 Representative thermogram from a DSC

This figure has three typical thermodynamic reactions shown in it. Going from low to high temperatures one can first see a change in specific heat (measured by an increased endothermic differential power level) as is typically seen in a glass transition. The exothermic event involves the removal of energy from the sample compared to the blank reference pan. A representative exothermic reaction is the crystallization event. Thus, a glass that crystallizes upon heating enters a more ordered state and heat must be released from the sample for this to happen. The final endothermic event is due to the melting of the crystalline phase.

Each of these events has assigned temperatures. The temperature for the onset of the glass transition, where the steepest part of the change in the specific heat part of the thermogram curve meets the pre-event baseline is known as the onset $T_g$. In similar fashion $T_{m\text{ onset}}$ (or $T_s$) for melting maybe determined. The onset end of melting is known as $T_{m \text{ endpoint}}$, whereas the temperature marking the crystallization is defined in the same onset way is known as the $T_x$ (onset) or $T_{x\text{ h}}$, whereas $T_C$ is the temperature at the thermogram exothermic minimum for the crystallization event).

Please note that the thermal events are referenced to a baseline, typically run just before the sample run. A baseline is run with no sample in either pan and the expected result is a flat signal. In the usual real case, the baseline will have some small deviation from being entirely
flat and software maybe used to both correct and subtract the baseline from an experimental run in order to normalize it to a flat baseline.

Calibration occurs by using materials with known melting points, typically metals such as indium, lead, and zinc.

### 1.3.1.2 Some Practical Considerations of DSC

Care must be taken to maintain the heating elements in good working order by routinely cleaning the sample cup areas. The modern DSC comes with software designed to run the temperature up and down in a cleaning cycle. Usually the heating elements are so well matched that damage to one side necessitates full replacement of the head where the heating elements reside. This is a fairly expensive repair at the level of thousands of US dollars.

The sample pans may be made of a variety of materials including aluminum (good up to 600°C), gold (useful up to 1000°C), platinum (may be used to near 1700°C), or ceramic (useful to a variety of temperatures). Usually the aluminum pans are discarded after single use. These aluminum pans typically cost a few dollars each.

### 1.3.1.3 Modulated DSC

This is a patented technique of the TA Instruments and to some extent reworked by other companies. To quote TA [16],

>M DSC offers all the benefits of standard DSC, overcomes its limitations, and provides further information for greater understanding of material properties. Specifically, MDSC permits separation of the total heat flow signal into its thermodynamic (heat capacity) and kinetic components. MDSC offers simultaneous improvements in sensitivity and resolution, and can separate overlapping events that are difficult or impossible to do by standard DSC.

This is a manifold topic and details beyond the introduction presented here are available from either vendors or more specialized works.

### 1.3.2 Differential Thermal Analysis

Differential thermal analysis (DTA) is a closely related technique to differential scanning calorimetry. In it a furnace heats two samples. One is a reference sample of alumina and the other a mixture of alumina and the glass in question. Each sample has its temperature measured by a thermocouple and the difference in temperature between the two thermocouples is plotted versus temperature of the sample as the furnace is ramped up in temperature. The plot may be converted to power difference as a function of sample temperature as in the DSC or directly plotted as temperature difference versus temperature of the sample, see Figure 1.19. The thermal events described for DSC show up in analogous manner in DTA.
Figure 1.19 A schematic of the operation of a DTA.

Its chief advantage over DSC is its relatively inexpensive way to reach high temperatures. On the other hand the rate of temperature change is harder to control due to the rather large thermal mass associated with the furnace.

Like in the DSC, calibration occurs by using materials with known melting points, typically metals.

1.4 INSTRUMENTATION USED FOR DETERMINING $T_g$ AND RELATED THERMAL EVENTS

1.4.1 DSCs

DSCs are sold commercially and come in several varieties. Shown in Figure 1.20 is a current TA® Modulated DSC. Typical temperature calibration accuracy is better than $+/- 0.1^\circ C$ whereas the error in $T_g$ is close to $+/- 3.0^\circ C$. 
DSCs need some accessories. These include sample pans, crimpers, cover lid reformers, standard metals for calibration, and more.

1.4.2 Differential Thermal Analysis

Many commercial versions of DTAs are available, see Figure 1.21. They consist of a furnace and typically two ceramic stalks on which the samples reside along with a thermocouple for each. Typical temperature calibration accuracy is better than $+/− 0.1^\circ$C whereas the error in $T_g$, $T_x$, or $T_m$, is of the order of $+/− 1.0$ to $3.0^\circ$C.
It is also possible to purchase simultaneous thermal analysis (STA) instruments. In such instruments, there are simultaneous DTA and thermogravimetric analysis (TGA) measurements that take place.

Similar accessories to the DSC are needed in DTA. Usually ceramic sample cups are used and aluminum oxide is coplaced with the sample in the ceramic sample cup.

### 1.5 ANALYSIS OF DATA AND EXTRACTION OF USEFUL INFORMATION

Figure 1.22 shows an experimental thermogram [17] from a lithium borate glass with composition 1.5Li₂O·B₂O₃. The thermal run was carried out at 10°C/min in a 404 Netzsch DSC. It has several clearly delineated thermal events as marked (all in °C):
<table>
<thead>
<tr>
<th>R, Li/B ratio</th>
<th>Mole % Li₂O</th>
<th>T&lt;sub&gt;y&lt;/sub&gt;</th>
<th>T&lt;sub&gt;x&lt;/sub&gt;</th>
<th>T&lt;sub&gt;c&lt;/sub&gt;</th>
<th>T&lt;sub&gt;m onset&lt;/sub&gt;</th>
<th>T&lt;sub&gt;m endpoint&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5</td>
<td>60.0</td>
<td>315</td>
<td>369</td>
<td>382</td>
<td>692</td>
<td>790</td>
</tr>
</tbody>
</table>

**Figure 1.22** A Typical DSC thermogram [17]. It is from a lithium borate glass with R = 1.5, where R is the molar ratio of alkali oxide to boron oxide. Note that endothermic/exothermic directions are reversed from what was given earlier in the chapter.

These temperatures are determined as shown in the figure. Proprietary software was used to determine onset or other values of the required temperatures.

The fictive temperature is defined as the temperature at which the melt that formed the glass was at as the sample solidified may also be found from DSC. This is beyond the present discussion.

### 1.6 CASE STUDIES FROM GLASS SYSTEMS

#### 1.6.1 The Glass Transition Temperatures of Barium Borosilicate Glasses [18]
The $T_g$s of a large series of barium borosilicate glasses of the form R$\text{BaO.B}_2\text{O}_3.\text{KSiO}_2$ were determined. The results are shown as families of $K$, with $R$ varying widely as shown in Figure 1.23. The next illustration, Figure 1.24, depicts $N_4$, the fraction of four coordinated borons present in these glasses as a function of $R$ for fixed $K$ families as well [19]. The following trends are observed.

- All $T_g$ trends from various $K$ families resemble the $K = 0$ family except the trends are shifted towards higher $R$ as $K$ increases. This is indicative of the sharing of alkali between the borate and silicate network with the borate network determining the $T_g$ trend.

- The $T_g$ maximum increases as $K$ increases. This increase of the $T_g$ maximum is attributed to the formation of a Si-O-B network. In contrast, Figure 1.25 shows this feature is not strongly present in calcium borosilicate glasses, implying the absence of strong network–network interactions.

- The $T_g$ trends resemble closely the trends for $N_4$. However, unlike in the lithium borosilicate case [20], Figure 1.26, the $T_g$s remain high as $R$ increases. This is likely due to crosslinking of Ba to two oxygens in the network. The same effect resulting in enhanced $T_g$ values is present in the calcium borosilicate system as shown in Figure 1.25.

**Figure 1.23** The $T_g$s of barium borosilicate glasses of the form R$\text{BaO.B}_2\text{O}_3.\text{KSiO}_2$ [18].
Figure 1.24 The fraction of four-coordinated borons, $N_4$, of barium borosilicate glasses of the form $\text{RBaO.B}_2\text{O}_3.\text{KSiO}_2$ [19].

Figure 1.25 The $T_g$ s of calcium borosilicate glasses of the form $\text{RCaO.B}_2\text{O}_3.\text{KSiO}_2$ [18].
1.6.2 Stability Parameters in Lithium Borate Glasses [18]

Lithium borate glasses make a particularly good system to study thermal stability because of their relatively wide glass formation range, through the use of roller quenching. For glasses written RLi₂O.B₂O₃, this continuous range is from R = 0 to 2.8 (0 to 74 molar percent Li₂O) [12].

Table 1.4 depicts various literature definitions of stability parameters. Once the thermograms of the lithium borate glasses were measured and analyzed the following results were obtained as shown in Table 1.5 [18].
**Table 1.4** Glass stability parameters (temperatures in K) [17].

\[
\begin{align*}
K_{LL} &= \frac{T^h_x}{T_g + T_m} \\
K_H &= \frac{T^h_x - T_g}{T_m - T^h_x} \\
K_W &= \frac{T^h_x - T_g}{T_m} \\
K_T &= \frac{T_g}{T_m} \\
K_{SP} &= \frac{(T^h_x - T_g) (T^h - T^h_x)}{T_g} \\
K_1 &= T_m - T_g \\
K_2 &= T^h_x - T_g \\
K_3 &= \frac{T^h_x}{T_m} \\
K_4 &= \frac{(T_x - T_g) (T_c - T^h_x)}{T_m}
\end{align*}
\]
Table 1.5 Characteristic temperatures (°C) from lithium borate glasses.

<table>
<thead>
<tr>
<th>Mole %</th>
<th>Method*</th>
<th>( T_g )</th>
<th>( T_x )</th>
<th>( T_c )</th>
<th>( T_s )</th>
<th>( T_{m,\text{onset}} )</th>
<th>( T_{m,\text{endpoint}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>20.0</td>
<td>Carbonate method</td>
<td>460</td>
<td>597</td>
<td>622</td>
<td>726</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Solution method</td>
<td>461</td>
<td>588</td>
<td>614</td>
<td>770</td>
<td>–</td>
</tr>
<tr>
<td>0.4</td>
<td>28.6</td>
<td>Carbonate method</td>
<td>489</td>
<td>576</td>
<td>585</td>
<td>722</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Solution method</td>
<td>489</td>
<td>583</td>
<td>591</td>
<td>716</td>
<td>–</td>
</tr>
<tr>
<td>0.5</td>
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<td>Carbonate method</td>
<td>463</td>
<td>510</td>
<td>516</td>
<td>806</td>
<td>908</td>
</tr>
<tr>
<td>0.7</td>
<td>41.2</td>
<td>Carbonate method</td>
<td>459</td>
<td>494</td>
<td>511</td>
<td>636</td>
<td>820</td>
</tr>
<tr>
<td>0.86</td>
<td>46.2</td>
<td>Carbonate method</td>
<td>439</td>
<td>491</td>
<td>500</td>
<td>–</td>
<td>825</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Solution method</td>
<td>436</td>
<td>494</td>
<td>500</td>
<td>–</td>
<td>823</td>
</tr>
<tr>
<td>1.0</td>
<td>50.0</td>
<td>Carbonate method</td>
<td>411</td>
<td>445</td>
<td>452</td>
<td>–</td>
<td>836</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Solution method</td>
<td>420</td>
<td>480</td>
<td>488</td>
<td>–</td>
<td>819</td>
</tr>
<tr>
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<td>Solution method II</td>
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<td>475</td>
<td>483</td>
<td>–</td>
<td>818</td>
</tr>
<tr>
<td>1.5</td>
<td>60.0</td>
<td>Carbonate method</td>
<td>315</td>
<td>369</td>
<td>382</td>
<td>–</td>
<td>692</td>
</tr>
<tr>
<td>2.0</td>
<td>66.7</td>
<td>Solution method</td>
<td>265</td>
<td>298</td>
<td>300</td>
<td>596</td>
<td>643</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Solution method II</td>
<td>272</td>
<td>311</td>
<td>313</td>
<td>595</td>
<td>630</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Carbonate method</td>
<td>272</td>
<td>303</td>
<td>306</td>
<td>–</td>
<td>629</td>
</tr>
</tbody>
</table>

Estimated error in temperatures is approximately ±3–5°C.

*Glasses were prepared in two ways, from lithium carbonates and boric acid heated using a traditional furnace approach and by a solution route to glass formation using lithium hydroxide and boric acid solutions.

Most of the parameters for stability work reasonably well as guides for relative glass stability. In Figures 1.27a, 1.27b, 1.28a, and 1.28b are some representative stability results to show how careful DSC experiments maybe used to track critical cooling rates. Note that in each figure there is a presentation of a calibration curve found from glasses in the literature that confirm the connection between critical cooling rates and the stability parameter. Thus, it is possible to determine close values for the critical cooling rates of lithium borate glasses.
Figure 1.27 (a), Critical cooling rate versus the glass stability parameter $K_{LL}$ for several glasses [GeO2 (G), PbO.SiO2 (PS), Na2O.2SiO2 (NS2), 2MgO.2Al2O3.5SiO2 (M2A2S5), Li2O.2SiO2 (LS2), CaO.MgO.2SiO2 (CMS2), CaO.Al2O3.2SiO2 (CAS2), Li2O.2B2O3 (LB2)]. (b), the same $K_{LL}$ versus composition in the Li$_2$O–B$_2$O$_3$ system [17].

Figure 1.28 (a), Critical cooling rate versus the glass stability parameter $K_3$ for several glasses [GeO2 (G), PbO.SiO2 (PS), Na2O.2SiO2 (NS2), 2MgO.2Al2O3.5SiO2 (M2A2S5), Li2O.2SiO2 (LS2), CaO.MgO.2SiO2 (CMS2), CaO.Al2O3.2SiO2 (CAS2), Li2O.2B2O3 (LB2)]. (b), Glass stability parameter $K_3 = T_x^h/T_m$ versus composition [17].

The glasses with low borate content have stability parameters that are readily translated to critical cooling rates using the calibration curves in Figures 1.27 and 1.28, See Table 1.5. The resulting critical cooling rates approach $10^4$ to $10^5$ K/s—exactly what was needed to make
these glasses using roller quenching.

1.7 CONCLUSION TO THERMAL PROPERTIES

Using modern instrumentation, a large variety of thermal measurements are possible. These include characteristic temperatures associated with the glass transition, crystallization, melting, and more. These measurements maybe compared with models for atomic arrangement. Critical cooling rates for glass formation may be deduced by suitable combinations of the thermal parameters.

Oftentimes, thermal properties provide a mirror to atomic-level or intermediate range structure.

The $T_g$ itself is an important intrinsic value when choosing reliable and stable glasses for practical commercial purposes.

ACKNOWLEDGMENTS

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Ethan Lawrence is thanked for help with the figures.

REFERENCES

References on Density


**References on Thermal Properties**

14. See the *SciGlass Database*, for example.


2 INFRARED SPECTROSCOPY OF GLASSES

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2.1 INTRODUCTION

Infrared (IR) and Raman are two complementary techniques of vibrational spectroscopy both of which have been used extensively over the years in glass studies [1]. Raman spectroscopy of glasses is presented in Chapter 3 of this book [2], while aspects of infrared spectroscopy and applications to glasses are reviewed here. The lack of long-range order in glasses makes the impact of vibrational spectroscopy in structural studies of glasses greater than in those of crystalline solids [3, 4], where diffraction methods are probably more advantageous because of long-range order. IR spectroscopy was proven very useful in investigating the nature of glasses and especially that of glasses modified by metal oxides. This is because IR can provide information on the short-range order structure, using mid-infrared bands which are characteristic of the glass-forming oxides and on the metal ion-site interactions by analyzing intense bands in the far-infrared which arise from localized vibrations of the metal ions in glass [4–6].

Because glasses are strong absorbers of infrared radiation, most of the early mid-infrared spectra were measured by transmission on pellets of powdered glasses dispersed in suitable matrix materials, for example, alkali metal halide salts. However, this technique often leads to ion exchange [7] and sample hydrolysis [8] during glass grinding and pellet processing at high pressures. The latter phenomena lead to frequency shifts of absorption bands, and even to the appearance of bands in the infrared which are not representative of the pristine glass. Also, the use of alkali halide salts as matrix materials causes spectral distortions and non-reproducible intensities of absorption bands because such spectra originate from combination of transmission and reflection phenomena [9]. As a result, a measured phonon frequency does not coincide with that of the IR active transverse optical (TO) vibrational mode as it should, but is intermediate to that of the TO and LO (longitudinal optical) vibrational modes. The extent of this phenomenon depends on size and aggregation of glass particles, as well as on the dielectric constant of the salt matrix.

Compared to transmission measurements on metal halide salt pellets of powdered glasses, infrared reflectance spectroscopy of bulk glasses is an advantageous technique since the same pristine glass sample, that is, a polished slab, is used for data acquisition over a broad frequency range covering both the mid- and far-infrared spectral ranges. This advantage when combined with the capabilities of modern Fourier-transform spectrometers, and the
availability of software for analysis of reflectivity data, leads to the quantitative determination of the frequency-dependent optical and dielectric properties of glass. Therefore, the true band shapes of the TO and LO modes can be obtained, and this allows for the quantitative analysis of glass structure. These features make IR reflectance spectroscopy a very powerful tool in glass science, and this is reflected by the steadily increasing interest as shown in relevant publications [8–41].

Due to its non-destructive characteristics, IR reflectance spectroscopy finds a broad range of applications in glasses. They include the evaluation of glass structure as a function of composition of various glass-forming systems (e.g., References 8–23), and the monitoring of glass structure as it evolves during chemical and physical processes. The latter may refer to corrosion of glass surfaces [24–27], the evolution of glass network during sol-gel processing [28–30], ion exchange phenomena in glasses [31–33], the effects of fictive temperature [34, 35] and stress [36, 37] on glass structure, the evolution of structure as a function of depth from the glass surface [38], and thermal poling-induced structural rearrangements in the sub-anodic layer of bulk glasses exhibiting nonlinear optical properties [39–41].

Besides bulk glasses, equally important in technology are glasses in thin film forms. In the field of semiconductor devices, dielectric glass films have found wide applications as surface passivation layers for active junctions in silicon and as diffusion sources into silicon for the fabrication of p-n junctions [42, 43]. Advances in solid electrolytes have led to the development of glass films with ion conduction properties and great potential for use in all solid-state electrochemical devices [44–47]. Lately, glass thin films are considered also in the field of planar photonic devices as they can combine low losses, high amplification by rare earth doping and efficient second order nonlinear optical properties induced by thermal poling [48, 49].

The assessment of glass films by infrared spectroscopy is more complicated compared to bulk glasses. For example, if the film is considerably thick (1–10 μm) and aligned at exactly 90° relative to the incident beam, an interference pattern develops and certain absorption bands may be distorted by the background interference wave [50]. In the case of oblique incidence of the infrared radiation the Berreman effect should be considered as well [51]. This effect refers to the excitation of LO modes besides the expected TO modes, when infrared transmission or reflection spectra of thin films are measured with natural or p-polarized light at oblique incidence [52, 53]. Despite such complications, infrared transmission on films remains a very useful technique for the qualitative investigation of glass structure. In certain cases it can be applied for quantitative studies like the measurement of hydroxyl content in silica glass [54] and the determination of the fraction of short-range order structural units in thin films of ionic glasses [55].

The purpose of this chapter is to introduce infrared spectroscopy and its potential in glass studies with emphasis on glasses in bulk and thin film forms. We first give a brief review of the basics on refractive index and dielectric function that allow defining the optical and dielectric properties measured in the infrared. Then we outline the main methods used to treat reflectivity data measured on bulk materials which absorb strongly in the infrared, and give the formalism
to treat spectra of thin films which are either free-standing or deposited on infrared transmitting or reflecting substrates. Key aspects of the Fourier-transform infrared (FT-IR) instrumentation are presented, and the procedure of measuring infrared spectra is outlined using as example the reflectance spectrum of silica glass. Results of analysis of infrared reflectivity data by different methods are compared and discussed, and attention is drawn when making conclusions about glass structure by direct consideration of transmittance spectra of thin films. Finally, case studies are presented for bulk glasses and thin films by focusing on examples for the evaluation of structural parameters from IR spectra and the correlation with glass properties. To this aim, we have used as examples borate glasses which facilitate the separation of IR bands characterizing the glass network from those related to metal ion-site vibration modes. We conclude by summarizing key points of glass studies by infrared spectroscopy.

2.2 BACKGROUND AND THEORY

2.2.1 Refractive Index and Dielectric Function
The theory of the propagation of light waves in a material and the relations between the optical and the dielectric response functions are reviewed in several books [56–60] and in general articles on infrared spectroscopy [61, 62]. Therefore, we will briefly review here only the equations required to define the terms used in this chapter. For an isotropic material in which no energy is dissipated, Maxwell’s relation provides the wave equation which holds for each component of the electric field $E$. For light propagating in the $x$-direction one may write

$$E_x = E_0 e^{-i \omega (t-x/v)}$$

where $t$ is the time, $\omega$ is the angular frequency and $v$ is the velocity of light in the medium. The angular frequency is related to the frequency $\nu$ and the period $T$ of oscillation by $\omega = 2\pi \nu = 2\pi/T$, with the SI units being $[\omega] = s^{-1} = \text{radian/s}$, $[\nu] = s^{-1} = \text{Hz}$ and $[T] = \text{s}$.

The velocity of light in the medium $v$ is given in terms of the velocity of light in vacuum $c$.

$$v = \frac{c}{n} = \frac{c}{\sqrt{\epsilon}}$$

where $n$ is the refractive index and $\epsilon$ is the relative permittivity of the medium, that is, the permittivity relative to the value in vacuum (8.854×10$^{-14}$ F/cm). The permittivity is known also as the dielectric constant of the material and is related to the refractive index by Maxwell’s formula $\epsilon = n^2$.

For absorbing media, the propagation of light is governed by the complex refractive index $n^*(\nu)$

$$n^*(\nu) = n(\nu) + ik(\nu)$$
where the real \( n(\nu) \) and imaginary \( k(\nu) \) parts of the refractive index are now frequency-dependent functions. Likewise, the dielectric response of an absorbing material is described by the complex dielectric function

\[
\varepsilon^*(\nu) = \varepsilon_1(\nu) + i\varepsilon_2(\nu)
\]  

(2.4)

Because of the relation \( \varepsilon^*(\nu) = [n^*(\nu)]^2 \), the computation of the real and imaginary parts of the dielectric function is straightforward in terms of \( n(\nu) \) and \( k(\nu) \).

\[
\varepsilon_1(\nu) = n^2(\nu) - k^2(\nu)
\]  

(2.5)

\[
\varepsilon_2(\nu) = 2n(\nu)k(\nu)
\]  

(2.6)

The dielectric function is an important property of the material because it is related to the complex polarizability \( p^*(\nu) \).

\[
\varepsilon^*(\nu) = 1 + Np^*(\nu)
\]  

(2.7)

where \( N \) is the number of oscillators in the sample and the polarizability \( p^*(\nu) \) is directly related to the chemical bonding in the material. In particular, the absorption component of the dielectric function, \( \varepsilon_2(\nu) \), is related to the number and type of polarizable bonds in the sample while the real part, \( \varepsilon_1(\nu) \), is the dispersion component.

Combination of Eqs. 2.1–2.3 for an absorbing medium yields the following modified form for \( E_y \):

\[
E_y = E_0 e^{-i\omega[\nu - n(\nu)/c]} e^{-\omega k(\nu)x/c}
\]  

(2.8)

Compared to Eq. 2.1, which holds for a transparent medium, the above expression shows that there is now an additional term which describes the damping of the light wave travelling in the \( x \)-direction. The energy carried by the wave is proportional to the mean square \( <E_y^2> = I \) which diminishes according to the Lambert's law:

\[
I(\nu) = I_0(\nu) e^{-2\omega k(\nu)x/c} = I_0(\nu) e^{-\alpha(\nu)x}
\]  

(2.9)

where \( \alpha(\nu) \) is the absorption coefficient defined by

\[
\alpha(\nu) = \frac{4\pi\nu k(\nu)}{c}
\]  

(2.10)

When the frequency is expressed in wavenumbers (cm\(^{-1}\)), the absorption coefficient takes the form \( \alpha(\tilde{\nu}) = 4\pi\tilde{\nu}k(\tilde{\nu}) \) where \( \tilde{\nu} = \nu/c \). The damping of light in the material can be expressed also in terms of its absorbance \( A(\nu) \),

\[
A(\nu) = \frac{\alpha(\nu)d}{2.303}
\]  

(2.11)
where \( d \) is the sample thickness. An optical function used also frequently in spectroscopy is the transmittance \( T(\nu) \) of the sample which is defined in terms of Eq. 2.9 as the ratio of the transmitted intensity to the intensity of the incident radiation,

\[
T(\nu) = \frac{I(\nu)}{I_0(\nu)} = e^{-\alpha(\nu)d}
\]  

Equations 2.11 and 2.12 give the simple relation \( A(\nu) = -\log T(\nu) \) between absorbance and transmittance.

It is clear from the above that the quantitative characterization of a material can be made by accurate determination of its frequency-dependent dielectric function or refractive index. These are fundamental material's properties which are related directly to chemical composition, structure and bonding. Other optical properties can be derived easily from the refractive index. Experimental techniques and analysis methods for the evaluation of dielectric function and refractive index in the infrared are considered next. Emphasis is placed on bulk materials and thin films as these forms of solids are encountered frequently in glass studies and applications.

### 2.2.2 Reflectance Spectroscopy of Bulk Materials

The reflectance spectrum \( R(\nu) \) of a sample is defined as the ratio of the reflected intensity \( I(\nu) \) to the intensity of the incident radiation \( I_0(\nu) \).

\[
R(\nu) = \frac{I(\nu)}{I_0(\nu)} = r^2(\nu)
\]  

where \( r(\nu) \) is the amplitude of the complex reflectivity coefficient \( r^*(\nu) = r(\nu)e^{i\theta(\nu)} \) and \( \theta(\nu) \) is the phase shift on reflection.

In this section we deal with bulk samples absorbing strongly in the infrared, that is, samples of semi-infinite thickness and negligible transmittance in the infrared region. In this case, only reflection from the first interface of air (vacuum) with the sample contributes to \( R(\nu) \) in Eq. 2.13. For samples of finite thickness (e.g., thin glass films) multiple internal reflections need to be considered for the correct interpretation of the reflectance and transmittance spectra. Therefore, the case of thin films will be examined separately in Section 2.3. In the following we will review the two broadly applied methods for the treatment of reflectivity data obtained from bulk samples, that is, Kramers–Krönig transformation and dispersion analysis.

#### 2.2.2.1 Kramers-Krönig Transformation

The relation between reflectance \( R(\nu) \) and optical properties \( (n(\nu), k(\nu)) \) of bulk samples depends on the angle of incidence and the polarization of the incident radiation [56]. For normal incidence of radiation \( R(\nu) \) is given by the expression
Also, for normal incidence the complex reflectivity coefficient \( r^*(ν) \) takes the form

\[
 r^*(ν) = r(ν)e^{iθ(ν)} = \frac{n^*(ν) - 1}{n^*(ν) + 1}
\]  

(2.15)

Equating the real and imaginary parts in the above equation leads to the following Fresnel formulae for normal incidence:

\[
 n(ν) = \frac{1 - r^2(ν)}{1 + r^2(ν) - 2r(ν) \cos θ(ν)}
\]  

(2.16)

\[
 k(ν) = \frac{2r(ν) \sin θ(ν)}{1 + r^2(ν) - 2r(ν) \cos θ(ν)}
\]  

(2.17)

Since \( r(ν) \) is obtained directly from the experimental reflectance spectrum, \( r(ν) = [R(ν)]^{1/2} \), the only parameter required to calculate the \( n(ν) \) and \( k(ν) \) spectra from Eqs. 2.16 and 2.17, respectively, is the spectrum of the phase shift \( θ(ν) \). This is calculated by the Kramers–Krönig (KK) transformation [63, 64] over the entire frequency spectrum

\[
 θ(ν) = \frac{2ν}{π} P \int_0^∞ \frac{\ln r(ν_i) - \ln r(ν)}{ν^2 - ν_i^2} dν_i
\]  

(2.18)

where \( P \) denotes the Cauchy principal value of the integral. Equations 16–18 show that the KK analysis of the experimental reflectance spectrum of a bulk material allows for the direct calculation of \( n(ν) \) and \( k(ν) \). The subsequent evaluation of dielectric properties from \( n(ν) \) and \( k(ν) \), Eqs. 2.5–2.7, relates the measured reflectance with the dielectric properties and, thus, with fundamental molecular vibrations, chemical bonding, and structure of the material.

### 2.2.2.2 Dispersion Analysis

The alternative method for treating reflectivity data is the dispersion analysis, where an appropriate model for the dielectric function is employed to calculate the optical properties from the model. The adjustable parameters of the model are then determined by best fitting the calculated reflectance to the experimentally measured reflectance spectrum.

According to the classical dispersion theory, which was originally applied for the treatment of infrared reflectance spectra of crystals [65], the sample is considered as a system of independent damped harmonic oscillators and the complex dielectric function \( ε^*(ν) \) is modeled as follows:
\[ \varepsilon^*(v) = \varepsilon_1(v) + i\varepsilon_2(v) = \varepsilon_\infty + \sum_j \frac{\Delta \varepsilon_j \nu_j^2}{\nu_j^2 - \nu^2 - i\nu \Gamma_j} \]  \hspace{1cm} (2.19)

where the summation is over \( j \) Lorentzian oscillators each one characterized by three parameters, \( \nu_j \) = resonance frequency (transverse-optical), \( \Gamma_j \) = bandwidth (homogeneous line broadening) and \( \Delta \varepsilon_j \) = dielectric strength. \( \varepsilon_\infty \) is the dielectric constant at high frequencies that takes into account the electronic contributions, and is often equal to the square of the refractive index measured in the visible region. The following analytical solutions for \( \varepsilon_1(v) \) and \( \varepsilon_2(v) \) can be easily derived from Eq. 2.19:

\[ \varepsilon_1(v) = \varepsilon_\infty + \sum_j \Delta \varepsilon_j \frac{\nu_j^2 - \nu^2}{(\nu_j^2 - \nu^2)^2 + \Gamma_j^2 \nu^2} \]  \hspace{1cm} (2.20)

\[ \varepsilon_2(v) = \sum_j \Delta \varepsilon_j \frac{\Gamma_j \nu}{(\nu_j^2 - \nu^2)^2 + \Gamma_j^2 \nu^2} \]  \hspace{1cm} (2.21)

Setting \( \nu = 0 \) in Eq. 2.20 yields the static dielectric constant \( \varepsilon_0 \) of the material, \( \varepsilon_0 \equiv \varepsilon_1(v = 0) \):

\[ \varepsilon_0 = \varepsilon_\infty + \sum_j \Delta \varepsilon_j \]  \hspace{1cm} (2.22)

The parameters \( \nu_j, \Gamma_j \) and \( \Delta \varepsilon_j \) of each oscillator and the value of \( \varepsilon_\infty \) are determined by best fitting the calculated reflectance to the experimental reflectance spectrum. The reflectance spectrum is calculated from Eq. 2.14 where \( n(v) \) and \( k(v) \) are written in terms of \( \varepsilon_1(v) \) and \( \varepsilon_2(v) \) as follows:

\[ n(v) = \left\{ \frac{1}{2} [(\varepsilon_1^2(v) + \varepsilon_2^2(v))^{1/2} + \varepsilon_1(v)] \right\}^{1/2} \]  \hspace{1cm} (2.23)

\[ k(v) = \left\{ \frac{1}{2} [(\varepsilon_1^2(v) + \varepsilon_2^2(v))^{1/2} - \varepsilon_1(v)] \right\}^{1/2} \]  \hspace{1cm} (2.24)

As an example of classical dispersion, Figure 2.1 shows the response of a model material comprising two Lorentzian oscillators with parameters \( \nu_1 = 1080 \text{ cm}^{-1}, \Gamma_1 = 55 \text{ cm}^{-1}, \Delta \varepsilon_1 = 0.65, \) and \( \nu_2 = 460 \text{ cm}^{-1}, \Gamma_2 = 40 \text{ cm}^{-1}, \Delta \varepsilon_2 = 0.90, \) and high frequency dielectric constant \( \varepsilon_\infty = 2.15. \) The dielectric properties are computed from Eqs. 2.20 and 2.21, the optical properties from Eqs. 2.23 and 2.24 and the reflectance of the material from Eq. 2.14. Besides visualizing different presentations of the infrared response of the model material, Figure 2.1 shows that the real part of the dielectric function goes through negative values in frequency ranges above resonances \( \nu_1 \) and \( \nu_2. \)
Figure 2.1 Infrared response of a two-Lorentzian-oscillator model; reflectance spectrum $R(\nu)$ (a), real $\varepsilon_1(\nu)$ and imaginary $\varepsilon_2(\nu)$ part of the dielectric function (b), and real $n(\nu)$ and imaginary $k(\nu)$ part of the refractive index (c). The dielectric function $\varepsilon^*(\nu)$ is modeled according to Eq. 2.19 using the parameters: $\nu_1 = 1080 \text{ cm}^{-1}$, $\Gamma_1 = 55 \text{ cm}^{-1}$, $\Delta \varepsilon_1 = 0.65$, and $\nu_2 = 460 \text{ cm}^{-1}$, $\Gamma_2 = 40 \text{ cm}^{-1}$, $\Delta \varepsilon_2 = 0.90$. The high frequency dielectric constant is $\varepsilon_\infty = 2.15$.

Galeener and coworkers [14] argued that, in analogy to polar crystals, peaks in the $\varepsilon_2(\nu)$ spectra of glasses mark the frequencies of strong absorption of TO electromagnetic waves for which the electric polarization $\mathbf{P}$ is transverse to the propagation vector $\mathbf{k}$ of the IR wave ($\mathbf{P} \perp \mathbf{k}$). Similarly, strong absorption of LO waves ($\mathbf{Pk}$) corresponds to peaks in the energy loss function which is defined as the imaginary part of $-1/\varepsilon^*(\nu)$.

$$\text{Im}\left(-\frac{1}{\varepsilon^*(\nu)}\right) = \frac{\varepsilon_2(\nu)}{\varepsilon_1^2(\nu) + \varepsilon_2^2(\nu)} = \frac{2n(\nu)k(\nu)}{[n^2(\nu) + k^2(\nu)]^2}$$  \hspace{1cm} (2.25)

The transverse-optical and longitudinal-optical responses of the two-Lorentzian-oscillator
model defined above are compared in Figure 2.2 and manifest large LO-TO splittings for this model: \( \text{LO}_1 - \text{TO}_1 = 160 \text{ cm}^{-1} \) and \( \text{LO}_2 - \text{TO}_2 = 63 \text{ cm}^{-1} \). Large values of LO-TO splitting characterize vibrations of polar bonds as in inorganic crystals and glasses, while a small LO-TO splitting indicates vibrations of covalent bonds as in organic molecules and polymers.

**Figure 2.2** Comparison of the reflectance spectrum \( R(\nu) \) (a) with the imaginary part \( \epsilon_2(\nu) \) (b) and the energy-loss function \( \text{Im}(-1/\epsilon^\ast(\nu)) \) (c) of the dielectric function \( \epsilon^\ast(\nu) \), for the two-Lorentzian-oscillator model used in Figure 2.1.

Instead of Eq. 2.19, some authors prefer the so-called factorized form of \( \epsilon^\ast(\nu) \) for classical dispersion.

\[
\epsilon^\ast(\nu) = \epsilon_\infty \prod_j \frac{\nu_{j\text{LO}}^2 - \nu^2 + i\Gamma_{j\text{LO}} \nu}{\nu_{j\text{TO}}^2 - \nu^2 + i\Gamma_{j\text{TO}} \nu} \tag{2.26}
\]

The adjustable parameters in Eq. 2.26 are the frequencies and bandwidths of the TO and LO
modes together with $\epsilon_\infty$. The dielectric strength $\Delta \epsilon_j$ of each vibrational mode is calculated from the LO-TO splitting according to the expression

$$\Delta \epsilon_j = \epsilon_\infty \sqrt{\frac{2}{v_{j\text{TO}}} \prod_{k \neq j} \frac{(v_{k\text{LO}}^2 - v_{j\text{TO}}^2)}{(v_{k\text{TO}}^2 - v_{j\text{TO}}^2)}}$$

(2.27)

Setting $\nu = 0$ in Eq. 2.26 yields the Lyddane–Sachs–Teller relationship:

$$\frac{\epsilon_0}{\epsilon_\infty} = \prod_j \frac{v_{j\text{LO}}^2}{v_{j\text{TO}}^2}$$

(2.28)

For a discussion on the merits of the factorized form for $\epsilon^*(\nu)$ and its applications to glasses the reader is referred to publications by Gervais and coworkers [16, 60].

Compared to crystals, the local structural environment in glasses is not uniform and this leads to inhomogeneous broadening of the resonance peaks. To treat this problem Efimov and coworkers [21] proposed the so-called convolution model, which is an extension of the classical dispersion theory and very useful for the quantitative treatment of infrared reflectance spectra of glasses. In this model, the complex dielectric function involves Lorentzian oscillators with Gaussian band broadening.

$$\epsilon^*(\nu) = \epsilon_\infty + \sum_j \frac{\Delta \epsilon_j v_j^2}{\sqrt{2\pi} \sigma_j} \int_{-\infty}^{+\infty} \frac{\exp[-(x-x_j)^2/2\sigma_j^2]}{x^2 - \nu^2 - i\Gamma_j \nu} \, dx$$

(2.29)

Here $x$ is the variable frequency of oscillators, $\sigma_j$ is the standard deviation expressing the distribution of frequency of the $j$th oscillator around its central frequency $v_j$, and $\Delta \epsilon_j$, $\Gamma_j$ and $\epsilon_\infty$ have the usual meaning. With four adjustable parameters per oscillator the convolution model is mathematically more flexible than classical dispersion theory, which has three adjustable parameters per oscillator. As a result, the convolution model gives better fits for the reflectance spectra of glasses.

The large number of adjustable parameters in the convolution model reduces its usefulness when analyzing complex reflectance spectra of glasses [26]. For cases where the inhomogeneous broadening is much larger than the homogeneous bandwidth, MacDonald and coworkers [26] approximated the absorption bands by simple Gaussian distributions. In this approach, known as Gaussian dispersion analysis, the imaginary part of the dielectric function is written as a sum of Gaussian terms (oscillators).

$$\epsilon_2(\nu) = \sum_j \frac{A_j}{\sqrt{2\pi} \Delta v_j} \exp \left[ -\frac{1}{2} \frac{(\nu - v_j)^2}{\Delta v_j^2} \right]$$

(2.30)
The number of adjustable parameters per oscillator is now reduced to three and involves the center resonance frequency $\nu_j$, the bandwidth $\Delta \nu_j$ and the amplitude $A_j$. Unlike classical dispersion, the real part of the dielectric function in the Gaussian dispersion analysis is calculated by Kramers–Krönig transformation of the corresponding imaginary part, Eq. 2.30. The two dielectric components are then employed to obtain the adjustable parameters by best fitting the reflectance spectrum. The Gaussian dispersion method was found very effective in surface studies of materials, for example, in probing the time evolution of the leaching process of glass surfaces.

Recently, De Sousa Meneses and coworkers [23] introduced a new dielectric function model for the quantitative analysis of infrared reflectance spectra of glasses. This model is known as the causal Voigt model, as it includes terms in the dielectric function based on the causal version of the Voigt profile (i.e., convolution of Gaussian and Lorentzian functions). The authors also developed the Focus software for curve-fitting and made it freely available on the web [66]. The Voigt model reproduces very satisfactorily reflectivity spectra of glasses both at high frequencies and in the far-infrared region of the spectrum. The reader may consult relevant publications for the formalism of the Voigt model, comparisons with the convolution model, and applications to glasses [23].

In closing this section we note that the reflectance-fitting methods, as the ones reviewed above, require a model for the dielectric function and need as input in the fitting procedure the number of oscillators in order to reconstruct $n(\nu)$ and $k(\nu)$ from the measured reflectance spectrum. Compared to fitting, the Kramers–Krönig analysis allows for the direct calculation of $n(\nu)$ and $k(\nu)$ from the experimental reflectance without reference to any model for the dielectric response. Comparison of results obtained by the two methods of analysis will be presented and discussed in Section 2.4.1.

### 2.2.3 Infrared Spectra of Thin Films

The transmittance, $T(\nu)$, of bulk glasses is zero in the infrared at least in the region of the fundamental vibrational modes of the glass network. This facilitates the measurement of good quality reflectance spectra, $R(\nu)$, and allows for the evaluation of the optical and dielectric properties by employing the methods reported above for analyzing $R(\nu)$. For free-standing glassy films, with thickness in the order of 1 $\mu$m, both $T(\nu)$ and $R(\nu)$ measurements can be made in the infrared and result in complicated spectra due to superposition of optical effects. These effects result from multiple reflections of the incident infrared beam inside the film, lead to the development of interference fringes in the measured spectra and affect strongly the actual spectrum of the film. This calls for special attention in order to separate the influence of optical effects from the structure-related vibrational signatures of the film material.

For thin films deposited on substrates, the measured spectra depend on the optical properties of both film and substrate. For substrates which are transparent in the infrared, the measured $T(\nu)$ and $R(\nu)$ spectra are characterized also by interference fringes which result from multiple reflections of the incident beam in both film and substrate. For thin films on metallic substrates, the infrared measurements can be made in the reflection-absorption configuration, R-A, which...
combines double transmissions through the film with reflections from the metallic surface. Besides the strong effect exerted by the dielectric response of the metallic substrate, the R-A spectrum is influenced by interference fringes due to multiple transmissions in the film.

The in-depth evaluation of the spectra of thin films can be made on the basis of rigorous expressions for reflectance and transmittance for the film substrate system, as reported in previous infrared studies of thin films of glassy materials [55, 67, 68]. A brief description of the necessary formalism for the analysis of transmittance and reflectance spectra of thin films is given here. In particular, we consider the case of normal incidence of light on a four-layer configuration vacuum(0)–film(1)–substrate(2)–vacuum(3), where each layer is characterized by a thickness \( d_k \) and components \( n_k \) (real) and \( k_k \) (imaginary) of the complex refractive index \( (k = 0−3) \). The complete formulae for \( T(\nu) \) and \( R(\nu) \) take into account all multiple interferences in both film and substrate and are as follows:

\[
T = \frac{i^2 t_1 t_2 t_3 e^{-2(y_1+y_2)}}{A + B \cos(2\theta_2) + C \sin(2\theta_2)} [6pt]
\]

\[
R = \frac{D + F \cos(2\theta_2) + G \sin(2\theta_2)}{A + B \cos(2\theta_2) + C \sin(2\theta_2)}
\]

where

\[
\theta_k = \frac{2\pi}{\lambda} n_k d_k
\]

and

\[
\gamma_k = \frac{2\pi}{\lambda} k_k d_k
\]

The frequency dependence has been omitted for convenience in the above expressions. Also, \( n_k, k_k, \) and \( d_k \) in Eqs. 2.33 and 2.34 denote the real and imaginary parts of the refractive index and the thickness of layers 1 (film) or 2 (substrate). The terms \( A, B, C, D, F, \) and \( G \) are functions of the thickness \( d \), the real \( (n) \), and imaginary \( (k) \) parts of the refractive index of thin film and substrate and are given in analytical form in Reference 67.

Optically polished silicon wafers of 0.6 mm in thickness were used in Reference 67 as typical transparent substrates for infrared measurements of deposited glassy films. The period of interference pattern due to multiple reflections in such Si substrates is \( \delta = 1/(2n_{Si}d_{Si}) \approx 2.5 \text{ cm}^{-1} \) using \( n_{Si} = 3.4 \) and \( d_{Si} = 0.6 \text{ mm} \). Therefore, the influence of Si interference pattern on the infrared spectra of glassy films can be optically averaged, and thus eliminated, by measuring infrared spectra at low resolution (e.g., 10 cm\(^{-1}\)). This is done theoretically be averaging Eqs. 2.31 and 2.32 with respect to variable \( \theta_2 \), and this allows the direct comparison of simulated spectra with low resolution infrared measurements. Averaging leads to the following expressions:
with $S = \sqrt{A^2 + B^2 + C^2}$.

The infrared spectra of free-standing films are simulated using Eqs. 2.31 and 2.32, or Eqs. 2.35 and 2.36, where the refractive index of substrate is replaced by the one for vacuum. To compare the infrared response of glass thin films deposited on Si or metallic (e.g., gold) substrates with those of the corresponding bulk glasses, one can simulate the $T(\nu)$ and $R(\nu)$ spectra of the thin film substrate system using as input the complex refractive index of the bulk glass and of the substrate, while leaving the film thickness as the only adjustable parameter. Optical properties of bulk glasses, that is, $n(\nu)$ and $k(\nu)$ spectra, can be determined from measured reflectance spectra through, for example, the Kramers–Krönig analysis presented above. Optical properties of silicon can be calculated by inversion of the measured low resolution transmittance and reflectance spectra [67]. The frequency-dependent refractive index of metallic substrates (e.g., gold) can be obtained by modeling the complex dielectric function with the Drude model and using known values for the plasma frequency and the damping constant of the metal.

We will use the formalism reviewed here to examine in Section 2.4.2 transmittance spectra of free-standing glass films as a function of thickness, in order to demonstrate the effect of interference patterns on the infrared spectral profiles. Also, we will show in Section 2.4.2 that the comparison of measured and modeled spectra of thin films on substrates is a very effective tool for revealing the real structure of glass thin films.

### 2.3 INSTRUMENTATION

Rapid-scan Fourier-transform spectrometers are used nowadays for the measurement of infrared spectra. As the monochromator (i.e., prism or grating) is the heart of conventional dispersive spectrometers, the key optical element of a Fourier-transform infrared (FT-IR) spectrometer is the Michelson interferometer. It consists of two perpendicular plane mirrors (one is stationary and the other moves at a constant velocity), and a beam splitter mounted at 45° relative to these mirrors. The radiation from the infrared source is partially reflected to the fixed mirror and partially transmitted to the movable mirror. After the two beams return to the beam splitter they interfere and the signal resulting from a polychromatic or continuous source takes the form

$$I(\nu) = 2 \int_0^\infty I(\nu)[1 + \cos(2\pi \nu s)] d\nu$$  

(2.37)
where \( s \) is the optical path difference of the two beams, also called retardation, and \( \tilde{\nu} \) is the wavenumber of radiation. The signal \( I(s) \) contains a constant part which is independent of \( s \),

\[
I_\infty = 2 \int_0^\infty I(\tilde{\nu})d\tilde{\nu}
\]

and an oscillating component which takes positive and negative values,

\[
F(s) = 2 \int_0^\infty I(\tilde{\nu}) \cos(2\pi \tilde{\nu} s)d\tilde{\nu}
\]

\( F(s) \) is responsible for the characteristic appearance of the interference signal and is called the interferogram function. In a FT-IR experiment, the infrared signal \( F(s) \) is measured first as a function of retardation \( s \) of the Michelson-interferometer mirrors and then it is Fourier-transformed to calculate the signal \( I(\tilde{\nu}) \), that is, the single-beam spectrum in the frequency domain.

\[
I(\tilde{\nu}) = 2 \int_0^\infty F(s) \cos(2\pi \tilde{\nu} s)ds
\]

According to Eq. 2.40, the calculation of \( I(\tilde{\nu}) \) requires the measurement of the interferogram \( F(s) \) in a range of \( s \) values from zero to infinity. In practice, the interferogram \( F(s) \) can only be recorded to a limited maximum retardation, \( s_{\text{max}} \). Because of this technical limitation, the calculation of the integral requires a mathematical manipulation called apodization. The maximum retardation \( s_{\text{max}} \) used in the FT-IR measurement and the type of apodization function employed for the calculation of \( I(\tilde{\nu}) \) determine the spectral resolution, \( \Delta \tilde{\nu} \). For rectangular apodization, the spectral resolution is given by \( \Delta \tilde{\nu} = 1/(2s_{\text{max}}) \) and for triangular apodization it becomes \( \Delta \tilde{\nu} = 1/s_{\text{max}} \). In contrast to infrared measurements with conventional dispersive spectrometers, the resolution of FT-IR measurements is constant over broad spectral ranges because no grating and slit alteration is necessary. The reader can consult specialized books on Fourier-transform IR spectroscopy for more details on data acquisition and treatment (see, e.g., References 69–71).

Contemporary FT-IR spectrometers are single-beam instruments. They include the Bruker Vertex 80v vacuum spectrometer [72] whose optical layout is shown in Figure 2.3. Radiation from either of the two sources (mid-infrared, MIR, and far-infrared, FIR) can be selected and passed through a variable aperture (APT) to the Michelson-type interferometer. The modulated infrared beam is then directed to the sample and detector (D1, D2) compartments. The MIR light source is a globar (i.e., a U-shaped silicon carbide piece) that emits mid-infrared radiation and the FIR source is a mercury lamp that emits in the far-infrared. A KBr beam splitter is used for MIR measurements (350–7500 cm\(^{-1}\)) and a multilayer beam splitter is used
in the FIR range (30–680 cm$^{-1}$). Typical detectors of the Bruker Vertex 80v spectrometer are RT-DLaTGS with KBr window for MIR and RT-DTGS with polyethylene window for FIR. Combination with a Mylar 125 μm beam splitter and a silicon bolometer cooled with liquid He can extend the FIR range to lower frequencies (35–5 cm$^{-1}$).

**Figure 2.3** Optical layout of the Fourier-transform Bruker Vertex 80v spectrometer. Infrared radiation from a mid-infrared (MIR) or far-infrared (FIR) source passes through the variable aperture (APT) to the beam splitter (BMS) of the Michelson-type interferometer and then directed to the sample and detector (D1, D2) compartments. (Reprinted with permission from Bruker Optics)

Besides transmission FT-IR measurements, commercially available accessories can be inserted in the sample compartment to permit measurements in specular reflectance, diffuse reflectance and attenuated total reflectance (ATR) modes [69–71].

Compared to conventional dispersive infrared spectrometers, FT-IR spectrometers always produce single-beam spectra. A typical experiment involves measuring both the reference and the sample interferograms. An example is shown in **Figure 2.4** for the process of measuring the specular reflectance spectrum of a polished slab of vitreous silica, v-SiO$_2$. The reflectance accessory used here allows for measurements at nearly normal incidence (11° off-normal). The
interferograms in Figure 2.4 were measured at room temperature with 4 cm$^{-1}$ resolution and represent the average of 200 scans. As observed in Figure 2.4a the signal (interferogram) measured from the sample (v-SiO$_2$) is greatly modified relative to that obtained for the reference gold mirror and this indicates strong interaction of the infrared radiation with the material through excitation of the infrared active vibrational modes of silica glass. The single-beam spectra in Figure 2.4b were obtained by Fourier-transformation of the corresponding interferograms, and are employed to calculate the reflectance spectrum $R$ shown in Figure 2.4c from the ratio of sample to reference single-beam spectra. The measured specular reflectance spectrum of v-SiO$_2$ is in good agreement with reported spectra [13, 14].

Figure 2.4 (a) Interferograms $F(s)$ (arb. units) measured in specular reflectance at 11° off-normal from a gold mirror (reference) and a polished slab of vitreous SiO$_2$ (sample); (b) Single-beam spectra $I(\tilde{v})$ (arb. units) obtained by Fourier-transformation of interferograms $F(s)$ shown in (a); and (c) Reflectance spectrum $R(\tilde{v})$ of silica glass in the far- and mid-IR range calculated by $R(\tilde{v}) = I(\tilde{v})_{sample}/I(\tilde{v})_{reference}$ (for details see text).

Uncertainties in determining the optical and dielectric properties of materials result from
errors associated with infrared measurements and with the method used to treat the measured data. For well-polished glass samples, the error in measuring reflectance spectra in the mid-infrared region is typically less than 0.5%. It is noted though that this error increases for measurements in the far-infrared if the surface roughness starts becoming comparable or greater than the wavelength of infrared radiation. Similar to reflectance measurements is the error involved in transmission measurements on thin films which have smooth and flat surfaces.

2.4 ANALYSIS OF INFRARED DATA

2.4.1 Bulk Glasses

The direct analysis of reflectivity data by Kramers–Krönig (KK) transformation requires evaluation of the phase shift integral, $\theta(\nu)$, according to Eq. 2.18. As discussed by Gaskell and Jonson [13], the KK analysis introduces errors for the following reasons.

- The integral extends over the entire frequency range, while the experimental spectrum is frequency-limited. This problem is considerably reduced now because modern spectrometers allow for the acquisition of continuous reflectivity spectra in a broad frequency range (e.g., 30–7500 cm$^{-1}$), and also appropriate modeling and software is available to extrapolate the reflectivity data to $\nu \to 0$ and $\nu \to \infty$.

- Equation 2.18 has singularities at the resonance frequencies $\nu = \nu_j$ and, thus, values of $\theta$ at frequencies near $\nu_j$ are subject to uncertainty. Computational methods to avoid the problem of singularities have been presented and discussed [13, 19, 73].

- At the high frequency edge of a strong reflection band, the value of $R(\nu)$ can be as low as $10^{-5}$. Because $R(\nu)$ enters Eq. 2.18 in logarithmic form, measurements over the region of low $R(\nu)$ should be made with an accuracy comparable to that of the rest of the spectrum. Experimental and computational methods to deal with this problem have been discussed [13].

In the infrared study of vitreous silica and quartz by KK transformation of the reflectance spectra, Gaskell and Jonson [13] estimated the maximum error in $\epsilon_2(\nu)$ to be about 5% at resonance frequencies and about 2.5% over the central regions of the spectra.

In comparison to KK analysis, the dispersion analysis of reflectivity data is not sensitive to the problems mentioned above. However, dispersion analysis requires more complicated computational procedures besides the need for a specific microscopic model for the dielectric function. To compare the two methods of analysis (i.e., KK transformation vs. reflectivity fitting), we present in Figure 2.5 results for the typical oxide glass $K_2O.2B_2O_3$. The infrared reflectivity was measured in the range 30–5000 cm$^{-1}$ as shown in part in Figure 2.5a by the solid line spectrum. The dotted line spectrum in the same figure is the result of best fitting Eq. 2.19 (i.e., classical dispersion) to the experimental reflectivity using 12 Lorentzian oscillators. As observed in Figure 2.5a, the agreement between the two spectra is very satisfactory.
Figure 2.5b compares the refractive index spectrum, \(n(\nu)\), obtained by the KK analysis (solid line) with that resulted from the reflectivity fitting procedure (dotted line). The corresponding spectra of \(k(\nu)\), \(\epsilon_1(\nu)\) and \(\epsilon_2(\nu)\) are shown in frames (c), (d), and (e) of Figure 2.5.

Figure 2.5 Comparison of results by Kramers–Krönig transformation (KK), Eq. 2.18, and reflectance fitting by classical dispersion theory (fit), Eq. 2.19, employed for the analysis of the infrared reflectance spectrum of glass \(\text{K}_2\text{O.2B}_2\text{O}_3\). The experimental reflectance spectrum (solid line) and the best fit spectrum (circles) are shown in (a). The results of KK analysis (full lines) and curve-fitting (circles) for the \(n(\nu)\), \(k(\nu)\), \(\epsilon_1(\nu)\) and \(\epsilon_2(\nu)\) spectra are shown in (b), (c), (d), and (e), respectively.

It is clear from Figure 2.5 that the results of the two methods of analysis are almost identical in very broad frequency ranges. Some discrepancies observed at very low frequencies are due to the fact that the experimental spectrum was extrapolated below 30 cm\(^{-1}\) in order to perform the KK transform. Besides fitting with classical dispersion theory, results of other models of dispersion analysis were shown to be comparable to those of the KK inversion including the convolution model [21] and the Voigt model [23].
As stated above, KK transformation and dispersion analysis give comparable results for the optical \( n(v) \) and \( k(v) \) and dielectric \( \epsilon_1(v) \) and \( \epsilon_2(v) \) properties of glasses. If additional information is required regarding the nature and number of oscillators giving rise to the infrared response of the material, then the dispersion analysis provides such information at this level of data treatment. This is because the nature \( (v_j, \Delta v_j, \text{and} \Delta \epsilon_j) \) and number of oscillators are adjustable parameters and required input, respectively, in the process of dispersion analysis. However, this is not needed for the KK transformation of reflectivity data. Thus, to obtain information on oscillators from KK analysis, a second stage of data treatment is required and this is done by deconvoluting a KK-derived response function. Such a function can be the absorption coefficient spectrum \( \alpha(v) \) \[^{[8,74]}\], which for typical glasses is best described by Gaussian profiles.

\[
\alpha(v) = \sum_j \alpha_j \exp \left[ -\frac{2(v - v_j)^2}{\Delta v_j^2} \right] \tag{2.41}
\]

Each Gaussian band is characterized by the resonance frequency \( v_j \), the bandwidth \( \Delta v_j \) and the value of the absorption coefficient at the resonance frequency, \( \alpha_j \). While these parameters determine the nature of oscillator \( j \), the number of \( j \)-type oscillators is related to the integrated intensity \( <A>_j \) of the \( j \)th Gaussian band.

\[
<A>_j \equiv \int_{-\infty}^{\infty} \alpha_j \exp \left[ -\frac{2(v - v_j)^2}{\Delta v_j^2} \right] dv = \sqrt{\pi/2} \Delta v_j \alpha_j \tag{2.42}
\]

An example of deconvolution of the \( \alpha(v) \) spectrum is shown in Figure 2.6a for the superionic glass 0.67CuI-0.33[Cu₂MoO₄-Cu₃PO₄]. Deconvolution of \( \alpha(v) \) using standard nonlinear least-square fitting showed that a reasonable fit requires at least 13 Gaussian bands below 1100 cm \(^{-1}\), with parameters listed in Table 2.1. The error in determining \( v_j \) is \( \pm 2 \) cm\(^{-1}\) for the stronger bands and \( \pm 5 \) cm\(^{-1}\) for the weaker bands. The corresponding accuracy for the bandwidth \( \Delta v_j \) is \( \pm 5 \) cm\(^{-1}\) and \( \pm 10 \) cm\(^{-1}\) and for the integrated intensity \( <A>_j \) is \( \pm 3\% \) and \( \pm 7\% \) for the stronger and weaker bands, respectively.
Table 2.1  Deconvolution parameters of the absorption coefficient spectrum according to Eq. 2.41 and fitting parameters of Eq. 2.19 to the reflectance spectrum for glass 0.67CuI-0.33[Cu₂MoO₄-Cu₃PO₄] (for details see text).

<table>
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<th>(v_j) (cm(^{-1}))</th>
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<th>(&lt;A&gt;_j) (10(^4) cm(^{-2}))</th>
<th>(v_j) (cm(^{-1}))</th>
<th>(\Gamma_j) (cm(^{-1}))</th>
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</table>

\(\epsilon_\infty = 3.95\)
Figure 2.6 (a) Deconvolution of the $\alpha(\nu)$ spectrum of glass 0.67CuI-0.33[Cu$_2$MoO$_4$-Cu$_3$PO$_4$] (solid black line) into Gaussian component bands according to Eq. 2.41 (solid grey lines). The simulated spectrum is shown by open circles. Inset, (b) shows the measured infrared reflectance spectrum (solid line) compared to the best fitting with Eq. 2.19 (open circles).

The inset of Figure 2.6 shows the best fitting of Eq. 2.19 (classical dispersion) to the experimental reflectance spectrum. Thirteen Lorentzian oscillators were required to reach a good agreement between experiment and fit (as in the case of $\alpha(\nu)$ deconvolution, Figure 2.6a), with fitting parameters given also in Table 2.1. The errors in $\nu_j$ and $\Delta\nu_j$ are similar to those for $\alpha(\nu)$ deconvolution, and for the oscillator strength $\Delta\epsilon_j$ are estimated at $\pm2\%$ and $\pm8\%$ for the stronger and weaker bands, respectively.

As seen in Table 2.1, the results obtained for resonance frequencies by KK analysis/deconvolution and reflectance fitting are similar. As for bandwidths, the main origin of the observed differences can be traced to the different fitting functions used in analyzing reflectivity and absorption data, that is, Lorentzian versus Gaussian line shapes.

The assignment of component bands to specific vibrations of the glass-forming molybdate and phosphate species requires consideration of group theory [75–77] as reported for CuI-containing molybdate glasses [74]. In this context, the strongest bands in Figure 2.6a at ca. 795
and 1020 cm\(^{-1}\) are assigned to the asymmetric stretching vibration of the monomeric MoO\(_4^{2-}\) and PO\(_4^{3-}\) oxoanions; \(\nu_3(\text{MoO}_4^{2-}) = 795 \text{ cm}^{-1}\) and \(\nu_3(\text{PO}_4^{3-}) = 1020 \text{ cm}^{-1}\). Additional modes of vibration of the same phosphate and molybdate species are responsible for the weaker bands above ca. 200 cm\(^{-1}\), while far-infrared activity below ca. 200 cm\(^{-1}\) arises from the rattling motions of Cu ions against their oxide and iodide sites. Therefore, the mid-infrared part of the spectrum in Figure 2.6 shows that the glass considered in this example has a completely ionic structure, that is, it has neither phosphate nor molybdate network connectivity. Information regarding the nature of copper ion sites in glass, as well as the effective charge of copper ions can be obtained using the spectroscopic parameters extracted from the analysis of the Cu ion sites [74].

We conclude from this section that KK transformation and dielectric dispersion models give equivalent results. Which of the two methods is selected for use depends on the level of analysis required and the kind of information sought. From the various functions available to present and discuss infrared spectra of bulk glasses, we will use in the following the absorption coefficient obtained through KK analysis of reflectance spectra.

### 2.4.2 Thin Films of Amorphous Materials

Very often the structure of glass thin films is discussed in relation to the structure of corresponding bulk glass, by comparing infrared spectra measured on thin film and bulk forms of the same glass composition (see, e.g., Reference 55 and the references therein). We use here the formalism presented in Section 2.2.3 to show that such comparisons and relevant conclusions on the structure of thin films should be made with caution.

We use as example a borate glass with composition 0.2AgI-0.8[Ag\(_2\)O-2B\(_2\)O\(_3\)]. The specular reflectance spectrum of the bulk glass was measured [55] and then KK-transformed to calculate the optical properties \(n(\nu)\) and \(k(\nu)\) shown in Figure 2.7. The \(n(\nu)\) and \(k(\nu)\) spectra are then used as input in Eq. 2.35 to calculate the transmittance spectra, \(T(\nu)\), of thin films. These films have different thickness, \(d\), but the same chemical composition and structure as they all have exactly the same \(n(\nu)\) and \(k(\nu)\) properties. The absorbance spectra, \(A(\nu)\), of the films were calculated from the simulated transmittance spectra by \(A(\nu) = -\log T(\nu)\), and the results are shown in Figure 2.8 as a function of film thickness.
Figure 2.7 Refractive index $n(\nu)$ and extinction coefficient $k(\nu)$ spectra of the bulk glass 0.2AgI-0.8[Ag$_2$O-2B$_2$O$_3$] obtained by Kramers–Krönig transformation of the measured reflectance spectrum.
Figure 2.8 Effect of film thickness on the calculated absorbance spectra of free-standing glass films with composition 0.2AgI-0.8[Ag$_2$O-2B$_2$O$_3$].

It is observed that all spectra exhibit similar profiles below 1500 cm$^{-1}$ with the strongest absorption envelopes centered at ca. 970 and 1330 cm$^{-1}$. In addition, the position of these envelopes varies from 965 to 985 cm$^{-1}$ and from 1320 to 1340 cm$^{-1}$, respectively, as the film thickness increases from 0.7 to 7.0 μm. It is noted that the 970 and 1330 cm$^{-1}$ envelopes result from vibrational modes of the borate network, with the ca. 970 cm$^{-1}$ feature attributed to asymmetric stretching modes of borate tetrahedra, BØ$_4^-$, and that at ca. 1330 cm$^{-1}$ to corresponding modes of triangular borate units, BØ$_3$ and BØ$_2$O$^-$ [8], where Ø denotes an oxygen atom bridging two boron atoms, and O$^-$ indicates a non-bridging oxygen atom.

Considering the origin of the bands at ca. 970 and 1330 cm$^{-1}$, it would be tempting to associate the obvious dependence of their frequency on film thickness with variations in the nature of the borate tetrahedral and triangular units. Likewise, the change in relative intensity of these envelopes could be interpreted as a change in the relative population of the corresponding
borate units with film thickness. Obviously, none of these interpretations are correct since all films have the same structure and bonding as they are dictated by \( n(v) \) and \( k(v) \) properties.

The phenomena described above result directly from the influence of film thickness on the vibrational profiles of glass. As seen in Figure 2.8, all films exhibit interference patterns which are well visible in the region above 1500 cm\(^{-1}\) where absorption is very small. Nevertheless, the interference patterns extend over the entire frequency region, and this results in absorption spectra which are superpositions of the true vibrational profiles of glass with a pure optical effect, that is, interference due to multiple reflections in the film. The period and amplitude of interference change with film thickness and, thus, these parameters influence the frequency and relative intensity of vibrational bands in a manner which depends on film thickness.

The example presented here shows that a safe interpretation of measured infrared spectra of thin films requires the comparison of measured and simulated spectra. Relevant case studies on glass thin films will be presented in Section 2.5.2.

2.5 CASE STUDIES

2.5.1 Bulk Glasses

For several reasons, borate glasses are ideal models to demonstrate the effectiveness of infrared spectroscopy in glass science relative to other types of glass. Boron has the smallest mass among the network-forming elements and, thus, the main vibrational modes associated with the glass network appear well above 500 cm\(^{-1}\) in the mid-infrared [8]. This prevents overlapping of bands characteristic of the short-range order in glass with metal ion-site vibrational modes active in far-infrared, that is, below ca. 500 cm\(^{-1}\) [4–9]. Borates have also a rich chemistry due to the ability of boron to change its coordination with oxygen between three and four, and this provides a wealth of short-range order structures and anionic environments that can coordinate the modifier metal ions. Therefore, borate glasses are prototype systems for investigating both short-range order structures (mid-infrared) and metal ion-site interactions (far-infrared).

2.5.1.1 Network Structure of Borate Glass

Alkali borate glasses \( xM_2O-(1-x)B_2O_3 \) (\( M^+ = \) alkali metal ion) have been studied extensively over the years to elucidate their structure, that is, the nature and relative population of the borate units building the glass network. The aim of those studies was to understand the structural origin of the non-monotonic variation of physical properties with alkali oxide content (\( x \)), a phenomenon known widely as the “boron anomaly” [78]. A representative property manifesting the “boron anomaly” is the glass transition temperature, \( T_g \). Addition of \( M_2O \) to \( B_2O_3 \) causes the progressive increase of \( T_g \), followed by the appearance of a maximum for compositions \( x \approx 0.25–0.33 \) and then by a decreasing trend at higher metal oxide contents.
The pioneering NMR work of Bray and coworkers [79] has set the basis for the quantification of the borate network structure, and this was proved essential for understanding the dependence of $T_g$ on the modifier alkali oxide content. Increasing $x$ was found to cause the transformation of neutral borate triangles, $\text{BO}_3^3$, into charged borate tetrahedra, $\text{BO}_4^4^-$, where $\text{O}$ indicates an oxygen atom bridging two boron atoms. For $x < 0.30$ the fraction of four coordinated boron atoms, $N_4$, was found to follow closely the law $N_4 = x/(1-x)$, which suggests that each added oxygen atom converts two $\text{BO}_3^3$ units into two $\text{BO}_4^4^-$ tetrahedra. Higher alkali contents were shown to induce the formation of non-bridging oxygen (NBO) atoms on borate triangular units, with increasing number of NBO's as $x$ increases toward $x = 0.75$. These NBO-containing units are the metaborate, $\text{BO}_2^2\text{O}^-$, pyroborate, $\text{B}_2\text{O}_5^4^-$, and orthoborate, $\text{BO}_3^3^-$, units. In subsequent works, the increase of $T_g$ was correlated with $N_4$ because the transformation of $\text{BO}_3^3$ to $\text{BO}_4^4^-$ adds a fourth bridging B–O bond per boron center and this increases the rigidity of the network, as opposed to NBO-formation that leads to network destruction [80–82].

Besides its $x$-dependence, $T_g$ shows a clear dependence on the type of alkali metal, $M$. As shown by Affatigato and coworkers [81] glasses of constant alkali oxide content exhibit $T_g$'s decreasing from Li to Cs. Propositions for the explanation of the $M$-dependence of $T_g$ were made and include the increasing trend of $N_4$ from Cs to Li especially for glasses with alkali oxide contents exceeding $x = 0.25$ [82–84].

Glass transition temperature data were also reported for alkaline-earth borate glasses [85], $x\text{MO}-(1-x)\text{B}_2\text{O}_3$ ($M^{2+} = \text{alkaline-earth metal ion}$), and show that alkaline-earth borates have considerably higher $T_g$'s than alkali borate glasses of the same metal oxide content. Also, $T_g$ decreases from Mg to Ba in line with the trend found in alkali borate glasses. However, compared to the last systems much less is known about the structure of alkaline-earth borate glasses including, for example, the $M$-dependence of $N_4$, and thus $T_g$-structure correlations are not well established in these glass systems. In this context, some results obtained by infrared spectroscopy will be highlighted in this section, based on a comparative IR and Raman study of alkaline-earth borate glasses over broad composition ranges [86].

Glasses suitable for infrared reflectance measurements were formed by splat-quenching the melts between two preheated copper blocks. This method gives glasses with quite good flat surfaces appropriate for reflectance measurements. However, glass formation in all four $x\text{MO}-(1-x)\text{B}_2\text{O}_3$ systems was possible only for composition $x = 0.45$ while for values of $x$ below or above 0.45 glass formation is limited to three borate systems. The splat-quenched glass samples were used for reflectance measurements without any further treatment (e.g., polishing) to avoid surface alteration due to hydrolysis.

Absorption coefficient spectra were obtained by KK analysis of the measured reflectance spectra, and typical spectra are shown in Figure 2.9 for $x = 0.33$ and 0.45. To facilitate spectral comparison, the spectra of glasses with the same MO content were scaled at
the high frequency absorption band. It is clear from Figure 2.9 that the absorption profiles depend not only on the MO content but also on the type of alkaline-earth metal. To understand the structural origin of these spectral differences, we will review briefly assignments for the main absorption profiles.

Figure 2.9 Comparison of infrared absorption coefficient spectra of alkaline-earth borate glasses $x\text{MO}-(1-x)\text{B}_2\text{O}_3$, with metal oxide contents $x = 0.33$ (a) and $x = 0.45$ (b). The spectra were obtained by KK transformation of the measured reflectance spectra.

As noted in Section 2.4.2, absorption in the range 800–1150 cm$^{-1}$ can be attributed to the B-Ø stretching vibration of BØ$_4^-$ tetrahedra [8, 82]. Glassy B$_2$O$_3$ ($x = 0$) is known to consist of boroxol rings and independent BØ$_3$ triangles and, thus, anhydrous B$_2$O$_3$ glass shows no absorption in this spectral range. The high frequency absorption profile (1150–1550 cm$^{-1}$) originates from the stretching vibration of B-Ø and B-O$^-$ bonds in borate triangular units, which are of the B$_3$ and BØ$_2$O$^-$ type for glasses below the metaborate stoichiometry, $x = 0.5$. For glasses of higher metal oxide contents, $x > 0.5$, asymmetric stretching vibrations of the
pyro-borate ($\text{B}_2\text{O}_5^{4-}$) and ortho-borate ($\text{BO}_3^{3-}$) units contribute to the infrared activity above ca. 1200 cm$^{-1}$. Therefore, the evolution of the 800–1150 cm$^{-1}$ envelope with $x$ in the range $0 < x \leq 0.40$ shows the progressive change of boron coordination number from three to four. For higher MO contents ($x \geq 0.45$), a decrease of the relative intensity of the BØ$_4$$^-$ absorption band was observed and this signals the destruction of BØ$_4$$^-$ units in favor of formation of borate triangles with increasing number of non-bridging oxygen atoms [8].

To quantify the effect of alkaline-earth oxide content and type on the short-range order structure by infrared spectroscopy, we have calculated the integrated intensity of the absorption envelopes 800 to 1150 cm$^{-1}$ (borate tetrahedral units) and 1150 to 1550 cm$^{-1}$ (borate triangular units) denoted by $A_4$ and $A_3$, respectively. The relative integrated intensity, $A_r = A_4/A_3$, was obtained and is shown in Figure 2.10 as a function of MO content and type. The change in boron coordination from three to four as the MO content increases toward the metaborate composition ($x = 0.50$) is illustrated clearly in this figure. It is also observed that the $x$ value at which $A_r$ exhibits its maximum is a function of the type of alkaline-earth oxide.
Figure 2.10 Relative integrated absorption $A_r = A_4/A_3$ as a function of metal oxide content in alkaline-earth borate glasses $x$MO-(1−$x$)B$_2$O$_3$. Integrated absorptions $A_4$ and $A_3$ correspond to tetrahedral and triangular borate units, respectively. Lines through data points are drawn to guide the eye.

The relative integrated intensity $A_r$ can be used to estimate the fraction of boron atoms in fourfold coordination, $N_4$, from the simple expression

$$N_4 = \frac{A_r}{\alpha + A_r}$$  \hspace{1cm} (2.43)

where $\alpha$ is the relative absorption coefficient of boron tetrahedra versus boron triangles [86]. The use of relative integrated intensities is particularly suitable when studying alkaline-earth borates because glass formation becomes difficult at the limits of glass-forming regions. This reduces the size and surface quality of the splat-quenched bulk samples, while polishing is usually avoided due to hydrolysis effects. While this problem reduces the accuracy of absolute
integrated intensities, it becomes greatly eliminated when the relative integrated intensity $A_r$ is employed.

While $A_r$ is obtained from infrared measurements (Figure 2.10), the use of Eq. 2.43 requires the knowledge of the relative absorption coefficient $\alpha$. This was achieved by comparing infrared data with reported NMR data by Huebert et al. [87], and gave $\alpha = 1.3$ for Ba, Sr and Ca-borate glasses and $\alpha = 1.9$ for Mg-borate glasses. Using these values for $\alpha$ and the infrared data ($A_r$), $N_4$ was calculated through Eq. 2.43 for glass compositions in all four alkaline-earth borate systems. The results are shown in Figure 2.11 versus MO content and are compared with the theoretical curve $x/(1-x)$, as well as with $N_4$ values obtained by NMR [88, 89], neutron diffraction and molecular dynamics simulations [90].
Figure 2.11 Fraction of four-coordinated boron atoms, $N_4$, as function of MO mole fraction in alkaline-earth borate glasses $x\text{MO}-(1-x)\text{B}_2\text{O}_3$. The $N_4$ values obtained by infrared analysis (IR) are compared to those of NMR spectroscopy [88, 89], neutron diffraction, and molecular dynamics studies [90] and the theoretical curve $N_4 = x/(1-x)$. The $N_4$ curve is obtained when one mole of added MO converts two moles of neutral BØ$_3$ triangular units into two moles of charged borate tetrahedral BØ$_4^-$ (Ø = bridging oxygen atom). Lines through IR data points are drawn to guide the eye.

The following observations can be made from Figure 2.11: (a) there is good agreement between the infrared results and those of other techniques, (b) for Ba− and Sr-glasses of low MO contents (up to ca. $x = 0.25$) $N_4$ follows the theoretical value, (c) the MO content at which $N_4$ attains its maximum value shifts to higher $x$ values as the field strength of the $M^{2+}$ ion increases, and (d) for glasses of the same MO content, $N_4$ tends to decrease with increasing field strength of the $M^{2+}$ ion, that is, from Ba to Mg. Note that this trend is opposite to that found for alkali borate glasses [83, 84]. Also, while the decrease of $N_4$ from Ba- to Ca-borates
appears smooth the Mg-borate glasses exhibit distinctly lower $N_4$.

To understand the peculiarity of Mg-borate glasses, the Raman spectra of alkaline-earth borates were also measured [86]. A key finding from Raman spectroscopy was that Mg-borate glasses around the metaborate composition ($x = 0.50$) are characterized by the coexistence of boroxol rings and over modified borate units, with a prominent appearance of pyroborate dimers $B_2O_5^{4−}$. The coexistence of boroxol rings and pyroborate units in glass structures with stoichiometry below the metaborate composition can be understood in terms of the disproportionation reaction:

$$\text{[ØB-O-BØO]} \rightleftharpoons \text{[BØ}^3\text{]} + \text{[Ø-B-O}_2^{\text{−}}\text{]}$$

The activation of the above reaction path was related to the very high field strength of Mg$^{2+}$ ions that require sites of high anionic charge density for their coordination. The charged oxygen atoms of the pyroborate-type unit, that is, Ø-B-O$_2^{2−}$, can be very suitable ligands for coordinating the magnesium ions. It is noted that the Raman spectra of Ba-, Sr- and Ca-borate glasses show no evidence for the presence of pyroborate units in glasses with $x \leq 0.50$. Thus, both Raman and IR spectroscopy show that the short-range order structures of Ba-, Sr-, and Ca-borate glasses with $x \leq 0.50$ are dictated by the coexistence of isomeric $BØ_4^{−}$ and $BØ_2O^{−}$ metaborate units ($BØ_4^{−} \Leftrightarrow BØ_2O^{−}$), in addition to neutral $BØ_3^{0}$ triangular units.

As noted in the beginning of this section, in alkali borate glasses, $T_g$ decreases from Li to Cs and this trend could be correlated with a decreasing rigidity of the borate network as $N_4$ decreases in the same order. However, the $N_4$ trend in alkaline-earth borate glasses was found to be opposite to that in alkali borates, suggesting that the connectivity of the boron-oxygen network should increase from Mg to Ba. On these grounds, the $T_g$ trend in alkaline-earth borates would appear opposite to expectations if the network connectivity provided by B–O bonding were the only factor determining $T_g$. To resolve this apparent discrepancy we will consider also the metal-oxygen (M-O) part of bonding since it provides additional cross-links across borate segments of the network which enhance the overall network rigidity and increase $T_g$ [85, 91]. The strength of M–O bonding can be quantified in terms of the corresponding force constant $F_{M-O}$ which can be derived directly from the far-infrared data presented in the following section.

### 2.5.1.2 Metal Ion-site Interactions

The short-range order structure of glass and the local anionic environments which host the modifier metal ions are very often discussed independently. However, during glass formation, a synergy develops between the requirements of metal ions for establishing suitable
coordination environments/sites and the ability of glass network to provide such anionic sites. In the case of crystallization, additional constraints are imposed by the need to establish long-range structural periodicity. As the glass state is approached by cooling a melt, thermodynamics drives the system toward the stable crystalline state but kinetics prohibits it from reaching the crystalline structure. Therefore, although the natural tendency for metal ions is to create in glass “crystal-like” sites, that is, sites similar to those in corresponding crystals, there is a strong possibility that additional types of site are created and contribute to the disordered nature of glass. The spatial distribution and nature of the anionic sites hosting metal ions are factors affecting the physical properties of glass. Information related to metal ion sites in glass can be extracted by probing the metal ion site vibration bands measured in the far-infrared spectra.

As seen in Figure 2.9, glasses of the same MO content exhibit asymmetric far-infrared bands with their peak frequency increasing upon decreasing the mass of metal ion. This trend suggests that such bands should be related to localized vibrations of metal ions in their equilibrium sites [4–6]. The asymmetric far-infrared profiles were analyzed into component bands, and a typical example is shown in Figure 2.12 for glasses in the series 0.45MO–0.55B₂O₃ (M = Mg, Ca, Sr, and Ba).
Figure 2.12 Far-infrared absorption coefficient spectra of glasses 0.45MO-0.55B$_2$O$_3$ (M = Mg, Ca, Sr, Ba), deconvoluted into Gaussian component bands. The experimental spectrum (solid black line) is compared with the simulated spectrum (open circles).

The two lower-frequency bands are marked by L and H in Figure 2.12, and their peak frequencies are plotted in Figure 2.13 versus the inverse square root of the metal ion mass, $M^{-1/2}$. A linear dependence on $M^{-1/2}$ is found for both $v_H$ and $v_L$ frequencies, indicating that the corresponding bands should be attributed to oscillatory modes which involve mainly the motion of metal ions. The motion of a metal ion relative to its site should be compensated by an appropriate motion of oxygen atoms forming the site, so that there is no net displacement of the center of mass of the metal ion-site entity. Although the reduced mass of metal ion-site vibration, $\mu$, depends on the mass of metal ion and oxygen in a way determined by the symmetry of the site [92], the metal ion has a predominant contribution on the oscillation frequency (Figure 2.13). This suggests that the reduced mass of the metal ion-site vibration can be approximated by the metal ion mass, $\mu \approx M_C$, implying that the metal ion vibrates against a quite rigid anionic site.
Figure 2.13 Metal ion-site vibration frequencies versus the square root of the inverse metal ion mass $M^{-1/2}$ for glasses $M_2O-3B_2O_3$ ($M = Li, Na, K, Rb$ and $Cs$) and $0.45MO-0.55B_2O_3$ ($M = Mg, Ca, Sr,$ and $Ba$) glasses. Frequencies denoted by $\nu_{M-O(H)}$ (a) and $\nu_{M-O(L)}$ (b) correspond to peak maxima of bands H and L, respectively, and were obtained from fitting the far-infrared spectra (Figure. 2.12). Frequency data for the alkali borate glasses $M_2O-3B_2O_3$ were obtained from Reference 93. Error bars are of the size of symbols. Lines are least-square fits to the data.

It is clear from Figure 2.13 that the frequencies of vibration of alkaline-earth ions against their sites are higher compared to those of alkali ions of similar mass. This suggests that the force constant of the average metal ion–oxygen bonding in alkaline-earth borates is higher than that in alkali borate glasses. The force constant of the metal ion–oxygen bonding, $F_{M-O}$, can be derived directly from far-infrared data. Considering the presence of two types of metal ion sites, an effective or average force constant for M–O bonding can be defined as follows:

$$F_{M-O} = 4\pi^2 c^2 \mu v_{eff}^2$$ (2.45)
where \( c \) is the speed of light, \( \mu \) is the reduced mass of cation-site vibration and \( \nu_{\text{eff}} \) is an effective cation-site vibration frequency obtained by

\[
\nu_{\text{eff}} = (f_H \nu_H^2 + f_L \nu_L^2)^{1/2}
\]  

(2.46)

The frequency-weighting factors \( f_H \) and \( f_L \) can be approximated by \( f_{H(L)} = A_{H(L)}/(A_H + A_L) \), where \( A_H \) and \( A_L \) are the integrated intensities of the \( H \) and \( L \) component band, respectively. To simplify the calculations, we assume here octahedral type of sites for all metal ions, noting that other site coordinations do not affect the general dependence of \( T_g \) on the average force constant. For octahedral sites, the reduced mass of vibration is \( \mu = m_C m_O/(m_C + 2m_O) \), where \( m_C \) and \( m_O \) are the masses of metal and oxygen atoms.

The glass transition temperature, \( T_g \), of the \( x = 0.33 \) alkaline-earth borate glasses is shown in Figure 2.14 versus the calculated effective force constant \( F_{M-O} \), and is compared with data for alkali diborate glasses, that is, \( x = 0.33 \) [93]. It is observed that in each glass family \( T_g \) varies linearly with \( F_{M-O} \), showing that besides \( B-O \) bonding the \( M-O \) interactions play an important role in determining \( T_g \). For glasses of the same \( MO \) content \( T_g \) increases with \( F_{M-O} \), that is, from Ba to Ca, and this occurs despite the fact that \( N_4 \) tends to decrease in the same order. Thus, the combined effect of \( B-O \) bonding and \( M-O \) interactions should be responsible for the observed trend of \( T_g \) in alkaline-earth borate glasses.
**Figure 2.14** Dependence of glass transition temperature, $T_g$, on the effective force constant, $F_{M-O}$, of the metal ion-oxygen (M–O) bond in alkaline-earth and alkali borate glasses of the diborate composition $0.33MO-0.67B_2O_3$ (note that glass with this composition is not formed in the Mg-borate system). Lines are least-square fits to data.

**Figure 2.14** shows also that for M–O bonding of the same strength, the alkaline-earth borates exhibit higher $T_g$s compared to alkali borate glasses. For example, the $T_g$ of Ba-diborate glass is higher by 130 degrees than that of Na-diborate glass, even though the two glasses have the same $F_{M-O}$ value and very similar $N_4$ values [82]. Such differences in $T_g$ can be attributed to the details of the M–O bonding, including the higher cross-linking efficiency of the divalent ions which have larger coordination numbers with oxygen atoms compared to alkali ions [91].

As for the two far-IR components H and L, we note that they suggest the existence of at least two distributions of anionic site environments which differ in charge density and microstructure. Metal ions occupying sites H and L were found to probe different local optical basicity [93, 94] and have different diffusion coefficients in borate glasses [95]. However, the
exact nature of such sites remains an open question.

2.5.2 Glass Thin Films

Glasses are in a metastable thermodynamic equilibrium, and thus they can assume structures that depend strongly on preparation conditions and thermal history. For glass films there is a great need to understand the effect of preparation conditions on structure and properties, because films can deviate much more than bulk glasses from the stable equilibrium state (i.e., crystal). This aspect was demonstrated in earlier studies of v-SiO$_2$ films developed by evaporation [96], dc-sputtering [97] and rf-magnetron sputtering [98], and more recently for lead-germanate glass films grown by pulsed laser deposition (PLD) [99]. Structural differences between bulk glasses and thin films were identified also in AgI-containing borate glasses despite the fact that both glass forms were prepared from the same borate melt [55]. In this section we present and discuss infrared spectra of glass films developed by rf sputtering from Li-borate targets, in comparison to spectra simulated using the optical functions of bulk glasses.

2.5.2.1 Glass Films Deposited on Transparent vs. Reflective Substrates

Infrared spectra of free-standing films were shown in Section 2.4.2 and demonstrated the effect of film thickness and related interference fringes on band profiles and relative intensities. The effect of substrate is examined here, as illustrated in Figure 2.15 where the spectrum of a free-standing film is compared with spectra of films deposited on Si (0.6 mm thick) and gold-covered Si substrates. Films on substrates were developed by rf sputtering of lithium-diborate, Li$_2$O-2B$_2$O$_3$, targets which were prepared from stoichiometric mixtures of crystalline B$_2$O$_3$ and LiBO$_2$ powders. Film deposition was done in argon atmosphere (1 Pa pressure) with rf power ranging from 1.5 to 2.5 W/cm$^2$. More experimental details are presented in Reference 67.
Figure 2.15 Infrared spectra of thin films deposited by sputtering from a Li-borate target with composition Li$_2$O-2B$_2$O$_3$. The spectra of films on Si and Au substrates were measured by transmission, $T$, and reflection-absorption, R-A, respectively. Comparison is made with the transmittance spectrum of a free-standing Li$_2$O-2B$_2$O$_3$ film of 1 μm thickness, as calculated from the optical response of the Li$_2$O-2B$_2$O$_3$ bulk glass. For details see text.

The transmittance spectrum of the free-standing Li-diborate film in Figure 2.15 was calculated from Eq. 2.35 using as input the $n(\nu)$ and $k(\nu)$ spectra of the bulk Li$_2$O-2B$_2$O$_3$ glass and film thickness of 1 μm. The spectra of films on Si and Au substrates were measured with low resolution (10 cm$^{-1}$). As observed in Figure 2.15, the two sputtered films give infrared spectra with marked differences both in shape and position of bands despite the fact that these films were prepared in the same way from targets having the same composition. The film on Si shows the strongest mid-IR envelopes at approximately the same frequency as the free-standing film, that is, at ca. 980 cm$^{-1}$ (BØ$_4^-$ tetrahedral units) and 1350 cm$^{-1}$ (BØ$_2$O$^-$ and BØ$_3$ triangular units), and both films exhibit the Li ion-site vibrational band at ca. 380 cm$^{-1}$ in the far-IR. The sharp band at 610 cm$^{-1}$ of the film/Si spectrum is due to the strongest lattice mode.
of silicon and is observed in the spectrum because the Si substrate is more than 300 times thicker than the deposited glass film. The R-A spectrum of the film/Au system retains the strong bands above 500 cm\(^{-1}\), although with pronounced shifts toward lower frequencies in comparison to those of the transmittance spectra. The striking characteristic of the R-A spectrum is the nearly absent Li-site vibration band which appears at \(ca\). 380 cm\(^{-1}\) in transmittance spectra.

Such differences between reflection-absorption (R-A) and transmittance (T) spectra of the same type of film appear at first sight surprising, but they can be understood if we consider the effect of optical properties of the metallic substrate on infrared spectra. This is demonstrated in Figure 2.16 which compares experimental and calculated R-A spectra of Li\(_2\)O-2B\(_2\)O\(_3\) thin films on Au. Calculation was made by Eq. 2.32 using as input the \(n(\nu)\) and \(k(\nu)\) responses of gold in the infrared, gold thickness of 100 nm, the \(n(\nu)\) and \(k(\nu)\) spectra of the bulk Li\(_2\)O-2B\(_2\)O\(_3\) glass and glass film thickness of 1.24 \(\mu\)m [67]. The comparison shows a good agreement between experiment and simulation, suggesting that the apparent absence of the Li-site vibration band should be due to the effective masking of the far-IR properties of glass by the overwhelming optical response of Au. Indeed, the \(n(\nu)\) and \(k(\nu)\) values of gold are at least two orders of magnitude higher than those of glass and Si substrate.
Figure 2.16 Comparison of infrared experimental and calculated reflection-absorption, R-A, spectra of thin films on Au having nominal composition Li$_2$O-2B$_2$O$_3$. For details see text.

The above discussion shows that the search for possible structural differences between thin films on substrates and bulk glasses should consider the influence of substrate optical properties, and especially those of metallic substrates which have strong optical response in the infrared. In the following, we consider thin films on Si substrates which are transparent in the infrared range.

2.5.2.2 Effect of Preparation Conditions on the Structure of Glass Thin Films

The low resolution (10 cm$^{-1}$) transmittance spectrum, $T_{\text{exp}}$, of a glass film with nominal lithium-diborate composition is shown in Figure 2.17a. This film was deposited on Si substrate (0.6 mm) by sputtering a Li$_2$O-2B$_2$O$_3$ target at rf power of 1.5 W/cm$^2$. The origin of the glass vibrational bands below 1700 cm$^{-1}$ was discussed in the previous section. We note here that in the region above 1700 cm$^{-1}$ the experimental spectrum exhibits a strong interference pattern due to multiple reflections in the glass film. We recall that measuring the
IR spectrum with 10 cm\(^{-1}\) resolution eliminates the interference pattern due to multiple reflections in the Si substrate (see Section 2.2.3).

![Graph showing transmittance spectra](image)

**Figure 2.17** Low resolution experimental transmittance spectrum, \(T_{\text{exp}}\), of a Li-borate thin film deposited by rf sputtering on Si substrate (0.6 mm) from a Li\(_2\)O-2B\(_2\)O\(_3\) target. The measured spectrum is compared with spectra calculated using the \(n(\nu)\) and \(k(\nu)\) infrared responses of bulk glasses \(x\text{Li}_2\text{O}-(1-x)\text{B}_2\text{O}_3\) with \(x = 0.33, 0.275,\) and 0.25. For details see text.

The measured transmittance spectrum is compared in **Figure 2.17a** with the spectrum calculated using Eq. 2.35 and the \(n(\nu)\) and \(k(\nu)\) optical properties of the bulk lithium-diborate glasses, which has Li\(_2\)O content (mole fraction) equal to \(x = 0.33\) in terms of the formula \(x\text{Li}_2\text{O}-(1-x)\text{B}_2\text{O}_3\). The fit in **Figure 2.17** was obtained for film thickness equal to 1.55 \(\mu\)m and shows a reasonable agreement with the measured spectrum. This suggests that the nature and relative population of the short-range order (SRO) borate units in films prepared by rf sputtering should be close to those in the bulk glass of the same nominal composition. However, there are two obvious differences between experimental and simulated spectra; the
experimental spectrum exhibits weaker Li ion-site band at ca. 370 cm$^{-1}$ and stronger the band at ca. 1360 cm$^{-1}$ which is due to triangular borate units (BØ$_2$O$^-$ and BØ$_3$). The good fit of the interference pattern above 1700 cm$^{-1}$ suggests that the nature and extent of optical effects should be the same in the experimental and simulated spectra of the films, and, thus, spectral differences below ca. 1700 cm$^{-1}$ should manifest real structural and/or compositional variations between film and bulk glass.

In searching for the origin of the above effects we note that the combined spectral differences in both mid- and far-IR regions would be consistent with Li ion content in thin films smaller than that in the bulk Li-diborate glass [8]. To examine this hypothesis, we compare in Figure 2.17b and 2.17c the experimental transmission spectrum of the sputtered Li-borate film with spectra calculated using the $n(\nu)$ and $k(\nu)$ properties of bulk $x$Li$_2$O-(1$-$x)B$_2$O$_3$ glasses with $x = 0.275$ and 0.25, that is, glasses with Li$_2$O content lower than that of the nominal diborate composition ($x = 0.33$) of the sputtering target. As observed in Figure 2.17b, the bulk glass with composition 0.275Li$_2$O-0.725B$_2$O$_3$ gives the best match in the mid-IR range between experimental and calculated spectra, and, in particular, very good agreement in the region of tetrahedral (800–1150 cm$^{-1}$) and triangular (1150–1600 cm$^{-1}$) borate units.

The above result shows that rf sputtering of Li-diborate targets leads to Li-borate thin films with lithium oxide content lower by ca. 16.7\% than that of the target material. This is an important aspect to be considered when designing thin film electrolytes for electrochemical applications.

Despite the good agreement in the mid-IR range of the spectra in Figure 2.17b a notable difference remains in the region of the Li ion-site vibration band in the far-IR, even when comparison is made with the spectrum calculated for the 0.275Li$_2$O-0.725B$_2$O$_3$ composition. This difference may result from the higher cooling rate of the thin film relative to the bulk glass, and could reflect the presence of local chemical/structural inhomogeneities as proposed by various models even for homogeneous glasses [100]. In terms of a potential energy landscape, this suggests that thin films would occupy local energy minima of higher enthalpy and volume than bulk glasses [101]. Therefore, it is of interest to probe the response of thin films to annealing processes that may change their frozen-in energy. Such annealing experiments at sub-$T_g$ temperatures were described in Reference 67 for sputtered Li-borate films, and were found to give almost perfect matching of the film spectrum measured after annealing with the simulated spectrum for a film having the composition and structure of the bulk 0.275Li$_2$O-0.725B$_2$O$_3$ glass.

The above shows that annealing of the “hyperquenched” thin film amorphous state leads to change toward the bulk glassy state prepared under slower cooling. The main effect has been observed for the Li ion-site vibration band, indicating that upon annealing Li ions trigger limited SRO structural rearrangements to modify/create sites of lower potential energy.

2.6 CONCLUSIONS
This chapter has addressed IR spectroscopy of glasses. Advances in instrumentation, sampling techniques, and methods for data analysis make infrared a powerful tool in glass science and technology. Ranges of applications were given in the introduction; the rest of the chapter has focused on infrared studies of glasses in bulk and thin films forms.

A brief review was given on the propagation of light in isotropic media like glasses, and the optical functions measured in the infrared were defined and discussed. Emphasis was placed on the frequency-dependent refractive index and dielectric function, because they are the fundamental properties related directly to structure/bonding and chemical composition.

The two methods employed to treat experimental reflectance spectra of bulk glasses, that is, Kramers–Krönig (KK) transformation and dispersion analysis were introduced and their limitations and advantages were discussed. Comparison of infrared results obtained on glasses showed that KK transformation and dielectric dispersion analysis give equivalent results. Thus, the method of choice for a particular application depends on the level of structural analysis required and the kind of information sought.

The potential of infrared reflectance spectroscopy for the quantitative assessment of glass structure was demonstrated by presenting results for alkaline-earth borate glasses. It was shown that the integrated intensity of borate tetrahedral units in the mid-IR relative to that of borate triangular units, $A_r$, depends on both alkaline-earth oxide content and type. When a good scaling with data from nuclear magnetic resonance (NMR) is available, $A_r$ can be converted into the fraction of four coordinated boron atoms, $N_4$. It was shown that $N_4$ exhibits similar trends with $A_r$ in good agreement with results from other experimental techniques.

Far-IR spectra measured on alkaline-earth borate glasses were found to exhibit broad distributions of anionic environments/sites hosting the metal ions. This is in line with the disordered nature of glasses, and with the richness of borate SRO structures in providing anionic sites for metal ions. The analysis of the far-IR profiles allowed the evaluation of the average strength of metal ion-site interactions, and this was found to scale linearly with the glass transition temperature for glasses of constant metal oxide content.

The general formalism to treat infrared transmittance and reflectance spectra of glass films on substrates was given. It was shown that low resolution transmittance spectra of glass films on transparent substrates present a combined contribution of the vibrational response of (i) the glass, (ii) the substrate, and (iii) the interference fringes due to multiple light reflections in the film. The corresponding transmission-absorption spectra of glass films on metallic (reflecting) substrates showed strong masking of glass bands in the far-IR due to the dominant high values of the optical functions of the metallic substrate.

The particular case of Li-borate glass films deposited by rf sputtering on Si (transmitting) substrates was examined by comparing experimental and calculated IR spectra. The latter spectra were obtained using the general formalism and, as input, the optical properties of the Si substrate and of the bulk glass having the same nominal composition with the target material used for film deposition. The comparison of experimental and simulated spectra of sputtered Li-borate films highlighted two effects; (i) variations in composition between thin films and
target material, and (ii) differences in energetics of the anionic sites hosting Li ions, which can be relaxed by sub-$T_g$ annealing of thin films.

We conclude by noting that a better understanding of the complicated response of glasses in the infrared can benefit greatly from recent experimental and theoretical developments in the field of vibrational spectroscopy of glasses. Recent advances include very low frequency infrared measurements on glasses by terahertz time-domain spectroscopy [102], hyper-Raman scattering [103] and calculations of infrared spectra by first-principles for bulk glasses [104] and thin films on substrates [105].

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3

RAMAN SPECTROSCOPY OF GLASSES

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3.1 INTRODUCTION

Vibrational spectroscopy is a very powerful technique for studying glass structure, which has been extensively used during the past 50 years. The instrumentation has also played an important role in spreading the use of this spectroscopic tool. In particular, the generalized use of Fourier-transform infrared (FTIR) spectrometers since the eighties and the introduction of powerful gas lasers for Raman spectroscopy since the seventies were decisive in boosting the worldwide use of these characterization techniques. Other less commonly used vibrational spectroscopy methods include inelastic neutron scattering and Brillouin scattering, as well as a range of nonlinear Raman effects (as opposed to the linear or spontaneous Raman effect) like stimulated Raman scattering (SRS), coherent anti-Stokes Raman spectroscopy (CARS) and surface-enhanced Raman spectroscopy (SERS). A new approach, tip-enhanced Raman spectroscopy (TERS) combines Raman spectroscopy at smooth surfaces with an Atomic Force Microscope. Raman and IR spectroscopies are by far the most commonly used ones. Although Raman and IR methods often provide complementary information, the present chapter is exclusively dedicated to Raman spectroscopy, whereas IR methods will be treated in a separate chapter of this book.

Raman spectroscopy is a well-known analytical tool for the identification of the chemical composition and structural groups present in different materials. In the case of glass, in particular, Raman is a powerful tool for the study of its structure, as well as structural changes like crystallization, for example, for the fabrication of glass-ceramic materials. The linear (spontaneous) Raman effect (or Raman effect, for short) was first theoretically predicted by A. Smekal [1] in 1923 and it was experimentally demonstrated by C.V. Raman [2] in 1928. It is an inelastic light scattering phenomenon (which means that the frequency of the monochromatic light used for excitation changes upon interaction with the sample being measured). The effect probes the vibrational levels of specific groups of atoms or ions, being often complementary to IR spectroscopy. Photons of the laser light are taken up by the sample into a non-stationary, very short-lived virtual state ($\sim10^{-15}$ s) and are then reemitted almost instantaneously. The frequency of the reemitted photons is shifted up (anti-Stokes Raman effect) or down (Stokes effect) relative to the original single frequency, by a value called the Raman shift. This in turn provides information about vibrational, rotational, and other low frequency transitions in molecules or molecular groupings of the sample being analyzed. Raman spectroscopy can be used to study solid, liquid, and gaseous samples. Although the vibrations of crystalline solids
are extended to the whole crystal (or grain for a polycrystalline solid), these are much more localized in the case of glasses [3]. The corresponding vibrational energy transitions for this case are essentially characteristic of molecular groupings, rather than the whole vitreous solid, especially in the highest frequency range.

Raman spectroscopy of glass usually does not provide specific structural information, but it can often identify the presence of terminal anions, like the non-bridging oxygen (NBO or O_{NB}) ions in oxide glasses, through the presence of typical high-frequency peaks in the spectra. Therefore, it is useful to combine theory with experimental Raman spectroscopy data when possible. One important early theoretical contribution was due to Bell, Bird, and Dean [4, 5], who constructed ball and spoke models of the glass structure containing a few hundred atoms, in agreement with short range structural information from X-ray and neutron diffraction data for the AX_{2} glasses SiO_{2}, GeO_{2}, and BeF_{2} [5]. The atomic coordinates were first measured and the vibrational spectra were then computed based on a harmonic force field with both central and noncentral force constants. These authors concluded that, for such tetrahedral network glasses, the vibrational modes had extended character at low frequencies, but localized at high frequencies, with more intense localization in the case of non-bridging anionic species (like the NBOs), or for large A/X atomic mass ratios [5].

A few years later, Sen and Thorpe [6] developed a model for the vibrational density of states (VDOS) of tetrahedral AX_{2} glasses like SiO_{2}, based on a random network of [AX_{4}] tetrahedra with nearest neighbor central forces only, which predicted that, as the A-X-A bridging angle θ increased from π/2 to π, the character of the vibrational modes changed from purely molecular (single frequency) to band-like (as in solids). Therefore, the value of the bridging angle determined to a large extent how solid state effects modified the characteristics of the isolated tetrahedral modes and simple expressions were derived for the positions of the main peaks in the VDOS, as a function of θ and the central force constant, α.

Another approach consists in calculating the Raman spectra of certain glasses with relatively simple compositions based on computer modeling (e.g., molecular dynamics, MD, or reverse Monte Carlo), followed by a comparison with the experimental spectra until the agreement is considered to be satisfactory and the structural model on which the calculation was based is validated. This approach may provide short- or even intermediate-range order (SRO or IRO, respectively) information concerning the glass structure. However, extracting structural information from vibrational spectra in this way is not trivial due to the complexity of the involved vibrations and coupling factors, requiring model structures of large enough size, involving significant CPU time. As an example, Simona Aspas et al. [7] calculated the Raman spectra of sodium tetrasilicate glass (Na_{2}Si_{4}O_{9}) based on ab initio and classical MD simulations. Their amorphous model, containing 90 atoms (24 Si, 54 O, and 12 Na) confined to a cubic box of 1.08 nm edge length, was generated both by an ab initio approach to the interatomic force field (performed in the framework of the density functional theory, DFT) and by using a classical valence force field, especially suited for partially covalent silicate glasses. The glass VDOS were then calculated based on these two MD simulations, having quite similar shape below 500 cm\(^{-1}\), but showing some significant differences above this
frequency. The polarized Raman spectra of the glass were subsequently calculated from those VDOS, within the bond-polarizability approximation. While an overall agreement was found with the experimental parallel-polarized (VV) spectrum, the agreement with the perpendicular polarized (VH) spectrum was not as good. In general, although classical modeling approaches to the vibrational properties are not sufficiently accurate, further structural refinement can be achieved with *ab initio* methodologies [8].

Yet another approach which has been considered in the past was the tentative use of group theory, by extending the Factor group method [9], strictly valid for crystalline solids only, to the interpretation of glass vibrational spectra [10].

In conclusion, there is no single theory for accurately predicting the first order vibrational spectra of glassy materials, so that certain types of approximate (simplified) models are necessary to interpret these data, in particular with regards to the Raman spectra. Compositional variations, whenever possible, are also very helpful in assigning the Raman spectra of glasses.

### 3.2 BACKGROUND

#### 3.2.1 Theory

The Raman effect is based on molecular deformations induced by the electric field of light, $\varepsilon$ and determined by the molecular polarizability, $\alpha$. The laser beam used for excitation can be considered as an oscillating electromagnetic wave with electrical vector $\varepsilon$. Upon interaction with the sample, it induces an electric dipole moment, $\mu = \alpha \varepsilon$, which deforms molecules or molecular groups. These vibrate with a characteristic frequency $\nu_m$, corresponding to the periodical oscillations of their constituent atoms or ions about their equilibrium positions.

When a photon with frequency $\nu_o$ hits a Raman-active molecular grouping (i.e., a grouping that scatters a Raman signal) which at the time of interaction is in its ground vibrational state, part of the photon's energy is transferred to the Raman-active mode with frequency $\nu_m$ and the resulting frequency of the scattered light is reduced to $\nu_o - \nu_m$; $\nu_m$ is also called the Raman shift (or frequency of the Raman effect), as shown in Figure 3.1. In particular, this Raman frequency is called the Stokes frequency, of the Stokes Raman effect. The anti-Stokes Raman effect is also possible, where the frequency of the scattered light increases to $\nu_o + \nu_m$. 
Mechanisms of normal (spontaneous) Raman scattering: S, Stokes; AS, anti-Stokes. Also in the figure: R, Rayleigh scattering; IR, infrared absorption; \( \nu = 0 \) or \( \nu = 1 \)—quantum number defining the vibrational level. The dashed lines represent the virtual state.

In addition, elastic Rayleigh scattering, with the laser frequency, \( \nu_o \), is also present as a strong peak centered at zero Raman shift. A dominant fraction of the incident laser light in spontaneous Raman effect undergoes elastic Rayleigh scattering; this type of signal is useless for practical purposes of structural characterization.

Only about 0.001% of the incident light produces useful inelastic Raman signal (both Stokes and anti-Stokes). Thus, spontaneous Raman scattering is very weak and special precautions must be taken to separate it from the predominant Rayleigh scattering. Instruments such as notch or edge filters, tuneable filters, laser stop apertures, or double and triple spectrometers are used to strongly attenuate Rayleigh scattering and obtain high-quality Raman spectra. Figure 3.1 shows schematically the two spontaneous Raman effects, together with Rayleigh scattering and IR absorption.

The spontaneous Raman effect can be treated in the framework of classical theory [11]. The electric field of the electromagnetic radiation propagating in the x-direction is given by
where \( n^* \) is the complex refractive index, \( k \) is the radiation wave vector and \( \omega_0 \) is the frequency of the exciting laser light.

The interaction between the laser light and the material under analysis is made possible through the polarizability of the valence electrons, expressed as the linearly induced polarization.

\[
P = \varepsilon_0 \chi \varepsilon \tag{3.2}
\]

where \( \chi \) represents the linear, first order, electric susceptibility tensor (directly proportional to the polarizability) and \( \varepsilon_0 \) is the permittivity of vacuum. The scattered photon is emitted by the induced oscillating electric dipole which radiates from the virtual state. For small displacements from the internuclear equilibrium configuration, that is, in the harmonic regime, the components of the electric susceptibility tensor are linear functions of the vibrational coordinate \( X \), being approximately given by the first two terms of the series expansion in terms of \( X \):

\[
\chi = \chi^0 + (\partial \chi / \partial X)_0 X \tag{3.3}
\]

Also, for small vibrational amplitudes, one can write:

\[
X = X_0 \cos [\omega(q)t] \tag{3.4}
\]

with \( X_0 \) representing the vibrational amplitude and \( \omega(q) \) representing the vibrational (or phonon) frequency for phonon wave vector \( q \). (Note that \( \omega(q) = 2\pi \nu_m \)). At the origin (\( \chi = 0 \)), the amplitude of the electric field of the incident laser light is simplified to

\[
\varepsilon = \varepsilon_0 \cos \omega_0 t \tag{3.5}
\]

and one can then write

\[
P = \varepsilon_0 \chi^0 \varepsilon_0 \cos \omega_0 t + \varepsilon_0 (\partial \chi / \partial X)_0 X_0 \varepsilon_0 \cos [\omega(q)t] \cos [\omega_0 t] = \varepsilon_0 \chi^0 \varepsilon_0 \cos \omega_0 t + 1/2 \varepsilon_0 (\partial \chi / \partial X)_0 X_0 \varepsilon_0 \times [\cos [\omega_0 + \omega(q)]t + \cos [\omega_0 - \omega(q)]t] \tag{3.6}
\]

\[
\uparrow \text{Rayleigh scatter} \quad \uparrow \text{Raman (AS)} \quad \uparrow \text{Raman (S)}
\]

where the induced polarization includes the terms for Raman (S plus AS) and Rayleigh scattering. At ambient and low temperatures, the anti-Stokes Raman intensity is usually quite low, since most oscillators will be in the vibrational ground state (\( \nu = 0 \)). The elastic Rayleigh scattering intensity is \( ca. 1/1000 \) of the incident laser light, whereas the Stokes Raman intensity is only \( ca. 1/1000 \) of the Rayleigh scattered light.

### 3.2.2 Selection Rules

Equation (3.6) shows also that, in order for Raman scattering to have non-zero intensity, it is
necessary that \((\partial \chi / \partial X)_o \neq 0\), that is, the electrical susceptibility, which is directly proportional to the polarizability for lasers with moderate power, must vary with a vibrational coordinate at the internuclear equilibrium configuration, such that at least one of the derivatives of the susceptibility (or polarizability) components must be non-zero. In fact, the intensity of the Raman effect at the frequency of a particular vibrational mode is proportional to the sum of squares of the individual \(\chi_{ij} \epsilon_k\) terms of the induced polarization (Eq. 3.2). Since each of these terms is proportional to the derivative of a susceptibility component \((\partial \chi_{ij} / \partial X)_o\) (Eq. 3.3), a given vibration must cause a change in the corresponding electric susceptibility (or polarizability), in order to give rise to spontaneous Raman scattering. This is a general selection rule for Raman activity of the vibrations of any materials. The other general selection rule for fundamental vibrations is that the vibrational quantum number change between the initial and final states must be \(\Delta v = 1\) (in the harmonic approximation). This arises from the requirement that the transition moment between the initial \((v = 0)\) and the final state must be non-zero. For the linear Raman effect, this transition moment is an integral taken over the product of the wavefunctions of the initial and final states of the transition and the induced electric dipole moment operator; since this is an odd function and the wavefunction for \(v = 0\) is even, for the integrand to be even and the integral non-zero the wavefunction of the final state must be odd, that is, it must correspond to the \(v = 1\) state.

A specific, although more qualitative selection rule was put forward by Almeida [12] for Raman spectroscopy of glasses: the Raman spectrum of a glass is usually dominated by high frequency symmetric stretching vibrations of non-bridging anion species about fixed network forming cations, since these are the vibrations which involve the largest polarizability changes.

### 3.2.3 Depolarization of Raman Lines

The recording of polarized Raman scattering, by discriminating and measuring the polarization properties of Raman lines, allows the determination of an additional parameter, the depolarization ratio (DR), which provides valuable information about the symmetry of the vibrational modes probed. The fact that the laser light used is usually strongly linearly polarized makes the determination of DR relatively simple.

Suppose that the scattering medium is formed by randomly oriented ions or molecular groupings, which is the case for a gas or liquid and also essentially true in the case of glasses. When the incident laser light is polarized with horizontal electric field \((H)\), two different scattering configurations may be considered: one is the parallel configuration \((HH)\), in which the scattered laser light is analyzed for the same polarization as that of the incident light; in the other, the perpendicular configuration \((HV)\), the polarization analyzer selects scattered laser light polarized perpendicularly to the electric field of the incident light. The DR is given by the ratio between the Raman scattered light intensities in the perpendicular and the parallel configurations: \(DR = I_{HV}/I_{HH}\). For a 90° scattering configuration, this can take values between 0 (completely polarized vibrations) for totally symmetric vibrations of cubic symmetry (e.g. symmetric stretching modes), and 0.75 (depolarized vibrations) for asymmetric vibrational modes [11]. Partially (not completely) polarized vibrations (symmetric modes of non-cubic
symmetry) will have $0 < \text{DR} < 0.75$.

When studying the Raman spectra of solids like glasses, since the different molecular orientations are not truly random, the previous theoretical analysis is not completely accurate and one has to interpret the observed DR values with some caution. If DR is found to be either 0 or 0.75, there is still a slight possibility that the vibration responsible for the spectral peak is actually partially polarized, rather than completely polarized, or depolarized, respectively. Conversely, if DR is close to 0 or 0.75, it is still slightly possible that the vibration is actually completely polarized, or depolarized, respectively. In such cases, one has to rely on some additional information concerning the molecular structure of the system under study. But when DR is definitely larger than 0 but clearly lower than 0.75, one may be confident that the glass vibration is indeed partially polarized. In conclusion, the main usefulness of determining the DR is to make available additional information allowing in principle the distinction between symmetric and asymmetric vibrations, which is not possible after recording unpolarized spectra only.

### 3.3 INSTRUMENTATION AND DATA ANALYSIS

In general terms, modern Raman instrumentation like the one shown in Figure 3.2, requires

- light source (laser);
- sample compartment, with filters, collimation optics, and the sample holder;
- spectrometer, with collection optics to collect the scattered Raman photons and a monochromator to separate them by frequency;
- detector, to count the number of photons with a certain energy which reach the detector;
- optical microscope, in the case of micro-Raman systems.
When choosing a Raman spectrometer, the above items should be considered and adapted to the type of work to be performed. The main issue with Raman instrumentation is the inherent weakness of the Raman effect ($\sim 10^{-6}$ of the incoming laser light). As a result, optics must be well aligned and detectors must be highly sensitive and present very low noise.

### 3.3.1 Light Source

Raman spectroscopy is quite a versatile technique and many light sources can be used, typically continuous wave (CW) lasers from the ultraviolet (UV) to the near infrared (NIR). Typical examples include (but are not limited to) in the UV: 244 nm, 257 nm, 325 nm, and 364 nm; in the visible: 458 nm, 473 nm, 488 nm, 514.5 nm, 532 nm, 586 nm, 633 nm, and 647 nm; and in the NIR: 785 nm, 830 nm, 980 nm, and 1064 nm.

The Raman scattering intensity is approximately proportional to $\lambda^{-4}$, where $\lambda$ is the excitation wavelength. Therefore, higher excitation frequencies, that is, shorter wavelengths in the visible and UV regions, provide higher Raman spectral intensity than longer wavelengths.
Unfortunately, shorter wavelengths can also excite fluorescence in many samples, obscuring the Raman bands.

The most obvious choice for a Raman light source is a laser and among the most used ones are gas lasers such as argon ion, krypton ion or the He–Ne laser. The Ar⁺ laser gives high power throughput with great stability, making it one of the most used lasers in Raman history. The most intense spectral lines of the Ar⁺ laser are the 488 nm (blue) and the 514.5 nm (green), but, apart from these frequencies, the argon laser has a series of other plasma lines, each of which can be used independently, from the violet to the green region. These lines can be selectively chosen whenever the Raman signal is obscured by fluorescence, or when absorbing species are present in the composition of the samples. This is the case of Er³⁺-doped glasses, which absorb near 488 and 514.5 nm, but the use of the 457.9 nm or 476.5 nm spectral lines yields clear and non-fluorescent spectra for these glasses [14, 15]. Sometimes, the only way to reduce the fluorescence signal of a sample is to lower the energy of the radiation, by using red or infrared radiation. This can be achieved with the He–Ne laser at 632.8 nm or the Kr⁺ laser at 647.1 nm, or a near infrared semiconductor diode laser at 785 nm. This can also be used for photosensitive samples such as chalcogenide glasses, which undergo photostructural changes when exposed to near-bandgap radiation [16]. On the other hand, the high power obtained in Ar⁺ lasers (up to ~10 W), makes it possible to use them in multiline mode to pump additional tuneable lasers such as a liquid dye or a Ti:Sapphire laser, broadening the range of possible wavelengths used.

Although ideal for Raman spectroscopy, the Ar⁺ laser ages quickly and it may lose half its output power after 2 or 3 years, with the plasma tube needing to be replaced every 5 to 8 years. Recently, single-mode diode lasers have been taking over as the choice for Raman measurements, especially in micro-Raman systems, which typically require ≤ 100 mW of power. Although limited to only one wavelength (which prevents the easy fluorescence discrimination possible with multi-wavelength lasers like Ar⁺ or Kr⁺), their good stability, together with unbeatable dimensions (bellow 10 cm, when compared to a standard ~1.5 m long Ar⁺ laser tube), make diode lasers an excellent choice for modern Raman systems. However, special attention should be devoted to the laser spectral bandwidth, that is, the degree of monochromaticity of the laser, usually indicated by the full width at half maximum (FWHM) of the laser peak. Gas lasers present output bandwidths of ~0.01 nm, while diode lasers have values ~1 nm. Since a laser wavelength difference of 1 nm for the 633 nm line corresponds to a Raman shift of ~25 cm⁻¹, this might be problematic especially at low frequencies.

### 3.3.2 Sample Compartment

Whenever a laser is used, it is necessary to introduce a dielectric filter designed to pass only the desired laser line and remove other plasma lines. This means that, for each laser line used, a specific filter must be inserted. Alternatively, a laser monochromator is introduced before the sample compartment in order to eliminate the plasma lines which can interfere with the Raman signal.
The scattering configuration usually involves collection of Raman scattered light at 90° from the incident laser direction. However, in micro-Raman spectrometers like the one shown in Figure 3.2, a 180° back-scattering configuration is adopted.

Generally speaking, glasses are weak Raman scatterers and in fact silicate glasses are often used as containers for Raman sampling due to their transparency to the visible and NIR lasers used. When the glasses themselves are the purpose of the analysis, the collection optics has to be carefully aligned in order to enhance their Raman signal. Investing in alignment time usually compensates, since only with proper alignment can good quality data be obtained. Therefore, the initial alignment should be done with a strong scatterer, such as CCl₄ (main peaks at 218, 314, and 459 cm⁻¹) or cyclohexane (main peaks at 801, 2853, and 2938 cm⁻¹) or Silicon (main peak at 520.7 cm⁻¹). Once the collimation optics is optimized, replacement of the reference by the sample should take place. Bulk glass samples usually yield more signal if focusing is made not at the surface, but slightly inside the glass, just below the surface, since the analyzed volume is higher and the scattered signal is stronger.

### 3.3.3 Spectrometer

There are two main types of spectrometers used in Raman spectroscopy: the dispersive and the Fourier-transform spectrometers. The most common is the dispersive type and among these the most used system for the study of glasses involves a double monochromator system, combining a high resolution and high stray light rejection with an adequate throughput. These characteristics are required to record the Raman signal close to the excitation line, where glasses present the characteristic boson peak, usually below 100 cm⁻¹. A typical dispersive spectrometer, where the incoming light is separated by gratings, passes through narrow band slits and is detected by a photomultiplier tube, typically requires at least ~30 minutes to scan the spectral region of interest (e.g., 10 to 4000 cm⁻¹) and, if good quality spectra are to be obtained, more than one scan may be necessary, increasing the overall time to record a spectrum to impractical values. For many years, this was the standard Raman system.

Nowadays, two alternatives are used to decrease this run time: the most common is the use of multi-channel detectors (see next item); a second type of spectrometer, the Fourier-transform (FT) Raman spectrometer is also being used. According to Chase and Hirschfeld [17], the most adequate laser for FT-Raman is the Nd³⁺:YAG solid state laser operating in the NIR at 1064 nm. With this long wavelength there is virtually no fluorescence, making it an ideal candidate for fluorescent materials. The scattered Raman signal is then filtered (to remove the 1064 nm radiation), modulated by an NIR interferometer and then sent to the detector. Since the FT-Raman system works with NIR radiation, the intensity of the Raman signal (roughly proportional to λ⁻⁴) becomes lower, making it less applicable for glasses, unless they have been doped or contain fluorescent impurities.

### 3.3.4 Detector

For many years, the photomultiplier tube (PMT), working in photon counting mode, was the best option for Raman signal detection. The PMT is a cascade electron amplifier with high
gain and low dark current, whose reduced cost led to its widespread use. The main disadvantage is the time necessary to record a spectrum, especially if several scans are needed. This also limits the use of Raman spectroscopy (with PMT detection) in kinetic studies.

More recently, PMTs have been progressively replaced by multi-channel detectors, such as charge coupled devices (CCDs). Their use drastically reduces the time necessary to collect a spectrum, since they register photons over a wide range of wavelengths at the same time. A CCD chip consists of a two-dimensional photodiode array of pixels, typically 1024 × 1024. When light hits a pixel, it creates a charge via the photoelectric effect, which is set in motion by an applied potential. The scattered light is focused as a line on the CCD and each line corresponds to a Raman spectrum. In this way several lines can be added, increasing the signal-to-noise ratio, or can be stacked in order to follow the kinetics of a chemical reaction. CCDs are commonly used for imaging and mapping. For imaging, the spectrometer lets just one particular wavelength of interest (at a Raman peak of the species under study) go through onto the CCD, which images the distribution of that particular species. Although imaging is a fast process, only a particular region is analyzed. On the other hand, mapping records the whole spectrum but is quite time consuming and can take days to complete. Each manufacturer has developed specific algorithm-based software to speed up the mapping capability.

CCDs, being multi-channel detectors, are generally less robust than single channel PMTs regarding possible damage from the laser light. Hence they are normally used together with notch or edge filters to guarantee efficient rejection of the laser line. These filters, however, cause simultaneous rejection of the lower frequency part of the Raman spectrum below ~70–100 cm\(^{-1}\), a spectral region which can be recorded by a good (long) double monochromator, together with PMT detection. In addition, edge filters prevent recording of the anti-Stokes part of the Raman spectrum, but this is seldom necessary. Recently, however, ultralow frequency filters have been proposed [18], based on Bragg gratings, which are transparent devices with a periodic variation of the refractive index, allowing measurements down to ~5–10 cm\(^{-1}\) as well as the simultaneous measurement of Stokes and anti-Stokes data.

Since the Raman signal is rather weak, the background noise is critically important. CCDs may work with nitrogen cooling (at ~130°C) in order to reduce the dark current, but thermoelectrically Peltier-cooled CCDs, working at ~70°C, are being increasingly used, due to easier operation and lower operational and maintenance costs.

### 3.3.5 Micro-Raman Spectrometers

For glass films, a Raman microscope system where the samples are positioned on a microscope slide and observed in a backscattering geometry is most adequate. Micro-Raman spectrometers include an optical microscope and a Raman spectrograph. A laser is directed to an objective lens of the microscope and focused onto the sample. The scattered Raman signal is collected by the same objective and guided to the monochromator, where it is separated by gratings and detected by a PMT or a CCD. The microscope is usually equipped with a 50/50 R/T (% reflection / % transmission) beamsplitter to direct the laser and collect the signal. The
laser is finely focused on the surface, but it will continue to penetrate the sample, as long as the glass sample is transparent to the exciting laser radiation. How far it penetrates depends upon the laser wavelength and the sample material itself and it can vary from as little as a few nm to several nm. For example, Dombrowski et al. [19] showed that, for silicon, the penetration depth goes from 300 nm for a visible laser ($\lambda = 485$ nm) to $\sim$15 nm for a UV laser ($\lambda = 364$ nm). The probed volume depends on the laser spot size and the beam penetration. At 633 nm, the He–Ne laser wavelength, the light will penetrate 3 µm, but this number changes rapidly with the wavelength. At 785 nm it is about 12 µm, but at 532 nm it is 0.7 µm and in the UV it can drop to 5–10 nm.

Micro-Raman systems with high magnification and high numerical aperture (NA) objectives use a highly focused laser beam yielding $\sim$1 µm lateral resolution [20]. Although Raman spectroscopy is a non-destructive technique, there is intense power at the sample which can lead to its degradation, especially for long exposure times. The use of a 10/90 beamsplitter can reduce sample damage. Another possibility is to disperse the sample in another medium with no Raman signal, such as KBr, or to immerse the sample in a liquid which acts as a heat absorber (such as water) [20], using immersion objectives. Sample degradation can also be reduced by defocusing the laser beam or rotating the sample. This will reduce the flux density and may allow a proper Raman spectrum to be obtained.

Another aspect of the micro-Raman systems is the low power necessary, since the laser beam is focused to a diffraction limited spot on the sample. This reduces the need for powerful lasers, so solid state lasers of $\sim$100 mW are more than enough to generate good Raman signals.

Generally, a set of objectives are used: a standard objective for sub-micron sized samples or structural features under study is the 100× magnification, with NA of 0.9. For transparent samples like bulk glasses, a 50× (0.80 NA) objective can yield higher intensity due to the higher volume analyzed and a 5× or 10× objective is usually used on a first approach to the area of interest. A long working distance objective, such as the 50× objective, is mandatory if samples are tilted or just not flat enough.

Apart from the lateral (XY) spatial resolution, micro-Raman spectrometers often give depth (Z) resolution. For this, confocal optics is required. The microscope contains a pinhole in its focal plane, whose adjustable aperture selects the depth from where the radiation is to be analyzed, allowing micron depth resolution, such that individual layers of a sample may be discretely analyzed, if there is no limitation due to their optical absorption [21].

### 3.3.6 Resolution

Spatial resolution is diffraction limited and is mainly dependent on the laser wavelength, but spectral resolution is strongly dependent on the individual components of the instrument. Although it is difficult to speak about a single spectrum resolution, since it varies over the spectral range due to grating dispersion, in dispersive Raman spectrometers, four main factors affect the spectral resolution: the diffraction grating, the detector, the slit or pinhole, and the distance between grating and detector (focal length of the spectrometer).
The diffraction grating determines the total wavelength range of the spectrometer: the more grooves (or lines) per mm (l/mm) the grating has, the higher the dispersion and the better the separation of the incoming wavelengths. However, this also means that a smaller part of the spectrum is observed at the same time by the CCD. The detector determines the size and number of collected points: the smaller the pixel of the CCD is, the higher the achievable spectral resolution. Furthermore, mechanical slits or confocal holes can also add some limitations, since the smaller the slit or the hole, the better the spectral resolution, although at the expense of signal intensity. In practice, the slits are kept as narrow as possible to ensure optimum resolution, as long as enough light reaches the detector. The longer the focal length of the spectrometer the higher the spectral resolution.

Usually, a grating of 1200 l/mm is considered for general use, since it delivers a wide spectral range with acceptable resolution. For high resolution (e.g., an average resolution of ~1 cm⁻¹), a 1800 l/mm grating with a red laser can be used and, for specific applications such as in the UV range, a 2400 l/mm grating can be used. On the other hand, for a large spectral range and an average resolution ~4 cm⁻¹, a 600 l/mm grating and a red laser may be used.

Resolution of a Raman system can be estimated if a neon or an argon lamp is used, since they present extremely narrow line widths (usually less than 0.001 nm [22]) and the FWHM of the Raman bands are a good indication of instrumental resolution.

### 3.3.7 Data Analysis

In order to extract reliable information from a Raman spectrum, calibration procedures have to be performed. These procedures consist in checking the linearity of the monochromator (for each grating), in order to insure spectral correctness. There is no universally accepted calibration standard and every spectroscopist has their own favorite standard materials, depending on the spectral range analyzed. From carbon tetrachloride, to cyclohexane, indene, Silicon or a Neon lamp, they all can tell you if the equipment's response is in line with the expected results. Nowadays, many Raman equipment use in-built software packages that can correct the obtained spectra automatically for a certain spectral region, once the calibration standards are run. In confocal micro-Raman systems, calibration procedures also include a confocality check.

Once the spectroscopist has confidence in the equipment's results, he can turn into analysis. Data analysis requires the knowledge of the wavenumber position of the bands, as well as their intensity. One of the main problems which may occur in Raman spectroscopy is the existence of a fluorescence background which can obscure the Raman signal completely. If the usual technique of using a different excitation wavelength is not possible or does not solve the problem, then the only thing to do, to recover the Raman signal, is to try to remove the broad background by using a polynomial or spline baseline function, or by looking into the first derivative of the Raman spectrum. In the latter case, only the Raman peak frequency can be obtained and no information regarding peak intensity is made available.

For some systems, particularly glasses, the Raman signal is usually broad and a straightforward analysis can be rather difficult. In many cases, it is helpful to analyze a set of
samples within a certain compositional range and to follow the increase or decrease of a particular band. Most Raman software is now integrated with Raman spectral libraries that can be searched to find a match and thus provide a chemical identification. Raman spectroscopy can then be used as a pass/fail test, as long as a proper spectrum is available in the database to be compared to a new spectrum obtained. This is the basis of routine applications of Raman spectroscopy. If, on the other hand, there is no previous knowledge about the analyzed sample, then peak fitting of broad Raman bands may give more information (see Section 3.4.1—Figure 3.5). However, it is always possible to fit a perfect Gaussian peak with two new Gaussian peaks, so peak fitting exercises should always be done with care in order to ensure some underlying physical meaning.

**Figure 3.3** (a) Polarized (HH and HV) Raman spectra of the 50 SiO$_2$-50 Na$_2$O glass composition (50SiNa); (b) depolarization ratio ($I_{HV}/I_{HH}$) of the 50SiNa composition.
**Figure 3.4** Polarized (HH) Raman spectra of \((100 - x) \text{SiO}_2 - x \text{Na}_2\text{O}\) glasses. (a) Raw data; (b) normalized data.
Figure 3.5 Peak-fitting of metasilicate Raman spectrum in the region between 800–1200 cm\(^{-1}\) with: (a) three Gaussian peaks; (b) four Gaussian peaks; (c) four Lorentz peaks, and (d) four Voigt peaks.

The Raman spectrum of most glasses is enhanced at low frequencies, exhibiting the so-called boson peak, which is a weakly polarized or depolarized band (DR \(\geq 0.6\)) usually below \(\sim 100\) cm\(^{-1}\). Low frequency peaks like this may be masked by the Bose–Einstein thermal phonon population factor, \(n(\omega) = 1 / [\exp(h\omega/k_B T) - 1]\), which increases with decreasing phonon frequency. According to Galeener and Sen [23], the temperature factor can be removed and the data reduced to absolute zero by dividing the raw data by \([n(\omega) + 1]\).

### 3.4 CASE STUDIES

This section presents four case studies that illustrate the use and application of Raman spectroscopy to different type of glasses, namely: (i) the effect of alkali incorporation in the structure of silicate glasses, (ii) the study of phase separation mechanisms in phosphate glasses, (iii) the study of germanosilicate glasses and glass ceramics, and (iv) Raman study of
3.4.1 Structural Effects of Alkali Incorporation in Silicate Glasses

Alkali incorporation in silicate glasses is known to promote structural changes responsible for their property modifications. One of the major structural changes is the breaking of the backbone structure of the glasses. According to Zachariasen's model [24], later refined by Warren and Biscoe [25], it is generally accepted that silica glass structure is based on corner sharing of [SiO$_4$] tetrahedra, with a broad dispersion of the bridging angles ranging from 120° to 180°, where each Si atom is surrounded by four oxygen atoms, each in turn connected to another Si atom, bridging two tetrahedral units which are called $Q^4$ species—tetrahedra with four bridging oxygens.

The addition of alkali ions to silica causes the breaking of the Si–O–Si bonds and the formation of Si–O$_{NB}$ bonds, where O$_{NB}$ represents a non-bridging oxygen (or NBO, bonded only to one Si atom), thus reducing the connectivity of the glass network and creating tetrahedral units with lower connectivity $Q^3$, $Q^2$, $Q^1$, and $Q^0$, which have three, two, one, and zero BOs, respectively. The structure of binary alkali silicate glasses has been studied by several techniques, which include, among others, vibrational spectroscopy and X-ray and neutron diffraction [26-30], but Raman spectroscopy, in particular, remains one of the best techniques to follow such structural changes.

As previously discussed by Bendow [31], a full description of the fused silica structure is not based solely on its Raman spectrum, such that confirming data from other techniques may be required. However, the progressive incorporation of alkali species in silicate glasses can be conveniently followed and understood based on their Raman spectra, since the presence of NBO ions can easily be identified by Raman spectroscopy. To illustrate this point, a series of sodium silicate glasses were prepared with nominal compositions (100 − $x$) SiO$_2$ − $x$ Na$_2$O, with $x$ = 20, 30, 33, 40, and 50 mol% [32]; $x$ = 33 refers to the disilicate glass structure with, on average, one NBO/tetrahedron, while $x$ = 50 corresponds to the metasilicate structure, with two NBO/tetrahedron and $x$ = 0 represents pure silica, lacking NBO species.

The glasses were synthetized according to the procedure described elsewhere [33]. The final melting temperatures ranged between 1000°C and 1450°C, depending on the composition. For pure silica, a commercial glass sample from Heraeus was used.

Raman spectroscopy measurements were performed with a double monochromator (Spex 1403), an Argon ion laser (Spectra-Physics, mod. 2016) operating at 514.5 nm (1W at source) and a PMT detector (Hamamatsu R928). Polarized Raman spectra (HH and HV configurations) were collected in the 90° scattering geometry, at room temperature, with a resolution of 4 cm$^{-1}$. The spectra were obtained with a time constant of one second, between 10 cm$^{-1}$ and 1300 cm$^{-1}$, with an estimated frequency accuracy of ±2 cm$^{-1}$.

Figure 3.3a shows the polarized Raman spectra of the sodium metasilicate glass, dominated by the polarized peaks at 617 and 978 cm$^{-1}$. The HV component indicates that, apart from the low
frequency region, all the Raman peaks are strongly polarized, indicating that they involve symmetric stretching vibrational motions, as observed in Figure 3.3b (DR < 0.2).

Figure 3.4 shows the polarized (HH) components of the Raman spectra of the different silicate glasses prepared. A general spectral intensity increase is observed with increasing sodium content in the intermediate/high frequency range, where silica glass peaks are rather weak. These Raman spectra can be analyzed by dividing them into three main regions: the low frequency region (10–200 cm\(^{-1}\)); an intermediate frequency region (300–800 cm\(^{-1}\)) and the high frequency region (800–1200 cm\(^{-1}\)).

The main information obtained from the low frequency region involves the boson peak (at ca. 50 cm\(^{-1}\) in pure silica glass), which is characteristic of most glasses, but whose origin remains controversial. The boson peak, which may originate from an excess in the VDOS of amorphous materials, has been associated with the presence of intermediate range order in glass [34–36] in the framework of the Martin and Brenig model [37]. More recent theories tend to associate the boson peak with the transverse acoustic van Hove singularity of the corresponding crystal [38], indicating that the glass has no additional modes in excess of the sound waves in the crystal. The boson peak has also been related to dynamical effects over the glass transition and to the early stages of the crystallization process [39–41]. In fact, it has been suggested that low frequency Raman spectra can be used to determine the \(T_g\) value of glasses [42, 43].

In order to observe this peak, a good discriminating spectrograph and optical quality samples are required. The thermal population may mask the peaks in this low frequency region of the spectrum, so the corrected (reduced) Raman spectrum should be computed whenever accurate peak position and shape are relevant. From Figure 3.4, it can be observed that, for some samples, the region below \~80 cm\(^{-1}\) is buried under the strong Rayleigh wing, whose high intensity may be due to local refractive index fluctuations in the samples of lower optical quality.

For vitreous silica, the dominant Raman band lies in the intermediate frequency region at \~430 cm\(^{-1}\) (Figure 3.4). The dominant band in a glass Raman spectrum is usually related to symmetric stretching (SS) vibrational modes and, in fact, Galeener [44] has assigned this band to SS modes of the Si-O-Si bonds, SS (Si-O\(_B\)), with the BO atoms oscillating along the bisector of the Si-O-Si (bridging) angle. This can be confirmed through the depolarization ratio, which for this band is close to zero (\~0.04). Near the main band, a sharp peak is observed at \~490 cm\(^{-1}\), which, together with the small peak at \~600 cm\(^{-1}\), have been attributed to four- and three-membered silicate rings, respectively [45]. With increasing Na\(_2\)O content, several modifications can be observed in this region: to begin with, the intensity of the broad polarized band at \~430 cm\(^{-1}\) decreases rapidly, while that of the \~490 cm\(^{-1}\) sharp peak appears to increase simultaneously with a blue shift (in Figure 3.4: 486 \~ 532 \~ 565 \~ 571 \~ 590 \~ 617 cm\(^{-1}\)). Although this conclusion seems rather straightforward, it is probably not correct as discussed by McMillan [46], since this peak and the \~600 cm\(^{-1}\) peak both decrease in intensity for very small additions of Na\(_2\)O, while new bands appear. The bands peaking within the \~532–617 cm\(^{-1}\) region are obviously related to the addition of sodium oxide. Since
these bands have high intensity and frequencies of the order of the main bands in pure silica, it was suggested [46] that they are related to similar vibrational modes, that is, SS (Si-O\textsubscript{B}), in lower bridged tetrahedra. Their increasing frequencies reflect, according to Furukawa et al. [27], the progressive depolimerization of the silica tetrahedral network or may indicate a decrease in the average Si-O-Si angle as may be inferred from the Sen and Thorpe model [6, 44].

The 800–1200 cm\textsuperscript{-1} region is, however, the most strongly affected by the incorporation of sodium oxide. In fact, new peaks appear which become progressively dominant. The peak at \sim 1100 cm\textsuperscript{-1} is found to increase in intensity from 0 to 33 mol\% of Na\textsubscript{2}O, but higher alkali contents lower its intensity (Figure 3.4a). On the other hand, a new band at \sim 950–980 cm\textsuperscript{-1} becomes more intense with increasing alkali concentration, reaching its highest intensity for the 50 SiNa composition. For this particular glass, another band occurs near 850 cm\textsuperscript{-1}. These polarized bands have been assigned to SS (Si-O\textsubscript{NB}) vibrations and are related to the \(Q^n\) signatures in Raman spectra [27, 46]. In fact, the main band at \sim 1100 cm\textsuperscript{-1}, which is most intense for the \(x = 33\) mol\% composition, corresponds to \(Q^3\) units, while the band at \sim 950–980 cm\textsuperscript{-1} is related to \(Q^2\) units, being strongest for the metasilicate structure. Figure 3.4b shows a frequency increase of the \(Q^2\) band from \sim 950 to \sim 980 cm\textsuperscript{-1} with increasing sodium oxide content from 40 to 50 mol\%, which is in accordance with the literature [46]. However, as pointed out by McMillan in his review [46], a careful examination of the polarized spectra revealed a more complex interpretation, since the 950 cm\textsuperscript{-1} band has a higher depolarization ratio than the 980 cm\textsuperscript{-1} band. According to McMillan [46], “the 980 cm\textsuperscript{-1} band becomes strongly Raman-active just close to the metasilicate composition” and although these two bands could be related, they might also correspond to two different vibrations. Figure 3.3b agrees with these results and in fact, we found a DR value of \sim 0.4 at 948 cm\textsuperscript{-1} for the compositions with \(\leq 33\) mol\% Na\textsubscript{2}O, while those with 40 and 50 mol\% Na\textsubscript{2}O present DR minima of \sim 0.1 at 953 and 977 cm\textsuperscript{-1} respectively.

According to the literature [46 and references therein], vibrations of the \(Q^I\) and \(Q^0\) units in alkali silicates correspond to the peaks at \sim 900 and \sim 850 cm\textsuperscript{-1}, respectively, but the \sim 900 cm\textsuperscript{-1} peak is only explicitly observed in alkaline-earth silicate glasses. In the alkali silicates, the \sim 900 cm\textsuperscript{-1} peak is unresolved under the 950–1000 cm\textsuperscript{-1} band [45] and peak-fitting of the Raman spectra [47] might be necessary.

In the present study, only the band at 850 cm\textsuperscript{-1} was observed, but a possible shoulder on the low frequency side of the \(Q^2\) band could be tentatively found through peak fitting of the region between 800 and 1200 cm\textsuperscript{-1} (Figure 3.5). The peak shape can be of Gaussian or Lorentzian types, as well as a combination of the two (Voigt shape). In the present case, although peak fitting with four Gaussian peaks (Figure 3.5b) yielded a better fit than with three (Figure 3.5a) (with unconstrained variables), it yielded shares of 8.5 \% for \(Q^0\), 46.2 \% for \(Q^I\), 23.4 \% for \(Q^2\) and 21.9 \% for \(Q^3\) units, for the 50SiNa composition, indicating a predominance of \(Q^I\) in this composition, which was not to be expected. However, considering Lorentzian
(Figure 3.5c) or Voigt (Figure 3.5d) shapes, a predominance of $Q^2$ was obtained (~50% in both cases), in agreement with the expected results.

The observed decrease in the frequency of the $Q^n$ peaks with increasing number of NBO ions per tetrahedron reflects the decreasing Si-O$_{NB}$ bond strength as the degree of modification of the glass network increases.

The effect of modifying alkali cations on the silicate glass structure can also be studied by Raman spectroscopy as reported by Santos et. al. [33], where the Raman spectra of binary silicate glasses with 80 SiO$_2$–20 R$_2$O (R = Li, Na, K) were studied and the $Q^3$ band was observed to shift to higher frequency (1085, 1099, and 1108 cm$^{-1}$), from the lithium to sodium and to potassium silicates, respectively (Figure 3.6). This behavior also reflects the increasing Si-O$_{NB}$ bond strength as the degree of modification of the glass network increases from Li → Na → K containing glasses.

Figure 3.6 Polarized (HH) Raman spectra of v-SiO$_2$ and 80 SiO$_2$–20 R$_2$O glasses, with R = Li, Na, K. (Reprinted from Reference 33.)
Although data from other techniques are necessary to better explain the glass structure, Raman spectroscopy gives a very important insight, especially when $Q^n$ units are present, as e.g. in multicomponent silicate glasses. However, care should be taken regarding peak fitting procedures. Moreover, when interpreting the Raman spectra of glasses, a set of samples with systematic compositional variations should preferentially be studied for a more definitive assignment of each particular Raman peak.

3.4.2 Phase Separation Mechanisms in Transition Metal Phosphate Glasses

An example of an interesting Raman study [48] focuses on the separation of crystalline phases within a transition metal phosphate glassy matrix as a precursor for the preparation of glass-ceramic materials, which are ceramics obtained by the controlled nucleation and crystallization of a glass precursor. While the structural transformation of a glass into a crystalline phase may be followed by Raman spectroscopy, the detailed determination of the mechanisms of phase separation within a glassy matrix by micro-Raman spectroscopy has been little explored until now.

Glass-in-glass phase separation phenomena may be of two general types [49]: (i) classical phase separation by nucleation and growth with a discrete, droplet-like morphology; (ii) spinodal decomposition, with an interconnected morphology. The driving force for phase separation is the lowering of the Gibbs free energy and while (i) requires large compositional fluctuations of small spatial amplitude, (ii) involves small compositional fluctuations of large spatial extent. In the case of metastable immiscibility below the liquidus temperature, $T_L$, fast quenching of the melt may actually lead to a homogeneous glass, whereas further reheating will lead to the occurrence of phase separation.

Crystallization, or the precipitation of crystals of a composition usually different from that of the initial glass, occurs also by a nucleation and growth mechanism. The nucleation phenomenon may be homogeneous, leading to bulk crystallization, or heterogeneous, normally leading to surface crystallization.

Mazali et al. [48] have studied phase transformations within glasses with the compositions 6 Li$_2$O-24 TiO$_2$-39 CaO-31 P$_2$O$_5$ (LTCP) and 6 Li$_2$O-18 Nb$_2$O$_5$-43 CaO-33 P$_2$O$_5$ (LNCP). For the devitrification study, glass discs 25 mm in diameter and 2 mm thick of both compositions were first submitted to a 20 hour nucleation step at 630°C. After cooling, the samples were reheated and heat treated at the crystal growth temperature, $T_c$: LTCP = 760°C and LNCP = 830°C, for periods of time between 2 and 30 minutes and also for a longer period of 12 hours. The $T_c$ values were obtained from differential thermal analysis (DTA) measurements. The micro-Raman spectra were measured with a Renishaw Raman Imaging Microprobe System 3000, coupled to an optical microscope with 1.0 μm spatial resolution, using a 8 mW He–Ne laser ($\lambda = 632.8$ nm) for excitation, at 2 cm$^{-1}$ resolution. The measured areas were located at the sample surfaces.

LTCP glass undergoes glass-in-glass phase separation by spinodal decomposition at 760°C
[50] and Figure 3.7 shows optical micrographs of the initial stages of devitrification of LTCP glass, treated at this temperature for 2 and 3 minutes, whereas Figure 3.8 shows the corresponding Raman spectra. The spectra of regions (b.1) and (c.1), in the frequency range above 500 cm$^{-1}$, are similar to that of the as-cast glass (a), which is characterized by a strong band at $\sim$930 cm$^{-1}$, related to the presence of TiO$_6$ octahedra in the glass network [51]. In the region between 100 and 700 cm$^{-1}$, when compared to the as-cast glass spectrum, it is clear that some new peaks are present in (b.1) and (c.1), which are due to newly formed crystalline phases. On the other hand, the spectra of regions (b.2) and (c.2) correspond to areas where the devitrification process has clearly reached a more advanced stage, with a large number of sharp peaks characteristic of crystalline phases. For any of the different heat treatments, the peaks in the 100–700 cm$^{-1}$ region are due to the presence of the NASICON-type (sodium superionic conductor) LiTi$_2$(PO$_4$)$_3$ phase [52]; the region between 100 and 400 cm$^{-1}$, in particular, contains crystal external modes that can be assigned rigorously by the factor group method. The NASICON-type phases include [PO$_4$] tetrahedral and [TiO$_6$] octahedra connected through oxygen bridges. The sharp and strong peak at 142 cm$^{-1}$ is due to the doubly degenerate E$_g$ mode characteristic of the anatase phase of TiO$_2$, whose intensity increases substantially on going from (b.2) $\rightarrow$ (c.2) (2 $\rightarrow$ 3 minutes at 760°C). The peaks at 1047 and 741 cm$^{-1}$ (b.2, c.2 and d) can be attributed to the $\beta$-Ca$_2$P$_2$O$_7$ phase [53] and the peak at 638 cm$^{-1}$, which is observed for the more advanced stages of ceramization, has been attributed to the Li(TiO)PO$_4$ crystalline phase [54]. The combination of the information available from Figures 3.8 and 3.9 show that the composition continuously changes during the phase separation phenomena, which is characteristic of spinodal decomposition. Therefore, one may conclude that, for the LTCP composition, glass-in-glass phase separation by spinodal decomposition, induced by the Ti$^{4+}$ ions (which may be considered to act as a nucleating species for the glass-ceramic material), is the precursor phenomenon to the crystallization of the LiTi$_2$(PO$_4$)$_3$ and anatase major phases. Between 5 minutes and 12 hours of thermal treatment, the Raman spectra exhibited no further changes. Raman micro-spectrometry, therefore, allowed the identification of the LiTi$_2$(PO$_4$)$_3$, Li(TiO)PO$_4$, anatase TiO$_2$, and $\beta$-Ca$_2$P$_2$O$_7$ phases in the devitrification process of LTCP glass.
Figure 3.7 Optical micrographs of the initial stages of devitrification of LTCP glass, treated at 760°C for 2 and 3 minutes. (Magnification: 40×).

(Reprinted from Reference 48.)
Figure 3.8 Micro-Raman spectra of LTCP glass in the different regions indicated in Figure 3.7 and (d) after 12 hours of heat treatment at 760°C.

(Reprinted and adapted from Reference 48.)

On the other hand, the phase transformations that occur when LNCP glass is transformed into a glass-ceramic are illustrated through the Raman spectra of Figure 3.9 (bottom). After the nucleation step at 630°C, crystallization heat treatments of 2 and 5 minutes at 830°C were performed. Figure 3.9 (top) shows that the devitrification process started at the surface, after heterogeneous nucleation and initially there was two-dimensional crystal growth along the surface, followed by growth toward the center of the sample. Figure 3.9 (top) illustrates the aspect of the interface ceramic/glass for both heat treatment times and the regions analyzed by micro-Raman spectroscopy, whereas the corresponding spectra are shown in Figure 3.9 (bottom). Region (i), within the glassy phase, had a spectrum similar to that of the as-cast glass shown in Figure 3.8a. In the nucleated region (ii), one observes the 914 cm$^{-1}$ band (typical of the Nb-O bonds in the glass), but also the sharp peak at 1047 cm$^{-1}$, attributed to the PO$_3^{2-}$ stretching vibration of the β-Ca$_2$P$_2$O$_7$ phase. At the interface region (iii), there is a reduction in
the intensity of the 914 cm\(^{-1}\) and an intensification of the 1047 cm\(^{-1}\) peak, together with the appearance of two new peaks at 739 and 487 cm\(^{-1}\), also assigned to the \(\beta\)-Ca\(_2\)P\(_2\)O\(_7\) phase [53]. In region (iv), corresponding to the crystallized region near the interface, the band at 914 cm\(^{-1}\) is no longer observed and only those bands typical of \(\beta\)-Ca\(_2\)P\(_2\)O\(_7\) are visible. Finally, in region (v), a crystallized region far from the interface, the Raman spectrum is completely different from that of region (iv), with new peaks at 1016 and 990 cm\(^{-1}\), which can be attributed to P-O vibrations. The peaks at 805, 462, 376, and 293 cm\(^{-1}\), are assigned to Nb-O vibrations, characteristic of the \(\alpha\)-NbPO\(_5\) phase [55]. This shows that nucleation is initiated with the formation of crystallization nuclei for the \(\beta\)-Ca\(_2\)P\(_2\)O\(_7\) phase, which cause classical (droplet-like) phase separation in the glassy matrix and then induce the formation of a new phase, \(\alpha\)-NbPO\(_5\).

\[\text{Figure 3.9} \] Ceramic/LNCP glass interface for both 2 and 5 minutes of heat treatment at 830°C (top); Raman spectra taken in the regions indicated (bottom).

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3.4.3 Raman Study of Niobium Germanosilicate Glasses And Glass-Ceramics

Niobium germanosilicate glasses are promising candidates to obtain transparent nanocrystalline glass ceramics with nonlinear optical properties. For this purpose, crystallization has to occur homogenously at the nanoscale and the nanocrystals should have nonlinear properties. Glasses in the GeO$_2$-SiO$_2$-Nb$_2$O$_5$-K$_2$O system are known to exhibit nanoscale crystallization [56–58] and phases with nonlinear optical properties such as K$_3$Nb$_3$Si$_2$O$_{13}$, KNbSi$_2$O$_7$, and KNbO$_3$ have been obtained [59–63]. Raman data have been used not only to study the structure of these glasses, but also to identify the different crystalline phases occurring upon heat treatment.

R. Santos et. al. [58] synthesized a set of glass samples in the 50(GeO$_2$-SiO$_2$)-25Nb$_2$O$_5$–25K$_2$O system, with compositional variation from pure germanate to pure silicate compositions and studied their structure by Raman spectroscopy. The low frequency Raman spectrum of the pure germanate composition (lower curve of Figure 3.10) presents a boson peak at 72 cm$^{-1}$ plus a broad band centered at 200 cm$^{-1}$ due to Nb-O bending modes [64–66]. The 486 cm$^{-1}$ and 856 cm$^{-1}$ peaks have been related to the SS mode of Ge-O-Ge and the SS mode of Ge-O$_{NB}$ species, respectively [58, 60–62]. The $\sim$740 cm$^{-1}$ band, which is absent in alkali germanate compositions [67, 68], has been related to the presence of Nb$_2$O$_5$ and assigned to NbO$_6$ octahedra [64, 66]; however, Takahashi et. al. [40] have assigned it to Ge-O-Nb bonds.
It is known that the addition of niobium oxide to a disilicate composition drastically reduces the silicate-related Raman bands, due to the large polarizability and therefore large Raman scattering cross section of the niobate-related vibrations. In fact, above 5 mol% of niobium oxide, the niobate-related bands completely dominate the spectra at the expense of the silicate-related ones, which disappear above 15 mol% Nb$_2$O$_5$ [64, 69, 70]. Therefore, the high frequency Raman spectrum of the potassium niobium silicate composition (top curve of Figure 3.10) is dominated by the ~694, ~809, and 894 cm$^{-1}$ peaks, which have all been attributed to Nb-O bonds [63, 71, 72]: the 694 cm$^{-1}$ peak has been related to vibrations of NbO$_6$ octahedra without NBOs, while the ~809 cm$^{-1}$ peak has been attributed to highly distorted NbO$_6$ octahedra without NBOs and/or to NbO$_6$ octahedra with non-bridging oxygens [71]. This high frequency peak was also assigned to NbO$_4$ tetrahedra by Kolobkova [64] and, in fact, the existence of NbO$_4$ units has also been proposed by Jehng and Wachs [73], based on

**Figure 3.10** Polarized (HH) Raman spectra of (50 − x)GeO$_2$ − x SiO$_2$ − 25 Na$_2$O − 25 K$_2$O glasses. (Reprinted from Reference 58.)
the Raman spectra of a series of niobium oxide reference crystals, who assigned the Raman peaks in the 500–700 cm\(^{-1}\) region to vibrations of slightly distorted NbO\(_6\) octahedra, the 790–830 cm\(^{-1}\) peaks to NbO\(_4\) tetrahedra and the 850–1000 cm\(^{-1}\) region to highly distorted NbO\(_6\) octahedra. EXAFS data have also suggested the possible coexistence of NbO\(_4\) tetrahedra and NbO\(_6\) octahedra in niobium alkali silicate glasses, for Nb\(_2\)O\(_5\) contents ~5 mol%; but only the octahedral form was proposed above 15 mol% [66]. The 894 cm\(^{-1}\) peak has also been related to highly distorted NbO\(_6\) octahedra with at least one NBO species [63, 69, 74, 75], as well as to NbO\(_4\) tetrahedra [65]; however, Figure 3.10 clearly shows that this peak is strongly dependent on the silica content and it can tentatively be attributed to SS (Si-O\(_{NB}\)).

The Raman spectra of mixed niobium germanosilicate glasses include the characteristic features of the pure germanate glass, plus a high frequency band at ~894 cm\(^{-1}\), similar to the high frequency band of the pure silicate glass. Therefore, the 486 cm\(^{-1}\) band indicates the presence of Ge-O-Ge bonds, while the band at ~740 cm\(^{-1}\) indicates the presence of NbO\(_6\) octahedra without NBOs and those at ~856 and 894 cm\(^{-1}\) are related to the presence of NbO\(_6\) octahedra with NBO species and to Si-O\(_{NB}\) bonds, respectively.

Based on the Raman spectroscopy analysis above, an overall structural picture has emerged, where the Nb\(^{5+}\) cations act as network formers and the germanosilicate glass structure can be described as an array of GeO\(_4\) and SiO\(_4\) tetrahedra, connected by NbO\(_6\) octahedra with some degree of distortion. The potassium ions tend to be located close to the NbO\(_6\) octahedra, compensating the excessive negative charge. A possible sketch of the germanosilicate glass structural motif is shown in Figure 3.11.
The progressive replacement of glass by crystalline phase upon heat treatment can also be followed by Raman spectroscopy. The crystallization of niobium oxide-containing glasses has been studied by several authors [40, 54, 75]. For example, the Raman spectrum of heat treated 40GeO$_2$–10SiO$_2$–25Nb$_2$O$_5$–25K$_2$O glass composition (Figure 3.12) revealed a decrease in intensity of the bands at 486, ~740, and 856 cm$^{-1}$, while the characteristic band of the crystalline K$_{3.8}$Nb$_5$Ge$_3$O$_{20.4}$ phase at ~600 cm$^{-1}$ became predominant. The high frequency peaks of this crystalline phase near 800 and 836 cm$^{-1}$ occurred only after more prolonged heat treatment, corresponding to a higher crystalline volume fraction.
Figure 3.12 Raman spectra of the 40GeO<sub>2</sub>–10SiO<sub>2</sub>–25Nb<sub>2</sub>O<sub>5</sub>–25K<sub>2</sub>O glass composition before and after heat treatments, plus the K<sub>3.8</sub>Nb<sub>5</sub>Ge<sub>3</sub>O<sub>20.4</sub> crystalline phase.

(Reprinted from Reference 58.)

Since the boson peak is characteristic of glass, its study with heat treatment might give an insight of the early stages of the crystallization process. Several authors followed the evolution of the boson peak with temperature [39–41] and found it to be highly sensitive to the glass transition. Stavrou et. al. [41] were able to determine $T_g$ from the Raman data, while Takahashi et. al. [39] reported a strong decrease of the boson peak frequency with increasing temperature, at $T/T_g \sim 1.0–1.1$, followed by a sudden increase at $T/T_g \sim 1.1–1.2$, attributed to the glass-super cooled liquid (SCL) and SCL-crystal transitions, respectively. A sudden increase of the FWHM of the boson peak was also observed at temperatures near $T/T_g = 1.1–1.2$. According to Takahashi et. al. [39], nucleation is expected to start in denser regions of the SCL phase, which may occur due to density fluctuations and are randomly distributed, similar to embryo formation in liquids. The sharp decrease of the boson peak frequency observed by Takahashi et. al. [39] near $T_g$ was accompanied with a sudden drop of the elastic modulus.
(caused by a decrease in viscosity), which enabled the atomic diffusion and the growth of denser regions which became the crystalline nuclei. In the case of the 50GeO₂–25Nb₂O₅–25K₂O glass composition [40], the boson peak frequency was found to decrease gradually with increasing temperature, with a sudden drop at \( T_g \) (632°C), corresponding to the glass-SCL transition, reaching a minimum at 720°C, which corresponded, according to Takahashi et. al. [40], to the SCL-crystal transition.

### 3.4.4 Raman Spectroscopy of Chalcogenide Glasses

The Raman spectra of vitreous chalcogenides such as GeS₂ or As₂S₃, as opposed to those of most oxide glasses, tend to exhibit sharp, molecular-like spectral features and a more pronounced mutual exclusion between IR and Raman-active bands. This behavior is also found in halide glasses like those based on zinc bromide and iodide and it is explained in the framework of the central force model [6] as due to the fact that the bridging (inter-tetrahedral) angle in these glasses is usually smaller than in oxide glasses and often close to 100° only.

One interesting recent example deals with the structure of a typical family of chalcogenide glasses, GeS₂–Sb₂S₃, studied by a combination of polarized Raman spectroscopy, DSC and laser-induced phase transformation studies [76], where particular attention was devoted to the intermediate range order (IRO) of these covalently bonded glasses. Pseudo-binary glasses with the molar composition \((100 - x)\text{GeS}_2 - x\text{Sb}_2\text{S}_3\) \((x \text{ varying from 0 to 90 mol%})\) were prepared by melt quenching in evacuated silica glass ampoules, after which they were annealed and cut into 1.2 mm thick disks, subsequently polished to optical quality. Glassy \(\text{Sb}_2\text{S}_3\) was prepared by thermal evaporation on a silica glass substrate, whereas c-\(\text{Sb}_2\text{S}_3\) was obtained by slowly cooling of molten \(\text{Sb}_2\text{S}_3\). Raman scattering spectra were recorded at room temperature upon excitation with an Ar ion laser at 488 nm, in the back-scattering geometry. This same CW laser was used as an irradiation source through a 50× microscope objective \((\text{NA} = 0.75)\) to study the phase transformation behavior of these glasses.

The polarized Raman spectra of \((100 - x)\text{GeS}_2 - x\text{Sb}_2\text{S}_3\) glasses \((0 \leq x \leq 100)\) are shown in Figure 3.13. Strong polarization dependences were observed in GeS₂ glass \((0\% \text{ Sb})\), as well as in those with low \(\text{Sb}_2\text{S}_3\) content. The inset of Figure 3.13a, which represents the HH and HV spectra of pure GeS₂ glass, shows that the intensity of the HV spectrum was about seven times less than that of the HH spectrum. Four main peaks were observed, at 290 (except for 0% Sb), 340, 370, and 432 cm⁻¹; as the \(\text{Sb}_2\text{S}_3\) content increased, the intensity of the 290 cm⁻¹ peak increased and that of the other three peaks decreased. The DR of the 340 cm⁻¹ peak of GeS₂ glass was ~0.13, corresponding to a polarized vibration. The 370 and 432 cm⁻¹ Raman modes, on the other hand, had a high DR, typical of asymmetric stretching vibrations. The peaks at 340 and 370 cm⁻¹ are assigned to [GeS₄] tetrahedra. A combination of two peaks formed the band at 290 cm⁻¹, which were separated through Gaussian peak fitting, yielding two component bands at ca. 280 and 308 cm⁻¹. As shown in Figure 3.13a, these are the frequencies of the main
vibrational modes of c-Sb$_2$S$_3$ crystallites, where all the Sb atoms are bonded to S atoms in [SbS$_3$] pyramids. In addition, the peak at 308 cm$^{-1}$ was strongly depolarized, so it can be assigned to an asymmetric stretching mode of these pyramids, whereas the 280 cm$^{-1}$ polarized component is assigned to the symmetric stretching vibration of those pyramids. Therefore, the polarized Raman spectra of all the GeS$_2$-Sb$_2$S$_3$ glasses are compatible with a structure composed of [SbS$_3$] pyramids and [GeS$_4$] tetrahedra.

![Figure 3.13](image)

Figure 3.13 (a) HH and (b) HV polarized Raman spectra of (100 − x)GeS$_2$ − x Sb$_2$S$_3$ glasses (0 ≤ x ≤ 100) and c-Sb$_2$S$_3$ crystallites. The inset of (a) represents the HH and HV spectra of GeS$_2$ (0% Sb) glass. (Reprinted with permission from Reference 76. Copyright 2012 American Chemical Society.)

So far, no specific structural order beyond the next-nearest neighbor units could be identified. Boolchand et. al. [77, 78] have shown that the composition dependence of $T_g$ in chalcogenide glasses contains vital clues regarding the connectivity of the network. Figure 3.14a shows the differential scanning calorimetry (DSC) curves of the present GeS$_2$-Sb$_2$S$_3$ glasses. Although only glasses with 90-70 mol% Sb$_2$S$_3$ showed clear crystallization peaks, it is apparent that both the $T_g$ and $T_x$ (onset of crystallization) values, as well as ($T_x$-$T_g$) increased with the GeS$_2$ content of the glasses. The behavior of $T_g$ is shown in Figure 3.14b: the fact that the Ge-S bond strength (232.2 kJ/mol) is higher than that of Sb-S bonds (204.2 kJ/mol) explains the
compositional variation of $T_g$; on the other hand, the fact that this variation is not linear suggests that the degree of connectivity of the glass network varies with composition as well [77, 78]. The slope $dT_g/dx$ was largest in region I, lowest in region II ($40 \leq x \leq 50$) and it increased again slightly in region III. The threshold behavior observed in region II indicates the occurrence of network demixing (or phase separation) in this quasi-binary, stoichiometric glass composition range [77, 78].

**Figure 3.14** (a) DSC curves for the $(100 - x)$GeS$_2$ – $x$ Sb$_2$S$_3$ glasses ($0 \leq x \leq 100$) at a heating rate of 10 K/min. (b) Glass $T_g$ as a function of the Sb$_2$S$_3$ content. The lines are only guides to the eye.

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In order to further investigate this threshold behavior, laser-induced changes were studied and followed by Raman spectroscopy. As a result, Sb$_2$S$_3$ crystals were found to precipitate in glasses with $50 \leq x \leq 60$, for high enough laser power ($\sim 2.5$ mW). Apparently, the threshold of phase transformation behavior was at $x = 50$. It is worth noting that, distinct from phase transition by heat treatment, the laser-induced change does not have a strong connection with the thermal stability ($\Delta T = T_x - T_g$), which increased continuously with the GeS$_2$ content of the glasses as shown in Figure 3.14a. The data of threshold behavior in $T_g$ and laser-induced phase transformation led to other insights into the atomic scale structure of the present glasses, as explained below.

Let us then consider the structural implications of the $T_g$ and Raman scattering behavior near $x = 40$ mol% Sb$_2$S$_3$. As previously argued, the glass network appears to be built by [SbS$_3$] pyramids and [GeS$_4$] tetrahedra [76]. For low $x$, one expects the pyramids to disperse uniformly within a continuous matrix of tetrahedral containing Ge-S-Ge bonding sequences, as shown in Figure 3.15a. Therefore, the question one can ask is: when $x$ decreases from a high value, where [GeS$_4$] tetrahedra are isolated and Sb-S-Sb bonding sequences occur as in
Figure 3.15c, what is the topological threshold where the $x$ value becomes small enough for all the [$SbS_3$] pyramids to be isolated by the tetrahedra? This situation can be described as each [$SbS_3$] pyramid being isolated by three [$GeS_4$] tetrahedra, while each tetrahedron is bonded to four pyramids, as shown in Figure 3.15b. This implies that the ratio of tetrahedral to pyramidal units is 3:4 or that $x = 40$, which is in excellent agreement with the threshold in $T_g$ at $x = 40$ as well. Further confirmation that [$GeS_4$] tetrahedra are isolated when $x \geq 40$ stems from the fact that the corresponding Raman spectra do not exhibit any features attributable to corner- or edge-shared tetrahedra in region II ($40 \leq x \leq 50$); in fact, while the Raman bands at 370 and 432 cm$^{-1}$ are assigned to asymmetric stretching vibrations of edge-shared [$GeS_4$] tetrahedra, the strongest peak at 432 cm$^{-1}$ disappears for $x \geq 40$, as shown in Figure 3.13.

**Figure 3.15** Schematic representation of the IRO structure of $(100 - x)GeS_2 - x Sb_2S_3$ glasses with different mol% $Sb_2S_3$. (Reprinted with permission from Reference 76. Copyright 2012 American Chemical Society.)
3.5 CONCLUSIONS

Raman spectroscopy is one of the most direct techniques for the study of glass structure, including both short and intermediate range order aspects. Compositional information is also simultaneously obtained. Although a direct calculation of glass structure from Raman spectral data is not possible, theoretical modeling may help, through a comparison between model predictions and experimental data. Glass phase separation, crystallization and other structural changes may also be conveniently followed by Raman spectroscopy. Microscopic structural and compositional details, in particular, can be easily followed with the increasingly sophisticated micro-Raman instrumentation available nowadays, with confocal capabilities. Permanent software developments, on the other hand, allow easy comparison between the experimental glass spectra and those of known reference materials, enabling easier identification of composition and structure. The main drawback of the Raman technique, which is not exclusive of glassy materials, is fluorescence interference, but even this is becoming less of a problem every day in view of the increasing availability of a larger number of laser sources of different wavelengths which allow the elimination of fluorescence through a suitable choice of excitation.

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4
BRILLOUIN LIGHT SCATTERING

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4.1 INTRODUCTION

Light scattering is caused by perturbations in the propagation of electromagnetic waves through matter, resulting in light emission in directions that are different from that of the incident wave. Essentially, this is due to a change in motion of the charges in a dielectric medium. The oscillating electric field vector of the incident light couples with the electronic or ionic charges in the scattering medium and induces oscillating dipoles. The latter, in turn, act as sources of electromagnetic radiation that emit the scattered light waves in all directions. If the scattering medium were perfectly homogeneous and if the incident light were the only factor causing linear response perturbations, all scattered light, except for that emitted in the same direction as the incident light, would destructively interfere, and all that could be observed would be light transmission.

The fact that we indeed observe light scattering is because the scattering medium is subject to a host of other perturbations that cause spatial and temporal fluctuations in the scattering intensity. Such effects may be caused by externally imposed thermal, mechanical, and electromagnetic fields, by intrinsic physicochemical processes, or by a combination thereof. In this chapter, we are concerned with the thermo-mechanical response of condensed matter, considering as a starting point the way matter stores thermal energy. Thermal energy imparted onto a molecular structure causes atomic vibrations, and because of the interactions between atoms, these vibrations are transmitted between them and propagate across the material. The overall vibrational motion of any atom can be decomposed into fundamental modes and effectively described using a linear combination of plane waves, called phonons, each with a given frequency, $\omega$, and wavelength, $\lambda$. Along with the wave character of a specific phonon comes its propagation direction, described by a wavevector $\mathbf{q}$, which is discussed in more detail below. The magnitude of this wavevector is $|\mathbf{q}| = q = 2\pi/\lambda$. This concept constitutes the basis for the Einstein and Debye models of the heat capacity of solids, and even though the phonon description is defined within the framework of periodic crystalline lattices, it serves well to describe the behaviors of amorphous solids and liquids for as long as processes are confined to the regime of linear dispersion, that is, where the sound velocity $v_g = \partial\omega/\partial q$ is a constant.

For the present context, we consider these thermal phonons as the origin of the fluctuations that cause light scattering, that is, the scattering events that are based on interactions between
photons and phonons. We will see that these scattering events can occur with or without momentum and energy exchanges. The latter events, in which the scattered light has the same frequency as the incident light, are referred to as elastic scattering, and the former events, which are characterized by a frequency shift in the scattered light, as inelastic scattering. The Brillouin light scattering technique then consists of analyzing the spectrum of scattered light and relating the observed spectral features to the phenomena that caused the scattering events in the material. Indeed, matching the type of scattering event, the Brillouin spectrum exhibits a strong central or Rayleigh line, due to elastic scattering, and Brillouin peaks doublets, due to inelastic photon–phonon interactions. Depending on the scattering geometry and the elastic anisotropy of the material probed, up to three Brillouin doublets can be observed, one corresponding to longitudinal and two to shear elastic deformations. First, and foremost, by simply connecting the Brillouin frequency shift \( \omega_{L/S} \) to the magnitude of the wavevector associated with the scattering event, \( q \), one can calculate the sound velocities, \( c_{L/S} = v_\phi = \omega_{L/S}/q \approx v_s \) and when the density of the material is known, the longitudinal and shear elastic moduli, \( M' = \rho_0 c_{L}^2 \) and \( G' = \rho_0 c_{S}^2 \). Note that for isotropic amorphous structures, there are only two independent elastic constants, and hence, these can be determined using a single Brillouin scattering measurement. Using the relationships from linear elasticity theory, one can then calculate other coefficients such as the bulk modulus, Poisson's ratio, Lamé's constants, the Young's modulus, etc. (see below). Moreover, because the orientation of the wavevector can be selected via the scattering geometry, one can determine these elastic coefficients along specific directions relative to the sample geometry. In crystalline materials, for example, one can measure elastic constants as a function of the crystallographic orientations.

However, as will be detailed below, a wealth of additional information can be extracted from Brillouin spectra. Recall that the elastic constants are derived from the propagation velocities of elastic deformation, which, in a first approximation, are described as plane waves. Under this assumption, every atomic-scale constituent undergoes periodic oscillatory motion, always returning to the same positions. In real materials, however, atomic motion is not that ideal and atoms sporadically effect non-periodic displacements. By not returning to the positions previously visited, the energy put into the elastic deformation of the structure is not restored, but instead it has dissipated from the phonon under examination and transmitted to a different phonon. On balance, the energy in the system is conserved, that is, as much energy as is lost by a given phonon to others is also returned by other phonons to this particular one. The amounts of energy so exchanged per oscillation constitute a small fraction of the total phonon energy, perhaps a few percent. This energy exchange between phonons is reflected in the broadening of the Brillouin peaks, that is, rather than being characterized by a narrowly defined amount of energy stored in the probed phonon \( (\omega_{L/S}) \), this phonon possesses a distribution of energies \( (\omega_{L/S} \pm \Delta \omega_{L/S}) \), that is, some energy quanta are a little higher and others a little lower, to match the gain and loss of energy.

The loss modulus of the material corresponds to the amount of energy dissipated per unit volume change of deformation. Along with the energy dissipation due to the aperiodic motion
of atomic-scale moieties comes a momentum exchange, that is, the quantity transported by such moieties from their position in the original elastic wave to the point of collision with new neighbors upon which they are incorporated into a new regiment of periodic motion, with different frequency and direction. This process of momentum exchange is equivalent to internal friction or viscous dissipation, depending on whether the context is the deformation of solids or flow of liquids. Accordingly, it is possible to derive the viscosity coefficient from a Brillouin spectrum, which is of particular interest when studying the relaxation behavior of supercooled liquids and glass formation.

The scattering of light by propagating acoustic phonons was first predicted by Léon Brillouin in 1922, but the technique became viable only after introduction of monochromatic coherent laser light sources, which allows one to probe phonons in the GHz frequency regime. Accordingly, the visco-elastic response of the material is measured on a time scale that leaves little or no time for the structure to relax. In other words, the underlying deformations and the corresponding moduli can be considered adiabatic. The wavelengths of the phonons probed are of the order of 200 nm. Considering that, at any given time, only about one quarter of that distance is significantly extended and another quarter significantly compressed, while the rest of the material exhibits close to equilibrium interatomic spacing, measuring elastic moduli using Brillouin scattering effectively amounts to sampling the mechanical response of a large number of dog bone specimens that are about 50 nm long and subject to oscillatory straining. At this scale, variations in molecular structure and defects significantly affect the statistical fluctuations in the measurement results.

Similarly, the loss modulus obtained using this technique probes the elementary mechanisms of momentum transport, much in the sense of the model proposed by Eyring [1], in which the frictional forces between molecular layers of liquid, sheared by an imposed velocity gradient perpendicular to the layers, are established by the impacts of atomic-scale moieties that migrate from layer to layer and upon arrival carry a different momentum than the molecules with which they collide. Note that this concept implies that particles must be mobile to some extent for there to be any viscous dissipation, which is important in interpreting the experimental observations. The molecular collision events sampled during the measurement are reflected in the Brillouin spectral features, which can be analyzed to reveal the loss moduli or viscosity coefficients of the scattering medium. Accordingly, Brillouin scattering is one of very few techniques that allow one to directly measure the bulk viscosity. Even though the technique probes high frequency processes, the viscosity measurement is actually carried out at zero shear rate. No shear deformation or any other kind of external forcing is externally imposed. Indeed, the photon–phonon interactions do not cause elastic deformation of the scattering medium, nor do they cause atoms to depart from the harmonic motion of a given phonon. The energy exchange due to the inelastic nature of the scattering event is less than 0.01% of a typical activation energy associated with atomic diffusion.

Hence, the Brillouin light scattering experiment does not perturb the thermodynamic equilibrium of the system under investigation, which allows one to study materials subject to delicate thermal, mechanical, and chemical conditions, such as fragile gels, supercooled liquids, or molecular organic materials undergoing polymerization reactions. Since the
measurement is contact-free, it is possible to measure the properties of materials under extreme conditions of temperature and pressure, as well as substances that are highly corrosive, radioactive, or toxic. Samples can be very small. Using standard optics one samples a scattering volume of 25 to 50 µm in diameter, but with microscope optics this can be reduced to the order of a micron. Only a few phonon wavelengths are necessary to occupy the scattering volume in order to achieve adequate scattering conditions.

The primary quantity of interest that is yielded by this measurement is the complex mechanical modulus. In principle, there are other parameters related to the way matter accommodates thermal energy that can be obtained using this technique, such as thermal diffusivity, the ratio of the heat capacities at constant pressure and constant volume, elasto-optic coefficients, etc. Measurement of some of these quantities requires a precision that surpasses routine use of the available instrumentation, and will not be dealt with here in detail. On the other hand, the complex mechanical modulus provides very unique insights into materials behaviors. On the face of it, Brillouin scattering yields mechanical properties, that is, the elastic storage and loss moduli of a material. Moreover, these quantities are tightly coupled: the abilities of a structure to store versus dissipate elastic energy balance one another, and in joint consideration the two components of this complex modulus uniquely reveal details about the physical state of the scattering medium, particularly with regard to its structure and dynamics. Thus, considering the scale at which the modulus is determined, Brillouin scattering can serve as an indirect structural probe, especially when applied to covalent and polymeric amorphous materials. The storage modulus reflects the structural integrity and the degree of connectivity in the network; it provides an assessment of the way structural units are connected with each other rather than of their positions in space. The loss modulus complements and validates this information in that it provides a measure of the mobility in the structure, that is, moieties that are free to move about do not contribute to structural stiffness, which explains how structural characteristics are identifiable in the balance between rigidity and mobility.

4.2 BACKGROUND AND THEORY

The electric field of light incident on a dielectric medium causes polarization of the local charge density. The spatial extent of this effect is limited to molecular dimensions, that is, much smaller than the wavelength of the incident light. The strength of the induced polarization density, \( \mathbf{P} \), is given by [2]

\[
P = \alpha \mathbf{E} = \alpha \mathbf{E}_0 e^{i(kr - \omega_0 t)},
\]

where \( \mathbf{E} \) is the local electric field, \( \alpha \) is the polarizability of the structural moiety located at position \( \mathbf{r} \), and \( \omega_0 = 2\pi c/\lambda \) is the angular frequency of the incident radiation. Here \( c \) is the speed of light, and \( \lambda \) is the wavelength of the incident light. The magnitude of the electric field that results from a dipole oscillating with frequency \( \omega_0 \), measured at distance \( L \) from this dipole, is
where $\theta_z$ is the angle between the direction of the incident electric field vector and the scattering direction. The intensity of the scattered light is proportional to the square of the electric field magnitude, that is,

$$I_s \propto (E')^2 = \alpha^2 \frac{16\pi^4}{L^2 \lambda^4} \left( E_0 e^{i(kr-2\pi c t/\lambda)} \right)^2 \sin^2 \theta_z = \alpha^2 \frac{16\pi^4}{L^2 \lambda^4} I_0 \sin^2 \theta_z. \quad (4.3)$$

If the incident light is not polarized, and assuming it propagates in the $x$-direction, the incident intensity is distributed evenly among the $y$- and $z$-polarities, $I_0 = (I_{0z} + I_{0y})/2$, and the above equation becomes

$$I_s \propto \alpha^2 \frac{8\pi^4}{L^2 \lambda^4} I_0 \left( \sin^2 \theta_z + \sin^2 \theta_x \right) = \alpha^2 \frac{8\pi^4}{L^2 \lambda^4} I_0 (1 + \cos^2 \theta), \quad (4.4)$$

where $\theta (= \theta_x)$ is the angle between the incident radiation and the direction defined by the scattering location and the point of observation, or simply, the scattering angle. Equation 4.4 describes the scattering intensity from a single isolated dipole associated with a particular molecular species. In case the scattering volume contains a number of polarizable species, the local electric field, $E_{\text{loc}}$, deviates from the external field due to the mutual influence of surrounding induced dipoles. The total dipole moment of a region containing $N_j$ individual dipole moments becomes $\mathbf{P} = \sum_j N_j \mathbf{p}_j = \sum_j N_j \alpha_j \mathbf{E}_{\text{loc}}$, and the relationship between this total dipole moment and the imposed external field $\mathbf{E}$ is $\mathbf{P} = \chi \mathbf{E}$, where $\chi$ is the dielectric susceptibility of the scattering medium. This formalism allows us to treat the scattering medium as a continuum, which allows us to replace the above summation of the effect individual dipoles with an integration over a region, provided we can describe the spatial dipole density distribution using a suitable functional form. At this juncture it is also convenient to develop the desired formalism in terms of the dielectric displacement field, $\mathbf{D} = \mathbf{E} + 4\pi \mathbf{P} = \varepsilon \mathbf{E}$, where $\varepsilon$ is the dielectric permittivity, or dielectric constant. We recognize that $\varepsilon = 1 + 4\pi \chi$. The dielectric permittivity represents the stiffness of the scattering medium with respect to charge displacement in response to an electric field, and it controls the intensity of the light scattered from a continuum in the way that the polarizability does for an individual dipole.

Next we account for the fact that the dielectric constant may vary as a function of the spatial coordinate, that is, it fluctuates about an average value according to $\varepsilon(\mathbf{r}) = \varepsilon + \Delta \varepsilon$. The important quantity here is the deviation from the average value of the dielectric constant. Indeed, if the scattering power were uniform across the illuminated volume, presumed to be significantly larger than the wavelength of the light, there would for every volume element be another one for which emitted light at the detector would have opposite phase, and thus mutually annihilate, except for the forward direction from incident. Conversely, if the
dielectric constant were non-uniform, any underlying repetitive pattern, even if it were only one component among overall random fluctuations, would give rise to constructive interference at a given scattering angle. This constitutes a diffraction condition that we are going to fold into the formalism for the scattering intensity.

Within reasonable approximation, the dielectric constant is proportional to the electron density, and the latter in turn is proportional to the mass density, \( \rho \), of the scattering volume. We can therefore relate the fluctuations in the local dielectric constant to those in the local density,

\[
\Delta \varepsilon = \left( \frac{\partial \varepsilon}{\partial \rho} \right)_T \Delta \rho. \tag{4.5}
\]

and express the density fluctuations in the form of a three-dimensional Fourier series,

\[
\Delta \rho = \sum_q \Delta \rho_q e^{iq\cdot r}, \tag{4.6}
\]

where the summation is carried out over all possible wavevectors \( q \) associated with the density fluctuation, and the individual Fourier coefficients are obtained as

\[
\Delta \rho_q = \frac{1}{V} \int_V \Delta \rho e^{-iq\cdot r} dV. \tag{4.7}
\]

This integral signifies that the scattering intensity observed in the experiment is sampled from the scattering volume \( V \), which, as stated, is typically much larger than the wavelength of the probing radiation. To derive the expression for the scattering intensity we begin with Maxwell’s equations (in the absence of magnetization and electrical currents)

\[
\nabla \times \mathbf{E}' = \frac{1}{c} \frac{\partial \mathbf{H}'}{\partial t} = i\omega_0 \mathbf{H}' / c \quad \text{and} \quad \nabla \times \mathbf{H}' = \frac{1}{c} \frac{\partial \mathbf{E}'}{\partial t} = -i\omega_0 \mathbf{D}' / c \quad [3], \]

which yields

\[
\nabla \times (\nabla \times \mathbf{E}') = \frac{\omega_0^2}{c^2} \mathbf{D}'. \tag{4.8}
\]

We now must account for the fact that in a scattering medium the dielectric displacement field has contributions from both the electric field of the incident and scattered radiation, that is, \( \mathbf{D}' = \varepsilon \mathbf{E}' + \Delta \varepsilon \mathbf{E} \Rightarrow \mathbf{E}' = \mathbf{D}' / \varepsilon - \Delta \varepsilon / \varepsilon \mathbf{E} \). Substituting into Eq. 4.8 yields

\[
\nabla \times (\nabla \times (\mathbf{D}' - \Delta \varepsilon \mathbf{E})) = \frac{\varepsilon \omega_0^2}{c^2} \mathbf{D}' \tag{4.9}
\]

Using the curl-of-curl identity, \( \nabla \times (\nabla \times \mathbf{D}') = \nabla (\nabla \cdot \mathbf{D}') - \nabla^2 \mathbf{D}' = -\nabla^2 \mathbf{D}' \), we obtain

\[
\nabla^2 \mathbf{D}' + \frac{\varepsilon \omega_0^2}{c^2} \mathbf{D}' = -\nabla \times (\nabla \times [\Delta \varepsilon \mathbf{E}]), \tag{4.10}
\]

which has the solution
\[ D' = \nabla \times \left( \nabla \times \left[ \frac{e^{ik'L}}{4\pi L} \int V \Delta \varepsilon E_0 e^{-ik'r} dV \right] \right). \]  

(4.11)

Taking the spatial phase of the incident light into account, that is, \( E = E_0 e^{-ik \cdot r} \), and after substituting \( \Delta \varepsilon \) with Eqs. (4.5) and (4.6), we obtain

\[ D' = \nabla \times \left( \nabla \times \left[ \frac{E_0 e^{ik'L}}{4\pi L} \left( \frac{\partial \varepsilon}{\partial \rho} \right) \int V \sum_q \Delta \rho_q e^{-i(k' - k - q \cdot r)} dV \right] \right). \]  

(4.12)

Here, \( k \) and \( k' \) are the wavevectors describing the incident and scattered light, respectively. Equation 4.12 can be solved to yield the expression first derived by Einstein,

\[ I = I_0 \frac{\pi^2 V_s}{2\Lambda_0^4 L^2} k_B T \left( \rho \frac{\partial \varepsilon}{\partial \rho} \right)_T \beta_T (1 + \cos^2 \theta), \]

\[ (4.13) \]

where \( \beta_T = \frac{1}{\rho} \left( \frac{\partial \rho}{\partial \rho} \right)_T \) is the isothermal compressibility of the scattering medium, which corresponds to the reciprocal of the bulk modulus, an elastic constant that is further examined below. We can further refine the above analysis to account for the polarization of the incident radiation relative to that of the scattered light and scattering plane, which is defined to contain the propagation directions of the incident and scattered light. Accordingly, we denote by the index \( VV \) the case when the polarization of the incident and scattered light are both perpendicular to the scattering plane, by \( HH \) when they are both parallel to the scattering plane, and by \( HV \) or \( VH \) when the incident light polarization is parallel and the scattered light polarization is perpendicular to the scattering plane, or vice versa. The intensity of the scattered light in each of these cases is [4]

\[ I_{VV} = I_0 \frac{\pi^2 V_s}{\lambda_0^4 L^2} k_B T \varepsilon^4 \frac{|P_{12}|^2}{\rho_0 v_L^2}, \]

\[ (4.14) \]

\[ I_{HH} = I_0 \frac{\pi^2 V_s}{\lambda_0^4 L^2} k_B T \varepsilon^4 \frac{|P_{44} + (P_{12} + P_{44}) \cos \theta|^2}{\rho_0 v_L^2}, \]

\[ (4.15) \]

and

\[ I_{VH} = I_{HV} = I_0 \frac{\pi^2 V_s}{\lambda_0^4 L^2} k_B T \varepsilon^4 \frac{|P_{14}|^2}{\rho_0 v_S^2} \cos^2 \left( \frac{\theta}{2} \right). \]

\[ (4.16) \]

In these expressions, the \( P_{ij} \) represent the Pockels elasto-optic coefficients. These coefficients are elements of a fourth-rank tensor, with simplified index notation, following the same convention as is used for elastic constants. Accordingly, the Pockels coefficient \( P_{ij} \) describes
the change in refractive index for light polarized in \(i\)-direction based on a strain applied in \(j\)-direction. The index 44 refers to shear deformation. Dimensionally, the Pockels coefficient multiplied with the refractive index to the fourth power is identical to the first term in parenthesis in Eq. 4.13, that is, \([\varepsilon^{	ext{Pockels}}_{ij}] = [(\rho \partial \varepsilon / \partial \rho)^2]^{\text{refractive index}}\).

The important aspects to note from this derivation are that (i) induced molecular-scale dipoles oscillate and emit light; (ii) the scattering intensity observed is proportional to the square of the electric field magnitudes averaged over the entire scattering volume, which takes into account the phase differences between different source points; (iii) if the scattering strength were truly homogeneous across the scattering volume, this phase difference would cancel the scattering intensity in all but the forward direction due to destructive interference; (iv) hence, scattering is measurable because of density inhomogeneities in the scattering volume. This has two important consequences concerning the information content of Brillouin scattering spectra, which we will examine in the following: one is the diffraction condition that allows one to identify the probed phonon wavevector, and other one is the ability to observe spatiotemporal behaviors of density fluctuations based on the appropriate formulation of the corresponding dynamic structure factor.

With Eq. 4.5 we related the origin of scattering to density fluctuations, and based on the discussion in Section 4.1, we attribute the source of these density fluctuations to thermal energy that is stored in condensed matter as phonons. The plane wave description of a given phonon implies a periodic repetition of density maxima and minima, and consequently, a moving spatial grating of the refractive index. At room temperature and above, the scattering volume is filled with phonons of a wide range of wavelengths and propagation directions. On the whole, light scattered from various points in the scattering volume, even when modulated according to the fluctuations in the local density and dielectric constant, will always annihilate through destructive interference, except in the case where the diffraction condition for the spatial grating is fulfilled, that is, when

\[
q = k_s - k_i
\]

This condition is already implicit in Eq. 4.12 and it is further illustrated in Figure 4.1. Hence, the fact that the density oscillations associated with a given phonon establish a diffraction grating allows one to filter out the direction and wavelength of one particular phonon. This diffraction condition is defined by the scattering geometry, as revealed in Figure 4.1. Assuming that the momentum magnitudes of the incident and scattered light are virtually identical, that is, \(|k_i| = |k_s| = 2\pi/\lambda\), Eq. 4.17 can be rewritten in terms of the magnitude of the phonon wavevector as

\[
q = \frac{4\pi n}{\lambda} \sin \theta/2,
\]  

where \(n\) is the refractive index of the medium. Next, we introduce the statistical-mechanical formalism, called dynamic structure factor, \(S(q, \omega)\), that relates the density fluctuations in the scattering medium to the governing principles. This dynamic structure factor, multiplied with a
population probability density, describes the spectrum of scattered light and ultimately allows one to extract the desired materials properties. For fluids, an expression for $S(q, \omega)$ can be derived using the generalized hydrodynamic theory [5–8] or the mode coupling theory [9–12]. Both approaches yield expressions of comparable structure, and here we illustrate the basis for the dynamic structure factor expression using the generalized hydrodynamic approach. The derivation of $S(q, \omega)$ is based on the simultaneous solution of the equations of balance for mass, momentum and energy, that is, the equation of continuity

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0,$$

(4.19)

the Navier–Stokes equation

$$\frac{\partial \mathbf{v}}{\partial t} + \mathbf{v} \cdot \nabla \mathbf{v} + \gamma^{-1} \left( \frac{\partial \rho}{\partial \rho} \right)^{1/2} \left[ \rho^{-1} \nabla \rho - \rho^{-1} \left( \frac{\partial \rho}{\partial T} \right) _\rho \nabla T \right] - \nu _S \left[ \nabla ^2 \mathbf{v} + \nabla (\nabla \cdot \mathbf{v}) \right] - \nu _B \nabla (\nabla \cdot \mathbf{v}) = 0,$$

(4.20)

and Fourier's second law

$$\frac{\partial T}{\partial t} + \mathbf{v} \cdot \nabla T - (\gamma - 1) \nabla \cdot \mathbf{v} / (\rho^{-1} (\partial \rho / \partial T) _\rho) - \left[ \kappa \nabla ^2 T + \phi _\eta / (\rho c_V) \right] = 0,$$

(4.21)

where $\gamma = c_p / c_v$ is the ratio of the heat capacities at constant pressure and constant volume, also known as the Landau–Placzek ratio, $\kappa$ is the thermal diffusivity $\kappa = (\lambda _{th} / \rho_0 c_V)$, where $\{\lambda _{th}\}$ is the thermal conductivity, $\nu _S$ and $\nu _B$ are the kinematic shear and bulk (or dilatational) viscosities, and $\phi _\eta$ is a term that accounts for the viscous dissipation of energy. Equations (4.19) through (4.21) are solved simultaneously using double Laplace–Fourier transformations to obtain a set of algebraic equations in frequency and wavenumber space. From the linearized solution for the density as a function of the transformed variables, one then constructs the correlation function that, after some manipulation, yields the desired dynamic structure factor. Accordingly, the normalized scattering intensity is given by the expression

$$\frac{S(q, \omega)}{S(q)} = \frac{(\gamma - 1)}{\gamma} \cdot \frac{2 q^2 \cdot \kappa}{\omega^2 + (q^2 \cdot \kappa)^2} + R _C \frac{2 \xi _0 ^2 \tau _B ^{-1}}{\omega^2 + (c _S ^2 \xi _0 ^2 \tau _B ^{-1})^2}$$

$$+ R _B \left[ \frac{q^2 \Gamma _S}{(\omega + c_s q)^2 + (q^2 \Gamma _s)^2} + \frac{q^2 \Gamma _S}{(\omega - c_s q)^2 + (q^2 \Gamma _s)^2} \right]$$

$$+ R _B \frac{q}{c_s ^2} \left[ (\Gamma _S + \kappa (\gamma - 1)) \frac{\omega + c_0 q}{(\omega + c_s q)^2 + (q^2 \Gamma _s)^2} + \frac{\omega - c_0 q}{(\omega - c_s q)^2 + (q^2 \Gamma _s)^2} \right],$$

(4.22)

where $\Gamma _S = \frac{1}{2} \frac{\eta _0}{\rho _0} + (2 \gamma - c_0 ^2 c_s ^2 - 1) + (1 - \gamma \kappa q^2 \tau _B) \frac{c _\infty ^2 - c _0 ^2}{1 + (c_s q \tau _B)^2} \tau _B$ is the sound attenuation
coefficient, $\rho_0$ is the average density, $c_S, c_0, c_\infty$, are the velocities of sound at the actual probing frequency $\omega_S = qc_S$, at zero frequency, and at infinite frequency, respectively. The coefficients $R_C$ and $R_B$ are given by

$$R_C = \left\{ \left[ 1 - \left( \frac{c_S}{c_0} \right)^2 \right] \left[ \left( 1 - \frac{1}{\gamma} \right) \left( c_0 q \right)^2 + \left( \frac{c_0}{c_S} \right)^4 \tau_B^{-2} \right] + \left( c_\infty^2 - c_0^2 \right) q^2 \right\} \times \left[ \omega_S + \left( \frac{c_0}{c_S} \right)^4 \tau_B^{-2} \right], \text{ and}$$

$$R_B = \left\{ \left[ 1 - \left( \frac{c_0}{c_S} \right)^2 \left( 1 - \frac{1}{\gamma} \right) \right] \left[ \omega_S^2 + \left( \frac{c_0}{c_S} \right)^2 \tau_B^{-2} \right] - \left( c_\infty^2 - c_0^2 \right) q^2 \right\} \times \left[ \omega_S + \left( \frac{c_0}{c_S} \right)^4 \tau_B^{-2} \right].$$

Figure 4.1 Schematic of how the wavelength and propagation direction of the phonon being probed in the Brillouin scattering process is controlled by the scattering angle. Density changes associated with the phonon are depicted as varying gray scale levels. The momentum vector balance diagram reflects the diffraction condition, which is that the light scattered from equivalent phase points along the sound wave superimposes at a path difference equal to an integral number of wavelengths.

The kinematic viscosity $v(\omega) = \frac{\eta_0}{\rho_0} + \frac{c_\infty^2 - c_0^2}{1 + (\omega/\omega_B)^2 \tau_B}$ is the real part of the Fourier transform of the time dependent viscosity, $v(t)$, and $\tau_B$ is a characteristic structural relaxation time. The reasoning behind this time dependence is explored in more detail below. The first term on the right-hand side of Eq. 4.22 corresponds to the Rayleigh peak, the second term describes the
effect of sound dispersion due to thermal relaxation on the shape of the Brillouin spectrum (also known as Mountain peak), the next two terms represent the symmetric parts of the Stokes and anti-Stokes lines of the Brillouin components, and the last two represent the asymmetric parts of these peaks. In the second and third line of Eq. 4.22, note the terms \( \pm c_S q \equiv \pm \omega_S \) that represent the Brillouin frequency shifts. These shifts are the hallmark of the inelastic process associated with scattering from propagating phonons. They occur because the absorbed photon contributes to the motion of a phonon that propagates with velocity \( c_S \), and upon reemission the photon wavelength is either compressed or extended, depending on whether the phonon propagates toward or away from the detector. The process is often described as analogous to the Doppler effect, except that in this case the sound wave is the vehicle and light is the signal that either increases or decreases in pitch.

Again, in the standard Brillouin scattering experiment (in contrast to stimulated Brillouin scattering), light is not creating sound waves, it merely probes the existing thermal phonons, that is, the atomic motion created by induced dipoles constitutes a negligible perturbation of the thermal vibrations of the atoms. For one, when visible light is used to carry out Brillouin scattering experiments, the probing frequencies are too high to couple directly with atomic motion. Instead, the vibronic excitations are achieved by polarizing the electron clouds surrounding the atomic nuclei. The vast majority of these excitations decay and reemit photons without interfering with the atomic motion (elastic scattering). In some cases, however, the induced charge oscillation superimposes onto the thermal vibrations of the atoms in such a way that the emitted light wave is compressed or expanded to give rise to the anti-Stokes and Stokes shifts in the Brillouin spectrum (inelastic scattering). Moreover, for transparent glass-forming systems, the amount of energy absorbed per unit time within the scattering volume is of the order of a microwatt, which, considering a typical thermal conductivity, results in a temperature rise of about one hundredth of a degree Kelvin. Even if this thermal energy were to be imparted into a single phonon, its frequency could not be resolved with the available spectrometers.

### 4.3 INSTRUMENTATION

The challenge with Brillouin spectroscopy is the resolution of the signal, both in terms of its frequency and its intensity. The phonons that are probed in this experiment have frequencies of the order of a GHz, whereas that of the probing electromagnetic radiation is half a PHz. Hence, on the frequency scale, one wants to achieve a resolution of one in a million. Similarly, the fraction of the total scattering intensity contained in the Brillouin peaks is only \( 10^{-5} \) or less—the other components include elastically scattered light and light scattered from impurities and chemical inhomogeneities. Spectrometers based on the principle of wavelength dispersion do not provide the desired resolving power, and hence, Brillouin spectroscopy is generally carried out using Fabry–Pérot interferometry.

In such an interferometer, the light to be analyzed is passed through an optical cavity delimited by two parallel, very flat, and partially transmitting mirror surfaces. The reflected light is
redirected several times inside the cavity, where it interferes with itself. The reflectivity, \( r \), of the mirrors is controlled via the type and thickness of the coating deposited on the mirror surfaces. Higher reflectivity results in better filtering quality but lower signal intensity and vice versa. A good compromise is sought at about 95% reflectivity. Every reflection on the back and front mirror adds an optical path difference of \( \Delta = \Delta_p + 2\Delta_r = 2d_1\cos\phi + \lambda \), where \( d_1 \) is the mirror spacing, \( \phi \) is the angle between the light propagation direction and the mirror surface normal, and the factor \( \lambda/2 \) upon each reflection arises when the refractive index in the gap is smaller than that of the mirror material. This causes a phase shift of \( \delta = k\Delta = \frac{2\pi}{\lambda}\Delta \), and constructive superposition is achieved when \( \delta = 2\pi \), that is, \( \Delta = m\lambda \), where \( m \) is an integer, and thus, \( 2d_1\cos\phi = m\lambda \). Adding up all reflected and transmitted fractions of the light intensity, accounting for their appropriate phase shifts, leads to a converging infinite series of terms, according to which the overall intensity of light transmitted by the interferometer is described by [13]

\[
\frac{T}{T_0} = \frac{1}{1 + F\sin^2(\delta/2)} = \frac{1}{1 + F\sin^2(2\pi d_1\cos\phi/\lambda)},
\]

(4.23)

where \( T_0 \) is maximum possible transmission of the cavity, and \( F = 4r^2/(1 - r^2)^2 \) is the coefficient of finesse, which is a quality factor that depends on the flatness and reflectivity of the mirrors. The expression in Eq. 4.23 is known as the Airy function. Accordingly, transmission is maximized whenever an integral number of half wavelengths fit exactly into the spacing \( d_1 \) between the mirrors. This is illustrated in Figure 4.2.
Figure 4.2 Illustration of the transmission orders across a Fabry–Pérot cavity for different mirror reflectivity. The higher the reflectivity, the better the filtering quality.

Note that the sharpness of the transmitted peaks increases with increasing reflectivity. Evidently, sharpness is needed to achieve adequate resolution. The Rayleigh criterion states that in order to resolve two adjacent peaks of equal height, they should be separated by approximately one full width at half maximum, which in terms of Eq. 4.23 translates to

\[
\frac{T}{T_0} = \frac{1}{1 + F \sin^2 \left( \frac{\Delta \delta_R}{4} \right)} = \frac{1}{2} \Leftrightarrow \sin \left( \frac{\Delta \delta_R}{4} \right) = \frac{1}{\sqrt{F}},
\]

where \( \Delta \delta_R \) is the phase shift between minimally resolved peaks, and since this quantity is small, \( \Delta \delta_R \approx \frac{4}{\sqrt{F}} \). In terms of the wavelength difference that can be resolved, use of the above relationship between optical path difference and phase difference yields

\[
4/\sqrt{F} = -\frac{4 \pi d_1 \cos \varphi}{\lambda^2} \Delta \lambda_R \Leftrightarrow \Delta \lambda_R = -\frac{\lambda^2}{\sqrt{F} \pi d_1 \cos \varphi}, \text{ and since } 2d_1 \cos \varphi = m\lambda,
\]
\[ \Delta \lambda_R = -\frac{2\lambda}{\sqrt{F \pi m}} \iff \left| \frac{\Delta \lambda_R}{\lambda} \right| = \frac{2}{\sqrt{F \pi m}}. \]  

(4.25)

With the available mirror qualities, resolutions of the order of \(10^{-6}\) are achievable, which is about two orders of magnitude better than that of diffraction gratings. Note that the resolution increases with increasing order of transmission, or increasing mirror spacing \(d_1\). Hence, it would be possible to increase the resolution almost arbitrarily by expanding the size of the interferometer cavity. However, there is a trade-off. Assume that there are two distinct wavelengths present in the signal, \(\lambda_1\) and \(\lambda_2\), such that \(\lambda_2 = \lambda_1 + \Delta \lambda\). As the mirror spacing is augmented to enhance the resolution of the interferometer, the peaks corresponding to the two wavelengths separate farther. At some point the \(m\)th order of \(\lambda_2\) to coincides with the \((m+1)\)th order of \(\lambda_1\), that is, \(m \lambda_2 = (m + 1) \lambda_1\). When this happens, identification of the wavelength difference between the two signals becomes ambiguous. Hence, the maximum wavelength difference, \(\Delta \lambda_{FSR}\), that can be unequivocally detected due to being contained inside one order of interference, that is,

\[ m \left( \lambda + \Delta \lambda_{FSR} \right) = (m + 1) \lambda \iff \Delta \lambda_{FSR} = \frac{\lambda}{m} = \frac{\lambda^2}{2d_1 \cos \varphi} \]  

(4.26)

is called the free spectral range of the instrument and constitutes the total span of spectral features that can be captured with the measurement. Typically interferometers are constructed so that \(\varphi = 0^\circ\), and we get \(\Delta \lambda_{FSR} = \frac{\lambda^2}{2d_1}\). Based on this analysis, increasing \(m\), or equivalently, the mirror spacing, simultaneously boosts resolution and limits the spectral range. Optimizing the balance between both performance characteristics means maximizing the quantity \(\frac{\Delta \lambda_{FSR}}{\Delta \lambda_R} = \frac{\pi \sqrt{F}}{2}\), simply called finesse, which serves as a key figure of merit for an interferometer. Accordingly, large \(F\) provides a wide spectral range and high resolution.

Charles Fabry and Alfred Pérot developed their interferometer concept around 1900. Maintaining the surfaces of the two mirrors that define the cavity parallel to each other was essential to the proper functioning of this instrument. In early interferometer designs, the mirror surfaces rested on a well-machined plate and spectral scanning was achieved by applying large pneumatic pressures to the outside surfaces of the mirrors, thereby deforming the glass and the metal plate they rest on so as to scan the cavity over several interference orders. Another means for realizing spectral filtering was to keep the mirrors at fixed distance and instead varying the refractive index of the medium in the cavity by gradually changing the pressure of a gas mixture contained in the space between the mirrors. With these approaches, a single frequency scan could take hours, and Brillouin spectroscopy was a rather tedious undertaking. Since then, technological advances have made a number to improvements possible, not only to preserve parallel mirror alignment during a frequency scan, but also in some fundamental aspects of interferometry. One such improvement is tandem interferometry, which allows for a dramatic increase in the free spectral range without compromising spectral resolution.
Consider the combination of two interferometers in series, where one cavity is scanned at a slightly different rate than the other, that is, \( d_2 = \zeta d_1 \), where \( \zeta \) is a number close to unity.

Assuming that \( \varphi = 0^\circ \), both cavities transmit simultaneously when

\[
2d_1 = m\lambda \quad \text{and} \quad 2d_2 = \xi \lambda = 2\zeta d_1 \Rightarrow \zeta = \frac{\xi}{m},
\]

(4.27)

where \( \lambda \) and \( m \) are integers. Hence, if the free spectral range of a single interferometer is \( \lambda/m \) or \( \lambda/(m+1) \) or \( \lambda/(m+2) \), etc., depending on the mirror spacing, that of a tandem interferometer is derived from the condition \( \lambda/(m+j) = \lambda/(\xi + i) \) such that \( \zeta(m+j) = \xi + i \Rightarrow i/j = \zeta \). Transmitting orders therefore occur at multiples of \( m \) or \( I \), and within that spectral range the assignment of peaks is unambiguous. Figure 4.3 shows a schematic of a Brillouin spectrum near the transmitting order obtained using a tandem Fabry–Pérot with a \( \zeta \)-value of 0.92 and a finesse of about 50. The adjacent lower and higher orders are significantly suppressed, allowing for clear identification of the Brillouin peaks. To appreciate this advantage, consider either one of the spectra transmitted by a single interferometer in the top half of the figure. In between the \( m \)th and \((m+1)\)th order of transmission of the taller Rayleigh peaks on can observe the Stokes component of the Brillouin peak corresponding to one order and the anti-Stokes corresponding to the other order of transmission. \textit{A priori}, however, it is not clear which Brillouin peak belongs to which order. If the Brillouin frequency shift were large, the left peak could belong to the \((m+1)\)th order of transmission and the right one to the \( m \)th. If the shift were small it would be the other way around. The suppression of nearby orders using tandem interferometry allows one to identify the correct peaks easily (lower part of the figure).
Figure 4.3 Principle of the spectral filtering using a tandem Fabry–Pérot interferometer. Because of the differential in the scanning amplitude between the two cavities, $d_2 = \zeta d_1$, where $\zeta$ is a fractional number close to but not equal to unity, simultaneous transmission through both cavities occurs only when the orders interference are $l = \zeta m$, which given that $l$ and $m$ are integers, increases the free spectral range by a factor $n$, such that $n\zeta$ is an integer. Within that free spectral range all intermediate orders are suppressed and the assignment of Brillouin peaks is unambiguous.

Despite the sophistication associated with this measurement, or perhaps because of it, Brillouin spectroscopy has remained somewhat of a niche specialty, and not many Fabry–Pérot interferometers are commercially available for this application. Tandem interferometry has been elegantly implemented in the instrument developed by J.R. Sandercock. This tandem interferometer has two sets of parallel mirrors. One mirror from each pair, is mounted on a translation stage that can be displaced horizontally in the direction of the optical axis by a piezoelectric transducer. The other two mirrors are mounted in stationary frames, but they are supported on hinges so that they can pivot about the horizontal and vertical axes contained in the mirror plane. This pivotal mobility serves to maintain the surfaces of the stationary and
translating mirrors in each pair parallel to each other, while the latter are scanned back and forth for spectral filtering. The necessary pivotal adjustments are also done via piezoelectric transducers, and they are electronically controlled based on the feedback obtained from monitoring the transmission characteristics of a reference beam [14]. The mirror surfaces are flat within a tolerance of about 2 nm over a diameter of 2”, and the pivotal corrections provide parallelism between mirrors within similar tolerances.

In this instrument the translation stage is moved in the direction of the optical axis of the first Fabry–Pérot cavity. However, the second cavity is positioned at an angle of about 18° to the first one. Hence, if the translating mirror of the first cavity is opened to a distance $d_1$, that of the second cavity is moved to a distance $d_2 = d_1 \cdot \xi$, where $\xi = \cos(18°)$. The light is redirected by a fixed mirror situated behind the first interferometer to pass through the second one, as illustrated in Figure 4.4. In fact, with the help of a prism mounted after the second interferometer and another mirror mounted near the entry of the instrument, the optical path of the light to analyzed is folded back and forth through the optical components so as to traverse each interferometer three times, for total of six filtering passes. Note how in Figure 4.3 the line widths of the spectral features narrows as a result of coupling consecutive filtering steps. Using Eq. 4.25 to derive an effective finesse of the coupled device, this can easily exceed 100. The multi-pass tandem Fabry–Pérot interferometer concept has been highly beneficial to both the increase in spectral resolution and free spectral range. Hence, unless the research-grade spectrometers used for Brillouin light scattering in laboratories around the world today are in-house development, they are very likely the tandem Fabry–Pérot interferometer developed and manufactured by Sandercock, or slight modifications thereof.

![Figure 4.4](image_url) Schematic of the tandem Fabry–Pérot interferometer design by J.R. Sandercock.
A relatively new, perhaps less tried and proven, yet promising alternative to the tandem Fabry–Pérot interferometer is the virtual image phased array (VIPA) spectrometer [15–20]. The central component of such an instrument is a thin glass plate that is coated on the entrance side with a coating that is 100% reflective, except for a thin horizontal slit toward the bottom end of the plate. This slit area may in fact be coated with an anti-reflective film to allow for the incident light to enter the plate. The other side of the plate is coated with a highly, but not entirely reflective coating, through which some light may exit. Collimated incident light is focused using a semi-cylindrical lens onto the back surface behind the inlet slit of the plate, to create the original beam waistline. The plate is inclined forward from the vertical by a small angle γ, so that the light reflected on the backside of the plate is guided upwards. Every time the light is reflected off the back and front surfaces, it acts as if it originated from a virtual source located at a distance $2 \cdot d$ farther back and $\delta z = 2d \sin \gamma$ further up from the position of the inlet slit, where $d$ is the thickness of the glass plate. As the light emanates from the backside of the coated glass plate, following a diverging path from every source of the virtual array, the waves interfere destructively or constructively, depending on the angle and distance from the original beam waist. The interference pattern for a given vertical plane behind the glass plate can be calculated analytically. Placing a spherical lens at the location of this plane, this interference pattern is then projected onto a charge-coupled device (CCD) detector and the image is recorded.

This image contains a series of transmission orders of Rayleigh and Brillouin peaks, dispersed in vertical direction. The dispersion angles resulting from the interference of an array of virtual sources is much larger than what can be achieved by conventional refractive gratings. VIPA interferometers have also been configured in multiple stages, for which an effective finesse of about 40 and a spectral resolution of 700 MHz have been reported [19]. Hence, VIPA interferometers do not have as good a spectral resolution as multi-pass Fabri-Pérots, nor do they provide the ability to control the free spectral range independently. The great advantage of VIPA spectrometers is their transmission efficiency and the high rate with which spectra can be acquired. VIPA does not require cavity scanning, and the entire spectrum is imaged at once on the CCD detector. This allows one to reduce the light collection time from minutes to, in some cases, hours for Fabry–Pérot interferometers to mere seconds for VIPA spectrometers.

Finally, in Brillouin light scattering, the optical path in the vicinity of the sample is also important. Unlike in Raman scattering, where the wavevector associated with the vibronic excitation is of lesser importance, in Brillouin scattering this wavevector represents the propagation direction of the acoustic phonons with which light interacts inelastically, and consequently the direction along which the visco-elastic response of the scattering medium is probed. This allows one, for example, to determine the elastic constants of minerals along all their crystallographic directions by performing the measurements on a single crystal mounted on a goniometer head. It is also possible to identify elastic anisotropies in materials that are strained or textured in a particular direction, that have developed preferred growth orientations upon deposition, or that possess built-in residual stresses depending on their processing history.

When carrying out a Brillouin scattering measurement, the sample is illuminated with
monochromatic light, typically coming from a laser operating in the visible range, which is focused onto some region inside the sample, that is, the scattering volume. From here, light scatters in all directions, but only the portion comprised within the solid angle delineated by the aperture of the collimating lens placed at a distance corresponding to its focal length away from the scattering volume is collected. The direction of the incident laser beam and that of the optical axis of this lens then define the scattering angle \( \theta \), as long as the light enters and exits the scattering medium through surfaces that are perpendicular to these respective directions. In all cases, though, the scattering angle refers to the light propagation directions internal to the sample. Hence, if the optical paths cross the sample surface at off-normal orientations, determination of the scattering angle must account for directional changes according to Snell's law.

In this respect, backscattering and 90°-scattering are two relatively convenient geometries. The corresponding optical paths are illustrated in Figure 4.5. In backscattering, the scattered light is collected in the same orientation as the incident beam, only traveling in the opposite direction. In fact, in this geometry the focusing lens also serves as the collimating lens. This configuration is also advantageous in terms of the efficiency in collecting scattered light, because the collimating optics is by default focused on the same spot as the incident beam. Moreover, the focal lengths of lenses typically used in this setup provide for a large depth of field, and by sampling such a sizeable scattering volume, this scattering geometry yields a strong scattering intensity. Backscattering probes phonons with the largest possible wavevector for a given incident radiation, resulting in the largest Brillouin peaks shifts. However, the disadvantage of backscattering is that, due to symmetry reasons expressed in Eq. 4.16, it does not resolve light scattered from shear acoustic waves. The process in 90°-scattering can be considered as observing the incident beam laterally through the collimating optics, preferably at the focal point. This allows for precisely pinpointing the scattering volume to a particular location in the sample, but by reducing this volume, the scattering intensity also drops compared to backscattering.
Figure 4.5 Common scattering geometries used for bulk samples: (a) backscattering and (b) 90° scattering. \( \mathbf{k}_i \) and \( \mathbf{k}_s \) designate the wavevectors of the incident and scattered light inside the sample, respectively; the additional subscript e designates the light propagation directions external to the sample. \( q \) designates the phonon probed.

To correctly identify the scattering angle and internal wavelength of probing light, both of which are required to compute \( q \), it is generally necessary to know the refractive index, \( n \), of the scattering medium. As we will see in the next section, the value of \( q \), in turn, is required to compute the storage and loss moduli. In some situations, however, the precise value of \( n \) is not easily accessible. For example, if the objective is to measure the elastic moduli as a function of temperature, and it is to be expected that the high temperature refractive index deviates significantly from that at ambient conditions, or if the sample is subject to a large strain deformation. Under these conditions, a simple geometric construct, known as the platelet scattering geometry, can be employed to eliminate the need for measuring the refractive index, for example, as a function of temperature or the state of strain. Consider a plate-like sample geometry, where the incident and exiting light crosses surfaces that are parallel to each other, and the angles at which the light enters and exits relative to the surface normal are equal. As shown in Figure 4.6a, under those conditions, the scattering angle is equal to twice the internal angle relative to the surface normal, that is, \( 2\alpha \). Using Snell’s law \( n_1 \sin \alpha = n_2 \sin \alpha' = \sin \alpha' \), with \( n_2 = 1 \) closely approximating the refractive index of air, we can relate \( \alpha \) to the external angle of incidence, \( \alpha' \), and hence the wavevector magnitude of the phonons probed is
Figure 4.6 Platelet scattering geometry used for studying layered structures with parallel surfaces or thin films: (a) light enters and exits on opposite sides of the sample at an angle that is bisected by the film plane; phonons probed propagate in the film plane. (b) if the transmitted beam is collimated and reflected on itself, a second peak appears in the Brillouin spectrum in addition to the one discussed for (a), which corresponds to phonons that propagate perpendicular to the film plane. (c) when the film is supported on a reflective substrate, light entering from the free surface gives rise to backscattering, while the light reflected from the substrate gives rise to platelet geometry scattering, similar to the case depicted in (a). For thin films, this geometry also produces two peaks in the Brillouin spectrum, one probing phonons propagating nearly perpendicular to and the other one propagating parallel to the film plane. \( \mathbf{k}_i \) and \( \mathbf{k}_s \) designate the wavevectors of the incident and scattered light inside the sample, respectively; the additional subscript e designates the light propagation directions external to the sample. \( q \) designates the phonon probed.

\[
q_p = \frac{4\pi n}{\lambda} \sin \alpha = \frac{4\pi}{\lambda} \sin \alpha'.
\]
Accordingly, the refractive index of the scattering medium is eliminated from the expression and the wavevector magnitude can be determined without the knowledge of \( n \). In Figure 4.6b, a second scattering geometry is illustrated, which can be realized either by letting the incident and scattered light cross the sample surface on the same side and with the same angle relative to the surface normal, or by keeping the platelet scattering geometry setup as before, but by placing a collimating lens and a mirror in the path of the transmitted light, right after it exits the sample, so that the reflected light doubles back onto its original path. In the second scenario, the scattered light, collected in the direction of \( k_{s,e} \), contains two spectra: that corresponding to probing the phonon wavevector \( q_P \), as before, and that corresponding to

\[
q_R = \frac{4\pi n}{\lambda} \cos \alpha = \frac{4\pi n}{\lambda} \cos(\sin^{-1}[\sin \alpha'/n]).
\]  

(4.29)

Note that the direction of \( q_R \) is perpendicular to that of \( q_P \). If the refractive index of the scattering medium is known from an independent measurement, this setup allows one to determine the elastic anisotropy of the material. Conversely, if the elastic properties are isotropic, then the setup allows one to determine both the modulus and the refractive index in a single measurement.

### 4.4 DATA ANALYSIS AND INFORMATION CONTENT

As collected Brillouin scattering spectra are affected by instrument broadening. The true signal can be obtained via deconvolution, provided the smearing function is known. A nonlinear least square fit of the refined spectrum by the expression shown in Eq. 4.22 then allows one to extract the quantities of interest, that is, principally the velocity of sound \( c_S \) and the attenuation coefficient \( \Gamma_S \), but with careful experimentation determination of quantities such as \( \tau_B \), \( \gamma \), and even \( \kappa \) is possible. Possible reasons for the signal broadening have already been discussed in the previous section. For example, as illustrated in Figure 4.2, depending on the coefficient of finesse, a unit impulse is broadened into an Airy function line shape. Another source of spectral broadening arises from the fact that scattered light is collected within a finite solid angle. This means that phonons within a narrow range of wavevectors are sampled, and since each one is characterized by a slightly different frequency, this leads to peak broadening. Generally, imperfections in the optical components or sample constitution affect the line width. The sum of all these contributions is captured in the smearing function, which is oftentimes expressed as a Gaussian. This can be done by analytically tracking the broadening effects due to each factor, by comparing the measured spectra for substances with known properties, or by a combination of both.

Figure 4.7 illustrates the spectral fitting procedure using the data obtained from a sodium tellurite melt [5]. The data points represent the photon counts as a function of the frequency. The dash-dotted line in the center represents the Rayleigh peak after instrumental broadening has been removed via deconvolution. The shorter and broader central spectral feature can be attributed to the thermal relaxation peak, shown as a solid line. This peak emerges above the
glass transition as a narrow feature initially. The Rayleigh line is shown as a dotted line. The remainder of the central spectral feature can be attributed to the thermal relaxation peak, shown as a solid line. This peak emerges above the glass transition as a narrow line. The remainder of the central spectral feature can be attributed to the thermal relaxation peak, shown as a solid line. This peak emerges above the glass transition as a narrow line. With increasing temperature it broadens, while its intensity rapidly diminishes. The Brillouin peaks, as shown in Figure 4.7, are asymmetric. This asymmetry is fully accounted for by the last couple of terms in Eq. 4.22. Using this procedure it is straightforward to determine the positions, linewidths, and intensities of the Brillouin and relaxation peaks.

**Figure 4.7** Typical Brillouin scattering spectrum from a molten alkali borate system. Circles represent the experimental data, and the lines represent the best fits of these data using Eq. 4.22. The contributions from the different terms of Eq. 4.22 are shown as labeled in the legend.

With regard to the visco-elastic properties of the scattering medium, the two most important quantities resulting from the best fit of Eq. 4.22 to measured Brillouin spectra are the elastic storage modulus
where $c_s q = \omega_S \Leftrightarrow c_s = \omega_S / q$, and the mechanical loss modulus

$$M''(\omega) = \alpha \eta'(\omega),$$

where $\eta'(\omega)$ is the dynamic viscosity. This term is frequency dependent because the structural relaxation undergone by the scattering medium is on the same time scale as the probing frequency. Accordingly, the viscosity coefficients that appear in the momentum balance (e.g., the Navier-Stokes equation), are assumed to be time dependent, that is,

$$\eta(t) = \eta_0 + \eta' e^{-t/\tau_B}.$$  \hspace{1cm} (4.32)

This formulation is based on empirical observations that viscous dissipation diminishes once the structure has adjusted to an imposed impulse. Transformed to the frequency domain, this yields

$$\eta'(\omega) = \eta_0 + \rho_0 \frac{c_0^2 - c_s^2}{1 + (\omega_s \tau_B)^2} \tau_B,$$  \hspace{1cm} (4.33)

which constitutes the first two terms of the attenuation coefficient

$$\Gamma_s = \frac{1}{2} \left\{ \frac{\eta_0}{\rho_0} + \frac{c_\infty^2 - c_0^2}{1 + (\omega_s \tau_B)^2} \tau_B + \kappa \left[ 2 \gamma - c_0^2 c_s^{-2} - 1 \right] - \gamma \frac{c_\infty^2 - c_0^2}{1 + (\omega_s \tau_B)^2} (q \tau_B)^2 \right\},$$  \hspace{1cm} (4.34)

and can be deduced from the full width at half maximum (FWHM) of the Brillouin peaks, $\Delta \omega_B = 2q^2 \Gamma_s$. The remaining contributions to the sound attenuation coefficient,

$$\kappa [2 \gamma - c_0^2 c_s^{-2} - 1 - \gamma \frac{c_\infty^2 - c_0^2}{1 + (\omega_s \tau_B)^2} (q \tau_B)^2]$$

are due to thermal relaxation processes involving the thermal diffusivity $\kappa$. This latter parameter can in principle be derived from the FWHM of the Rayleigh peak

$$\Delta \omega_R = 2q^2 \frac{\kappa}{\rho_0 c_p}.$$  \hspace{1cm} (4.35)

Similarly, the structural relaxation time constant $\tau_B$ can be obtained from the FWHM of the thermal relaxation peak underlying the Rayleigh peak

$$\Delta \omega_C = 2c_0^2 c_s^{-2} \tau_B^{-1}.$$  \hspace{1cm} (4.36)

Furthermore, the factor $\gamma$ can be approximated by [21–23]

$$\gamma = I_R / 2I_B + 1.$$  \hspace{1cm} (4.37)
where $I_R$ and $I_B$ are the Rayleigh and Brillouin peak intensities. For liquids at or below the melting temperature, however, the dynamic viscosity is dominated by the terms of Eq. 4.33. This is because both $\kappa$ and $\tau_B$ are small, so that $\gamma \kappa q^2 \tau_B \ll 1$. Moreover, the magnitudes of $\gamma$ and $c^2 \rho c_S^{-2}$ closely track one another within the temperature range of interest and approach unity. Hence, in Eq. 4.34 the terms grouped in square brackets and multiplied by $\kappa$, that is, those describing thermal relaxation, do not contribute significantly to the width of the Brillouin peak compared to those describing viscous relaxation.

Depending on the scattering geometry and the polarization of the scattered light relative to the incident light, it is possible to differentiate between longitudinal viscosity $\eta_L$ and shear viscosity $\eta_S$. The longitudinal viscosity is defined as $\eta_L = 4/3 \eta_S + \eta_B$, where $\eta_B$ is the bulk viscosity. The difference between the velocity of sound at infinite and zero frequencies, multiplied with average density of the material, is commonly known as the relaxational modulus, that is, $\rho_0 (c^2 \infty - c^2_0) = M_2$. Accordingly,

$$M''(\omega_S) = \omega_S \eta''(\omega_S) = \omega_S \eta_0 + \rho_0 \frac{c^2 \infty - c^2_0}{1 + (\omega_S \tau_B)^2} \omega_S \tau_B = \omega_S \eta_0 + M_2 \frac{\omega_S \tau_B}{1 + (\omega_S \tau_B)^2}, \quad (4.38)$$

of which the last term represents the imaginary component of the complex mechanical modulus, $M''(\omega)$, in the framework of Maxwell’s theory for a linear visco-elastic medium. In this formalism, the dynamic process is characterized by a single relaxation time, $\tau_B = \tau_0 e^{E_a/k_B T}$. Here, $\tau_0$ is a time constant and $E_a$ the activation energy of the relaxation process. Hence, $\eta''(\omega) = \omega \eta_0 + M_2 \frac{\omega \tau_0 e^{E_a/k_B T}}{1 + \omega^2 \tau_0^2 e^{2E_a/k_B T}}$, \quad (4.39)

and $\eta'(\omega) = \eta_0 + M_2 \frac{\tau_0 e^{E_a/k_B T}}{1 + \omega^2 \tau_0^2 e^{2E_a/k_B T}}$. \quad (4.40)

Equations (4.39) and (4.40) reveal both the frequency and temperature dependence of the loss modulus and dynamic viscosity, respectively. In a Brillouin scattering experiment, the probing frequency, which is in fact the frequency of the phonon that is being probed, is controlled by the selection of the phonon wavevector. To this end one can vary the scattering angle and the wavelength of the probing radiation. The latter is rather difficult to accomplish, as it would require a tunable laser source and the replacement of the interferometer mirrors, because the mirror coatings are optimized for a narrow wavelength range. Changing the scattering angle is not always trivial, since the angle at which incident and scattered light cross the sample surface must be carefully established, but it is doable. Nevertheless, in practice the frequency range that can be covered this way is limited to about one order of magnitude, because at small
scattering angles the Brillouin peaks tend to become overshadowed by the significantly more intense elastically scattered light.

It is therefore more commonplace to carry out relaxational spectroscopy of glass-forming systems by varying the sample temperature. Indeed, the probing frequency in a typical Brillouin scattering experiment is relatively constant, even if the consistency of the material under investigation changes from that of a supercooled liquid to a glass. In the context of the discussion that follows, the principal features of the loss modulus as a function of temperature also apply to behavior of the viscosity. Given the GHz-range probing frequencies, significant relaxation can only be expected for matter in the liquid state. However, under these conditions, the probing frequencies tend to resonate with those of elementary transport processes, such as diffusional jumps of atoms and small molecules, and reorientations of dangling moieties of larger molecules.

Figure 4.8 shows a series of curves representing the viscosity according to Eq. 4.40, for different probing frequencies, and as a function of the temperature. This graph reveals the general trends one should expect to observe in experimental data. Note that at zero frequency Eq. 4.40 yields the familiar Arrhenius expression for the viscosity in simple liquids, which appears as a straight line on the log $\eta$ versus $1/T$ plot. At finite probing frequencies, however, Eq. 4.40 exhibits a maximum, which occurs at higher temperatures the higher the frequency. At very high temperatures, viscosity values determined at different probing frequencies all converge. This is the case when the characteristic relaxation time has dropped below the reciprocal of even the highest frequency. The relaxation process then comes to completion well within the period of the selected phonon. At low temperatures the viscosities drop off sooner the higher the probing frequency. The fact that viscosities vanish when approaching zero temperature, or equivalently, increase with temperature in the low temperature regime, may seem odd at first sight. However, this merely reflects the fact that no viscous processes are sufficiently activated to effect any measurable energy dissipation within the period of the probe. As alluded to above, using Brillouin scattering, viscous processes are detected based on the momentum transported and exchanged between structural sites, and for there to be momentum transport, there has to be finite molecular mobility. Obviously, at zero frequency an infinite amount of time is provided, during which all viscous processes come to completion.
Figure 4.8 Schematic showing the viscosity attributed to a single relaxation mechanism as a function of temperature according to Eq. 4.40, probed at different frequencies. Inset: comparison of the viscosity of a polyolefin standard as determined by Brillouin scattering at ~$10^{10}$ Hz (squares) and rotating cylinder viscometry at 0 Hz (circles).

This explains why, when probed at finite frequency, the viscosity at first increases with temperature and decreases only after reaching a maximum. Many laboratory viscometers provide the ability for oscillatory shearing up to frequencies of hundreds of Hz. The reason why maxima in viscosities are not observed with those instruments is because these maxima would occur at temperatures below the glass transition. Based on the comparison between Eqs. (4.39) and (4.40), the maximum in viscosity essentially maps onto that of the loss peak in the mechanical modulus, which is perhaps a more familiar concept. Importantly, viscosities measured in the GHz frequency regime using Brillouin scattering extrapolate rather accurately to the same quantities measured at zero frequency simply by adjusting the magnitude of the frequency in Eq. 4.40. The inset in Figure 4.8 shows the kinematic viscosity coefficient of a viscosity standard polyolefin, measured by Brillouin scattering, as a function of temperature. The data are compared to the viscosity determined by rotating cylinder viscometry (as
determined by the National Institute for Standards and Technology). Note that the data coincide at high temperatures and deviates at low temperatures, as predicted above and illustrated in the inset of Figure 4.8. Both data sets were fitted by the expression in Eq. 4.40 and in both cases yielded the same parameters within experimental error, that is, \( M_2 = 2.064 \times 10^8 \text{ Pa} \cdot \text{s}; \tau_0 = 1.67 \times 10^{-15} \text{ s} \), and \( E_a = 30.122 \text{ kJ/mol} \).

Probing viscous processes at high frequencies has the disadvantage of being limited to viscosities of about \( 10^5 \text{ Pa} \cdot \text{s} \) or less, due to the short relaxation times that can be accommodated under these circumstances. Then again, since Brillouin scattering also yields the complementary storage modulus, this may not really be a shortcoming. There are several advantages to measuring viscosities at high frequencies. As mentioned before, in the GHz regime one directly probes the atomistic mechanisms of momentum transport, by resonating with these processes. The high probing frequencies allow one to discern different relaxation mechanisms more easily. It is well known (and can be easily shown) that the maximum in the loss modulus or viscosity, as described by Eqs. (4.39) or (4.40), respectively, occurs when \( \omega \tau = \omega \tau_0 e^{E_a/k_B T_p} = 1 \). From this follows that the loss modulus or viscosity peaks at a temperature given by

\[
T_p = \frac{E_a}{-k_B \ln(\omega \tau_0)} = \frac{-E_a}{k_B(\ln \omega + \ln \tau_0)}.
\]

In the context of Maxwell’s theory for linear visco-elasticity we identify relaxation mechanisms based on their activation energy \( E_a \) and characteristic time constant, \( \tau_0 \). The peak temperature being an easily recognizable and unambiguous quantity in relaxational spectroscopy, using Eq. 4.41 we can evaluate the extent to which each of these quantities affects the location of mechanical loss peak on the temperature scale, that is,

\[
\Delta T_p = \left( \frac{\partial T_p}{\partial E_a} \right)_{\tau_0} \Delta E_a + \left( \frac{\partial T_p}{\partial \tau_0} \right)_{E_a} \Delta \tau_0
= -1/(k_B \ln(\omega \tau_0)) \Delta E_a + E_a/(k_B \ln(\omega \tau_0))^2 \Delta \ln \tau_0.
\]

Note that because \( \omega \tau_0 = e^{-E_a/k_B T_p} \), with all quantities on the exponent being positive and finite, \( \omega \tau_0 \) is always smaller than one. Consequently, \( \ln \omega \tau_0 \) is always negative and decreases in magnitude as the frequency increases. Thus, the higher the frequency the larger the factors that multiply \( \Delta E_a \) and \( \Delta \ln \tau_0 \) in the above expression, and the more markedly the peak temperature is affected by variations in these quantities. Or, in other words, high probing frequencies separate energy loss peaks more clearly and allow one to distinguish relaxation mechanisms that would blend when probed at lower frequencies. Furthermore, Brillouin scattering allows one to measure the viscosity without mechanical contact, without imparting external forcing, that is, without disturbing the thermodynamic equilibrium of the system, or the metastable state it may be in. It therefore yields the zero-shear rate viscosity.

The complex modulus, \( M^*(\omega) \), describes elasticity and dissipation as two conjugate quantities,
which characterize a given dynamic process

\[ M^*(\omega) = M'(\omega) + iM''(\omega) = M_0 + M_2 \frac{\omega^2 \tau^2}{1 + \omega^2 \tau^2} + iM_2 \frac{\omega \tau}{1 + \omega^2 \tau^2} \]  

(4.43)

where \( M_0 \) is the static modulus. The real components in Eq. 4.43, and their temperature dependence, are derived from the frequency shift between Brillouin and Rayleigh peaks, that is, \( M_0 + M_2 \frac{\omega^2 \tau^2}{1 + \omega^2 \tau^2} = \frac{\nu \omega^2}{\sigma^2} \). When describing the response to longitudinal actuation, each component of the modulus includes the bulk modulus, \( K \), and the shear modulus, since

\[ M = K + 4/3G, \]  

(4.44)

whereas for a shear actuation, the moduli contain only the shear components, \( G \).

### 4.5 EXAMPLES OF CASE STUDIES

In this section we describe several research scenarios in which Brillouin scattering has become the method of choice for the investigation. This description is not intended to provide a complete account of all possible applications for the Brillouin technique, nor is it meant to provide an exhaustive literature survey of the work that had been done in the areas of research exemplified in the following. A number of scholars have contributed to this body of knowledge and we are making an effort to reference the most pertinent work, but to attempt giving a comprehensive list is beyond the scope of this chapter.

#### 4.5.1 Room-Temperature Glass

The typical notion we have of glass is that of a homogeneous, mechanically isotropic, and transparent solid. Brillouin light scattering is ideally suited to determine the elastic properties of such a material: transparency provides access to any location in the interior or near the surface of the specimen, and isotropy means that only two elastic constants are required to fully characterize the elastic response of the material. Indeed, Hooke's law for a homogeneous isotropic material in three dimensions can be expressed as

\[ \sigma = \lambda \text{tr} (\epsilon) I + 2\mu \epsilon, \]  

(4.45)

where \( \lambda \) and \( \mu \) are the first and second Lamé coefficients, respectively, \( \sigma \) and \( \epsilon \) are the stress and strain tensors, respectively, and \( I \) is the identity matrix. Here, \( \mu \) corresponds to the shear modulus, that is,

\[ \mu = G', \]  

(4.46)

and \( \lambda \) is related to the longitudinal modulus as

\[ \lambda = M' - 2G'. \]  

(4.47)

Using Eq. 4.44 we get
Depending on the scattering geometry, these two quantities can be obtained in a single measurement, that is, the spectrum of scattered light exhibits two peaks, one associated with shear waves and the other one with longitudinal waves. Figure 4.9 shows a typical Brillouin spectrum collected from a fused silica sample in the 90°-scattering geometry. Note that we can separately resolve the longitudinal and shear peaks based on the fact that the light scattered from shear waves tends to depolarize. This means that, assuming the incident light is vertically polarized, the light scattered from longitudinal phonons remains vertically polarized, whereas that scattered from transverse phonons is horizontally polarized. Hence, a polarizer filter mounted in the collection path with its polar direction parallel to the orientation the incident light's electric field vector (VV configuration) suppresses the light scattered from shear waves. Mounting the polarizer with its polar direction perpendicular to the incident electric field vector (HV configuration) suppresses the light scattered from longitudinal waves. In other words, the VV configuration yields the longitudinal peaks (shown as circles in Figure 4.9) and the HV configuration the shear peaks (inverted triangles). Without polarizer, both Brillouin doublets appear in the collected spectrum. The line represents a fit of this data using Eq. 4.22.
Figure 4.9 Typical Brillouin scattering spectrum of fused silica: triangles are measured in the HV polarization directions, resolving the shear peaks, and circles are measure using the VV directions, resolving the longitudinal peaks.

From the measurement of these two quantities we can calculate the constants of linear elasticity, as summarized in Table 4.1.
Table 4.1 Relationships between various elastic constants relevant to homogeneous isotropic media.

<table>
<thead>
<tr>
<th>Elastic Constant</th>
<th>Expression</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st Lamé coefficient</td>
<td>( \lambda )</td>
<td>( \lambda = M' - 2G' )</td>
</tr>
<tr>
<td>2nd Lamé coefficient</td>
<td>( \mu )</td>
<td>( \mu = G' )</td>
</tr>
<tr>
<td>Poisson's ratio</td>
<td>( \nu = -2\frac{\varepsilon_{11}}{\varepsilon_{11}} \left( \varepsilon_{22} + \varepsilon_{33} \right) )</td>
<td>( \nu = \frac{\lambda}{2(\lambda + 2\mu)} = \frac{M' - 2G'}{2(M' - G')} )</td>
</tr>
<tr>
<td>Bulk modulus</td>
<td>( K = -V \left( \frac{\partial p}{\partial V} \right)_T )</td>
<td>( K = M' - \frac{4G'}{3} )</td>
</tr>
<tr>
<td>Young's modulus</td>
<td>( E = \frac{\sigma_{11}}{\varepsilon_{11}} )</td>
<td>( E = \frac{G'(3M' - 4G')}{M' - G'} )</td>
</tr>
<tr>
<td>( C_{11} )</td>
<td></td>
<td>( C_{11} = M' )</td>
</tr>
<tr>
<td>( C_{12} )</td>
<td></td>
<td>( C_{12} = \lambda = M' - 2G' )</td>
</tr>
<tr>
<td>( C_{44} )</td>
<td></td>
<td>( C_{44} = \mu = G' )</td>
</tr>
</tbody>
</table>

Inorganic glasses, at least those that are relatively stable under ambient conditions, can easily be drawn into fibers, which yields a convenient geometry for mechanical testing, both in tensile or torsional deformation modes. It is therefore straightforward to measure two independent elastic constants using conventional mechanical testing equipment. The major advantage of Brillouin scattering, in this regard, is the spatially resolved access to materials properties it provides. As mentioned earlier, with conventional optics the volume of material probed with Brillouin scattering measures on the order of 25 μm in diameter. Hence, by focusing the incident beam and collection optics on various locations inside a transparent glass, it is possible to scan the material for spatial inhomogeneities in its elastic properties [17].

As an example, the elastic moduli of a tempered borosilicate glass plate are shown in Figure 4.10 as a function of the distance from the surface. Of the elastic moduli plotted in this figure, the longitudinal and shear moduli are directly measured by Brillouin scattering, whereas the other two are calculated using the corresponding relationships in Table 4.1. The fluctuations in the data for \( M' \) and \( G' \) compound accordingly in the calculated values for \( K \) and \( E \). We notice, however, that all elastic moduli are lower near the surface of the glass plate than in the interior. This is due to the compressive stress that is imparted in the near-surface regions of the glass as a result of the tempering process. Silica is the predominant network former in this glass, and because silica glass exhibits an anomalous pressure dependence of its elastic properties, that is, its stiffness decreases with increasing pressure [24–30], compressive residual stresses cause a decrease in elastic moduli. Using an approximate value for the coefficient \( \frac{\partial M'}{\partial p} \), derived from the data given by Grimsditch [24], we can estimate the compressive stress at the surface of this glass plate to range between 80 and 100 MPa.
Figure 4.10 Elastic longitudinal ($M'$), Young's (E), bulk (K), and shear ($G'$) moduli of a tempered borosilicate glass plate as a function of the distance from the surface. The decrease of the moduli near the surface reflect the compressive state of the glass.

The small scattering volume required for Brillouin scattering measurements allows for relatively arbitrary sample size and shape, and generally very little sample preparation is needed. Most important is to provide for a clean optical path to the region of the specimen to be examined. This is accomplished by creating a smooth and ideally a flat surface. While not entirely precluding the ability to collect spectra, exceedingly rough surfaces may cause spurious reflections and introduce considerable uncertainty with respect to determining the angle of incidence of the probing beam, which translates to inaccuracy in identifying the wavevector of the scattering phonons. Using microscope objectives, the required sample size can be reduced to only a few micrometers, and the glassy phase of interest can be embedded inside other materials constituents, such as at grain boundary junctions or in between reinforcing fibers of a polymer composite [31, 32].

To illustrate the appeal of Brillouin measurements, in Figure 4.11 we compare the longitudinal...
moduli of a series of binary sodium borate glasses measured using Brillouin scattering with those determined using an ultrasonic pulse echo overlap technique [33, 34]. The latter method requires samples with uniform density and of specific geometry, that is, cylinders of 12 mm length and 15 mm diameter, true to within 2 μm for each sample. The flat ends of each sample are polished optically smooth and parallel to each other before applying X-cut and Y-cut quartz transducers to each end for the generation and detection of longitudinal and shear the ultrasonic pulses, respectively. The data so obtained, using a fundamental frequency of 10 MHz, are shown as open circles. By contrast, the samples used for the Brillouin measurements consist of a droplet of material suspended via surface tension in a double-loop platinum wire, created by simply dipping the wire into a melt reservoir just before measurement [35]. The two loop on the wire are arranged like the rims on a barrel, to facilitate a roughly cylindrical shape of the droplet. The incident beam enters the sample from the bottom and the scattered light is collected from the side of this cylinder. The entire assembly is placed in a small resistively heated furnace with bottom and side windows. A bit of bulging of the droplet is inevitable, and the curvature causes some inaccuracy in determining the magnitude of the phonon wavevector, which is the main reason for the scatter in the Brillouin data, shown as blue circles.
Figure 4.11 Longitudinal elastic moduli of sodium borate glasses and melts as a function of the Na$_2$O concentration. Small open circles represent data measured using ultrasound propagation at room temperature, solid circles and solid squares represent data measured using Brillouin scattering at room temperature and 1000°C, respectively.

However, considering possible differences in composition and thermal history, the agreement between the modulus data obtained using the two methods is very good. Given this procedural convenience, the Brillouin technique has been very popular for scanning the compositional dependence of elastic moduli of a variety of multi-component glass systems [5,23,36, 37,37–46].

4.5.2 Temperature Dependence, Glass Transition, and Visco-Elasticity

The minute sample size and the contact-free nature of Brillouin measurements allow for a great deal of liberty in the design of sample containment, and make this technique highly suitable for the measurement of visco-elastic properties of glass-forming systems over a wide temperature
range, including the liquid state and glass transition region. Thus, a number of researchers have used this technique to study the temperature dependence of the complex mechanical moduli of glasses and supercooled liquids [5,45–53]. The data shown as red squares in Figure 4.11 correspond to the longitudinal moduli of the various sodium borate compositions in their molten state at 1000°C. The strong compositional dependence of the modulus observed at room temperature has now all but vanished, that is, mechanically these melts act very similarly, regardless of the glass former contents, suggesting that the network is by and large disintegrated at this temperature.

The common perception is that in simple liquids the shear elastic modulus vanishes. Considering Eq. 4.44, this would mean that the remaining longitudinal modulus essentially consists of the bulk modulus, that is, the reciprocal of the isothermal compressibility, 
\[ \beta = -\frac{1}{V} \frac{\partial V}{\partial p} \] (see Table 4.1). (Another common assumption in fluid dynamics is to treat liquids as incompressible, that is, \( \beta = 0 \). Evidently this cannot be the case, or else the bulk modulus would be infinite.) Therefore, given such finite compressibility, it is not surprising to observe a finite longitudinal modulus, \( M' = K \). However, for glass-forming systems, the conclusion is not as simple as that. The assumption that the shear elastic moduli vanish in liquids may be reasonable for zero-frequency actuation, but for high frequency elastic deformations, this is not the case. Figure 4.12 shows both the longitudinal and shear elastic moduli of three common oxide network formers, SiO\(_2\), GeO\(_2\), and B\(_2\)O\(_3\), measured using Brillouin scattering as a function of temperature [54]. These data exemplify several key characteristics of glass-forming compounds. First, we note that all three systems exhibit signs of thermo-mechanical anomalies, that is, temperature ranges over which the modulus increases with temperature. This is the case for SiO\(_2\) over the entire temperature range measured, for GeO\(_2\) almost over the entire range, except for a small region just above the glass transition, and for B\(_2\)O\(_3\) mostly in the liquid state above 800°C.
Figure 4.12 Longitudinal and shear elastic moduli of three major glass formers, SiO$_2$, GeO$_2$, and B$_2$O$_3$, measured as a function of temperature using Brillouin scattering. Note the anomalous increase in stiffness with temperature for all three compounds. Also note the abrupt change in slope for GeO$_2$ and B$_2$O$_3$ at their glass transition temperature.

Glass transition temperatures, $T_g$, are indicated with vertical arrows. For B$_2$O$_3$ and GeO$_2$ the glass transition is revealed by a cusp, that is, an abrupt change in slope of the modulus versus temperature data. Indeed, the behavior exhibited by B$_2$O$_3$ is characteristic of most normal glass-forming systems: below $T_g$, the elastic storage capacity of the glassy network changes very little with temperature. At $T_g$, the modulus drops precipitously, and levels out toward high temperatures at a value that is likely dominated by the bulk modulus, characteristic of the molten state. However, as can be seen in Figure 4.12, the shear modulus measured at GHz frequencies never vanishes, not even at 1650°C—about a thousand degrees above the melting temperature of this compound. This means that the tendency to form a three-dimensional network remains strong. Even at these very high temperatures the characteristic relaxation time associated with the rupture of network bonds is significantly longer than a nanosecond.
The thermo-mechanical anomaly, evident in all three systems, can also be explained by the persistence of a relatively intact network topology. The average ring size in these amorphous networks is about six, comparable to that in high symmetry crystalline modifications of these compounds. At low temperatures, the framework of polygonal joints that delineate network crevices are collapsed, with segments pointing inward to facilitate dense packing of network constituents. To accommodate the increased thermal motion at elevated temperatures, the crevices inflate and the collapsed segments unbuckle to assume a configuration more optimized for isotropic load bearing. In short, the network stiffens. The structural motives present in the amorphous network, and the reversible buckling transitions they undergo are similar to those in high and low density crystalline polymorphs of the corresponding compounds. Of these, the low density modifications, which are stable at high temperatures, all possess higher elastic moduli, for example, α- and β-cristobalite, or \( \text{B}_2\text{O}_3\)-I and \( \text{B}_2\text{O}_3\)-0. A detailed explanation of this phenomenon and its underlying mechanisms can be found in References [25, 26, 30, 55–57].

With increasing modifier cation concentration in the glass, the covalent bonding pattern that constitutes the glassy network becomes progressively disrupted, and the anomalous thermo-mechanical behavior is gradually suppressed. Figure 4.13 shows the temperature dependence of the elastic moduli of binary alkali silicates, germanates, and borates, as a function of the alkali oxide concentration. We observe that the higher the alkali concentration, that is, the greater the degree of network modification, the more steeply the elastic storage capacity of the glassy network decreases with increasing temperature above the glass transition. This is the case whether the pure network former has greater stiffness than its modified alloys, such as for silicates, or whether the opposite is true, as is the case for borates. Even for germanates, for which the room-temperature modulus goes through a maximum at about 10 mol% potassium oxide, this seems to be the case, although it is difficult to tell due to the gap in the data in the range of strongly supercooled liquids. The modulus data shown in Figure 4.13 are obtained by placing the sample in a small windowed furnace and by taking measurements at temperature intervals of 10 or 20°C. The most time consuming aspect of this procedure is the wait for the furnace temperature to equilibrate. Hence, the samples are cooled or heated very slowly, and for sample compositions near the edges of the glass-forming regions, crystallization may occur. This has been the reason for these data gaps. Typically, we collect data upon cooling samples after the sample holder has been dipped in the melt reservoir. In case samples crystallize while holding it in the strongly supercooled state, we obtain the data below the temperature gap by first rapidly quenching the sample into a glass and then conducting measurements upon heating. For good glass-forming systems, the moduli measured upon cooling and heating typically coincide to within less than a percent relative error.
Figure 4.13 Longitudinal elastic moduli of (a) potassium silicates; (b) potassium germatates; and (c) sodium borates, as a function of temperature and for various alkali oxide concentrations, measured using Brillouin scattering. Discontinuities in slope indicate the glass transition temperature.

The elastic modulus, especially when determined at this 50 nm scale characteristic for Brillouin scattering, can be viewed as a measure of network connectivity. The rate of decay of network integrity generally follows the same trend as the fragility index of the glass-forming melt. Because of the more significant change in slope of the modulus versus temperature data for highly modified or fragile glass formers, the signature of the glass transition, that is, the cusp or kink in the data is more evident. Its location on the temperature scale can be identified with the same precision as scanning calorimetry, and consequently, Brillouin scattering has become a popular method for determining the glass transition temperature [5,45,46,48–53,58–61], especially when samples are difficult to access or very little sample volume is available [40]. This is the case, for example, when glasses develop during thin film deposition. We will revisit this scenario in the following section.
Viscosity and viscous relaxation processes are a key aspect of glass formation. As detailed in Section 4.4, Brillouin scattering probes the momentum transport at the atomistic level, and thereby provides unique insights into the mechanisms of viscous dissipation. The temperature dependence of the characteristic relaxation time $\tau$ in Eq. 4.43 allows one to use Brillouin scattering for relaxational spectroscopy, in a way that is very similar to dielectric impedance spectroscopy, except that here we measure the complex mechanical modulus. The ability to observe mechanical loss peaks, that is, maxima in the imaginary component of the complex modulus, with the temperature range of supercooled liquids bears promise to reveal the structural relaxation mechanisms that are at play during glass formation. Furthermore, being able to discern such peaks in their entirety, and not just the descending flank, as is the case with low frequency and steady-state rotating cylinder viscometry, eliminates significant ambiguity when fitting expressions such as Eq. 4.40 to such data in order to extract fundamental physical constants. To demonstrate the capabilities of Brillouin scattering for the investigation of visco-elastic relaxation during glass formation, we first examine the behavior of pure $\text{B}_2\text{O}_3$ and afterwards compare the complex modulus of an alkali borate with that of an alkali tellurite system.

Figure 4.14a shows the mechanical loss modulus of pure $\text{B}_2\text{O}_3$, normalized with respect to its average density, as a function of temperature. A small peak is apparent in these data near 500°C and the magnitude of this specific loss modulus increases again toward higher temperatures, ostensibly to describe the flank of a second, larger peak, whose maximum is not reached within the temperature range of the measurement. The experimental data are fitted with the expression

$$
M''(\omega_s)/\rho_0 = \omega_s\eta_0/\rho_0 + \sum_j \frac{c_\infty^2 - c_0^2}{1 + (\omega_s\tau_{B,j})^2}\omega_s\tau_{B,j}
$$

(4.49)

where $\tau_{B,j} = \tau_{0,j}e^{E_{a,j}/k_BT}$ is the characteristic relaxation time of the $j$th mechanism, and the sum is carried over all active mechanisms. The number of these mechanisms is not known a priori, but is determined as the minimum number needed to provide a good fit of the data. Based on the argument presented earlier in conjunction with Eq. 4.42, namely that the high frequencies probed by the Brillouin technique result in a broader dispersion of relaxation peaks on the temperature axis, this approach is reasonable and good fits are achieved with the assumption of relatively few distinct relaxation mechanisms. For pure $\text{B}_2\text{O}_3$, we identified three mechanisms with clearly separated maxima.
Figure 4.14 (a) Specific loss modulus for B$_2$O$_3$ as a function of the temperature, revealing three energy-dissipating mechanisms: the dissolution of boroxol rings, the network disintegration, and the diffusion of impurities; (b) comparison of the viscosity of B$_2$O$_3$ measured using rotating cylinder viscometry and Brillouin light scattering, the latter being converted to zero-frequency quantities (contributions of all three dissipation are shown as lines, but the overall viscosity is dominated by network disintegration); (c) superposition of bulk, shear, and longitudinal viscosities of B$_2$O$_3$ measured using Brillouin scattering; (d) real and imaginary components of the Poisson ratio as a function of temperature. Note the positive values of Im($\nu^*$) in the temperature range in which the bulk viscosity dominates.

We will further discuss these relaxation processes, but first, we ascertain the validity of the viscosity coefficient so obtained [41]. To this end we set the remaining frequency in the denominator of Eq. (40) to zero, and compare it with the viscosity derived from rotating cylinder viscometry. The results are shown in Figure 4.14b. Accordingly, the zero-frequency viscosity extrapolated from Brillouin measurements is in excellent agreement with the literature data [62–64]. At high temperatures, the Brillouin data track the rotating cylinder data.
very nicely. The slight difference in magnitude is to be expected, since Brillouin measurements yield the longitudinal viscosity, \( \eta_L = 4/3 \eta_S + \eta_B \), whereas rotating cylinder viscometry yields only \( \eta_S \). At low temperatures, the result from the two methods deviates more strongly. This can be ascribed to the non-Arrhenius behavior of the viscosity, which is characteristic of the quantity measured using conventional viscometry. By contrast, the viscosity derived from Brillouin scattering is dominated by the strongest term in the linear combination of Eq. 4.49, which is four orders of magnitude larger than the second-strongest term, and which does obey Arrhenius behavior. Of the possible explanations for this discrepancy, we would like to point out that, while rotating cylinder viscometry requires a finite shear rate for the measurement, this restriction is absent in Brillouin scattering. The effect that such an imposed shear deformation has on the structural, and thus mechanical integrity of a glass-forming liquid near \( T_g \) is at present unknown.

For as long as Brillouin spectra reveal both longitudinal and shear elastic peaks, it is possible to differentiate between bulk and shear viscosity. These two measures for \( \text{B}_2\text{O}_3 \) are plotted versus temperature in Figure 4.14c. Interestingly, the smaller low temperature peak can be predominantly attributed to bulk viscosity, that is, dissipative mechanical energy losses that occur upon isotropic dilational deformations, while shear deformations are responsible for the majority of energy dissipation in the high-temperature loss peak. To complete our understanding of the underlying relaxation mechanisms, we examine the temperature dependence of the complex Poisson ratio,

\[
\nu^* = \frac{M^* - 2G^*}{2(M^* - G^*)} = v' + iv''.
\] (4.50)

The real and imaginary components of this complex Poisson ratio for \( \text{B}_2\text{O}_3 \) are shown as a function of temperature in Figure 4.1d. The room temperature value of the real component of \( \nu^* \) is just under 0.3, and does not change with temperature until the glass transition is reached. Starting at \( T_g \), \( v' \) suddenly increases and gradually levels out at its high temperature value of 0.35. This behavior qualitatively reflects the decrease in elastic storage modulus in the same temperature range. Note that at 1100°C, clearly above the melting point of crystalline \( \text{B}_2\text{O}_3 \), \( v' \) has not reached the value of 0.5, characteristic of an incompressible fluid, which again underlines the fact that on short time scales the \( \text{B}_2\text{O}_3 \) melt does not behave like a simple liquid and its network topology prevails even under the influence of strong thermal motion. The imaginary component of \( \nu^* \) exhibits small positive values at low temperatures and negative values above about 700°C. To understand the meaning of the sign of \( \nu'' \), consider Hooke's law for one-dimensional oscillatory stress,

\[
\varepsilon_{11} = \frac{\sigma}{M^*} = \frac{\sigma_0}{(M' + iM^*)} e^{i\omega t} = \frac{\sigma_0}{|M^*|} e^{i(\omega t - \phi)},
\] (4.51)

where \( \sigma_0 \) is the amplitude of the applied uniaxial stress and \( \tan \phi = M''/M' \). The phase angle \( \phi \) represents the time lag with which deformation follows the applied stress in a particular
direction. The Poisson ratio is defined as the negative ratio of the strains perpendicular to and in the direction of the applied stress responsible for this deformation, that is, \( \nu^* = -\epsilon_{22}/\epsilon_{11} \), and hence

\[
\epsilon_{22} = -\nu^*\epsilon_{11} = -|\nu^*| \frac{\sigma_0}{|M^*|} e^{i(\phi - \delta)} = -\frac{\sigma_0}{|M^*|} e^{i(\phi - \delta + \delta)} ,
\]

(4.52)

where \( \tan \delta = \nu''/\nu' \). Hence, \( \delta \) represents the phase angle between the strain in direction of the applied stress and the accompanying cross-contraction. Accordingly, if \( \delta \) is negative, the material first expands in response to the applied stress before it contracts perpendicular to it. The delay is very short, on the order of \( 10^{-13} \) s, is comparable to the oscillatory period of atomic vibrations near the Brillouin zone edge of the acoustic branch or of a lower-frequency optical mode. Such a lag is what one might intuitively expect, but it is not a given. Indeed, at low temperatures \( \delta \) is positive, which means that the structure first cross-contracts before it yields in the direction of the applied stress. The observation of a positive imaginary Poisson ratio, in conjunction with the predominance of the bulk viscosity in the same temperature range, allowed us to infer a possible mechanism for the disintegration of the borate network upon heating above \( T_g \). It is generally believed that B\(_2\)O\(_3\) glasses contain high concentrations of boroxol rings, whereas at high temperatures these rings disappear. Given the above evidence from Brillouin scattering, we surmise that for the network to significantly expand, thermal motion first must cause adjacent boroxol rings to collide, exchange two bonds, and by joining two six-membered rings into a 12-membered ring, raise the compliance of the network. For this mechanism to be active, momentum is exchanged during the collision of rings, which requires local compaction and manifests as bulk viscous dissipation. Similarly, the bond exchange requires proximity of structural constituents before expansion, hence the positive imaginary component of the Poisson ratio.

The use of Brillouin scattering for relaxational spectroscopy and the identification of relaxation mechanisms is demonstrated using the data shown in Figure 4.15. Here we compare the complex mechanical moduli, that is, their real and imaginary components, for two glass-forming systems as a function of temperature. The two systems differ by the nature and concentration of modifier cations, but more importantly, by the type of network former, B\(_2\)O\(_3\) in one and TeO\(_2\) in the other system. Indeed, the observations highlighted here are common to borates and tellurites with a wide variety of compositions, respectively. The fundamental revelation from the data in Figure 4.15 is that the glass transition delineates the changeover between two thermodynamically distinct forms of matter, as opposed to merely an exponential slowing of relaxation processes so that below \( T_g \) the structure appears rigid on laboratory time scales. If the latter were the case, the quantities \( M' \) and \( M'' \) in Eq. 4.43 would relate to each other via Kramers–Krönig transformation [5,8,51,65], and \( M_0 \) would be a constant, that is, the materials fundamental constitution and structure would not change when crossing from slow to fast relaxation regimes. An easy way to tell whether Kramers–Krönig transformation applies is when the maximum magnitude of the loss modulus amounts to half the difference between the high and low frequency, or low and high temperature limits of the storage modulus. As can be
seen from Figure 4.15, this is not nearly the case. In previous sections, we have ascertained that the magnitude of the storage and loss moduli determined using Brillouin scattering agree well with those measured by other means. Hence, to describe the behavior observed in Figure 4.15, we must account for the fundamental structural and thermodynamic changes that occur upon glass transition of these materials.

Figure 4.15 Storage and loss moduli of (a) 38Na$_2$O·62B$_2$O$_3$ and (b) 20K$_2$O·80TeO$_2$ as a function of temperature. Symbols represent the data measured using Brillouin scattering and the lines represent best fits of Eq. 4.54. Note that the borate system exhibits two relaxation mechanisms, whereas the tellurite system has only one. The areas shaded in color represent the energy stored and dissipated in respective mechanisms. Underlying to the storage modulus is the change in static modulus due to structural changes associated with the glass transition.

One way to do this is to modulate the static modulus $M_0$ by a temperature-dependent factor $\phi(T)$, where

$$\phi(T) = \frac{n_R}{n_R + n_V} = \frac{1}{1 + e^{-\Delta H(T_c-T)/k_B T c}}. \tag{4.53}$$

Equations 4.53 describes a simple two-state model, in which one state represents a rigid glass (subscript R) and the other state a visco-elastic fluid (subscript V). The quantities $n_R$ and $n_V$ represent the number of moles of the substance in these respective states, $\Delta H$ the enthalpy difference between these states, and $T_c$ the temperature at which the free energies of the two
states are equal. Modifying Eq. 4.30 accordingly, and allowing for multiple relaxation mechanisms labeled by \( j \), yields

\[
M^*(\omega) = M_0\phi(T) + M_2(1 - \phi(T))\sum_j \frac{\omega^2 \tau_j^2 + i\omega \tau_j}{1 + \omega^2 \tau_j^2}.
\]

This model has been successful in that it is applicable to a wide variety of glass-forming systems, including silicates, germanates, borates, phosphates, and tellurites [5,35,45,52,54]. The data in Figure 4.15 are fitted using Eq. 4.54, which illustrates the quality of this approach. All borate systems require assumption of at least two distinct mechanisms to describe structural relaxation during the glass transition, whereas tellurites never require more than one. In the storage modulus data for tellurites we also typically observe a first kink at \( T_g \) and a second kink when the network degradation is completed, but the resulting liquid is still too viscous to relax on the time scale of Brillouin scattering. Seemingly, the network degradation mechanism for tellurites is frictionless, whereas that for borates incurs viscous dissipation. For additional details, the reader may refer to References [5, 52].

### 4.5.3 Spatially Confined Systems (e.g., Thin Films)

Because Brillouin scattering requires such a small scattering volume, it is highly suitable for the characterization of specimens with small dimensions in one or more directions. Indeed, Brillouin scattering has been extensively used to study the elastic properties of thin films [66–74] and even single isolated silica spheres of sub-micron dimensions [66, 75]. In this latter experiment, light scattered from a sphere as small as 260 nm was measured. The spectral analysis of this light does not yield the conventional Brillouin spectrum, resulting from the acoustic plane waves propagating in a direction that satisfies Bragg's condition (see Figure 4.1). Instead, this spectrum has many more peaks, which correspond to the frequencies of the harmonic modes of deformation of the nano-sphere [66].

Light scattered from free standing films as thin as 29 nm has produced Brillouin spectra [69, 76, 77]. For such thin films, scattering occurs from film-guided acoustic phonons, known as Lamb modes. These modes are dispersive, and their group velocity varies with \( qh \), where \( q \) is the wavevector of the guided mode, and \( h \) is the film thickness. For thin films, when \( qh \leq 1 \), only two modes prevail, one with predominantly transverse and the other with predominantly longitudinal molecular displacements. In the limit of \( qh \to 0 \), the velocity of the transverse mode tends to zero and that of the longitudinal mode to a constant value. As detailed in the previous section, the temperature dependence of the sound velocity or, equivalently, elastic modulus, serves as a way to determine the glass transition temperature, \( T_g \). The effect of spatial confinement of a material on its \( T_g \) is of interest for elucidating the nature of the glass transition phenomenon. Specifically, in polymeric glass-forming systems, structural relaxation near the glass transition is facilitated by the segmental motion of the polymer chains, and when the overall specimen dimensions reach a characteristic length of the polymer, such as its average end-to-end distance, chain dynamics is affected by the proximity of constraining or free
surfaces.

In this context, polystyrene has been investigated by several groups [69, 72, 76–79], and in each case, Brillouin light scattering was the method of choice for determining $T_g$. For high molecular weight polystyrene these researchers found that with decreasing film thickness $T_g$ remains constant until the thickness reaches the average end-to-end distance of the polymer. Subsequently, it decreases linearly by up to 70°C. Accordingly, the threshold at which $T_g$ begins to decrease is molecular weight dependent. Below a certain molecular weight, this molecular weight dependence subsides and the $T_g$ versus film thickness data of all systems, which still show the same decrease, overlap. The authors explain their observations by a superposition of two mechanisms: for high molecular weight polymer, as soon as essentially every polymer chain in the specimen is exposed to a free surface, their mobility is enhanced, and consequently, $T_g$ drops. In addition, the fact that for low-molecular weight polymer the onset of the $T_g$ drop becomes independent of the chain length suggests that the glass transition is governed by an inherent length scale beyond the characteristic size of a structural building block, perhaps cooperative motion among these units.

Another unique opportunity afforded by Brillouin scattering is for determining the elastic modulus in the direction perpendicular to the film plane, that is, across the film thickness. In Section 4.3 we already described the scattering geometries that allow one to measure the elastic modulus in the plane of a film and perpendicular to it, which can reveal elastic anisotropies in materials that form under high aspect ratio growth conditions. Recall that the phonon wavelengths probed using visible light, for example, 532 nm green light, are of the order of 200 nm. It therefore takes a minimum film thickness of about 0.5 to 1 μm for phonons that travel perpendicular to the film plane to develop and to establish an adequate Bragg grating. However, if the film is thin enough and transparent, we can configure the scattering geometry shown in Figure 4.6c. The scenario shown is that of a film deposited onto a reflective substrate, and the external light path corresponds to the conventional backscattering geometry. The focal point of the focusing and collimating lens is perhaps half way in between the film's free surface and the interface with the substrate. Backscattered light from this region is collected by the collimating lens and guided to the interferometer. At the same time, the incident beam continues to the substrate surface, where it is reflected and eventually exits the film through its free surface. In effect, the reflected beam acts like a second light source that enters from the bottom of the sample. Because of the small film thickness, the reflected light is not defocused much yet when it passes near the volume of most intense backscattering. Any light scattered from the reflected beam in this region is then also collected by the collimating lens. However, as shown by the wavevector balance in this figure, the light reflected by the substrate probes phonons that travel in the plane of the film.

Hence, this scattering geometry produces two longitudinal peaks: one probing the in-plane elastic response of the thin film, and the other the elastic response nearly perpendicular to the film, or nearly the film growth direction. The slight offset from truly perpendicular has the advantage that it does not likely probe standing acoustic waves across the film thickness, for which spectra would be more difficult to interpret. An example of the results from such a
The in- and out-of-plane elastic moduli, $c_{11}$ and $c_{33}$, respectively, of a layer-by-layer deposited thin film composed of chitosan (chit), poly(sodium styrenesulfonate) (PSS), and cellulose nano-fibers (cellN) are plotted versus the cellN volume fraction. The layers are deposited in the sequence $[(\text{chit/cellN})_x/\text{(chit/PSS})_y]$, and the chit volume fraction is controlled by varying the number of layers $x$ and $y$. Throughout the composition range, $c_{11}$ is higher than $c_{33}$, which reflects the reinforcing role of the stiff cellulose nanofibers. The out-of-plane elastic modulus is strongly affected by the ability of interfacial bonding to transmit normal forces. Indeed, at high cellN concentration the contact between polymer and fibers starts to become spotty, allowing for large-amplitude fiber bending in the film normal direction, and the out-of-plane modulus decreases again. The lines shown in the graph are best fits to the data using a modified rule of mixing model described in Reference [80].

**Figure 4.16** Longitudinal elastic moduli of layer-by-layer deposited polymer-cellulose nanofiber thin-film composite, as a function of the cellulose fiber volume fraction. $c_{11}$ refers to the in-plane and $c_{33}$ to the out-of-plane modulus.
4.5.4 Systems Under Pressure

The visco-elastic behavior of materials under high pressure is of great interest both in geological sciences and materials engineering. Again, the small sample volumes required and the ability to probe materials properties without mechanical contact to the sample, has led to the development of diamond anvil technology for the investigation of mechanical response of systems under high pressure. A schematic of a diamond anvil cell is shown in Figure 4.17. It consists of two diamonds with their tips flattened. By orienting the faces so created toward each other, they provide the top and bottom enclosure for the sample. Lateral confinement is achieved with a gasket, typically a ductile metal, a fraction of a millimeter thick and with a central aperture of about 250 μm, placed in between the flattened diamond tips. The sample is placed inside the aperture, along with a pressure-transducing fluid to fill void space and provide for hydrostatic pressure conditions. Pressure is then applied by pushing the diamonds toward each other, upon which the gasket deforms and seals the cavity. The pressure inside the cavity can be determined, for example, by placing minuscule ruby crystals alongside the sample. Ruby fluoresces at a wavelength that possesses a well-characterized pressure dependence, and the sample pressure can be inferred by comparing the ruby fluorescence wavelength with a calibration curve.
Given the strength and hardness of diamond, pressure of up to 200 GPa can be reached with such a setup. Beyond 15–20 GPa, most pressure-transducing media are densified to the extent that they transmit shear forces, and it is no longer guaranteed that the pressure state the sample is subject to is purely hydrostatic. On the other hand, because of their relatively open structure and the lack of periodicity, most glasses are sufficiently ductile to not require a pressure-transducing medium at all. Upon squeezing the diamonds onto the gasket and sample cavity, the glass deforms plastically until the entire cavity is filled. Despite the non-trivial shape of cut diamonds, by maintaining the two anvil faces parallel to each other, one can easily establish the platelet scattering geometry of Figure 4.5a, and thus eliminate the need to determine the refractive index of the sample. This is an important experimental simplification, as the refractive index typically depends quite strongly on the materials density.

To date, the behavior of glasses under pressure has been relatively little explored, possibly because of the constrained experimental conditions. The combination of the small sample volume required for diamond anvil cells, and the non-contact probing mechanism of inelastic
light scattering provides relatively convenient access to the mechanical properties of materials under high pressure. Of particular interest in this context is that as-quenched melt-processed glasses exhibit an open and loose molecular packing, and that a more compact packing can be achieved upon compression [25, 26, 29, 81]. The high density structures are stable under ambient conditions, but revert to the low density packing upon heating the glass above the glass transition temperature. Detailed inquiries into this behavior, starting with the seminal work by Grimsditch et al. [24, 82], have given rise to the concept of polyamorphism, that is, the existence of more than one structurally and thermodynamically distinct non-crystalline state of a given material [24, 55, 56, 81, 82].

Evidence for polyamorphism manifests in various materials properties, such as density, mechanical moduli, refractive index, etc. One example of this is illustrated in Figure 4.18. Vitreous boron oxide has been subjected to compression-pressure release cycles, in which the maximum pressure was varied. As shown in Figure 4.18, the sound velocity of B$_2$O$_3$ glass changes with the applied pressure. Upon compression it increases monotonously, and upon releasing the pressure it decreases again, albeit at a lower rate. However, irrespective of the maximum imposed pressure, the pressure dependence of the sound velocity exhibits a marked discontinuity at about 3 GPa, which is the signature of a second-order phase transition in crystalline materials. Subsequent molecular dynamics simulations have shed light on this observation, by predicting the existence of a previously unknown low density crystalline phase of B$_2$O$_3$, as well as by revealing the occurrence of similar structural motives in compressed and expanded vitreous B$_2$O$_3$ [55, 56, 81]. Nevertheless, it is remarkable that the transition between these high and low density structural states in the glass is continuous upon compression and discontinuous upon decompression, and that cycling through these transitions is reversible and repeatable.
Figure 4.18 Longitudinal sound velocity of B$_2$O$_3$ glass as a function of pressure, measured using Brillouin scattering. Filled symbols represent data upon compression and open symbols upon decompression. Data for different maximum pressures are shown. While the change in sound velocity is continuous upon compression, all decompression data exhibit a discontinuity at around 3 GPa, regardless of the maximum pressure reached during the compression-decompression cycle.

4.5.5 Mechanically Fragile Systems, Soft Matter, and Gels

The contact-free non-invasive nature of Brillouin scattering allows one to study structural developments in situ, while a materials system is undergoing thermo-chemical changes. Because the light scattering probe does not actuate the system, it does not interfere with its instantaneous thermodynamic equilibrium or natural path toward equilibrium. While this investigatory tactic can be applied to a wide variety of scenarios, ranging from displacive phase transformations to rheology in supercooled liquids, we limit our discussion here to two illustrative examples.
In Figure 4.19 we show the real and imaginary component of the complex mechanical modulus of silica gels, measured using Brillouin scattering, as a function of the silica volume fraction for two different preparation pathways, that is, with and without an aging step before drying the gel. Measurements began after gelation or aging treatment, respectively. The change in the volume fraction of SiO$_2$ results from the evaporation of the pore fluid. The critical points, that is, when the meniscus between pore fluid and ambient atmosphere begins to recede inwards from the gel’s periphery, are marked by arrows. The critical point represents the instant when the meniscus that establishes the pressure gradient causing the fluid to flow from the pore interior to the surface has the strongest curvature, and the gel is most likely to crack.

**Figure 4.19** Longitudinal storage and loss moduli of two silica hydrogels, one aged and not the other before they were dried, as a function of the silica volume fraction.

Aging of gels is used as a strategy to preventing gels from cracking, and the general perception is that aging strengthens the gel backbone by allowing the backbone structure to coarsen. Comparing the storage moduli of the two gels at their respective critical points, they have about the same magnitude—that of the aged gel is in fact a bit lower. On the other hand, the
loss modulus of the aged gel is significantly lower than that of the non-aged gel. The loss modulus in these gels reflects the energy dissipated by aperiodic motion of molecular species in the network, and it includes the viscous interaction between pore fluid and backbone. Accordingly, it is not the stiffness of the network backbone that controls whether the gel can sustain the lateral forces exerted by the network, but the reduced frictional forces due to the smoothing of the internal pore walls during aging simply require less of a pressure gradient to maintain the balance between fluid flow and evaporation rate.

Besides Brillouin scattering there are few experimental techniques, if any, that allow one to measure the complex mechanical modulus of fragile materials systems with such ease and provide the insights described above. Perhaps the most notable aspect of this study is that we were able to assess the amount viscous dissipation inside the pore structure of a gel. Indeed, when extrapolating the loss modulus data to zero silica content, and after dividing by the Brillouin shift frequency, we obtain the viscosity coefficient of the solvent used to prepare the gels.
Figure 4.20 Longitudinal, shear, Young's, and bulk moduli, as well as the Poisson ratio of an epoxy system as a function of time while it was curing, measured using in situ Brillouin scattering.

The final example, the in situ investigation of the epoxy cure, illustrates several important aspects of using Brillouin scattering for studying the nature of amorphous materials. First, given that epoxy is a thermoset polymer, the crossover from a liquid to a glass in this system is controlled by chemical reactions rather than by the withdrawal of thermal energy. The reader may therefore want to compare the general behavior observed in Figure 4.20 with that in Figs. 4.12 and 4.13. Second, the mechanical behavior of epoxy allows us to clearly distinguish between adiabatic and isothermal elastic moduli. Figure 4.20 shows the longitudinal, shear, Young's, and bulk moduli of an epoxy system as a function of time, measured using Brillouin scattering while it undergoes curing reactions. The graph also shows the Poisson ratio, calculated using Eq. 4.50. The epoxy system consists of DGEBA resin (Epon 862) and amine hardener (Epikure 9553), mixed at a 1:1 stoichiometry. From the start, the mixture exhibits a finite longitudinal modulus, which rapidly increases with time, reflecting the progressive polymerization and cross-linking in the network structure. For the first 40 min. of cure, the
longitudinal modulus is identical to the bulk modulus. This follows from Eq. 4.44 and the fact that during this period, no shear peak is apparent, that is, the material does support shear deformations and can be considered a liquid. At around 40 minute cure, a shear peak suddenly appears in the Brillouin spectra. The shear elastic modulus and Young's modulus rise abruptly at a degree of cure that can be considered as the chemical glass transition. Concurrently, bulk and longitudinal moduli decouple, and the Poisson ratio drops from 0.5, the value for a liquid, to about 0.41. From here on, all elastic moduli increase at a decelerating rate to plateau at their final values, corresponding to an ultimate degree of cure of about 85% in this system, while the Poisson ratio decreases in a similar fashion.

The plateau value for the Young's modulus measured by Brillouin scattering is about 5.0 GPa, while that obtained under steady state loading (e.g., tensile tester, nano-indenter) is 3.8 GPa. This difference is the result of probing the modulus at zero Hz versus GHz-frequencies, the former yielding the isothermal and the latter the adiabatic elastic modulus. The isothermal modulus is that of a fully relaxed structure, which upon compliance to the imposed stress may have released some of the elastic energy into heat and dissipated to the environment. Conversely, the adiabatic modulus is that of a structure in which all imparted strain energy is still stored as elastic energy and fully available by giving rise to a restoring force. In inorganic glasses, the difference between isothermal and adiabatic moduli is generally negligible, because the structure of such glasses has little capacity for relaxation at ambient temperatures. The situation is different for organic glasses, whose \( T_g \) is often only a few tens of degrees above room temperature. Even in a system such as epoxy, which is a relatively stiff elastomer, the difference between adiabatic and isothermal moduli can be quite large (about 30% in this case). Ultimately, whether one measures the adiabatic or isothermal modulus is a matter of the probing frequency, and the difference between the two, in the terminology of visco-elastic theory, is coined the relaxational modulus. In the spirit of the time–temperature superposition principle, the glass transition is sometimes modeled using Debye relaxation formalisms and attributed to the changeover between the isothermal modulus (prevailing in the liquid state) and the adiabatic modulus (characteristic of the solid state). This, however, is not advisable, since time–temperature superposition strictly applies to a material in a given physical state, probed at different effective frequencies, while the glass transition may indeed involve the changeover between two thermodynamically distinct states of matter [50, 51, 65].

4.6 SUMMARY

Brillouin light scattering is a technique based on the interactions between light and thermal phonons in materials. The spectrum of scattered light contains information about the rates of propagation and attenuation of the phonons, from which one can derive the complex mechanical modulus of the material. The real component of this modulus accounts for the amount of energy stored elastically per unit volume in the material. Longitudinal and shear elastic moduli can be obtained. The imaginary component of the complex modulus measures the amount of energy per unit volume dissipated by aperiodic motions of the molecular constituents of the material. In visco-elastic media, this loss modulus can be related to its high
frequency zero-shear rate viscosity coefficient. Brillouin scattering allows one to measure mechanical properties materials without mechanical contact. The technique is non-destructive, and for all practical purposes, non-invasive. The minute amounts of energy exchanged between photons and phonons when causing vibronic excitations, do not disturb the thermodynamic equilibrium of the materials system. Furthermore, the visco-elastic properties are measured by probing molecular displacements in specific directions inside the material, and the measurement only requires very small amounts of matter. Based on these characteristics, the technique is ideally suited to measure visco-elastic properties of small specimens or material in confined spaces, materials under delicate thermodynamic conditions, such as supercooled liquids, fragile gels, or systems undergoing chemical reactions, as well as materials that are chemically aggressive, that are at high temperatures or high pressures.

REFERENCES

5

NEUTRON DIFFRACTION TECHNIQUES FOR STRUCTURAL STUDIES OF GLASSES

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5.1 INTRODUCTION

Neutron diffraction (ND) is an important experimental technique for the investigation of the structure of glasses. It can be used to study oxide glasses, chalcogenide glasses, metallic glasses, amorphous semiconductors, molecular glasses, amorphous polymers, organic glasses, and so on. An ND experiment yields a measurement of the distribution of interatomic distances that can be more accurate than for any other experimental method. The shortest distances in the glass (the short range order, SRO) can be characterized in terms of coordination numbers, bond lengths, and other short distances. These can be measured very accurately by ND, and used to determine the coordination polyhedra that form the basis of the glass structure. The way in which these units connect together (the intermediate range order, IRO) is also probed by ND, although in a more subtle way, and its investigation usually requires some kind of modeling of the ND results. The results of an ND experiment can be predicted exactly for a structural model, and hence ND provides a rigorous test of structural models.

The main aim of this chapter is to provide empirical information to enable a new researcher, such as a research student, to plan and perform an ND investigation of the structure of glass samples, to analyze the experimental data, and to begin to interpret the results. A brief outline is given of the theory of ND for glasses; particular emphasis is given to subjects such as incoherent scattering, which new researchers tend to find especially troubling. The study of glass structure by ND is best not considered in isolation, but instead in the wider context of both the study of other types of material, and the use of other techniques to study glass structure. Therefore, whilst the main emphasis of this chapter is very much on ND from glasses, this is set in the wider context of liquid and crystalline materials when relevant; the experimental approaches described here can also be of use in the study of these other types of material. It is also worth mentioning that there are other neutron scattering techniques of use in the study of glass, such as inelastic scattering and quasi-elastic scattering, which are beyond the scope of this chapter.

5.2 INSTRUMENTATION

5.2.1 The Neutron
The neutron was discovered relatively recently by Chadwick in 1932, for which he received the Nobel Prize for physics in 1935. Soon after that, Fermi received the Nobel Prize in physics for studies of the interactions between neutrons and matter, but it was many years before the Nobel Prize in physics was belatedly awarded to Brockhouse and Schull for the development of neutron scattering techniques for studies of condensed matter. It is useful to consider the properties of the neutron, as given in Table 5.1, because they lead to some important advantages and limitations for the use of ND.

**Table 5.1** Properties of the neutron.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass</td>
<td>$m_n = 1.00866491600$ amu</td>
</tr>
<tr>
<td>Mean free lifetime</td>
<td>881.5 s</td>
</tr>
<tr>
<td>Charge</td>
<td>zero</td>
</tr>
<tr>
<td>Spin</td>
<td>$\frac{1}{2}$</td>
</tr>
<tr>
<td>Magnetic dipole moment</td>
<td>$\mu_n = -1.91304272 \mu_N$</td>
</tr>
</tbody>
</table>

Bound neutrons in a stable nucleus are stable, but free neutrons undergo $\beta$-decay with a mean lifetime of approximately 15 minutes. Thus a nuclear reaction of some sort is required to produce a beam of neutrons for a diffraction experiment. In practice the number of neutrons produced by a radioactive source is insufficient for a useful diffraction experiment, and the only two methods currently capable of producing enough neutrons are either nuclear fission in a nuclear reactor, or the interaction of an accelerated particle beam with a target. Accelerators and reactors are large, expensive facilities, and hence their availability is limited; the total number of neutron sources in the world is probably less than 30. The use of a diffractometer at most neutron sources may be requested by submission of an experimental proposal, and further information about the application procedure should be sought on the internet.

### 5.2.2 The Interactions between a Neutron and a Sample

As implied by its name, the neutron is neutral. The lack of a charge means that a neutron does not interact with the electric field in a sample, and this is part of the reason why the interaction between a neutron and a sample is relatively weak. The main interaction between a neutron and a sample is the nuclear force between the neutron and the nuclei of the sample, and this interaction occurs for all samples. The neutron has spin $\frac{1}{2}$ and a non-zero magnetic dipole moment, and consequently there is a magnetic interaction between a neutron and the unpaired electrons in the atoms in a sample. Therefore, for samples containing magnetic ions, there is a magnetic interaction between a neutron and the sample, in addition to the nuclear interaction. A detailed consideration of magnetic diffraction is beyond the scope of this chapter, but Section 5.4.7.1 indicates how paramagnetic self scattering can be taken into account.

The interaction between a neutron beam and a sample (via nuclear forces and the magnetic interaction) is relatively weak, compared to the interaction between an X-ray beam and a sample (via the electromagnetic interaction), and hence ND is an intensity-limited technique.
Thus it is always important to ensure that an ND experiment yields results with sufficiently
good statistical accuracy; this is achieved by using relatively large samples (the volume of a
typical ND sample is of order 1 to 2 cm$^3$), and the longest possible counting time.
Nevertheless, the relatively weak interaction for neutrons is highly advantageous because the
experimental corrections (for absorption, multiple scattering, etc.) can often be performed
much more reliably for ND, leading to more accurate results.

It is useful to consider the simple case of a neutron beam with wavevector $\mathbf{k}$, parallel to the $z$-
axis (see Figure 5.1), which is incident on a single fixed nucleus. In this case the incident
wavefunction can be represented as

$$\psi_{\text{inc}} = \exp(ikz). \quad (5.1)$$

If the neutron wavelength is of the order 1 Å, then this is larger than the size of a nucleus by a
factor $ca. 10^5$. Therefore the waves scattered by different parts of the nucleus will all be in
phase, with the result that the total scattered wave is spherically symmetric. In this case the
scattered wavefunction at the point $\mathbf{r}$ is

$$\psi_{\text{sc}} = -\frac{b}{r} \exp(ikr) \quad (5.2)$$

where $b$ is a constant, known as the scattering length of the nucleus. The scattering length
determines the amplitude of the wave scattered by the nucleus, and it is defined so that a
positive value corresponds to a phase change of $\pi$ between the incident and scattered waves. It
is very important to note that the scattered wave is spherically symmetric, so that $b$ is not a
function of scattering angle; instead $b$ is a simple constant. Thus, nuclear neutron scattering
does not involve a form factor (unlike X-ray diffraction, or magnetic ND), with the result that
reliable information can be measured up to high momentum transfer, leading to high resolution
in real space and accurate bond lengths.
The neutron mass is similar to the mass of a proton \((m_n/m_p \approx 1.0014)\), and thus inelastic scattering processes (where the neutron exchanges energy with the sample) are of great importance, especially for samples containing hydrogen (i.e., protons which are not bound in a larger nucleus). A neutron with energy \(E\) has a de Broglie wavelength, \(\lambda\), given by the non-relativistic expression

\[
E = \frac{\hbar^2}{2m_n\lambda^2}
\]  

(or \(E = 81.787/\lambda^2\) in convenient units of meV and Å, respectively), and thus the neutron exhibits wavelike behavior including diffraction. Diffraction effects are most clearly observed if the wavelength is similar to the distances between the scattering centers. For example, the silicon–oxygen bond length in SiO\(_2\) glass is 1.61 Å, and a neutron with this wavelength has an energy ca. 31 meV. Thus neutrons with a wavelength suitable for a diffraction experiment also have an energy which is similar in magnitude to the vibrational energies in solids (e.g., the largest vibrational energy in SiO\(_2\) glass is ca. 170 meV). Consequently, inelastic scattering phenomena are of great importance, and inelastic neutron scattering experiments can provide an important fundamental probe of the structure of glasses.

5.2.3 Neutron Sources
5.2.3.1 Reactor Sources

Neutron beams for ND first became available in the 1940s, with the advent of nuclear reactors in which neutrons are produced by the fission of $^{235}$U nuclei. The cross-section for neutron-induced fission of $^{235}$U is high only for slow neutrons with energies in the meV range, whereas the fast neutrons produced by fission have much higher energies in the MeV range. Hence, in order to sustain the fission process, a reactor includes a component, known as a moderator, which slows down the neutrons. The neutrons undergo inelastic collisions (see Section 5.2.2) with the nuclei in the moderator, so that they are in thermal equilibrium at the temperature of the moderator. The moderator normally contains large numbers of low mass nuclei (usually H or D), because the energy transferred in the inelastic collisions is maximized when the mass of the colliding nucleus is as close as possible to the neutron mass. The peak flux within the moderator is at a neutron speed $v_p$ given by

$$E = \frac{1}{2} m_n v_p^2 = k_B T,$$

where $T$ is the temperature of the moderator. For example, a temperature of 290 K corresponds to a neutron energy $E$ of 25 meV, a neutron wavelength $\lambda$ of 1.8 Å, or a neutron speed $v$ of 2200 m/s. It is thus fortuitous that the process of moderation produces neutrons which, as well as being slowed down for maintaining the fission reaction, also have a wavelength suitable for performing ND experiments.

A neutron diffractometer uses a beam of neutrons that is obtained by viewing a moderator through a beam-tube or neutron guide which passes through the shielding around the neutron source. Note that in practice the moderator used as a source of neutrons for ND experiments at a reactor may be separate from the moderator used to slow the neutrons in order to maintain the fission reaction. Figure 5.2 shows the neutron flux for three different moderators at the world's pre-eminent reactor source of neutrons, the Institut Laue-Langevin (ILL) in Grenoble, France. Reactor neutron sources produce a high flux of thermal neutrons ($E \sim 25$ meV, $T \sim 290$ K) and cold neutrons ($E \sim 1$ meV, $T \sim 12$ K), but they have little flux at higher epithermal energies ($E \sim 1$ eV, $T \sim 12000$ K). This is a consequence of the fact that a reactor can only produce neutrons which are in thermal equilibrium with a moderator, and there are practical limitations on the maximum temperature of the moderator.
The neutron flux produced by a normal nuclear reactor is unchanging with time and covers a wide range of neutron wavelengths. In order to perform an ND experiment it is thus necessary to monochromate the neutron beam from a reactor so that it covers a narrow range of neutron wavelengths, and the vast majority of the flux from the source is lost at this stage.

5.2.3.2 Accelerator Sources

Since the 1960s, ND experiments have increasingly come to be performed using sources of neutrons that are based on a particle accelerator. A beam of charged particles is accelerated to a high energy and then fired at a target. Interactions between the particle beam and the nuclei in the target produce high energy neutrons that are then slowed down by a moderator.

The earlier accelerator-based neutron sources used an electron linear accelerator to accelerate an electron beam to relativistic energies (~50 MeV), which was then fired at a dense target made of a heavy element, usually uranium, and neutrons were produced by a two-stage
process. Firstly, the electrons were slowed down extremely rapidly due to the strong interaction with the electromagnetic field of the target nuclei, producing a cascade of bremsstrahlung photons. Secondly, some of these photons went on to produce neutrons by photo-neutron reactions, where the photon excites a target nucleus that subsequently decays with the emission of a neutron. Approximately 20 electrons must be accelerated for each neutron produced.

More recent accelerator-based neutron sources use a linear accelerator, sometimes in combination with a synchrotron, to accelerate a beam of protons to a high energy (~800 MeV). The proton beam is fired at a heavy metal target (made for example of tantalum, tungsten, uranium, or mercury), and neutrons are produced by the spallation process. Spallation is a violent interaction between the proton and the target nucleus that results primarily in the emission of neutrons, but also a variety of light nuclear fragments. In effect, the protons chip pieces off the target nuclei, and each proton produces about 15 neutrons for a non-fissile target (or about 25 neutrons for a fissile target).

Accelerator-based sources are usually pulsed\(^1\) (typically with a pulse repetition rate of order 50 Hz), and so they produce a pulsed neutron flux that is ideally suited to the time-of-flight ND technique. This technique involves measuring the time-of-flight (T-O-F), \(t\), for a neutron to travel the total flight path, \(L\), from the moderator to the detector, via the sample. On the assumption of elastic scattering (i.e., initial and final neutron energies are the same, \(E_i = E_f\)) then

\[
    t = \frac{m_n}{\hbar} L \lambda,  \tag{5.5}
\]

(or \(t = 252.82 L \lambda\) in convenient units of \(\mu s\), meters, and Ångstroms, respectively), and it is straightforward to determine the neutron wavelength. The use of the T-O-F technique removes the need to monochromate the neutron beam and thus, even though the raw flux produced initially by an accelerator-based source is much less than that produced by a reactor source, the final flux available for ND is of a comparable order of magnitude (see Figure 5.2).

The moderator at an accelerator-based neutron source is used to slow the neutrons down so that they have suitable wavelengths for ND, in the same way as for a reactor neutron source. However, in order that the moderation process does not broaden the pulsed time structure of the neutron flux too much, the moderator must be relatively small. (Also note that, unlike a reactor, the process of moderation plays no role in the production of neutrons at an accelerator-based source.) This has the consequence that the neutrons produced by an accelerator-based source are under-moderated and there are many more epithermal neutrons (i.e., neutrons with energy greater than thermal neutrons, see Figure 5.2) than for a reactor source. Figure 5.2 also shows the neutron flux for a moderator at the ISIS spallation neutron source at the Rutherford Appleton Laboratory, UK. The epithermal neutrons at a pulsed neutron source allow diffraction patterns to be measured up to high momentum transfers, and it is this which enables high resolution in real space to be achieved (see Section 5.4.2.2).
5.2.4 Neutron Diffractometers

5.2.4.1 Neutron Diffractometers—General Principles

The purpose of a total neutron diffractometer is to measure the differential cross-section

$$I_N(Q) = \left(\frac{d\sigma}{d\Omega}\right)_{tot} = \frac{R_{tot}}{N\Phi d\Omega}, \quad (5.6)$$

where $R_{tot}$ is the rate at which neutrons of wavelength $\lambda$ are scattered into the solid angle $d\Omega$ in the direction $(2\theta, \phi)$ (see Figure 5.1), irrespective of whether or not they are scattered elastically (i.e., total neutron scattering). $N$ is the number of atoms in the sample and $\Phi$ is the flux of neutrons of wavelength $\lambda$ that is incident on the sample.

In general the differential cross-section depends upon the scattering vector

$$Q = k_i - k_f, \quad (5.7)$$

where $k_i$ and $k_f$ are the neutron wavevector before and after scattering. The term momentum transfer (i.e., the momentum transferred to the sample) is commonly used for $Q$, although strictly speaking this term should be used for $\hbar Q$. Diffraction data are treated by considering the scattering to be totally elastic so that the magnitudes of the initial and final neutron wavevectors are the same,

$$|k_i| = |k_f|. \quad (5.8)$$

Most glass samples are isotropic (i.e., their properties are the same in all directions), and for an isotropic sample it is only the magnitude of the momentum transfer that is significant, in which case the differential cross-section is a function of a single variable

$$Q = |Q| = \frac{4\pi \sin \theta}{\lambda}. \quad (5.9)$$

For ND experiments on polycrystalline powders it is usually more convenient to treat the differential cross-section as a function of d-spacing, $d$ ($= 2\pi/Q$), defined according to Bragg's law by

$$2d \sin \theta = \lambda. \quad (5.10)$$

Bragg peaks are then observed in the differential cross-section whenever the d-spacing satisfies

$$d = d_{hk\ell}, \quad (5.11)$$

where $d_{hk\ell}$ is a d-spacing between atomic planes (with Miller indices $(hk\ell)$) in the crystal for which the structure factor is non-zero.

To produce high quality data, a neutron diffractometer must satisfy several requirements: (i)
The data must have a good statistical accuracy, which is obtained by having a high count rate. This is achieved by such factors as an intense source, a large total detector solid angle, and a sufficiently large sample. (ii) The corrections that are made to the data must be as small as achievable. In particular the background must be small, featureless and unchanging. (iii) The range in $Q$ must be as wide as possible, in order to provide high resolution in real space. (iv) The reciprocal-space resolution must be as narrow as possible.

Due to its lack of charge, a neutron cannot be detected by directly producing an electrical current in a detector. Instead a more indirect method of detection is used, involving a nuclear reaction that releases energy, which is then turned into an electrical signal, such as the absorption of a neutron by a $^3$He nucleus

$$\frac{3}{2}{\text{He}} + ^0\text{n} \rightarrow ^3\text{H} + ^1\text{p} + 0.770 \text{MeV}. \quad (5.12)$$

Neutrons are usually detected using single particle counting.

### 5.2.4.2 Reactor Source Diffractometers

A schematic of the layout of a typical neutron diffractometer at a continuous (reactor) source is illustrated in Figure 5.3. The neutron beam coming from the moderator at a conventional reactor covers a wide range of wavelengths and is unchanging with time. Therefore a single crystal monochromator is used to produce a monochromatic beam. The general principle of operation of a neutron diffractometer at a steady state source is the same as for a conventional laboratory X-ray diffractometer, since both have a well-defined incident wavelength. The differential cross-section is measured as a function of $Q$ by moving the detector to different scattering angles, $2\theta$, and measuring the scattered count rate. That is to say, $Q$ (or $d$) is scanned by varying $2\theta$ whilst keeping the neutron wavelength $\lambda$ constant (c.f. Eq. 5.9).

![Schematic of a neutron diffractometer for a continuous source.](image)
Figure 5.4 shows the D4c diffractometer [1] at the ILL reactor which, for many years, has been the most successful reactor-based diffractometer for studying the structure of liquids and amorphous materials. The diffractometer uses neutrons from a hot graphite moderator at a temperature of 2400 K, because this produces neutrons with short wavelengths and hence a high maximum $Q$ can be achieved, leading to good real-space resolution. A copper monochromator is used to produce neutrons with a wavelength of 0.7 Å, 0.5 Å or 0.35 Å, depending on which copper reflection is selected. Most of the neutron flight path is evacuated in order to minimize background due to the scattering of neutrons by air. There are nine one-dimensional position sensitive detectors, each of which is a micro-strip detector with 64 elements. The large number of detectors is used to provide a large detector solid angle and hence a high count rate. The detectors can cover a range in scattering angle, $2\theta$, from 1.5° to 140°, and with a wavelength of 0.5Å the $Q$-range of D4c extends from 0.3 to 24 Å$^{-1}$. (A higher maximum $Q$ may be attained with a wavelength of 0.35 Å, but the flux available at this wavelength is an order of magnitude lower and is too low for regular use.)

Figure 5.4 The D4c liquids and amorphous diffractometer at the Institut Laue Langevin [1].

5.2.4.3 Pulsed Source Diffractometers

A schematic of the layout of a typical T-O-F neutron diffractometer at a pulsed source is illustrated in Figure 5.5. The T-O-F technique (see Eq. 5.5) is used to determine the wavelength of the detected neutrons and hence a monochromator is not needed. The differential
cross-section is measured as a function of $Q$ with the detector at a fixed scattering angle, $2\theta$, and $Q$ (or $d$) is scanned by varying the neutron wavelength $\lambda$ (c.f. Eq. 5.9). The T-O-F technique is thus a dispersive technique and a white beam covering a wide range of wavelengths is incident on the sample. For diffraction from a crystalline powder, pulsed source data have the simplifying property that T-O-F is proportional to d-spacing:

$$t = \frac{2m_\mu Ld \sin \theta}{h}, \quad (5.13)$$

(or $t = 505.64Ld\sin\theta$ in convenient units of $\mu$s, meters, and Ångstroms, respectively). A noteworthy advantage of the ability to measure a full diffraction pattern at a single fixed scattering angle is that complex sample environment equipment can be used (e.g., for high pressures) with two well-collimated flight paths for the incident and scattered beams so that background from the equipment is minimized.

**Figure 5.5** Schematic of a time-of-flight neutron diffractometer for a pulsed source.

**Figure 5.6** shows the GEneral Materials diffractometer, GEM [2], at the ISIS spallation neutron source, which is arguably the best neutron diffractometer in the world for high real-space resolution studies of glass structure. The neutron beam comes from a liquid methane moderator at a temperature of 110 K. A cooled moderator is used in order to reduce the correction for inelasticity effects. The length of the incident flight path, $L_i$, is 17.0 m, leading to a high resolution in reciprocal space. In practice a T-O-F diffractometer has several different detector banks at different scattering angles, $2\theta$, in order to extend the $Q$-range of the data, and GEM has detector banks at eight different scattering angles. The detectors are ZnS scintillators with narrow 5 mm active elements so as to minimize the angular contribution to the reciprocal-space resolution, and the best resolution ($\Delta Q/Q \sim 0.35\%$) is obtained from the backward angle detectors. The detectors cover a very large solid angle (area~10 m$^2$, maximum azimuthal angle~45$^\circ$) so as to achieve a high effective count rate. A nimonic $t_0$ chopper at a distance 9.3 m from the moderator is used to close off the beam at $t = 0$, and thus prevent very fast neutrons
and prompt gamma rays from reaching the sample. This prevents high energy neutrons from thermalizing in large pieces of sample environment equipment (e.g., high pressure equipment) and then giving rise to a substantial background. In addition, two disc choppers are used at flight paths of 6.5 m and 9.5 m to define a restricted wavelength range for the beam reaching the sample. This is done so as to avoid frame overlap, which can be a significant problem for a diffractometer with a longer flight path. Frame overlap occurs when slower neutrons from a pulse of the source are overtaken by faster neutrons from the subsequent pulse. If the flux of the slower neutrons is significant, then a diffraction peak which in reality is detected at the long T-O-F \( t \), appears to be detected at the earlier time \( t - \tau_0 \) (where \( \tau_0 \) is the period of the source), and this leads to spurious peaks in the data. The sample tank contains an oscillating radial collimator, made of \(^{10}\text{B}\)-coated mylar vanes, which collimates the secondary flight path from sample to detector, thus reducing background, especially from bulk sample environment such as high pressure equipment. However, for most simple glass structure studies, the oscillating collimator is removed because it imposes a rapidly changing profile on the scattered neutrons, which may be problematic for the experimental corrections.

**Figure 5.6** The GEneral Materials diffractometer, GEM, at the ISIS Facility [2].
5.3 THEORETICAL ASPECTS OF NEUTRON DIFFRACTION ON GLASSES

5.3.1 The Static Approximation

The outline of ND in this chapter is given within the static approximation, in which the atoms in a sample are fixed, so that their positions do not change and they do not exchange energy with a neutron beam. For a more rigorous theoretical derivation of results, including the effects of inelastic scattering, the reader should consult other more fundamental texts [3–7].

5.3.2 Scattering from a Single Nucleus

For the single fixed nucleus considered above in Section 5.2.2, the cross-section can be evaluated using Eq. 5.6. The incident neutron flux is $\Phi = |\psi_{\text{incl}}|^2 = 1$ (see Eq. 5.1), whilst the rate at which neutrons are scattered into the area $dS$ is $R_{\text{tot}} = |\psi_{\text{sc}}|^2 dS = b^2 d\Omega$ (see Figure 5.1 and Eq. 5.2). The differential cross-section for the single fixed nucleus is then

$$I^N(Q) = \left( \frac{d\sigma}{d\Omega} \right)_{\text{tot}} = b^2. \quad (5.14)$$

Integrating this expression over all possible directions for the scattered neutron gives the total cross-section for the nucleus as $\sigma = 4\pi b^2$, and the transmission of a thickness $x$ of identical non-interacting atoms with number density $\rho^0$ is given by the Beer–Lambert law,

$$T = \frac{I(x)}{I_0} = \exp(-\rho^0 x \sigma). \quad (5.15)$$

Usually scattering lengths are given in units of fm (i.e., $10^{-15}$ m), but cross-sections are given in units of barns ($10^{-28}$ m). This can lead to an error by a factor of 100 if sufficient care is not taken when using tabulated scattering lengths to calculate a cross-section.

5.3.3 Scattering from an Assembly of Nuclei

Figure 5.7 shows the scattering geometry for a single atom, $j$, at position $R_j$ relative to an arbitrary origin O. For the wave scattered from the atom, there is a path length difference ($\Delta_i - \Delta_f$) relative to the origin. This is equivalent to a phase difference ($Q.R_j$) (using Eq. 5.7). For an assembly of $N$ nuclei, the scattered wavefunction involves a sum over the phase factors for all the nuclei,

$$\psi_{\text{sc}} = \sum_{j=1}^{N} -\frac{b_j}{r} \exp(iQ.R_j). \quad (5.16)$$

The differential cross-section is then given by
Thus the scattered intensity depends on a sum over all the interatomic vectors, \( \langle R_j - R_k \rangle \), in the sample.

\[
I^N(Q) = \frac{r^2}{N} |\psi_{sc}|^2 = \frac{1}{N} \sum_{j=1}^{N} \sum_{k=1}^{N} b_j b_k \exp(iQ.(R_j - R_k)).
\]

(5.17)

Figure 5.7 The scattering geometry for a single atom, \( j \), at a position \( R_j \) relative to an arbitrary origin \( O \). For the wave scattered from the atom, there is a path length difference \( \Delta_i - \Delta_f = R_j(\hat{k}_i - \hat{k}_f) \) relative to the origin.

### 5.3.4 Isotropic Samples

Glasses and crystalline samples are usually isotropic, in which case the scattered intensity depends on the magnitude of the momentum transfer, \( Q = |Q| \), but not on the direction of \( Q \). In this case, averaging Eq. 5.17 over all directions of \( Q \) leads to the Debye equation,

\[
I^N(Q) = \frac{1}{N} \sum_{j=1}^{N} \sum_{k=1}^{N} b_j b_k \frac{\sin(QR_{jk})}{QR_{jk}},
\]

(5.18)

where \( R_{jk} \) is the magnitude of the interatomic vector, \( \langle R_j - R_k \rangle \), that is, \( R_{jk} \) is the distance between atoms \( j \) and \( k \).

### 5.3.5 Coherent and Incoherent (Distinct and Self) Scattering

A significant difference between ND and XRD (X-ray diffraction) concerns the incoherent scattering from the sample. For XRD, the scattering power (i.e., the form factor) of all atoms of the same element may be regarded as identical. However, for ND, the scattering length \( b_j \) (i.e., the amplitude of the neutron wave scattered by a nucleus) is not the same for all nuclei of a particular element due to two factors, isotopic incoherence and spin incoherence. Isotopic incoherence arises as a result of the presence of more than one isotope of a particular element.
Spin incoherence is due to the fact that a neutron and a nucleus of spin $I$ can form two different compound nuclei of spin $I \pm 1/2$; the amplitude of the neutron wave scattered by the nucleus, and thus the scattering length, is generally different for the two different compound nuclei. For a consideration of coherent and incoherent scattering it is convenient to write Eq. 5.18 in the form

$$I^N (Q) = \sum_{j=1}^{N} \sum_{k=1}^{N} b_j b_k \langle j, k \rangle, \quad (5.19)$$

The value of $b_j$ is not the same for all the nuclei of a single element, due to isotopic and spin incoherence, and hence to obtain a useful result Eq. 5.19 is averaged over all possible distributions of scattering length for atoms of the same element, making the assumption that there is no correlation between the values of $b_j$ for any two nuclei. Now the average value of $b_j b_k$ differs, depending whether or not $j = k$ is satisfied.

$$\bar{b}_j b_k = (\bar{b})^2, \quad \text{if } j \neq k \quad (5.20)$$

$$\bar{b}_j b_k = \bar{b}^2, \quad \text{if } j = k$$

where $\bar{b}$ is the average scattering length (also called the coherent scattering length) for all nuclei of a particular element, whilst $\bar{b}^2$ is the average of the squared scattering length for the relevant element. (In Eq. 5.20, it is assumed that $j$ and $k$ can refer to two nuclei of the same element.) The double summation of Eq. 5.19 may thus be separated into $j \neq k$ (distinct) terms and $j = k$ (self) terms;

$$I^N (Q) = i^N (Q) + I^S (Q), \quad (5.21)$$

where the self scattering is given by

$$I^S (Q) = \sum_{l} c_l \bar{b}_l^2 = \langle \bar{b}^2 \rangle_{av}, \quad (5.22)$$

in which $c_l = N_l/N$ is the atomic fraction for element $l$, and $\langle \bar{b}^2 \rangle_{av}$ is the average squared scattering length for the sample (i.e., a weighted average over all the elements in the sample). The average scattering cross-section per atom is thus $\sigma_{\text{scatt}} = 4\pi \langle \bar{b}^2 \rangle_{av}$. The distinct scattering is given by

$$i^N (Q) = \sum_{l,l'} \bar{b}_l \bar{b}_{l'} \sum_{j=1}^{N_l} \sum_{k=1}^{N_{l'}} \frac{1}{N} \frac{\sin(QR_{jk})}{QR_{jk}}, \quad (5.23)$$

where the $l$ and $l'$ summations are over the elements in the sample (e.g., for PbO-SiO$_2$, $l = \text{Pb}$,
Si, O). The \( j \) (or \( k \)) summations are then over all the \( N_l \) (or \( N_{l'} \)) atoms of element \( l \) (or \( l' \)), excluding terms where \( j \) and \( k \) refer to the same atom.

In Eq. 5.21 the differential cross-section, \( I^N(Q) \), is separated into two parts, the distinct and self scattering: the distinct scattering is an interference term which contains structural information about the interatomic distances in the sample, whilst the self scattering is essentially a background which does not contain structural information. In order to extract structural information about the sample it is necessary to perform a satisfactory subtraction of the self scattering from the measured diffraction data.

The separation into distinct and self terms arises naturally in diffraction theory, and is useful for the study of glass structure, and hence this is the formalism that is used in this chapter. However, there is an alternative formalism, in terms of coherent and incoherent scattering, which is also widely used. By the algebraic trick of adding and subtracting a \( \sum_i \tilde{b}_j^2 \langle j, j \rangle \) term to Eq. 5.19, the differential cross-section may be separated into its coherent and incoherent parts.

\[
I^N(Q) = \sum_{l,l'} \tilde{b}_j \tilde{b}_{j'} \sum_{j=1}^{N_l} \sum_{k=1}^{N_{l'}} \frac{1}{N} \frac{\sin(QR_{jk})}{QR_{jk}} + \left( \langle \tilde{b}^2 \rangle_{av} - \langle \tilde{b}^2 \rangle_{av} \right),
\]

in which self terms \( (j = k) \) are now included in the summation. The incoherent cross-section of the sample is

\[
\sigma_{inc} = 4\pi \left( \langle \tilde{b}^2 \rangle_{av} - \langle \tilde{b}^2 \rangle_{av} \right),
\]

in which \( \langle \tilde{b}^2 \rangle_{av} = \sum_l c_l \tilde{b}_l^2 \), and \( \sigma_{coh} = 4\pi \langle \tilde{b}^2 \rangle_{av} \) is the average coherent scattering cross-section for the sample. The interpretation of the coherent contribution to the differential cross-section is that this is what would be measured from a sample for which all nuclei of element \( l \) had a scattering length of \( \tilde{b}_l \). The coherent contribution to the differential cross-section contains the interference information relating to the positions of atoms in the sample. For most elements the incoherent cross-section is relatively small, but a notable exception to this is hydrogen for which the incoherent cross-section is very large, so that the measured experimental diffraction pattern is dominated by the incoherent contribution, and this can be a severe problem as is discussed in Section 5.4.6.2.

Figure 5.8 illustrates how the differential cross-section, \( I^N(Q) \), can be separated into either distinct and self contributions, or coherent and incoherent contributions. Experimental data for liquid CCl\(_4\) are used for this illustration because this compound has a larger incoherent cross-section than most materials, due to the fact that chlorine has two isotopes with very different scattering lengths, and both isotopes have a significant abundance. The average level of \( I^N(Q) \) is given by the self scattering, and the distinct scattering, \( I^N(Q) \), oscillates about this average level; this is an important underlying principle for the treatment of experimental data.
Figure 5.8 The lower Q region of the corrected differential cross-section, $I^N(Q)$, for liquid CCl$_4$, showing how it can be separated into either self and distinct contributions, or into coherent and incoherent contributions.

As shown by Eq. 5.23, the distinct scattering contains information about the structure of the sample, in the form of the interatomic distances, weighted according to the coherent neutron scattering lengths of the atoms. The magnitude of the coherent scattering length of an element is determined by the strong interaction between the nucleus and the neutron, and hence it varies haphazardly across the periodic table, as shown in Figure 5.9. This behavior leads to certain advantages for ND, compared to XRD. For example, XRD is not good at distinguishing elements which are adjacent in the periodic table, because their X-ray scattering powers (i.e., their atomic numbers) are almost the same. Also, ND is much better than XRD for determining the position of oxygen atoms, since oxygen scatters weakly for XRD, but relatively strongly for ND.
Figure 5.9 The bound atom coherent neutron scattering length of the natural elements (and deuterium) as a function of atomic number [32]. Elements with a negative scattering length (and deuterium) are indicated by the element symbol.

5.3.6 Atomic Vibrations

5.3.6.1 The Effect of Inelasticity on the Self Scattering

An important stage in the analysis of ND data is to obtain the distinct scattering, $i^N(Q)$, by subtracting the self scattering from the measured differential cross-section (see Figure 5.10). It appears from Eq. 5.21 that this should be simple, since in the static approximation the self scattering is a constant, $I^S(Q) = \sum_l c_l \bar{b}_l^2$, independent of $Q$. However, this is not the case; in practice the effect of inelastic scattering of neutrons on $I^S(Q)$ must be taken into account.
Figure 5.10 Key stages in the analysis of (corrected and normalized) neutron diffraction data from a glass: subtraction of self scattering, Fourier transformation, addition of $T^0(r)$.

In the static approximation it is assumed that neutrons do not exchange energy with the sample, but actually a scattered neutron may have a non-zero energy transfer

$$E = E_i - E_f,$$  \hspace{1cm} (5.26)

where $E_i$ and $E_f$ are the neutron energy before and after scattering. A non-zero value of $E$ corresponds to inelastic scattering. The effect of inelastic scattering for diffraction was first considered by Placzek [8] (who showed that, fortunately, to first order, there is no inelasticity effect for the distinct scattering, $i^N(Q)$), and it is still widely known as “the Placzek correction”. The effect can be calculated within an approximation (first derived for a reactor diffractometer by Johnson et al. [5] and for a T-O-F diffractometer by Wright [9] and later by Howe et al. [10]), and a full treatment of this topic is beyond the scope of this chapter; the reader should consult more advanced texts for full details [11]. However, the salient points can be understood from the following equation;

$$F^S(Q) = \sum_i c_i E_i^2 (1 - P_i(Q, 2\theta, M_l, T, \varepsilon(E_f), \Phi(E_i))).$$ \hspace{1cm} (5.27)
The Placzek correction, $P_{\theta}$, depends on the scattering angle, $2\theta$, so that the self scattering becomes smaller at higher angles. The correction depends on the sample temperature, $T$, so that the effect is more severe for a hotter sample. The correction also depends on the masses of the atoms in the sample, so that the effect is more severe for lighter elements. Furthermore, the correction depends on the energy efficiency, $\epsilon(E)$, of the detector, on the energy distribution of the source, $\Phi(E)$, and on the $Q$-$E$ locus for neutrons detected with the same apparent momentum transfer. These last three factors all depend on the parameters of the diffractometer, and in particular the inelasticity effect has marked differences between reactor and T-O-F diffractometers. Figures 5.11 and 5.12 show the corrected differential cross-section, $I^N(Q)$, for B$_2$O$_3$ glass, as measured on the D4 [12] and GEM [13] diffractometers, respectively, together with the calculated self scattering, $I^S(Q)$. For a reactor diffractometer (Figure 5.11), the main effect is that the self scattering becomes smaller at higher angle (i.e., at higher $Q$). For a T-O-F diffractometer (Figure 5.12), the self scattering also becomes smaller at higher angle (i.e., the self scattering is smaller for detector banks at higher angle). However, for a T-O-F diffractometer the $Q$-dependence of the self scattering is different, with a very strong increase at the lowest $Q$, followed by a minimum at intermediate values of $Q$, arising from the energy distribution of the neutrons from the source, which is characteristic of the temperature of the moderator. For the analysis of T-O-F diffraction data, it is important to note that, because the Placzek correction (see Eq. 5.27) depends on scattering angle, $2\theta$, this correction must be made before data from different scattering angles are combined to form the final determination of the distinct scattering, $i^N(Q)$. 
Figure 5.11 The differential cross-section of B$_2$O$_3$ glass, $I^N(Q)$ (corrected and normalized), measured on the D4 diffractometer, together with the calculated self scattering [12].
Figure 5.12 (a) The calculated self scattering, $I^S(Q)$, for B$_2$O$_3$ glass on the GEM diffractometer. (b) The (corrected and normalized) differential cross-section of B$_2$O$_3$ glass, $I^N(Q)$, measured on the GEM diffractometer (continuous line), together with the calculated self scattering (dashed line) [13]. The curves for the different detector banks are shown with vertical offsets for clarity.

5.3.6.2 The Effect of Atomic Vibrations on Diffraction

The Debye equation in the form given above (Eq. 5.23) does not explicitly include the effect of atomic motions, but these may be included as follows:

$$I^N(Q) = \sum_{l,l''} I_{l,l''}^N(Q) = \sum_{l,l''} c_{l,l''} \tilde{b}_l \tilde{b}_{l''} (S_{l,l''}(Q) - 1),$$  \hspace{1cm} (5.28)
where \( R_{jk} \) is the mean distance between the pair of atoms \( j \) and \( k \), and \( u_{jk}^2 \) is the mean square variation in the distance between these two atoms. Thus the effect of atomic vibrations is to introduce the Debye–Waller factor, \( \exp(-2W_{jk}) \), which leads to a reduction (i.e., a damping) of the distinct scattering at higher \( Q \). In Eq. 5.28, the distinct scattering is separated into partial structure factors, \( S_{ll'}(Q) \), for each pair of elements, \( l \) and \( l' \), in the sample; these are often called Faber–Ziman partial structure factors [14]. Some workers also find it useful to define a total coherent structure factor, \( S^N(Q) \), for example by

\[
i^N(Q) = (S^N(Q) - 1) \langle \tilde{b}^2 \rangle_{av}.
\]

Figure 5.13 shows a simple application of Eqs. 5.28 to 30 to simulate the distinct scattering for SiO\(_2\) glass, by calculating the distinct scattering for an ideal SiO\(_4\) tetrahedron (using physically realistic thermal displacement factors \( \langle u_{\text{SiO}}^2 \rangle^{1/2} = 0.041 \text{ Å} \) and \( \langle u_{\text{OO}}^2 \rangle^{1/2} = 0.081 \text{ Å} \)). For this tetrahedron, there are only two interatomic distances, the bond length \( r_{\text{SiO}} = 1.614 \text{ Å} \), and the oxygen–oxygen distance, \( r_{\text{OO}} = \sqrt{8/3}r_{\text{SiO}} = 2.636 \text{ Å} \). There are thus two simple contributions to the simulation, \( i^N_{\text{SiO}}(Q) \) and \( i^N_{\text{OO}}(Q) \), both of which are damped sinc functions, as shown in the lower parts of Figure 5.13. The Si–O distance has a smaller variation, so that it damps less severely to high \( Q \), and hence it is possible to estimate the length of the Si–O bond from the period (\( \Delta Q \)) of oscillation of \( i^N(Q) \) at high \( Q \), according to \( r_{\text{SiO}} \approx 2\pi/\Delta Q \).
The distinct scattering, $i^N(Q)$, for SiO$_2$ glass (dashed line), together with a Debye equation simulation for an ideal SiO$_4$ tetrahedron with realistic thermal displacement factors (continuous line). The Si–O and O–O contributions to the simulation are shown (together with the experimental result shown again as a dashed line) with vertical offsets. The inset shows the corresponding correlation function, $T^N(r)$, for the simulation, and a SiO$_4$ tetrahedron.

The simulated function in Figure 5.13 gives a reasonably close description of the observed features in the distinct scattering, $i^N(Q)$. Thus the general shape of the distinct scattering for a glass is determined by the basic structural unit. For pairs of atoms which are further apart than those in the basic structural unit, the RMS (root mean square) variation in distance, $\langle u^2_{jk} \rangle^{1/2}$, is relatively large and hence their contribution is concentrated mainly at lower $Q$; this is why the simulation in Figure 5.13 is less satisfactory at lower $Q$.

The Debye equation method of simulating diffraction data can be very powerful, for example for predicting the scattering from extremely small particles (i.e., nanoparticles). However, it rapidly becomes hard to perform the calculation as the model gets bigger, because the number of interatomic distances involved is proportional to $N^2$.

The Debye–Waller factor defined according to Eq. 5.30 is not exactly the same as used in crystallography. In crystallographic analysis (which is essentially a description of the long range order) the Debye–Waller factor for a pair of atomic sites, $d$ and $d'$, is $\exp(-(W_d + W_{d'}))$, where $W_d = Q^2 \langle u^2_d \rangle / 2$ and $u^2_d$ is the mean square displacement of the atom from the site. Thus the crystallographic Debye–Waller factor treats the two sites as independent oscillators, and it is not related to the interatomic distance between two atoms. If two atoms are close
together, especially if they are bonded, their thermal motions are highly correlated, with the result that the value of $\langle u^2 \rangle^{1/2}$ is smaller for short distances $R_{jk}$ than would be predicted by the crystallographic Debye–Waller factor [15].

Although the Debye equation is able to give a reasonable description of the diffraction pattern (i.e., the distinct scattering), each atomic pair provides a contribution which extends over the full $Q$-range, and hence the Debye equation does not provide a useful means of separating the contributions arising from different pairs of atoms in the structure. In order to obtain specific information about the different interatomic distances in the glass, it is necessary to adopt a Fourier transform approach, so that a correlation function in real space can be studied.

5.3.7 Real-space Correlation Functions

So far, the diffraction from a glass has been considered in terms of the scattering in reciprocal space, but it is immensely powerful to consider how this may be related to information in real space by means of Fourier transformation.

The simplest correlation function to understand is the radial distribution function (RDF) of a monatomic system, $n(r)$. This may be defined so that $n(r)dr$ is the number of atoms inside a spherical shell with radii $r$ and $r + dr$, with an average atom at the center. Figure 5.14 gives a graphical representation of how such functions are related to the atomic structure. The total correlation function, $t(r)$, and pair correlation function, $g(r)$, of the monatomic system may then be defined according to

$$n(r) = rt(r),$$  \hspace{1cm} (5.32)

$$t(r) = 4\pi rg(r).$$  \hspace{1cm} (5.33)
Figure 5.14 The neutron correlation function, $T_N^N(r)$, for B$_2$O$_3$ glass [13], together with a fragment of a two-dimensional B$_2$O$_3$-like network, showing how the peaks in the correlation function arise from the interatomic distances.

Very few samples of interest are monatomic; it is important to consider samples containing more than one element, in which case the different scattering lengths of the elements must be taken into account, and this is done by means of partial correlation functions. The partial RDF, $n_{ll'}(r)$, is defined so that $n_{ll'}(r) dr$ is the number of atoms of type $l'$ in a spherical shell $(r, r+dr)$ with an average atom of type $l$ at the center, and there are corresponding partial functions, $t_{ll'}(r)$ and $g_{ll'}(r)$, which are defined in the same way as in Eqs. 5.32 and 5.33.

The total correlation function measured in an ND experiment, $T_N^N(r)$, is obtained by Fourier transformation of the distinct scattering,

$$T_N^N(r) = T_0^0 (r) + D_N^N (r) = T_0^0 (r) + \frac{2}{\pi} \int_0^\infty Q t_N^N (Q) M (Q) \sin (rQ) \, dQ ,$$

(5.34)
where $D^N(r)$ is the differential correlation function, $M(Q)$ is a modification function introduced to take account of the finite $Q$-range of the experimental data (see Section 5.4.2.2), and the average density contribution is defined by

$$T^0 (r) = 4\pi r g^0 \langle \tilde{b} \rangle^2_{av}, \quad (5.35)$$

where $g^0 = N/V$ is the macroscopic atom number density, and $\langle \tilde{b} \rangle_{av} = \sum I_i \tilde{b}_i$ is the average coherent neutron scattering length for the sample. $D^N(r)$ is the function which is obtained directly by Fourier transformation of the distinct scattering, and it arises from deviations of the scattering length density from the average.

The total neutron correlation function is related to the partial functions according to

$$T^N (r) = \sum_{l,l'} c_l \tilde{b}_l \tilde{b}_{l'} t_{ll'} (r). \quad (5.36)$$

It is of great importance to note that the $l - l'$ and $l' - l$ partial correlation functions are not independent, but are related according to

$$t_{ll'} (r) = t_{l'l} (r) \frac{c_l}{c_{l'}}. \quad (5.37)$$

A simple way to understand this point is to consider that the number of Si–O bonds in a silicate sample is equal to the number of O–Si bonds; hence the ratio of coordination numbers depends on the relative numbers of the two types of atom,

$$n_{OSi} = n_{SiO} \frac{c_{Si}}{c_{O}} \quad (5.38)$$

that is, the coordination numbers $n_{SiO}$ and $n_{OSi}$ are not independent.

Figure 5.15 shows a measurement for GeO$_2$ glass [16] of the various neutron correlation functions introduced above. The total neutron correlation function, $T^N (r)$, is the most widelyfavoured of these functions for use in studying glass; for example, its use has often been advocated by Wright [3]. The RDF was used extensively in the past, such as in the pioneering XRD work of Warren [17], but is not widely used now. It has the advantage of suppressing artefacts at low $r$, but also suppresses the nearest neighbor peak(s), and arguably these are the most important peaks in the measured correlation function. The pair correlation function, $g^N (r)$, is more commonly favoured in studies of liquid structure [18]. It does not suppress the nearest neighbor peak(s), but it does suppress the longer range peaks (which are not so significant in a liquid), and it amplifies artefacts at low $r$. The total correlation function, $T^N (r)$, is the function which arises directly from the Fourier transform in Eq. 5.34 without multiplication/division by a factor $r$, and it provides a reasonable compromise between suppressing or amplifying both the low $r$ artefacts and the longer range information.
Figure 5.15 Neutron correlation functions for GeO$_2$ glass [16]: (a) the total correlation function, $T^\text{N}(r)$; (b) the differential correlation function, $D^\text{N}(r)$; (c) the pair correlation function, $g^\text{N}(r)$; and (d) the radial distribution function $n^\text{N}(r)$. In each case the experimental result is shown as a continuous line, whilst the relevant average density term is shown as a dashed line.

Figure 5.14 shows graphically how the total correlation function is related to the atomic structure for a simple oxide glass. Usually the first peak arises from bond lengths in the basic structural unit (e.g., the B–O bond length in B$_2$O$_3$ glass), and this is followed by a peak which arises from the oxygen–oxygen distance in the basic structural unit (e.g., the O–O distance in BO$_3$ units in pure B$_2$O$_3$ glass). The total correlation function can be measured experimentally for any isotropic sample, and Figure 5.16 shows the distinct scattering and $T^\text{N}(r)$ for three samples, liquid, glass and crystal, which all have a tetrahedral structural unit. It is striking that the first two peaks, arising from the two distances within the tetrahedron, are similarly well defined in all three phases, that is, the basic structural units in glasses are neither less well defined than in crystals, nor more well defined than in liquids. The differences between the three different phases occur mainly at longer distance. For the liquid, there is only slight order beyond the structural unit. For the glass there is more order than the liquid in the medium range, whilst the crystal has much greater order at longer range. The experimental approach (i.e., correlation functions) described here was originally developed mostly for the study of glasses and liquids, but in recent years it has increasingly been applied to the study of crystalline
structures [19], in which case it is often called the PDF method [20] (see Section 5.4.10). The term PDF is an abbreviation for Pair Distribution Function, and this function is equivalent to the differential correlation function, $D^N(r)$, introduced above in Eq. 5.34.

**Figure 5.16** The distinct scattering, $i^N(Q)$ (left-hand side), and the neutron correlation function, $T^N(r)$ (right-hand side), for liquid carbon tetrachloride, GeO$_2$ glass, and GeO$_2$ in its quartz crystalline form [16].

A difficulty of this field, especially for newcomers, is that there is not a generally agreed convention for the exact definition of correlation function or scattering function; different workers may use the same notation for different functions, or different notation for the same function. A detailed discussion of this issue has been given by Keen [21], but here are some guidelines that may be of use in determining exactly what correlation function has been used in a publication:

- What is the long range trend of the correlation function? Is it proportional to $r^2$, $r$ or a constant (i.e., is the definition $n^N(r)$, $T^N(r)$ or $g^N(r)$)? If the correlation function is non-zero
at high $r$, then the dependence on $r$ should be apparent at high $r$ (as in Figure 5.15a, c and d). If the correlation function oscillates about zero (as in Figure 5.15b), then the dependence on $r$ should be apparent from the low $r$ region.

- Has the average density contribution been subtracted, to yield a correlation function which oscillates about zero? (e.g., in Figure 5.15b, $T^0(r)$ has been subtracted to yield the differential correlation function, $D^N(r)$).

- In this chapter, a consistent normalization to one atom is used (i.e., the equations involve a factor $1/N$, where $N$ is the total number of atoms in the sample). Another normalization (often used by Wright [3]) is in terms of a composition unit (for SiO$_2$ this involves three atoms, and hence the correlation function is three times larger). An alternative approach is to define the correlation functions so that they oscillate about one, and this is more popular in the study of liquid structure [18]. The pair correlation function, $g^N(r)$, consistent with the definitions above, oscillates about $g^0(\bar{b})^2$, but it oscillates about one if divided by this factor. For a monatomic sample, this normalization is attractive because then the pair correlation function indicates how the local density varies with distance from an average atom. However, for other samples, the situation is not so simple, due to the weighting of each partial contribution by the scattering lengths of a pair of atoms, and so this normalization is less attractive.

In a more complete theory of ND, the pair correlation function is shown to be the distinct van Hove correlation function [22], $g_{ll'}(r) = G^D_{ll'}(r,0)$, where

$$G^D_{ll'}(r, t) = \frac{1}{N_i} \sum_{j=1}^{N_i} \sum_{l'=1}^{N_{l'}} \int \left\langle \delta(r' - R_j(0))\delta(r' + r - R_k(t)) \right\rangle dr'.$$

(5.39)

$R_j(t)$ represents the position of atom $j$ at time $t$, and thus $G^D_{ll'}(r, t)$ represents the correlation between atoms of type $l$ at time zero with atoms of type $l'$ at later time $t$. Thus the exact interpretation of total diffraction is that it yields an instantaneous “snapshot” of the interatomic vectors.

The Fourier transformation of experimental data (Eq. 5.34) is in practice performed numerically by software, and for equally spaced data this can be done efficiently by use of Filon's quadrature [23]. Fast Fourier transform techniques can also be used for the purpose; at first sight these may appear unsuitable, due to the requirement for $2^n$ points, but this requirement can be met by padding with zeroes at high $Q$. For unequally spaced data numerical integration methods can be used. The numerical evaluation of the Fourier transform in Eq. 5.34 essentially involves a weighted sum over the measured intensity points, $y_i \pm e_i$, and Toby and Egami [24] have shown that the error on the Fourier transform can also be evaluated by a suitable summation of the intensity errors, $e_i$. To a reasonable approximation, their result can be simplified for equally spaced data to give the error on $D(r)$ as
where $\Delta Q$ is the spacing between the intensity points. It is also possible to derive the correlation function using inverse methods [25]. This involves having a trial real-space correlation function, comparing its Fourier transform with the experimental data in $Q$ space, and adjusting the real-space correlation function so that the agreement in $Q$ space is optimized. An advantage of inverse methods is that the effect of $Q$-resolution can readily be incorporated. On the other hand, it is not clear how to evaluate the errors on a correlation function produced in this way. More importantly, for inverse methods, the mathematical description of the real-space resolution function is not clear, which is a disadvantage for peak-fitting methods of peak deconvolution (see Section 5.4.3), and for differentiating between small genuine peaks and artifacts (such as termination ripples, see Section 5.4.2.2).

5.4 THE APPLICATION OF NEUTRON DIFFRACTION TO STUDIES OF GLASS STRUCTURE

5.4.1 Experimental Corrections

ND has the advantage that the scattering length, $\bar{b}$, is a constant which is independent of $Q$ (unlike X-ray or electron diffraction, which involve a $Q$-dependent form factor), with the result that the diffraction pattern can be measured reliably to very high $Q$, with a reliable normalization between the low and high $Q$ regions. Furthermore, because the interaction between the neutron and matter is relatively weak, experimental corrections can often be performed relatively reliably. As a consequence of these advantages, highly reliable results may be obtained, leading to trustworthy determinations of coordination numbers, distributions of bond lengths, etc.

The Fourier transformation of the experimental data required to obtain the correlation function (see Eq. 5.34) involves integrations of the distinct scattering, $i^N(Q)$, over the full $Q$-range that has been measured. For this to be reliable, it is essential that the different regions of $i^N(Q)$ are correctly weighted relative to each other, and for this to be achieved it is necessary to correct the data for all the various experimental effects that cause the data to have any kind of $Q$-dependent suppression/amplification. Furthermore, ND has the ability to produce results that are accurately normalized on an absolute scale, and this leads to an ability to provide accurate coordination numbers. However, for reliable absolute normalization to be achieved, it is necessary to perform a full set of experimental corrections on the data for the following effects [26]:

- **Detector dead-time.** After a detector chain has counted a neutron, it is unable to count another neutron for a period of time. Thus more intense regions of the signal are suppressed, and it is necessary to correct for this effect.
- **Subtraction of backgrounds.** It is necessary to subtract the contribution to the scattering...
that arises from general backgrounds, and from the sample container.

- **Absorption.** This is when a neutron is permanently absorbed by a nucleus.
- **Attenuation.** This is when the incident and scattered flux of neutrons are reduced due to further scattering events.
- **Multiple scattering.** When neutrons are scattered more than once, this is called multiple scattering. Multiply scattered neutrons are removed from the incident and scattered beams, as considered by the theory described above, but they are still detected, and hence they lead to a further ‘background’ signal which must be subtracted.

In principle, these effects (apart from multiple scattering) are relatively simple to understand and account for. For example, the effects of absorption and attenuation can be calculated by means of a generalization of Eq. 5.15, involving an integration over all possible neutron paths through the sample. However, in practice the various absorption and scattering events are all interrelated [27]; for example, the multiple scattering from the sample may be absorbed by the container, the single scattering from the container may be multiply scattered by the sample, etc. Therefore the evaluation of a full set of corrections is a complex and convoluted process, and sophisticated software is required. Perhaps the most complete and reliable software currently available for this process is Soper's GudrunN program [28], which is available on the internet [29].

Although it is possible to correct the experimental data for all of the effects outlined above, it is best to use an experimental setup in which they are made as small as possible. A useful rule of thumb for diffraction is that the sample should not scatter more than 5% of the incident beam. Most samples are available in the form of a powder or coarse grains, in which case it is essential to use a sample container, and this should be designed so that the container scattering is minimized. Sometimes it is possible to make a glass sample in the form of a cylindrical rod, in which case a container is not required, and this is the ideal experimental setup.

As is apparent from Figure 5.9, vanadium has a smaller coherent neutron scattering length than any other element. Thus the scattering from vanadium is almost entirely incoherent (see Eqs.5.24 and 5.25), with the consequence that the Bragg peaks observed from a sample of pure vanadium metal are extremely small. Thus vanadium plays a special role in neutron scattering; for example, vanadium is often used to make sample containers because of its very small Bragg peaks. Perhaps the best sample containers for ND on glasses are cylinders made of thin vanadium foil, say 25 or 40 μm in thickness, because this minimizes the container scattering which must be subtracted in the corrections process. Another special metal for neutron scattering is Ti$_{62}$Zr$_{38}$ alloy which has an average coherent neutron scattering length of zero, and hence is a null alloy with no Bragg peaks [30]. It is possible to make a null alloy in this way, firstly because the two elements concerned have coherent scattering lengths of opposite sign (as shown in Figure 5.9, a few elements, such as titanium, have negative scattering lengths), and secondly because the Ti-Zr system forms a substitutional solid solution. Ti$_{62}$Zr$_{38}$ alloy is useful for making sample containers for use with demanding sample environment equipment, such as is used for high pressure. However, it suffers from the disadvantages that it is not
available as a thin foil, and its diffraction pattern has diffuse scattering due to local order. Another important use of vanadium, due to its mostly incoherent scattering, is as a calibration standard, which can be expressed simply by the following equation:

\[
\text{Normalized sample spectrum} = \left( \frac{\text{sample} - \text{empty container background}}{\text{vanadium} - \text{background}} \right).
\]  \tag{5.41}

In an ND experiment on a glass it is normal to also measure the diffraction pattern of a vanadium standard (either a cylinder if the detectors cover a wide angular range, or a flat plate if the detectors are all at low scattering angles), so that this normalization can be performed. This provides correct inter-normalization of results from different detectors, allows the corrected differential cross-section to be normalized on an absolute scale (since the differential cross-section of vanadium can be calculated according to Eqs.5.24 and 5.25, using the known cross-section, \(\sigma_{\text{inc}}\), and since \(\bar{b}\) for vanadium is almost zero, see Figure 5.9), and for a pulsed source diffractometer allows the flux distribution, \(\Phi(\lambda)\), arising from the moderator to be normalized out. Figure 5.17 illustrates the effect of flux normalization for pulsed diffraction data, using data from the former LAD diffractometer. The vanadium T-O-F spectrum is closely related to the flux distribution \(\Phi(\lambda)\) arising from the moderator. The upturn in \(\Phi(\lambda)\) at low times is due to high energy epithermal neutrons whilst the broad peak at intermediate times is the peak of a Maxwellian distribution whose position depends on the moderator temperature (c.f. Eq. 5.4).
Figure 5.17 Time-of-flight spectra for (a) vanadium; (b) polycrystalline silicon; and (c) GeO$_2$ glass. Also shown are the normalized spectra for (d) polycrystalline silicon and (e) GeO$_2$ glass.

For values of $r$ less than the shortest interatomic distance in the glass, the total correlation function, $T^N(r)$, should ideally be equal to zero. However, as shown in Figures 5.10, 5.14, 5.15 and 5.16, real experimental results are not identically zero in this region. Firstly, there are Fourier ripples and experimental noise in this region. Secondly, an unphysical peak is often observed at a short distance in the range below 1 Å, which arises because of imperfections in the experimental corrections. Most corrections change relatively slowly in $Q$ space, compared to the genuine experimental information, and hence inadequacies in the corrections give rise to the unphysical peak at low $r$. As Wright has advocated [31], the behavior of the low $r$ region of an experimental correlation function can be used to indicate how well the experimental corrections have been performed. Nevertheless, there are inverse methods of obtaining the correlation function [25], which usually involve setting the correlation function to zero below a minimum distance, in which case it is not possible to determine the quality of the corrections
from the low \( r \) region.

For neutron energies in the thermal region (i.e., for \( T \) of order 300 K or lower in Eq. 5.4), many nuclei have an absorption cross-section known as a “1/\( v \) cross-section”, which means that it is proportional to the neutron wavelength; \( \sigma_{\text{abs}}(\lambda) = \lambda\sigma_0 \). For this reason, absorption cross-sections are conventionally quoted for a neutron speed of 2200 ms\(^{-1}\), and Table 5.2 gives the absorption cross-sections at this speed for the 10 most absorbing natural elements, together with a few other relevant elements. As a rule of thumb, if the average absorption cross-section for a sample is of order 1000 barns or greater, then absorption is too large for it to be feasible to measure a useful diffraction pattern. On the other hand, if the average absorption cross-section is of order 100 barns or less, it is possible to obtain a meaningful diffraction pattern which can be corrected successfully. For example, chlorine has a significant absorption cross-section, and thus the correlation function for liquid CCl\(_4\) shown in Figure 5.16 is relatively noisy at low \( r \), due to the significant correction for absorption. Boron is an important element in the glass field, but samples containing higher concentrations of natural boron are too absorbing for useful ND results to be obtained; for example, if a B\(_2\)O\(_3\) sample containing natural boron is used, it may not be possible to observe any scattered neutrons, due to the high absorption. However, the isotopes of boron are available at relatively low cost, and hence it is normal to make samples using highly enriched \(^{11}\)B (\( \sigma_{\text{abs}}(^{10}\text{B}) = 3835 \) barns, \( \sigma_{\text{abs}}(^{11}\text{B}) = 0.0055 \) barns [32]). Boron is also widely used as a shielding material in neutron diffractometers, usually in the form of boron carbide or boron nitride. Cadmium and gadolinium are also widely used for shielding, but they are of more limited benefit at a pulsed neutron source, because they are virtually transparent to higher energy neutrons.

### Table 5.2

Absorption cross-sections of natural elements for the 10 most absorbing elements and some other elements of interest [32].

<table>
<thead>
<tr>
<th>Element</th>
<th>B</th>
<th>Cd</th>
<th>In</th>
<th>Sm</th>
<th>Eu</th>
<th>Gd</th>
<th>Dy</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \sigma_{\text{abs}}(2200 \text{ ms}^{-1})/\text{barns} )</td>
<td>767</td>
<td>2520</td>
<td>193.8</td>
<td>5922</td>
<td>4530</td>
<td>49700</td>
<td>994</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Element</th>
<th>Ir</th>
<th>Hg</th>
<th>Pa</th>
<th>O</th>
<th>Si</th>
<th>Cl</th>
<th>Ge</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \sigma_{\text{abs}}(2200 \text{ ms}^{-1})/\text{barns} )</td>
<td>425</td>
<td>372.3</td>
<td>200.6</td>
<td>0.00019</td>
<td>0.171</td>
<td>33.5</td>
<td>2.2</td>
</tr>
</tbody>
</table>

### 5.4.2 Resolution

#### 5.4.2.1 Reciprocal-space Resolution

As shown in Figure 5.16, the features in the ND pattern of a glass are much broader than the Bragg peaks observed in the diffraction pattern of a crystalline powder. The glass diffraction features are thus much broader than the reciprocal-space resolution of a typical neutron diffractometer, and this can give the impression that the \( Q \)-resolution is not an important effect when studying glasses; this is not correct. Grimley et al. [33] have given the following simple consideration of the effect of \( Q \)-resolution, which has been confirmed by other more
sophisticated approaches [24, 25, 34, 35]. The measured diffraction pattern is a convolution of the ideal diffraction pattern (i.e., measured with perfect resolution) with the resolution function. According to the convolution theorem, the measured correlation function is then the product of the ideal correlation function with the Fourier transform of the resolution function. A simple description of the resolution function is a Gaussian centered at the origin, and hence in real space this corresponds to another Gaussian centered at the origin. In conclusion, this shows that the effect of Q-resolution is that the measured differential correlation function, \(D^N(r)\), becomes increasingly damped at higher \(r\). The coordination numbers determined from ND are normally slightly below the expected value (e.g., for SiO\(_2\) glass a value of 3.9 has been obtained by ND [5], and this is typical, whereas the expected value for this tetrahedral glass is four), and this can be ascribed to the damping of the peaks in the correlation function that arises from the Q-resolution. Nevertheless, for a modern diffractometer with high Q-resolution, coordination numbers closer to the ideal values tend to be measured, see Section 5.4.3.

### 5.4.2.2 Real-space Resolution

The Fourier transform in Eq. 5.34 requires that the distinct scattering, \(i^N(Q)\), is known to infinitely large values of \(Q\), but in practice it is only possible to measure experimental data up to some finite value, \(Q_{\text{max}}\). If the Fourier transform is calculated from the experimental data with a sharp cut-off at \(Q_{\text{max}}\), then the resultant correlation function has significant termination ripples, which can easily be mistaken for real features (e.g., see Figure 5.18c). Hence it is common [36] to multiply the distinct scattering by a modification function, \(M(Q)\), which is chosen so as to reduce the termination ripples, though at the expense of some loss of resolution in real space. The most commonly used modification function is the Lorch function [37], defined as follows:

\[
M_{\text{Lorch}}(Q) = \frac{\sin(\Delta r Q)}{\Delta r Q}
\]

\[
M_{\text{Lorch}}(Q) = 0 \quad Q > Q_{\text{max}}.
\]

The use of the Lorch function reduces the termination ripples to a very large extent. (Indeed with the high \(Q_{\text{max}}\) of pulsed ND, the effect of thermal motion is often to entirely remove the termination ripples from the correlation function). However, this gain is achieved at the expense of some loss of resolution, with a full width at half maximum (FWHM) \(\Delta r_{\text{Lorch}} = 5.437/Q_{\text{max}}\). If the Fourier transform is performed without a modification function (i.e., with a “step” modification function which equals unity for \(Q \leq Q_{\text{max}}\) and is zero for \(Q > Q_{\text{max}}\) ) this yields the best possible real-space resolution, with a FWHM \(\Delta r_{\text{step}} = 3.791/Q_{\text{max}}\), but at the expense of relatively large termination ripples on either side of a real peak in the correlation function, \(T^N(r)\). In earlier work, [38] a pseudo Debye-Waller factor, \(\exp ( - \alpha^2 Q^2)\) (see Eqs.5.29 and 5.30), with an arbitrary ‘thermal factor’ \(\alpha\), was used as a modification function, but this reduces the termination ripples less than with the use of the Lorch function.
Occasionally other modification functions have been proposed [39, 40], but currently the use of the Lorch function is pre-eminent [41].

Figure 5.18 Neutron diffraction results for 2CaO·Na₂O·3P₂O₅ glass [2, 42]. (a) The distinct scattering, \( i^N(Q) \), with the high Q region shown in an inset. (b) The step and Lorch modification functions [37] for \( Q_{\text{max}} = 55\text{Å}^{-1} \). (c) The total neutron correlation function, \( T^N(r) \), obtained using the two modification functions shown in part (b) with the first peak region shown in an inset.

The high energy neutrons which are available only for an accelerator source (see Section 5.2.3.2) make it possible to measure diffraction patterns to higher values of \( Q_{\text{max}} \) than is possible for a reactor source, so that a narrower real-space resolution width, \( \Delta r \), can be obtained. For example, Figure 5.18a shows the distinct scattering for 2CaO·Na₂O·3P₂O₅ glass [2, 42]; for phosphate glasses oscillations are often observable to very high momentum transfer [43], and for this glass they can be discerned up to \( Q_{\text{max}} = 55\text{Å}^{-1} \), as shown in the inset to the figure. Figure 5.18b shows the Lorch and step modification functions, evaluated for this value.
of $Q_{\text{max}}$, whilst Figure 5.18c shows the corresponding total correlation neutron functions, $T_N(r)$. The inset to Figure 5.18c shows the detail of the first peak region, for interatomic distances of order 1.5 Å, which are due to P–O bonds. For the step modification function there is a clear splitting into two peaks at 1.4800(6) Å and 1.5977(10) Å, due respectively to bonds to non-bridging and bridging oxygen. The step modification function gives the best possible resolution, but at the cost of significant termination ripples in the correlation function; on the other hand, the Lorch modification function [37] greatly reduces the termination ripples, but at the cost of an increase in the resolution width, so that the two types of P–O bond lead to an asymmetry in the first peak, rather than a clear splitting.

Figure 5.19 shows simulations of the total neutron correlation function for an ideal GeO$_4$ tetrahedron with bond length $r_{\text{GeO}} = 1.7369$ Å, using physically realistic values for the RMS variation in interatomic distance ($\langle u_{\text{GeO}}^2 \rangle^{1/2} = 0.0422$ Å and $\langle u_{\text{OO}}^2 \rangle^{1/2} = 0.1005$ Å). The two peaks are due to interatomic distances between Ge–O and O–O atom pairs. The simulations in Figures 5.19a and 5.19b were calculated using the Lorch modification function [37] and values of $Q_{\text{max}}$ that are typical of what can be achieved in an experiment at a good reactor source (24 Å$^{-1}$) and at an accelerator source (40 Å$^{-1}$), respectively. The effect of the value of $Q_{\text{max}}$ on the real-space resolution width is evident, but the figure also illustrates how the high values of $Q_{\text{max}}$ available at an accelerator source can virtually remove the termination ripples. This effect occurs if the resolution width, $\Delta r$, is not larger than the width which arises from the RMS variation in interatomic distance (which has a FWHM given by $\sqrt{8 \log e 2 \langle u_{jk}^2 \rangle^{1/2} \approx 2.355 \langle u_{jk}^2 \rangle^{1/2}}$, and often occurs using an accelerator source.
Figure 5.19 Simulation of the total neutron correlation function, $T^N(r)$ (as obtained using the Lorch modification function [37]), for an ideal GeO$_4$ tetrahedron, showing the effect of maximum momentum transfer, $Q_{\text{max}}$, on real-space resolution and termination ripples. (a) $Q_{\text{max}} = 24$ Å$^{-1}$, (b) $Q_{\text{max}} = 40$ Å$^{-1}$.

Pulsed ND at an accelerator source has played an important role in investigations of the bond lengths in phosphate glasses, because it is the only experimental technique which has proved able to resolve the difference in the lengths of the two types of P–O bond [43], due to the high values of $Q_{\text{max}}$ ($\sim 50 – 60$ Å$^{-1}$) which can be achieved. In pure P$_2$O$_5$ glass [44], 40% of the oxygen atoms bond to only one phosphorus atom, and they are described as terminal oxygens (TOs). As modifier oxide is added to P$_2$O$_5$, the number of oxygens which are truly terminal (i.e., bonded to only one cation) decreases, whilst the number of non-bridging oxygens (i.e., oxygens which are bonded to one phosphorus and also one or more modifier cations) increases. However, the ND data show that there is no clear distinction between the lengths of the P-TO and P-NBO bonds [43].
In view of the importance of real-space resolution, it is worthwhile to discuss the factors which determine the value of $Q_{\text{max}}$. For a reactor source, $Q_{\text{max}}$ is determined simply by the maximum achievable scattering angle, which is limited at $2\theta = 180^\circ$, and the wavelength, $\lambda$, which depends on the parameters of the monochromator and the temperature of the moderator. For an accelerator source, very high energy epithermal neutrons are often available, and in principle experimental data can be measured up to several hundred Å$^{-1}$. However, in practice the useful value of $Q_{\text{max}}$ depends on the rate at which the oscillations in the distinct scattering, $i^{N}(Q)$, diminish at high $Q$. The width, $\langle u_{jk}^2 \rangle^{1/2}$, of the first peak in the correlation function determines the Debye–Waller factor, $\exp(-Q^2 \langle u_{jk}^2 \rangle / 2)$, which governs the rate at which the amplitude of the oscillations in $i^{N}(Q)$ decrease at high $Q$ (see Eqs.5.29 and 5.30). Thus the information in the diffraction pattern diminishes rapidly at higher $Q$. Also the statistical accuracy of the ND pattern measured at an accelerator source becomes progressively worse as $Q$ increases (as is apparent in Figure 5.12, for example), and furthermore the $Q$-resolution width at high $Q$ is proportional to $Q$, so that the diffraction features are increasingly broadened as $Q$ increases. Therefore in practice the value of $Q_{\text{max}}$ is the point at which the amplitude of the oscillations in $i^{N}(Q)$ becomes small in comparison with the size of the error bars on the experimental data. For each sample, the width of the first peak in $T^{N}(r)$ is different, and hence the useful value of $Q_{\text{max}}$ depends on the sample. All of the factors discussed cause it to rapidly become harder to observe the oscillations in $i^{N}(Q)$ as $Q$ increases, and hence the prospect of measuring ND to significantly higher values of $Q_{\text{max}}$ than currently available is very challenging.

### 5.4.3 Peak Fitting and Integration

The previous section shows how ND can be very powerful for determining bond lengths in glasses, but it can also be very powerful for determining coordination numbers. The concept of coordination number is very important in structural studies of glasses. A simple definition is that the coordination number is the total number of neighbors of a central atom. When this concept is applied to glasses it must be recognized that usually it is only possible to determine the average coordination number (i.e., the coordination number averaged over all relevant central atoms) since different types of atomic site cannot necessarily be differentiated. Coordination numbers for a glass can be determined experimentally from the area under a peak in the correlation function. If a peak in $T^{N}(r)$ at a distance $r_{\text{ll'}}$, due to a pair of elements $l - l'$, has an area $A_{ll'}$, then the corresponding coordination number is given by

$$
N_{ll'} = \frac{r_{ll'} A_{ll'}}{(2 - \delta_{ll'}) c_l b_l b_{l'}}.
$$  \hspace{1cm} (5.43)

where $\delta_{ll'}$ is the Kronecker delta. To determine the coordination number from a peak in $T^{N}(r)$, it is necessary to identify the pair of elements, $l - l'$, which give rise to the peak, and to determine the area of the peak, $A_{ll'}$, which can be determined either by fitting or integration.
For a discussion of the area of a peak it is necessary to consider the factors which give rise to the broadening of the peak:

1. **Real-space resolution.** This has been discussed in the preceding section, and its effect can be calculated analytically.

2. **Thermal motion of the atoms.** The thermal motion of the atoms gives rise to a broadening of a peak in the correlation function which, in the harmonic approximation, can be described by a Gaussian. Even at very low temperature there is significant thermal broadening due to zero-point motion.

3. **Static disorder.** If there is structural disorder in the interatomic distances then this also gives rise to a broadening of a peak in the correlation function. For example, the two P–O distances in a phosphate glass (e.g., see Figure 5.18c) give rise to a broadening of the first peak in the correlation function. If a peak in the correlation function is asymmetric, then this is definite evidence of static disorder. However, generally speaking, it is not possible to distinguish static disorder from thermal disorder, in which case the RMS variation in interatomic distance has contributions from both effects.

The contribution to the partial correlation function $t_{ll'}(r)$ due to a single interatomic distance $r_{jk}$ with RMS variation in distance $\langle u_{jk}^2 \rangle^{1/2}$ is

$$
t_{jk}(r) = \frac{n_{jk}}{r_{jk} \left( 2\pi \langle u_{jk}^2 \rangle \right)^{1/2}} \exp \left\{ -\frac{(r - r_{jk})^2}{2 \langle u_{jk}^2 \rangle} \right\},
$$

where $n_{jk}$ is the coordination number, that is, the average number of $k$ type atoms around a $j$ type atom. In reciprocal space, this corresponds to

$$
i_{jk}(Q) = n_{jk} \tilde{b}_j \tilde{b}_k \frac{\sin(Qr_{jk})}{Qr_{jk}} \exp \left\{ -\frac{\langle u_{jk}^2 \rangle Q^2}{2} \right\}.
$$

It is simpler computationally to take the effect of real-space resolution into account by using Eq. 5.45 to calculate the reciprocal-space function, and then to Fourier transform to real space, using the same modification function and value of $Q_{\text{max}}$ as for the experimental data. This procedure gives the function which is then fitted to the experimental correlation function.

Figure 5.20a shows the results of fitting a single peak to the neutron correlation function of GeO$_2$ glass (determined using the Lorch modification function with $Q_{\text{max}} = 40$ Å$^{-1}$) [16], and the corresponding parameters are given in Table 5.3. A very close fit to the peak is obtained, as is apparent from the oscillations in the residual, which are of similar magnitude to the oscillations in the experimental data on either side of the peak. There is no apparent asymmetry.
in the observed peak, and probably the static disorder in the Ge–O bond lengths is very small. The fitting method is well suited to determining the area under such a peak, because it allows the (positive and negative) contributions from the termination ripples to be taken into account correctly. The coordination number of the fit (see Table 5.3) is within 1% of the ideal value of four for this tetrahedral glass, and a major reason for the high accuracy of this result is the high Q-resolution of the modern diffractometer that was used (see Section 5.4.2.1).

**Table 5.3** Parameters from fitting the total neutron correlation function, $T_N^N(r)$.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$Q_{max} / \text{Å}^{-1}$</th>
<th>Atom pair, $l - l'$</th>
<th>$r_{ll'} / \text{Å}$</th>
<th>$\langle u_{ll'}^2 \rangle^{1/2} / \text{Å}$</th>
<th>$n_{ll'}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>GeO$_2$</td>
<td>40</td>
<td>Ge-O</td>
<td>1.737(2)</td>
<td>0.0422(3)</td>
<td>4.032(8)</td>
</tr>
<tr>
<td>2CaO·Na$_2$O·3P$_2$O$_5$</td>
<td>55</td>
<td>P-NBO</td>
<td>1.4800(6)</td>
<td>0.0362(5)</td>
<td>1.87(3)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>P-BO</td>
<td>1.5977(10)</td>
<td>0.0490(9)</td>
<td>1.96(4)</td>
</tr>
</tbody>
</table>
Figure 5.20 The first peak region of the total neutron correlation function, $T_N(r)$, for (a) GeO$_2$ glass [16] (thick grey line is experiment, thin black line is fit, dashed line is residual); (b) 18Cs$_2$O-88GeO$_2$ glass [16]; and (c) 2CaO·Na$_2$O·3P$_2$O$_5$ glass (thick grey line is experiment, thin line is fit, dashed line is fitted P-NBO component, dotted line is fitted P-BO component, dot-dashed line is residual (offset)) [2, 42].

Figure 5.20c shows the results of fitting the sum of two peaks to the neutron correlation function of 2CaO·Na$_2$O·3P$_2$O$_5$ glass (determined using the step modification function with $Q_{\text{max}} = 55$ Å$^{-1}$) [2, 42], and the corresponding parameters are given in Table 5.3. In this case, it is expected that the structure of a phosphate glass involves two discrete, different bond lengths (P-NBO and P-BO), and clearly fitting is well suited to determining them accurately. The software which has been used to produce the correlation function fits shown in this chapter (and which can also fit X-ray correlation functions) is available on the internet [45].

On the other hand, Figure 5.20b shows the neutron correlation function of a binary germanate glass containing 18 mol% Cs$_2$O (determined using the Lorch modification function with $Q_{\text{max}} =$
The position of the peak maximum is shifted to slightly longer distance, compared to pure GeO$_2$ glass, but the more marked effect is the appearance of a significant shoulder on the right hand side of the peak. This peak asymmetry is definite evidence of a distribution of Ge–O bond lengths in this glass. It is generally accepted that the addition of modifier to GeO$_2$ results in the average Ge–O coordination number increasing above four, and then decreasing back towards four when larger amounts of modifier are added, and ND has provided the main proof for this effect [16, 46, 47]. However, it is not yet fully established whether the higher coordinated germanium atoms are six-coordinated or five-coordinated (or both). Nevertheless, in either case the higher coordination is likely to involve more than one bond length; for example, it is well known that octahedral coordination usually involves two different bond lengths (axial and equatorial) due to the Jahn–Teller effect. If several different bond lengths (or a distribution of bond lengths) are expected within the envelope of a single correlation function peak, then it is debatable whether the fitting approach is the best way to characterize the peak. The advantages of fitting are that the contributions to the peak area from the termination ripples are included, and that it provides a reasonable way of taking into account the overlap with an adjacent peak (such as the O–O peak which is centered at approximately 2.8 Å in germanate glasses—see Figure 5.20b. In this way, the experimental peak can be fitted using a small number of discrete distances, and thus the peak can be parameterized and a reasonable estimate of its area obtained [47]. A pitfall of this approach is that it provides values for several bond lengths which are not meaningful, with the hazard of overinterpretation.

In cases where there is an extended distribution of interatomic distances, it is preferable to determine the area under a peak in the experimental RDF by integration, which avoids the problem of potential overinterpretation, and then to use the coefficient $(2 - \delta_{pp})c_{ij}\mathbf{b}_i\mathbf{b}_j$ from Eq. 5.43 to determine the coordination number. For this approach it is necessary to choose the limits for the integration, and usually the best choice is to use the position of the first minimum on either side of the peak. For example, integration of the RDF for the peak shown in Figure 5.20b between the two adjacent minima (at 1.48 and 2.30 Å) gives a Ge–O coordination number of 4.36, and this could correspond to 36% of the germaniums being 5-coordinated, or 18% being 6-coordinated [16]. Although it is not necessary to explicitly specify the distance range for a simple case like GeO$_2$, where there is a narrow distribution of bond lengths that is well separated from any other interatomic distances (see Figure 5.20a), for an extended, overlapping distribution (as for 18CsO·82GeO$_2$, Figure 5.20b) it is essential.

### 5.4.4 Normalization of Data

An ND measurement has the potential to measure coordination numbers which are more accurate than can be obtained by any other technique, because of the lack of a form factor and the ability to achieve a reliable normalization of the experimental data. However, as discussed below, for accurate coordination numbers to be obtained it is essential that the density and chemical composition of the sample are well known. Indeed, it is doubtful whether it is meaningful to determine a particular coordination number unless the composition of the sample
is known.

As shown in the previous section (see Eq. 5.43), the coordination number is derived from the area, \(A_{\parallel\parallel}\), under a peak in the measured correlation function, \(T_N^N(r)\). However, an accurate coordination number can only be obtained if firstly the experimental corrections are performed as well as possible (see Section 5.4.1), and secondly the final correlation function is normalized as well as possible; if the normalization of the correlation function is not reliable, then the value obtained for the peak area, \(A_{\parallel\parallel}\), is not reliable. The coefficient \((2 - \delta_{\parallel\parallel})c_j\bar{b}_j\bar{b}_n\) in Eq. 5.43 depends on the atomic fraction for element \(l\), and hence it is clear that the chemical composition of the sample must be well known for a reliable coordination number, \(n_{\parallel\parallel}\), to be derived from the peak area, \(A_{\parallel\parallel}\). However, the density of the sample is also of great importance due to the role it plays in determining the average density contribution, \(T_0^0(r)\) (see Eq. 5.35). The quantity determined directly from the diffraction experiment is the differential correlation function, \(D^N_N(r)\), and then this is added to \(T_0^0(r)\) to finally obtain the total correlation function, \(T_N^N(r)\) (see Figure 5.10). Thus, for \(T_N^N(r)\) to be reliable, it is required that \(T_0^0(r)\) is reliable, and \(D^N_N(r)\) is correctly normalized relative to \(T_0^0(r)\).

If the composition and density of the sample are both well known, then the average density contribution, \(T_0^0(r)\), can be calculated reliably and it can be used to optimize the normalization of \(T_N^N(r)\), leading to accurate coordination numbers [48]. To illustrate this procedure, experimental data are shown for crystalline \(Y_2O_3\); the structure of this crystal is well known [49], and there can be little doubt that the coordination is octahedral with \(n_{YO} = 6\), and that the values for the density and chemical composition are reliable. Figure 5.21a shows the measured differential correlation function, \(D_{\text{meas}}^N(r)\), as obtained by Fourier transformation of the corrected experimental diffraction pattern of \(Y_2O_3\), and also the negative of the average density contribution, \(-T_0^0(r)\), calculated from the density and chemical composition,

\[
T_0^0(r) = 4\pi r g_0^0 \left( \bar{b}_n \right)_n^2 = -S_0^0 r. \tag{5.46}
\]

In the low \(r\) region before the first peak, in principle \(T_N^N(r)\) is zero (i.e., there are no interatomic distances below a certain minimum) and \(D_N^N(r)\) should equal \(-T_0^0(r)\). In practice \(D_N^N(r)\) is expected to oscillate about \(-T_0^0(r)\), due to the presence of termination ripples and experimental noise. It is apparent in Figure 5.21a that \(D_{\text{meas}}^N(r)\) for \(Y_2O_3\) does not agree closely with \(-T_0^0(r)\). Figure 5.21a shows the result of a fit to the first peak in \(D_{\text{meas}}^N(r)\) of a single peak (Eq. 5.44) together with a linear term, \(-S_{\text{fit}}^0 r\), where \(S_{\text{fit}}^0\) is a constant. The area of the fitted peak shown in Figure 5.21a gives a \(Y-O\) coordination number of 6.53. However, if the renormalizing factor \(S_0^0/S_{\text{fit}}^0\) is applied, then the renormalized \(Y-O\) coordination number is 5.93, which agrees closely with the ideal value of six, with an error of about 1%. Figure 5.21b shows the total correlation function calculated according to

\[
T(r) = T_0^0(r) + \frac{S_0^0}{S_{\text{fit}}^0} D_{\text{meas}}^N(r), \tag{5.47}
\]
together with a simulation of the total neutron correlation function, derived from the reported crystal structure [49]. The quality of the final normalization is apparent from the close agreement between the areas under the simulated and measured functions. The question arises as to why the data may not be perfectly normalized after careful corrections have been performed, and there are several possible reasons. For example, it may not be possible to determine the number of atoms in the beam accurately (the sample may not be perfectly uniform, the definition of the beam may not be precise, the beam profile may not be uniform, etc.), or there may be a sample-dependent contribution to the background.

**Figure 5.21** The low \( r \) region of the correlation function for crystalline \( \text{Y}_2\text{O}_3 \), showing (a) \( D_{\text{meas}}(r) \) prior to renormalization (thick grey line), together with \(-T^0(r)\) (dashed line) and a fit to the first peak in \( D_{\text{meas}}(r) \) (thin black line) and (b) \( T^N(r) \) after renormalization (thick grey line), together with a simulation (thin black line).

### 5.4.5 Scattering at low \( Q \)
5.4.5.1 Homogeneous Samples

Ideally, the Fourier transform (Eq. 5.34) requires that the distinct scattering is measured to a minimum $Q$-value of zero, but this cannot be achieved experimentally. However, it has long been established [50] that for a homogeneous sample (i.e., a sample which has no small angle scattering—see Section 5.4.5.2) the low $Q$ limit may be represented as

$$i(Q) = A + BQ^2. \quad (5.48)$$

This form may be justified by considering that the scattering must be symmetric, that is, the same diffraction pattern must be measured for negative values of $Q$ as for positive values. It can be useful to fit Eq. 5.48 to the low $Q$ region (say below 1 Å$^{-1}$ or less) of the measured distinct scattering as a means of extrapolating to $Q = 0$, prior to Fourier transformation. A simple way of performing such a fit is to plot $i(Q)$ versus $Q^2$, and then to perform a linear fit to the low $Q$ region.

For a single phase liquid (i.e., a liquid without variations in chemical composition or density) at temperature $T$, the $Q = 0$ limit of the structure factor (for ND or XRD) is given by [51]

$$S(0) = g^0 k_B T \kappa. \quad (5.49)$$

where $k_B$ is the Boltzmann constant and $\kappa$ is the isothermal compressibility of the liquid. Strictly, this equation does not apply to a glass, because glasses are not in true thermodynamic equilibrium. However, a glass made by melt quenching can be regarded as a liquid which has been frozen at the glass transition temperature, $T_g$, and Wright et al. [52] have shown in a careful study of SiO$_2$ glass that the zero $Q$ limit of the diffraction pattern of the glass is given by evaluating Eq. 5.49 for the melt at the glass transition temperature, using the high frequency determination of the isothermal compressibility. This has important implications for the nature of the glassy state, since it shows that the fluctuations of the melt are frozen in at temperature $T_g$; this is a strong argument against the formation of a micro-crystalline structure for the glass.

5.4.5.2 Inhomogeneous Samples

If a sample has microstructure (i.e., inhomogeneities on a length scale, $L$, of order say 10–1000 Å) then the diffraction pattern will exhibit additional scattering at low $Q$ (less than say 0.1 Å$^{-1}$), known as small angle neutron scattering (SANS) because it is normally measured at small scattering angles. The only true Bragg peak which arises from non-crystalline samples is the (000) reflection, which cannot be observed because it coincides with the transmitted beam. However, microstructure in the sample leads to a broadening of the Bragg peaks, and at low $Q$ this is observed as SANS. A detailed discussion of microstructure is beyond the scope of this chapter, but it is worth noting that a fine powder sample will exhibit a significant SANS signal in the diffraction pattern.

To illustrate the phenomenon of SANS, it is worthwhile to consider an isolated (surrounded by empty space) sphere of radius $R$, with a uniformly distributed scattering length density, $\rho_b$. 
containing \( N \) atoms. For this uniform sphere, the distinct scattering is calculated analytically [53] as

\[
i^N(Q) = 9I_0 \left( \frac{\sin y - y \cos y}{y^3} \right)^2,
\]

where \( y = QR \), and the \( Q = 0 \) limit is \( I_0 = \rho_b^2 V_s^2 / N \), with sphere volume \( V_s = 4\pi R^3 / 3 \). (This is one of the very few uniform geometric objects for which an analytic result exists.) Figure 5.22a shows this function for a sphere of radius 20 Å. The scattering rises very strongly at low \( Q \) (less than about 0.2 Å\(^{-1}\)) to values greatly in excess of those observed at higher \( Q \) (see Figure 5.16). It is fundamental to note that SANS is observed if there is a contrast between the scattering length density of the object, \( \rho_b \), and its surroundings.
Figure 5.22 (a) The predicted distinct scattering for an isolated sphere of radius 20 Å, with $I_0 = 1000$. The inset shows a Guinier plot of the prediction, together with the corresponding Guinier approximation. (b) The measured nuclear SANS for amorphous Dy$_7$Ni$_3$. The inset shows a Porod plot of the experimental data, together with a Porod fit to the data.

If the scattering length density varies over a characteristic distance, $L$ (e.g., the particle size), and the $Q$-values of the experimental data are small in comparison with $L^{-1}$ (i.e., $QL < 1$), then the SANS can be described in terms of the Guinier approximation [54]. In this approximation, the coherent differential cross-section for a sample with $N_p$ particles of uniform scattering length density $\rho_{bp}$, embedded in a matrix of uniform scattering length density $\rho_{bm}$, is

$$\frac{d\sigma}{d\Omega}^{\text{coh}} = \frac{V_p^2 N_p^2}{N} (\rho_{bp} - \rho_{bm})^2 \exp\left(-Q^2 R_G^2 / 3\right), \tag{5.51}$$

where $R_G$ is the radius of gyration (i.e., the RMS distance of part of the particle from its center). In this regime it is useful to plot the experimental data as $\log_e(I)$ versus $Q^2$, as shown...
in the inset to Figure 5.22a, in which case the slope of a linear fit yields an estimate of the particle size, $R_G$.

If the experimental $Q$-values are large in comparison with $L^{-1}$ (i.e., $QL \sim 1$), then the SANS can be described in terms of the Porod approximation [55],

$$\frac{d\sigma}{d\Omega} = \frac{2\pi A_p N_p}{N} (\rho_{bp} - \rho_{bm})^2 Q^{-n} \quad (5.52)$$

where $A_p$ is the surface area of a particle. If the structures giving rise to the SANS are compact and smooth then the dimensionality, $n$, has the value of four, but if the structures are fractal in nature then the value of $n$ differs from four [56, 57]. Figure 5.22b shows a measurement of the nuclear SANS for the melt-spun amorphous metal Dy$_7$Ni$_3$ [58] (measured on the former D17 small angle diffractometer at the Institut Laue Langevin). In the Porod regime it is useful to plot the experimental data as $\log(I)$ versus $\log(Q)$, as shown in the inset to Figure 5.22b, in which case the slope of a linear fit yields the dimensionality. The Porod fit shown in Figure 5.22b yields a slope close to four, indicating that the SANS arises from the structure of the surface of the melt-spun ribbons. Contrast matching is an important experimental technique for SANS; this involves placing the sample in liquids of different scattering length density (which may be prepared, for example, by mixing $H_2O$ and $D_2O$ in different proportions) and observing the effect on the SANS signal. For example, this technique has been applied to melt-spun amorphous metal ribbons [59, 60]; it was possible to almost entirely remove the observed SANS, showing again that it arises from the surface structure of the ribbons.

The ordinary ND pattern (sometimes known as WANS—wide angle neutron scattering), as described elsewhere in this chapter, has conventionally been analyzed separately from the SANS signal. However, the advent of new ND instrumentation, particularly the Near and Intermediate Range Order Diffractometer [61] (NIMROD) at the ISIS Facility, which covers a $Q$-range wide enough to measure both regions simultaneously enables the interesting possibility of modeling both the microstructure and the atomic level structure at the same time.

### 5.4.6 Sample-Related Difficulties

As discussed in Section 5.4.4, for reliable and meaningful results to be obtained from an ND experiment on a glass, it is essential that the composition and density of the sample are well known. Thus glass samples studied by ND should always be well characterized, using as many different experimental techniques as possible.

#### 5.4.6.1 Nuclear Resonances

A nucleus absorbs neutrons very strongly if the neutron energy is close to the energy of an excited state of the nucleus; this phenomenon is known as a nuclear resonance [62, 63]. It is extremely hard to obtain useful ND data if the neutron energy is close to a resonance, due to the very strong absorption, but fortunately the great majority of isotopes do not have a resonance in the energy range used for ND.
Table 5.4 lists the energies for all resonances of stable nuclei which are less than 4 eV [62, 63]. If a sample contains any of these nuclei then the effect of the resonance needs to be considered in an ND experiment. For a constant wavelength diffractometer it is necessary to choose a neutron wavelength so that the energy (see Eq. 5.3) is not close to a resonance energy. For a T-O-F diffractometer, the effect of resonances is more complex, and this is illustrated by Figure 5.23 which shows the corrected differential cross-section for a 10K₂O.90TeO₂ glass [64], measured on the former LAD diffractometer [65]. The ¹²³Te nucleus has a resonance at 2.334(8) eV (see Table 5.4) [62], so that there is strong absorption in the region of the spectra which correspond to this energy, and this gives rise to a negative peak in the experimental data. The negative peak occurs over a different Q range for each detector angle, illustrating an important point in understanding experimental problems with T-O-F diffraction; if a problem is due to a diffraction effect then the related feature occurs at the same Q-value for different detector angles, but if a problem is due to a constant-energy effect (such as a resonance) then the related feature occurs at different Q-values for different detector angles. For the data shown in Figure 5.23, there is also a strong positive peak for the intermediate detector angles (20°, 35°, 60°, and 90°) because these detectors were sensitive to γ-rays; when a neutron is absorbed by a nucleus it may give rise to a prompt γ-ray which arrives at the detector before neutrons with the energy of the resonance. However, modern neutron detectors should have very low sensitivity to γ-rays, so that this phenomenon is not observed. For a sample containing an element with a resonance, a reliable result (covering a full Q-range) can be obtained from a T-O-F diffractometer if the detectors cover a large range of angles; in this case a reliable result is obtained by combining the spectra from the different angles so that the Q-range for each angle that is affected by the resonance is avoided. Nevertheless, Table 5.4 shows that there are very few elements which are ill-suited to study by ND. For example, europium and gadolinium have a large number of resonances in the thermal region so that they are effectively “black” and useful ND results cannot be obtained. Neutron resonances are particularly common for rare earth (RE) elements, and hence (considering the chemical similarity of REs) it may be advisable when planning an experiment to choose to study samples containing REs for which resonances are not a problem.

Table 5.4 Energies of nuclear resonances below 4 eV for stable nuclei [62, 63].

<table>
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<th>Element</th>
<th>Isotope</th>
<th>Resonance energies/eV</th>
</tr>
</thead>
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<td>Sr</td>
<td>⁸⁷Sr</td>
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</tr>
<tr>
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<td>Rh</td>
<td>¹⁰³Rh</td>
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</tr>
<tr>
<td>46</td>
<td>Pd</td>
<td>¹⁰⁸Pd</td>
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</tr>
<tr>
<td>48</td>
<td>Cd</td>
<td>¹¹³Cd</td>
<td>0.178(2)</td>
</tr>
<tr>
<td>49</td>
<td>In</td>
<td>¹¹³In</td>
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</tr>
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</tr>
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<td>Properties</td>
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<td>---</td>
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<td>-------------</td>
<td>------------</td>
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<tr>
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<tr>
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<td>3.397(20)</td>
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<td></td>
<td></td>
<td>$^{149}$Sm</td>
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</tr>
<tr>
<td>63</td>
<td>Eu</td>
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<td>0.321(1) 0.460(1) 1.055(3) 1.815(7) 2.717(5) 3.368(6) 3.710(6)</td>
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<tr>
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<td>2.156(4)</td>
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</tr>
<tr>
<td>92</td>
<td>U</td>
<td>$^{235}$U</td>
<td>0.290(5) 1.124(5) 2.028(4) 2.76(1) 3.145(5) 3.615(5)</td>
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Figure 5.23 The (corrected and normalized) differential cross-section of $10\text{K}_2\text{O} \cdot 90\text{TeO}_2$ glass, $I^N(Q)$, measured on the former LAD diffractometer [65]. The curves for the different detector banks are shown with vertical offsets for clarity.

5.4.6.2 Hydrogen Contamination

It is always important to minimize chemical contamination of the sample, but for ND the effect of hydrogen contamination is especially profound. Some glasses, such as borates or phosphates, are particularly prone to pick up moisture (in the form of either $–\text{OH}$ or $\text{H}_2\text{O}$) [66, 67], and much better ND results will be obtained if this contamination is reduced or eliminated. It may be advisable to place a sample under vacuum or in a sealed, dry environment as soon after manufacture as possible. Sometimes moisture contamination can be removed by drying in a vacuum oven, but this is only effective at removing surface $\text{H}_2\text{O}$, and has little effect on $–\text{OH}$ or $\text{H}_2\text{O}$ in the bulk. If the chemical formula of the sample of interest includes hydrogen, then ND results can be greatly improved if the sample is deuterated (i.e., if the hydrogen atoms are replaced with deuterium atoms). Nevertheless, it should be borne in
mind that if a deuterated sample is exposed to normal atmosphere, the deuteration may be reversed within a few minutes, due to exchange with hydrogen in atmospheric moisture, which can be rapid.

For some scientific studies, however, it is desirable to measure ND for a sample with a significant hydrogen content. For example, Figure 5.24 shows experimental data for a sample of an amorphous zeolite precursor, which contains a large amount of hydrogen [68]. This illustrates the problems that arise with hydrogen; first, the very large incoherent cross-section of hydrogen (see Section 5.3.5) leads to a large incoherent background, and second, the inelasticity effect for hydrogen (see Section 5.3.6.1) is very severe, causing a strong rise in the self scattering at low $Q$. In fact, the approximate methods which are commonly used to calculate the self scattering (such as that originally proposed by Placzek [8]) break down if the sample contains hydrogen (because the neutron and proton mass are very similar), and it is necessary to remove the self scattering by an empirical method. Figure 5.24 shows a smooth fit to the experimental $I^N(Q)$ data which was achieved by using a cubic spline with variable knot spacing, together with the estimate of the distinct scattering that was obtained by subtraction of this fit [68]. Although such empirical methods are useful, it is always preferable to remove hydrogen from the sample if possible.
Figure 5.24 (a) The differential cross-section measured by Bank5 (93°) of the GEM diffractometer [2] for amorphous zeolite precursor LTA$_5$ [68], together with a smooth cubic spline fit. (b) The estimate of the distinct scattering which is obtained from a difference of the two curves in (a).

As shown in Section 5.3.6.1 (see Figures 5.11 and 5.12), the effect of inelasticity is much reduced at low scattering angle, and for this reason T-O-F neutron diffractometers with all of the detectors at low angle, such as SANDALS [69] (Small Angle Neutron Diffractometer for Amorphous and Liquid Samples) and NIMROD [61] at the ISIS Facility, are available for the study of samples with low atomic mass (e.g., aqueous solutions).

5.4.6.3 Crystal Contamination

ND is much more penetrating than XRD (which may only probe a short distance into the surface of the sample, depending on the X-ray wavelength and the sample composition), and thus for a sample containing a crystalline impurity the ND pattern is more likely than the XRD pattern to exhibit Bragg peaks. Furthermore, ND (especially time-of-flight ND) tends to have
high $Q$-resolution, which also acts to make Bragg peaks more apparent. It is thus common for samples which appear fully amorphous by laboratory XRD to be shown to contain a significant crystalline contamination when ND is performed.

Of course it is preferable to study phase pure glass samples that do not contain crystalline material, but sometimes this is not possible, and then it may be desirable to remove the Bragg peaks from the diffraction pattern. As a simple example, Figure 5.25 shows diffraction data for a tin borate-based glass of nominal composition $70\text{SnO} \cdot 30\text{B}_2\text{O}_3$ [13], which exhibits Bragg peaks due to crystalline impurities. In this case, the Bragg peaks have been removed by the simple expedient of fitting a straight line underneath the Bragg peak. Figure 5.25 also shows a simulation of the diffraction pattern of crystalline SnO$_2$ in the rutile phase [70], calculated using CrystalMaker® software [71]. The predominant crystalline impurity is clearly SnO$_2$, due to disproportionation and then oxidation of tin in the melt [72]. The example in Figure 5.25 illustrates the difficulty of Bragg peak removal. As $Q$ increases, the Bragg peaks become closer together, and it becomes impossible to remove them individually; thus the contribution from the crystalline impurity cannot be removed at higher $Q$. It is also not possible to remove the crystalline contribution to the diffraction pattern well by using a conventional crystallographic simulation method (e.g., the Rietveld method [73]), because such methods do not correctly describe the short range order (especially the effects of correlated atomic motion, see Section 5.3.6.2) and hence they do not predict the higher $Q$ region of the diffraction pattern. Therefore, the best way to remove the contribution due to a crystalline impurity may be to measure ND for a pure sample of the impurity, followed by a suitable subtraction of the correlation functions [74].
Figure 5.25 The distinct scattering, $i^N(Q)$, for a tin borate glass sample with nominal composition 70SnO·30B$_2$O$_3$ before and after removal of Bragg peaks (see text) [13]. Also shown is a simulation of the diffraction pattern for crystalline SnO$_2$ and vertical tick marks indicate the positions of the Bragg peaks.

5.4.7 Partial Correlation Functions

5.4.7.1 Isotopic Substitution

A limitation of a standard ND experiment is that the information obtained is not element-specific. The neutron correlation function, $T^N(r)$, has contributions from all possible pairs of elements in the sample (e.g., Si–Si, Si–O, and O–O for SiO$_2$), and as $r$ increases the contributions from the different pairs rapidly overlap and cannot be resolved. Isotopic substitution (first reported by Enderby et al. in a study of liquid Cu$_6$Sn$_5$ [75]) is a very important technique that can address this problem [18]. In this section, the method is first illustrated by a particularly elegant example, and is subsequently discussed from a general
There are a few elements which have isotopes with both positive and negative scattering lengths (H, Li, Ti, Cr, Ni, Sm, Dy, and W), in which case isotopic substitution can be used so that the coherent scattering length for the element is zero. This is known as the null technique; if an element has a coherent scattering length of zero, then this element does not contribute to the distinct scattering, and none of its partial correlation functions contribute to the measured correlation function. This technique is especially powerful if it can be applied to both elements in a sample with two elements—this has been called the double-null isotopic substitution technique [76].

The total correlation function measured in a single diffraction experiment is a sum of pairwise partial correlation functions (see Eq. 5.36), and for the binary amorphous metal Dy\textsubscript{7}Ni\textsubscript{3} the total neutron correlation function is given by

\[ T^N(r) = c_{\text{Dy}} b^2_{\text{Dy}} t_{\text{DyDy}}(r) + 2c_{\text{Dy}} b_{\text{Dy}} b_{\text{Ni}} t_{\text{DyNi}}(r) + c_{\text{Ni}} b^2_{\text{Ni}} t_{\text{NiNi}}(r), \] \hspace{1cm} (5.53)

where \( c_{\text{Dy}} = 0.7 \) and \( c_{\text{Ni}} = 0.3 \) are the atomic fractions for the two elements. There are three independent partial correlation functions, because the Dy–Ni and Ni–Dy functions are not independent (see Eq. 5.37). (In general, a sample with \( N_e \) elements has \( N_e(N_e + 1)/2 \) independent partial correlation functions.) ND was measured for all four samples, \( \text{NatDy}_7\text{NatNi}_3, \text{NatDy}_7\text{0Ni}_3, \text{0Dy}_7\text{NatNi}_3, \) and \( \text{0Dy}_7\text{0Ni}_3 \) (where \( \text{0Dy} \) and \( \text{NatDy} \) indicate dysprosium with the null and natural isotopic compositions, respectively) and the measured diffraction data are shown in Figure 5.26. For the \( \text{0Dy}_7\text{0Ni}_3 \) sample, there is no coherent nuclear scattering from either element, and this enables the magnetic scattering, \( I^M(Q) \), to be measured, so that it can be subtracted from the results for the other three samples. At room temperature, which is greatly in excess of the 35 K magnetic ordering temperature for Dy\textsubscript{7}Ni\textsubscript{3}, the magnetic scattering is almost entirely self scattering, given by

\[ I^{MS}(Q) = \frac{2}{3}(\gamma r_0)^2 \sum_l c_l |f_l(Q)|^2 \langle \mu^2_l \rangle, \] \hspace{1cm} (5.54)

where \( \gamma \) is the neutron magnetic moment in nuclear magnetons and \( r_0 \) is the classical electron radius. \( f_l(Q) \) and \( \mu^2_l \) are respectively the magnetic form factor and mean square magnetic moment for element \( l \). Thus \( I^M(Q) \) is proportional to \( |f_{\text{Dy}}(Q)|^2 \), where \( f_{\text{Dy}}(Q) \) is the dysprosium magnetic form factor. For the \( \text{NatDy}_7\text{0Ni}_3 \) sample, \( \bar{b}_{\text{Ni}} = 0 \), and hence Eq. 5.53 shows that the experimental correlation function yields a direct measurement of the \( t_{\text{DyDy}}(r) \) partial correlation function. Similarly, the \( \text{0Dy}_7\text{NatNi}_3 \) sample has \( \bar{b}_{\text{Dy}} = 0 \) and yields a direct measurement of the \( t_{\text{NiNi}}(r) \) correlation function. These two like-atom partial correlation functions can then be combined (according to Eq. 5.53) with the correlation function measured for the \( \text{NatDy}_7\text{NatNi}_3 \) sample to obtain the unlike-atom correlation function, \( t_{\text{DyNi}}(r) \). Figure 5.27
shows the three partial correlation functions for Dy$_7$Ni$_3$, obtained by use of the double-null isotopic substitution technique [58]. The figure also shows the partial correlation functions calculated for a Dy$_7$Ni$_3$ hard sphere liquid, according to the Percus–Yevick equation [77, 78]. For a binary hard sphere system, the interatomic distance for unlike-atom contacts is midway between the two distances for like-atom contacts, but (as is shown by the comparison with the hard sphere calculation in Figure 5.27) this is not the case for Dy$_7$Ni$_3$. Instead the measured partial correlation functions show that pairs of nickel atoms are close but not touching. The amorphous metal has a more ordered structure than a hard sphere liquid, and the observed Ni–Ni nearest neighbor distance is similar to that in crystalline Dy$_3$Ni$_2$ [79], where it arises from two nickel atoms packed into the recess on either side of a square of four dysprosium atoms (as shown in the inset to Figure 5.27).
Figure 5.26 The differential cross-section, $I^N(Q)$, of amorphous Dy$_7$Ni$_3$ for three different isotopic compositions (superscripts Nat and 0 indicate the natural isotopic composition and the null isotopic composition), shown as a continuous line [58]. The dashed line indicates the sum of the magnetic scattering, $I^M(Q)$, and the calculated nuclear self scattering, $I^S(Q)$, for each sample.
Figure 5.27 The three measured partial correlation functions for amorphous Dy$_7$Ni$_3$ [58], together with the partial correlation functions for a Percus–Yevick calculation of the partial correlation functions for a binary hard sphere liquid. The inset in the figure shows how a similar Ni–Ni distance arises in crystalline Dy$_3$Ni$_2$ [79] (large, translucent spheres are Dy, smaller, solid spheres are Ni).

For most elements, it is not possible to use the null technique, but nevertheless isotopic substitution can be performed (although there are some elements for which isotopic substitution is not feasible, either because there is only one stable isotope, or because the difference between the scattering lengths of the available isotopes is too small). If only one substitution is performed, then this is known as a first difference. In this case, let A be the element on which isotopic substitution is performed so that two samples are made in which it has scattering lengths $\bar{b}_A$ and $\bar{b}_A'$. The correlation functions measured for these two samples are $T(r)$ and $T'(r)$. Using these two measurements it is possible to separate any two of the three combinations A–A, A–X and X–X (where X is any element other than A). However, the two most useful combinations are a simple difference, or a weighted difference, derived from Eq. 5.36 as
follows:

\[
T(r) - T'(r) = c_A \left( \bar{b}_A - \bar{b}'_A \right) \left( (\bar{b}_A + \bar{b}'_A) t_{AA}(r) + 2 \sum_{k \neq A} \bar{b}_k t_{Ak}(r) \right),
\]

Equation 5.55 shows that the result of a simple difference only includes correlations which involve element A; that is, it eliminates correlations which do not involve A. Equation 5.56 shows that the result of the weighted difference eliminates all correlations involving A except the A–A correlation, that is, it eliminates all unlike-atom correlations which involve A. Note that a first difference, as in Eq. 5.55, is equivalent to a XAFS (X-ray Absorption Fine Structure) measurement at the absorption edge of element A, but with the added advantage that it yields longer range information, which is not accessible to the XAFS experiment due to the absence of data at low wavevector.

If another substitution is performed, say a measurement in which the scattering length of element A is changed to \( \bar{b}'_A \), so that the correlation function is \( T''(r) \), then this is known as a second difference. It is then possible to obtain a complete separation into A–A, A–X and X–X contributions, for example,

\[
t_{AA}(r) = \frac{\bar{b}_A \left( T'(r) - T''(r) \right) + \bar{b}'_A \left( T''(r) - T'(r) \right) + \bar{b}''_A \left( T(r) - T'(r) \right)}{c_A \left( \bar{b}_A - \bar{b}'_A \right) \left( \bar{b}_A - \bar{b}''_A \right) \left( \bar{b}'_A - \bar{b}_A \right)}.
\]

For a sample containing \( N_e \) elements, there are \( N_e (N_e+1)/2 \) independent partial correlation functions, and hence this number of isotopic substitution measurements must be made in order to achieve a complete separation of all the partial pairwise atomic correlation functions; this rapidly becomes prohibitive as the number of elements increases.

For simplicity, consider a sample containing two elements A and B (e.g., Dy\(_7\)Ni\(_3\)). If three correlation functions, \( T(r) \), \( T'(r) \), and \( T''(r) \), are measured for three samples with scattering lengths \( \bar{b}_A, \bar{b}_B, \bar{b}'_A, \bar{b}'_B, \) and \( \bar{b}''_A, \bar{b}''_B \), respectively, then the measured correlation functions are related to the partials by

\[
\begin{bmatrix}
T(r) \\
T'(r) \\
T''(r)
\end{bmatrix} = [A]
\begin{bmatrix}
t_{AA}(r) \\
t_{BB}(r) \\
t_{AB}(r)
\end{bmatrix} =
\begin{bmatrix}
c_A \bar{b}_A^2 & c_B \bar{b}_B^2 & 2c_A \bar{b}_A \bar{b}_B \\
c_A \bar{b}'_A^2 & c_B \bar{b}'_B^2 & 2c_A \bar{b}'_A \bar{b}'_B \\
c_A \bar{b}''_A^2 & c_B \bar{b}''_B^2 & 2c_A \bar{b}''_A \bar{b}''_B
\end{bmatrix}
\begin{bmatrix}
t_{AA}(r) \\
t_{BB}(r) \\
t_{AB}(r)
\end{bmatrix}.
\]
The three partial correlation functions can then be obtained by means of an inversion of the matrix $A$,

$$\begin{align*}
[t (r)] &= [A]^{-1} [T (r)].
\end{align*}$$

(5.59)

Thus the partial correlation functions are essentially obtained by solving simultaneous equations, and Eq. 5.57 shows that the extraction of the partials depends critically on the difference between scattering length values. Even if the scattering length values are known very precisely, the matrix inversion amplifies the errors on the measured correlation functions. Thus the differences in scattering length need to be as large as possible, for the derivation of partials to be well-conditioned. As Livesey and Gaskell have proposed [80], Turing's number, $T_n$ [81], can be used as a figure of merit for isotopic substitution experiments. $T_n$ gives an upper limit on the factor by which the fractional error in the partial functions exceeds the fractional error in the measurements, and is given approximately by

$$T_n = |A|_E |A^{-1}|_E,$$

(5.60)

where the Euclidean norm is given by adding in quadrature the components of the matrix $A$,

$$|A|_E = \left( \sum_{i,j} A_{ij}^2 \right)^{1/2}.$$

(5.61)

For example, the study of Dy$_7$Ni$_3$ using the double-null isotopic substitution technique is one of the most well-conditioned of all isotopic substitution studies, with $T_n = 12.3$. For most isotopic substitution studies in the literature, the value of $T_n$ is typically an order of magnitude larger. Consequently, there are severe experimental requirements on an isotopic substitution experiment if a satisfactory separation of partials is to be achieved. First, it is essential that the samples be identical, apart from their differing isotopic composition, and XRD is usually the preferred way to verify this. Furthermore the measurements on the isotopic samples must be performed in the same way, to reduce the effect of systematic errors. High statistical accuracy diffraction data are required, which requires long counting times and also high detector stability.

An excellent example of isotopic substitution on a glass has been given by Eckersley and Gaskell who have reported both first difference [82] and second difference [83] isotopic substitution for 48CaO·49SiO$_2$·3Al$_2$O$_3$, using calcium isotopes. The first difference showed that modifier ions have a well-ordered nearest neighbor shell and also ordering at longer distances up to $\sim$10Å. Another example of a second difference measurement has been given by Petri et al. [84] for GeSe$_2$ glass, using both Ge and Se isotopes to obtain a full separation of the partial functions, finding evidence for defects in the form of homopolar (i.e., Ge–Ge and Se–Se) bonds. The method of H/D substitution has made a big impact in the study of molecular liquids, especially aqueous solutions [85], because there is a large difference between the hydrogen and deuterium scattering lengths ($\bar{b}_H = -3.739$ fm and $\bar{b}_2H = 6.671$ fm [32]), and
deuterated samples are available relatively cheaply, with the possibility of deuterating specific molecular sites.

### 5.4.7.2 Other Methods

An impediment to the widespread use of isotopic substitution is the very high financial cost of isotopic material (especially since ND requires relatively large samples, say a few grams), and also the lack of suitable isotopes for some elements. However, other methods may also be used to help to differentiate the various partial contributions to the total correlation function. The most widely applicable of these methods involves the combination of ND and XRD. The strength of X-ray scattering for a given element is proportional to the atomic number, $Z$, whereas the coherent neutron scattering length varies haphazardly across the periodic table (see Figure 5.9). Thus the relative weights of the various partial functions are different in the X-ray and neutron correlation functions (the X-ray correlation function, $T^X(r)$, is usually more strongly dominated by the contributions involving heavier elements). Hence the use of both ND and XRD on a sample can reveal more than can be obtained by the use of one radiation alone.

A detailed discussion of the combined use of ND and XRD is beyond the scope of this chapter, but a good example of the method has been given by Benmore et al. [86] in a study of calcium aluminate glasses. Another good example of the application of the method can be found in a study of a high lead silicate glass, 80PbO·20SiO$_2$ [87], for which $T^N(r)$ is dominated by partials involving Pb or O, whilst $T^X(r)$ is dominated by partials involving Pb; simultaneous modeling of the two correlation functions provides information that is much more element-specific than is possible using only one radiation, and for the first time it has been possible to derive a detailed structural model showing how the lone-pairs of electrons are arranged relative to each other in a glass network containing lone-pair cations.

Another approach which has been used to differentiate the various partial contributions to the total correlation function is isomorphous substitution. This method involves performing diffraction on two samples that are identical, except that one element is substituted for another, and the two elements are assumed to be structurally identical. Mostly this approach has been applied to amorphous metals [88], although it has also been applied successfully to investigate the environment of rare earth (RE) ions in phosphate glass. [89] Clearly the requirement that the two substituted elements are structurally identical is a limitation of the technique, but RE elements are probably the best suited of all to this technique.

In some cases, ND can be used in more novel, specialized ways to obtain element-specific information. For example, a magnetic difference ND technique has been applied to directly observe the distribution of Tb–Tb distances in a phosphate glass, 24.6Tb$_2$O$_3$·72.2P$_2$O$_5$·3.2Al$_2$O$_3$ [90]. First, the ND pattern was measured with the sample at a temperature 4 K, with the sample in the paramagnetic state. Second, the ND pattern was measured again, after application of a high magnetic field of 4 T, which is large enough to cause a high degree of alignment of the Tb magnetic moments. Figure 5.28a shows the two measured diffraction patterns, whilst Figure 5.28b shows their difference. In the absence of a magnetic field, with the sample in the paramagnetic state, there is no correlation between the
orientations of pairs of Tb magnetic moments, and hence there is no structural information in
the magnetic contribution to the scattering. However, with the high applied magnetic field,
there is a high degree of alignment of the magnetic moments, with the result that the magnetic
scattering contains structural information. Thus the difference shown in Figure 5.28b depends
exclusively on Tb–Tb correlations. Figure 5.29a shows the differential correlation function,
$D^N(r)$, measured before and after application of the magnetic field, whilst Figure 5.29b shows
their difference, together with a simulation of the first two peaks. The first peak at 3.9 Å is due
to pairs of Tb ions which are both bonded to the same non-bridging oxygen, whilst the second
peak at 6.4 Å is due to two Tb ions which are bonded to different oxygens in the same PO$_4$
tetrahedron. Knowledge of the RE–RE distances in glass is of particular interest for laser and
optoelectronic applications. Figure 5.29c shows a reverse Monte Carlo (see Section 5.4.9)
simulation of the partial Er-Er differential correlation function for erbium metaphosphate glass
[91] (together with an arbitrary scaling of $\Delta D^N(r)$); there is a remarkable agreement between
the two independent results.
**Figure 5.28** The differential cross-section for $24.6\mathrm{Tb}_2\mathrm{O}_3\cdot72.2\mathrm{P}_2\mathrm{O}_5\cdot3.2\mathrm{Al}_2\mathrm{O}_3$ glass at 4 K, showing (a) the diffraction pattern with and without the application of the 4 T magnetic field; and (b) the field-on minus field-off difference, $\Delta I^N(Q)$. [90].
Figure 5.29 The differential correlation functions for 24.6Tb₂O₃·72.2P₂O₅·3.2Al₂O₃ glass at 4 K [90], showing (a) the differential correlation function with and without the application of the 4 T magnetic field; (b) the field-on minus field-off difference, $\Delta D^N(r)$ (together with the simulation of the contribution from the first two distances described in the text); and (c) a reverse Monte Carlo simulation of the partial Er–Er differential correlation function for erbium metaphosphate glass [91] (together with an arbitrary scaling of $\Delta D^N(r)$).

Diffraction with polarized neutrons can also be used to measure partial functions for magnetic materials [92]. However, it is worth noting that novel techniques which make use of magnetic scattering are limited to a very small $Q$-range (with $Q_{\text{max}}$ in the range 5–10 Å⁻¹) due to the magnetic form factor (e.g., see Figure 5.26).

For some elements it is also possible to measure partial functions using the anomalous dispersion technique. For this technique, it is necessary that the element of interest has a nuclear resonance at low energy (see Section 5.4.6.1). The method makes use of the fact that there is a strong wavelength-dependence of both the real and imaginary parts of the scattering length close to an absorption resonance. Although it is potentially a very powerful technique,
anomalous dispersion is experimentally challenging, since it necessarily involves measurements for which absorption is very high, and thus far it has only been applied to glasses containing samarium (14Sm$_2$O$_3$·13Al$_2$O$_3$·73GeO$_2$ [93] and 20.5Sm$_2$O$_3$·79.5P$_2$O$_5$ [94, 95]).

### 5.4.8 Interpretation of Results

It is beyond the scope of this chapter to exhaustively review methods of interpretation of glass diffraction results. Instead a number of general concepts that are useful for gaining an understanding of ND results on glass structure are presented.

#### 5.4.8.1 Crystallite Models

The diffraction pattern of a glass consists of a series of peaks that are much broader than the sharp Bragg peaks normally measured for a polycrystalline powder (see Figure 5.16). However, it is well known that when crystallites become very small there is an observable broadening of the Bragg peaks, according to the Scherrer equation [96], which gives the FWHM of a Bragg peak as

\[
\Delta Q = \frac{2\pi K}{L},
\]

where \(L\) is the crystallite dimension and \(K (\sim 1)\) is a shape factor. Thus it has often been regarded as attractive to describe glass structure in terms of a model involving very small crystallites to account for the broad diffraction peaks [97–99]. Figure 5.30 shows the ND patterns of normal polycrystalline PdO and of hydrous PdO, which involves extremely small crystallites of diameter about 18 Å (illustrated by the inset to the figure) [100]. The simulation in the figure was calculated for a spherical particle of PdO of diameter 18 Å (inset) using the Debye equation (Eq. 5.28), and the SANS for this model was removed by use of Eq. 5.50, which is equivalent to placing the model in a hole in a homogenous medium of the same scattering length density. Even though the crystallites in hydrous PdO are extremely small, the diffraction pattern retains the broadened Bragg peaks of normal PdO, and it is also apparent from the differential correlation function (Figure 5.31) that the order extends to a relatively long distance compared to that observed in a glass. For a microcrystalline model to give a reasonable representation of diffraction results for a glass, it is necessary that the crystallite dimension be of order one unit cell, in which case there is no translational symmetry and the model ceases to be crystalline. Thus microcrystalline models of glass structure are not viable, because the crystallites contain too few unit cells to be considered crystalline, and because they lack a description of the region between crystallites [101] (see also Section 5.4.5.1). Instead, disordered models involving a distribution of atomic sites are to be preferred, such as the random network model [99, 101–103] which is commonly used to describe the structure of covalently bonded glasses.
Figure 5.30 The measured distinct scattering (thick grey lines), $i^N(Q)$, for anhydrous PdO (vertically offset) and for hydrous PdO [100]. Also shown (thin black line) is a simulation of $i^N(Q)$ for a spherical particle of PdO of diameter 18 Å (inset) embedded in a homogenous medium.
Figure 5.31 The measured differential neutron correlation function (thick grey lines), $D^N(r)$, for anhydrous PdO (vertically offset) and for hydrous PdO [100]. Also shown are simulated (see text) differential neutron correlation functions (thin black lines).

5.4.8.2 Bonding and Bond Lengths

When planning an ND experiment on a glass, it is useful to estimate the nearest neighbor distances likely to be observed; it can be preferable to choose to study a system in which there is little or no overlap between the nearest neighbor peaks in the correlation function, because then the peak parameters (e.g., bond lengths and coordination numbers) can be determined more reliably. This can be done by reference to the structure of crystalline materials of similar composition, or by use of tabulated values for the sizes of atoms. The ionic radii provided by Shannon [104] are often used for this purpose; for example, the ionic radii of Ge$^{4+}$ and O$^{2-}$ (with coordination numbers of 4 and 2, respectively) are 0.390 Å and 1.35 Å, giving a Ge–O distance of 1.74 Å, which is a good estimate of the bond length in GeO$_2$ glass (see Table 5.3). For amorphous metals, it is usual to make use of the Goldschmidt radii for 12-fold coordination [105], simply because coordination numbers in metals are usually much larger.
Electrostatic bond strength (EBS) is another very simple concept, first proposed by Pauling [106], which can be of great use in understanding glass networks. If a cation with formal charge $\zeta e$ is coordinated by $\nu$ anions (all of the same type), then the bond going from the cation to each anion has an EBS, $s$, defined as

$$s = \frac{\zeta}{\nu}. \quad (5.63)$$

Pauling [107] postulated that in a stable structure the magnitude of the formal charge, $-\zeta e$, of an anion is exactly or nearly equal to the sum of the strengths of the bonds to it from the adjacent cations, so that

$$\zeta = \sum_k s_k = \sum_k \frac{\zeta_k}{\nu_k}. \quad (5.64)$$

This criterion may be considered to be an expression of the necessity for charge balance in stable structures. It is of great use in determining which anion environments are likely to occur [47, 108].

The neutron correlation function, $T_N(r)$, provides information on the distribution of interatomic distances which can be much more detailed than a single bond length, and the concept of bond-valence (BV) can be of great use in obtaining a more profound understanding of the results. BV is an empirical concept, based on information from a large number of crystal structures, according to which the valence of an atom, $i$, may be expressed in the form

$$V_i = \sum_j v_j = \sum_j \exp \left( \frac{R_{ij} - d_{ij}}{b} \right), \quad (5.65)$$

where the summation is performed over its neighbors, $j$. $d_{ij}$ and $v_{ij}$ are respectively the length and the valence of the bond between atoms $i$ and $j$. $R_{ij}$ is the BV parameter for the atom pair $(i,j)$ (tabulated values for $R_{ij}$, based on numerous crystal structures, are given by Brese and O'Keeffe [109]) and $b$ is a universal constant ($= 0.37\text{Å}$). If we make the simplifying assumption that all of the $n_{ij}$ neighbors to atom $i$ have the same bond length, $r_{ij}^{bv}$, then this interatomic distance is given by

$$r_{ij}^{bv} = R_{ij} + b \log_e \left( \frac{n_{ij}}{V_i} \right). \quad (5.66)$$

Although the BV method has been developed for crystal structures [110], it is becoming increasingly clear that it is a powerful tool for understanding glass structure [111]. Equation 5.66 shows that the bond length increases as the coordination number increases. For example, for Ge–O coordination numbers of 4, 5, and 6, Eq. 5.66 predicts Ge–O bond lengths of 1.7480, 1.8306, and 1.8980 Å, respectively [16]; thus the appearance of a shoulder on the right hand side of the Ge–O peak for 18Cs$_2$O.82GeO$_2$ glass (in **Figure 5.20b**) is clearly associated with the presence of a significant fraction of germanium atoms with a coordination number greater
than four. The BV method is also of great use in considering the environment of bridging oxygens, especially in glasses such as tellurites in which there can be a large difference in the lengths of the bonds [64, 112].

5.4.8.3 Coordination Polyhedra

As well as understanding the bond lengths (or interatomic distances) between pairs of atoms in the glass, it is also of interest to understand the geometry of the coordination shell around each atom, that is the coordination polyhedron of each atom. For example, we may wish to determine the number and geometry of anions X (e.g., O$^{2-}$) around a cation A (e.g., Si$^{4+}$) in a glass.

Obviously the coordination number for each type of atom is of great relevance for a consideration of the coordination polyhedra. However, it must be acknowledged that coordination numbers cannot usually be measured as accurately as the bond lengths. As discussed in Section 5.4.4, the accuracy of the coordination numbers depends on many factors, including the sample composition and density, and in the most favourable cases coordination numbers can now be measured to within about 1% of the expected value (e.g., see the fit results for GeO$_2$ in Table 5.3, or the results for crystalline $\alpha$-TeO$_2$ [112] which give $n_{\text{TeO}} = 3.95(3)$, compared to the expected value of four), but in less favourable cases the accuracy will not be as good as this, for example if the sample contains any hydrogen. As illustrated by the small errors on the bond lengths in Table 5.3, the interatomic distances in a sample can be measured very accurately, especially if their distribution is symmetric, as would be obtained if the distribution of static distances is very narrow. (In fact, the bond lengths obtained from the neutron correlation function are a true measure of the bond lengths in a material, because the effects of correlated motion are treated correctly. This is in contrast to standard crystallographic methods, which do not allow for correlated atomic motion, and hence sometimes underestimate bond lengths [113]).

It follows from the discussion of the previous paragraph that it is important not to rely solely on measured coordination number to determine the coordination polyhedron, but also to consider the longer interatomic distances in the polyhedra (i.e., X–X). The $r_{\text{XX}}/r_{\text{AX}}$ ratio (or the X–A–X bond angle) are very important signatures of the basic structural units in the glass. For example, if $r_{\text{XX}}/r_{\text{AX}}$ is close to 1.6330 (implying a bond angle close to 109.47°), then this is strong evidence that the basic structural unit is a tetrahedron, which is the most common unit in network glasses.

Table 5.5 gives the structural properties of some simple coordination polyhedra with coordination numbers of six or less, since these are relevant for glass forming cations in network glasses. These structural units are also shown in Figure 5.32. All of the values in Table 5.5 are given for a regular, undistorted unit, in which all A–X distances are the same, and all equivalent pairs of X atoms have the same separation, $r_{\text{XX}}$ (for the square pyramid the values are based on a reasonable angle value, $\beta\sim 10^\circ$). If the units are not distorted, then the bond angle $\theta$ is given by
\[
\theta = 2 \sin^{-1} \left( \frac{r_{XX}}{2r_{AX}} \right), \tag{5.67}
\]

and if the atoms are considered to be spheres in contact then their radius ratio is

\[
\frac{r_A}{r_X} = \frac{2r_{AX}}{r_{XX}} - 1. \tag{5.68}
\]

**Table 5.5** Structural properties of coordination polyhedra in network glasses (see Figure 5.32).

<table>
<thead>
<tr>
<th>Unit</th>
<th>Coordination number, (n_{AX})</th>
<th>Coordination distance ratio(s), (r_{XX}/r_{AX})</th>
<th>Radius ratio, (r_A/r_X)</th>
<th>Bond angle(s), X-Å-X</th>
<th>Example(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triangle AX(_3)</td>
<td>3</td>
<td>1.7321</td>
<td>0.1547</td>
<td>120°</td>
<td>B(_2)O(_3) [12]</td>
</tr>
<tr>
<td>Trigonal pyramid AX(_3)</td>
<td>3</td>
<td>2\sin(\theta/2)</td>
<td>((1/\sin(\theta/2))-1)</td>
<td>(\theta)</td>
<td>As(_2)O(_3) [118], tellurites [119]</td>
</tr>
<tr>
<td>Tetrahedron AX(_4)</td>
<td>4</td>
<td>1.6330</td>
<td>0.2247</td>
<td>109.47°</td>
<td>Silicates [120], GeO(_2) [16], GeSe(_2) [84], GeS(_2) [121], phosphates [43], aluminates [122], gallates [123]</td>
</tr>
<tr>
<td>Disphenoid AX(_4)</td>
<td>4</td>
<td>1.4142, 2.0</td>
<td>0.4142</td>
<td>90°, 180°</td>
<td>Tellurites [124] [125]</td>
</tr>
<tr>
<td>Trigonal bipyramid AX(_5)</td>
<td>5</td>
<td>1.7321, 1.4142</td>
<td>0.1547, 0.4142</td>
<td>90°, 120°, 180°</td>
<td>Germanates [16]</td>
</tr>
<tr>
<td>Square pyramid-based AX(_5)</td>
<td>5</td>
<td>planar ~1.4, 2.0 apical ~1.5</td>
<td>planar ~0.43 apical ~0.31</td>
<td>planar ~90°, 160° apical ~100°</td>
<td>Ti in K(_2)O·TiO(_2)·2SiO(_2) [114]</td>
</tr>
<tr>
<td>Octahedron AX(_6)</td>
<td>6</td>
<td>1.4142, 2.0</td>
<td>0.4142</td>
<td>90°, 180°</td>
<td>Ca in 48CaO·49SiO(_2)·3Al(_2)O(_3) [82], germanophosphates [126]</td>
</tr>
</tbody>
</table>
Important examples of coordination polyhedra for glasses. (a) AX$_3$ triangle; (b) AX$_3$ trigonal pyramid; (c) AX$_4$ tetrahedron; (d) AX$_4$ disphenoid; (e) AX$_5$ trigonal bipyramid; (f) AX$_5$ square pyramid-based unit; (g) AX$_6$ octahedron; (h) AX$_6$ trigonal prism; (i) AX$_8$ Archimedean antiprism; (j) AX$_{12}$ icosahedron.

The assumptions of equal A–X distances and equal equivalent X–X distances are likely to be least good for the square pyramid-based AX$_5$ unit, for which it is highly likely that the apical A–X distance will be markedly different from the other bond lengths. For example, in K$_2$O·TiO$_2$·2SiO$_2$ [114] Ti occurs in TiO$_5$ square pyramid units with four bridging Ti–O bonds of length 1.96 Å to oxygens in the plane, and a non-bridging titanyl Ti=O bond of length 1.65 Å to an apical oxygen. Similarly, the presence of terminal oxygens in P$_2$O$_5$ and phosphate glasses leads to relatively large distortions of the PO$_4$ units from the geometry of an ideal tetrahedron [44]. Also, in AX$_6$ octahedra there is likely to be a difference between equatorial and axial A–X bond lengths due to the Jahn–Teller effect. Similarly, there is a pronounced difference between the equatorial and axial Te–O bond lengths in a TeO$_4$ disphenoid [112]. Nevertheless, despite the distortions of the units that occur in many materials, it is still a useful starting point to consider the ratio of distances (or the bond angle) as an important stage in identifying the coordination and geometry around the atoms in a glass.

For amorphous metals and for larger modifier cations in network glasses, polyhedra with larger coordination numbers than those given in Table 5.5 are usually appropriate (e.g., trigonal prism, Archimedean antiprism, icosahedron—see Figure 5.32) [115–117].

### 5.4.8.4 Comparison with Crystalline Structures

Glasses are structurally different from crystals (see sections 4.5.1 and 4.8.1). However, the same interatomic potentials (or bonding interactions) occur between atoms, regardless of
whether they are in a glass or in a crystalline solid, and therefore the local structure in a relevant crystal can provide a useful indication of the local structure in a glass. Nevertheless, sometimes there are important structural differences between glasses and crystals; for example, B₂O₃ glass contains a large proportion of highly planar B₃O₆ boroxol groups, but these superstructural units are not found in the crystalline forms of B₂O₃ [12]. Therefore, ND results on a glass should be compared critically with related crystals, rather than simply assuming that the local structure is exactly the same. For example, the addition of modifier to GeO₂ usually leads to crystal phases in which there are octahedrally coordinated germanium atoms, but there is evidence that in the corresponding glasses the higher coordination may be more uniformly distributed due to the formation of 5-coordinated germanium atoms [16].

For a full comparison of ND results for a glass with a crystal structure, it is essential to simulate Tᴺ(r) for the crystal structure [127], taking into account both the real-space resolution of the measurement, and the broadening effect of atomic motion. The effect of real-space resolution is included in the simulation by convoluting the ideal correlation function of the crystal (i.e., the correlation function calculated from the crystallographic positions of the atoms) with the resolution function appropriate to the experimental measurement. This resolution function depends on the modification function, and in particular the value of Q_max used in the Fourier transformation of the experimental data (see Section 5.4.2.2). The effect of thermal motions of the atoms is included in the simulation by convoluting the ideal partial correlation functions of the crystal with a Gaussian whose standard deviation is \( \langle u^2 \rangle^{1/2} \), the RMS variation in distance between a pair of atoms of types \( l \) and \( l' \). Due to the effects of correlated motion, the thermal width \( \langle u^2 \rangle^{1/2} \) is a function of distance, \( r \), with smaller values for short distances [15]. For example, a reasonable simulation of the correlation function of the quartz form of GeO₂ can be obtained with a thermal of 0.040 Å for Ge–O bonds, and 0.100 Å for all longer distances between Ge and O atoms.

It is an intricate procedure to simulate the correlation function of a crystal, and a computer program, XTAL, is available on the internet for this purpose [128, 129]. Examples of the use of this program are shown in Figure 5.31 and Figure 5.33b and c.
Figure 5.33 The total neutron correlation function, $T^N(r)$, of crystalline $U_4O_9$. (a) The experimental correlation function, $T_{\text{exp}}(r)$, compared with the U–O and U–U contributions, $T_{\text{Conr}}(r)$, as determined by EXAFS [163]. (b) The experimental correlation function, compared with the total neutron correlation function, $T_{\text{XTAL}}(r)$, simulated from the crystallographically determined structure of $U_4O_9$ [160]. (c) The experimental correlation function, compared with the partial components of $T_{\text{XTAL}}(r)$ [160].

5.4.8.5 The First Sharp Diffraction Peak

The peak in the diffraction pattern of a glass with the smallest $Q$-value is usually the sharpest peak (e.g., see Figure 5.11 or 5.13), and this so-called first sharp diffraction peak (FSDP) has attracted a great deal of attention [130]. Since the FSDP occurs at the lowest $Q$-value of any diffraction peak, it relates to the longest “periodicity” in the glass structure. Furthermore, if the first peak is the sharpest peak, then it is also the most slowly decaying correlation in real space. Thus, the FSDP relates to the longest range order that exists in the glass (in the absence of microstructure, which gives rise to small angle scattering), and this is why it has received
special attention, as key evidence for intermediate range order (IRO). Furthermore, the FSDP has physical properties (e.g., temperature-dependence) that are anomalous, and similar in different glass systems, which some workers interpret as evidence of a universal phenomenon.

Wright has shown that the low $Q$ side of the FSDP is well described by a Lorentzian, which provides a convenient form with which to fit the peak and to determine its position, $Q_1$, width, and height [101]. There have been many phenomenological studies of the way in which the properties of the FSDP depend on other parameters, such as composition, pressure, etc., but these have shed little light on its origin. There is a longstanding interpretation of the FSDP as arising from crystalline-like layers in the glass structure [131, 132], such that its position is $Q_1 \approx 2\pi/L$, where $L$ is the inter-layer spacing. More recently a view has emerged which is more consistent with the non-crystalline structure of glass, in which the FSDP results from the periodicity arising from the boundaries between a succession of the cages which comprise the structure of a three-dimensional covalent network [133]. Alternatively, Elliott [134] has interpreted the FSDP as arising from the arrangement of the voids in the network structure, but this is essentially equivalent to the cage interpretation, since it is the contrast between the voids and their boundaries that gives rise to the FSDP (as for small angle scattering—see Section 5.4.5.2).

5.4.9 Modeling

The clearest information on a glass that can be obtained by ND concerns the short range order (SRO). The interatomic distances and coordination numbers derived from ND are potentially more accurate than for any other experimental technique, and much of this chapter describes the means by which they may be determined reliably, so that the coordination polyhedra can be investigated. Nevertheless, the way in which the structural units connect together to form the extended structure of the glass (i.e., the intermediate range order, IRO) is also of considerable interest. However, as the interatomic distance, $r$, increases, the peaks in the correlation function become closer together, and their thermal widths become larger because there is less correlation between the atomic motions [15]. Hence there is increasing overlap of the peaks at higher $r$, with the result that ND is sensitive to IRO in a more subtle way than for SRO, and it is necessary to employ modeling techniques to make progress with the investigation of IRO.

The ideal modeling solution would be to determine the three-dimensional position of every atom relative to the other atoms in the sample. In principle, this is feasible when performing single-crystal diffraction because information is obtained as a function of the momentum transfer vector, $Q$. However, glasses are usually isotropic, or almost isotropic, with the result that the measured diffraction pattern is condensed down to a function of a single variable, the magnitude of the momentum transfer, $Q = |Q|$; that is, the measured distinct scattering, $i(Q)$, is an average over all possible orientations of the sample relative to the incident neutron beam. This results in a loss of information so that it is not possible to deduce the positions of all the atoms in the sample. Conversely, there may be an enormous number of different sets of atomic coordinates which would all give rise to the same observed distinct scattering, $i(Q)$. This situation is called the uniqueness problem. For a structural model of a glass to be correct it is
necessary that it agrees with the observed diffraction pattern. However, if a model is consistent with the diffraction pattern, this is not proof that the model is right—it is merely evidence that the model is not wrong. Thus, unique structure determination is not possible.

The random network model for the structure of covalent glasses was proposed by Zachariasen in 1932 [102], and this provides a description of the SRO in a glass in terms of structural units which connect together with a degree of randomness (such as a distribution of bond angles and dihedral angles). Originally there was some doubt whether it was possible to form an extended three-dimensional structure on the basis of the model, and this concern was allayed by the early ball-and-stick modeling technique. A ball-and-stick model would be constructed by hand, and then photographed from more than one direction so that the coordinates of the atoms could be digitized [135, 136]. A similar approach was adopted for metallic glasses, in which a dense random packing of hard spheres was modeled by filling a bag with ball bearings [137]. The correlation functions of these models showed reasonable agreement with experiment. However, the method is laborious, and has largely been superseded by computer modeling methods. It is worth noting that most computer modeling methods make use of periodic boundary conditions, and hence the model needs to be sufficiently large that its crystalline nature is not a problem; according to the minimum image convention, this may be achieved if the size of the unit cell is twice the longest significant distance in the glass [138].

Recent years have seen the development of techniques for obtaining structural models of disordered materials in which a computer programme is used to move atoms around inside a box so as to optimize the agreement with diffraction data. The most widespread of these is the reverse Monte Carlo (RMC) method in which the atoms are moved according to a variant of the standard Monte Carlo algorithm [138]; a move which improves agreement with diffraction data is accepted, but if the move worsens the agreement then it may be rejected or accepted according to a probability factor [139, 140]. Thus the aim is to produce a model for which the deviation from experiment has been minimized (whereas for the standard Monte Carlo method it is the energy that is minimized). For a large number of atoms, \( N \) (say \( N \approx 1000 \) or more), there are \( 3N \) parameters; with such a large number of parameters a very close fit to the diffraction data can potentially be obtained. According to the “uniqueness problem” there are many models which may be produced by this method, and in fact it tends to produce the most disordered model that is consistent with the diffraction data (and constraints) [141]. Thus early RMC models of glass were not consistent with what was already known about glass structure; for example, for SiO\(_2\) glass, which is well described as a random network of corner-sharing SiO\(_4\) tetrahedra, many of the silicon atoms were 3- or 5-coordinated, or had a 4-coordinated coordination polyhedron which was not tetrahedral [142].

In response to the problems with early RMC models, the method was developed to include constraints; for example, there can be restrictions on the distances between a pair of atom types, or restrictions on the coordination numbers for a pair of atom types [143]. There have also been other variations on the RMC method, such as the inclusion of a constraint based on BV [144] (see Section 4.8.2), which are intended to produce more reasonable models. A more recent RMC variation, which appears promising, minimizes the difference from diffraction for
each of the individual atomic sites (whereas the standard RMC method minimizes the difference from diffraction for the average atomic site) [145]. With the addition of constraints, the RMC method has been able to produce structural models which are consistent with diffraction data and are consistent with what is already known about the nature of bonding in materials. However, the danger introduced by the use of constraints is that the RMC simulation can no longer sample configurations with different IRO (e.g., different ring statistics) to the starting model; RMC is then a means of refining a starting model so that it has better agreement with experiment, rather than a means of finding a fundamentally new model [140, 146].

A rather different method of modeling glass structure is provided by molecular dynamics (MD) simulations [147, 148]. This involves filling a box with atoms, and determining their trajectories by solving Newton's equations of motion, using a particular set of assumed potentials to describe the interactions between the various pairs of atoms. Usually the system is simulated at a very high initial temperature so that it is liquid, and then the temperature is reduced to mimic the quenching of a glass; an inherent difficulty with the technique (due to computer limitations) is that the melt is quenched at a very high rate ($\sim 10^{12} \text{ K/s}$), which is much faster than for the quenching of real glasses ($\sim 1 - 10^6 \text{ K/s}$). A common problem with the use of MD to simulate glass is that the comparison with experiment is cursory: one reason for this is that it is difficult to know how to change the input potential to improve the agreement. However, it is essential that models are compared quantitatively with experiment to assess their worth [149]. A promising new development is thus the use of RMC to refine an MD model so that it agrees well with diffraction data [150]. The DL_POLY package is perhaps the most widely used MD software for glass simulation, and is readily available on the internet [151]. DL_POLY performs classical MD simulations which use empirical potentials, but a more recent development has been \textit{ab initio} MD, which calculates the forces between the atoms using quantum mechanics—a parameter-free, first-principles approach [152, 153].

In the early days of RMC, the debate about the legitimacy of the method was almost theological in character [154]. One criticism of the method is that it is unphysical, and in particular that it does not involve the use of a potential. The aim of modeling a glass structure is to produce a model that is consistent with all the available experimental data, by whatever means the model is produced; in this author's opinion, it is ironic that RMC was criticized for producing models without the use of a potential, when those models agree well with experiment, whereas MD modeling (which does use a potential) is often unable to closely reproduce diffraction data. Nevertheless, this criticism was recently addressed by the development of the empirical potential structure refinement (EPSR) modeling technique [155]. This method is similar to RMC, but with the important difference that the atoms are moved around in the box by use of the Monte Carlo method, using potentials to describe the interatomic interactions, and then the potentials are adjusted to optimize the agreement with diffraction data. Significantly, there is little requirement for constraints and the structural model obtained is not dependent on the assumptions used to form the initial model. Nevertheless, the method is more successful if XRD data can be used, in addition to ND data, and an excellent example of this has recently been given in a study of 80PbO.20SiO$_2$ glass by Alderman et al. [87].
A striking example of a successful result from the use of RMC has already been mentioned in Section 5.4.7.2. The structure of several RE metaphosphate glasses was simulated by RMC, using experimental data from both ND and XRD [91]. At the same time a completely independent study used ND with a magnetic difference technique to isolate the Tb–Tb correlation function in a terbium metaphosphate glass [90], and it was found to show a remarkable similarity to the RE–RE partial function from the RMC study (see Figure 5.29). The results of a diffraction experiment depend on the distances between pairs of atoms in the sample, and so they can be used to determine a two-body correlation function. Thus RMC simulation of diffraction data has the potential to be able to extract two-body correlations well, as shown by the example of RE–RE correlations in metaphosphate glasses. However, the IRO in a glass (e.g., the distribution of rings) is characterized in terms of many-body correlations, which are not measured directly by diffraction. Thus diffraction is sensitive to IRO in an indirect way—essentially information about IRO is built up from diffraction results by a process of “triangulation” of the various pairwise distances (as for the determination of coordination polyhedra, see Section 5.4.8.3). For example, as yet, RMC [156, 157] and EPSR [158] have been unable to reliably extract information on the presence of boroxol rings in B₂O₃ glass, in contrast with what is known from other experimental techniques, such as Raman scattering and NMR [12].

5.4.10 The PDF Method

The analysis of diffraction data by Fourier transformation to a real-space correlation function was first used in a study of a crystalline form of sulphur in 1934 [159], but for the next few decades the approach was developed almost entirely for the study of non-crystalline samples (glasses and liquids), whilst almost all diffraction studies of crystalline materials used reciprocal-space analysis methods, such as Rietveld refinement [73]. However, in recent years the real-space correlation function method has increasingly been applied to the study of crystal structures, in which case the method is often called the PDF (pair distribution function) method [19, 20]; the function which is called the PDF in such studies is usually the differential correlation function, \( D^N(r) \), introduced above in Eq. 5.34. The reason for using \( D^N(r) \), rather than \( T^N(r) \) which is generally preferred for glasses, is that the differential correlation function is better suited to the display of the much greater order at longer range in crystals (for example, see Figure 5.31). The PDF method has proved very useful for structural investigations of disordered crystals (i.e., crystals in which the contents of the unit cells are not all exactly the same, and for which the local structure may differ from the average structure), and sometimes it is even useful for ordered crystals. Although “the PDF method” essentially concerns the structure of crystalline materials, there is currently increasing overlap between the study of the structure of non-crystalline materials and of disordered crystalline materials, and thus it is useful for a glass scientist to be aware of the method. A brief illustration of the PDF method is given here using crystalline U₄O₉ as an example of its use [160], because this is of at least some passing interest to glass scientists due to the proposed presence of a “glassy part” in the structure, and the use of X-ray spectroscopy.
Crystalline UO$_2$ has the calcium fluorite structure, in which each uranium atom has eight oxygen neighbors at a distance 2.368 Å, whilst the oxygen atoms are separated by 2.734 Å [160]. By means of a modification of the UO$_2$ structure, a larger concentration of oxygen can be incorporated, resulting in the formation of U$_4$O$_9$. The crystal structure of U$_4$O$_9$ has been determined by single-crystal ND [161, 163], and the oxygens are arranged around the center of a vacant cube with the geometry of a cuboctahedron. The unit cell of U$_4$O$_9$ is relatively large and complex, containing 828 atoms on average, with mean coordination number and bond length $n_{\text{UO}} = 8.328$ and $r_{\text{UO}} = 2.354$ Å, respectively. However, a radically different structural view emerged on the basis of a XAFS study, using the uranium L$_{\text{III}}$ edge [163]. The results were interpreted as showing first that there is separation into two phases, one with the UO$_2$ structure, and one which is glassy and is spectroscopically invisible (i.e., with a distribution of U–O bond lengths which is too broad to be observed by XAFS), and secondly that there are short oxo bonds (i.e., terminal U=O bonds) in the material. Figure 5.33 shows the total neutron correlation function, $T_{\exp}(r)$, which was measured for a sample of U$_4$O$_9$ [160]. The first two peaks at around 2.33 Å and 2.66 Å arise from U–O and O–O correlations, respectively. It is important to note that ND is sensitive to all atomic pairs in the sample, and there is no possibility of a portion of the sample that is spectroscopically invisible. Figure 5.33a also shows a simulation of the total neutron correlation function, $T_{\text{Conf}}(r)$, calculated according to the results of the XAFS study [163]. Firstly, it should be noted that whereas the XAFS results give rise to a peak at 1.76 Å due to oxo bonds, there is no such peak in the ND measurement. Figure 5.33b shows a simulation of the total neutron correlation function, $T_{\text{XTAL}}(r)$, calculated from the known crystal structure of U$_4$O$_9$ using the XTAL program [128, 129], and Figure 5.33c shows the three partial contributions to the simulation. This simulation gives a fairly good account of the observed $T_{\exp}(r)$; there are small differences, which may arise because the local structure is not exactly the same as the average structure. Nevertheless, the similarity of peak areas shows that the observed $T_{\exp}(r)$ is consistent with a coordination number, $n_{\text{UO}}$, similar to that of the crystallographic result. The XAFS results are sensitive to U–O and U–U correlations, but not O–O correlations. In practice, this means that the XAFS simulation, $T_{\text{Conf}}(r)$, in Figure 5.33a should give a full account of the experimental correlation function only in the region of the U–O peak at around 2.33 Å. However, the XAFS results underestimate the area under $T_{\exp}(r)$ in this region by a factor of order two, that is, the XAFS results severely underestimate the U–O coordination number. Thus the ND results [160] do not support the structural conclusions based on the XAFS results [163]; no evidence was found for oxo bonds or a glassy component of the structure in U$_4$O$_9$.

An important reason why XAFS studies can give highly inaccurate coordination numbers is that there is a very high correlation between the coordination number and the variation in bond length. This high correlation arises because of the lack of information in the low momentum transfer region for XAFS results. For the simulation shown in Figures 5.33b and c, the thermal variation in interatomic distances was adjusted empirically to optimize the agreement with the
experimental measurement, leading to $\langle u_{U-U}^2 \rangle^{1/2} = \langle u_{O-O}^2 \rangle^{1/2} = 0.1 \text{ Å}$ and $\langle u_{U-O}^2 \rangle^{1/2} = 0.13 \text{ Å}$ [160]. These values are in contrast to the Debye–Waller factors from the XAFS experiment which are typically 0.045 Å [163]. Thus the probable reason for the highly inaccurate coordination numbers from the XAFS study is that a poor value was chosen for the Debye–Waller factor, and indeed an earlier XAFS study [164] of $U_4O_9$ used Debye–Waller factors in closer agreement with those obtained from the crystallographic simulation, $T_{XTAL}(r)$, and also gave coordination numbers which are closer to the expected values.

Considerable structural insight can be gained by making a detailed comparison of a measured correlation function for a glass with the simulation for a related crystal structure. The model correlation function, $T_{XTAL}(r)$, shown in Figure 5.33b was calculated using the program XTAL [128] which is available on the internet [129] and can be used to simulate neutron or X-ray correlation functions for either crystalline or non-crystalline model structures. For PDF studies of crystalline materials other programs are also available. These include the program PDFfit [165], which essentially performs a structural refinement in real space (although the crystallographic symmetry is not maintained), and the program RMCprofile [166], which may be used to perform an RMC simulation for a crystalline structure.

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**FURTHER READING**

Further information of general relevance to neutron diffraction on glasses may be found in the following references.


**Notes**

1Accelerator-based neutron sources which are quasi-steady-state or intensity-modulated also exist. Furthermore pulsed neutrons have also been produced in Russia by using a pulsed reactor.

2Also the study of crystalline structures has the huge advantage that it is only necessary to determine the coordinates of the atoms in one unit cell, which is then reproduced by translations to build up the full three-dimensional structure.
6
X-RAY DIFFRACTION FROM GLASS

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6.1 INTRODUCTION

For a proper understanding of structure-property relations in any material, a detailed knowledge is needed at the atomic level. X-ray diffraction from crystalline powdered materials exhibits sharp Bragg peaks associated with long-range ordering, which may be accurately indexed with a lattice, positional, and thermal displacement parameters corresponding to a well-defined space group. Furthermore, single crystal diffraction experiments in three dimensions allow absolute structure determination. Yet glass quenched from the liquid state has an inherently disordered structure on both intermediate- and long-range length scales, making absolute structural determination impossible, although the local bonding characterizing the short-range ordering is often pronounced. Consequently, the most information that can be reliably extracted currently from an X-ray experiment from an isotropic glass is a one-dimensional pair distribution function from which the three-dimensional structure cannot be directly generated. Progress in the case of amorphous structures made using measurements with coherent X-ray beams may overcome these limitations (to some extent) in the future. Nonetheless, depending on the composition and fictive temperature of the glass, the structure itself may vary significantly. The degree of disorder and structural variability lends itself to ambiguity in structure determination, and generally several techniques are required to obtain a clear picture of the structure of a particular glass. In this sense, glasses are by definition “polyamorphic” since the structure depends on their thermal history [1]. However, this term has come to be associated with a first-order phase transition in recent years, despite the fact that theoretically this can only occur in the liquid state [2]. It is also the reason that for most X-ray measurements on glasses, computer modeling and simulation play a vital role in interpreting and understanding the glass structure distribution function at the atomic level.

In 1932, Zachariasen proposed the random network theory of glasses on the basis that the chemical bonding rules are likely to be the same as for crystals [3]. An empirical observation for conventional binary oxide glasses led to a set of four rules: (i) no oxygen atom may be linked to more than two cations; (ii) the cation coordination number should be small, that is 3 or 4; (iii) oxygen polyhedra preferably share corners, rather than edges or faces; and (iv) for 3D networks, at least three corners must be shared. Zachariasen suggested that all four rules should be satisfied for glass formation to occur since low coordination numbers and corner sharing polyhedra are more likely to result in open, low density variable structures. Violation of one of these criteria does not necessarily prevent glass formation but simply means it is
energetically less favorable, and such structures may occur for glasses produced from highly non-equilibrium conditions. Wright [4] has subsequently modified this theory by omitting the word “random”, since steric hindrance usually limits the interconnection of adjacent polyhedra to a fixed range of torsion angles. For glasses with three or more components, the cations are often classified as network formers or modifiers based on their field strength, although this definition can become unclear for intermediates.

For covalently bonded chalcogenide glasses, the structures are usually more complex than for oxides since homopolar bonding between like atoms may occur. In contrast to a chemically ordered system which contains the maximum number of bonds between unlike atoms, like-like bonds allow a greater variability in the range of entities which can be formed. Nonetheless, the number of bonds is generally governed by the 8-n rule [6]. For metallic glasses that are wholly or in part ioni
cally bonded, the relative sizes of the atoms largely determine the polyhedral packing. Small molecule organic glass formers often interact via van der Waals forces but may have polarized structures due to intermolecular hydrogen bonding or changes in molecular conformation, leading to variable or different orientational correlations than observed in the crystalline state. Due to the complex disorder associated with larger organic molecules, glassy polymers often do not fully crystallize, and it becomes important to try and separate the winding intramolecular chain structure from the intermolecular chain interactions.

The X-ray Pair Distribution Function (PDF) technique was first pioneered by Warren [7, 8] in the 1930s using X-rays to study noncrystalline forms of matter. Narten and colleagues made considerable progress in the 1970s by carefully refining the data analysis techniques associated with the X-ray pair distribution function method, using conventional X-ray sources [9, 10]. In the meantime, the PDF technique had gained much popularity within the field of neutron scattering [11], which was expanded further in the 1980s, with the development of high flux spallation neutron sources, providing access to high momentum transfers. A similar leap in instrumentation occurred for X-ray diffraction with the development of the high energy X-ray technique (commonly defined as energies in excess of 60 keV) in the mid-1990s. Based on a γ-ray diffraction technique, the breakthrough was made by Poulsen and Neuhefeind [12], when they first used synchrotron radiation of 100 keV to study the structure of glass out to high momentum transfers (Q > 20 Å⁻¹). The high energy X-ray PDF technique became widespread in the last decade and current synchrotron beamlines that routinely perform measurements on glasses include those at the Advanced Photon Source (USA), SPring-8 (Japan), HASYLAB (Germany), and the European Synchrotron Radiation Facility (France).

The measured X-ray pair distribution function represents the probability of finding an atom at a distance r away from a central atom. The coordination number is therefore determined by the number of atoms of type j which are located around an atom of type i within a specified shell given by the radii r and r + dr. It has been proposed that the distribution function for an amorphous solid can be quantified in terms of four ranges of order [4] (see Figure 6.2): (i) The structural unit (polyhedra) identified by the average bond length r₁, coordination number nᵢⱼ and bond angle α; (ii) the relative orientation of adjacent units described by the connectivity, bond angle β and torsion angle γ; (iii) the intermediate range order, which can be described by
the ring size distribution to identify the network topology and dimensionality; and (iv) longer range density fluctuations. It should be understood that the X-ray structure factor and associated X-ray pair distribution function represent an average of the interactions within the bulk glass and as such provide an overview of the structure over a range of distances. In addition, it should be realized that ranges (i), (ii), and (iii) are dependent upon one another and are therefore correlated, since the coordination and regularity of the short range order will affect the connectivity and overall topology. Consequently, the PDF places stringent constraints on any atomistic model of the glass in question.

**Figure 6.1** Zachariasen–Wright [4] network model of a glass in which the structure is “random” within the steric packing constraints of the local units. The dashed lines of periodicity \( Q_1 \) arise from correlations between rings, which comprise the glassy network. \( Q_2 \) represents the length scale of the bulk connectivity of the network. The black circles represent the modifier atoms which break up the connectivity of the network, often in clusters for oxide glasses [5], and the shaded regions represent different ring sizes.
**Figure 6.2** Shows three ranges of order, from the local short range unit, to the packing of adjacent tetrahedra and associated torsion angles, to the intermediate range structures over longer distances (see text).

The X-ray PDF method is most powerful when interpreted along with information from other methods, both experimental (e.g., neutron diffraction, anomalous X-ray diffraction, EXAFs, NMR) as well as computational (e.g., Monte Carlo, molecular dynamics, density functional theory.). Most notably, neutron diffraction and anomalous X-ray diffraction provide a means of experimentally extracting partial structure factor information by direct combination with X-ray diffraction data.

### 6.2 BACKGROUND/THEORY

X-ray scattering theory has been covered comprehensively in many excellent texts and for brevity the readers will be referred to the literature [13, 14]. Rather this section will concentrate on the extraction of the pair distribution function from the measured scattered X-ray intensity. An important difference between X-ray and neutron diffraction is that X-rays
essentially measure an electron distribution function rather than a nuclear distribution function. For elastic scattering, the magnitude of the momentum transfer $Q$ for a monochromatic photon beam of wavelength $\lambda$, at scattering angle $2\theta$ is still given by

$$Q = \frac{4\pi}{\lambda} \sin \theta$$  \hspace{1cm} (6.1)

There are many different formalisms for the total structure factor $S_X(Q)$, which have been summarized by Keen [15]. Experimentally, they all derive from the measured elastic contribution of the scattered intensity $I_X(Q)$ that represents the electron-electron interactions. To extract the elastic scattering, the self-scattering of the atoms or molecules needs to be subtracted from $I_X(Q)$, given by $f^2(Q) + C(Q)$ where $f^2(Q)$ represents the materials' electron density distribution and $C(Q)$ is the Compton scattering contribution [13–15].

X-ray form factors represent the scattering from the electron cloud and their amplitude therefore increases with atomic number $Z$. Practically the decrease in $f(Q)$ with increasing $Q$ limits the maximum value of $Q$ that it is obtainable with X-rays. As can be seen in Figure 6.3, the relative magnitude of the $Q$-dependence for heavier elements is also significantly higher at larger $Q$-values. At wavelengths around which specific atoms strongly absorb (absorption edges) the X-ray scattering factor changes due to anomalous dispersion, changing the magnitude and phase of the photon collision. The anomalous X-ray scattering technique can be used to obtain element-specific partial structure factor information [16], even at high energies (extending the maximum accessible high $Q$ limit) although the contrast is much lower. Electron form factors can be calculated from the X-ray form factors using the Mott–Bethe formula [17] and primarily differ only in the low-$Q$ region.
Figure 6.3 The free atom form factors for the elements H, O, Ge and Pb normalized to their number of electrons at $Q = 0$ [18]. The insert shows a zoomed in region of the atomic form factor for H using the independent atom approximation (solid line) compared to the modified atomic form factor for H obtained using Eq. 6.2 with $z_\alpha = 0.5$ corresponding to the electron residing halfway along the bond and $\delta = 2.0$ obtained from fitting to the quantum mechanical calculations of Wang et al. for H$_2$O [19].

The magnitude in electron units of the X-ray form factor for independent (free) atoms at $f(Q = 0)$ is $Z$. However, the non-spherical shape of the electron cloud in liquids or glasses with few electrons, such as hydrogenous or light element materials, requires a re-distribution of charge to be taken into account. This effects the shape of the $S(Q)$ at low $Q$-values, typically $Q \leq 1$ Å$^{-1}$. In the case of water, the spherical independent atom approximation form factors have been successfully modified to give the Modified Atomic Form Factor (MAFF) [20] using the equation,
where $Z$ is the fractional electron charge on the $\alpha$ atoms and it is required that $\sum_{\alpha} Z_{\alpha} = 0$ to conserve charge. Hydrogen-related correlations represent a worst-case scenario for extracting reasonable atom–atom bond lengths and coordination numbers from X-ray PDF data because the scattering electrons reside partway along the bond.

A direct Sine Fourier transformation of the X-ray intensity $I_X(Q)$ yields the electron distribution function, which contains information on the shape of the electron cloud surrounding the nucleus. In order to obtain a pseudo-atomic function, it is necessary to divide by a so-called “sharpening function”. The most common formalism [13–15] is to divide by the average scattering $f^2(Q)$,

$$S_X(Q) - 1 = \frac{I_X(Q) - \left( \sum_{i=1}^{n} f_i^2(Q) \right) - C(Q)}{f^2(Q)}$$

(6.3)

where $i$ and $j$ represent the different atomic species in the material. The average scattering is given by

$$f^2(Q) = \left[ \sum_{i,j=1}^{n} c_i f_i(Q) \right]^2$$

(6.4)

The measured $S_X(Q)$ is most commonly expressed using the Faber–Ziman formalism [21] as the sum of the X-ray weighted element-specific partial structure factors $S_{ij}(Q)$,

$$S_X(Q) - 1 = \left( \frac{\sum_{i,j} c_i c_j f_i(Q) f_j(Q) [S_{ij}(Q) - 1]}{f^2(Q)} \right)$$

(6.5)

It is worth reiterating that $S_X(Q)$ is a pseudo-nuclear function since it derives a nuclear function from a measurement of the electron density distribution. By definition, $S_X(Q)$ still tends to unity at high $Q$-values, and for homogeneous liquids, the normalized $I_X(Q)$ tends to the isothermal compressibility as $Q$ tends to zero. This behavior is described by the equation

$$I(Q \rightarrow 0) = \rho k_B T \chi_T Z$$

(6.6)

where $Z$ is the total number of electrons in a single molecule, $k_B$ is the Boltzmann constant, $T$ is the absolute temperature, and $\chi_T$ is the isothermal compressibility. For homogeneous glasses, this equation is generally valid at conditions corresponding to the glass transition temperature where the liquid structure is frozen in.

Theoretically the measured electron–electron function $I_X(Q) - \left( \sum_{i=1}^{n} f_i^2 Q \right) - C(Q)$ may be Fourier transformed into real space (provided a wide enough $Q$ range is measured) to give the
electron density distribution directly. However, in the large majority of cases, the pseudonuclear pair distribution function $G_X(r)$ is obtained via a Sine Fourier transformation of $S_X(Q)$ using

$$G_X(r) - 1 = \frac{1}{2\pi^2 r \rho} \int_{Q_{\min}}^{Q_{\max}} Q[S_X(Q) - 1]M(Q, \Delta)\sin(Qr)dQ \quad (6.7)$$

In Eq. 6.7 $Q_{\min}$ and $Q_{\max}$ represent the finite range in reciprocal space over which the X-ray data are measured and $\rho$ is the atomic (or molecular) number density in Å$^3$. Of these two limits, the $Q_{\max}$ often has the most noticeable effect on the Fourier transform. If the $S_X(Q)$ curve is not truncated at a node corresponding to unity, a step function is Fourier transformed into real space and large “ringing” oscillations are superimposed on the pair distribution function masking out structural features. Fourier noise can also be added to the transform if the curve does not oscillate evenly about 1.0. In addition, missing features between the measured $Q_{\min}$ and $Q = 0$ can lead to omitted long wavelength oscillations due to density fluctuations or particle sizes at high r-values in $G_X(r)$. A Lorch [22] or other modification function $M(Q, \delta)$ is often used to minimize the oscillations generated during the Fourier transform over a finite Q-range, where the parameter $\delta$ describes the average width in real space. Other commonly used real space representations [23] include the total pair distribution function, $T_X(r)$ which is useful for peak fitting for glassy spectra,

$$T_X(r) = 4\pi \rho r G_X(r) \quad (6.8)$$

The differential pair distribution function, $D(r)$, which removes the bulk density, emphasizes the longer r correlations,

$$D_X(r) = 4\pi \rho r [G_X(r) - 1] \quad (6.9)$$

Also, the radial distribution function $N_X(r)$ has a direct physical interpretation as the number of atoms that are present within the range $r$ and $r + dr$,

$$N_X(r) = 4\pi \rho r^2 G_X(r) \quad (6.10)$$

The Bhatia–Thornton formalism [24] is also sometimes used to provide information on the topology and chemical ordering in a liquid or a glass. For a binary system the Bhatia–Thornton representation is linked to the Faber–Ziman formulation using linear equations, which convert the element-specific partials to topological and chemical ordering partials (see [25] for a full description). These are the so called number–number (which describes the glass topology), concentration–concentration (which describes the chemical ordering), and the cross term number–concentration partial structure factors. The Bhatia–Thornton formalism has been successfully used to explore the extent of longer range correlations in real space known as “extended range ordering” in glass which relates to feint correlations persisting out to long distances, for example, $r \sim 60$ Å [25]. However, it should be noted that the magnitude of these oscillations show that the degree ordering only represents a very small fraction of the bulk
6.3 ANALYSIS OF DATA, EXTRACTION OF USEFUL INFORMATION

In this section, we first consider the differing origins of effects which can influence the accuracy of the extracted X-ray static structure factor and associated PDF, and how to assess them. These effects include those related to (i) the source (polarization, energy resolution and beam size); (ii) sample and environmental effects (container, attenuation, multiple scattering, fluorescence); and (iii) detector effects (geometrical arrangements, oblique incidence, detector efficiency, flat field, electronic dark currents). Many of these have been discussed in detail in the literature and can be found here [9, 13, 14, 27–30]. These corrections and the order they are applied must be considered carefully, together with the removal of the background scattering (air or vacuum plus any windows) and the composition-dependent Compton scattering contribution.

Beam polarization effects depend solely on the X-ray source [9, 13, 14]. For synchrotrons, the incident photons are almost completely polarized, such that corrections in the vertical plane are minimal [28]. For X-ray tube sources, an unpolarized beam factor needs to be taken into account when comparing measured intensities as a function of scattering angle $2\theta$. The energy resolution is ultimately limited by the quality of the monochromator and optics, but for the study of diffuse diffraction peaks in glasses for most powder diffractometers, this generally has a negligible effect on the quality of the data unless performing anomalous X-ray diffraction measurements. Similarly, X-ray beam sizes of $<0.5$ mm, when compared to the sample-to-detector distances of ca. 500 mm, are usually well below the limit for detecting significant peak broadening.

The sample-dependent absorption corrections to the scattered X-ray intensity $I_x(Q)$ from a liquid or glass can be reliably applied using the method of Paalman and Pings [31], by independently measuring the sample scattering in a vessel $I_{SV,0}$, the empty vessel $I_{V,0}$ and the background $B$,

$$I_x(Q) = K \left( \frac{I_{SV,0}^V - B}{A_{S,SV}^V} - \frac{A_{V,SV}^V (I_{V,0}^V - B)}{A_{S,SV}^V A_{V,V}^V} \right) - f^2(Q) M_{SV} - C(Q) \tag{6.11}$$

where the coefficient $A_{S,SV}$ represents the attenuation of the sample in the presence of the sample plus vessel, $A_{V,SV}$ the attenuation of the vessel in the presence of the sample plus vessel and $A_{V,V}$ the attenuation of the vessel in the presence of the vessel. For thin samples with few electrons, the ratio of multiple to single scattering [32] of the sample in the vessel $M_{SV}$ is negligible at high energies, so the second term in Eq. 6.1 can be discarded. However, at the energies used in conventional laboratory sources both absorption and multiple scattering effects can be significant and require geometry-dependent computational algorithms to
calculate their $Q$-dependence accurately since the volume of the sample probed varies with scattering angle. Low energy X-ray reflection geometry measurements may also be more sensitive by surface effects. In the case of X-ray fluorescence emitted from a material, the correction is usually approximated as a constant background to the measured signal. The incoherent Compton signal dominates the scattering at high $Q$-values and can be eliminated using an energy discriminating detector at high scattering angles provided the peak is sufficiently separated from the elastic scattering peak. However at low $Q$-values, there is overlap between the elastic and Compton scattering peaks, and the peak fitting of the energy spectrum at each $Q$-value is required in any case. For this reason, in most cases, the entire energy spectrum is measured and the element-specific calculated Compton cross sections are used instead. At high energy synchrotron sources, the Compton scattering contributions are subject to a relativistic quantum correction as described by the Klein-Nishina formula [13, 14]. $K$ is the normalization factor required to formalize $I_X(Q)$ to the number of electrons such that $S_X(Q)$ oscillates about unity at high $Q$-values.

Detector corrections can vary drastically depending upon the type and details of the detection mechanism used. For energy discriminating solid state detectors, bremsstrahlung background radiation can be minimized during the experiment but dead time effects need to be carefully considered if moderate to high intensity fluxes are used [12]. Accurate geometrical corrections are essential in any X-ray experiment, since different paths thorough absorbing filters, sample shapes, and detector elements can alter measured signal significantly. For 2D flat plate area detectors, which have been used in many of the example illustrations in this chapter, dark currents need to be regularly monitored for electronic drift throughout the experiment, and flat field experiments performed to obtain a detector gain map of different pixel efficiencies within the detector paneling [29]. In addition, oblique incidence corrections due to vastly different path lengths of hard X-rays at the edges of area detectors are required [33].

All corrections described above can be minimized to a fraction of one percent in state-of-the-art monochromatic high energy X-ray synchrotron sources, but cumulatively often result in overall accuracies of 1 or 2\% (at best) in $S_X(Q)$ [12, 29]. Moreover, it has been demonstrated that many of the $Q$-dependent corrections have similar shapes and are inter-dependent so tracking data analysis errors is often problematic [12]. The sample-dependent corrections often become much more difficult to calculate using lower energy X-ray tube sources and the overall accuracy is not as good as for synchrotron X-rays, but the detector efficiencies often improve at lower energies. The situation for energy dispersive X-ray diffraction is exacerbated since the myriad of corrections need to be performed over a wide range of energies, however, this technique has the advantage that measurements can be made very quickly mapping out large regions of phase (pressure or temperature) space.

With several $Q$-dependent corrections to the X-ray data, accurate normalization in absolute units can sometimes be problematic, although this becomes less of an issue when higher energy X-rays are used. This is because for hard X-rays (say, 60–120 keV) the measured data tend towards the number of electrons in the system corresponding to the dominant Compton scattering contribution at high $Q$. For good quality X-ray data, the Krogh-Moe/Norman
technique [35, 36] can be used, which employs sum rules to normalize the $S_X(Q)$ data for a given density using the low $r$ region, but this can become difficult for data containing a significant amount of systematic or statistical errors.

Ultimately there are consistency checks which can be applied to fully analyzed X-ray diffraction data, such as the isothermal compressibility limit at $Q = 0$ (described by Eq. 6.6 which usually corresponds to that of the liquid at $T_g$ for a glass). However, the quality of the experimental data can be most easily evaluated by the behavior of the Fourier transform at low $r$, below the first real peak in the pair distribution function. If the oscillations in this region are small compared to the magnitude of the first real peak and alternate about the theoretical limit (shown in Figure 6.6), the data can be assessed as being of good quality. However, it has been pointed out that there are many ways to disguise poorer quality data [37], including omitting the data in this region in the published figure.

**Figure 6.4** Measured X-ray intensity for GeSe$_2$ glass normalized to the sum of the constituent atomic form factors squared plus the Compton scattering (dashed line) at high $Q$. The insert shows the normalization in the high-Q region.
Figure 6.5 The measured X-ray structure factor for GeSe$_2$ glass, multiplied by $Q$, to illustrate the extent of the oscillations at high momentum transfers.
Different representations of the X-ray pair distribution function for GeSe₂ glass; $G_X(r)$ oscillating about unity at high $r$ and zero at low $r$, $T_X(r)$ oscillating about zero at low $r$ and $4\pi\rho r$ at high $r$, $D_X(r)$ oscillating about $-4\pi\rho r$ at low $r$ and zero at high $r$, and $N_X(r)$ oscillating about zero at low $r$ and $4\pi\rho r^2$ at high $r$.

Secondly, in this section, we consider the information that can be extracted from the measured $S_X(Q)$ and $G_X(r)$ functions. The first sharp diffraction peak (FSDP) at position $Q_1$ in the X-ray (or neutron) diffraction $S(Q)$ is associated with the existence of intermediate or medium range order in glass with a periodicity of $2\pi/Q_1$ (as illustrated in Figure 6.1, although its origin is still controversial) [4, 38, 39]. Medium range order has been loosely defined as covering the region $5–20$ Å [38, 39]. The FSDP is often fitted with a Lorentzian or Gaussian peak in the diffraction data to accurately extract $Q_1$ as well as the peak width, which is related to the coherence of the structural units giving rise to it, as described by the Scherrer equation. For tetrahedral network glasses, the $Q_2$ peak has been associated with chemical ordering within the bulk glass [25]. However, it is worth noting that in reciprocal space the highest frequency Fourier components decay the most rapidly, and for a glass the peaks invariably become broader with increasing $Q$, until only the one arising from the sharpest real space peak remains
(which is often related to the first interatomic distance in real space). Although the $G_X(r)$ function is often used to extract bond distances and local coordination numbers, the appropriate X-ray weighting factors need to be accounted for to accurately obtain this information. In many studies in the literature the $Q$-dependent weighting factor is replaced with a constant approximation when evaluating the coordination number. This has been done by taking either the average value over the $Q$ range of the experiment (which can lead to misleading coordination numbers) or the value at the $Q = 0$ limit, where $f(Q = 0) = Z$ in the independent atom form factor approximation. Although the latter method is more accurate, there is still the question of knowing the effective number of electrons associated with each atomic species. The flaws in the averaging approximation are illustrated in Figure 6.8, which shows a significant $Q$-dependence of the weighting factors for specific partial structure factors, for example, Si–Si or O–O in glassy SiO$_2$. Therefore, for X-rays the local structural peaks are best fitted in $Q$-space using a Gaussian approximation to take into account the $Q$-dependent variation in the weighting factor. For molecules or well-defined “molecular units” we can fit individual “intramolecular” peaks to the X-ray $S_X(Q)$ through [9]

$$S_{\text{intra}}(Q) = \sum_{i,j=1}^{m} \frac{Nc_i c_j f_i(Q) f_j(Q)}{2} \text{sinc}(Q r_{ij}) \exp \left(-Q^2 \sigma_{ij}^2 \right)$$

where

$$S_X(Q) = S_{\text{intra}}(Q) + S_{\text{inter}}(Q) \quad (6.12)$$
Figure 6.7 Photon scattering cross-sections for SiO$_2$ as a function of incident energy [34]. The photoelectric absorption cross-section (dash-dot line) dominates for energies below ~50 keV, above which the incoherent Compton scattering dominates (dotted line). The K-edge absorption from Si occurs at 0.14 keV.
Figure 6.8 Q-dependent X-ray weighting factors for the three partial structure factors of glassy SiO$_2$ [18].

$N$ denotes the coordination number, $r_{ij}$, are the atomic separations of the intramolecular interactions, and $\sigma_{ij}$ are the associated values for half the mean square variation, where $\sigma_{ij} = <r_{ij}^2>/2$. Using this method has the advantage that the area under all the Fourier termination oscillations either side of the main peak in real space are accounted for (e.g., see Figure 6.12). In addition, the model fit is applied to the same momentum transfer range as the measured data and truncated at the same $Q_{\text{max}}$. The main disadvantage is that the peak in real space is assumed to be symmetric, which may not necessarily be the case. This can be circumvented by multiple peak fits or by dividing out the appropriate partial weighting factor for isolated peaks of a known correlation and integrating to find the coordination number. When using Eq. 6.12 it should be stressed that overlapping correlations from neighboring peaks need to be accounted for when fitting and that the information extracted from this process corresponds to average values. This is because diffraction is generally not sensitive to the speciation of elements in the same way as NMR, that is, the relative populations of species like AlO$_4$, AlO$_5$, and AlO$_6$, cannot be uniquely determined since their peaks overlap strongly. Rather the coordination
number extracted from the PDF fit will correspond to the sum of these contributions, that is, the bulk average Al–O coordination number.

Figure 6.9 Bragg–Brentano reflection geometry (top) versus high energy transmission (direct) geometry [13,16].
Figure 6.10 Weighted X-ray structure factors, $Q[S_X(Q)-1]$, for two diffraction experiments on glassy $\text{P}_2\text{O}_5$ made with Ag Kα X-rays $\lambda = 0.561$ Å (open symbols) and X-ray synchrotron radiation $\lambda = 0.088$ Å (filled circles). Digitized from Hoppe et al. [51]).
Figure 6.11 The X-ray structure factor for glassy SiO$_2$ measured at the Advanced Photon Source synchrotron (circles). The line represents a fit to the first three peaks in $G_X(r)$, Si-O, O-O and Si-Si using Eq. 6.12 with the parameters in Table 6.1.
The X-ray and neutron pair distribution functions are shown for glassy SiO$_2$ (lines). Also shown is the fit to the first three peaks in $G_X(r)$ corresponding to, Si–O, O–O, and Si–Si, respectively, obtained using Eq. 6.12 with the parameters in Table 6.1 (circles). Inset shows a comparison of the direct and Lorch Fourier transforms of the fit to the Si–O peak.

The Fourier transformation from $S_X(Q)$ to $G_X(r)$ can sometimes appear to be a black art to those unfamiliar with the technique. Truncation effects due to data sets not ending at precisely unity or from limited $Q$ ranges can lead to Fourier artifacts, which take the form of strongly varying periodic oscillations superimposed on the real space structure. As a starting point, useful information for the interpretation of $G_X(r)$ can often be obtained from a comparison with the corresponding crystalline structures of a similar density. This does not imply crystalline models are suitable for describing glass structure, as the local structural units are usually more distorted in the glass and the range of connectivity considerably broader. However, the local chemistry bonding arrangements are often similar between glass and crystal analogues. A comprehensive discussion of the validity of crystal-based models (quasi-crystalline, strained-crystalline, and para-crystalline) as well as cluster, molecular, and layered models for
amorphous materials has previously been given by Wright [37].

Since the X-ray PDF function provides an average correlation function of the bulk structure over a range of distances, the information from several complimentary experimental techniques can be used in combination. The use of additional information for data interpretation is important because for a system of \( n \) atom types there are \( n(n + 1)/2 \) contributing partial structure factors, although low \( Z \) contributions can often be neglected since they are weakly weighted by X-rays. Neutron diffraction in particular is a sister technique to X-ray diffraction and the data are generally combined directly to eliminate specific partial structure factors and deconvolute overlapping peaks in \( G(r) \). Many other element-specific techniques can be used to help interpret X-ray PDF data. These include NMR spectroscopy which has made great strides in glass science in recent decades and provides information not obtainable using the PDF technique, such as speciation and molecular conformation. Two other common element-specific X-ray absorption methods include; extended X-ray absorption fine structure (EXAFS) and the X-ray absorption near edge structure (XANES). More sophisticated X-ray difference techniques such as anomalous X-ray scattering and isomorphic substitution are very powerful in determining partial structure factor information, but can only be applied to a limited range of elements and are often limited by the accuracy of the corrections or approximations used [40].

In any glass diffraction study, the interpretation can become clearer if a systematic study is made. Variations in composition, pressure or temperature, for example, can aid in the extraction of useful information.

One of the most important uses of the X-ray PDF technique is that \( S_X(Q) \) or \( G_X(r) \) provide a rigorous test of structural models over a range of length scales, typically from 1–20 Å. In the first instance, the average number density is a simple yet strong indicator of the soundness of any structural model. Beyond that, it has been suggested a goodness of fit \( R \)-factor for \( \chi \)-squared fitting of models to real space data should be used to assess the accuracy of the model [4]. With modern day computers ball-and-stick or Percus–Yevick models are rarely used. Widely used methods to model PDF data using computer-generated models are Reverse Monte Carlo (RMC) modeling [41,42], and Empirical Potential Structural Refinement (EPSR) [43]. The RMC method uses random and/or crystalline starting structures and iteratively refines a three-dimensional atomistic model of the material that is consistent with PDF data sets. During the RMC process, favorable changes in structure are accepted, and unfavorable changes are allowed with some probability to avoid local minima, on the basis of a \( \chi \)-squared fit to \( S(Q) \). These techniques can be very powerful for modeling pairwise additive interactions, provided enough constraints are used from other sources, such as chemical knowledge, density, neutron, and NMR or EXAFS data. If too few constraints are used, unrealistic chemical structures may be obtained that still fit perfectly with the X-ray diffraction pattern. In addition, RMC will often fit the data with the most disordered models possible. EPSR is, in concept, a similar method compared to RMC or Rietveld refinement, targeting mainly molecular systems, whereby it refines an arbitrary interatomic potential until the three-dimensional atomic model for the system is in agreement with the measured PDF data. Both RMC and EPSR modeling techniques can be considered as analogous to a Rietveld refinement in crystallography.

Classical molecular dynamics (MD) predict the X-ray PDF by moving atoms within a
simulation box according to predefined interatomic potentials [44]. The main advantage is that the essential underlying forces within the system can be determined and used to predict both the structure and dynamical behavior. *Ab initio* molecular dynamics simulations [45] combine the advantages of MD and density functional theory (DFT), and generally provide more accurate models than classical MD simulations with the added cost of computational time. For accurate potentials a three-dimensional model consistent with all the measured data can be obtained, from which additional information such as bond angle distributions, orientational correlations and ring statistics can be extracted. One drawback of comparing limited size DFT atomistic models is that artificial broadening in reciprocal space and Fourier transform artifacts arise from the restricted $r_{\text{max}}$.

The bond angle distributions obtained from 3D models represent the populations of atoms at specific angles and are often broader in the case of the more distorted local polyhedra found in glasses compared to their crystalline counterparts. Bond angle information has important implications for ring size distributions, since narrower angles could correspond to smaller ring sizes and vice versa. The ring size distribution is usually determined by a shortest path criteria and describes the topology of the glass structure [46]. Good glass forming ability is often associated with a broad range of ring sizes, in contrast to crystals, which normally only have a few well-defined ring sizes. For systems made up of non-spherical molecules, orientational correlation functions can be obtained from computer models which depend on the relative arrangements of neighboring molecules. Although this information cannot be extracted from X-ray diffraction data alone, the EPSR modeling technique [43] bridges this gap by using diffraction data as a constraint on the three-dimensional model used to extract the angular correlation functions.

### 6.4 INSTRUMENTATION

Monochromatic X-ray beams generally provide the most accurate PDF data. For laboratory X-ray tubes, the diffractometer is most commonly configured in Bragg–Brentano reflection geometry [47], which can be arranged in either of two ways. For a fixed tube, the geometry is, $\theta-2\theta$, whereas if the tube moves and the sample is fixed the geometry is referred to as, $\theta-\theta$. The essential characteristics are that (i) a Mo or Ag Kα source is used to access a reasonable maximum momentum transfer range, (ii) the angle between the specimen surface and the incident X-ray beam ($\theta$) and the angle between the incident beam and the detector slit ($2\theta$) is maintained throughout the experiment. (iii) the source slit-to-sample and sample-to-detector distance are fixed and equal defining a diffractometer circle with the sample at the center.

In contrast, in a synchrotron high energy X-ray, a monochromatic beam of high energy X-rays scatters in transmission geometry, passing through the entire sample into a detector in the forward direction [48–50]. High energy X-rays ("hard" rays) at synchrotron sources typically have energies of 60–120 keV and very high fluxes. The main advantages of conducting experiments on glasses using high energy photons include the following: (i) Much higher momentum transfers can be accessed, leading to high real space resolution at short distances in the pair distribution function. This can lead to more accurate determination of bond distances
at low r, particularly between two average bond distances which are very close together. (ii) The high penetration allows experiments to be conducted in air and in the scattering is concentrated in the forward direction with minimal polarization effects. The penetration also allows for the use of a variety of bulky sample environments and a large area flat-plate detector arrangement (iii) Photo absorption strongly depends on the atomic number of the material and is greatly reduced at higher energies, so millimeter-sized samples that contain heavy elements can be studied. (iv) The radiation damage in biological samples is massively reduced. (v) The measured X-ray structure factors and pair distribution functions are directly comparable to neutron diffraction studies measured over similar Q ranges.

Figure 6.10 clearly illustrates the additional information obtained in a high energy X-ray experiment at a synchrotron source compared to a laboratory X-ray tube apparatus. Taking, for example, the high energy X-ray beamline at 11-ID-C at the advanced photon source [50], this automated diffractometer operates at a fixed energy of 115 keV (0.108Å where $\frac{d\lambda}{\lambda} \approx 10^{-3}$) and has three pairs of horizontal and vertical collimating slits. The detector axis is aligned to the beam to within 0.05 milliradian from the beam center and the detector stepper motor position precision is within 100 μm. The wavelength is calibrated using standard gamma-ray sources when using a solid state Ge point detector or by using the radial plots of crystalline LaB$_6$ and CeO$_2$ at several different sample-detector distances over the range 50–150 cm when using a 2D area detector. For area detectors, the asymmetry of the powder patterns at the longer (high resolution) distance is used to determine the perpendicular tilt of the detector panel, which is usually $<1$ milliradian. An ion chamber measures the incident flux from the direct beam. The incident beam typically has square dimensions of 0.5 mm $\times$ 0.5 mm and the beam transmitted through the sample is blocked by a tungsten beamstop mounted in front of an area detector. The sample is positioned on a goniometer with three-dimensional motor control. Alignment is initially performed using an optical telescope and laser beam system, and precise adjustments (to within 10 microns) are made using the X-ray beam and a moveable photodiode detector which also measures the sample transmission. For area detectors, regular dark current measurements need to be performed between scans to minimize the effects of electronic drift.

Most modern day synchrotrons are fully automated with limit switches to control the large array of motor movements remotely by computer. Although in principle hard X-ray diffraction measurements are quite straightforward, problems can sometimes arise. The main pitfalls from these types of experiments are keeping the count rate to below 60,000 counts per second, above which detector dead time corrections become difficult for most solid state detectors or area detectors begin to saturate. Sample thickness therefore needs to be considered carefully to balance the optimum signal versus absorption and multiple scattering effects. The incident collimation is also important in order to reduce slit scattering and secondary background scattering into the detector. However, one of the most vital issues is beamstop alignment. Tilted beamstops can lead to asymmetric background scatter and so beamstops should be perfectly aligned prior to the experiment. If the beamstop alignment changes even slightly during the experiment (since the beamstop position is often very sensitive to even the slightest knock), the background may change significantly making previous measurements worthless. At the current time, most area detectors are image plates and do not carry out energy discrimination, thus
suffering from memory effects where residual images from previous (usually strongly scattering crystals) remain as trapped excited states in the detector pixels. These memory effects are usually only a few percent of the measured signal but can ruin the measurements from a diffuse and weakly scattering glass. Care therefore needs to be taken to eliminate detector memory effects (as they decay slowly with time over hours or days), before the experiment starts, by exposing the detector to a high flat field of radiation to release the trapped excited states in the detector, evening out the pixels' response [29].

### 6.5 CASE STUDIES

#### 6.5.1 SiO$_2$ and Oxide Glasses

Silica glass is the archetypal network forming glass with a plethora of technological applications. From X-ray diffraction, we can determine that the structure is comprised of an open network of corner shared SiO$_4$ tetrahedra, commonly referred to as AX$_2$ type glasses. The A refers to a positively charged atom at the center of each tetrahedron, for example, Si, Ge, Be, and the negative charged X atoms are at the corners, for example, O, F, Se, S. For most network glasses, some structural information can be inferred regarding the intermediate range order from the measured structure factor, $S_X(Q)$, itself. AX$_2$ tetrahedral glasses typically have a FSDP at $Q_1r_1 \sim 2.5$ and a second peak at $Q_2r_1 \sim 4.5$ [37], where $r_1$ is the position of the first peak in real space, which in this case refers to the Si–O bond length. The peak at $Q_1r_1 \sim 2.5$ can usually be associated with cages surrounding open regions (voids) in the network and ring statistics which give rise to the intermediate range order. In other materials, the FSDP may arise from other entities, such as layers or clusters. The peak at $Q_2r_1 \sim 4.5$ in AX$_2$ glasses corresponds to the packing of the atoms and has a large contribution from the concentration–concentration partial structure factor in the Bhatia–Thornton formalism. Curiously, the $Q_2$ peak is the strongest feature in GeSe$_2$ glass and in the neutron $S_N(Q)$ for SiO$_2$, but is missing in the X-ray $S_X(Q)$ for SiO$_2$ glass. This is because the $Q_2$ peak is strongly correlated with the oxygen–oxygen atom interactions in glassy SiO$_2$, which dominate the neutron spectra due to the high concentration and neutron scattering length of oxygen. However, the O–O correlation is weaker in the X-ray spectra and is cancelled out by the heavily weighted Si–O interactions which are manifested by a strong negative dip is Q-space [52] (the physical origin of this negative feature is more easily interpreted in the real space representation described later in Figure 6.12). The peaks at $Qr_1 > 7$ correspond to details of the local tetrahedral unit (Si–O and O–O distances and root mean square deviations).

For SiO$_2$, the X-ray structure factor comprises three partial structure factors, Si–Si, Si–O and O–O given by the equation

$$S_X(Q) - 1 = \left( \frac{1}{f^2(Q)} \right)$$
For SiO$_2$ glass, we use Eq 6.12 to fit the Si–O, O–O, and Si–Si peaks in the pair distribution function corresponding to the interactions within the tetrahedral unit and its nearest neighbor. The bond lengths extracted have been noted to differ slightly (<1%) from that obtained from neutron data. This gives an indication of how surprisingly well the spherical electron cloud approximation around the silicon and oxygen atoms works for X-ray PDF. The number of bonding or lone pair electrons that distort the shape of the electron cloud compared to the total number of electrons will give an indication of how good the spherical cloud approximation is. However, the main effects are restricted to the lowest Q-values as shown previously for hydrogen in the insert for Figure 6.3. As discussed previously in the section on X-ray form factors.

In real space, a direct comparison of the X-ray and neutron pair distribution functions reveals the origin of the differences in the measured diffraction patterns. Both X-rays and neutrons accurately measure the position, width, and coordination number associated with the Si–O and O–O peaks. However, while features from all three partials (i.e., the Si–O, O–O and Si–Si) are observed in the X-ray function, the neutron function is dominated by the oxygen-containing correlations.

The effect of using a modification function on the $S(Q)$ truncated at a $Q_{\text{max}} = 29.2$ Å$^{-1}$ is also shown in Figure 6.12. The Lorch function used here has the effect of smoothing out the satellite oscillations on either side of the main peak but this comes with the loss of real space resolution. The experimental resolution itself is inversely proportional to the maximum measured Q-value, $Q_{\text{max}}$. The Si–O, O–O and Si–Si Gaussian peak fits to the data in Figure 6.12 have been summed and convoluted with a sinc function and truncated at the same $Q_{\text{max}}$ as the data. Using the high resolution G(r) functions, Neufeld and Liss [53] were able to determine the Si–O–Si bond angle distribution in SiO$_2$ glass much more accurately than the pioneering work by Mozzi and Warren [54] which used laboratory-based X-ray sources decades previously. Both investigators used Monte Carlo approaches to extract the most probable bond angles associated with the diffraction data rather than assuming that these are first and second neighbor distances.

The measured X-ray structure factor and corresponding pair distribution function for glassy SiO$_2$ are directly comparable to theory and simulation. Using an aerodynamic levitation technique, Mei et al. [52] were able to measure the X-ray pair distribution function of liquid SiO$_2$ and compare their results to both ab initio and classical molecular dynamics simulations. Both simulations showed a significantly broader Si–O peak in the liquid compared to the glass, whereas the experimental X-ray data show that the differences in structure between liquid and glass are much more subtle, consistent with SiO$_2$ being a strong glass former.

Given the different weighting factor information for the X-ray and neutron diffraction measurements illustrated in Figure 6.12, the techniques are most powerful when combined. Benmore et al. [52] have exploited this contrast to extract the Faber–Ziman partial structure
factors of SiO$_2$ glass (using isotopic neutron diffraction and high energy X-ray diffraction) and thereby obtain element-specific pair distribution function information (see Figure 6.15). Combined X-ray and neutron measurements are often very useful in the study of oxide glasses, chalcogenide glasses and amorphous organic molecules. The coordinated use of X-ray and neutron structure factors often depends on the ability to isolate or extract information on an element-specific feature that might otherwise be obscured by overlapping correlations and often relies on a significant contrast between the scattering of the constituent atoms.

**Figure 6.13** The Si–O–Si bond angle (β) determined from combined high-energy X-ray and neutron data by Neufeld and Liss [53] (solid line) compared to that from the early X-ray data of Mozzi and Warren [54] (circles).
Figure 6.14 The X-ray pair distribution functions for glassy and liquid SiO$_2$ obtained from experiment (circles), compared to classical MD simulations (dashed line) [56] and ab initio MD simulations (solid line) [45].
The measured partial distribution functions Si–Si, Si–O and O–O obtained with a combination of X-ray diffraction and neutron diffraction data (circles) [52] compared to the results of an earlier RMC simulation of Kohara et al. (line) [57].

The corresponding Si–Si, Si–O and O–O partial pair distribution functions are shown in Figure 6.16 along with the representative “element-specific” interactions that they correspond to. While both the RMC and molecular dynamics simulations appear to be in reasonable agreement with the measured X-ray pair distribution function for SiO$_2$ glass in Figure 6.14, the disagreements for the $r > 3$ Å region are important as they can lead to glass structures with different topologies. For example, although the extracted ring statistics from the RMC and MD models both show a broad distribution of rings centered on a ring size of 6, the MD model has a much narrower ring-size distribution, while the RMC favors a higher population of larger ring sizes (see Figure 6.17). This probably reflects a combination of the disordered nature of models produced by the RMC modeling process and the usually rigid potentials used in describing the SiO$_4$ tetrahedra.
Figure 6.16 The partial pair distribution functions $T_{ij}(r)$ for glassy SiO$_2$ corresponding to the measured circles in Figure 6.15 shown together with schematics of the atom–atom interactions within the bulk structure of the glass.
Figure 6.17 The ring size distribution for SiO₂ glass calculated from the RMC model of Kohara et al. (white bars) [58] and the classical MD simulation by Rino et al. (black bars) [58].

6.5.2 Chalcogenide Glasses

Chalcogenide glasses have been used as the basis for network rigidity theories [59, 60] because they form homogenous bulk glasses over a wide compositional range and have a continuous variation in average coordination number, $\bar{n}$. The “eight minus $n$-rule” was proposed by Mott in 1969 [61] to describe the structure of chalcogenide glasses but is equally applicable to organic polymers. The rule ensures that all of the valence electrons of the constituent atoms are taken up in bonds, by counting the number of covalent bonds necessary to complete the atoms’ outermost shell of electrons. Using this chemical condition, the nearest neighbor coordination number of the atom Z is given by $Z = 8 - n$ where $n$ is the number of s and p type electrons in the atom. Furthermore, mean-field theory predicts an onset of network rigidity for $\bar{n} > 2.4$, reaching a fully polymerized network at $\bar{n} = 2.67$ [62, 63]. The structural arrangements are generally more complex in chalcogenide glasses compared to oxide glasses because there are a significant number of “wrong” or homopolar bonds present.

The changes in the X-ray structure factor versus composition also generally appear quite
dramatic as changes occur both in the region of the FSDP and at high $Q$. In this case, the FSDP is sensitive not only to changes in the intermediate range order but also to variations in different short-range order bonding arrangements. Bychkov et al. [64] have monitored both the peak height and position as a function of composition in several binary chalcogenide glasses and found trends corresponding to three distinct structural regions. At low concentrations (<15% network forming cations, NFC) no significant variation was observed in the FSDP height and this region was associated with a random distribution of NFCs. For most of the binary Se glasses studied, the compositional range $15\% < \text{NFC} < 33\%$ showed an increase in FSDP height and this was associated with network formation consistent with network rigidity theory. Beyond NFC $> 20\%$--$40\%$ (or n-bar $> 2.4$, see Figure 6.18) the large number of homopolar bonds dramatically changes the FSDP amplitude, which can either result in a rise if cage molecules such as $\text{P}_4\text{Se}_3$ or $\text{As}_4\text{Se}_3$ form, or a decrease in amplitude if the network is depolymerized as in the Ge–Se system. In contrast, the Te–Se system showed little variation with composition since the structure is dominated by chains. The height of the FSDP has also been found to correlate with changes in the molar volume in ternary chalcogenide glasses such as GeAsS [65].
Figure 6.18 The behavior of the height of the first sharp diffraction peak (FSDP) versus concentration of network forming cations, for a series of selenium binary glasses, Bychkov et al. [64].

Another way of depolymerizing the glassy network by increasing the coordination number is to apply pressure. The study by Mei et al. [67] on GeSe$_2$ glass at high pressure provides an example of how open structure network glasses densify. In this case, Raman spectroscopy shows a transition from edge- to corner-sharing units up to pressures of 3 GPa resulting in a more flexible network. This is associated with a rapid decrease in the FSDP height in the X-ray diffraction pattern and a breakdown of intermediate range order. At higher pressures (beyond 4 GPa), the pair distribution functions show a gradual increase in the average coordination number as the density increases. The application of pressure is therefore a powerful way of understanding the relationship between polyhedral coordination, connectivity, intermediate range order, and changes in macroscopic properties such as density, viscosity, and compressibility. Indeed, slight movements of the position of the first peak in the pair distribution function of bulk metallic glasses have also been used to measure the anisotropic strain, which can be related to fatigue and fracture [68].

6.5.3 Amorphous Materials, Gels, Foams and Fibers
In addition to glasses, X-ray diffraction equally can be applied to a range of amorphous materials made in ways other than quenching from the melt. These include (i) pressure-induced amorphization, where a glassy structure factor is obtained by disordered the crystalline lattice through intense pressure, for example, amorphous ice [68]; (ii) chemical reactions ending in an amorphous or nanocrystalline product, for example, calcium-silicate-hydrate which results from the reaction of silicate phases of Portland cement with water [69]; (iii) bioactive glass, foams and gels which react in physiological environments [70]; (iv) amorphous biological fibers which have strong anisotropy, for example, spider silks, whale baleen. [72]; (v) amorphous pharmaceuticals produced by containerless techniques which usually results in more effective drugs with higher solubility and bioavailability [72].

6.6 CONCLUSIONS

X-ray diffraction is often the first step in characterizing glass structure since the measurements are straightforward and generally robust. Information on both the intermediate range order (≈5–20 Å) as well as the short range order (1–5 Å) can be obtained. This includes accurate bond distances, local coordination numbers and bond angles, provided overlapping correlations from neighboring peaks are adequately taken into account. Some care needs to be taken because the PDF only measures an average distribution function, making extrapolation to a three-dimensional structure problematic. The main difficulty with the analysis of X-ray diffraction data from glasses is that of uniqueness, as even if the model precisely fits the measured data, other models may also fit just as well. Nonetheless, the X-ray PDF technique does (perhaps most importantly of all) provide a stringent test of any model and if the model is not consistent with the X-ray data, it is wrong and needs to be modified or rejected.

The future of the application of X-ray diffraction to glass lies in advances in three main areas: (i) instrumentation, (ii) dedicated sample environment equipment, and (iii) software development and modeling. Advances in focusing optics and more intense photon beams will lead to smaller beam sizes which may address the question of structural heterogeneity between the ergodic and non-ergodic regimes during glass formation through faster time resolved measurements [73, 74]. High energy discriminating large area detectors are not currently available, but would significantly improve the accuracy of X-ray data at high Q-values and significantly extend the Q range achievable to those obtainable at spallation neutron sources. The combination of simultaneous small angle X-ray scattering (SAXS) and wide angle X-ray scattering (WAXS) experiments using medium to high energy X-ray are already possible, but have not yet been fully utilized by the glass community to explore local structure concurrently with longer-range density fluctuations. Anomalous X-ray scattering (AXS) has long held the promise of extracting partial structure factor information, by varying the incident photon energy in the vicinity of an absorption edge of one of the constituent elements in the glass. The resulting change in X-ray form factor can readily provide differential structure factors for glass forming elements over a limited Q range using high energy resolution photon beams, provided the data can be reliably corrected for Compton scattering and fluorescence problems [40]. Recently it has been shown that high energy AXS can extend the accessible Q range and
provide high resolution PDF data, even though the anomalous dispersion is much smaller [75]. However, the accessible absorption edges in the energy range > 40 keV are largely limited to the rare earths and heavier elements, so could be applied to find modifier environments in glasses (see Figure 6.20). Coherent high energy photons from X-ray free electron lasers (XFEL) hold the promise of extracting three-dimensional images of glass structures using the technique of ankylography [76], although at the time of writing the limitations of this technique are still under debate [77].

![Figure 6.19](image1.png)  
**Figure 6.19** The low Q dependence of the X-ray structure factor of glassy GeSe₂ as a function of increasing pressure [66].

![Figure 6.20](image2.png)  
**Figure 6.20** The energy dependence of the X-ray form factor for lead. The inset highlights the small absorption edge at 88 keV. (Taken from [78]).

The study of glassy materials under realistic operating conditions like high or low temperatures [79], high pressures [80], stress/strain, in magnetic or electric fields or by containerless levitation [81] will require the development of specialized sample environment equipment. Nanoparticles have not been mentioned in this chapter, but as the borders between length scales blend together, the study of bulk versus surface effects represents another area of research which may extend to the study of glasses and amorphous materials at interfaces. Lastly, more sophisticated software is needed to process the huge amount of data sets that are now generated at high flux synchrotron sources, and advances in computational scattering science are necessary to make full use of the data we already measure through combination with computer simulation. Two recent examples of advances in this area include (i) the data
reduction of anisotropically scattering materials of amorphous fibers [71] and (ii) combining RMC models based on X-ray diffraction data with density functional theory simulations [82] to provide a direct link to NMR spectroscopy and the dynamical behavior of glasses.

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Table 6.1 Measured values of silica coordination numbers and distances.

<table>
<thead>
<tr>
<th>Atom type $i$</th>
<th>Atom type $j$</th>
<th>Atom number, $N_{ij}$ (Typical error ± 0.3)</th>
<th>The average distance between atoms, $r_{ij}$ (Å) (Typical error ± 0.005)</th>
<th>The root mean square deviation, $\sqrt{\langle r_{ij}^2 \rangle}$ (Å) (Typical error ± 0.005)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>O</td>
<td>4.0</td>
<td>1.61</td>
<td>0.038 ± 0.005</td>
</tr>
<tr>
<td>O</td>
<td>O</td>
<td>5.6</td>
<td>2.62</td>
<td>0.075</td>
</tr>
<tr>
<td>Si</td>
<td>Si</td>
<td>3.5</td>
<td>3.06</td>
<td>0.085</td>
</tr>
</tbody>
</table>

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7

XAFS SPECTROSCOPY AND GLASS STRUCTURE

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7.1 INTRODUCTION

Geometrical and thermal atomic disorder makes the structural and dynamical characterization of glassy systems particularly complex. A satisfactory description must rely on the experimental results of several probes providing measurements of atomic positions, their disorder, their correlations, chemical bonds, etc., but all these average data are not enough; it is useful to resort to modeling techniques that describe glasses as the sum of individual sites or local configurations. A model can be considered appropriate if it interprets all the available experimental results. The more the complementary results fit the model, the more it is reliable.

Available structural probes are sensitive to atomic order to different extents: X-ray and neutron scattering techniques are more sensitive to short and intermediate range order while others, like XAFS, NMR, EELS, etc. are sensitive to the short-range order only and so they are particularly suited to study the local structure of disordered systems. Some techniques are site-sensitive while others are not.

X-ray absorption spectroscopy (XAS) and X-ray Diffraction (XRD) were known as structural techniques since the beginning of the second decade of the twentieth century, but while XRD produced long-range structural results since its birth, the evolution of XAS as structural technique started many years later, in the 1970s, when an adequate theoretical interpretation of the fine structure observed beyond the absorption edges was proposed. The contemporaneous advent of synchrotron radiation sources facilitated its development. At present XAS is better known with the acronym XAFS: X-ray absorption fine structure spectroscopy.

XAFS studies the modulation of the X-ray absorption probability that appears at energies near and above the core-level binding energies of a given atomic species in a sample. Such modulation depends on the chemical and physical state of the sample. Element specificity and independency on the aggregation state (solid, liquid, or gas) and on the presence of long-range order are the main peculiarities of XAFS.

XAFS spectra are sensitive to valence state, species, number, and distances of the atoms immediately surrounding the selected element and to their local thermal and static disorder.

XAFS probes the local structure of gaseous and condensed matter; it is routinely used in research activities including liquid and solid state physics, chemistry of catalysis, biology,
environmental science, and material science.

XAFS is particularly important for glass structure investigations; it is used to determine the local environment around the several atomic species present in glasses. Many applications concern the local arrangement of impurities purposely inserted in glasses to change their functional properties, even at high dilutions. The use of XAFS for nanocrystalline glass-ceramic systems is very important, since the obtained information is complementary to that determined by the XRD.

This chapter gives a brief description of XAFS theory and analysis methods with particular attention to glasses. Examples of state-of-the-art studies in different glassy systems will be presented along with a critical assessment of XAFS potential for such systems.

7.2 THE ORIGINS OF X-RAY ABSORPTION SPECTRA

XAS was discovered just 1 year after of the discovery of X-ray diffraction by Laue. In 1913, the duke Maurice de Broglie [1], the elder brother of Louis de Broglie, by recording the emission spectrum of an X-ray tube by a monocrystal mounted on the rotating drum of a recording barometer, observed a spectrum composed by lines and bands. Two bands were recognized as the Ag and Br absorption K-edges of the AgBr emulsion of the photographic detector (May 1914) [2]. However, while XRD provided structural information since its birth, almost five decades passed before Lytle [3] realized that it is possible to extract structural information from XAS [4]. In the 1970s, thanks to the collaboration of Lytle with Stern and Sayers, the foundations of the modern XAFS theory were laid [5, 6], based on the application of Fourier transform of the experimental signal. High resolution spectra measured at the new X-ray synchrotron facilities favored the development of XAFS spectroscopy. Exhaustive, accurate, and interesting historical reviews on the X-ray absorption fine structure have been written by Stumm von Bordwehr [7] and Lytle [8]. History of the subsequent theoretical advances is described by Rehr et al. in Reference 9.

The absorption phenomenon of radiation by matter is ruled by the statistical law of Beer–Lambert

\[ I = I_0 e^{-\mu(E)x} \]  

(7.1)

where \( I_0 \) is the intensity of a collimated and monochromatic beam incident on a sample of thickness \( x \), \( I \) is the intensity transmitted through the sample, and \( \mu \), the absorption coefficient of the sample, a measure of the probability that the radiation is absorbed. \( E \) is the radiation energy. In the X-ray regime (\( \sim 500 \text{ eV} \sim 50 \text{ keV} \)), the photoelectric absorption process prevails over elastic (Thomson) and inelastic (Compton) scattering processes. In a photoelectric process, an X-ray photon is absorbed by an atom through the transition of an electron (photoelectron) from a tightly bound quantum core level (such as the 1s, 2s, or 2p level) to an unbound electronic state. Transitions occur when \( E \geq E_0 \), where \( E_0 \) is the electron binding energy (Figure 7.1). The X-ray photon disappears and the remaining energy \( E - E_0 \) is
acquired by the photoelectron as kinetic energy. At energy $E \equiv E_0$, an abrupt increase of the absorption coefficient $\mu$, called the absorption edge, appears. Transitions of 1s electron of the atomic levels $K$ give rise to the K-edges; transitions of electrons 2s, or $2p_{1/2}$ or $2p_{3/2}$ of the electronic levels $L$ give rise to the $L_1$, $L_2$, $L_3$ edges, respectively, and so on for the 5 M-edges at lower energies, etc. By increasing the atomic number, the energy of K-edges increases from a few tens of eV to hundreds of keV while L-edges occur at lower energies [10]. In polyatomic gases and condensed matter, an oscillating fine structure is observed just near the edge and up to more than 1000 eV beyond the edge: it constitutes the XAFS. In Figure 7.2, the XAFS spectra at the As and Se K-edges in arsenic selenide, As$_2$Se$_3$, are shown. For interpretation convenience, XAFS is currently analyzed into two separated energy regions: XANES and EXAFS. XANES (X-ray absorption near edge structure), sometimes denoted also NEXAFS, spans from a few eV before the edge to some tens of eV past the edge; EXAFS (extended X-ray absorption near edge structure) extends from tens of eV to more than 1000 eV past the edge. The energy border of these two regions is not well-defined and depends on the case under study. XANES and EXAFS regions at the K-edge of Se are shown in Figure 7.2. Both substructures are present in polyatomic gases and condensed matter.

**Figure 7.1** XAFS origins from the electronic transitions excited by X-ray photons from core levels to unoccupied levels just below of the conduction band (excitation) or to the continuum of free states (ionization).
Figure 7.2 K-edges of As and Se in As$_2$Se$_3$. The XANES and EXAFS regions are indicated at the Se K-edge.

XAFS spectroscopy can be applied to almost all the elements of the periodic table through XANES, always accessible, and EXAFS spectra. The lighter elements, starting from $Z \leq 10$, show only XANES spectrum; the EXAFS signal at K-edge of elements with atomic number $Z \leq 11$ to 20 attenuates not far from the edge and so its analysis is often rather difficult owing to its short energy range; the elements up to approximately $Z = 50$ are investigated by recording XANES and EXAFS at the K-edge; the heavier atoms are easily accessible through L-edges.

7.3 XAFS INSTRUMENTATION

A schematic typical experimental set-up for XAFS measurements is shown in Figure 7.3; it is composed by an X-ray synchrotron source, an optical beamline, containing devices for conveying, geometrically defining, monochromatizing the white X-ray beam emitted by the source and focusing it on the sample inside a XAFS apparatus. There are several methods to measure the XAFS spectra depending on the detection mode (Figure 7.4).

Figure 7.3 Schematic synchrotron beamline for XAFS measurements.
Direct measurements are made in transmission mode (Figure 7.3), indirect measurement techniques include X-ray fluorescence yield (FLY), Auger electron yield, total electron yield (TEY) and the photoluminescence yield mode (PLY). The transmission mode detects the X-ray photons that pass through the sample without being absorbed. In Figure 7.5, a typical apparatus for transmission measurements is shown; it consists of a first detector which measures the intensity $I_0$, proportional to the flux and energy of photons impinging on the sample, a sample holder and a second detector which measures the intensity of photon, $I$, not absorbed by the sample. Often, X-ray intensity is measured by gas ionization chambers. These consist of gas-filled boxes where two parallel electrodes collect all the charges created by direct ionization within the gas through the application of an electric field. Ionic current is proportional to X-ray intensity. This is the minimal apparatus present in most of the XAFS facilities. Sometimes the absorption coefficient of a standard sample $\mu_s$, is measured by means of a third detector. This allows calibrating the X-ray energy scale with high accuracy referring to the positions of characteristic absorption peaks or inflection points with known energies of reference samples. This set-up is particularly useful for chemical shift measurements.
Figure 7.5 Apparatus for transmission XAFS experiments. The beam intensities $I_0$ and $I$, measured by ionization chambers, are enough for recording the XAFS spectra; sometimes a third chamber is used to accurately calibrate the energy scale by recording the XAFS spectrum of a standard such as, for instance, a metal foil. The X-ray beam crosses the chambers through thin low absorbing windows. The electrodes collecting the electrons and ions generated by the ionization of the gas contained in the ion chambers are shown in figure. The measured currents are proportional to X-ray fluxes crossing the chambers.

The absorption signal $\mu(E)$ is generally measured by scanning the energy step by step and halting the monochromator at each energy point. Scanning transmission mode is by far the most used method because its simplicity and for the highest accuracy of the obtainable results. Sample preparation is one of the most critical phases of a measurement since a set of artifacts can corrupt XAFS data. To avoid or reduce artifacts the sample should be uniform, free of pinholes, and its thickness should be optimized on the basis of its composition and the measurement mode [11].

The duration of measurements can range from tens of minutes to some hours depending on beam intensity, sample absorbance and the required signal-to-noise ratio. Measurements can last seconds when resorting to Quick-XAFS apparatuses [12–14] using a quick-scanning monochromator and fast data acquisition. A unique way of collecting XAFS spectra in a sufficient energy range within a few milliseconds is carried out by Energy Dispersive-XAFS spectrometers [15–17]. In these set-ups a bent crystal focuses and disperses a polychromatic X-ray beam onto the sample (Figure 7.6). The beam transmitted by the sample diverges toward a position-sensitive detector, where position is correlated to X-rays energy. This scheme has the advantage of an intrinsic stability in focal spot position and in energy scale, since there are no moving components. It benefits from a high acquisition speed since all energy points are acquired all together in parallel. QuicK-XAFS and Dispersive-XAFS allow time resolved studies of chemical reactions, catalysis [18], phase transitions [19] and various aspects of solid state chemistry [20–22].

Sometimes the characteristics of the sample do not permit the use of the transmission mode. For instance, for measuring EXAFS from minority components in much diluted systems, one resorts to the fluorescence mode (Figure 7.7).
Figure 7.6 Energy Dispersive XAFS. Sub-second data collection set-up. The optical elements are static. It is usable only in transmission mode; energy range and resolution are more limited than scanning techniques.
Figure 7.7 Schematic set-up of a fluorescence detection mode: $I_0$ is the X-ray beam intensity impinging onto the sample and $I_F$ the X-ray fluorescence intensity emitted from the selected atomic species of interest. A metallic filter and a Soller slit absorb the unwanted radiation. Often the incoming X-ray flux is monitored by collecting the total electron yield $I_0$ excited by the X-ray beam in a polyethylene foil covered by a metallic thin film.

This detection mode is preferred in the following cases: (i) for concentrations down to the ppm level and for thin samples, (ii) for too thin samples, when the sample is too absorbing (a typical situation that occurs in soft X-ray experiments (below 5 KeV), and (iii) when the preparation of samples with enough homogeneity for transmission experiments is not possible. In fluorescence mode the X-ray-excited fluorescence yield (FLY), caused by the radioactive decay of the core hole created by X-ray absorption, is measured. However, the intensity scattered from the sample includes not only the fluorescence $I_F$ coming from the selected atomic species of interest, but also the fluorescence lines from other elements in the sample as well as elastically and inelastically scattered radiation (Compton). When possible, the unwanted fluorescence intensity is reduced before reaching the detector by means of metallic filters and Soller slits, that is, sets of parallel metallic foils that slice the incident radiation into small parallel beams (Figure 7.7). The absorption coefficient is given by $\mu x = C \cdot I_F/I_0$, where $C$ is approximately constant and is eliminated in the XAFS signal extraction process. Although the X-ray fluorescence spectra have the same structural content as the transmission ones, the amplitude of the features might be different [23]. This fact is particularly true for the near-edge structures and has to be considered when comparing XANES measured with different detection modes. The fluorescence intensity is generally collected by single or multi-elements solid-state
detectors. Although the signal-to-noise ratio in fluorescence mode is often better than that in transmission mode, more systematic errors can affect fluorescence spectra [24, 25].

To investigate the structure near the surface, one resorts to the total electron yield detection mode (TEY) [26]. In this method, the Auger electrons escaping from the sample, which is tilted with respect to the incoming beam as in the fluorescence mode, are collected. Alternatively, the intensity of escaping electron is monitored by an electrometer connected to the sample holder, which measures the compensating current that flows into the sample. It has been [26] shown that TEY can reproduce XAFS spectra obtained from the other detection modes. The sampling depth of TEY is mainly determined by the effective penetrations range of the Auger electrons which depends on the photon energy and on the material density. For instance, the effective penetration range for silicon changes from about 10 Å to 10^4 Å in the energy range 10^2÷10^4 eV; at the Si K-edge (1839 eV) it is about 10^3 Å.

Some luminescent materials can be studied by recording the VIS/UV photoluminescence yield excited by the incoming X-rays [27, 28]; the resulting XAFS spectra are denoted X-ray excited optical luminescence (XEOL) spectra.

### 7.4 THE PHYSICAL MECHANISM OF XAFS

The photoelectrons extracted from the inner levels of the absorbing atoms are backscattered by the surrounding atoms: the interference between the outgoing and backscattered photoelectron wave is the common origin of XANES and EXAFS oscillations beyond the edge. In the frame of the electric dipole and one-electron approximations, the absorption coefficient μ, is given by the Fermi’s Golden rule,

$$
\mu(E) \propto \left| \langle \tilde{\Psi}_f | \mathbf{p} \cdot \mathbf{A}(r) | \tilde{\Psi}_i \rangle \right|^2 \rho(E_f)
$$

where $E$ is the X-ray energy, $| \tilde{\Psi}_f \rangle$ and $| \tilde{\Psi}_i \rangle$ are the final and initial states having energies $E_f$ and $E_i$, respectively. The summation extends to all final states $f$. $\mathbf{p}$ is the momentum operator and $\mathbf{A}(r)$ is the vector potential of the incident electromagnetic wave. $\mathbf{A}(r)$ can be considered as a classical wave $A(r) \equiv \hat{\epsilon} A_0 e^{i \mathbf{k} \cdot \mathbf{r}}$ where the polarization versor $\hat{\epsilon}$ is perpendicular to the wavevector $\mathbf{k}$. Often, by approximating $e^{i \mathbf{k} \cdot \mathbf{r}} \approx 1$, the spatial dependence of the electromagnetic field can be neglected allowing to describe the core excitation by electric dipole transitions. However, in some cases, the quadrupolar transitions must be taken into account as in the case of transition metal K-edges [29].

For monatomic gases, $\tilde{\Psi}_i$ corresponds to a spherical wavefunction leaving the absorbing atom; for polyatomic molecules and condensed matter, it interacts with the part of itself backscattered by the neighboring atoms (Figure 7.8a). The interference between the outgoing electronic wavefunction, $\tilde{\Psi}_i$, with the one scattered by the neighboring atoms, $\tilde{\Psi}_f$, gives rise to the modulations of the absorption coefficient $\mu$ as a function of the X-ray photon energy, depending on the physical properties of the absorbing atom and on the geometrical and
electronic properties of the atomic environment around it. When the photoelectron follows a unique path going from the absorbing atom \( A \) to the backscattering atom \( B \) and back to the origin, the scattering is called \textit{single} (SS) (Figure 7.8a); when it follows longer paths, as shown in Figure 7.8b, the scattering is \textit{multiple} (MS). Single scattering is often prevalent in EXAFS, thus allowing sometime a simpler analysis, while XANES can be quantitatively interpreted only in the framework of multiple MS. Since XAFS is an interference phenomenon between the outgoing and the backscattered wave, the coherence of the final state is fundamental; so any cause that changes the energy of the photoelectron, as losses for inelastic scattering, or perturbations of the instantaneous atomic positions as thermal agitation, acts as dephasing effect.

![Figure 7.8](image.png)

\( \text{Figure 7.8} \) (a) Single scattering of the photoelectron wave outgoing from the absorbing atoms, \( A \), from parts of it back-scattered from the neighboring atoms, \( B \). (b) Some possible multiple scattering paths followed by the photoelectron.

### 7.5 EXAFS

The measured fine structure, phenomenologically defined as the modulation above a given absorption edge of the absorption coefficient \( \mu(E) \) with respect to the atomic absorption coefficient \( \mu_0(E) \), is expressed by

\[
\chi(E) = \frac{\mu(E) - \mu_0(E)}{\mu_0(E)} \tag{7.3}
\]
χ(E) denotes the XAFS signal. The subjects that actually probe the structure of matter are not the X-ray photons but the photoelectrons that they excite from the binding energy $E_0$ to unfilled electronic states or to continuum. Then, since XAFS is an interference effect, dependent on the wave-nature of the photoelectron, it is convenient to express the XAFS signal in terms of the photoelectron wavenumber, $k$, rather than its kinetic energy $E - E_0$; these quantities are related by the relationship

$$k = \sqrt{\frac{2m}{h^2}}(E - E_0),$$

where $m$ is the electron mass and $h$ the Planck's constant.

The EXAFS signals extracted some tens of eV past the K-edge of Ge in crystalline and amorphous Ge are shown in Figure 7.9.

![Figure 7.9](image)

**Figure 7.9** XAFS spectra at the K-edge of Ge in crystalline Ge at 10 K and 300 K are reported for comparison with the XAFS of an amorphous Ge. The effect of disorder (thermal and structural) is evident comparing the spectra (vertically and horizontally, respectively).

The EXAFS equation, in the plane wave and SS approximations, was first formulated by Stern et al. [6] on the basis of a semi-phenomenological approach, as

$$\chi(k) = \sum_i \chi_i = \sum_i \frac{S^2_i N_i |F_i(k, \pi)|}{kR_i^2} e^{-2k^2 \sigma_i^2} e^{-2R_i/\lambda(k)} \sin \left(2kR_i + \varphi_i\right)$$

where the index $i$ runs over all the coordination spheres (shells) around the absorbing atom, $\chi_i$ is the EXAFS contribution corresponding to the $i$th shell, $N_i$ represents the coordination number, that is the number of identical atoms at the same average distance $R_i$ from the
absorbing atom; \( \sigma_i \) is the variance of a Gaussian distribution of neighbors belonging to the \( i \)-th shell; \( S_0^2 \) is the passive electrons reduction factor; \(|F_i(k, \pi)|\) is the modulus of the backscattering amplitude; \( \lambda \) is the photoelectron mean free path (MFP); and \( \varphi_i \) is the phase shift due to the atomic potentials. The finite MFP of the photoelectron, typically less than 10 Å, reduces the EXAFS structural sensitivity to few coordination shells around the absorbing atom. This reduction is further enhanced by the Debye–Waller factor, \( \sigma_i^2 \), which is due to thermal atomic movements and structural disorder, as can be seen in Figure 7.9 by comparing the \( \chi(k) \) signals of \( c- \) and \( a-Ge \). The three structural parameters: interatomic distance, \( R_i \), coordination number, \( N_i \), and the Debye–Waller factor, \( \sigma_i^2 \), can be extracted from Eq. 7.4 when the other terms are estimated by theoretical calculations or extracted from reference compounds.

A procedure for extracting such data from the EXAFS signal was first proposed by Stern et al. [6]: it is based on the Fourier transform (FT) of the EXAFS signal

\[
FT(r) = \sqrt{\frac{2}{\pi}} \int_{k_{\text{min}}}^{k_{\text{max}}} \chi(k)W(k)k^ne^{-2ikr}dk
\]

where \( k_{\text{min}} \) and \( k_{\text{max}} \) denote the range of the FT \( W(k) \) is a window function; the factor \( k^n \), where \( n \) is an integer typically equal to 1 or 2, is used to compensate the signal reduction in the \( k \) range at high \( k \) values.

The transformation from the reciprocal \( k \)-space to the real \( R \)-space, yields a pseudo-radial distribution function having peaks corresponding to the first few near-neighbor distances (Figure 7.10): the peak positions, however, do not coincide with the real distances \( R_i \) because of the presence of phase \( \varphi_i \), in Eq. 7.4. Through subsequent Fourier filtering, in which the single shells in the \( R \)-space are singled out (when possible), one can obtain the EXAFS contribution, \( \chi_i \) of each coordination shells and, thereby, the relative structural parameters. Width and height of the peaks in the \( R \)-space, are related to the spread of the interatomic distances caused by thermal and static disorders. Low disorder is accounted for the Debye–Waller factor \( \sigma_i^2 \) for Gaussian distributions; high disorders have to be expressed through asymmetric distributions \( \rho(r) \) as it will be shown below.
Figure 7.10 Fourier transforms of the spectra in Figure 7.9. The peak positions are related to the coordination shells around the absorbing atoms. In amorphous Ge the dramatic effect of structural disorder cause the disappearance of the shells beyond the first one.

EXAFS is very sensitive to local disorder. Very soon, it was recognized that Eq. 7.4, which is valid for Gaussian distributions only, can lead to approximate results or significant errors when applied to disordered systems. For instance, apparent bond length contractions with increasing temperature were found in crystals with positive thermal expansion when data were analyzed with the incorrect assumption that the distribution was a Gaussian [30, 31]. This anomaly is due to the fact that the effect of disorder cannot be simply described by a $k^2$-weighted Debye–Waller factor (Eq. 7.4), because the backscattering amplitude and phase shift of the EXAFS signal are influenced by further terms [32]. So the validity of Gaussian distribution was restricted to low temperatures and very weak structural disorder. At high temperature and for asymmetric distributions, adequate analysis techniques must be used. Moreover, since the very beginning, the plane wave approximation had proved to fail at low $k$, producing unacceptable errors in the structural parameters, especially for light atoms whose backscattering function generally assumes negligible values at high $k$. This problem was overcome by the spherical wave approximation of EXAFS [33]. Very soon the validity limits of the SS approximation, especially for the shells beyond the first one, stimulated the development of MS theories. At present, a general theoretical MS formalism, developed by Rehr et al. [9] (which allows also for disorder influence and the curve wave effect by an effective scattering amplitude $f_{\text{eff}}(kR)$) interprets the EXAFS signal $\chi(k)$ as a summation of contributions due to all the possible scattering geometries in addition to the SS one.

### 7.5.1 EXAFS Formula for Glasses

In glassy systems, besides the thermal disorder caused by the thermal motion of the neighbors of the absorbing atom (that in Eq. 7.4 is expressed by a Gaussian distribution of distances with variance, $\sigma_i$), the distribution of interatomic distances is further enlarged by the structural disorder. This is taken into account by substituting the Gaussian distribution with an asymmetric radial distribution function that may be described by some analytical forms. In the single scattering and plane wave approximation, as in Eq. 7.4, the EXAFS equation for a single coordination shell with a radial distribution function $\rho(r)$ (RDF) around the absorbing atom is given by
where $\delta_1$ is the central atom phase shift. There are several methods to obtain quantitative structural information from $\rho(r)$ starting from the experimental signal $\chi(k)$. A first approach assumes a physically reasonable shape for $\rho(r)$, and optimizes its parameters by fitting the calculated single-shell EXAFS (Eq. 7.5) to the experimental signal. This method has been widely described in Reference 32 with great emphasis to liquids and high temperature studies, where a Gaussian distribution is absolutely inadequate. These model-dependent techniques allow a significant reduction of fitting parameters and their mutual correlation, when the true RDF shape can be reasonably reproduced by the model used to best fit Eq. 7.5. In other cases, an arbitrary shaped RDF is necessary, as described in References 34–36. These model independent approaches assume an arbitrary shaped distribution of a single type of atoms around the absorbing species, whose details or evolution (e.g., as a function of temperature or of glass composition) can be successively analyzed and quantified. Of course, this kind of analysis is necessary when the local environment of the absorbing atoms is quite complex, for example, when it is impossible to single out close bond lengths, because of a broad and asymmetric distribution of distances. In some other cases, like in melts, it is almost impossible to separate the contributions of different atoms that are present more or less at the same distance. Thus, $\rho(r)$ can be considered as a superposition of several pair radial distribution functions, which can be modeled and optimized through a best-fitting procedure. The peak fitting method has been developed and intensively used by Filipponi et al. [37] who have been able to reconstruct the distributions of many disordered solid and liquid systems. Another approach, very useful in presence of moderate disorder, is based on the expansion of the integral present in Eq. 7.5 as the exponential of a Maclaurin series around $k = 0$:

$$\int_0^\infty \left[ \rho(r)e^{-2r^2/\lambda^2} \right] e^{2ikr} = \exp \left[ \sum_{n=0}^\infty (2ik)^n C_n/n! \right]$$  \hspace{1cm} (7.6)

The coefficients $C_n$ of the series are called cumulants [38–40]. These terms are linear combinations of the moments of the distribution $\rho(r)(e^{-2r^2/\lambda^2}) = P(r, \lambda)$, called effective distribution. $C_0$ depends on the normalization of the distribution, $C_1$ represents the mean value, $C_2$ the variance, $C_3$ depicts the asymmetry, and $C_4$ the distribution flattening with respect the Gaussian shape, and so on. Even cumulants affect the EXAFS amplitude, while the odd ones affect the EXAFS phase, as can be seen by substituting the integral in Eq. 7.6,

$$\chi(k) = \frac{NS^2_0}{k} \exp \left( C_0 - 2k^2C_2 + 2k^4C_4/3 \ldots \right) \cdot \sin \left( 2kC_1 - 4k^3C_3/3 \ldots \right)$$  \hspace{1cm} (7.7)

When the cumulant series is quickly convergent, the first four cumulants, together with the coordination number, may be extracted from the EXAFS signal by means of the amplitude ratio
and phases difference methods [40]. The method is very accurate when relative cumulants are obtained by using the physical parameters $S^{2}_{0}$, $F(k, \pi)$ and $\lambda$ present in Eq. 7.5 extracted experimentally from a known reference compound. The reliability of results obtained depends on: i) quality of the experimental data, ii) reliability and correctness of single-shell extraction, iii) reference compound validity, iv) correctness of theoretical functions contained in EXAFS formula, and v) the convergence properties of the cumulants series. For not too disordered systems, the cumulants of the real radial distribution $\rho(r)$ are almost equal to the ones of the effective distribution $P(r, \lambda)$, except for the first one whose difference from $C_{1}$ depends on $\lambda$ and can amount at thousandth of Å, growing with the distribution width. A detailed description of applications of the cumulants method can be found in References 41 and 42. The cumulants method has been successfully exploited in studies of thermal disorder in crystalline compounds [43] and glasses [44], but it is certainly useless for very disordered systems like high temperature solids and melts; in these cases, the splice method [45], which is an extension of the cumulants method, or the peak fitting method [30] are preferred. The reliability of the cumulants method for amorphous solid systems should be validated case by case. For instance in an EXAFS study of amorphous germanium thin films [46], the distribution reconstructed from cumulants was found in good agreement with the one obtained by the peak fitting method [32]. On the other hand, in silver borate glasses $g$-Ag$_{2}$OnB$_2$O$_3$($n = 2, 3$) EXAFS analysis methods at the K-edge of Ag, based on Fourier filtering and cumulants expansion, provided only averaged results, due to the presence of several sites of Ag ions [47]. In some cases, it is impossible to extract, directly from Eq. 7.5, unambiguous information about the average local environment of the absorbing species, because of the complexity of the structural situation. In these cases, instead of the inversion of Eq. 7.5, it is highly preferable to follow an opposite procedure using the XAS spectra for driving or checking the modeling/simulation of the structure via molecular dynamics calculations [48] or other statistical methods (Reverse Monte Carlo or similar) [49]. The local information provided by XAFS experiments is, in many cases, an essential complement to neutron or X-ray scattering studies that are currently used to model the structure of glasses.

### 7.6 XAFS DATA ANALYSIS

The objective of data analysis is the extraction of structural information, such as interatomic distances, $R$, coordination numbers, $N$, and disorder parameters of the coordination shells around the absorbing atoms starting from the absorption coefficient $\mu = \mu(E)$. For extracting the XAFS spectrum from the absorption coefficient, $\mu$, several operations have to be performed; generally they are (i) corrections for instrumental errors; (ii) pre-edge background subtraction; (iii) normalization; (iv) Fourier filtering, consisting of (a) Fourier transform from the energy $E$ (or the wavenumber $k$-space) to the distance $R$-space; (b) the inverse Fourier transform; (v) fitting procedure. We describe these operations shortly and refer the reader to the book of G. Bunker [50] where they are treated in great detail.

#### 7.6.1 Corrections for Instrumental Errors
Rough data need to be cleaned by instrumental errors. Spurious instrumental peaks, due to reflections of the monochromator or other optical elements, may appear superimposed to the absorption coefficient spectrum; they are called *glitches*, are generally narrow in energy and may be much greater than the XAFS oscillations. Since their noisy effect can be magnified by the Fourier transform, it is preferable to remove them from the rough data. Their small energy width facilitates the removal which is carried out by interpolating the spectrum just before and after the glitch with a polynomial [51].

### 7.6.2 Pre-edge Background Subtraction

The first objective of data analysis is to extract the XAFS oscillation present above the absorption edge ([Figure 7.11a](#)). This requires the subtraction of the pre-edge background which extends throughout the region beyond the edge. The removal is generally done by fitting the pre-edge region before the edge to a polynomial function in a range of ~ 50÷100 eV. ([Figure 7.11b](#)). The pre-edge polynomial is extrapolated throughout the entire energy range of the post-edge region [51]. A Victoreen polynomial, \( \mu(\lambda) = a\lambda^4 + b\lambda^3 + c \), is often appropriate for transmission data; when the removal is done in the energy space, higher-order polynomials may be necessary especially if the background shows a marked curvature as it can occur in some fluorescence measurements or when the total absorption is very high in respect to the edge jump. Generally pre-edge background removal is a critical operation influencing the determination of the accuracy of coordination number and Debye–Waller factor, but at a lesser extent in comparison with other systematic errors affecting the EXAFS amplitude.
Figure 7.11 (a) Rough XAFS spectrum of Ge at 10K, (b) pre-edge background removal, (c) removal of the atomic absorption contribution $\mu_0(E)$, and (d) $k$-weighted XAFS signal.

### 7.6.3 Post-edge Background Subtraction

This operation aims to evaluate the atomic absorption coefficient $\mu_0(E)$ present in Eq. 7.3. This is the most critical and difficult analysis procedure because it is not possible to unquestionably distinguish the contribution due to the environment surrounding the absorber from the atomic-like absorption of the isolated atom. As a matter of fact, since the electronic state of an absorber bound to other atoms is, in general, dissimilar from its electronic state in atomic gaseous phase, $\mu_0$ is not the same of an isolated atom and neither is measurable independently nor calculable with enough accuracy. So it must be artificially evaluated. Often $\mu_0(E)$ is approximated by the smooth background averaging the oscillatory part of $\mu(E)$ deduced by fitting the post-edge of $\mu(E)$ using, for instance, a cubic spline procedure [52] (Figure 7.11c). This operation requires particular attention because it could alter the frequency content of the extracted EXAFS signal, so the spline method should remove only the very low frequency
components of $\mu(E)$ without damaging the signal. Cubic spline procedure and Bayesian smoothing are reviewed together with other post-edge background removal methods by K.V. Klementev [53]. In the same paper, the estimation of the uncertainty in the $\mu_0$ construction, which contributes essentially to the systematic errors of results, is reported.

7.6.4 Normalization

The data function $\mu = \mu(E)$ is usually normalized in order to compensate for the uncertainties in the concentration and sample thickness. The normalization, consisting in the reduction to a unit step height, is done in two ways: energy dependent or energy independent. The energy dependent method defined in Eq. 7.3, $\chi(E) = [\mu(E) - \mu_0(E)]/\mu_0(E)$, is used when a rigorous comparison with the theoretical EXAFS expression is to be attempted [54]; this method compensates for the uncertainties in the sample thickness or concentration. In the energy independent method, the modulations of the absorption coefficient $\mu - \mu_0$ are divided by the size of the constant edge-jump $\Delta\mu(E_0)$ (Figure 7.11b) so giving rise to the XAFS signal. The jump $\Delta\mu(E_0)$ is determined at the edge position $E_0$, which is the position of the maximum of derivative of $d\mu(E)/dE$, by fitting low order polynomials to two intervals data of a few hundred eV below and above the edge, extrapolating them to the edge position, and calculating their difference $\Delta\mu(E_0)$. This method is applied when the experimental data are to be compared with that of a reference compound which has the same absorbing element and the same monotonic function $\mu_0(E)$. In this case, the systematic difference is canceled in the comparison. An alternative accurate normalization of X-ray absorption data for quantitative analysis of near-edge features is reported in Reference 55.

7.6.5 Conversion to $k$-Space, Choice of Threshold Energy $E_0$ and Weighting

For calculating the wavevector $k$ from the relationship $k = \left[\frac{2m}{\hbar^2}(E - E_0)\right]^{1/2}$, the knowledge of the threshold energy $E_0$ is required. The correct determination of $E_0$ is reflected in the accuracy of bond lengths determination. $E_0$ cannot be experimentally determined from the spectrum because complex physical and chemical processes influence shape and position of the edge. Often $E_0$ is fixed at the position of the maximum of the first derivative of the absorption coefficient, $d\mu/dE$, for both reference and unknown compounds. This choice is valid only if the local chemical environment of the absorbing species of the examined samples is expected to be very similar. In general, this situation does not occur especially if reference and unknown samples have different ionicity or valence. The difficulty is overcome by assuming $E_0$ as one of the adjustable parameters of the analysis procedure.

The EXAFS function $\chi(k)$ is often weighted by $k^n$ where $n$ is an integer variable between 1 and 3 (Figure 7.11d); this to amplify the oscillations at high $k$, where the signal amplitude decreases, thus allowing the smaller oscillations to contribute to the determination of atomic distances, which depend on the frequency of oscillations and not on the amplitude, at the same
level as the larger ones.

7.6.6 Transformation from \( k \)-Space to \( R \)-Space

Equation 7.4 can be simply regarded as a summation of sinusoidal functions
\[
\chi(k) = \sum_i A_i \sin(2kR_i + \phi_i(k))
\]
where \( A_i \) represent the amplitude of the XAFS contribution \( \chi_i(k) \) of the \( i \)th coordination shell. The \( k^n \chi(k) \) Fourier transform gives a pseudo-radial distribution function of radii of the atomic shells \( R_i \) around the absorbing atom. The peaks in Figure 7.10 represent the coordination shells around Ge in c- and a-Ge; their positions are shifted with respect to the real \( R_i \) shell radii because of the phase \( \phi_i(k) \). Amplitudes and widths of the peaks depend on the structural parameters \( N_i \) and disorder parameters as well as also from the range in K-space, FT window function type, amplitude and phase scattering functions for each atom type, and \( k^n \)-weight. It should be borne in mind that FT is not a radial distribution function and thus cannot be used for extracting any type of conclusions on the structure. It is suitable mainly to separate contributions from different shells or just to compare the XAFS behavior in R-space of different systems.

7.6.7 Fourier Filtering: Reverse Transformation: from \( R \)-Space to \( k \)-Space

The inverse-transform from the \( \Delta r \) interval of a peak corresponding to the \( i \)th single shell to the \( k \)-space allows the filtering of the XAFS signal, \( \chi_i(k) \), from the overall spectrum. In Figure 7.13 the XAFS signals of the first three shells of Ge in c-Ge have been obtained by back-transforming the first three peaks of the Fourier transform reported in Figure 7.12. The extraction of the structural information of each coordination shell is finally carried out in two ways: by the "log amplitude-ratio and phases-difference" method or by a best fit procedure.
**Figure 7.12** Fourier transform of the XAFS signal reported in Figure 7.11d.

**Figure 7.13** Fourier filtering: the XAFS signals of the first three coordination shells of Ge obtained by reverse Fourier transforming the peaks reported in Figure 7.12.

### 7.6.8 Log Amplitude Ratio and Phases Difference Method

This method is mainly used for analyzing the first coordination shell when it is well separated from the higher shells. The extension to a higher shell is possible only if it is spectrally isolated from all the others and MS contribution is expected to be negligible. This method has been widely applied for studying the evolution of disorder parameters and variations of bond lengths in glasses as function of temperature. It consists in comparing the data of an unknown compound to a well-known standard. In the case of a thermal study on the same sample, the spectrum at the lowest temperature (usually liquid helium or nitrogen temperature) is assumed as standard. The analysis is performed on the Fourier-filtered EXAFS signal. The log of the ratio between the amplitude of the $\chi(k)$ functions of the unknown and the reference spectra plotted as a function of $k^2$ are fitted by polynomials; the same for the difference of the phases of $\chi(k)$ functions. The analysis yields the differences between the cumulants of the radial
distribution of the unknown sample with respect to the standard.

### 7.6.9 Fitting Procedure

An alternative approach and the unique way to analyze multiple shell contributions or the whole unfiltered EXAFS spectrum, is the numerical fitting procedure using the EXAFS parameterized function (Eq. 7.7). Fitting procedures use phase shifts and backscattering functions calculated or extracted from reference materials. A typical procedure is done by a nonlinear least-squares fitting code, using a high speed algorithm, based on the multi-shell Gaussian/cumulant model within single scattering or MS approximation. Simultaneous analysis up to many shells with several fitting parameters in each like $N_i$, $S_i^2$, $R_i$, $\sigma_i^2$, $\Delta E_{0i}$, $C_{3i}$, $C_{4i}$, .... are allowed. The range of values for any fitting parameter can be limited by boundaries or fixed to constant values. Covariance and correlation matrices can be also calculated.

Remarkable progress in theoretical calculations has taken place in the last 10–15 years. Modern codes for calculating theoretical XAFS spectra are accurate enough to fit experimental data directly. FEFF [56, 57] is a leading and most renowned program for calculating spectra. Good open-source software programs like Artemis/Athena [58, 59], Viper [60], EDA [61–63], etc. [64] are available both for processing the EXAFS signal and for using FEFF-calculated spectra to fit the data by starting from an ansatz structure; the GNXAS package [65] is an advanced software for EXAFS data analysis based on multiple-scattering (MS) calculations and a rigorous fitting procedure of the raw experimental data [66]. Calculation of vibrations and some multi electron excitations is an active research area, though parameterizing the fitting process can be quite involved.

In comparison with the fitting procedure, the previously described procedure, if applicable, has the advantage that experimental amplitudes and phase shifts extracted from a reference compound can be transferred to the unknown compound if the environment around the absorbing atom is very similar in both samples. Moreover, the comparison of empirical spectra permits the cancellation of some instrumental effects such as the amplitude suppression at low $k$ due to poor instrumental resolution. A further advantage of the approach with regard to the best-fit procedure is a direct check of the quality of the analyzed intermediate data. Nonlinear least square fitting can be affected by parameters correlations and multiple minima as well as over fitting. On the other hand, Fourier filtering introduces distortions related to transformation intervals, windowing and $k^n$ weighting. So it is necessary to apply to both the reference and calculated XAFS spectra the same filtering procedure applied to the experimental spectrum under analysis [67].

Once the physical parameters contained in Eq. 7.4 or in Eq. 7.5, that is $S_0^2$, $F(k, \pi)$, $\varphi$, and $\lambda$, are extracted from reference compounds or theoretically calculated, structural information of a given coordination shell may be obtained from the EXAFS signal. The information consists in the coordination number $N$, the interatomic distance $R$, the Debye–Waller factor $\sigma^2$, and other order parameters characterizing the radial distribution $\rho(r)$ of the shell. These data are obtained by simulating the EXAFS signal and optimizing the structural parameters together
with the $E_0$ value, until the best fit of the filtered experimental spectrum [67] is obtained. It should be noted, however, that the information content is limited by the finite range of the available signal. It has been reported [68] that, according to the Nyquist sampling theorem, the number of independent parameters obtainable by an EXAFS spectrum is \( n \approx 2\Delta k\Delta r/\pi + 2 \) where \( \Delta k = k_{\text{max}} - k_{\text{min}} \) and \( \Delta r = r_{\text{max}} - r_{\text{min}} \) are the intervals of the direct and inverse Fourier transforms, respectively. If in the fitting procedure is applied to the whole \( \Delta k \) and \( \Delta r \) intervals of the EXAFS spectrum, \( n \) can be less than the number of physical quantities related to all shells and multiple paths needed to fit the spectrum. Limiting the fit to reduced \( \Delta k \) and \( \Delta r \) intervals related to one or two overlapped shells decreases \( n \) as well as the number of the fit parameters [69]. Of course, the reduction of free parameters decreases their mutual correlation.

### 7.7 EXAFS ACCURACY AND LIMITATIONS

As soon as EXAFS began to be routinely used as structural technique in many different scientific areas, the need to establish criteria for evaluating EXAFS accuracy and limitations was recognized. It was soon realized that the accuracy of the structural parameters extracted from EXAFS spectra depends not only on data statistical errors, but also on sample preparation [70], experimental set-up, standards used for modeling EXAFS, transferability of theoretical or experimental phase shifts and backscattering functions, data processing and analytical procedures [71]. While the exact accuracy of EXAFS parameters is still under debate [72, 73], some standards and criteria about experiment, data analysis, theory, and XAS standards database have been established by the International XAFS Society [74]. The accuracy on the determination of \( R \) can vary between 0.01 and 0.001 Å depending on the quality of experimental data and the reliability of backscattering amplitudes and phase shifts. In order to resolve splitting of close distances, \( \Delta R \), XAFS signal must extend at least up to a maximum wavelength \( k_{\text{max}} = (\pi/2\Delta R) \) which corresponds to half of the maximum exchanged momentum in diffraction techniques.

Typical systematic errors reported in literature are: for \( N \), ± 10%; \( R \), ± 0.01 Å; and \( \sigma^2 \), ± 20%, the statistical error generally being much smaller. These figures can, however, be remarkably reduced by following the cited standards and criteria closely. Very accurate results on small changes of structural or thermal parameters are currently obtained in relative measurements carried out on the same sample as a function of temperature, or pressure, or external fields. Sensitivity to mean differential atomic motion of one femtometer, that is a factor of 100 times more sensitive than that normally available, has been published [75] using an X-ray dispersive spectrometer. For Ge isotopes, the effect of isotopic mass difference on the amplitude of relative atomic vibrations has been neatly evidenced by the dependence on temperature of the difference of Debye–Waller factors [76]. The isotopic effect has been also detected on the difference of nearest neighbors average interatomic distances, thanks to a spatial resolution better than 10 fm [71].

In the study of disordered systems, the discrepancies between EXAFS and XRD results
appeared more severe until the limits of the harmonic approximation and the effect of $k_{\text{min}}$ on the accuracy of coordination number were clarified [77]. Several forms of disorder can affect the XAFS spectrum of a glassy system. The presence of two or more slightly different interatomic distances can contribute to the same coordination shells and different structural sites can surround a given atomic species. Another form of disorder, more difficult to analyze, is the *compositional* one which is due to the presence of different atomic species within the same coordination shells. Thus, the characterization of the short-range order in glassy materials needs the choice of an appropriate method for data analysis. In presence of multiple sites around the absorbing species only average results are obtainable.

### 7.8 XANES

In the XANES region, the photoelectron energy is comparable to the free electron states just above the valence band, so the photoelectron is able to probe the bottom of the conduction band. In some cases, a pre-edge structure, caused by electronic transitions to bound states, is present in the absorption spectrum: it is also related to the local geometry around the absorbing atom and the bonding characteristics. XANES are often used as fingerprint, comparing the pre- or above-edge structure of reference compounds with the one of the unknown compound. From the energy edge position and the near edge structure, it is possible to get information about ligand type, coordination chemistry (e.g., tetrahedral, octahedral coordination) and the formal oxidation state of the absorbing atomic species. Normally the edge shifts to higher energy with an increased oxidation state, and a shift up to 5 eV per one unit charge (chemical shift) can be measured [78]. XANES oscillations may be interpreted as related to the structure of the final state density (Eq. 7.2).

Currently, the XANES region is calculated in terms of full multiple scattering (MS) of the photoelectron from the atoms surrounding the absorbing atom. At low energies, the outgoing photoelectron wavefunction has a large mean free path (MFP) and remarkable amplitude from being strongly backscattered by the atomic environment. It occurs that the photoelectron wave function outgoing from the central atom is scattered by other atoms and, after following double, triple, and longer paths (*Figure 7.8b*), is scattered back to the origin. The absorption coefficient is given by a series of terms $\chi_i(k)$ representing all the MS contributions, the first term, $\chi_2(k)$, of the series being the single-shell contribution which corresponds to the EXAFS signal calculated by Eq. 7.5. So, in principle, from XANES it is possible to extract not only the pair correlation function, $g_2$, but also many body correlation function $g_j$, with $j > 2$ (*Figure 7.14*) [32, 79].
Figure 7.14 Beyond the two-body correlation functions: $\chi_i(k)$ represent the SS and MS contribution to the EXAFS signal, $g_j$ represent a pair and multi-body correlation functions (Reference 30).

This approach to XANES points out the importance of the local geometry around the absorbing atom: atomic positions of neighbors, interatomic distances and bond angles can be extracted. XANES contains information about the atomic structural organization over distances up to about 6 Å. In general, it is rather complex and difficult to get structural information over such large distances in glasses. At present, this is becoming possible thanks to MS calculations in real space which are able to mimic XANES spectra [80–83]. Such an approach requires a good starting structural model. Structural models constructed by classical or ab initio molecular dynamics (MD) simulations are currently used satisfactorily [84]. Adequate choices of the cluster size and the final state potential are necessary to get a good agreement between calculations and experimental spectra.

The fact that XANES depends on both local and global properties of the material makes it rich of information but, at the same time, very difficult for a complete theoretical description. At present, the XANES theory in terms of full MS is not yet fully established and the existing software codes are not of simple general use. A different situation occurs with EXAFS, where each MS path can be independently evaluated: this formulation permits fast and accurate calculations of the most important MS paths. Apart from the treatment of inelastic losses and disorder, the common theoretical approaches allow fast and reliable calculations of EXAFS in any material.

7.9 XAFS SPECTROSCOPY APPLIED TO GLASS STRUCTURE: SOME EXAMPLES
Since its advent, XAFS has been exploited to study the local structure in multicomponent atomic systems, thanks to its accessibility to almost all the chemical elements of the periodic table and site sensitivity. It soon appeared to be very useful to the study of glassy structure because the standard diffraction technique showed its fair insensitiveness of the topology of the glass network [85, 86]. This is due to the strong correlations present in the network forming units that hide the weak correlation between modifying cations and the oxygen sublattice. At present NMR, X-ray and neutron diffraction and XAFS are the main experimental techniques used, often together, to elucidate glassy structure. Here we present some examples of application of XAFS to various glassy systems just to emphasize its peculiarities. A wide ranging paper on many inorganic oxide glasses and non-oxide glasses and the liquids from which they derive, investigated by several experimental and theoretical methods, has been published by G.N. Greaves and S. Sen [87]; it reviews the current understanding of the atomic structure of glasses ranging from the local environment of individual atoms to the long-range order up to many interatomic distances.

7.9.1 Silicate Glasses

One pioneering EXAFS study on glasses that still constitutes a milestone of EXAFS application to glassy systems was carried out by G.N. Greaves et al. [88]. This work was carried out at the dawn of the development of the EXAFS technique when the multiple scattering approach and the problems of asymmetric distributions around given species in disordered systems were still in their infancy. The authors investigated the local structure of alkali cations in alkali silicate glasses. The importance of this work stems from the fact that it has provided the basis for the formulation of the modified random network (MRN) model of glassy structure [89]: an extension of the Zacharasen's continuous random network (CRN) model for modified glasses. The CRN model localizes the cations like Na randomly in the holes and voids created inside the covalent network by the topological disorder, so ruling out the presence of defined coordinations around cations. Contrary to this expectation, G.N. Greaves et al., examining the K-edges of Si and Na in sodium disilicate, \( \text{Na}_2\text{Si}_2\text{O}_5 \), and soda-lime-silica, \( \text{Na}_2\text{CaSi}_5\text{O}_{12} \), glasses (Figure 7.15), found in each glass well-defined EXAFS spectra at the Na K-edge, indicating the presence of a different characteristic atomic environment around Na modifier. So, the Na–O coordination, scarcely recognizable by diffraction measurements, was highlighted by EXAFS.
Two clearly distinct environments were observed around Si and Na. The local Si environment appears indistinguishable from that of the reference compounds silica and α-quartz dominated by a single shell of 4 (±1) oxygens at 1.61 Å belonging to the rigid SiO$_4$ unit common to all four samples. On the contrary, the Na environment varies considerably with composition reflecting the situations existing in similar crystalline compounds. However, even weakly bonded elements such as Na have a reasonably well-defined average oxygen first coordination shell depending on the modifier concentration. So two principal sites for oxygen are present in the same glass: one, bridging, coordinated with Si and another, non-bridging, coordinated with Na. The authors envisaged the structure of silicate glasses as a natural extension of the structure of crystalline silicates. A structure made up of two interlacing continuous random sub-lattices: a covalent network consisting of the SiO$_2$ component intercalated by fraction of the modifier component was proposed. The link between the two sub-lattices is affected through the non-bridging oxygens [88] (NBO). The existence of an ionic Na$_2$O sublattice, sufficiently continuous to support percolation paths, would allow the correlated transport
mechanism of sodium [89].

Systematic XANES and EXAFS measurements at the K-edge of Si on a series of sodium silicate glasses at various concentrations of Na$_2$O (15–40 mol%) were carried out 15 years later by G.S. Henderson [90] in total yield mode (TEY). They were still analyzed in the harmonic approximation but considering the multiple shell contribution. The EXAFS data indicate that the Si–O bond distance increases as Na$_2$O is added up to 30 mol%, then decreases. However, this decrease was found inconsistent with the results of the neutron scattering study of Wright et al. [91] who had observed a continuous increase in Si–O bond length up to 50 mol% added Na$_2$O. Such discrepancy was attributed to the sensitivity of TEY to the surface of glass. The increase of the Si–O distance up 30 mol% of Na$_2$O is primarily determined by the network depolymerisation, confirmed also by the energy shift of the Si K-edge, while for higher concentrations the Si–O distance is controlled by NBO formation. The XAFS data are considered by the author consistent with reorganization and ordering of glass network beyond the second coordination sphere as Na$_2$O is added. Such ordering is related to the micro-segregation predicted by molecular dynamics [92] and by the previous EXAFS measurements [89], according to which, with increasing Na$_2$O, the network modifiers micro-segregate and are separated from the silicate network by NBO-rich regions.

The structural evidence of the micro-segregation of alkalis in oxide glasses first observed by G.N. Greaves et al. [88] was afterwards reviewed in relation with the ionic transport mechanism in different silicate glasses by G.N. Greaves and K.L. Ngai [93]. This work distinguishes the hopping mechanism of alkalis in silicate glasses where changes in the configurations of neighboring bridging and non-bridging oxygens are expected, as described by the MRN, from the alkalis hopping in fully charge compensated aluminosilicate glasses where the absence of NBO and the minimization of conformational changes in the network suggest a compensated CRN.

These and more recent XAFS results on alkali silicate glasses [94], together with the results of other techniques, notably magic angle spinning NMR [95], IR [96] and Raman [97] spectroscopy and XPS [98], as well as sophisticated MD simulations [99, 100], have provided a considerable contribution to elucidate structure and ionic diffusion mechanism.

**7.9.2 Silica Glass**

From the theoretical viewpoint, silica glass has become a prototype system for understanding the disordered state. Despite the large number of research papers on glassy silicon dioxide, this subject continues to arouse a remarkable interest as SiO$_2$ is one of the most interesting insulator materials having great applicability in many fields of technology like optoelectronics, microelectronic devices, etc. In glasses, structural information over distances beyond 10 Å from a given atomic species are difficult to obtain. Generally structural and dynamical disorder does not allow to extract EXAFS information beyond the first coordination shell. One possible way to go further is trying to reproduce experimental XANES by applying MS calculations to an assumed atomic cluster. In the case of glassy silica, this has been done by
Levelut et al. [101] at the K-edge of Si combining molecular dynamics (MD) and multiple scattering (MS). Structural models for MS calculations are obtained by classical and ab initio MD, taking into account the site disorder of the absorber by averaging several clusters. The agreement with experiment appears good and is independent on the model extracted from classical and ab initio MD. The results show the influence of the medium-range order on XANES up to more than 5 Å (Figure 7.16).

![Figure 7.16](image)

**Figure 7.16** XANES spectrum at the K–Si edge in silica: comparison between the experimental spectrum and two theoretical spectra corresponding to two samples generated by classical MD and ab initio MD calculations each averaged over two clusters [101].

### 7.9.3 Silica at High Temperature

XANES measurements at the Si K-edge in fluorescence mode were carried out on SiO$_2$ α-quartz from room temperature up to 2030 K at the microfocus beamline Lucia of the French synchrotron radiation facility Soleil [102] by D. de Ligny et al. [103]. Silica polymorphic transformations were observed in situ up to the liquid phase looking at Si environment in...
crystals and glasses as a function of temperature. From the comparison of the silica polymorphs with amorphous and molten silica, a better understanding of the local order present in the glass and liquid within the XANES sensitivity range of 6 Å was obtained.

The interpretation of the experimental spectra combines two approaches of the XANES study: the quantitative reconstruction of the spectra and the qualitative evaluation of their features as fingerprints of particular structural arrangements.

In Figure 7.17, the room temperature spectra of different well-known silica polymorphs are compared. The vertical dashed lines, labeled from A to F, indicate the features present on the α-quartz spectrum. Between 1850 and 1880 eV strong modifications are observed in the polymorphs; a close similarity between α-cristobalite and glass spectra is pointed out by the authors. Si K-edge XANES spectra for α-quartz from room to high temperature are shown in Figure 7.18 with the indications, on each spectrum, of the phases deduced from the calculated spectra. Some similarities are noticed between the XANES spectra with increasing temperature and the evolution observed at room temperature in Figure 7.17: in particular α-cristobalite and glass correspond to high temperature silica polymorphs quenched to room temperature even if no direct comparison among the spectra can be done. Moreover, the liquid and glass spectra are very similar especially in the E and F regions. In order to better identify the different β polymorphs which should appear as temperature increases, XANES spectra calculation were performed on α-cristobalite. The calculations were done on different cluster sizes, considering the atomic radial distribution around the central atom. The FDMNES (Finite Difference Method Near-Edge Simulation) software provided by Y. Joly [104] and the cell parameters and atomic position drawn from XRD studies were used. Calculations on clusters of 51 and 69 atoms were then performed respectively for β-quartz and β-cristobalite (Figure 7.3 in Reference 103); these theoretical spectra were similar to the high temperature experimental spectra shown in Figure 7.18, so the 970 K spectrum was assigned to β-quartz and the 1940 K to β-cristobalite. This result was considered in good agreement with the findings of neutron total scattering experiments which showed the same structure up to 7.5 Å for silica glass and β-cristobalite.
**Figure 7.17** Room temperature Si K-edge XANES spectra for SiO$_2$ polymorph [103].
Figure 7.18 Si K-edge XANES spectra for SiO2 α-quartz brought to high temperature. Phases were assigned from calculated spectra. The liquid was assigned from the thermodynamic stability field [103].

It is not always the case that XANES calculations, when compared with experimental data, are able to fit all details of a spectrum, its energy position and its absolute intensity. Nevertheless, they provide useful information on structure and size of the cluster adequate to reproduce the main features of the spectrum. Recently a first principle calculation based on the continued fraction approach and ultra-soft pseudo-potentials has been able to reproduce XANES spectra at the Si and O K-edges of SiO2 quartz [105].

7.9.4 Silica and Germania Glasses under High Pressure

7.9.4.1 XANES Measurements

The changes induced by pressure in structure and properties of noncrystalline materials constitute a topic of high interest for condensed matter. Changes in silica and germania, GeO2,
are of interest not only in high pressure physics but also in geophysics and material science. Molecular dynamics simulations suggest the occurrence of these structural changes is accompanied by an increase of the coordination number of oxygen atoms around Si or Ge from 4 to 6. Synchrotron X-ray absorption and diffraction technique currently allow the study of the behavior of materials at high pressure. In the case of silica, the measurements carried out by different techniques are few and controversial: while X-ray diffraction and other techniques indicate that the coordination number changes from 4 to 6 only at pressures greater than 20 GPa [106, 107], X-ray Raman scattering at the O K-edge [108] suggests that the change occurs between 10 and 20 GPa. Germanates are structural analogues to silicates and are more accessible to XAFS experiments because the higher energy of the K-edge of Ge with respect to Si facilitates the measurements in the pressure diamond-anvil cells. Like silica, germania under pressure undergoes amorphous–amorphous transformations whose kinetic study highlights a number of anomalous features that make them different from ordinary first-order transitions and from transition in liquids [109]. Earlier in situ XAFS spectra were performed on amorphous and crystalline Ge by Itié et al. [110] using a diamond-anvil cell adapted to an energy dispersive spectrometer at various pressures up to 29 GPa. The first direct evidence of complete coordination change in α-quartz GeO₂ and in amorphous GeO₂ was shown. The coordination of Ge was found to change from fourfold to sixfold coordination at pressures between 7 and 9 GPa. The progressive evolution of the Ge–O distances together with the modifications of the XANES suggested the presence of two different sites rather than a progressive site modification. The phase transition observed in amorphous phase was found to be reversible in contrast to that observed in crystalline phase [110]. The evidence of the coexistence of two different sites in α-quartz in the pressure range of phase transition is depicted by the spectrum at 7.4 GPa in Figure 7.19c. This spectrum is well reproduced as a linear combination of the spectra of α-quartz GeO₂ below and above the phase transition (Figure 7.19a and 7.19b, respectively) which are very close to the spectra of α-quartz GeO₂ at ambient pressure, showing fourfold coordination, and rutile α-quartz GeO₂ characterized by a sixfold coordination. The change of the coordination number in amorphous GeO₂ follows a similar pressure trend to that of α-quartz GeO₂. In this work, the change in Ge–O distance versus pressure was quantitatively investigated by analyzing the EXAFS spectra.
Figure 7.19 Evidence of the coexistence of two different sites in \( q \)-GeO\(_2\) in the pressure range of the phase transitions. XANES spectrum of c (7.4 GPa) is well reproduced in d by a weighted addition of XANES spectra in the low and high pressure phase (a and b, respectively) [110].

Similar investigations have been extended to LiO\(_2\)-4GeO\(_2\) glass and pure GeO\(_2\) gel compressed to 14 GPa at room temperature by O. Ohtaka et al. [111]. In Figure 7.20, the XANES of the LiO\(_2\)-4GeO\(_2\) glass (g-GeO\(_2\)) is reported together with the GeO\(_2\) reference compounds in rutile and quartz (q-GeO\(_2\)) forms. EXAFS measurements confirm that, on compression, the Ge–O distance in the LiO\(_2\)-4GeO\(_2\) glass gradually becomes shorter below 7 GPa, showing the conventional compression of the GeO\(_2\) tetrahedron, while between 8 and 10 GPa, when the number of oxygen atoms around Ge changes from 4 to 6, the Ge–O distance undergoes an abrupt increase.
Figure 7.20 Experimental Ge K-Edge XANES spectra of LiO$_2$-4GeO$_2$ glass ($g$-GeO$_2$) together with the XANES of the reference compound of GeO$_2$ in rutile and quartz ($q$-GeO$_2$) forms. The arrows indicate the two shoulders characteristic of sixfold coordination of Ge [111].

The comparison of the XANES spectra of complex systems of unknown structure with spectra of reference compounds with known coordination is a common use of XANES. This qualitative method of using the XANES of simple known compounds as fingerprints in complex systems is typical in the analyses of multicomponent glasses or composites used to corroborate EXAFS speculations.

7.9.4.2 EXAFS Measurements

A more recent detailed EXAFS analysis on amorphous, a-GeO$_2$, and crystalline, q-GeO$_2$, confirmed the transformation from four- to sixfold coordination [112] under pressure. For q-GeO$_2$ it appears abrupt at 8.5 GPa but the whole 6–12 GPa pressure range has to be considered as a transition region; for amorphous GeO$_2$ the transition is more gradual but the full octahedral state is not reached at 13 GPa as commonly believed. The moduli of the
EXAFS Fourier transforms at the K-edge of Ge in both crystalline and amorphous GeO₂ are reported in Figure 7.21 for some selected pressures [112]. The spectra drawn with continuous lines correspond to the low pressure phase, while in the dashed lines to the transition region and in dotted line (only for q-GeO₂) to the high pressure phase. According to the authors, in both compounds, the main peak at about 1.3 Å is due to the nearest neighbor oxygen atoms, which at ambient conditions are tetrahedrally coordinated to the central Ge atom [112]. In crystalline GeO₂ at ambient pressure, the structure from about 1.8 to 3.4 Å is due to second and third coordination shells (made up of four germanium and six oxygen atoms, respectively) and to multiple scattering contributions. In the case of amorphous GeO₂, the signal beyond the first coordination shell is attributed to an intermediate range order in the glass. The behavior of the first distance Ge–O as a function pressure is reported in Figure 7.22 for both compounds.

**Figure 7.21** Moduli of the EXAFS Fourier transforms at the K-edge of Ge in crystalline and amorphous GeO₂; the peak positions are backward shifted with respect to the actual interatomic distances as the transforms were performed without phase shift correction [112].
Figure 7.22 Ge–O first coordination distance in crystalline and amorphous GeO₂ versus pressure [112].

At low pressures, the Ge–O distance is practically constant with increasing pressure (top panel): the predominant bulk compression mechanism in q-GeO₂ corresponds to a distortion of the tetrahedron arising from changes in O–Ge–O angles, so that the average Ge–O bond lengths are almost constant in spite of an overall decrease of lattice parameters as a function of pressure. The phase transition is quite sharp at about 8.5 GPa but it is present in whole region 6–12 GPa. The authors find that the first shell coordination number qualitatively reflects the Ge–O distance evolution: it is equal to $N = 4$ (constant) in the low region then sharply increases reaching a high pressure value compatible with $N = 6$. A more gradual transition occurs in amorphous GeO₂ for both distance and coordination number which becomes about 5 at 13 GPa.

7.9.5 Nanoparticles Embedded in Glasses

Dispersion of nanoparticles in glass is a technique known since Roman time when composite
materials made by nanoparticles embedded in glass were exploited to produce stained glasses with beautiful colors. Nowadays metal nanocluster composite glasses are the object of numerous studies not only for the simple coloration process but because their optical and magnetic properties can be adjusted by controlling mean particle size and size distribution. The physical properties of nanoparticle-glass composite strongly depend on morphology, mean size, size distribution, concentration and interaction of nanoparticles with the host matrix. The technological interest toward these systems stems from the capability of tailoring the behavior of the glass-based structures as well as from the potentially low cost, ease of processing, high durability, resistance, and transparency. Scientific research aims at describing and understanding the dynamics of the processes of nucleation and growth of nanoparticles, their structure, size, size distribution and stability [113] in relation with their physical properties, the host material and the preparation methods.

EXAFS spectroscopy is one of the most suitable techniques for studying the structure of nanoparticles dispersed in glassy matrices since it provides information about their local structure and vibrational dynamics, irrespective of their size. By in situ XAFS measurements the local structural vibrational disorder of diluted species and the oxide phases formation in the host matrices can be followed after each state of preparation thus obtaining an effective description of nucleation and growth processes [114].

Two XAFS investigation on dopants in glasses are reported in this chapter: silver nanoparticles embedded in soda-lime glasses and Erbium doping in silica-based host matrices.

### 7.9.5.1 Ag Nanoparticles Embedded in Soda-Lime Silicate Glasses

Silicate glasses with embedded silver nanosized particles have attracted much interest as materials with potential applications in optoelectronics. Ag nanoparticles fabricated in soda-lime glass of varying ion oxide content by Na\(^+\)/Ag\(^+\) ion exchange and subsequent thermal treatment have been studied by XAFS and other structural techniques by several groups [114, 115].

By EXAFS measurements at the K-edge of Ag, information on structural and vibrational behavior of silver particles in dependence of particle size and temperature have been reported by Dubiel et al. [116] for particle sizes ranging from 1.7 to 7 nm. Cumulant EXAFS analysis has been done through UWXAFS code [117] using the theoretical amplitude and phase functions calculated by FEFF8 [56]. The extracted EXAFS data, like Ag–Ag distance, Debye–Waller factor and higher cumulants aim to get an insight on the influence of quantum size effects, interaction between nanoparticles and matrix and thermal effects induced by preparation at elevated temperatures. The Fourier transform of a glass containing particles of 1.5 nm, is shown in Figure 7.23 both the Ag–Ag and Ag–O correlations can be recognized.
Figure 7.23 Modulus of Ag K-Edge EXAFS at 10 K for ion exchanged glass containing particles of 1.5 nm. The dashed line represents the result of fitting [116].

The presence of Ag–Ag correlations constitutes the prerequisite for Ag particles formation; the Ag–O correlations is due to the oxygen environment of silver ions in the glassy matrix. The Ag–Ag distance in nanoparticles of 1.5 nm in size has been found to be less than 3.4% as compared to Ag bulk (Figure 7.24). The authors relate this reduction not only to the lattice contraction of small particles but also to the presence of clusters having structures similar to those found in silver oxides, like in Ag₆O₂, so they assume the formation of silver oxide-like clusters as predecessors or intermediates in the formation of crystalline Ag nanoparticles [118]. In Figure 7.24, the Ag–Ag first-shell interatomic distances R of different silver nanoparticles, measured as a function of temperature, are compared to the corresponding data for crystalline silver obtained by XRD. Usually, the interatomic distances determined by EXAFS are always larger than the distances between the centers of probability functions measured by XRD [119], owing to mean-squared vibrational displacements perpendicular to the line connecting the average position of the observed pair of atoms. For larger particles, the discrepancy between Ag–Ag distance in nanoparticles and in Ag bulk appears only as a slight shift of R(T) values, possibly caused by thermal treatment at elevated temperatures [116]. In Figure 7.24, for the larger nanoparticles with sizes of 4 and 7 nm, R(T) presents two slopes...
below and above the critical temperature $T_C = 400K$: below $T_C$, the lower slope is due to tensile stresses caused by the strong interaction of the particles with the host matrix; above $T_C$, the thermal expansion is similar to that of bulk material. In Figure 7.25, the second cumulant $\sigma_2(T) = C_2(T)$ of the radial distribution of the $Ag–Ag$ coordination is reported for 4 nm Ag nanoparticles as a function of temperature. $\sigma_2$ contains a component dependent on temperature, which gives information on thermal vibration, and a static component, $\sigma_{2S}$, evaluable at $T\equiv0K$, related to the static disorder in Ag nanoparticles.

Figure 7.24 Ag–Ag bond lengths of nanoparticles compared with XRD data of single-crystalline Ag [116].
Figure 7.25 Experimental data of Debye–Waller factor. The theoretical fit function yields a static part and a dynamic part [116].

The behavior of $\sigma_{2S}$ as a function of all particle sizes is reported in Figure 7.26 in comparison with the static disorder of the polycrystalline foil. The lower the particle size, the larger the static disorder especially for particles with sizes less than 5 nm. This behavior is attributed to the large number of atoms on the particles surface as well as to the interaction of the particles with the host glassy matrix.
Figure 7.26 The static Debye–Waller factor of all the samples with different average particle size [116].

7.9.5.2 Rare-Earth Impurities Dispersed in Glassy Matrices

Rare-earth elements present unique photoluminescence properties; their inclusion in glasses has been known for a long time as a convenient way for the fabrication of novel advanced optoelectronic devices. In the last few years the great development of optical communications has yielded increasing research and development activity on the design and manufacture of fiber optic and integrated optic lasers and amplifiers, especially of those based on Er$^{3+}$-doped glasses [120]. Er$^{3+}$-activated glass derived materials are used for the construction of Er$^{3+}$-doped waveguide amplifiers which are integrated optical devices providing high optical amplification in reduced sizes. The higher the Er content, the higher the amplification; but for small size devices Er$^{3+}$ concentration must below (typically ~1 mol%) in order to avoid Er$^{3+}$ clustering and its consequent intensity quenching. Since clustering depends on the hosting material, to combine small size and high Er content, the solution is to find new materials based on SiO$_2$ glass. Research has indicated two ways: (1) co-doping SiO$_2$ with other oxides in glassy form and (2) embedding Er$^{3+}$ ions in nanocrystals of co-dopant oxides. At any rate, the knowledge of the Er$^{3+}$ local structure is fundamental for the optimization of systems with the best optical properties. For this purpose EXAFS, thanks to its element sensitivity, plays a key role: it allows a careful description of the local environment of rare-earth elements within the
glassy network, that is useful for a better understanding of the spectroscopic properties and for selecting systems with optimized optical and spectral properties. Local structure around Er$^{3+}$ ions incorporated in SiO$_2$-HfO$_2$ waveguides in glassy and in glass-ceramics regimes has been studied by EXAFS at the Er L$_3$-edge by Afify et al. [121]. Waveguides containing various concentrations of HfO$_2$ and Er annealed at different temperatures have been investigated (Table 7.1); in Figure 7.27a and 7.27b the EXAFS signals $k\chi(k)$ and the relative $k^2\chi(k)$ Fourier Transforms are shown for all the samples.

**Table 7.1** Structural data obtained from EXAFS investigations on some different Er-doped waveguides [121].

<table>
<thead>
<tr>
<th>HfO$_2$ content (mol%)</th>
<th>10</th>
<th>20</th>
<th>30</th>
<th>40</th>
<th>50</th>
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<tr>
<td>Er$^{3+}$ content (mol%)</td>
<td>0.3</td>
<td>0.3</td>
<td>0.5</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>Thickness (micron)</td>
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<td>1.280</td>
<td>0.690</td>
<td>0.960</td>
<td>0.722</td>
</tr>
<tr>
<td>Heat treatment time at 900° C</td>
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<td>3.5 hour</td>
<td>5 minutes</td>
<td>5 minutes</td>
<td>2 minutes</td>
</tr>
<tr>
<td>First coordination</td>
<td>N (atom)</td>
<td>5.1(1)</td>
<td>5.1(1)</td>
<td>4.8(1)</td>
<td>5.0(2)</td>
</tr>
<tr>
<td>Shell</td>
<td>R (Å)</td>
<td>2.34(1)</td>
<td>2.33(1)</td>
<td>2.34(2)</td>
<td>2.33(2)</td>
</tr>
<tr>
<td>(Er$^{3+}$-O)</td>
<td>σ(Å$^2$)</td>
<td>0.011(2)</td>
<td>0.012(2)</td>
<td>0.012(2)</td>
<td>0.013(2)</td>
</tr>
<tr>
<td>Second coordination</td>
<td>N (atom)</td>
<td>4.0(7)</td>
<td>3.9(7)</td>
<td>3.4(1)</td>
<td>3.8(2)</td>
</tr>
<tr>
<td>Shell</td>
<td>R (Å)</td>
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<td>3.52(1)</td>
<td>3.51(1)</td>
<td>3.50(1)</td>
</tr>
<tr>
<td>(Er$^{3+}$-Hf)</td>
<td>σ(Å$^2$)</td>
<td>0.015(4)</td>
<td>0.013(4)</td>
<td>0.011(2)</td>
<td>0.014(4)</td>
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</table>
Figure 7.27 (a) Er L3-edge EXAFS spectra of Er$^{3+}$-doped SiO$_2$-HfO$_2$ waveguides at different concentrations of HfO$_2$ (see Table 7.1 for details). Spectra are vertically shifted for clarity. EXAFS signals $k\chi(k)$, (b) Fourier transforms moduli of the EXAFS signals $k^2\chi(k)$ [121].

In the range 0.8–3.3 Å, the moduli of their Fourier transforms $k^2\chi(k)$ (Figure 7.27b) show a major peak at about 1.7 Å and a contribution at about 2.9 Å. These structures can be attributed to the first two coordination shells around Er$^{3+}$ ions, as well as to multiple-scattering effects. However, the analysis has demonstrated that the multiple-scattering contribution is negligible, and that the structures are due to the first shell Er$^{3+}$-O pair correlation and second shell Er$^{3+}$-Hf pair correlation, respectively.

EXAFS signals were modeled employing the EDA [61] code on the basis of the usual multi-shell fitting procedure. To fit EXAFS signals, the backscattering phase and amplitude functions of different atomic pair correlations were extracted experimentally resorting to reference compounds, or calculated using the FEFF8 [52] code. The fit quality is depicted in Figure 7.28.
Figure 7.28 Modeling results of Er L3-edge EXAFS signals $k^2\chi(k)$ of different waveguides. Spectra are vertically shifted for clarity. (a) Comparison between experimental data and calculated spectra of the waveguides containing the lowest molar concentration of HfO2 (W1: 10%), and the largest (W5: 50%): calculated Er-O and Er-Hf EXAFS contributions are shown with their summation and the residual signal, and compared with the experimental EXAFS data (empty circles). The residual (black curve) EXAFS signals $k^2\chi(k)$. (b) Experimental and best-fit calculated Fourier transforms of the $k^2\chi(k)$ EXAFS signals for different waveguides (see Table 7.1). The calculated Modulus and the imaginary parts lie over the respective experimental data (dashed lines).

According to the results of the EXAFS analysis, summarized in Table 7.1, the first coordination sphere around Er$^{3+}$ is composed of five to six oxygen atoms at an average interatomic distance of 2.33 Å. Hafnium is the main atomic species present in the second coordination shell. Both the first and the second coordination shells of Er$^{3+}$ ions are independent on Er$^{3+}$ mol% concentrations. These results indicate that Er$^{3+}$ is preferentially dispersed in HfO$_2$-rich regions of the waveguide, starting from the lowest concentrations of HfO$_2$, differing in this respect from previously studied SiO$_2$-based binary or ternary glassy host matrices. No Er$^{3+}$-Er$^{3+}$ coordination shell has been detected; this fact rules out the Er clusterization. On the basis of the current EXAFS results and the photoluminescence studies, HfO$_2$ co-doping yields two effects: (i) an increase of Er$^{3+}$ solubility in the host glass and (ii) modification of the crystal field around Er$^{3+}$ sites, keeping the sites unchanged for a wide range of HfO$_2$ concentrations.

7.9.6 Study of Ionic Conductivity in Superionic Glasses Doped with AgI
Fast-ion-conducting glasses are systems characterized by values of ionic conductivity comparable to those of liquid electrolytes. They are of wide interest for potential applications in solid electrochemical devices. The understanding of transport properties in these glasses is still a challenging problem both from the applied and the basic research point of view; its solution may allow the design of new glasses with optimized properties for various applications. Here we refer to an EXAFS work by Sanson et al. [122], concerning superionic glasses doped with silver iodide (AgI) at the K-edge of iodine, with the objective to correlate the local environment of I to the high mobility of Ag\(^+\) cations. Twenty-four AgI-based fast-ion-conducting glasses, belonging to three different glass families (silver-borate, silver-molibdate and silver-tungstate) and having different activation energies have been examined. In Figure 7.29 the $k\chi(k)$ EXAFS signal and the corresponding Fourier transforms are reported. The EXAFS measurements were done in transmission mode; to get homogeneous samples of uniform thickness, the glasses were powdered, dispersed in alcohol and slowly deposited on polytetrafluoroethylene membranes. The thickness was chosen to have, when possible, an absorption edge jump $\Delta \mu = 1$ to optimize the signal-to-noise ratio.
Figure 7.29 EXAFS at the I-K-edge and the corresponding Fourier transforms for the reference compound $\beta$-AgI at 300 K (panel a) and three glasses AgI$_{0.50}$ (Ag$_2$O:4 B$_2$O$_3$)$_{0.50}$ (panel b), AgI$_{0.50}$ (AgPO$_3$)$_{0.50}$ (panel c) and AgI$_{0.30}$ (Ag$_2$WO$_4$)$_{0.70}$ (panel d) at liquid nitrogen temperature. Dashed and continuous lines in the Fourier transform are the imaginary part and the modulus, respectively.

The EXAFS signals, extracted from the experimental spectra according to well-established procedures [40], display good quality up to 15 $\text{Å}^{-1}$ (Figure 7.29). All glasses display a striking similarity in the Fourier transform; like in $\beta$-AgI, the structure between about 1.5 and 3 is due to the contribution of nearest neighbor Ag ions (the double peak is due to the shape of the backscattering amplitude of silver).

A nearest-neighbor link between negative iodine and oxygen ions is highly improbable. No neat contribution from farther neighbors is visible, owing to the effect of disorder. The experimental data for the glasses have been extracted from the EXAFS signals using crystalline $\beta$-AgI at liquid nitrogen temperature as reference material for backscattering amplitudes, phase shifts, and inelastic terms. The cumulant analysis allows one to determine the main parameters
which describe the distance distribution between the EXAFS absorbing atom and its nearest neighbors, namely mean distance, variance, skew parameter, and coordination number.

Figure 7.30 shows, for each of the 24 analyzed glasses, the I–Ag distance obtained from EXAFS measurements, plotted against the corresponding activation energy for dc ionic conductivity. A general correlation between the first shell I–Ag distance measured by EXAFS and the glass activation energy for dc ionic conductivity has been found out: glasses with longer I–Ag distances display higher ionic conductivity, independently from the chemical composition of their host glassy matrix.

Figure 7.30 Mean I–Ag distance measured by EXAFS in different families of AgI-based glasses at liquid nitrogen temperature, plotted against their activation energy for dc ionic conductivity. The symbols refer to the glass family: ⊙ = AgI – Ag₂O – 2 · B₂O₃, ⊠ = AgI – Ag₂O – 3 · B₂O₃, • = AgI – Ag₂O – 4 · B₂O₃, • = 1/4AgI – AgPO₃, = AgI – Ag₂MoO₄, ♦ = AgI – Ag₂WO₄. Dashed line is the reference value of crystalline β-AgI at liquid nitrogen temperature.

As a result, the I–Ag distance plays a key role on the conductivity enhancement of AgI superionic glasses, independently from the chemical composition of the host glassy matrix.
This fact has been related to a theoretical model for the ionic conduction [122].

7.10 SUMMARY AND CONCLUSIONS

The ability to investigate almost all atomic species of multicomponent systems and even dopants diluted down to concentrations of less than 100 ppm makes XAFS a useful and powerful structural tool for studying glassy materials. Let us summarize XAFS main features:

- **XAFS length scale** is a few Angstroms. XAFS probes short-range ordering in matter irrespective of aggregation state.

- **XAFS time scale** depends on the core hole lifetime of the excited atom ($\sim 10^{-15}$s), that is much faster than any atomic motion ($\sim 10^{-13}$s). Each absorption event takes a picture of the instantaneous atomic positions; each measurement point integrates over many absorbers and many snapshots. So the final result of the absorption measurement is the atomic distribution through a space and a time averaging.

- **XAFS measurements** need intense synchrotron radiation sources. Measurement times vary from hours to milliseconds depending on experiment aims and experimental set-up. Phase transitions under extreme conditions of pressure and temperature are detectable. Kinetics of physico-chemical processes like crystallization, amorphization, melting, etc. can be recorded by ultrafast techniques.

- **EXAFS is essentially a one-dimensional tool.** Its elemental specificity allows for the extraction of partial pair correlation functions around the chosen absorbing species. Many body correlation functions can be extracted resorting to multiple scattering.

- **EXAFS provides information** about mean distance, coordination number, radial distribution variance, and distribution asymmetry. Often, for disordered systems, only the coordination shell of the nearest neighbors and sometime the next-nearest are detectable.

- **EXAFS yields information** about disorder in interatomic distances; measurements as a function of temperature allow for the discrimination between static and thermal disorder. The parameters characteristic of thermal disorder, like the thermal Debye–Waller factor, Einstein and Debye temperatures, etc., can be used to study the local vibrational dynamics.

- **XANES can be used as a fingerprint** to empirically and qualitatively extract information about coordination chemistry, molecular orbitals, and electronic band structure.

- **XANES is commonly used** to determine the valence state through the measurement of the shift of the edge position.

- **XANES analysis based on linear combinations of known reference spectra of model compounds** yields the ratios of valence states and phases present in an unknown compound.

- **Theoretical quantitative reproduction** of XANES is complex, time-consuming and not always reliable. Increasing progress in *ab initio* calculations and software codes is reported in the literature.
Bond angles and direct measurement of three-body correlations can be obtained through multiple scattering.

However, there are many other probes that measure atomic positions, their atomic correlations, their thermal and static disorder, etc. that differ from XAFS by length and time scale (neutron and X-ray diffraction, nuclear magnetic resonance, nuclear quadrupole resonance, electron energy loss spectroscopy, Mössbauer spectroscopy, etc.). Only the joined use of these techniques may help to give an accurate and deep description of the structure of glassy materials.

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8
NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY OF GLASSES

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8.1 INTRODUCTION

If the invention of nuclear magnetic resonance (NMR) spectroscopy had preceded that of X-ray diffraction, our concept of structure in the solid state may have been different. The predominance of X-ray diffraction in determining crystal structures led to the establishment of a structural vocabulary incompatible with the nature of the glassy state. The term “structure” is often associated with unit cells in crystalline materials due to this historical chronology. However, the lack of long-range periodic translational order in glasses requires a different description of structure due to the preponderance of short-range order, in particular, one in which geometrical environments are elaborated from a specific point in the material.

NMR is a technique ideally suited for such a description as it probes the local environment of a nucleus. Indeed, NMR has a long history of providing valuable insight into glass structure. Little more than a decade after its invention, NMR was being used to determine the relative populations of three- and four-coordinate borons in alkali borate glasses [1]. These early studies suffered from a lack of peak resolution due to the anisotropies associated with internal interactions and the intrinsic geometric disorder present in glasses. However, advances in the technique of magic-angle spinning (MAS) during the 1970s revolutionized the use of NMR in glass studies as it dramatically increased peak resolution and allowed distinctly different local environments to be identified and quantified [2, 3].

NMR spectroscopy is capable of detecting nuclear spins from across the periodic table. Peak positions indicate such geometric parameters as coordination number, the nature of the bonded atoms, degree of polyhedral regularity, and polyhedral connectivity. Peak intensities are directly related to the population of the corresponding species, leading to a straightforward quantitative determination of short-range order. Furthermore, other spin interactions (e.g., quadrupolar, anisotropic shielding, indirect spin–spin coupling, and direct dipolar) may also be present and can provide valuable additional structural information relating to coordination geometry and connectivity. Finally, taking advantage of the multinuclear nature of NMR can provide complementary structural viewpoints of a given glass to build a consistent and comprehensive picture of the disordered structure.

8.2 THEORETICAL BACKGROUND
8.2.1 Zeeman Effect

NMR spectroscopy is based on the measurement of energy differences between nuclear spin states in nuclides with spin quantum number, $S \geq 1/2$, using radiofrequency fields. In the absence of a magnetic field, these spin states, characterized by the orientational quantum number $m_s$, have the same energy. However, the presence of a magnetic field, $B_0$, lifts this degeneracy and induces a splitting of the energy levels associated with nuclear magnetic dipole moments into $2S + 1$ levels, among which $2S$ single-quantum transitions are allowed (Figure 8.1). This Zeeman effect increases linearly with the applied magnetic field such that resonance frequencies of common nuclides generally lie in the 100–1000 MHz range on modern instrumentation. For a given nuclide, the transition energy, $\Delta E$, is governed by the magnetogyric ratio, $\gamma$, a characteristic property (Table 8.1) such that

$$\Delta E = \gamma \hbar B_0$$  \hspace{1cm} (8.1)

Table 8.1 Nuclear properties of selected nuclides of interest in glass science.*

<table>
<thead>
<tr>
<th>Nucleus</th>
<th>$S$</th>
<th>Natural abundance (%)</th>
<th>$\gamma/10^7$ rad T$^{-1}$ s$^{-1}$</th>
<th>$10^{31}$ Q/m$^2$</th>
<th>Receptivity$^+$</th>
<th>$\nu_0$ at 11.74 T (MHz)</th>
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<td>7/2</td>
<td>3.5277</td>
<td>-3.43</td>
<td>2730</td>
<td>65.560</td>
<td></td>
</tr>
<tr>
<td>Ba</td>
<td>3/2</td>
<td>2.988</td>
<td>245</td>
<td>4.47</td>
<td>55.547</td>
<td></td>
</tr>
<tr>
<td>La</td>
<td>7/2</td>
<td>3.801</td>
<td>200</td>
<td>342</td>
<td>70.606</td>
<td></td>
</tr>
<tr>
<td>Tl</td>
<td>1/2</td>
<td>15.589</td>
<td>-</td>
<td>791</td>
<td>288.329</td>
<td></td>
</tr>
<tr>
<td>Pb</td>
<td>1/2</td>
<td>5.540</td>
<td>-</td>
<td>11.4</td>
<td>104.570</td>
<td></td>
</tr>
</tbody>
</table>

Source: Adapted from Reference [4].

* Quadrupole moments (mb) from Pyykko [5]; NMR frequencies, ν₀, based on IUPAC Commission I.5, 2001.

† Receptivity relative to ¹³C, a partial indicator of a nuclide’s suitability for NMR observation, as defined by Harris [4].
Figure 8.1 Generalized energy-level diagram for an $S = 3/2$ nuclide as a function of applied magnetic field. Arrows indicate energies for the central (CT) and satellite (ST) transitions.

The energy-level populations follow the Boltzmann distribution such that a larger $\Delta E$ generates a greater population difference and hence greater intrinsic signal sensitivity. From a classical physics standpoint, the spins can be understood to precess in a conical path about the magnetic field axis at the Larmor frequency,

$$\nu_0 = \frac{|y|B_0}{2\pi} = \frac{\omega_0}{2\pi}$$

(8.2)

thereby generating bulk magnetization along $\vec{B}_0$ (Figure 8.2a).
Figure 8.2 Spin description of an NMR experiment: (a) precession of a nuclear spin about the magnetic field vector, representing an ensemble of precessing spins with the bulk magnetization aligned with \( \vec{B}_0 \); (b) after rotation by a \( B_1 \) field directed along the y-axis, the bulk magnetization lies in the observable x–y plane.

8.2.2 Magnetic Shielding

The Zeeman effect provides the fundamental basis which makes NMR spectroscopy possible, but its use to distinguish different chemical environments arises from the relatively small energy-level perturbations induced by local magnetic effects in molecules and materials. Electron motion in the surrounding bonds generates magnetic fields which alter the net field to which the nuclei are subject, resulting in subtle changes in the transition frequencies. This internal magnetic shielding interaction proves to be measurable in an NMR experiment, producing resonance shifts which are characteristic of local electronic environments. The absolute shielding is the frequency difference between the (hypothetical) bare nucleus, \( \nu_n \), and its frequency in the local electronic environment in the sample, \( \nu_s \),

\[
\sigma \text{(ppm)} = \left( \frac{\nu_n - \nu_s}{\nu_n} \right) \times 10^6
\]  

These differences are typically very small and are reported as parts per million (ppm). This fundamental electronic property is exceedingly difficult to measure, so experimentalists opt to report chemical shifts, \( \delta \), relative to the shielding of an accepted reference standard, \( \sigma_{\text{ref}} \), for convenience

\[
\delta \text{(ppm)} = \left( \frac{\sigma_{\text{ref}} - \sigma_s}{1 - \sigma_{\text{ref}}} \right) \times 10^6 = \left( \frac{\nu_s - \nu_{\text{ref}}}{\nu_{\text{ref}}} \right) 10^6 \approx (\sigma_{\text{ref}} - \sigma_s) 10^6
\]  

The magnetic shielding interaction depends on the orientation of the local electronic
environment with respect to the external magnetic field vector. This \textit{anisotropy} manifests as a continuous range of transition frequencies corresponding to the different orientations typically present in bulk materials. Measurements of chemical shielding anisotropy have the potential to provide detailed information regarding the bonding about a particular nucleus; however, the broad signals often observed experimentally in NMR studies of polycrystalline and amorphous solids tend to obscure features arising from chemically distinct environments and limit the information content of their NMR spectra.

\subsection*{8.2.3 Quadrupolar Interaction}

The majority of NMR-active nuclides also possess an electric quadrupole moment that simultaneously interacts with the anisotropic electric field gradient (EFG) generated by the surrounding electron density. This \textit{quadrupolar interaction} results in additional peak splitting and broadening effects for nuclides with $S > 1/2$. It has a different orientational dependence than chemical shielding, often producing peaks with complicated shapes and further variations in the chemical shift. The strength of the interaction—and therefore the extent of the peak shift and broadening—is quantified by the quadrupolar coupling constant $C_Q$, which is the product of the electric quadrupole moment ($eQ$) and the largest component of the EFG tensor ($eq_{zz}$)

\begin{equation}
C_Q = \frac{(eQ) \ (eq_{zz})}{h}
\end{equation}

The peak shape is further influenced by the asymmetry parameter, $\eta$, which is a measure of the relative magnitudes of the EFG tensor components.

\begin{equation}
\eta = \frac{eq_{xx} - eq_{yy}}{eq_{zz}}
\end{equation}

where

\begin{equation}
|eq_{zz}| \geq |eq_{yy}| \geq |eq_{xx}|
\end{equation}

The magnitude of the quadrupolar interaction relative to the Zeeman interaction has a decisive influence upon the appearance of NMR spectra of quadrupolar nuclides. For the large class of half-integer quadrupolar nuclides ($S = 3/2, 5/2, 7/2, 9/2$), if the quadrupolar interaction is weak enough to be treated as a first-order perturbation to the Zeeman energy levels, the central transition ($-1/2, +1/2$) behaves analogously to that observed for spin-1/2 nuclei, whereas the resonance frequencies of the satellite transitions ($m_s, m_s - 1$; where $|m_s| > 1/2$) are orientationally dependent. In glasses and polycrystalline materials, this anisotropy results in severe peak broadening, often rendering satellite transitions difficult to observe under non-spinning conditions. It is frequently the case that first-order perturbation theory is insufficient to account for the quadrupolar interaction, and second-order effects are observed. Under such circumstances, the central transition is also anisotropically broadened. In crystalline compounds or solids with well-defined local coordination environments, this second-order interaction produces characteristic lineshapes [6–9], which can be readily simulated to
determine $C_Q$ and $\eta$. However, the geometric distributions present in glasses typically result in a distribution of EFG tensor components, obscuring the lineshape features and making precise determinations of these parameters impossible.

### 8.2.4 Dipolar Interactions

A third type of internal interaction that affects the energy levels arises from the magnetic dipole–dipole coupling between nuclei. *Indirect spin–spin coupling* (a.k.a. *J*-coupling) operates via polarization of electrons in the intervening bonds between spin-active nuclei, whereas the *direct dipolar interaction* operates through space. Both mechanisms are anisotropic and described by second-rank tensors to yield spectral manifestations similar to the foregoing. The direct dipolar coupling can be analyzed in terms of internuclear distance distributions. While these are seldom directly measurable in typical glasses due to the large peak widths arising from structural disorder, they can serve as valuable spin-transfer mechanisms for detecting interatomic connectivity and spatial proximity among spins using the methodologies of multidimensional and double-resonance NMR (see Chapter 9).

### 8.2.5 High Resolution Methodologies

MAS is employed in the majority of NMR studies of glasses to improve spectral resolution. Without spinning, the predominance of anisotropic spin interactions (e.g., chemical shielding, dipolar, quadrupolar) generally gives rise to broad and featureless peaks, from which little structural information can be extracted. Rapid rotation of the sample introduces a scaling factor of $(3\cos^2\theta - 1)$ to the anisotropic components which depends on the angle, $\theta$, of the rotational axis with respect to the magnetic field direction. For most interactions, the scaling factor can be set to zero by adjusting the angle to $54.74^\circ$, hence averaging out most of the anisotropic broadening and leaving only the isotropic parts of the magnetic shielding and indirect dipole–dipole interactions.

If the spinning rate is faster than the non-spinning (a.k.a. “static”) linewidth of the anisotropic interaction, the signal intensity is concentrated into narrow isotropic peaks, the number of which depends on the number of chemically distinct local environments. If the spinning speed is slower than the static linewidth, and the linewidth is dominated by the magnetic shielding anisotropy or heteronuclear dipolar interactions, the isotropic center bands are flanked by *spinning sidebands* located at integer multiples of the spinning speed ([Figure 8.3](#)). For this reason, fast spinning is generally desirable to obtain sideband-free spectra and maximize the intensity of the isotropic peak. If the resonances are strongly broadened by distributions of isotropic magnetic shieldings and/or quadrupolar interactions, the spinning speed must be sufficiently rapid to ensure separation of the central peak from the spinning sidebands (e.g., see [Figure 8.4](#)). Spinning sidebands are often ignored as artifacts if only information about the central peak is needed, but they can also be a source of valuable information about the extent of anisotropy and can provide better site resolution in certain cases [10, 11].
Figure 8.3 Schematic anisotropically broadened chemical shielding powder pattern under conditions of: (a) non-spinning (static), (b) slow MAS, and (c) fast MAS.
Figure 8.4 $^{71}$Ga MAS NMR spectra of a lead galloborate glass under various experimental conditions: (a) $B_0 = 14.1$ T, $v_{\text{rot}} = 38$ kHz; (b) $B_0 = 21.1$ T, $v_{\text{rot}} = 32$ kHz; (c) $B_0 = 21.1$ T, $v_{\text{rot}} = 62.5$ kHz. Four-, five-, and six-coordinate gallium peaks are modeled using a Czjzek distribution. Spinning sidebands are marked by grey dots.

A significant complication often encountered in NMR studies of glasses arises for sizeable quadrupolar interactions. Second-order anisotropic effects are incompletely averaged by MAS, leaving a residual lineshape and linewidth (Figure 8.5). Broadening due to such effects can cause peak overlap, lowering spectral resolution and reducing the information content. A convenient approach to achieving isotropic spectra devoid of second-order broadening is multiple-quantum (MQ) MAS NMR. Developed in the mid-1990s, MQMAS is a 2D method that results in one dimension which closely approximates the standard MAS spectrum and a higher resolution dimension in which second-order broadening is eliminated [12, 13].

Applications of this method to vitreous systems are typified by its use to resolve overlapping peaks corresponding to different coordination numbers in $^{27}$Al MAS spectra (vide infra, see Section 8.5.2) and to resolve $^{17}$O peaks associated with different types of bridging oxygens in oxide glasses (vide infra, see Section 8.5.2). Drawbacks include long acquisition times due to its two-dimensional nature and the inherently low excitation and coherence conversion efficiencies for multiple quantum transitions. Moreover, the $C_Q$-dependence of peak intensities demands that caution be exercised in drawing conclusions about site populations.
Figure 8.5 Schematic depictions of half-integer quadrupolar central-transition NMR lineshapes: (a) crystalline environment under non-spinning conditions, (b) crystalline environment under MAS, and (c) glassy material under MAS. All three spectra are based on the same NMR parameters.

The measurement of internal NMR interactions provides the means by which structural information can be obtained from NMR spectra. Chemical shifts and quadrupolar coupling constants can be interpreted in terms of local structural environments (i.e., short-range order). MAS is generally sufficient to reduce or eliminate direct dipolar broadening for heteronuclear spin pairs, but homonuclear dipolar interactions (e.g., $^{19}$F–$^{19}$F) can be difficult to average by MAS and require very high spinning frequencies. The greatest value of dipolar interactions in studies of glass structure is their use to probe connectivity by double-resonance methods (see Chapter 9). More detailed treatments of NMR theory are readily available in References [4, 9, 14–18].

8.3 INSTRUMENTATION
NMR instrumentation consists broadly of four major components: a magnet, a probe, a radiofrequency transmitter and receiver, and a computer to control excitation and data acquisition. A comprehensive overview of the basic instrumentation and operation of NMR spectrometers can be found in References [19 and 20].

8.3.1 Magnet

The purpose of the magnet is to establish the initial conditions of the spin system by inducing the Zeeman effect, whereby nuclear spin states split into energy levels which can be probed by radiofrequency spectroscopy. Most commercial NMR systems are based on superconducting, vertical-bore magnets with magnetic flux densities ranging from 9.4 to 21.1 T, although lower and higher fields exist. Due to the importance of $^1$H NMR in routine chemical applications, magnets are often colloquially referred to by their proton frequency—for example, 400 MHz and 900 MHz, respectively—although this nuclide is seldom used in glass studies. The term “ultrahigh” is sometimes applied to fields of 18.8 T and higher, although this may change as higher field strengths become available.

The niobium-titanium and niobium-tin superconducting coils are generally cooled to cryogenic temperatures by liquid helium ($T = 4$ K) surrounded by a buffering dewar of liquid nitrogen ($T = 77$ K). Some higher field magnets (e.g., 18.8 T) are actively cooled by evaporating helium via pumping within a closed cycle to reduce the helium temperature to 2.2 K, thereby lowering the critical temperature for superconductivity at a particular magnetic field. This has the added benefit of stabilizing the magnet against variations due to atmospheric effects. Recent innovations in magnet technology include actively shielded magnets with significantly reduced stray fields and “cryogen-free” magnets with no need for liquid nitrogen. The latter utilize refrigeration and recirculating helium dewars to reduce helium consumption and require replenishment only once a year. Considering the growing threat of global helium shortages, such magnets are likely to become popular.

Typical bore diameters are 54 mm (“narrow” or “standard” bore) and 89 mm (“wide” bore); the former tends to be less expensive, more stable and ubiquitous in solution-state NMR laboratories, whereas the latter can accommodate the larger and more versatile probes often needed in solid-state NMR.

The magnetic field strength has a major impact on the spectral appearance, and consequently, its information content. This is particularly true when the nuclei in a sample are subject to multiple spin interactions which have different field dependencies. In the simplest case, $^{29}$Si is a dilute spin-1/2 nucleus affected only by magnetic shielding, which scales linearly with field strength. In a disordered material, distributions in the isotropic shift will also scale, resulting in no appreciable field dependence of the MAS NMR spectrum and little benefit to high fields, aside from greater magnetization. $^{207}$Pb is also a dilute spin-1/2 nucleus; however, its chemical shift is much more sensitive to local structure and correspondingly produces very broad peaks due to the structural disorder inherent in glasses. Typical $^{207}$Pb NMR signals can extend over hundreds of kHz, making it difficult to excite the resonance homogeneously. Hence, lower fields are advantageous because the overall signal breadth is reduced (in frequency units) and
easier to acquire. $^{19}$F is another spin-1/2 nucleus with a fairly large shielding range. It is 100% naturally abundant and possesses a large magnetogyric ratio (Table 8.1); therefore, spectra of glasses with an appreciable fluoride concentration are likely to be affected by broadening due to homonuclear dipolar interactions. Under such circumstances, a combination of low magnetic field and very fast spinning rates is optimal for obtaining high resolution $^{19}$F MAS NMR spectra of glasses.

For most quadrupolar nuclei, it is advantageous to use as high an external magnetic field as possible to reduce the influence of second-order quadrupolar effects on the spectra. For example, the determination of different aluminum coordination numbers using $^{27}$Al MAS NMR is difficult at low-to-moderate fields (e.g., 4.7–11.7 T) because the quadrupolar lineshapes for four-, five-, and six-coordinate Al overlap significantly. At high field (e.g., >16.4 T), resonances arising from these coordination environments are narrow relative to their respective chemical shift differences and higher spectral resolution can be readily obtained. Likewise, the spectral distinction between three- and four-coordinate borons in borate glasses requires lineshape deconvolution at applied fields lower than 11.7 T, but full resolution is achieved at higher fields. A similar situation can be described for $^{17}$O MAS NMR, where bridging oxygens can often be differentiated from non-bridging oxygens (NBOs) at sufficiently high magnetic fields. Furthermore, oxygens bridging different network formers can sometimes be resolved, depending on the network-forming cations and the magnetic field strength. In other cases, more sophisticated NMR methods are required to achieve site resolution. The advantages of high field extend also to MQMAS spectra, where the multiple-quantum excitation efficiency increases with decreasing magnitude of the quadrupolar broadening effect. Finally, high magnetic field strengths favor the study of low-$\gamma$ nuclides, as the signal-to-noise ratio scales with the size of the magnetization and the value of the Larmor frequency detected in the probe. As both of these quantities scale linearly with the magnetic field strength, significant time savings can be realized [21].

### 8.3.2 Probe

The sample is located in the probe, situated within a coil of wire which is part of a radiofrequency (rf) circuit. The simplest NMR probe is a tuned circuit with the sample placed in a horizontal solenoid coil in the most homogeneous region of the external magnetic field, and the capacitance is adjusted to the excitation frequency required to achieve resonance. Alternating current oscillating with the excitation frequency, $\omega_0$, is passed through the coil in the form of a pulse, generating an oscillating magnetic field, $B_1$, at the sample. At the nucleus-specific resonance condition, $\omega_1 \approx \omega_0$, this field interacts with the spins and rotates the bulk magnetization away from its original alignment with the static magnetic field. This leads some component of the magnetization to lie in the plane orthogonal to the static field, where it precesses around $\vec{B}_0$ (Figure 8.2b). The maximum excitation occurs when the magnetization vector is rotated by 90° into the transverse plane, constituting a “90° tip angle.” After excitation, the rf field is turned off and the voltage induced in the coil by a precessing ensemble of nuclear spins in the transverse plane is detected as an oscillating signal as a
function of time (Figure 8.6). Various relaxation mechanisms act to realign the magnetization vector with the static, external field, causing a reduction in the measured signal. This free-induction decay (FID) constitutes the raw time-domain response of the nuclei in the sample. This procedure can be repeated after a suitable delay to allow the signal to relax to its equilibrium position along $\vec{B}_0$, followed by signal averaging of all such acquired transients to increase the signal-to-noise ratio.

**Figure 8.6** Typical single-pulse (a.k.a. Bloch decay) pulse sequence for the acquisition of an NMR signal: a 90° rf pulse followed by detection of the free-induction decay. Fourier transformation (FT) of this time-domain signal produces a frequency-domain spectrum.

For most experiments on glassy samples where peak resolution is required, the coil is positioned at the magic angle with respect to the external magnetic field vector. Sample spinning is accomplished using streams of bearing and drive gases. Because reliable and stable spinning rates require that the mass be evenly distributed about the axis of rotation, MAS experiments are generally performed on finely ground samples. At the time of writing, spinning speeds in commercial probes range from about 2 kHz to 65 kHz, depending primarily
on the outer diameter of the rotor, typically 7 mm to 1.2 mm, respectively. The choice of spinning speed (and hence, the appropriate probe purchase) is based on a trade-off between how much sample is required to obtain suitable spectra in a practical amount of time and the spinning speed required to obtain the necessary peak resolution. Due to the mechanical demands of MAS NMR experiments, as well as the many options for rotor sizes and advanced experiments, most solid-state NMR facilities are equipped with a selection of different probes.

8.3.3 Radiofrequency Components

The radiofrequency fields used to excite the nuclei and produce detectable signals are generated by digital frequency synthesizers and amplified by linear amplifiers to provide oscillating magnetic field amplitudes corresponding to nutation frequencies ranging from 10 to 150 kHz, depending on the application. Modern electronics can deliver very short pulses with precise amplitudes and timing control down to 25 ns. This leads to sharp rise and fall times which can very closely approximate a “square” pulse or can be programmed to have different shapes and phases as needed for particular applications.

8.3.4 Computer Control

As with all modern analytical instrumentation, computer control is essential for programming pulse sequences and processing the detected signals. Pulse sequences range from a single square rf pulse followed by the acquisition of the FID (Figure 8.6), to highly sophisticated multidimensional and multiresonance sequences with precise control of pulse timings, lengths, amplitudes, and phases in relation to the sample spinning rotor cycle. Hundreds of pulse sequences are typically included in commercial spectrometer libraries and may be selected for particular applications. Basic spectral processing begins with Fourier transformation of the time-domain signal to yield the frequency-domain spectrum (Figure 8.6), where peaks appear at discrete offsets relative to the rf transmitter frequency and are referenced to standard reference compounds. Phasing, baseline correction, and other processing functions can be applied to improve spectral appearance and facilitate spectral interpretation.

8.3.5 Measurement Uncertainty

Measurement uncertainties in NMR spectroscopy fall under two general categories: those related to peak positions and those related to peak intensities. Uncertainties associated with NMR parameters obtained by deconvolution will be discussed in Section 8.4. The magnetic field and rf electronics can drift slightly over the course of long acquisition times or series of experiments, causing minor errors in the measured peak positions. Regular optimization of probe tuning, pulse calibration, magnetic field homogeneity (i.e., “shimming”), and standard referencing reduces these experimental indeterminacies to levels lower than those associated with NMR parameter determinations. Magnetic susceptibility differences can also introduce small errors in peak positions, especially when calibrating the probe response or referencing samples using solution standards; however, the differences between solutions and typical glass samples are not expected to exceed 1 ppm. In principle, the measurement of peak maxima can be limited by digital resolution, but the large peak widths normally found in solid-state NMR
spectra of glasses mean that this is generally not a handicap. An exception might be when the indirect dimension of a two-dimensional data set (e.g., MQMAS) has a restricted number of points due to rapid spin–spin relaxation. For most practical purposes, the direct measurement of peak positions in NMR spectra of glasses is simply limited by their comparatively broad peaks, even under MAS conditions, and uncertainties of less than 1 ppm are rare.

Although NMR is an inherently quantitative technique, several experimental factors and sample characteristics can result in non-quantitative results. From an instrumental perspective, finite pulse durations result in characteristic excitation profiles, in which the $B_1$ field strength depends systematically on the frequency offset. Shorter pulses have broader bandwidths which ensure more homogeneous excitation than longer pulses over the spectral region of interest, and this is seldom a major concern. More troublesome is the finite bandwidth of the probe, which can lead to uneven excitation and non-quantitative intensities in studies of low-$\gamma$ nuclides with large signal breadths. One time-consuming but effective solution is to record a series of spectra at different transmitter offsets and co-add the spectra post-acquisition. A more elegant approach is to utilize WURST (wideband uniform rate smooth truncation) pulses to excite a broader bandwidth more homogeneously [22].

Samples containing species with widely varying quadrupolar coupling constants exhibit different signal responses for a given excitation pulse and cannot be simultaneously maximized by a single rf pulse length. Under such circumstances, pulses must be kept short to remain in the linear excitation regime (Figure 8.7). For example, due to the different quadrupolar interactions of three- and four-coordinate borons, direct comparison of intensities is only valid if small tip angles are used to ensure homogeneous excitation. Additional minor corrections may also be required to account for overlap of central transition intensity with satellite transitions, or the loss of central transition intensity to spinning sidebands [23]. The use of more complex multipulse sequences introduces greater scope for non-quantitative intensities, such as MQMAS, spin-echo experiments, and cross-polarization. Careful consideration of relative integrated peak intensities must be made in each case with reference to the shortcomings of a particular sequence.
Figure 8.7 Variation of bulk magnetization for a spin-3/2 nucleus as a function of excitation pulse duration for small-$C_Q$ (solution-like) and larger-$C_Q$ (solid) sites. Shaded portion indicates regime of linear excitation.

Some sources of uncertainty in the peak areas arise from the sample characteristics. Spin–lattice relaxation times can differ for different sites in a material. This is particularly problematic for phase-separated or composite glasses. Under such circumstances it is necessary to ensure that sufficiently long relaxation delays are being used to allow for equilibrium to be reached for all the nuclei present in the sample. This can be tested by comparing the absolute signal area measured for the sample of interest with that of a standard material with a known concentration of the observed nucleus. Moreover, the presence of paramagnetic constituents or impurities can result in rapid spin–spin relaxation of some fraction of the nuclei under observation, rendering them effectively invisible on the acquisition timescale. Similarly, highly distorted local environments can generate very strong quadrupolar interactions for quadrupolar nuclides, producing broad peaks which dephase during the “dead time” between the end of the pulse and the beginning of the acquisition period, which are therefore not detected (see Figure 8.6).
8.4 DATA ANALYSIS AND STRUCTURAL INTERPRETATION

NMR parameters are inherently sensitive to local structural environments. Typically, this is synonymous with short-range order in glasses, such as coordination number, site symmetry, and the chemical nature of nearest neighbors. In some cases, insight about medium-range order can be obtained in the form of second- and third-nearest-neighbor identities. In the simplest cases, the chemical shift of the nucleus under observation will vary measurably for different coordination numbers, allowing for the identification of distinct “sites.” For quadrupolar nuclei, the shape of the peak can also provide valuable information about the local geometry. Although seldom observed in glassy materials, peaks can be split into multiplets due to J-coupling with other spin-active nuclei, leading to insight about atomic connectivity. Finally, NMR is considered a quantitative spectroscopic method, such that peak areas are proportional to the fraction of the chemical environment giving rise to a particular peak with respect to the total NMR signal observed for that nucleus. Hence, a comparison of relative integrated intensities for all peaks in an NMR spectrum readily provides site populations in glasses.

8.4.1 Chemical Shift Assignments

Key to the effective use of NMR in this capacity is making reliable peak assignments. For most commonly studied nuclei, chemical shift ranges for different coordination numbers are well-defined based on comparison with the NMR peaks of known crystalline compounds. For example, four-coordinate silicon invariably falls into the −60 to −120 ppm region, as calibrated by many minerals, whereas six-coordinate silicon can be found from −180 to −200 ppm, based on crystal structures such as stishovite [24, 25]. More generally, it is widely found that chemical shifts become more shielded (i.e., lower in frequency) as the coordination number increases (see references in [26]). While the identity of the nearest neighbor (e.g., F, O, S) can influence the precise chemical shift of the nucleus under observation, the ordering of coordination number ranges remains unaltered. This relationship can be used to assign specific coordination numbers where well-defined polyhedra are likely to be present (e.g., high field-strength cations; network formers) or to detect a progressive change in the coordination number of irregular polyhedra (e.g., low field-strength cations, network modifiers).

Chemical shifts are also sensitive to the degree of polymerization. In pure silicates, fully polymerized $Q^4$ species are generally found within the range of −105 to −120 ppm, whereas $Q^3$ species are shifted into the range of −90 to −100 ppm [17]. Similar effects are observed for other cations such as phosphates, borates, and vanadates, but the shifts may be subtle and masked by other effects. Progressive depolymerization results in deshielded peaks (i.e., increasing chemical shifts) such that the degree of polymerization can often be determined with reasonable accuracy by careful peak-fitting. It should be noted, however, that the chemical shift differences may be small and peak overlap is common, leading to uncertainty in the fitted populations.

Another secondary effect which can measurably influence chemical shifts is the identity of the
next-nearest neighbors. Particularly in the case of network-forming cations, the nature of the neighboring polyhedra can alter the chemical shift range. For example, $^{29}$Si chemical shifts are well documented to increase—shift to more positive values—with the number of bonded AlO$_4$ units, a relationship that has been used extensively in determining the Si/Al ratio in zeolites [27]. Such correlations have also been established for $^{11}$B, where four-coordinate boron peaks shift about $-0.5$ ppm with each bonded silicate unit and about $-1.8$ ppm with each bonded phosphate unit [28, 29].

These relationships have traditionally been inferred from NMR studies of appropriate crystalline compounds, but ab initio calculations have emerged as an alternate approach to determine peak identities for less well-studied nuclei or unusual bonding arrangements lacking known crystalline analogs. For example, the effect of neighboring phosphate units on four-coordinate boron chemical shifts was studied by model clusters containing zero- to four-bonded phosphate tetrahedra [28]. The direction and magnitude of the trend is consistent with experimental data on crystalline model compounds and a series of glass compositions. The reliability of density functional theory calculations of NMR parameters has reached the point where trustworthy trends can be determined, even if the magnitudes of the shielding tensor elements may not be accurate.

The existence of multiple structural effects on chemical shifts means that changes in peak positions must be interpreted cautiously. In multicomponent systems it may be difficult to disentangle peak shifts due to depolymerization, changes in network connectivity, and even charge compensation due to network modifiers. Recourse to literature values for constraining peak positions in highly overlapping patterns can also be unreliable when shifts are small and compositions variable. While it is often necessary to make assignments based on prior knowledge about the likely glass structure, this can lead to circular arguments or biased interpretations. Especially dangerous is the attribution of unresolved intensity in complex patterns to particular chemical species expected to be present by “intuition” or when lineshape fitting of the resolved peaks fails to account for the full spectral envelope. Spectral fitting should be strictly based on clearly observed peaks rather than marginal or ambiguous residual intensity. When routine experiments fail to deliver adequate resolution, valuable fitting constraints can often be obtained by more advanced NMR methods which selectively excite or filter out spectral components on the basis of their dipolar interactions (see Chapter 9).

### 8.4.2 Information from Quadrupolar Effects

The spectral appearance of quadrupolar nuclei is further influenced by the strength and distribution of the EFG, manifested as the quadrupole coupling constant (Eq. 8.5) and quadrupolar asymmetry parameter (Eq. 8.6). The magnitude of $C_Q$ depends on the EFG at the nucleus. Since the EFG reflects local symmetry, the size of $C_Q$ for a given nucleus provides insight into coordination environments, where measurable. In particular, larger $C_Q$s can be interpreted as arising from more distorted sites, whereas smaller $C_Q$s indicate highly regular polyhedral environments. Early work on $^{27}$Al demonstrated a relationship between $C_Q$ and the
polyhedral distortion in crystalline minerals [30], which has subsequently proven valuable for the assignment of peaks in amorphous materials. Extensions of this work to other nuclides have been less successful, implying that effects beyond the first coordination sphere have a decisive influence on the EFG [31]. In silicate glasses, the $^{17}$O $C_Q$ and $\eta$ values associated with bridging oxygen species are found to be sensitive to the Si–O–Si angle, providing detailed insight into the molecular structure of disordered solids [32].

Due to the very wide range of quadrupole moments, $C_Q$s can be so large that the signal is distributed over such a wide frequency range that it is practically indistinguishable from the noise (e.g., $^{75}$As, $^{115}$In, $^{121}$Sb); or $C_Q$s can be so small that standard lineshape analysis is dominated by other broadenings effects, precluding a precise measurement of this parameter (e.g., $^{133}$Cs, $^6$Li, $^7$Li, $^9$Be). In the intermediate range, it can also happen that some sites in a given glass have $C_Q$ values that permit observation, whereas others are so distorted that the intensity is effectively “invisible.” Such cases can lead to incorrect site populations [33]. The availability of high magnetic fields and fast MAS has led to the successful acquisition of spectra of previously inaccessible nuclides such as $^{73}$Ge, $^{71}$Ga, and $^{33}$S. In such cases, spectra tend to be dominated by quadrupolar broadening, and multiple sites, if present, are often unresolved [31, 34].

NMR parameters derived from complex and/or overlapping lineshapes by spectral simulation or deconvolution are subject to much larger uncertainties, depending on the complexity of the spin system. Spectral simulation of a typical second-order quadrupolar central-transition MAS lineshape in an ordered solid yields the isotropic chemical shift, quadrupolar coupling constant, and the quadrupolar asymmetry parameter. From a practical standpoint, the precise measurement of $C_Q$ in glasses is complicated by the sensitivity of the corresponding lineshape to disorder. Except in rare circumstances, a distribution of $C_Q$s for a given site results in peak broadening which obscures the features necessary for an unambiguous determination of $C_Q$ and $\eta$. Measurement of the full-width at half-maximum (FWHM) permits an estimate of the average $C_Q$ value, provided only a single type of local environment contributes to the peak. Multifield measurements can be used to obtain more precise values of the $C_Q$ and $\delta$ in disordered systems due to the known field dependencies of these interactions [17]. Peak shapes can also be simulated using assumed distributions of the chemical shift and EFG parameters [35]; however, the final parameter set may not be unique and should be used with caution. MQMAS is a viable alternative for assessing the NMR parameters in disordered systems as it eliminates second-order quadrupolar broadening. However, the resulting isotropic peaks may still be subject to distributions due to structural disorder and it may not be possible to independently obtain both $C_Q$ and $\eta$. Under such circumstances, it may be necessary to content oneself with the determination of the quadrupolar product, $P_Q = (C_Q^2 + \eta^2/3)^{1/2}$, which differs from $C_Q$ by up to 15% depending on the value of asymmetry parameter [9]. For relatively small quadrupolar interactions, an estimate of $C_Q$ can be obtained from the full breadth of the satellite transition spinning-sideband manifold, with appropriate corrections for the spin
number [7].

Despite the potential wealth of structural insight available from quadrupolar nuclides, careful consideration of the intrinsic properties of a given nuclide vis-à-vis the desired information is essential prior to launching an NMR study. For example, the high reactivity of $^{23}$Na makes it an attractive nucleus for MAS NMR studies of sodium environments in glasses. However, clear structural interpretations can be confounded by significant overlap due to its small chemical shift range and sizeable quadrupolar broadening. Furthermore, like $^1$H and $^{19}$F, its 100% natural abundance and high magnetogyric ratio make homonuclear dipolar interactions prominent and add additional broadening which is difficult to remove by MAS alone. From a structural perspective, its low field strength results in a wide range of coordination environments. These effects combine to produce $^{23}$Na MAS NMR spectra of glasses which are often featureless. Interpretation of peak positions—calibrated by comparison with crystalline structures—in terms of coordination numbers is approximate at best, and implicitly assumes that a single local environment dominates the peak shape [36].

8.4.3 Low-γ Nuclei

Nuclides with magnetogyric ratios lower than those of $^{15}$N are typically classified as “low-γ nuclei” and present unique challenges for NMR acquisition [37]. Fundamentally, low-γ nuclei suffer from an unfavorable Boltzmann population difference and consequently poor sensitivity. From a technical viewpoint, their low resonance frequencies can cause acoustic ringing in the probe which interferes with signal acquisition, particularly the detection of broad peaks which decay rapidly in the time domain. Furthermore, many low-γ nuclei are also beset by low natural abundance and/or large quadrupole moments, exacerbating the limitations arising from the low magnetogyric ratio. All of these challenges are mitigated by acquiring spectra at the highest possible magnetic field, and the advent of “ultrahigh” magnetic fields around the turn of the millennium has opened up new opportunities for NMR studies of low-γ nuclei [21]. Renewed interest in Carr-Purcell-Meiboom-Gill (CPMG) [38] and WURST [39, 40] pulse sequences have also contributed to significant recent advances in the collection of broad, low intensity NMR signals.

Many nuclei of interest in glass science possess low magnetogyric ratios and significant quadrupole moments, for example, $^{33}$S, $^{43}$Ca, $^{25}$Mg, $^{47/49}$Ti, $^{39}$K, $^{87}$Sr, and $^{73}$Ge. Successful NMR studies of these nuclei have been largely restricted to well-characterized crystalline compounds, where NMR parameters can be correlated with local structure [31, 41–45]. The disorder present in glassy materials broadens NMR peaks and effectively reduces sensitivity even further. In many cases, attempts to obtain NMR spectra of low-γ nuclei in glasses result in very broad, featureless signals which obscure information about individual sites and their quantities [31, 46]. The low sensitivity and necessity of quadrupolar CPMG methods render resolution enhancement techniques such as MQMAS impractical. At the time of writing, it is fair to say that whereas major progress has been made in the NMR acquisition of low-γ nuclei, structurally informative applications to glasses remain underdeveloped.
8.4.4 Paramagnetic Effects

Paramagnetic ions introduce unpaired electrons which interact with nuclear spins over relatively long distances through various mechanisms [47]. At low concentrations (e.g., < 0.5 mol%), the most tangible effect on the NMR experiment is a sharp reduction in spin–lattice relaxation times, $T_1$, which can be advantageous to accelerate spectral acquisition [48]. For example, $^{29}$Si $T_1$ values of several minutes in silicate glasses can be reduced to seconds with the addition of 0.2 mol% dopant (e.g., Co$_3$O$_4$, MnCl$_2$), corresponding to time-savings of days for typical MAS NMR spectra. However, paramagnetic interactions also induce peak broadening, which can render poorly resolved spectra entirely undifferentiated and structurally uninformative. Depending on the structural role of the paramagnetic ion, it is conceivable that some structural units may be preferentially relaxed and possibly even rendered unobservable due to a combination of peak broadening and rapid relaxation. While the incorporation of paramagnetic dopants for relaxation enhancement is a common practice in NMR of glasses, caution is advisable as it may introduce errors into the spectral analysis.

8.5 CASE STUDIES

Four case studies have been selected from the recent literature to illustrate the effective use of NMR spectroscopy in the determination of valuable structural aspects in glasses. These studies exemplify the application of routine one-dimensional MAS NMR of spin-1/2 and quadrupolar nuclei to obtain information about short-range order in mixed network-former glasses [29], as well as highlighting some of the challenges that may be encountered in probing less receptive modifier nuclides [26]. The utility of two-dimensional MQMAS for resolution enhancement of quadrupolar nuclides is also demonstrated for the detection of multiple aluminum coordination environments in geologically relevant aluminosilicate glasses [49] and for the elucidation of glass homogeneity in borosilicate glasses of commercial interest [50].

8.5.1 Borophosphate Glasses

NMR can be used to conveniently probe the structural changes induced by altering the composition of the network in the ion-conducting sodium borophosphate glass system [29].

Straightforward one-dimensional $^{31}$P and $^{11}$B MAS NMR experiments provide sufficient information to quantify the coordination numbers, degree of polymerization, and network connectivity. In so doing, the distribution of mobile sodium ions can be indirectly determined according to the anionic charges in the network structure.

Peaks in the $^{31}$P MAS NMR spectra of glasses are generally unresolved, but provide enough lineshape features for effective deconvolution (Figure 8.8). This procedure is generally unambiguous because $^{31}$P is a spin-1/2 nucleus and signals arising from a particular local environment are expected to be symmetrical with a mixed Gaussian/Lorentzian lineshape. As with $^{29}$Si MAS NMR, $^{31}$P peaks for four-coordinate phosphorus associated with different numbers, $n$, of bridging oxygens, $Q^n$, appear in different chemical shift regions with discrete
increases in frequency upon the replacement of each bridging oxygen by an NBO. Consequently, the spectrum of (Na$_2$O)$_{0.4}$(P$_2$O$_5$)$_{0.6}$ consists simply of $Q^3$ and $Q^2$ units in a 1:2 ratio. With the successive replacement of phosphorus by boron, the peaks are subject to two distinct structural changes which influence the peak position: progressive repolymerization of the phosphate network through the formation of four-coordinate boron species, and increasing connectivity between phosphate and borate polyhedra. Like depolymerization, B–O–P linkages have the effect of increasing the $^{31}$P NMR frequency of a given phosphate unit. In the absence of additional constraints, the fitted peak positions and intensities must be assigned to the appropriate phosphorus species under the assumption that complete peak overlap does not occur; alternately, all possible assignments must be considered. The authors take the latter approach and “assign” the measured peaks to combinations of $Q^2$ and $Q^3_{2B}$, for example, to indicate that a given peak may correspond to both types of species. At high boron concentrations, well-resolved peaks clearly corresponding to terminal ($Q^1$) and isolated ($Q^0$) phosphate species are observed.
Figure 8.8 $^{31}$P MAS NMR spectra of (Na$_2$O)$_{0.4}$[(B$_2$O$_3$)$_x$(P$_2$O$_5$)$_{1-x}$)$_{0.6}$ glasses. Signals from phosphates with 0, 1, 2, and 3 bridging oxygens are labeled. Asterisks denote spinning sidebands. (Adapted from Reference [29].)

$^{11}$B MAS NMR spectra of this series may be interpreted analogously (Figure 8.9), with the proviso that quadrupolar interactions may influence the peak shapes. In glasses with low boron content, a narrow peak is observed in the region known to indicate four-coordinate boron. The high local symmetry of such species generally generates a very weak quadrupolar interaction and no observable second-order effects on the lineshape. This peak drifts gradually to higher chemical shifts with increasing boron content as the number of phosphate neighbors decreases. While this change would be expected to occur in steps, discrete $^{4}$B peaks corresponding to different connectivities are rarely observed in $^{11}$B MAS NMR. Due to the breadth of these peaks and the presence of multiple connectivity arrangements in a given material, the average number of next-nearest-neighbor P atoms may be inferred from a plot of the peak position and composition [28].
With increasing boron content in these glasses, a broader peak begins to appear at higher frequency. The breadth and second-order lineshape are known to arise from the stronger quadrupolar interaction associated with three-coordinate boron species possessing all bridging oxygens [51]. That the shape remains recognizably “quadrupolar” is attributed to the relatively narrow geometrical distributions associated with these species. At sufficiently high magnetic fields ($B_0 \geq 11.7$ T), three- and four-coordinate boron resonances are resolved in $^{11}$B MAS NMR spectra and their integrated intensities provide a convenient measure of their relative amounts. The breadth of these three-coordinate boron peaks makes it difficult to measure peak shifts with the precision available for the four-coordinate boron peaks, and more detailed assignment of network connectivity is seldom directly accessible. Finally, in the pure sodium borate glass a change in the shape of the $[^3]$B peak indicates that some degree of depolymerization has occurred, generating three-coordinate boron species with one NBO. The quadrupolar parameters for such species have been carefully documented [51] and—although
they are difficult to measure precisely in $^{11}$B MAS NMR spectra where multiple $^{3}$B species are present—can be reliably identified even at fairly low concentrations.

Combining these two data sets with charge-balance and compositional constraints, a complete inventory of the short-range species can be generated, including coordination number (for boron), the degree of polymerization (i.e., number of NBOs), and next-nearest-neighbor identity. This compositional breakdown implies that P–O–B linkages between phosphorus $Q^3$ units and $^{4}$B are favorable. The average number of bridging oxygens per network former can be readily calculated from these data and shown to correlate with $T_g$, whereas the bulk ionic conductivity correlates with the presence of anionic four-coordinate boron species.

### 8.5.2 Aluminosilicate Glasses

The application of $^{27}$Al NMR to a series of calcium aluminosilicate glasses along the tectosilicate join (CaO/Al$_2$O$_3$ = 1) provides a straightforward quantification of the concentration of fivefold-coordinated aluminum [49]. Raman spectroscopy and Al K-edge X-ray absorption near-edge spectroscopy (XANES) of these samples show subtle changes interpreted in terms of increased Al coordination numbers. High field ($B_0 = 17.6$ T, 750 MHz $^1$H frequency) $^{27}$Al MAS spectra are also suggestive of high-coordinate aluminum, but the peaks overlap significantly (Figure 8.10a). By contrast, the use of $^{27}$Al MQMAS reveals fully resolved peaks in the isotropic dimension for four- and five-coordinate Al (Figure 8.10b). Multifield MQMAS data are analyzed in parallel using a Czjzek distribution to arrive at a single set of NMR parameters. Because the quadrupolar parameters prove to be very similar for these two sites, no correction factor is required to account for inhomogeneous excitation and the intensities may be taken to represent the true relative populations. Further confirmation of the site populations is obtained by simulation of the unresolved high field one-dimensional $^{27}$Al MAS spectra. Despite the very different appearances of these data sets, the results are in remarkable agreement, inspiring confidence in the measured concentrations of $^{5}$Al. It may also be noted that a hint of $^{6}$Al is inferred from fitting the 1D spectrum, but is not directly observed in the MQMAS contour plot.
Previous work had found evidence of non-negligible concentrations of $^{[5]}\text{Al}$ in related compositions, but not enough to justify the fraction of NBOs measured using $^{17}\text{O}$ NMR [52, 53], prompting a model based on three-coordinate “tricluster” oxygens to account for the composition and charge-balance. With these more accurate—and higher—$^{[5]}\text{Al}$ values, the NBOs can be quantitatively associated with five-coordinate Al and triclusters are not needed to rationalize the compositions. From a glass science perspective, this finding is significant because of the major role $^{[5]}\text{Al}$ is thought to play in governing transport properties [54].

### 8.5.3 Borosilicate Glasses

Much of the early NMR work on glasses focused on the spectroscopic observation of cations, due in part to their generally favorable NMR properties, and led to a tendency to conceptualize network glass structure in terms of cationic nodes. Historically, $^{17}\text{O}$ NMR has been less popular due to its low natural abundance (Table 8.1), necessitating costly and sometimes tricky isotopic enrichment, as well as its significant quadrupolar interaction which tends to obscure site resolution. Notwithstanding some early successes by other NMR methods, the advent of MQMAS has opened up the use of $^{17}\text{O}$ NMR in oxide glasses as a means of directly observing bonded cations and hence probing network connectivity.

Stebbins and coworkers have advanced the study of oxide glasses using $^{17}\text{O}$ MQMAS NMR to
study connectivity in a wide variety of systems. For example, they apply this methodology to a series of alkali borosilicate glasses both outside and within the known metastable immiscibility region of the phase diagram [50]. Although macroscopic phase separation can often be observed optically, NMR proves to be able to detect segregation effects at the nanoscale even in the absence of such visual evidence.

Whereas one-dimensional $^{17}$O MAS spectra at the moderately high field of 14.1 T—and indeed, even at higher fields—are known to be poorly differentiated [55], two-dimensional MQMAS spectra clearly distinguish among a variety of oxygen sites (Figure 8.11a). NBOs are spectroscopically distinct from bridging oxygens in $^{17}$O MQMAS, which is especially valuable for low field-strength modifiers, where NBO peak positions overlap with those of the bridging oxygens in the MAS dimension. The sensitivity of NBO chemical shifts to charge-balancing cations provides an indirect probe of modifier identity and proximity. More importantly, oxygens bridging different network formers are also resolved, with B–O–B, Si–O–B, and Si–O–Si appearing as separate peaks in the two-dimensional depiction as well as the one-dimensional isotropic projection. Remarkably, even finer resolution can be teased out of these projections, as careful comparisons reveal that oxygen peaks are sensitive to whether the bonded boron is three- or four-coordinated. This level of spectroscopic resolution permits the $^{17}$O MQMAS spectra to be broken down into five types of bridging oxygens, the quantification of which leads to an unprecedented level of detail in the network connectivity (Figure 8.11b).
Figure 8.11 $^{17}$O NMR spectra ($B_0 = 14.1$ T) of borosilicate glasses: (a) triple-quantum 2D MQMAS of lithium borosilicate glass ($K = \text{SiO}_2/\text{B}_2\text{O}_3 = 0.2; R = \text{M}_2\text{O}/\text{B}_2\text{O}_3 = 0.75$) with non-bridging and three types of bridging oxygens labeled; (b) isotropic 1D projections of MQMAS spectra of sodium borosilicate glasses ($K = 0.2$) with bridging oxygens labeled. (Adapted from Reference [50].)

Naturally, $^{11}$B NMR can also be applied to these systems. One-dimensional MAS spectra show the usual separation of three- and four-coordinate borons, with additional evidence of overlapping $[^3]B$ environments which can be deconvolved to represent ring and non-ring borons. While this is not new, the facility with which these contributions can be separated in an MQMAS experiment makes measurements of their populations more convenient, as isotropic peaks can be directly monitored (Figure 8.12). For example, $^{11}$B MQMAS reveals that compositions annealed below their $T_g$ show higher ring fractions than quenched glasses, signifying the presence of boron-rich regions, as expected for phase-separated materials. Interestingly, the $^{11}$B MQMAS spectra also provide marginally better resolution of the four-coordinate borons than do the MAS spectra. These high-resolution $^{11}$B MQMAS isotropic projections permit the detection of four-coordinate borons bonded to zero and one neighboring silicate tetrahedra.
Figure 8.12 Isotropic projections of $^{11}$B MQMAS NMR spectra ($B_0 = 14.1$ T) of sodium borosilicate glasses with peak assignments for three- and four-coordinate borons; compositions listed according to $K = \text{SiO}_2/\text{B}_2\text{O}_3$ and $R = \text{M}_2\text{O}/\text{B}_2\text{O}_3$. (Adapted from Reference [50].)

Taken together, the high resolution $^{11}$B and $^{17}$O MQMAS experiments provide the basis for a complete elaboration of the network structure in terms of individual boron and oxygen species and their respective connectivity with silicon. This experimental approach is applied to evaluate the extent and type of boron-silicon mixing for a series of compositions cutting across the known metastable immiscibility region, as well as compositions with different alkali modifiers and glasses with different thermal histories and macroscopic properties. The results indicate that the atomic-level resolution of NMR can be used to study phase separation phenomena that fall well outside the detection limits of optical microscopy.

8.5.4 Modifier Cations in Alkali Borate Glasses

The most common use of NMR to study glass structure involves the direct observation of
network components. However, in favorable cases, NMR can also be used to study network-modifying cations [26]. The NMR properties of the alkali and alkaline-earth cations vary widely, with $^7\text{Li}$, $^{23}\text{Na}$, and $^{133}\text{Cs}$ being quite receptive to NMR investigation while $^{39}\text{K}$, $^{43}\text{Ca}$, and $^{87}\text{Sr}$ remain very challenging (Table 8.1). Nevertheless, limited structural information can be gleaned from systematic studies of these cations.

Direct NMR observation of the alkali cations in analogous binary borate glasses reveals a universal trend to higher chemical shifts with increased alkali loading. Whereas this effect is clear for the highly receptive $^{23}\text{Na}$ and $^{133}\text{Cs}$ nuclides (e.g., Figure 8.13a), it is more subtle for $^{6/7}\text{Li}$ because of its very narrow chemical shift range, and appears in $^{39}\text{K}$ and $^{87}\text{Rb}$ MAS NMR spectra only upon direct comparison due to the very broad peak widths produced by large quadrupolar interactions (e.g., Figure 8.13b). Unlike high field-strength network formers which typically possess relatively small geometric distributions, the more ionic modifiers are generally characterized by wide distributions in coordination numbers and local geometrical parameters. Correspondingly, NMR spectra of low field-strength cations are often broad and featureless, a result which is exacerbated by the unfavorable NMR properties of many such cations. Despite this lack of resolution, the observed shifts to higher frequencies can be interpreted according to the well-documented correlation with reduced average coordination number. While it is not possible to determine the actual coordination numbers without careful calibration, the trend is consistent with greater negative charge being made available to the alkali cations as the fraction of anionic $^{[4]}\text{B}$ species increases, which provides more effective charge-compensation and lower coordination numbers. Furthermore, it is interesting to note that if the measured changes in chemical shifts are scaled by the known chemical shift region for each nuclide, these normalized chemical shifts are remarkably commensurate (Figure 8.14). The exception is lithium, which tends to form low-coordinate polyhedra due to its small size. Nevertheless, this apparent near-universality of modifier behavior for alkali metal cations implies that their effect on the glass network is surprisingly similar, despite the vast differences in ionic radii. This example illustrates that even when individual NMR spectra are dominated by internal broadening effects (e.g., quadrupolar) and/or severe geometric disorder, comparisons among a series of compositions can provide valuable structural insight.
Figure 8.13 MAS NMR spectra of alkali borate glasses. (a) $^{133}$Cs MAS NMR ($B_0 = 14.1$ T) spectra of cesium borate glasses; (b) $^{39}$K MAS NMR ($B_0 = 21.1$ T) of potassium borate glasses. The lines are added as guide for the eye. Crystalline impurities are marked by asterisks. (Adapted from Reference [26].)
8.6 CONCLUSIONS

The attractiveness of NMR for glass studies lies in its fundamental sensitivity to local environments, leading to structural descriptions which are naturally compatible with the disordered nature of glass. Experimental procedures and data analysis are straightforward for many nuclides of interest in glass science. However, the particular properties of NMR-active nuclides vary widely across the periodic table and must be considered carefully prior to attempting a study. Whereas some nuclei common to glasses are well established and can be considered routine (e.g., $^{29}$Si, $^{27}$Al, $^{11}$B, $^{31}$P, $^{23}$Na), others require greater effort to obtain the desired information (e.g., $^{17}$O, $^{19}$F, $^{71}$Ga, $^{77}$Se, $^{89}$Y). Moreover, there remains a class of nuclides that are just now becoming accessible with magnetic field increases and new pulse sequences, but have not yet reached the point where structurally informative spectra can be reliably obtained for disordered materials (e.g., $^{25}$Mg, $^{43}$Ca, $^{87}$Sr, $^{39}$K, $^{73}$Ge, $^{75}$As, $^{33}$S). Peak assignments for all these categories will be aided by careful studies of relevant crystalline compounds combined with improvements in theoretical calculations.
Several frontier areas can be identified that will expand the scope of NMR in the characterization of glassy materials. New strategies for enhancing sensitivity and obtaining high resolution spectra of low-γ and large-eQ nuclides in disordered environments are needed to realize the full multinuclear potential of NMR. More research on glasses with appreciable paramagnetic character must be done to deepen our understanding of these phenomena and develop innovative approaches to address the many such systems of interest in geology and materials science. The development and implementation of double-resonance NMR methodology to directly exploit dipolar interactions between spin-active nuclei will further advance the characterization of medium-range order. Finally, high-temperature NMR spectroscopy with sufficient spectral resolution is required to probe the structure and dynamics of network-forming glasses as they approach the glass transformation range.

Over the last half-century, NMR spectroscopy has made many important contributions to glass science. Beginning with clever approaches using low-field magnets and non-spinning samples, through the development of MAS, to the ultrahigh-field magnets and high resolution methodologies such as MQMAS used today, instrumental and technical innovations continue to advance the study of glasses by NMR and add to the body of knowledge. This steady progress defines a trajectory that promises to encompass more complex and exotic glasses by improvements in spectral sensitivity and resolution, and to strengthen the capacity of NMR as a glass characterization technique.

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REFERENCES


9 ADVANCED DIPOLAR SOLID STATE NMR SPECTROSCOPY OF GLASSES

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9.1 INTRODUCTION

Compared to crystalline solids, glasses present a formidable challenge to structure elucidation. Owing to the lack of long-range periodicity in the glassy state, diffraction techniques are fairly powerless, and the structural concepts typically emerge from the joint interpretation of numerous complementary spectroscopic experiments. For a comprehensive view, glass structure must be discussed on different length scales: (i) short-range order involving only the first atomic coordination spheres (distance region 0.15–0.3 nm), (ii) second-nearest neighbor environments (0.3–0.5 nm), (iii) nanostructure (0.5–3 nm), (iv) mesostructure (3–500 nm), and finally, (v) microstructure (> 500 nm). Spectroscopic methods such as NMR, Raman scattering, photoelectron and extended X-ray absorption fine structure (EXAFS) provide primarily local information about the first few coordination spheres. While the utility of solid state NMR for characterizing the short-range order of glasses was discussed in the preceding chapter, the present contribution concerns the study of structural issues on the 0.3–3 nm length scale (domains (ii) and (iii), particularly in the sub-nanometer region commonly denoted as medium-range structure. The structural issues addressed include (i) the connectivity between different network former species, (ii) the distance correlations involving network former and network modifier species, and (iii) the overall spatial distribution of the network modifier ions (see Figure 9.1).
As discussed in the preceding chapter, and also recently reviewed in Reference 1, important information about these questions can be obtained from chemical shift measurements using magic-angle-spinning NMR. However, a more direct and more powerful approach makes use of the \textit{indirect and direct magnetic dipole–dipole interactions} between the nuclei. The magnetic nuclei not only feel the externally applied magnetic field, moderated by shielding effects caused by their surrounding electron clouds, but they also sense the magnetic moments of their neighbors. In most cases, these interactions are considerably weaker than those dominating the lineshape of the NMR spectra in the solid state. The research challenge then consists of (i) selectively extracting reliable dipolar coupling information from the complex internal NMR Hamiltonian, and (ii) translating this information into a structural description. For task (i) the NMR spectroscopist's toolbox contains a considerable number of powerful selective averaging strategies to measure, in a site-selective fashion, both homo- and heteronuclear indirect and direct spin–spin interactions. Based on this highly specific and accurate information, it is then possible to address task (ii), which is putting structural models for glasses to a quantitative test. The present contribution is focused on this aspect of glass
structure and reports important progress made in this direction made during the past few years, complementing recent summaries already available in the literature on this topic [1, 2]. Of course the information obtained by such experiments is combined with that gathered on the short-range order from standard solid state NMR spectra. As detailed below, such studies have given important insights into the local environments and the spatial distribution of the network former and the network modifier species in numerous glass-forming systems.

9.2 THEORETICAL ASPECTS

The total spin Hamiltonian determining the spectroscopic energy levels in solid-state NMR can be written as [3–7],

\[ H_{\text{total}} = H_z + H_{\text{ms}} + H_D + H_J + H_Q \]  

(9.1)

where \( H_{\text{ms}} + H_D + H_J + H_Q \) define the relevant Hamiltonians of distinct types of internal interactions, namely, (a) the magnetic interactions of the nuclei with the surrounding electrons (magnetic shielding), \( H_{\text{ms}} \), (b) the internuclear direct and indirect magnetic dipole–dipole interactions, \( H_D \) and \( H_J \), respectively, and (c) interactions between the electric quadrupole moments of spin > 1/2 nuclei and the electrostatic field gradients sensed by these nuclei (quadrupolar interaction), \( H_Q \). In the solid state, all of these interactions are anisotropic, that is, their influence on the precession frequency depends on molecular orientation in the magnetic field. As a result, extensive line-broadening is produced in powdered samples.

Magnetic shielding (\( H_{\text{ms}} \)) and nuclear electric quadrupolar interactions (\( H_Q \)) have been discussed in detail in the preceding chapter. In general, the anisotropies of these interactions are described by second-rank tensors in the limit of first-order perturbation theory. Using the technique of magic-angle-spinning, the anisotropy of the magnetic shielding can be removed, resulting in high resolution spectra, where different local environments can be generally differentiated by resolved resonances characterized by distinct isotropic chemical shift ranges. For example, in silicate and phosphate glasses, the various types of Q\( ^{(n)} \) environments (4 ≥ n ≥ 0, n being the number of bridging oxygen atoms on a particular unit) can be differentiated by distinct isotropic chemical shift ranges. This is also true for the central transition of quadrupolar nuclei in the limit of first-order perturbation theory. In the case of stronger quadrupolar interactions (\( H_Q > 0.05 H_z \)), however, second-order perturbation theory must be used, resulting in more complicated lineshapes, for which the averaging by MAS is incomplete. In favorable cases (e.g., \(^{11}\)B MAS-NMR in glasses) distinct lineshapes can be observed from which the electric field gradient size and asymmetry can be deduced by lineshape simulation methods. In most cases, however, the variation of local environments and topologies results in distributions of both isotropic chemical shifts and nuclear electric quadrupole coupling constants, which dominate the MAS-NMR lineshape [1]. By comparison, the magnetic dipole–dipole interactions are considerably weaker and have normally a negligible influence on the MAS-NMR lineshape. To extract this information from the spectra, special selective averaging and two-dimensional techniques are required. It is the purpose of
this chapter to review the most important ones of these techniques and highlight some recent applications of them for the quantitative structural analysis of glasses.

There are two distinct mechanisms, through which magnetic dipole–dipole interactions are being transmitted: first, there are the \textit{direct} magnetic dipole–dipole couplings which act merely through space and hence depend only on distance and relative orientation with respect to the NMR quantization axis (the direction of the externally applied magnetic field). Second, there are the \textit{indirect} spin–spin couplings, which are transmitted via the polarization of bonding electrons. These indirect couplings do not depend straightforwardly on internuclear distances as their magnitudes are greatly influenced by the extent of orbital overlap and covalency. For each mechanism, one has to differentiate between \textit{homonuclear} and \textit{heteronuclear} spin–spin interactions. As discussed in more detail below, the various types of interactions can be discerned from each other and addressed selectively using suitable selective NMR averaging methods.

\subsection*{9.2.1 Direct Magnetic Dipole–Dipole Coupling}

The Hamiltonian of the direct dipole–dipole interaction (“through-space”) is proportional to the inverse cube of the internuclear distance, providing a straightforward connection to geometric structure. In the limit of first-order perturbation theory, it is given by the expressions [3]

\begin{align}
H_{D\text{-homo}} &= - \left( \frac{\mu_0}{4\pi} \right) \frac{\gamma_i^2 \hbar^2}{r_{ij}^3} \left( \frac{3 \cos^2 \theta - 1}{2} \right) \left( \mathbf{I}_z \mathbf{I}_z - \mathbf{I}^2 \right) 
\tag{9.2}
\end{align}

\begin{align}
H_{D\text{-hetero}} &= - \left( \frac{\mu_0}{4\pi} \right) \frac{\gamma_i \gamma_s \hbar^2}{r_{is}^3} \left( \frac{3 \cos^2 \theta - 1}{2} \right) \left( \mathbf{I}_z \mathbf{S}_z \right) 
\tag{9.3}
\end{align}

The orientational dependence is described by the \((3 \cos^2 \theta - 1)\) term where \(\theta\) is the angle between the internuclear distance vector and the magnetic field direction. Dipolar interactions in two-spin systems can be treated straightforwardly by considering the eigenstates whose energies are modified according to a treatment on the basis of first-order perturbation theory. In systems characterized by multiple-spin interactions, this approach is not practical and one specifies an average mean square of the local field (called \textit{second moment}). The relation to internuclear distance distributions is given by the van Vleck formulae [8], which predict

\begin{align}
M_{2\text{homo}} &= \frac{3}{5} \left( \frac{\mu_0}{4\pi} \right)^2 I(I+1) \gamma_i^4 \hbar^2 \sum_{i \neq j} r_{ij}^{-6} 
\tag{9.4}
\end{align}

\begin{align}
M_{2\text{hetero}} &= \frac{4}{15} \left( \frac{\mu_0}{4\pi} \right)^2 S(S+1) \gamma_i^2 \gamma_s^2 \hbar^2 \sum_{s} r_{is}^{-6} 
\tag{9.5}
\end{align}

for homo- and heteronuclear interactions, respectively.
As described below, both homo- and heteronuclear dipole–dipole couplings can be measured selectively under static conditions using different versions of spin echo decay spectroscopy. It is frequently desirable, however, to measure the strength of magnetic dipole–dipole interactions under high resolution (i.e., under MAS) conditions, in order to obtain the dipolar coupling information in a site-resolved fashion. Magic-angle spinning, however, by its very experimental design, averages the direct homo- and heteronuclear magnetic dipolar interactions to zero. To overcome this dilemma, special dipolar recoupling techniques are available. In the following sections, the most important techniques used for measuring and quantifying direct and indirect magnetic dipole–dipole interactions are being reviewed. Thus, methods are available to selectively measure $M_{2\text{homo}}$ as well as $M_{2\text{hetero}}$ contributions. These values can then be compared with average values of second moments calculated via (9.4) and (9.5), respectively, from the distance distributions of any structural scenario or computer-simulated model. By means of this quantitative comparison, the model can be either corroborated or discounted.

### 9.2.2 Indirect Spin–Spin Coupling

Indirect spin–spin coupling proceeds via polarization of bonding electrons linking the nuclei involved; typically via one, two, or three linkages ($^1J$, $^2J$, or $^3J$-coupling, respectively). The relevant Hamiltonian is given by the tensor product

$$\mathcal{H}_J = \hat{I} \vec{J} \hat{S} \quad (9.6)$$

where $\vec{J}$ is the indirect spin–spin coupling tensor. Its magnitude and anisotropy depend to a great extent on the symmetry of the electron distribution in the chemical bond, but also on the sizes of the magnetic moments involved. For a two-spin interaction, the tensor is generally axially symmetric, and can be split into an isotropic component $J_{\text{iso}}$ and an anisotropic component $\Delta J$. While the anisotropic part is averaged out by magic angle spinning, the isotropic part produces peak splittings that are frequently observable in the spectra of crystalline solids. In glasses, such splittings are generally not observable because they are obscured by line-broadening effects resulting from distribution effects affecting $\delta_{\text{iso}}$; thus two-dimensional measurements are generally needed to identify them. Both homo- and heteronuclear spin–spin interactions of the observed nuclei to $n$ nuclei having spin quantum number $I$ yield a peak multiplicity of $\Pi(2nI + 1)$, where the product comprises all contributions from magnetic nuclei in the sample. In the solid state, the spectra are influenced both by isotropic and anisotropic $J$-couplings, however, the anisotropy can be eliminated by MAS.

The magnitudes of the $\vec{J}$ tensor components depend not directly on distance, but are greatly influenced by the electronic properties and bonding characteristics. DFT calculations of $J_{\text{iso}}$ values with GAUSSIAN or TURBOMOLE are possible in principle [9, 10], even though the accuracy is lower than that of magnetic shielding calculations. Nevertheless, the experimental detection of isotropic indirect spin–spin coupling in MAS-NMR spectra provides direct evidence of bond connectivity and the observed peak multiplicity gives information about the
number of spins to which the observe-nuclei are coupled.

9.3 HETERONUCLEAR EXPERIMENTS

9.3.1 Spin Echo Double Resonance

Spin echo double resonance (SEDOR) measures the strength of the heteronuclear dipole–dipole interactions between two different spin species I and S in an incremented Hahn spin echo experiment \((90^\circ-t_1-180^\circ-t_1)\) conducted on the observed S nuclei [11]. While this interaction is being refocused by the \(\pi\) pulses applied to the observed spins I, this refocusing can be un-done by a \(\pi\) pulse applied to the non-resonant S spins at some time during the dipolar evolution period \(2t_1\). One then compares the spin echo intensity of the observed nuclei as a function of dipolar evolution time (a) in the absence and (b) in the presence of these recoupling pulses. Experiment (a) produces a decay \(F(2t_1)/F_0\), which is largely governed by homonuclear dipole–dipole interactions (see below), while experiment (b) results in an accelerated decay reflecting the contribution from the heteronuclear dipole–dipole interaction. For multi-spin systems, a Gaussian decay is expected, the rate of which is given by the heteronuclear second moment \(M_{2hetero}^2\)

\[
\frac{I(2t_1)}{I_0} = \frac{F(2t_1)}{F_0} \cdot \exp \left( -\frac{(2t_1)^2M_{2hetero}^2}{2} \right) \tag{9.7}
\]

The first applications of SEDOR to amorphous systems involved spatial proximity studies of boron and phosphorus in compensated semiconductors based on amorphous silicon [12] and the speciation of selenium atoms in P-Se glasses [13]. Later on, \(^{23}\text{Na}\{^7\text{Li}\}\) and \(^{23}\text{Na}\{^6\text{Li}\}\) SEDOR were applied to investigate the relative spatial distribution of Na\(^+\) and Li\(^+\) ions in mixed-alkali lithium silicate [14–16], borate [17], and chalcogenide glasses [18]. Recently, this approach has been extended to study Li–F interactions in Li ion conducting oxyfluoride glasses [19]. Figure 9.2 illustrates an application to measure heteronuclear \({^6\text{Li}}\{^7\text{Li}\}\) dipole–dipole interaction strengths in a sample of \(^6\text{Li}\)-enriched lithium carbonate. The Hahn spin echo amplitude of the residual \(^7\text{Li}\) nuclei is measured as a function of dipolar evolution time \(2t_1\) in the absence and the presence of the \(^6\text{Li}\) recoupling pulses. An important limitation of the SEDOR sequence is its sensitivity to imperfections of the \(\pi\) pulse lengths and resonance offset effects affecting the dephaser nuclei S. The latter issue is particularly serious if S is a quadrupolar nucleus interacting with a local electric field gradient. As pointed out in the preceding chapter, the anisotropy of the nuclear electric quadrupolar interaction produces strong line broadening effects for the non-central Zeeman transitions, resulting in incomplete population inversion for the nuclei contributing to those transitions and hence a weakening of the SEDOR effect. While it is sometimes possible to account for such deviations by calibrating the technique with crystalline model compounds having similar spin dynamics as the system under study, the accuracy of the SEDOR method may be limited to those applications where experimental data are compared to distinct structural scenarios making vastly different
predictions.

**Figure 9.2** Measurement of the $^7\text{Li}\{^6\text{Li}\}$ dipolar second moment in isotopically enriched lithium carbonate (95% $^6\text{Li}$), using the SEDOR sequence. Filled squares, $F(2t_1)/F(0)$; open triangles, $I(2t_1)/I(0)$. The dashed curve is a fit to Eq. 9.7, while the solid curve was calculated with this expression using the $M_2$ value calculated with Eq. 9.5 from the known internuclear distances in lithium carbonate.

### 9.3.2 Rotational Echo Double Resonance

The Rotational echo double resonance (REDOR) experiment introduces the SEDOR concept into MAS-NMR experiments, affording site-selective heteronuclear dipole–dipole coupling information in high resolution spectra [20]. Figure 9.3 shows a typical pulse sequence used for such purposes [21]. Recoupling is accomplished by 180° pulse trains applied to the I-spins, while the S-spin signal is detected by a rotor-synchronized Hahn spin echo sequence. One measures the normalized difference signal $\Delta S/S_0 = (S_0 - S)/S_0$ in the absence (intensity $S_0$) and the presence (intensity $S$) of the recoupling pulses. A REDOR curve is then generated by plotting $\Delta S/S_0$ as a function of dipolar evolution time $NT_r$, the duration of one rotor period.
multiplied by the number of rotor cycles.

**Figure 9.3** Top: Timing of a REDOR pulse sequence, showing the evolution of the dipolar coupling Hamiltonian during the rotor cycle [21]. Bottom: Experimental and calculated $^{11}\text{B}^{(31}\text{P})$ REDOR curve of crystalline BPO$_4$. The dotted curve shows the parabolic approximation.
Figure 9.4 Constant time (CT-REDOR). Top: pulse sequences, in (a) the pulse position $t_{pp}$ of the I-spin dephasing pulses are stepped from 0 to $T_R$ (CT-VPP-REDOR; variable pulse position); in (b) the pulse widths $t_{PD}$ of the I-spin dephasing pulses are stepped from 0 to 2$\pi$ (CT-VPD-REDOR; variable pulse duration). Bottom: $^{11}\text{B}^{31}\text{P}$-CT-VPP-REDOR results for BPO$_4$ for $N = 2$ (filled black circles); $N = 4$ (open black circles); $N = 6$ (filled red circles); and $N = 8$ (open red circles). Dotted curves show results of a two-spin calculation employing the theoretical $M_2$-value of $1.87 \times 10^7$ rad$^2$/s$^2$; solid curves show results of a two spin calculation assuming $M_2$ values of $1.77 \times 10^7$ rad$^2$/s$^2$ ($N = 2$); $1.60 \times 10^7$ rad$^2$/s$^2$ ($N = 4$), $1.57 \times 10^7$ rad$^2$/s$^2$ ($N = 6$), and $1.34 \times 10^7$ rad$^2$/s$^2$ ($N = 8$).
Figure 9.5 Timing diagram of the rotational echo adiabatic passage double resonance (REAPDOR) pulse sequence.
Figure 9.6 Top: Pulse sequence used for cross-polarization. The rf field applied to the I nuclei during the contact time is phase shifted by 90° relative to the corresponding preparation pulse. Bottom: Relaxation processes and corresponding time constants involved in the cross-polarization experiment.
Figure 9.7 \( ^{19}\text{F} \)\(^{11}\text{B} \) heteronuclear correlation experiment of a lead fluoroborate glass. Top: Contact time 200 µs; preferential detection of the B-bonded F species. Bottom: Contact time 5 minutes, proportional detection of both B-bonded and non-B-bonded F species.
Figure 9.8 Heteronuclear DQ filtering experiment based on J-coupling. Top: Pulse sequence timing diagram. Bottom: Results of the \( ^{113}\text{Cd} \) \( ^{31}\text{P} \) DQ filtering experiment on Zn\(_{0.875}\)Cd\(_{0.125}\)GeP\(_2\). (a) Single-pulse \( ^{31}\text{P} \) spectrum, (b) selective detection of the signal component attributed to \( ^{113}\text{Cd} \)-bonded P atoms (originating from the PCdZnGe\(_2\) site).

For isolated two-spin-1/2 pairs, the REDOR curve has universal character and can be directly used to extract the internuclear distance. In contrast, for larger spin-clusters, the REDOR curve depends on the detailed shape and distance geometry of the spin system [22, 23]. In glasses, one generally expects a distribution of spin geometries and magnetic dipole coupling strengths, which is a priori unknown. As previously shown, this problem can be circumvented by limiting the REDOR data analysis to the initial curvature, where \( \Delta S/S_0 < 0.2 \) [2, 23–25]. In this limit of short dipolar evolution times, the REDOR curve is found to be geometry-independent and (for spin-1/2 non-observe nuclei) can be approximated by

\[
\frac{\Delta S}{S_0} = \frac{S_0 - S}{S_0} = \frac{4}{3\pi^2(NT_r)^2}M_2
\]  

(9.8)
where the average van-Vleck second moment defined by Eq. 9.5 can be extracted from a simple parabolic fit of the experimental data. Figure 9.3, bottom shows an application to BPO$_4$, a crystalline model compound for borophosphate glasses. In this compound, each of the boron atoms forms four B–O–P linkages to phosphate units. Equation 9.8 turns out to be an excellent approximation to the theoretically simulated REDOR curve, yielding a dipolar second moment of 14.5 \times 10^6 \text{rad}^2/\text{s}^2 in reasonable agreement with the value (18.7 \times 10^6 \text{rad}^2/\text{s}^2) calculated from the crystal structure. Other ternary crystalline borophosphates yield a similar level of agreement [26, 27]; there appears to be a trend that slightly underestimates $M_2$ by 10–20%, owing to experimental imperfections (resonance offset effects, non-perfect 180° flip angles. The performance of the sequence can be improved by applying a compensation scheme, that corrects for pulse imperfection and resonance offset effects. In this compensation scheme, a second reference signal $S_D$ is obtained, with an additional $\pi$ pulse applied to the non-observed spins in the middle of the dipolar evolution period [24]). Under perfect conditions, the difference signal $S_0 - S_D$ should be zero, as the extra $\pi$ pulse serves to cancel the recoupling effect. In reality, however, a non-zero difference signal is invariably observed. Simulations show that the magnitude of this extra difference signal produced by deviations of the recoupling pulses from the exact 180° flip angle is approximately equal to the extent to which the REDOR effect is weakened by this imperfection [24]. Hence a compensated REDOR curve can be constructed by taking the sum $(S_0 - S)/S_0 + a(S_0 - S_D)/S_0$, where the scaling factor $a$ has a value near unity, depending on the duty cycle. The $\pi$ pulse lengths for both I and S nuclear species should be as close as possible, as the compensation method only works if both pulses are applied at exactly the same time and for the same duration.

The initial curvature analysis of REDOR data discussed above has the disadvantage that owing to spinning speed limitations, only a few data points may be available for parabolic fitting. This drawback can be overcome by a variation of REDOR, in which the number of rotor cycles is held constant, but the timing of the recoupling $\pi$ pulse is changed systematically during the rotor cycle (“constant time, CT-REDOR”, see Figure 9.4) [28, 29]. This method is advantageous for systems with very strong magnetic dipole couplings, short spin–spin relaxation times and/or experiments done with low spinning speeds.

9.3.3 Rotational Echo Adiabatic Passage Double Resonance

Compared to the S{I = 1/2} case, REDOR curves of S-spins coupled to I > 1/2 spins are affected by two additional aspects [30, 31]. First of all, the extent of dephasing of the S nuclei depends on the Zeeman state of the particular I nuclei they are coupled to, reflecting the dependence of the $z$-component of the I magnetic moment on the orientational quantum number. In the presence of nuclear electric quadrupolar interactions, first-order perturbation theory results in a wide spectral dispersion of the non-central Zeeman transitions, rendering coherent $\pi$ recoupling pulse trains ineffective due to resonance offset problems. Then, in the case of large quadrupole splitting of the I spins, only those S nuclei that are coupled to I spins in the central Zeeman levels will give a REDOR response. Both effects can be accounted for with the help of simulations if the quadrupole tensor components are known, and a dipolar analysis is
still possible [32]. Alternatively, the rotational echo adiabatic passage double resonance (REAPDOR) method can be used, which recouples the dipolar interaction to the non-observed spins in all of the Zeeman states [33], see Figure 9.5. Here, a long continuous-wave pulse, lasting at least 1/3 of the MAS rotor period, leads to a mixing of I-spin Zeeman states, thereby resulting in more effective dipolar recoupling of the S-spins. In this case, the extent of the dipolar recoupling depends—besides on the magnitude of the dipole–dipole coupling—on the I-spin quadrupolar frequency, the MAS rotor frequency and the amplitude of the applied radio frequency field (expressed as the I-spin nutation frequency). Based on reliable input data, the effect can be taken into account by simulation, yielding quantitative dipolar coupling information to be compared with experimental data.

9.3.4 Cross-polarization

Another common approach for recoupling heteronuclear magnetic dipole–dipole interactions into the MAS Hamiltonian is the cross-polarization experiment [34]. This experiment utilizes the heteronuclear dipole–dipole coupling as a mechanism for transferring magnetization from a spin reservoir of source nuclei (labeled I) to recipient nuclei S, whose signal is then detected. Figure 9.6 shows the pulse sequence involved. In general, transverse spin magnetization of the source nuclei is created by a 90° pulse and spin-locked by applying a strong radiofrequency field along the direction of the magnetization in the rotating frame. During the application of this radiofrequency field, the spin states are now quantized in a direction orthogonal to $B_0$ and the transverse magnetization is forced to precess around this direction with the I-spin nutation frequency $\omega_{\text{I}} = \gamma_I B_{\text{I}}$. As the spin-locked magnetization is much higher than the value corresponding to the value of $B_{\text{I}}$, this situation reflects a non-equilibrium state, from which the system seeks to escape via relaxation. This can be accomplished via magnetization transfer to the recipient S nuclei, utilizing magnetic dipole–dipole interactions. For transfer to be possible, the I and S nuclei must have identical precession frequencies in the rotating frame. The S nuclei are irradiated on resonance for a duration (contact time) of several milliseconds, with their radio frequency amplitude $B_{\text{S}}$ chosen according to the Hartmann–Hahn matching condition [35].

$$\gamma_I B_{\text{I}} = \gamma_S B_{\text{S}}$$  \hspace{1cm} (9.9)

During the contact time, I-spin polarization is then transferred to the S-spins, whose signal is subsequently detected. The rate of this process is characterized by the cross-relaxation time $T_{\text{IS}}$ (see Figure 9.6), which depends on the strength of the heteronuclear magnetic dipole–dipole interactions. Competing relaxation mechanisms involve energy interchange with the lattice (spin lattice relaxation in the rotating frame, characterized by the time constant $T_{1\rho}$ (see Figure 9.6).

As the dipole–dipole couplings utilized by cross-polarization experiments on inorganic glasses are usually relatively weak, fast MAS modulates the Hartmann–Hahn matching condition, leading to $\gamma_I B_{\text{I}} = \gamma_S B_{\text{S}} \pm n \omega_r$, where $n$ is an integer and $\omega_r$ is the angular rotor frequency. To account for this modulation, one now frequently uses a ramped cross-polarization variant,
where the nutation frequency of the I or S nuclear species is systematically stepped up linearly during the contact time period. This important modification has led to significant signal-to-noise gains, particularly in cross-polarization experiments involving source nuclei other than $^1$H.

As the rate of the magnetization transfer depends on the strength of the magnetic dipole–dipole interactions (and hence on spatial proximity), qualitative information about relative internuclear distances can be extracted from systematic cross-polarization experiments as a function of contact time. In a useful two-dimensional version of CPMAS, an incremented evolution period $t_1$ is inserted between the I-spin preparation pulses and the subsequent spin-locking field. In this way, resolved resonances of the source nuclei can be correlated with resolved resonances of the recipient nuclei [36]. To illustrate the utility of such heteronuclear correlation experiments, in connection with variable contact time studies, Figure 9.7 shows a $^{19}$F$^{11}$B NMR result obtained on a lead fluoroborate glass. The $^{19}$F NMR signal comprises two distinct contributions, at −108 and −50 ppm versus CFCl$_3$. The minority signal at −108 ppm, which is preferentially detected at short contact time, is assigned to F species directly bonded to tetrahedral boron (BO$_{3/2}$F species), whereas the signal near −50 ppm comes from F species that are more remote from boron and thus require longer contact times for magnetization transfer [37]. Other applications of cross-polarization and heteronuclear correlation experiments to structural studies of glasses have been recently reviewed by Edén [1]. In many applications, the “source” I nuclei are highly abundant quadrupolar nuclei such as $^7$Li, $^{11}$B, $^{23}$Na, and $^{27}$Al. The fact that such quadrupolar nuclei have usually relatively short $T_1$ values makes them attractive source nuclei for CPMAS experiments. It is important, however, to be aware of some potential complications when using them. As discussed in the literature [38], spin-locking such quadrupolar nuclei under MAS conditions leads to level crossings and mixing of spin states causing very rapid loss of transverse magnetization. The rotating-frame spin-lattice relaxation time $T_{1\rho}$, which characterizes how long spin-lock can be maintained, depends critically on the strength of the quadrupolar coupling, the nutation frequency, and the rotor speed. With the latter two parameters under the experimenter's control, it is at first necessary to find those radiofrequency amplitudes with which good I-spin-locking can be accomplished, before the Hartmann–Hahn matching conditions can be adjusted. Finally, the recycle delay to be used for signal accumulation must be adjusted in accordance with the spin-lattice relaxation time $T_1$ of the source nuclei.

9.3.5 Connectivity Studies Based on the Detection of Indirect Spin–Spin Interactions

Even though their detection constitutes direct proof of interatomic connectivity, heteronuclear indirect spin–spin interactions have thus far been little utilized for structural studies of glasses. Potentially useful two-dimensional experiments include the heteronuclear J-resolved experiment [39] and correlation spectroscopy based on the detection of heteronuclear double quantum coherences [40, 41]. If the isotope with which J-coupling is to be detected has a low natural abundance, the indirect detection of the abundant spin species is often preferable and
can be used for HETCOR experiments [42]. Furthermore, this method can be used for spectral editing purposes. Figure 9.8 shows the pulse sequence stimulating heteronuclear double quantum (DQ) coherences [40–42] and an application of this sequence as a heteronuclear double quantum filter for the \(^{31}\)P resonance of a crystalline chalcopyrite alloy of composition Zn\(_{0.875}\)Cd\(_{0.125}\)GeP\(_2\). In these alloys, the P atoms are coordinated to two Ge and two Group-12 atoms. At the composition chosen, two \(^{31}\)P signal contributions are dominant, corresponding to the PGe\(_2\)Zn\(_2\) and the PGe\(_2\)ZnCd local environments. As illustrated by this figure, the latter resonance can be detected selectively by exciting (and detecting) the \(^{31}\)P–\(^{113}\)Cd heteronuclear double quantum coherence, thereby offering a useful lineshape constraint for the deconvolution of the full spectrum [42]. In recent years, it was shown that this sequence, improved with refined DQ excitation schemes, may have potential for counting Si–O–Al connectivities in aluminosilicate glasses [43–46].

9.3.6 Instrumental Considerations and Caveats.

All of the above experiments can be conducted on standard NMR instrumentation constructed during the past two decades. Obviously, the spectrometer must have at least two distinct heteronuclear radio frequency channels that can be separately addressed by the pulse programmer. As commercial spectrometers are usually furnished with a separate \(^1\)H/\(^{19}\)F channel, a three-channel instrument is needed. In addition, probes are necessary, which can be tuned simultaneously at the resonance frequencies of the two heteronuclei involved. The minimum frequency separation amounts to about 30 MHz; at lower values it becomes difficult to accomplish rejection of the frequency of nucleus X in the Y-channel of the probe and vice versa. “Crosstalk” problems of this kind generating a lot of noise are even more serious if both nuclei are pulsed simultaneously (like in CP) or if the signal of nucleus X must be acquired with high-power Y-decoupling. In our experience, passing the high power rf amplifier output through narrow band pass filters on both sides prior to entering the probe goes a long way toward beating noise problems. If the two frequencies are very close (such as is the case for the combinations \(^{31}\)P/\(^7\)Li, \(^{27}\)Al/\(^{13}\)C or \(^{23}\)Na/\(^{51}\)V, it is possible to conduct the experiment using a modified single-tuned probe that is sufficiently broad-banded to accept both frequencies [47–51].

One important caveat, which applies to the interpretation of heteronuclear second moments \(M_2^{SI}\) extracted from either S\{I\} REDOR or REAPDOR data has to be pointed out here: in glasses these quantitative dipole coupling data are frequently used to infer the number of “connectivities”, that is, S···I linkages, based on reasonable assumptions (or experimental results from EXAFS, diffraction, or MD simulations) of S···I internuclear distances in either the first or the second coordination spheres. Several examples of such an application are discussed in the “Case studies” below. Because of the through-space mechanism of dipolar coupling, however, bond connectivity is not a pre-requisite for measuring a REDOR effect. The translation of \(M_2\) values into bond connectivity values is based on the inherent assumption that the dipolar coupling strength associated with such first or second coordination sphere S···I linkages is much higher than that from through-space interactions at longer distance ranges. We
have found this inherent assumption to be generally justified, also in view of the $r^{-6}$ dependence of second moment values. More rigorous information about bond connectivities comes from heteronuclear J-based spectroscopic methods such as those discussed in Section 3.5.

### 9.4 HOMONUCLEAR EXPERIMENTS

#### 9.4.1 Static Spin Echo Decay Spectroscopy

Homonuclear magnetic dipole–dipole interactions can be measured selectively by Hahn spin echo decay spectroscopy, using the pulse sequence shown in Figure 9.9 [52]. For a spin-1/2 system the normalized echo intensity $I/I_0$ is only influenced by homonuclear dipole–dipole interactions, while all of the other abovementioned types of interactions plus the heteronuclear dipole–dipole couplings are being refocused. For a multi-spin system, one observes a Gaussian decay as a function of evolution time $2t_1$,

$$\frac{I(2t_1)}{I_0} = \exp \left[-\frac{M_{2\text{homo}}}{2}(2t_1)^2\right]$$ \hspace{1cm} (9.10)

affording a reliable measurement of the homonuclear van Vleck second moment $M_{2\text{homo}}$. 

The method has been validated by measurements on crystalline model compounds [53] and widely applied for examining the spatial distribution of $^{31}\text{P}$ spins ($I = 1/2$) in a variety of non-oxide glasses [54–58]. Of course it is necessary that dynamic motional narrowing effects are absent. Any change in resonance frequency for a given nucleus during the dipolar evolution time $2t_1$ because of nuclear motion or reorientation will accelerate the spin echo decay and thus not provide valid information upon the structure of the material. As pointed out in Reference 53, the method is quantitatively reliable only if the magnitude of the dipole–dipole interaction (in Hz) is smaller than the difference in resonance frequency of the participant nuclei. This situation is usually the case in glasses because a wide chemical shift distribution exists. As a result, the resonance frequencies of neighboring nuclei are rather different, and the spin-exchange term that is usually part of the homonuclear dipolar Hamiltonian can be neglected. The homonuclear dipolar Hamiltonian then takes form $\mathcal{H}_D \sim I_{z1}I_{z2}$, which is analogous to that present in heteronuclear dipole couplings. As a consequence, the pre-factor 3/5 in Eq. 9.4 needs to be replaced by the pre-factor 4/15.
It was also possible to extend this method to the study of certain quadrupolar nuclei such as $^{23}\text{Na}$, where the first-order quadrupolar splitting is sufficiently large such that the Hahn spin echo pulse sequence selectively acts on the central $1/2 \leftrightarrow -1/2$ Zeeman transition [59, 60]. For the case of spin-3/2 nuclei, $M_2$ is given by [60]

$$M_2 = 0.9562 \left( \frac{\hbar_0}{4\pi} \right)^2 \gamma^4 \hbar^2 \sum_j r_{ij}^{-6}. \quad (9.11)$$

The validity of Eq. 9.11 was confirmed experimentally for homonuclear $^{23}\text{Na}--^{23}\text{Na}$ dipole–dipole interactions in crystalline solids, for which the $M_2$ values are readily calculable from the known crystal structures [60]. Comprehensive studies of $^{23}\text{Na}$ spin echo decays as a function of ion concentration have been published for a wide range of binary oxide glasses (see Reference 61 and Section 9.5). Unfortunately, significant deviations from Gaussian decays (Eq. 9.10) are often observed, particularly if the observed nuclei are quadrupolar. These deviations reflect the influence of higher moments contributing to the description of the echo decay. To minimize such additional interferences, the data range for quantitative analysis is frequently curtailed to just the initial decay in the limit of short evolution times, where the second moment dominates. There are a number of other caveats. The $180^\circ$ pulse length has to be well-defined, that is, $\mathcal{H}_Q \gg \mathcal{H}_Z$ (selective excitation of the central transition, Eq. 9.11) or $\mathcal{H}_Q \gg \mathcal{H}_Z$ (non-selective excitation of all the Zeeman transitions) must hold; in the second case, an equation different from (Eq. 9.11) has to be used [59]. To test whether the regime of validity for this sequence is realized in a given situation, a nutation experiment yielding clear sinusoidal behavior of signal amplitude on pulse length is expected. In addition, erroneous results are obtained, if the observed nuclei I are coupled to another spin species S, which are strongly coupled among themselves and hence undergo rapid spin state fluctuations compromising the formation of an echo. Finally, for nuclei with spin quantum number $> 3/2$, the method is less well-tested and presumably also less reliable.

### 9.4.2 Homonuclear Dipolar Recoupling Experiments

To re-introduce homonuclear dipole–dipole couplings into the MAS Hamiltonian, many different approaches exist [62–68], using the build-up of zero-quantum (ZQ) or double-quantum (DQ) coherences via direct or indirect dipole–dipole interactions. To date, the large majority of applications to glasses have been of a qualitative nature, using a variety of two-dimensional NMR approaches for correlating resonances on the basis of the spatial proximity of the nuclei associated with them. Most recently, second-moment information at the same level of quantitative detail has become available by either DQ excitation spectroscopy [68] or the DQ-DRENR experiment (Double-Quantum-based Dipolar Recoupling Effects Nuclear Alignment Reduction; see Section 9.4.2.1).

#### 9.4.2.1 Two-Dimensional Correlation Methods Based on ZQ or DQ Coherences

A large number of dipolar recoupling methods utilize zero-quantum (ZQ) or double quantum
(DQ) coherences for spectroscopically correlating resonances of dipolar-coupled spins. **Zero-quantum coherences** are the result of spin diffusion (coupled “up and down” transitions) which can occur even under MAS conditions. The simplest probe of this effect is the radio frequency driven recoupling (RFDR) experiment shown in Figure 9.10a [65]. Following excitation by a 90° pulse, the spins are frequency-labeled during the evolution time $t_1$. The subsequent 90° pulse terminates the evolution and stores the magnetization along the magnetic field direction. During the mixing time $t_m$, spin diffusion among spatially close nuclei occurs, and the corresponding frequency exchange picked up during the detection period $t_2$ (following the final 90° pulse) manifests itself as a cross-peak in the corresponding two-dimensional correlation plot. The spin diffusion during $t_m$ is enhanced by coherently applying trains of 180° pulses. Figure 9.10b shows a simple application to the ion conductor $\text{Ag}_7\text{P}_3\text{S}_{11}$. This compound has three crystallographically distinct sites, giving rise to the resolved resonances A, B, and C. A represents an isolated $\text{PS}_4^{3-}$ ion, while B and C are the signals of a $\text{P}_2\text{S}_7^{4-}$ group. In the RFDR spectrum, the homonuclear magnetic dipole–dipole coupling between the two P atoms of this pyrothiophosphate group results in cross peaks between resonances B and C. As discussed in Reference 1, applications of this technique to glasses have concentrated on $31\text{P}$ connectivities in various phosphate glass systems.
Figure 9.10 Top: The RFDR sequence with two $\pi/2$-pulses sandwiching the $t_1$ evolution period. The mixing period is comprised of rotor-synchronized $\pi$-pulses. The third $\pi/2$-pulse produces transverse magnetization. Bottom: $^{31}$P RFDR spectrum of the ion conductor Ag$_7$P$_3$S$_{11}$. The two crystallographically distinct phosphorus sites B and C belonging to the P$_2$S$_7^{4-}$ group give rise to a cross-peak indicating the presence of homonuclear magnetic dipole–dipole coupling between them. The weaker dipolar couplings between more distant P atoms are not observed under the experimental conditions used.

Alternatively, the excitation of homonuclear **double-quantum (DQ) coherences** can be used [66]. If the individual nuclei have resonance frequencies $\omega_{L1}$ and $\omega_{L2}$, the double quantum coherence oscillates with the sum frequency of the spins $\omega_{L1} + \omega_{L2}$ during an evolution period $t_1$. Subsequently, it is reconverted to observable single-quantum coherence by applying an analogous de-excitation scheme. For detection, a $90^\circ$ pulse is applied, generating detectable single-quantum coherence (transverse magnetization) which is sampled during the detection period $t_2$. Fourier transformation with respect to both time domains results in a two-
dimensional plot, in which the single-quantum spectrum is correlated with the double quantum spectrum, see for example, Reference 67. For the excitation (and reconversion) of such DQ coherences a number of different schemes exist. The simplest one involves two 90° pulses, which are phase-shifted relative to each other and applied directly “back-to-back” (BaBa-sequence) [68]. Other schemes utilize windowless symmetry-based pulse sequences in which the nutation frequency is a sevenfold multiple of the MAS rotation frequency (C7-pulse sequence) [67, 69, 70]. Figure 9.11 illustrates an application to Ag$_7$P$_3$S$_{11}$. The strongest magnetic dipole–dipole coupling occurring within the pyrothiophosphate group results in the strongest cross-peak intensity. In addition, the weaker dipolar couplings (A–A, A–B, A–C, B–B, and C–C) are also being observed.

**Figure 9.11** $^{31}$P Homonuclear single quantum (SQ)/ double quantum (DQ) NMR correlation spectrum of the ion conductor Ag$_7$P$_3$S$_{11}$. The two crystallographically distinct phosphorus sites B and C belonging to the P$_2$S$_7^{4–}$ group give rise to the strongest cross-peak owing to the strongest homonuclear magnetic dipole–dipole coupling between them. Weaker couplings are also observed and give rise to the correlation peaks A–A, A–B, A–C, B–B, and C–C.
9.4.2.2 Second Moment Measurements

The goal of quantifying homonuclear second moments in REDOR-analog experiments has been realized only recently. A viable strategy is to measure the rate with which DQ coherences are excited by suitable schemes. Indeed, experiments on a number of crystalline thiophosphates revealed that the rate of such build-up curves is correlated with the homonuclear dipole–dipole coupling strengths. However, accurate second moment information is not available by this technique, because the build-up is superimposed by a decay caused by the creation of higher order coherences. In addition, the intensities are often limited by low DQ excitation efficiencies, which are greatly affected by resonance offset effects. Nevertheless, a rough distinction between different kinds of thiophosphate binding was possible. In addition, the conversion of lithium pyrothiophosphate glass with P–S–P linkages to Li$_4$P$_2$S$_6$ (containing a phosphorus–phosphorus bond) upon crystallization could be demonstrated by this method [71]. Recently, the DQ-spin counting approach has been greatly improved by including a constant-time approach [72], introducing super cycles and normalizing the DQ intensities, taking advantage of the fact that the DQ Hamiltonian changes sign upon 90° phase shifting [68]. Using this improved method, Saalwächter et. al. were able to measure accurate site-resolved second moments from initial build-up rates in MgP$_4$O$_{11}$ [68]. Based on the successes of this method, applications to glasses can be envisioned in the future. Recently, a different variant of this principle has been implemented, where no DQ coherence intensities are measured, but rather a diminution of z-magnetization based on the excitation of DQ coherences [73, 74]. In this method, recoupling is accomplished in the form of an effective DQ Hamiltonian created by a symmetry-based POST-C7 sequence consisting of two excitation blocks [70], attenuating the signal (intensity $S'$). For comparison, a reference signal $S_0$ with the dipolar recoupling absent is generated by shifting the phase of the second block by 90° relative to the first block. As in REDOR, the homonuclear dipole–dipole coupling constant can then be extracted from a plot of the normalized difference signal $(S_0 - S')/S_0$ versus dipolar evolution time. Figure 9.12 illustrates this method, which has been dubbed DQ-DRENAR (Double-Quantum-based Dipolar Recoupling Effects Nuclear Alignment Reduction) [74]. For short dipolar evolution times (usually $\Delta S/S_0 < 0.5$), a parabolic approximation analogous to Eq. 9.8 in the heteronuclear case is applicable.

\[
\frac{S_0 - S'}{S_0} = \frac{0.86\pi^2}{15} \sum_{j<k} b_{jk}^2 (N\tau_r)^2
\]

(9.12a)

where the term $\sum_{j<k} b_{jk}^2$ is directly proportional to the van Vleck dipolar second moment. In the case of an effectively heteronuclear interaction (with the exchange term $I_j^+I_k^-$ quenched by large differences in resonance frequencies) one obtains

\[
\frac{S_0 - S'}{S_0} \bigg|_{(t=N\tau_r)} = 0.0717M_2(N\tau_r)^2
\]

(9.12b)
Figure 9.12 DQ-DRENAR pulse sequence [74], based on the excitation of DQ coherences by POST-C7 blocks. In the C' block, the phases of all pulses are shifted by 90° relative to those in the C block. Implicit in the C7 scheme, the $^{31}$P nutation frequency is seven times as high as the spinning rate.

Figure 9.13 shows an application of this technique to Ag$_7$P$_3$S$_{11}$. The dipolar dephasing curves of the PS$_4$$^{3-}$ and P$_2$S$_7$$^{4-}$ groups are well-differentiated in this experiment, yielding dipolar second moment values in close agreement with those calculated from Eq. 9.4. Also this Figure illustrates the applicability of this method to phosphate-based glasses. The data obtained for a binary sodium phosphate glass of composition 60Na$_2$O-40P$_2$O$_5$ clearly reveal the ability of homonuclear REDOR of differentiating between the different types of Q($n$) species on the basis of their different numbers of P–O–P linkages. In addition, data are shown for a mesoporous sol-gel glass of composition 0.5AlPO$_4$-0.5SiO$_2$. This material had been previously conjectured, but never proven, to be phase separated on the nanoscale [75]. The identical second moments, measured for this material and for pure glassy AlPO$_4$ provides strong evidence for this assertion. Quantitative $^{31}$P dipolar coupling measurements via DRENAR or
DQ-build-up curves have been also reported for various bioactive silicate glasses containing phosphate species [76], as well as ion-conducting Ag$_3$PO$_4$-AgI glasses [77] (see Figure 9.13, bottom), and the dipole–dipole coupling strengths have been related to the spatial distribution of the phosphate species. Overall, these results indicate the suitability of DQ-based methods for characterizing the spatial spin distribution and for detecting and quantifying the extent of nanoscale segregation and phase separation processes in glasses, glass-ceramics, and nanocomposite materials.

**Figure 9.13** Top left: DQ-DRENAR results on Ag$_7$P$_3$S$_{11}$ [74]. Top right: Results on some phosphate glasses: squares and circles, data for Q$^2$ and Q$^1$ units in (Na$_2$O)$_{0.6}$(P$_2$O$_5$)$_{0.4}$ glass (inset, spectra for measurement of $S_0$ and $S'$ at $NT_r = 0.89$ ms). Up-triangles, Q$^0$ units in gel-prepared AlPO$_4$; down-triangles, Q$^0$ units in 0.5AlPO$_4$-0.5SiO$_2$ glass [73]. Solid curves represent parabolic fits to the initial data range. Bottom left: Experimental results on (Ag$_3$PO$_4$)$_x$(AgI)$_{1-x}$ glasses ($0 \leq x \leq 1$) and crystalline Ag$_3$PO$_4$. Right: Linear dependence of the average mean squared dipolar coupling constant on phosphate concentration as expected from a random spatial distribution of the phosphate ions [77].
Figure 9.14 Top: Two-dimensional homonuclear J-resolved spectroscopy. Following the preparation by a $\pi/2$ pulse, evolution takes place under the influence of homonuclear J-coupling during the evolution time $t_1$. Chemical shift and heteronuclear J-coupling evolution are refocused by the central $\pi$ pulse, and direct dipolar couplings are averaged out by MAS. The evolution is stopped by the second $\pi/2$ pulse, while the third $\pi/2$ pulse is used for detection. During the acquisition period $t_2$ the regular MAS Hamiltonian is effective. Bottom: Two-dimensional-J-resolved spectroscopy of Ag$_7$P$_3$S$_{11}$.

9.4.2.3 Recovery of Homonuclear Indirect Spin–Spin Interactions

The detection of indirect spin–spin interactions is valuable as it usually constitutes direct proof of bond connectivity, rather than mere spatial proximity. Two pulse sequences that have been quite useful for the structural analysis of glasses are homonuclear J-resolved spectroscopy (Figure 9.14) and refocused INADEQUATE (Figure 9.15). J-resolved spectroscopy combines the two types of selective averaging afforded by MAS and the Hahn spin echo, in a two-dimensional experiment [78, 79]. In glassy solids, the MAS-NMR peak is generally
inhomogeneously broadened by distributions of isotropic chemical shifts, which makes it impossible to resolve peak splitting produced by indirect spin–spin interactions in directly acquired spectra. This problem is solved by conducting a Hahn spin echo in the indirect ($t_1$) dimension of a two-dimensional NMR experiment: at the end of each evolution period $t_1$, the inhomogeneous broadening is refocused so that the amplitude and phase of the signal are exclusively governed by the strength of the isotropic J-coupling. Thus, the corresponding signal observed after Fourier-transforming the data acquired along the time domain $t_1$ allows a selective measurement of the homonuclear indirect dipole–dipole coupling constant. Figure 9.14 shows the application to crystalline Ag$_7$P$_3$S$_{11}$, which is an excellent compound for optimizing the experimental set-up. The two crystallographically distinct P atoms of the P$_2$S$_7^{4-}$ group are unambiguously identified by doublets in the second dimension of the two-dimensional spectrum. From the individual cross-sections, the indirect spin–spin coupling constant is available. Recently, two-dimensional homonuclear through-bond correlation and J-resolved spectroscopy results were successfully applied for the study of P–P and P–Se–P connectivities in P–Se glasses [80], extending earlier work based on through-space dipolar spectroscopy [54, 55].
Figure 9.15 Top: Timing and coherence level diagrams of the INADEQUATE pulse sequence. Bottom: Two-dimensional single-quantum/double-quantum correlation spectrum recorded by the INADEQUATE sequence on Ag₇P₃S₃₁. Note the complete suppression of the ³¹P resonance of the monomeric PS₄³⁻ group at 103 ppm. See Figure 9.14 for comparison.

An alternative method of recovering indirect spin–spin interactions is the INADEQUATE experiment (Figure 9.15) [81]. The 90°-τ-180°-τ-90° pulse block utilizes the homonuclear indirect magnetic dipole–dipole interactions (“J-couplings”) for creating double quantum coherences between the nuclei involved. For maximum DQ intensity, the preparation time 2τ should be equal to 1/2J, where J is the isotropic spin–spin coupling constant. In practice, frequently smaller values are used as a good compromise between maximum DQ yield and irreversible signal decay during τ due to spin–spin relaxation. Following a short evolution time t₁, during which they evolve under their combined resonance offsets, the DQ coherences are transferred to observable magnetization, which is then detected via a rotor-synchronized Hahn spin echo, while all single quantum coherences are completely eliminated by phase cycling. Figure 9.15 illustrates the application to Ag₇P₃S₃₁, leading to the selective detection of
the $P_2S_7^{4-}$ units, while the $PS_4^{3-}$ resonance is removed by the double quantum filter. Note the absence of all the other cross peaks that were observable in Figure 9.11 (peaks A–A, B–B, A–B, A–C, and C–C) as a result of DQ coherence build-up effected by direct dipole–dipole couplings. In the INADEQUATE spectrum, only the B–C peak is visible as DQ coherence build-up occurs selectively through the indirect spin–spin interactions, making this method a very powerful tool for proving through-bond connectivity in glasses. Indeed, INADEQUATE has been widely applied to phosphate glasses, for creating two-dimensional P–O–P connectivity maps between the various phosphate units linked to each other; this has been reviewed in Reference 1. If a singular short value of $t_1$ is used (typically $\sim 10 \, \mu$s), the experiment can also be used in a one-dimensional mode and used for double quantum filtering.

In recent years, dipolar and J-based homonuclear recoupling methods utilizing the stimulation of DQ coherences have been extended successfully to quadrupolar nuclei [82]. Successful applications to glasses have been comprehensively reviewed by Edén [1]. Particularly noteworthy is recent progress leading to the detection of Al–O–Al connectivities in various aluminosilicate and aluminate glasses [83–86], giving insights about the structural role of alumina as an intermediate oxide, which can act both as a network former and a network modifier species.

### 9.4.3 Instrumental Considerations and Caveats

From the experimental viewpoint, an important limitation regarding the feasibility of these two-dimensional experiments is the spin–spin relaxation time $T_2$. In many cases, $T_2$ values are shortened by strong homonuclear dipole–dipole interactions and/or dynamical processes. In addition, pulse sequences based on windowless pulsed excitation of DQ coherences (such as the DQ-DRENAR technique) require spectrometer hardware with short switching times ($\sim 50$ ns) to function properly. Quite generally, chemical shift anisotropy and resonance offset effects tend to interfere with the efficiency of two-dimensional NMR pulse sequences and seriously affect the quantification of dipole–dipole interactions. For these reasons, fast spinning ($\sim 30$ kHz), hard pulses (nutation frequencies near 100 kHz), and moderately weak external magnetic field strengths (4.65 or 7.05 T) present ideal conditions for such measurements, at least when spin-1/2 nuclei are involved.

Finally, it must be stated, that the two-dimensional NMR methods reviewed here are only a small group within a plethora of techniques available for homonuclear recoupling. This field is still under active development and new pulse sequences appear regularly. The design of these methods and the analysis of experimental results obtained with them are greatly aided by the availability of program packages that calculate the behavior of the spins under the influence of the external and internal interaction Hamiltonians using standard time-dependent perturbation theory. Especially noteworthy is the “SIMPSON” program, which enables the simulation of complex NMR experiments under the precise conditions used in the spectrometer [87]. This freeware has proven invaluable in the analysis of complex experiments and profoundly influenced NMR research in many laboratories.
9.5 CASE STUDIES

9.5.1 Spatial Distributions of Mobile Ions in Alkali Silicate and Borate Glasses

Application of $^{23}$Na spin echo decay spectroscopy to a wide range of oxide glasses provided detailed quantitative information about the spatial distribution of sodium ions in various binary oxide glass systems [61]. Figure 9.16 compares the results obtained for sodium silicate and sodium borate glasses. In the silicates, a more or less constant value of $M_2 = 4.5 \times 10^6 \text{ rad}^2/\text{s}^2$, observed at Na concentrations below $1.5 \times 10^{28} \text{ m}^{-3}$ (20 mole% Na$_2$O), indicates significant clustering of the sodium ions. In contrast, much smaller $M_2$ values are observed in the sodium borate glass system, where $M_2$ ($^{23}$Na$-$$^{23}$Na) is found to be proportional to the sodium number density, consistent with a random ion distribution in space. The inhomogeneous distributions of alkaline ions in silicate glasses are consistent with the proposal of ion-conducting channels, maintaining the possibility of long-range ion transport even at relatively low cation contents [88]. In contrast, a statistical mobile ion distribution results in very large average jump distances at low cation contents, making ion transport improbable. On this basis it is now possible to understand why at a given number density the ionic conductivities of alkali silicate glasses are significantly larger than those of the corresponding alkali borate glasses, as reported in Reference 89.
In principle, the same approach could be used to measure $^7$Li-$^7$Li dipolar second moments in the analogous lithium oxide-based glass systems. Owing to the much weaker $^7$Li nuclear electric quadrupolar interactions, very soft $^7$Li π pulses have to be used in this case, to avoid excitation of the outer Zeeman transitions. While progress in this direction has been recently reported [90], a suitable alternative is to conduct a heteronuclear experiment, using $^7$Li{$^6$Li} SEDOR on $^6$Li-enriched glasses [91]. **Figure 9.17** compares experimental results for a lithium silicate and a lithium borate glass with comparable lithium oxide contents (10 mol%) and a $^6$Li enrichment level of 95%. Clearly, the $^7$Li spins in the silicate glass dephase much more rapidly in the dipolar field of the surrounding $^6$Li spins, indicating much stronger dipolar interactions that in the borate glass. Systematic studies of the dependence of $M_2$ on the lithium content in these glasses show completely analogous results to the situation in **Figure 9.16**, consistent with lithium clustering in the silicate, but not in the borate glass systems.
Figure 9.17 Top: $^{7}\text{Li}^{6}\text{Li}$ SEDOR measured on $(\text{Li}_2\text{O})_{0.1}-(\text{SiO}_2)_{0.9}$ glass (top) and $(\text{Li}_2\text{O})_{0.1}-(\text{B}_2\text{O}_3)_{0.9}$ glass (middle). Both glasses have a $^{6}\text{Li}/^{7}\text{Li}$ isotope ratio of 9:1. The Hahn spin echo amplitude of the residual $^{7}\text{Li}$ nuclei is measured as a function of dipolar evolution time $2t_1$ in the absence (solid symbols) and the presence (open symbols) of the $^{6}\text{Li}$ recoupling pulses. The dotted curves are fits to the experimental data using Eq. 9.7. Bottom: Dipolar second moment $M_2(^{6}\text{Li}^{-^{7}\text{Li}})$ measured via $^{7}\text{Li}^{6}\text{Li}$ SEDOR in lithium silicate and lithium borate glasses as a function of cation number density.

It is important to realize that any kind of clustering affecting the spatial distribution of cations must be accompanied by analogous clustering of the charge-compensating anions. In alkali silicate glasses with relatively low alkali oxide contents (< 33 mole %) these anions are the non-bridging oxygen atoms associated with the $Q^{(3)}$ units. Cation clustering thus implies also preferred associations among the $Q^{(3)}$ species as proposed by the “modified random network model” (MRN) based on molecular dynamics simulations [88]. The scheme of Figure 9.18, bottom, suggests that the modifier cations are concentrated in cluster regions and coordinated...
primarily by non-bridging oxygen atoms [92], resulting in the formation of “ion-conducting channels” at higher concentrations [93]. Such an arrangement implies that the $^{29}\text{Si}-^{7}\text{Li}$ dipolar interactions are significantly stronger for the anionic $Q(3)$ sites than for the neutral $Q(4)$ sites.

Figure 9.18 Top: Site-resolved $^{29}\text{Si}\{-^{7}\text{Li}\}$ REDOR data on a lithium silicate glass containing 15 mole% Li$_2$O. Middle: Dependence of $M_2(29\text{Si}\{-^{7}\text{Li}\})$ for the $Q(3)$ and $Q(4)$ units on lithium oxide content $x$ in the $(\text{Li}_2\text{O})_x(\text{SiO}_2)_{1-x}$ glass system. Bottom: Schematic illustrating lithium clustering in lithium silicate glasses, bringing multiple Li ions into proximity of multiple $Q(3)$ units.

This hypothesis can be probed by measuring the magnetic dipole–dipole interactions between the nuclei associated with the network formers and those of the network modifiers. Thus, Figure 9.18 shows $^{29}\text{Si}\{-^{7}\text{Li}\}$ REDOR data of lithium silicate glasses containing less than 20 mole% Li$_2$O [92]. While the $Q(3)$ units show a substantial REDOR effect, the signal of the $Q(4)$ units is essentially unaffected by $^{7}\text{Li}$ irradiation, indicating that bridging oxygen atoms connecting between two $Q(4)$ units make essentially no contribution to the local Li environment. Thus the $Q(4)$ species reside in spatial regions that are largely cation-depleted, consistent with
the known tendency of lithium silicate glasses to phase-separate. By combining the $Q^{(3)}$–Li and $Q^{(4)}$–Li pair distribution functions $f_{SiLi}(r)$ extracted from complementary MD simulations with these NMR results new information is available about the structural organization of the lithium-rich nanophase. Based on the average $Q^{(3)}$–Li distances determined from the maxima in these curves (~318 pm), we can estimate the number of Li nearest neighbors to a $Q^{(3)}$ silicon unit from the experimental $M_2$ values. Thus, taking $r_{SiLi} = 318$ pm as the relevant average $Q^{(3)}$–Li closest distance in the $x = 0.1$ glass, each closest lithium neighbor would—on average—produce a contribution of $3.3 \times 10^6$ s$^{-2}$ to $M_2(29Si\{7Li\})$. Based on the experimental $M_2$ values near $11–12 \times 10^6$ rad$^2$/s$^2$ and considering that these values also include minor contributions from more remote $^7$Li spins, we can conclude that the $Q^{(3)}$ units are surrounded by three closest lithium ions. Independent confirmation for the model illustrated in Figure 9.18 comes from a study of the dipole–dipole interactions among the lithium spins, studied by $^7$Li\{$^6$Li\} SEDOR [91]. The limiting $M_2(7Li\{6Li\})$ value near $10 \times 10^6$ rad$^2$/s$^2$ measured at low lithium contents (see Figure 9.17) is quantitatively consistent with the presence of four lithium ions in the second coordination sphere at an average Li-Li distance of 273 pm [61].

Analogous results have been obtained for sodium silicate glasses [94]. Again, the combined analysis of $^{23}$Na spin echo decay spectroscopy and $^{29}$Si\{$^{23}$Na\} REDOR experiments indicates that the sodium arrangement is highly non-statistical, with large and constant dipolar second moments at low Na concentrations. In contrast, REDOR results on sodium borate glasses reveal a strikingly different picture [94]. In this case, the neutral species are trigonal BO$_{3/2}$ units and the anionic species are four-coordinate BO$_{4/2}^-$ species. The $^{11}$B resonances of both structural units are nicely resolved by MAS, thereby facilitating site-resolved $^{11}$B\{$^{23}$Na\} REDOR measurements. Figure 9.19, top, shows a typical REDOR curve: Clearly, the extent of dephasing is rather similar for both types of boron structural units. In agreement with the conclusions from Figure 9.16, this result argues strongly against cation clustering in sodium borate glasses. With increasing sodium content, the $M_2$ values characterizing the $^{23}$Na–$^{11}$B dipole–dipole interactions for the BO$_{3/2}$ groups increase linearly (Figure 9.19, bottom), consistent with a random distribution. In contrast, the $M_2(23Na–11BO_{4/2}^-)$ data approach a constant “baseline” value as expected for isolated Na$^+$–BO$_4^-$ charge compensation pairs. The second moment analysis indicates that the average Na–B distance is near 340 pm [95].
Figure 9.19 $^{11}\text{B}^{23}\text{Na}$ REDOR results on sodium borate glasses. Top: Site-resolved REDOR data on trigonal and tetrahedral boron species. Bottom: Site-selective $M_2^{\text{B-Na}}$ values extracted from these data as a function of sodium oxide content. (From Reference 95).

9.5.2 Connectivity Distribution in 70 SiO$_2$-30 [(Al$_2$O$_3$)$_x$(P$_2$O$_5$)$_{1-x}$] Glasses

Advanced dipolar NMR methods have been successfully applied to characterize the connectivity distribution in glasses with the composition 70 SiO$_2$-30 [(Al$_2$O$_3$)$_x$(P$_2$O$_5$)$_{1-x}$] [96]. The $^{31}\text{P}$ and $^{27}\text{Al}$ magic-angle spinning NMR data are highly sensitive to the P/Al ratio suggesting that there are clear Al–O–P connectivity preferences as might be expected based on bond valence considerations. At low phosphorus contents (e.g., in glasses with Al/P ratios $>1$) the MAS-NMR spectra reveal a constant local phosphorus environment with parameters similar to those of amorphous AlPO$_4$ (prepared by sol-gel methods) [97]. The $^{31}\text{P}$ spin echo decay data (Figure 9.20) show, however, very low $M_2^{(31\text{P}-31\text{P})}$ values at low P content and a
linear increase with increasing P content. These results (including the comparison with the spin echo data measured on the amorphous AlPO$_4$) indicate that despite the Al–O–P connectivity preference, the orthophosphate species are widely dispersed and do not form AlPO$_4$-like clusters in this compositional domain. In glasses with compositions exceeding the Al/P ratio of unity ($x > 0.15$), the strength of the $^{31}$P–$^{31}$P dipole–dipole coupling remains more or less constant. In this compositional domain, both AlPO$_4$-like environments as well as metaphosphate ($Q^2$)-like environments with P–O–P linkages are present. As both species are characterized by comparable $^{31}$P–$^{31}$P interaction strengths, no strong compositional change is observed here.

![Figure 9.20](image)

**Figure 9.20** Static $^{31}$P NMR spectra (top) and spin echo decay (bottom) of glasses in the system 70 SiO$_2$–30 [(Al$_2$O$_3$)$_x$(P$_2$O$_5$)$_{1-x}$]. (From Reference 96).

The extent of P–O–Al connectivity in this glass system was extracted from $^{27}$Al{$^{31}$P} REDOR and $^{31}$P{$^{27}$Al} REAPDOR experiments. The average number of P atoms linked to aluminum, $n_p$(Al), is estimated by comparing the $M_2(^{27}$Al{$^{31}$P}) values to that measured ($4.7 \times 10^6$
rad\(^2/s^2\)) for sol-gel prepared AlPO\(_4\) glass, in which each aluminum atom is tetrahedrally surrounded by four P atoms. For the low-aluminum glasses (Al/P < 1), these \(M_2\) values are of similar magnitude, albeit always by a factor \(\beta = 0.8\) to 0.85 smaller, suggesting that \(n_p(Al^{IV})\) always remains somewhat below the maximum value of four. In a similar vein, the \(M_2(\text{^{27}Al\{^{31}P\}})\) values measured for the Al\(^V\) and Al\(^VI\) species are comparable to, but somewhat lower than those measured in ternary aluminophosphate glasses with Al/P ratios < 1 [98]. Assuming that the same scaling factor \(\beta\) applies for the Al\(^V\) and Al\(^VI\) species in this composition domain as determined for the Al\(^IV\) species, we can estimate \(n_p(Al)\) from the expression

\[
n_p(Al) = (f(IV) \times 4 + f(V) \times 5 + f(VI) \times 6) \times \beta
\]

where \(f(IV), f(V), \text{ and } f(VI)\) represent the fractional contributions of the various aluminum coordination states, as determined via \(^{27}\text{Al}\) MAS-NMR peak integration. For glasses with Al/P > 1, no such site-resolved second moment information is available; thus \(n_p(Al)\) is approximated by the formula

\[
n_p(Al) = 4 \times M_2(\text{^{27}Al\{^{31}P\}}_{\text{exp}}) / M_2(\text{^{27}Al\{^{31}P\}}_{\text{AlPO}_4})
\]

Analogously the average number of Al atoms linked to phosphorus, \(n_{Al}(P)\), can be extracted from \(^{31}P\{^{27}Al\}\) REAPDOR experiments (see Figure 9.21). While in this case no second moment analysis is possible, \(n_{Al}(P)\) can be estimated by interpolating the simulated REAPDOR curves for 0 < \(n\) < 4, so as to make a satisfactory fit to the experimental data. Following this approach, \(n_{Al}(P)\) is close to one in the sample with \(x = 5\%\), and about 2.3 for the sample with \(x = 10\%\). For higher \(x\) values, \(n_{Al}(P)\) remains approximately constant close to 3, that is, distinctly below the number 4 expected for AlPO\(_4\) glass. Figure 9.21 illustrates that the REAPDOR dephasing of the latter reference material is indeed significantly stronger than for any of the present glasses. The bottom of this figure summarizes the total numbers of P–O–Al linkages, \(n_{P-O-Al}\), obtained either by multiplying \(n_p(Al)\) with the aluminium content 2\(x\), or by multiplying \(n_{Al}(P)\) with the phosphorus content \(2 \times (30 - x)\). Note that these values, obtained via two independent experiments, are in excellent agreement with each other, thereby validating the above analysis. In Figure 9.21, these values are compared to a clustering scenario, which maximizes the number of Al–O–P linkages. It is evident that the numbers \(n_{P-O-Al}\) are always consistently lower than those predicted by the cluster scenario, suggesting that the glass structure is more homogeneous than that predicted from an AlPO\(_4\) segregation scenario.
Figure 9.21 Top and middle: $^{31}\text{P}\{^{27}\text{Al}\}$ REAPDOR curves for the $\text{Al}_2\text{O}_3:(30-x)\text{P}_2\text{O}_5:70\text{SiO}_2$ glasses. The experimental data are compared with simulations based on P interacting with one, two, and three $^{27}\text{Al}$ neighbors (two-spin, three-spin, and four-spin system, respectively). Experimental data for glassy sol-gel-prepared AlPO$_4$ glass are also included. Bottom: Total number of P–O–Al linkages $n_{\text{P-O-Al}}$ as extracted from $^{27}\text{Al}\{^{31}\text{P}\}$ REDOR (circles) and $^{31}\text{P}\{^{27}\text{Al}\}$ REAPDOR analysis (open triangles). Solid curves illustrate the prediction from the extreme aluminum phosphate cluster scenario. See plate section for a color version of this figure. (From Reference 96).
Studies of this kind, addressing the structural role and connectivity of aluminum species, have been reported for numerous other Al-containing phosphate glasses, prepared either via melt-cooling or sol-gel methodology [97–102]. In all cases, a distinct Al–O–P connectivity preference has been noted. As described in detail in Reference 1, in the case of the system 50K2O–xAl2O3–(50 − x)P2O5, a complete P–O–P and P–O–Al connectivity analysis in terms of the various Q^{(n)}_{mA} species was possible based on 27Al{31P} REDOR, 31P{27Al} REAPDOR, CP-HETCOR, and 31P-J-resolved spectroscopy [101, 102]. If Al2O3 is replaced by Ga2O3, completely analogous behavior is observed [103]. A detailed examination of glasses in the system NaPO3–Ga2O3 by 71Ga{31P} REDOR indicates that the number of Ga–O–P linkages is close to the maximum number possible. Ga can be considered a network modifier,
resulting in the successive transformation $P^2 \rightarrow P^1 \rightarrow P^0$ as $x$ increases. Furthermore, the Ga coordination number appears to be controlled by the type of phosphate species present. While Ga(VI) dominates in the region of small $x$, where the majority of phosphate is present as $P^2$ or $P^1$ units, it is successively transformed to Ga(IV) as the number of $P^0$ units increases [103]. The composition $x = 0.25$ corresponds to the maximum value for which a structure can be formed consisting entirely of Ga(IV)–O–P linkages. For glasses with higher $x$ values up to the glass-forming border ($x = 0.35$), $^{71}$Ga$\{^{31}$P$\}$ REDOR results evidence the formation of Ga–O–Ga linkages. Homo- versus heteroatomic connectivity distributions were also analyzed in a number of aluminoborate glasses by $^{11}$B($^{27}$Al) and $^{27}$Al($^{11}$B) REDOR experiments [104–107].

For sodium aluminoborate glasses, these experiments indicate a rather chemically ordered structure. The conversion of the network follows the hierarchy $Al^4$ - $B^4$ - $B^2$. No higher coordinated Al is formed unless the Al/Na ratio exceeds one. The anionic $B^4$ and $Al^4$ units are preferentially linked to neutral $B^3$ species. There is a particularly strong avoidance of $B^4$–O–$Al^4$ connectivity, as can be rationalized based on bond valence considerations [104]. Aluminoborate glasses containing alkaline earth or rare-earth ions as network modifiers do not show such behavior and contain larger amounts of higher coordinated Al atoms over the entire composition range [105–107]. A predominance of Al–O–B connectivity can be noted here as well, however.

### 9.5.3 Speciations and Connectivity Distributions in Borophosphate and Thiaborophosphate Glasses

The large majority of technically relevant ion-conducting glasses are based on more than one network former species. The combination of several network formers usually offers the possibility of fine-tuning physical property combinations to special technological demands and in certain cases the interaction between the various network former components results in improved physical properties. For example, the ionic conductivities of alkali borophosphate glasses along the compositional series $[Na_2O]_y[(B_2O_3)_x(P_2O_5)_{1-x}]_{1-y}$ are significantly higher than those of either the binary alkali borate or the alkali phosphate glass systems having the same concentration of network modifiers, $y$ [108]. During the past few years, detailed solid state NMR experiments have given a quantitative structural explanation for such trends on the basis of the local environments of the borate and phosphate network former species, their bond connectivities, and their overall competition for the network modifier [109–117].

The preceding chapter already reviewed some important structural insights obtained for glasses in the system $[Na_2O]_{0.40}[(B_2O_3)_x(P_2O_5)_{1-x}]_{0.60}$ ($0.0 \leq x \leq 1.0$) on the basis of $^{31}$P and $^{11}$B MAS-NMR results [109]. That information is complemented with $^{11}$B$\{^{31}$P$\}$ and $^{31}$P$\{^{11}$B$\}$ REDOR results, obtained within a more recent study of the compositionally closely related system $[M_2O]_{0.33}[(B_2O_3)_x(P_2O_5)_{1-x}]_{0.67}$ ($0.0 \leq x \leq 1.0$; $M$ = Li, K, Cs) [110]. The single-pulse NMR data reveal similar spectra and essentially the same compositional trends as the earlier work on the $y = 0.40$ system. In the most recent study, double quantum filtering by the Refocused INADEQUATE method was used as an additional spectral editing method. Owing
to the absence of P–O–P linkages, the lineshape components attributed to the P$_{2B}^2$ and P$_{3B}^3$ units are not observed in such experiments, making it possible to (i) refine their lineshape parameters by difference spectroscopy, and (ii) remove ambiguities in the lineshape deconvolution of the remaining signal. Based on this work, a complete analysis of the $^{31}$P NMR spectra in terms of the individual P$_{mB}^n$ units ($0 \leq n \leq 4; m \leq n$) was possible. The results are summarized in Figure 9.23. The structural transformation caused by the successive replacement of the network former P$_2$O$_5$ by B$_2$O$_3$ can be summarized as follows: Up to $x = 0.5$, metaphosphate, P$^2$ units are successively replaced by anionic tetrahedral B$^4$ species. The dramatic increase of ion mobility in this compositional domain can be attributed to the change in the nature of the charge compensating species. The B$^4$ units offer more effective charge dispersal, as the negative charge is delocalized over four bridging oxygen atoms, rather than two non-bridging oxygen atoms in the case of P$^2$ units. Bond valence considerations show further that in the case of B$^4$–O–P$^3$ linkages (which are prevalent particularly for $x < 0.5$); the charge is actually spread out over the non-bridging oxygen atoms of the P$^3$ units. These delocalization mechanisms result in shallower Coulomb traps than in case of the binary metaphosphate glasses, thus increasing the probability of cation jumps. Beyond $x = 0.5$, where the ionic conductivity remains independent of composition, the NMR results show that the principal change is the substitution of neutral P$^3$ species by neutral B$^3$ species.

Figure 9.24 summarizes typical results from the $^{11}$B{$^{31}$P} REDOR NMR measurements on this system, indicating that the B$^4$ and the B$^3$ units differ significantly with regard to the $^{11}$B–$^{31}$P dipolar coupling strengths, as previously observed for other alkali and silver borophosphate glass systems [113–115]. The numerical $M_2$(B{$^3$P}) values extracted from these data via Eq. 9.8 and shown in the bottom part of the figure express the extent of P–O–B connectivity, with a contribution of about $4 \times 10^6$ rad$^2$/s$^2$ per B–O–P linkage. The data reflect the expected decrease of B–O–P connectivity from predominantly B$^4_{4P}$ units at low $x$ values, P$_2$O$_5$ rich glasses, to predominantly B$^4_{0P}$ units at high $x$ values, B$_2$O$_3$ rich glasses, along with the decreasing P/B ratio. Assuming $m = 4$ for $x = 0.1$ and based on $m = 0$ for $x = 1.0$, estimates of $m$ for the B$^4_{mP}$ units can be obtained from the measured $M_2$ values by interpolation. As illustrated by Figure 9.24c, these values are generally well-correlated with those estimated from the average $^{11}$B NMR chemical shifts of the B$^4$ species (as discussed in the preceding chapter).
Figure 9.23 Network former unit species concentrations (normalized to 100 %) obtained via $^{11}$B MAS-NMR for the $B^n$ species and deduced for the $P^n$ species on the basis of charge balance (solid) and obtained independently via deconvolution of the $^{31}$P MAS-NMR spectra (dashed), for glasses of the system $[K_2O]_{1/3}[(B_2O_3)_x(P_2O_5)_{1-x}]_{2/3}$ [110]. Lines are guides to the eye.

Based on the boron and phosphorus speciations and the REDOR data, total concentrations of P–O–P, B–O–P, and B–O–B linkages can be derived. Figure 9.25 compares these results with two distinct structural scenarios. The dashed curves in this plot represent the distribution according to a random linkage scenario, which is clearly not applicable here. Rather, heteroatomic P–O–B connectivities are strongly preferred over homolatonic P–O–P and B–O–B linkages, despite the fact that as suggested by Figure 9.24c, only few B$^3$–O–P linkages appear to exist in these glasses. Alternatively, the solid lines in Figure 9.25 show the predicted numbers of B–O–P linkages under the assumption that no B$^3$–O–P linkages occur and the number of B$^4$–O–P linkages always corresponds to the maximum number possible based on the composition. This scenario is in excellent agreement with the experimental data. This study concludes that B$^4$–O–P linkages, particularly those of the B$^4$–O–P$^3$ type, have special stability and are thus preferentially formed in this glass system. While previous $^{31}$P/$^{11}$B REDOR studies had further suggested the absence of B$^3$–O–P connectivity, their presence has been subsequently suggested on the basis of heteronuclear dipolar and J-based experiments [116,
Furthermore, two different types of B\(^4\) species could be discriminated based on the extent of B–O–B connectivity as probed by \(^{11}\text{B}\) double quantum NMR spectroscopy [116].

**Figure 9.24** (a) \(^{11}\text{B}\{^{31}\text{P}\}\) REDOR curve of \([\text{K}_2\text{O}]_{1/3}(\text{B}_2\text{O}_3)_x(\text{P}_2\text{O}_5)_{1-x}\)]_{2/3}-glass (x = 0.6). Red curves correspond to parabolic fits to Eq. 9.8. Measurements were done at 9.4 T and MAS-rotor frequencies of 8, 10, and 12 kHz. (b) \(M_2\) values as a function of x for glasses of the systems \([M_2\text{O}]_{1/3}(\text{B}_2\text{O}_3)_x(\text{P}_2\text{O}_5)_{1-x}\)]_{2/3} (M = Li, K, Cs). (c) Values of \(m\) determined by REDOR versus values of \(m\) determined from the \(^{11}\text{B}\) isotropic chemical shifts for glasses of the systems \([M_2\text{O}]_{1/3}(\text{B}_2\text{O}_3)_x(\text{P}_2\text{O}_5)_{1-x}\)]_{2/3} (M = Li, K, Cs) [110]. The solid line represents the identity case.

Similar studies have been published for a number of other oxide-based mixed-network former (MNF) systems in recent years [61, 118–122]. Heteroatomic bond formation is also favored in the (Na\(_2\)O)\(_{0.33}[(\text{P}_2\text{O}_5)_x(\text{Ge}_2\text{O}_4)_{1-x}]\)\(_{0.67}\) [118], NaPO\(_3\)-GeO\(_2\) [119] and NaPO\(_3\)-MoO\(_3\) systems [120], whereas the bond distribution is close to random in NaPO\(_3\)-TeO\(_2\) glasses [121, 122]. Finally, a number of recent dipolar NMR applications have focused on the characterization of
Phase separation phenomena in glasses and partially crystallized glass ceramics [123–127]. Here solid state NMR can furnish quite specific information of domain sizes, chemical segregation phenomena, and the medium range order of residual glassy phase.

Phase separation phenomena are also omnipresent in mixed-network-forming chalcogenide glasses. Quantitative details regarding the concentrations of individual local environments, their connectivities and the partitioning of the network modifier $M_2S$, where $M$ is an alkali, between the various network former components were elaborated for the system $[\text{Na}_2\text{S}]_{2/3}[(\text{B}_2\text{S}_3)_{x}(\text{P}_2\text{S}_5)_{1-x}]_{1/3}$, $0.0 \leq x \leq 1.0$ [128]. Figure 9.26 summarizes the $^{31}$P solid state MAS-NMR spectra of the glasses. At low thioborate contents, $x \leq 0.3$, three overlapping contributions near 93, 84, and 107 ppm are observed. The nature of these species was further explored by homonuclear J-resolved spectroscopy (Figure 9.27). The 84 ppm peak, which forms a singlet in the second frequency domain, is attributable to an isolated $\text{PS}_4^{3−}$ unit, while the 93 ppm peak, which forms a doublet in the second frequency domain ($J \sim 20$ Hz), can be assigned to a pyrothiophosphate, $\text{P}_2\text{S}_7^{4−}$ moiety. The downfield component near 107 ppm is correlated with a second doublet characterized by a substantially larger spin–spin coupling constant ($J \sim 80$ Hz). Based on the chemical shift and the size of this coupling constant, this species can be unambiguously assigned to a hexahypothiophosphate, $\text{P}_2\text{S}_6^{4−}$ species, in which a phosphorus–phosphorus bond is present. These results are further corroborated by the Refocused INADEQUATE spectrum of a glass with composition $[\text{Na}_2\text{S}]_{2/3}[(\text{B}_2\text{S}_3)_{0.3}(\text{P}_2\text{S}_5)_{0.7}]_{1/3}$, Figure 9.27, right. Note that in the double-quantum filtered spectrum, the dominant resonance attributed to $\text{PS}_4^{3−}$ groups is eliminated and only those species are being detected that are involved in $\text{P}−\text{P}$ or $\text{P}−\text{S}−\text{P}$ linkages. Overall, aided by the assignment made via the results of Figure 9.27, Figure 9.26 shows that with increasing thioborate content the monomeric $\text{P}^0$ units at 84 ppm become increasingly dominant. Qualitatively, these results illustrate that the thiophosphate groups function as an alkali metal scavenger species, accumulating a higher negative charge and attracting more network modifier than would be expected on the basis of proportional sharing of the network modifier.

Consistent with these findings P–S–B linkages are not detected in either $^{11}\text{B}\{^{31}\text{P}\}$ or $^{31}\text{P}\{^{11}\text{B}\}$ REDOR experiments. Figure 9.28 shows the $^{11}\text{B}\{^{31}\text{P}\}$ REDOR results obtained on a sample with $x = 0.5$, B/P = 1:1. The comparison of these curves to those in Figure 9.24 indicate that the heteronuclear magnetic $^{11}\text{B}−^{31}\text{P}$ dipole–dipole interactions are extremely weak, and the $M_2(11\text{B}\{^{31}\text{P}\})$ values of $0.2 \times 10^{-6}$ rad$^2$/s$^2$ and $0.3 \times 10^{-6}$ rad$^2$/s$^2$ for $\text{B}^4$ and $\text{B}^3$ units, respectively, are one order of magnitude lower than expected in the case of $\text{B}−\text{S}−\text{P}$ linkages.
Figure 9.25 Connectivity distribution of the bridging oxygen atoms in \([\text{K}_2\text{O}]_{1/3}\left[(\text{B}_2\text{O}_3)_x(\text{P}_2\text{O}_5)_{1-x}\right]_{2/3}\) glasses derived from NMR data and comparison with different linkage scenarios. Dashed curves, random linkage scenario; solid curves, scenario corresponding to the maximum possible number of \(\text{B}^4\text{-O-P}\) linkages excluding the formation of \(\text{B}^3\text{-O-P}\) linkages [110].
Figure 9.26 $^{31}$P MAS-NMR spectra of $[\text{Na}_2\text{S}]_{2/3}[\text{(B}_2\text{S}_3)_x\text{(P}_2\text{S}_5)_{1-x}]_{1/3}$ glasses [128]. Black curves show experimental spectra and red curves display simulations, with individual deconvolution components shown as dashed curves.
Figure 9.27 $^{31}$P J-resolved spectrum of \([\text{Na}_2\text{S}]_{2/3}[(\text{B}_2\text{S}_3)_{0.1}(\text{P}_2\text{S}_5)_{0.9}]_{1/3}\) glass with \(x = 0.1\) (left) and 1-D $^{31}$P refocused INADEQUATE spectrum of \([\text{Na}_2\text{S}]_{2/3}[(\text{B}_2\text{S}_3)_{0.3}(\text{P}_2\text{S}_5)_{0.7}]_{1/3}\) glass (bottom) [128].
Figure 9.28 Top: $^{11}\text{B}^{31}\text{P}$ REDOR curves for $B^3$ and $B^4$ units of a $[\text{Na}_2\text{S}]_{2/3}[(\text{B}_2\text{S}_3)_x(\text{P}_2\text{S}_5)_{1-x}]_{1/3}$ glass with $x = 0.5$ and parabolic fits of the $\Delta S/S_0 < 0.2$ region [128].

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REFERENCES


10
ATOM PROBE TOMOGRAPHY OF GLASSES

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10.1 INTRODUCTION

Atom probe tomography (APT) is an analytical microscopic analysis technique that combines field-ion microscopy (FIM) with time-of-flight mass spectrometry (TOF-MS). With this technique, individual atoms are field ionized from the surface of a sharp conical-shaped specimen one by one, accelerated through an electrostatic field, and collected by a position-sensitive, single-atom-sensitive detector. The individual ions are reconstructed into a three-dimensional, element-specific atom map with near-atomic resolution in depth and sub-nanometer lateral resolution. Traditional, voltage-pulsed APT has been used for the last ~30 years but has been limited to the study of conductive, metallic specimens, including metallic glass. The introduction of commercially available laser-pulsed APT systems over the last several years has opened the door to APT examinations of electrically insulating materials systems, which significantly includes insulating glasses. Simultaneous advancements in APT sample preparation using dual-beam scanning electron (SEM)/focused-ion beam (FIB) systems have enabled the manufacture of site-specific APT specimens from virtually any material. Together, these advancements have revitalized the field and enabled novel APT experiments on a wide array of materials systems. To date, there are only very limited examples of APT applied to insulating glass materials, but it is our hope that this chapter might encourage others to explore the potential of APT in this area of materials science.

The most unique feature of APT is its unrivaled combination of compositional identification and three-dimensional spatial reconstruction. Atomically resolved images can be produced with many techniques, including transmission electron microscopy (TEM) and atomic-force microscopy (AFM). Additionally, compositional profiling can similarly be obtained with sub-micron precision with X-ray photoemission spectroscopy (XPS), secondary ion mass spectrometry (SIMS) and analytical TEM. APT, however, uniquely combines these capabilities to generate three-dimensional, nanoscale composition measurements in small volumes of material (~100 × 100 × 300 nm³). It is equally important to mention up-front the limitations of APT. Most importantly, APT does not provide information on local chemical bonding. Furthermore, not all materials are suitable for APT analysis. Most significantly, the APT specimen must be mechanically robust to withstand the large mechanical stress associated with field ionization. This latter requirement is only determined through experiment and cannot be known with certainty a priori. Indeed, several materials systems have surprised experienced practitioners of APT with examples of unexpected success and failure. We will discuss these limitations further in due course.
In this chapter, we explore the fundamentals of APT, the evolution of the technique, practical aspects of an APT experiment, data reconstruction, analysis and common errors and aberrations encountered. Specific attention is given to details unique to glass science. A detailed discussion is also presented of the application of APT on the study of corrosion in a traditional oxide glass. Finally, a forward-looking perspective is presented on the potential of APT in the near future for glass science and areas where APT could make novel contributions.

10.2 BACKGROUND AND THEORY

APT is an analytical technique that provides three-dimensional, spatially resolved composition measurements of small volumes of material with sub-nanometer resolution. The technique is an extension of FIM, which was developed by Erwin Müller at the Pennsylvania State University. In 1955, FIM became the first experimental technique to image individual atoms [1–5], decades before the development of other atomic-resolution techniques such as AFM, scanning tunneling microscopy (STM) and TEM. The further development of FIM led to the introduction of several new forms of field-ion microscopes. Some of the most significant designs include the atom probe field ion microscope (first use of time-of-flight for elemental identification) [6], the imaging atom probe (combining imaging and element identification) [7], the position-sensitive atom probe (PoSAP) [8], and the similar tomographic (or three-dimensional) atom probe (TAP/3DAP) [9]. The final major advancement to the modern APT instrument was the introduction of a microelectrode nearer the specimen in the local electrode atom probe (LEAP) instruments [10–12], which are currently the most common atom probe design.

Regardless of the specific design, all of the above mentioned instruments rely on a large (positive) electric field to ionize individual atoms from the surface of a sharp needle-shaped specimen. These ions are accelerated away from the tip onto a detector to produce atomic or near-atomic resolution images. In the case of FIM, the ionized atom is an imaging gas (typically He, Ne, or Ar) that adsorbs onto the specimen surface, resulting in an atomic-resolution image of the specimen surface. In contrast, an atom-probe instrument does not use an imaging gas. Instead, individual atoms from the specimen are removed from the surface by the same field ionization process that is generally referred to as field desorption. A schematic of this process is exhibited in Figure 10.1, which depicts the potential energy diagram of an atom and an ion (the latter under the application of an electric field) as a function of distance from the specimen surface. At equilibrium, an atom occupies a steady-state distance from the specimen surface (\( x_0 \)) and escape from the specimen surface of a neutral atom can occur via sublimation with sufficient energy (\( \Lambda \)). Under no applied field, the potential energy curve of an ion resides at much higher energy than that of an atom above the sublimation energy. However, the application of an electric field lowers the energy curve for an ion by \(-neFx\), where \( n \) is the ionization state of the ion, \( e \) is the fundamental charge of an electron, \( F \) is the applied field, and \( x \) is the distance from the specimen surface. In this case, an ion that overcomes the substantially lowered energy barrier (\( Q(F) \)) can escape the specimen surface. This can be accomplished either by thermal agitation (over the energy barrier) or by quantum mechanical tunneling (through the barrier), provided that the energy barrier is sufficiently thin. More rigorous
discussions of the field ionization process can be found in other texts [13–16]. Regardless of the precise mechanism involved, the application of a strong electric field results in the reduction of the energy barrier that must be overcome for the escape of an ionized atom. During APT analysis, the barrier is reduced by a strong dc electric field that is not quite strong enough to cause uncontrolled ionization of atoms. The ionization of individual atoms is instead achieved by a brief excitation of the specimen by either an ultrafast voltage pulse (momentary decrease in the energy barrier height/shape) or an ultrafast laser pulse (thermal excitation over the barrier). This required timing sensitivity is critical to compositional identification via TOF-MS.

Figure 10.1 Schematic diagram of the potential energy curves associated with field ionization of atoms from a sample surface. In zero-field, an atom sits on the specimen surface at an equilibrium position \( (x_0) \) and must reach the sublimation energy \( (\Lambda) \) to escape. In contrast, the energy barrier for an ion to escape the specimen surface in the presence of an electric field \( (Q(F)) \) is substantially decreased, allowing ionized atoms to escape at a critical separation distance \( (x_c) \). (Adapted from Reference [13]).
Traditionally, APT has been limited to the analysis of electrically conductive and mechanically robust specimens. These requirements stem from the application of a strong voltage bias (thus great mechanical stress) and voltage pulse (thus needing conductivity) to the specimen to induce timed field ionization of individual atoms from the specimen apex. The electrical conductivity limitation was largely overcome in the 1980s when several researchers found they could induce timed field ionization with timed laser pulses [17–19]. This new variant of the atom probe instrument was termed the pulsed laser atom probe (PLAP). Laser pulsing effectively applies a brief thermal excitation to the APT specimen to induce field ionization [20]. A schematic plot of the fundamental difference between voltage and laser pulsing is displayed in Figure 10.2. A dashed black line is shown on the axes of electric field versus temperature to depict a constant ionization rate (or ionization probability) for a given species.

In an APT experiment, the specimen is maintained at a constant base temperature \(T_0\) and electric field (dc voltage of \(V_0\)) that is far below the ionization line. Controlled field ionization is induced in traditional voltage pulsed mode by applying a voltage pulse to the specimen, thereby raising the electric field applied the specimen along the vertical axis to the target ionization rate at a fixed base temperature, \(T_0\). In laser pulsing mode, the voltage applied to the specimen is fixed at \(V_0\) but the temperature on the tip is raised momentarily by \(\Delta T\) to reach the target ionization rate.
The early work on PLAP systems was marginally successful and proved that thermal pulsing enabled the analysis on electrically insulating specimens, including the very first example of an insulating glass analyzed by Kellogg and Tsong in 1982 [21]. Despite this early success, pulsed-laser atom probe systems were largely ignored for decades. This situation changed substantially in the early 2000s with the introduction of commercial atom probe systems that incorporated (relatively) reliable, user-friendly laser modules [22–24]. This reintroduction of pulsed-laser atom probe systems coincided with the introduction of LEAP systems and the mainstream use of FIB-based APT specimen preparation. From a practical perspective, the LEAP design provided substantial improvements in data collection rate, field-of-view, and flexibility of specimen geometry (micropost arrays of specimens over individual wire specimens—see Sample Preparation for more details) over previous APT designs. These
advancements have transformed APT from a very niche, time-consuming experiment to a more practical and routine experiment. For example, prior to the LEAP a typical “good” APT data set would consist of an analyzed sample volume of \(15 \times 15 \times 200 \text{ nm}^3\) and would require several days to acquire. Analysis of that same specimen in a modern LEAP system would produce a larger data set (\(120 \times 120 \times 200 \text{ nm}^3\)) that could be collected in approximately one hour. Secondly, the common availability and flexibility of dual-beam SEM/FIB microscopes has enabled tremendous versatility in the preparation of site-specific specimens and also specimens of materials systems that were not amenable to traditional electropolishing specimen preparation, including bulk and site-specific oxide-based glass materials systems. These combined advancements have sparked renewed interest in APT and an explosion of its application to novel materials systems, including insulating glass materials [25].

10.3 INSTRUMENTATION

A schematic is presented in Figure 10.3 of the primary components of a LEAP tomograph. The main analysis chamber is maintained in ultrahigh vacuum (\(<10^{-10} \text{ Torr}\)) with a combination of turbomolecular and ion pumps. The specimen stage is cryogenically cooled by an external cryostat. Typically the minimum temperature achieved at the sample is \(~15 \text{ K}\) and the experimentally relevant maximum temperature is \(~100 \text{ K}\). The cryogenic cooling is necessary during the analysis of specimens to minimize surface diffusion of atoms on the specimen surface during analysis. The specimen stage of a LEAP tomograph has a mechanical drive with micron precision in the three Cartesian directions. This level of placement control is necessary to position the specimen relative to a spatially fixed metallic annulus that acts as a local counter electrode to the APT specimen. The size of the aperture opening is approximately 30–60 \(\mu\text{m}\). Coarse alignment of the APT specimen with the aperture opening is accomplished with a pair of orthogonal CCD cameras aimed at the local electrode. More precise alignment is accomplished during data collection by centering the impact of ions on the detector and moving the specimen closer/further from the local electrode to optimize the field of view.
Figure 10.3 Schematic illustration of the primary components of a modern local-electrode atom probe system (not to scale).

During field ionization, a strong positive dc voltage bias of several kV is applied to the APT specimen by an external high voltage power supply, typically limited to <15 kV. The local electrode is connected to a high voltage power supply that, when running in voltage pulse mode, applies a ~nanosecond voltage pulse to the local electrode to induce timed field ionization of atoms. The voltage pulse is adjusted during the experiment to maintain a constant percentage of the dc voltage applied to the specimen and is typically on the order of 5–30% of the dc voltage. The ratio of the voltage pulse to the dc voltage is known as the pulse fraction and must be optimized for each material system being analyzed. Voltage pulsing is typically only used for mechanically robust, electrically conductive specimens (generally strong metals). For non-conductive (e.g., oxides or semiconductors) or mechanically delicate specimens (e.g., thin films with poor adhesion or weak glasses), it is more common to induce field ionization by laser pulsing (see Section 10.2).

An ultra-fast laser pulse (generally sub-nanosecond to sub-picosecond pulse duration; ca. 13 ps
pulse width in LEAP systems) is guided from the laser table through a window in the side of the chamber toward the APT specimen. Most APT systems use either a 532 nm (green) or 355 nm (ultraviolet) wavelength laser. Longer-wavelength lasers (infrared wavelengths) have been tested, but there is a general consensus that shorter wavelengths are more advantageous for the analysis of oxide-based specimens. The focusing of the laser spot in some systems is accomplished with in-vacuum optics systems to a spot size of <3 μm diameter, which also requires that the entire APT system be mounted on an air table to minimize vibrations from the environment. Systems without in-vacuum optics utilize larger spot sizes ~10–30 μm diameter and do not utilize an air table. The energy delivered per pulse can be adjusted during the APT experiment. Note, however, that the difference in spot size results in tremendous variability in the experimentally controlled energy per pulse to achieve similar evaporation conditions, ranging from the pJ energy range in the small spot size systems to μJ range in less focused systems. In general, smaller spot sizes are advantageous [22, 26] for improving the mass-resolving power of the collected mass spectrum. We have also observed anecdotally that the reduced spot size achieved with in-vacuum optics also enables a broader spectrum of specimen geometries (i.e., smaller tip diameter and smaller tip shank angle) to provide high quality data.

After an atom is ionized from the tip apex, the ion is accelerated through the electric field to a position sensitive detector. A schematic illustration of the position-sensitive, single-atom detector commonly found in most modern atom-probe tomographs is shown in Figure 10.4. The first portion of the detector is a microchannel plate (MCP). The detection efficiency of the MCP detector is limited by the percentage of open space on the MCP and is typically ~60%, although overall detection efficiency can be significantly lower. The MCP is sensitive to the impact of a single ion, which initiates an electron cascade and produces an electron cloud on the backside of the MCP. This electron cloud is focused onto a stack of crossed delay lines. The interaction of the electron cloud induces an electrical signal that is transmitted to either end of each delay line. Interpretation of the signal timing at either end of each delay line provides the spatial coordinate at which the electron cloud intersected the delay line according to the simple equation:

\[
X_D = L \frac{T_{x_2} - T_{x_1}}{2T_{p_x}}
\]

where \(T_{x_1}\) and \(T_{x_2}\) are the times at either end of the \(X\) delay line, \(T_{p_x}\) is the total propagation time along the line, and \(L\) is the physical length of the line. Note that the deduced spatial coordinates \((X_D, Y_D)\) are physical coordinates on the detector that need to be converted to spatial coordinates on the APT specimen. Simultaneously, these signals encode the time-of-flight \(t_D\) of the detected ion.
Figure 10.4 Schematic illustration of a position-sensitive APT detector depicting a microchannel plate with single-atom sensitivity backed by a stack of crossed delay line detectors for both time of flight measurement and spatial positioning of the detected ion.

In the case of a single-ion event, the two coordinates measured are sufficient to determine a specific location on the detector. It is often the case, however, that more than one ion impacts the MCP from a single laser or voltage pulse being applied to the tip. This can lead to ambiguous spatial information on the delay line detectors. Most modern atom probes incorporate a third set of delay lines (45° rotation) to deconvolute these mixed signals. This is an especially poignant issue for the APT analysis of non-metallic materials (such as oxide-based glasses) in which multi-hit events are very prevalent (~20–50% of all detected events). This issue is less common in metals in which single-ion evaporation events are more dominant (<5% multi-hit events). Multi-hit events should be minimized through experimental parameter optimization whenever possible, but generally >90% of multi-hit events are resolved for silica-based glass material.

In some systems, an energy compensating reflectron lens (not shown in the instrument schematic) is located between the local electrode and the detector. The reflectron lens improves the mass resolution (increased flight path) and eliminates some background noise in the collected data (energy filtering) [27]. This improved mass resolution comes at the cost of decreased detection efficiency as the ions must pass twice through a fine Cu mesh with approximately 90% open space. This degrades the overall detection efficiency from approximately 56% in a straight-flight path tool (no reflectron—MCP limited) to 37% with a
reflectron. This is an important consideration for the analysis of a specific materials system and problem. A reflectron system provides significantly better mass-resolving power (in particular in voltage-pulsed mode) and is therefore often preferred for the analysis of compositionally complex materials or for mapping low concentration dopants where minimizing the noise background is essential. On the other hand, the higher detection efficiency of the so-called straight flight path tool without the reflectron can be advantageous for the analysis of extremely small features (nanoprecipitates or thin films) in which the better counting statistics within small regions may be more important than the overall mass resolving power of the instrument. Importantly, note that the reflectron lens is a semi-permanent option for each atom probe instrument and is not a feature that can be switched on or off during the analysis of different materials.

### 10.3.1 APT Specimen Preparation

The specimen itself is the primary imaging optic in APT. Thus, as is often the case in high resolution microscopy, the data collected is only as good as the specimen. APT specimens (often referred to as “tips”) are needle-shaped with an end diameter generally ~50–200 nm. This specimen geometry is necessary to achieve the large electric field at the specimen apex for field ionization. The presence, for example, of a flat region in close proximity and orthogonal to the tip axis can strongly decrease the local electric field and prevent field ionization. Alternatively, additional sharp spires in close proximity to the tip can exhibit field ionization and cause substantial degradation to data quality. Compositional and structural defects can also be introduced during sample preparation, such as Ga ion-beam implantation and damage or altered near-surface chemistry as a result of electrochemical etching. Therefore care must be taken to achieve a proper, clean, tip-shaped geometry during sample preparation while also minimizing inadvertent compositional or structural changes to the sample.

Metallic APT specimens were traditionally prepared by electropolishing small pieces of wire into sharp needles. Further details can be found elsewhere [13, 15, 16] More recently, dual-beam SEM/FIB systems have become much more popular for producing APT specimens from a wide range of materials systems, ranging from metals to insulating bulk glass specimens and complex thin-film materials [28, 29]. The most common FIB-based approach to APT specimen preparation is the lift out method [30]. This approach is an adaptation of well-established FIB lift out methods for site-specific TEM sample preparation [31, 32]. Generally speaking, those proficient with the well-established TEM lift out methods can quickly adapt those experiences to produce APT specimens as well.

A series of images from a standard FIB-based lift out procedure is depicted in Figure 10.5. Typically, the sample from which the APT specimens are to be extracted is a polished surface suitable for SEM imaging, although unpolished surfaces and even powder samples are also feasible so long as the region of interest (ROI) is within ~10 μm of the surface. The example depicted in Figure 10.5 is a thin film sample (a magnetic tunnel junction stack measuring ~80 nm total thickness) on a Si substrate. The ROI is first identified by SEM and/or ion-beam imaging and a protective layer of C or metallorganic Pt (~100–500 nm thickness and ~2 × 25 μm² lateral dimensions) is deposited using the in situ gas-injection system of the FIB. This
layer marks the ROI and simultaneously protects it from ion-beam damage during subsequent FIB processing. Two cuts are then made using the FIB at 30° from sample normal, as shown schematically in panel (a). These cuts define the so-called lift-out bar. The corresponding SEM image of the sample after these cuts is shown in panel (b). An *in situ* micromanipulator is then used to extract the small bar of material from the bulk material. The extracted piece of material is then mounted onto an array of premanufactured Si microposts. A low magnification SEM of a typical commercial micropost array is depicted in panel (d). This particular array design can accommodate 36 individual APT specimens (one per micropost). Note that the micropost array specimen geometry is unique to local-electrode atom probe instruments. The local microelectrode, in contrast to a large far-field counter electrode in other atom probe designs, permits the enhancement of the electric field over one particular micropost at a time. Thus the local electrode is a very pragmatic advancement when combined with FIB-based specimen fabrication. The lift-out bar is brought to the apex of an individual micropost (panels e and f). The *in situ* Pt deposition system is then used to attach small pieces of the bar (~2 × 2 × 3 μm³) onto individual microposts. An average 25 × 2 μm² lift-out bar can be used to prepare ~8 individual APT specimens.
**Figure 10.5** Generalized FIB-based APT specimen preparation. (a) Schematic cross-section of the lift out sample geometry. (b) SEM image of an undercut lift-out bar ready for extraction. (c) Extraction of the lift-out bar using an *in situ* micromanipulator. (d) Low magnification SEM image of a pre-manufactured Si micropost array used for mounting FIB-prepared APT specimens. This particular array can hold 36 individual APT specimens. (e) Approach of the lift-out bar to an individual Si micropost. (f) Mounting a small piece of the lift-out bar onto an individual micropost.

After mounting a small piece of material onto the Si micropost it must still be sharpened into a sharp needle. This is accomplished by tilting the specimen so the focused ion beam is normal to the wafer and microposts. A series of annular patterns (typically ~20–30 kV Ga⁺ beam) with progressively smaller inner diameters sculpt the lift-out piece of material and Si micropost below into the desired needle shape. The final tip diameter and shank angle can be manipulated, with experience, by varying the annular mill routine. A series of SEM images displayed in **Figure 10.6** illustrates this process for a thin film specimen on an Si substrate. Panel (c) depicts a high magnification SEM image of the specimen after coarse milling. In this higher-resolution image, a distinct layer of contrast between the Si substrate and the speckled contrast of the FIB-deposited protective Pt cap. This Pt cap is not suitable for APT analysis and must be removed prior to APT analysis. This is accomplished by imaging the tip with a low energy ion beam (~2–5 kV) until the Pt cap is removed. This clean up procedure is critical to minimizing the Ga ion beam damage to the specimen. The finished specimen is shown in panel (d). In this instance, an extremely sharp tip geometry was desired, approximately 40 nm diameter at the apex. With experience it is possible to produce APT specimens reliably with
approximately ±50 nm lateral positioning accuracy and ±30 nm vertical positioning accuracy, assuming the target ROI or nearby fiducial markers provide sufficient contrast for SEM imaging during processing. This procedure is applicable to nearly all materials systems, including bulk or thin film glasses, both electrically insulating and conductive. For insulating glass materials, it is often advantageous to sputter-coat a polished glass surface with a conductive metallic film (~50–100 nm of Cr or Ni are suggested) which aids the FIB lift-out procedure (robust electrical grounding to prevent specimen drift while milling) and limits ion-beam damage into the more sensitive glass substrate. This protective film can remain at the specimen apex and be used for specimen alignment and laser focusing at the onset of subsequent APT analysis.

**Figure 10.6** SEM images of the sharpening of a thin-film APT specimen. (a) Mounted specimen prior to annular milling. (b) Same specimen after coarse milling at 30 kV. (c) Same tip at higher magnification. (d) Same tip after low kV cleanup and positioning in the thin-film region of interest.

**10.3.2 Experimental Procedure and Parameters**
The APT experiment begins with coarse alignment of the individual micropost specimen to the local electrode (in a LEAP system) using the CCD cameras focused at the analysis position. The laser, which has been pre-aligned to the proper analysis position with a standard Al or Si specimen, is then enabled at a small pulse energy by opening the shutter. A secondary coarse alignment is performed by driving the tip to the laser analysis position, which is made apparent by a bright reflection of the laser from the tip apex in the CCD camera. Data collection proceeds by setting the laser to the desired pulse energy and slowly increasing the dc voltage applied to the specimen. As ionized atoms begin to be collected, final specimen alignment is achieved by centering the detected events on the detector. As the specimen position is perfected, the laser position and focus must also be adjusted to maximize the detected ionization rate as a function of laser position. This laser positioning optimization can be very challenging with oxides that do not exhibit strong changes in detection rate as a function of laser position/focus. It is therefore advantageous to use a sacrificial sputtered metallic capping layer on top of the target glass substrate (~50 nm thickness of Cr or Ni) to perform these final laser alignments. The computer-controlled specimen voltage is adjusted throughout the analysis to maintain the target evaporation rate. Occasional laser scans can be performed during analysis to adjust and maintain the laser position at the tip apex. Data collection concludes when either the specimen fractures or a user-determined threshold is reached (commonly a feature of interest has been reached or the maximum voltage exceeded). As a general rule of thumb, the file size of a successful APT analysis is on the order ten megabytes to tens of gigabytes.

One of the most appealing aspects of APT is the ease with which the data acquisition is performed. While other advanced analytical techniques require hours of painstaking, tedious work to align and calibrate the instrument, an APT experiment can begin collecting “good data” in a matter of minutes. Furthermore, once an atom-probe experiment is initiated, the tool can often be left unattended under pre-programmed computer control for the duration of the data acquisition (typically several hours). It is important to remember that an APT experiment applies an extremely high stress to the nanoscopic specimen at a very low temperature. Therefore specimen fracture is very common and some material systems that are not mechanically strong enough may not be able to withstand APT analysis or be limited to relatively small data sets (~50 × 50 × 50 nm³). It is our experience that this is a common issue with many insulating glass compositions of interest.

Experimental variables should be optimized for every material type. The specimen temperature is chosen to be as cold as possible while allowing the mechanical stability of the tip. For robust materials, the temperature is taken to the lower-limits of the cryostat (~20–30 K), while more delicate samples, including many insulating glass samples, are analyzed at substantially higher temperatures (~50–100 K) to improve the mechanical stability of the specimen. Colder base temperatures generally lead to better APT data quality by preventing surface diffusion of atoms on the specimen surface (which leads to improved spatial resolution) and improved compositional accuracy (larger thermal gradient in laser-pulsing mode results in a better mass resolving power). Other experimental parameters that should be optimized are the target detection rate and either the voltage pulse fraction (voltage mode only) or the laser pulse
energy (laser mode only). For laser operation mode, the laser energy is set at the lowest possible energy that avoids untimed field ionization between laser pulses and premature specimen fracture. Untimed field ionization, referred to as dc noise, is the result of a high standing voltage applied to the specimen ($V_0$ in Figure 10.2) that permits field ionization without the additional energy pulse of the laser. This undesirable effect is apparent as a higher-than-normal noise floor (flat signal in the raw time-of-flight spectrum or power-law decay in the converted mass-to-charge-state ratio) and can result in significant compositional errors as the element with the lowest evaporation field is most sensitive to this artifact. Increasing the laser power can be advantageous in delicate specimens, such as glasses, that easily fracture during analysis as it decreases the standing voltage and thus mechanical stress on the specimen. The target detection rate is measured as the percentage of pulses that induce a detected ion at the detector. This is reported as either the number of detected ions per pulse (typically ~0.001–0.05 detected ions per pulse) or as an equivalent percentage of pulses inducing a detected event (e.g., 0.1–5%). The detection rate is computer-controlled during data collection by adjusting the applied dc voltage. The detection rate of most oxide-base materials (ordered or glass) is typically in the range of 0.1–0.3%, which is smaller than is typical for metallic specimen. Higher detection rates require a higher mechanical stress on the specimen, resulting in an unacceptably high failure rate in oxides.

Other parameters that are monitored during an APT experiment include the background noise (usually qualitatively through visual inspection of the mass spectrum), the percentage of multi-hit events to single-hit events, and the charge-state-ratio of a specific species of interest. A high background or dc noise can significantly degrade the quantitative accuracy of the technique, sometimes to the extent of precluding an accurate compositional analysis as noted above. This is usually either indicative of poor sample geometry or a need for further optimization of experimental parameters. The percentage of multi-hit events is strongly dependent on the material system being analyzed. Oxide-based materials commonly exhibit ~33% multi-hit events, while for metallic specimens only ~5% of detected events are multi-hit. In general multi-hit events should be minimized to maximize the compositional accuracy of the analysis, but this is a fairly minor concern as >90% of multi-hit events are usually resolved using the third set of delay lines in the detector design.

A summary of key experimental parameters that are available before or during the APT experiment is given in Table 10.1. Each parameter can have multiple effects on the probability of experimental success and data quality, so should be considered in experimental planning and execution.
<table>
<thead>
<tr>
<th>Parameters established Prior to data</th>
<th>Parameters available During data acquisition</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Atom probe instrument</strong></td>
<td><strong>Atom probe instrument</strong></td>
</tr>
<tr>
<td>• Local electrode or far-field electrode</td>
<td>• Pulse repetition rate (typically fixed)</td>
</tr>
<tr>
<td>• Flight path (sometimes adjustable)</td>
<td>• Target evaporation rate (typically fixed)</td>
</tr>
<tr>
<td>• Reflectron lens or straight-flight path</td>
<td>• Laser pulse energy or voltage pulse fraction (usually fixed)</td>
</tr>
<tr>
<td>• Laser wavelength (sometimes adjustable)</td>
<td></td>
</tr>
<tr>
<td><strong>Specimen</strong></td>
<td><strong>Specimen</strong></td>
</tr>
<tr>
<td>• Preparation method (electropolishing or FIB)</td>
<td>• Specimen base temperature (typically fixed)</td>
</tr>
<tr>
<td>• Orientation of region of interest (i.e., parallel or perpendicular to an interface)</td>
<td></td>
</tr>
<tr>
<td>• Tip diameter</td>
<td></td>
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<tr>
<td>• Tip shank angle</td>
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10.3.3 Data Reconstruction

The experimentally measured raw data (voltage, time-of-flight, detector coordinates, and ion sequence) must be reconstructed into a three-dimensional atomic map (real-space \(x,y,z\) coordinates and elemental identity of each ion) for analysis. This is accomplished using modern adaptations [33–36] of the reconstruction protocols detailed by Bas et al. [37]. A detailed understanding of the entire reconstruction algorithm is not necessary to obtain reasonable three-dimensional reconstructions, and we therefore leave those discussions to more thorough technical reviews by others [13, 15]. Here we approach the reconstruction procedure from the perspective of the experimentalist, focusing on the requirements for an accurate three-dimensional reconstruction using commercially available data reconstruction routines. We divide our discussion into two critical categories: mass-spectra analysis and three-dimensional spatial reconstruction.

10.3.3.1 Mass Spectra Interpretation for Reconstruction

The time-of-flight signal from the atom-probe instrument contains the information for elemental composition identification. The raw time-of-flight signal is first converted from time-of-flight measurements (time in ns) to a mass-to-charge-state ratio (measured in Da or a.m.u.) as:

\[
\frac{m}{n} = 2eV \frac{t^2}{\delta^2}
\]  

(10.2)
where \( m \) is the mass of the ion, \( n \) is the charge state of the ion (number of electrons removed in the field ionization process), \( \delta \) is the flight distance (specimen to detector), \( V \) is the voltage applied to the specimen, \( e \) is the fundamental charge of an electron, and \( t \) is the measured time of flight. A spectral histogram (usually referred to as the mass spectrum) of the resulting mass-to-charge-state ratios is compiled for all collected ions. Representative mass spectra are exhibited in Figure 10.7 for a simple binary metal specimen (Ni-5Cr) and a simple binary oxide (MgO). Each element has its own natural abundance of isotopes. This isotopic fingerprint is used to identify the elements present throughout the mass spectra. In the case of the Ni-5Cr metal alloy this is very straightforward. Nickel consists of five natural isotopes with atomic masses between 58 and 64 a.m.u. Ions of Ni atoms are apparent in two sets within the mass spectrum, one with a 1+ charge state (between 58 and 64 a.m.u.) and a more abundant set of peaks with a 2+ charge state (between 29 and 32 a.m.u.). The identification of Cr (4 isotopes between 50 and 54 a.m.u.) is even simpler, as it appears exclusively at the 2+ charge state between 25 and 27 a.m.u. On the other hand, the MgO mass spectrum is substantially more complicated. Magnesium consists of three isotopes (24, 25, and 26 a.m.u.) and ionic peaks are apparent for elemental Mg at both the 1+ and 2+ charge states. Similarly a clear peak exists for the only major isotope of O (16 a.m.u.) at the 1+ charge state only. In addition to the elemental peaks of Mg and O, several peaks associated with combinations of Mg and O are apparent in the mass spectrum. Four different sets of these so-called molecular-ion or complex-ion peaks are apparent in the spectrum: \( \text{MgO}^{1+} \), \( \text{MgO}^{2+} \), \( \text{Mg}_2\text{O}^{2+} \) and \( \text{O}_2^{1+} \). Peaks such as these are very prevalent in the atom probe analysis of materials with strong non-metallic bonds, whether they be covalently bonded (e.g., C-based materials) or ionically bonded (oxides, nitrides, sulfides, and fluorides). As many glass materials exhibit strong non-metallic bonds, this issue is particularly pertinent for the APT analysis of glasses. The prevalence and size of the molecular ions is strongly affected by the APT analysis conditions, especially the laser pulse energy: a higher laser energy generally results in more molecular ions and larger molecular ions. For simple oxides such as MgO, the added complexity of these additional peaks is little more than a nuisance. However, for more complicated materials the added complexity of molecular ions can degrade the quantitative accuracy (due to peak overlaps) and spatial resolution. Note, however, that even in the simple case of MgO a prominent peak overlap is apparent at 32 a.m.u. between \( ^{16}\text{O}_2^{1+} \) and \( ^{24}\text{Mg}_2^{16}\text{O}^{2+} \). The mass resolving power of APT (\( m/\Delta m \approx 1000 \)) is insufficient to separate the contributions of \( ^{15.9949}\text{O}_2^{1+} \) and \( ^{23.9850}\text{Mg}_2^{15.9949}\text{O}^{2+} \) at the integer 32 a.m.u. peak. In this simple example, the contribution of \( ^{24}\text{Mg}_2^{16}\text{O}^{2+} \) can be estimated based on the natural isotopic abundance of \( ^{24}\text{Mg}_2^{16}\text{O}^{2+} \) relative to the other \( \text{Mg}_2\text{O}^{2+} \)-type peaks that do not overlap with oxygen. This kind of peak deconvolution is common in atom-probe analyses of compositionally complicated materials.
Figure 10.7 Representative mass spectra from two binary materials systems: MgO (a) and Ni-5Cr (b). Each data set contains ~1.5 M detected ions. The metallic spectrum is composed primarily of so-called “elemental” single-atom peaks, while the spectrum for MgO is comprised of both single-atom peaks and several multi-atom complex ions. Note the significant peak overlap at 32 a.m.u. between $^{16}O_2^{1+}$ and $^{24}Mg_2^{16}O^{2+}$ which must be deconvoluted for proper oxide stoichiometry measurement. (MgO mass spectrum courtesy of Dr. Arun Devaraj, PNNL.)

Accurate peak identification is of paramount importance to the quality of all APT data. All subsequent aspects of three-dimensional reconstruction and data analysis rely on proper interpretation of the mass spectrum. Only identified ions are used in the three-dimensional tomographic reconstruction. Omission or misidentification of a peak can therefore substantially distort the tomographic reconstruction in addition to being compositionally inaccurate. The mass spectrum exhibited in panel (b) of Figure 10.7 depicts the shaded bin widths of peaks used in a so-called Range File that contains a list of all peak identifications used for the data reconstruction and analysis. When working with a new or compositionally uncertain material, this Range File will be iteratively improved by using the tomographic reconstruction to better understand elemental distributions and peak identification. It is common for several iterations to be made between the mass spectrum range identification and tomographic imaging to improve the compositional accuracy of the peak identification and subsequent spatial
10.3.3.2 Tomographic Reconstruction

The three-dimensional tomographic reconstruction proceeds after peak identification in the mass-to-charge-state ratio spectrum by estimating the geometry of the analyzed specimen. Most often this reconstruction is based on the so-called Bas protocol [37], and subsequent modifications for wide-field-of-view APT systems by Geiser [33]. Here we only discuss the reconstruction in a conceptual way as the reconstruction details are handled primarily by automated routines in the APT analysis software. The spatial positioning of a given ion is governed by a few key equations and assumptions. The first of these is the back-projection of a given ion's spatial coordinates on the detector to its original \((x,y)\) coordinate onto the (assumed) hemispherical tip apex. No direct measurement is made during data collection of the precise tip geometry. Instead, the radius of the assumed hemispherical end form is deduced from the measured voltage applied to the specimen using the equation

\[
F = \frac{V}{kR} \quad \text{or} \quad R = \frac{V}{kF} \tag{10.3}
\]

where \(F\) is the electric field required for field ionization (V/nm), \(R\) is the tip radius, \(V\) is the voltage applied to the specimen, and \(k\) is a geometric field factor that accounts for the effect of the specimen geometry on the enhancement or reduction of the electric field. The electric field \(F\) can be estimated from simple models for most elements and are reported in tables in standard APT references [13, 15, 16, 38]. Additionally, \(k\) can be estimated in some crystalline materials based on the indexing of crystallographic poles in either field ion maps or field desorption maps [34]. Typically, the value of \(k\) ranges from 2.5 to 6, although there is a great deal of uncertainty for this value in electrically insulating specimens. Since crystallographic poles do not exist in glass materials, it is not possible to use this method to estimate \(k\). Furthermore, values of \(F\) for complicated alloys, heterogeneous materials systems and ionically bonded systems cannot be estimated by simple models and reference tables do not exist at present. Instead, a reasonable estimate for the combined factor \(kF\) is obtained by evaporating the APT specimen to a known final voltage \((V_F)\) and measuring the final tip radius \((R_F)\) with complementary electron microscopy techniques (SEM or TEM). Currently this is the most common and reliable method for estimating reconstruction parameters for insulating glass specimens. Note that the initial specimen radius prior to APT analysis \((R_i)\) and initial specimen voltage \((V_i)\) can also be used to estimate \(kF\). This latter method is problematic, however, because the APT specimen reshapes to a steady-state voltage-to-radius ratio during initial field ionization and the voltage–radius relationship before ionization is often ambiguous.

After establishing the radius of the tip (based on experimentally measured voltage and estimated product \(kF\)) the detector coordinates for a given ion are converted to reconstructed coordinates using a point-projection model. A schematic illustration of this simple model is depicted in Figure 10.8. Conceptually, an ion follows a slightly compressed radial trajectory from the specimen to the detector. The magnification \((M)\) of the point projection is defined as
the ratio of the distance from the detected ion to the center of the detector \((D)\) to the distance of the original atom position from the center axis of the specimen \((d)\). The magnification can also be written in terms of the specimen radius and distance between the specimen and the detector as follows:

\[
M = \frac{D}{d} = \frac{L + \xi R}{\xi R} \approx \frac{L}{\xi R}
\]  

(10.4)

where \(L\) is the distance between the detector and the specimen (typically 90–400 mm), \(R\) is the specimen radius (determined by specimen voltage as above) and \(\xi\) is the so-called image compression factor, which is typically estimated based on prior experience and instrument calibrations. Since \(L \approx \xi R\), the sum in the numerator can be simplified as simply \(L\). This magnification factor converts the detector coordinates to spatial coordinates on the specimen surface by

\[
x = \frac{X_D}{M} \quad \text{and} \quad y = \frac{Y_D}{M}
\]  

(10.5)

where \(x\) and \(y\) are the lateral coordinates of each ion on the specimen surface.

**Figure 10.8** Schematic illustration of ion trajectories and geometric considerations for data reconstruction. (not to scale.)

Lastly, the \(z\)-coordinate is calculated based on an iterative increase in specimen depth for each
successive ion, expressed as
\[
  z_{i+1}^{\text{ref}} = z_i^{\text{ref}} + \Delta z_i
\]  

Conceptually, this equation depicts the progression of a reference coordinate system (\(z^{\text{ref}}\)) of a hemispherical shell from which ions are being emitted. As ions are collected, the position of this reference hemispherical shell increases in \(z\) by a small increment, and the absolute coordinate of each ion (\(z_i\)) is fitted onto this hemispherical shell, the radius of which was established by the above equations. The depth increment of each ion (\(\Delta z_i\)) is calculated based on an estimate of the volume taken up by that ion, irrespective of position. In practice, each detected ion is assigned some volume (\(\Omega_i\)). This individual ion volume is then (mathematically) distributed across the entire specimen surface area (\(A\)). The depth increment from this single ion is then calculated as
\[
  \Delta z_i = \frac{\Omega_i}{\zeta A}
\]

where \(\zeta\) is the detector efficiency (i.e., a correction factor for the volume of ions that are not included in the reconstruction). Obviously, the volume of each ion when spread over an area as large as the hemispherical surface translates to a very small length parameter. It is this small depth that increments the reference coordinate system for each detected ion and progressively iterates the calculated \(z\)-coordinate. The assumed volume of each ion (\(\Omega_i\)) can be a global average based on a known/assumed atomic density (often preferred for fairly homogeneous materials) or it is assigned a specific value for each ion based on its elemental composition (often preferred for heterogeneous materials with disparate atomic densities). Atomic volumes are assigned to each element automatically by the Range File, but care must be used that these values are sensible for a given materials system. Interestingly, this means that no two ions are assigned the exact same \(z\)-position within the sample. Operationally, however, the \(\Delta z_i\) parameter is so small (on the order of 1/10000 Å) that this is irrelevant.

Considering the relative simplicity of the reconstruction process in comparison to other tomographic reconstruction methods, it may be surprising that APT reconstructions routinely result in sub-nm three-dimensional spatial resolution. This is not to say the reconstruction is perfect—far from it, in fact. Recently there has been renewed interest in using TEM micrographs of APT specimens prior to and after APT field evaporation to both better understand the spatial aberrations apparent in the three-dimensional reconstruction and also to use these observations to assign better estimates of reconstruction parameters (especially specimen radius and image compression factor) [39–41]. This trend is likely to continue in the future and will be particularly important to the improved reconstruction of glass materials that do not exhibit internal scaling markers such as ordered atomic planes.

10.4 ANALYSIS METHODS
At its most basic level, every reconstructed atom-probe data set comprises a three-dimensional map of (generally) millions of individual data points. Each data point contains two primary pieces of information: its spatial coordinate \((x,y,z)\) and its elemental identity (mass-to-charge-state ratio). All subsequent analyses of these data consist of counting these individual atoms in local subvolumes to quantify the local composition. Direct visualization of the data set is also possible using the spatial distribution of specific ionic species (so-called atom maps). This approach provides a quick visual overview of the data, but it is qualitative and subject to interpretation. More rigorous data analysis requires the quantification of the local composition to remove this subjectivity from the analysis.

The most basic form of quantitative analysis is the measurement of the bulk composition of the analyzed specimen volume. This is done in a straightforward manner by first decomposing complex molecular species into their individual atomic species (e.g., \(\text{MgO}^+\) contains one atom of Mg and one atom of O). The elemental composition, directly measured in atomic \%, is then the ratio of the detected atoms of the species of interest divided by the total number of detected atoms. Conveniently no further adjustments to the measured composition are needed as the MCP detector is equally sensitive to all elements. Note, however, that the typical APT mass spectrum generally contains a few peaks from the residual gas in the analysis chamber, namely a prominent hydrogen signal (\(\text{H}^+, \text{H}_2^+, \text{and H}_3^+\)) and minor hydroxide signals (\(\text{OH}^+\) and \(\text{OH}_2^+\)). Typically these peaks are discarded for quantitative compositional analyses. In the event of peak overlap within the mass spectrum, the individual contributions of each species are estimated using the natural isotopic abundance of other surrounding peaks, as described in the discussion of the mass spectrum. The success of this method depends strongly on the extent of peak overlap and availability of other peaks to enable deconvolution. In extremely complex materials or materials that do not have multiple isotopes, this problem can be severe and limit the compositional accuracy of all subsequent measurements. For this reason, APT is likely not the best technique to quantitatively probe homogeneous glass composition.

APT is much more powerful when used to describe interfaces between compositionally dissimilar materials. The analysis of this type of data set is typically accomplished using an isoconcentration surface [42, 43]. To begin, a three-dimensional grid of local elemental composition is calculated for the entire specimen volume. This is accomplished using voxels (three-dimensional pixels) of a user-defined size (typically cubes \(~0.8–2\) nm in size) and counting the atoms within each voxel to establish the local composition. Since these sampling volumes are very small and prone to large statistical noise, the composition is then smoothed over adjacent voxels using a Gaussian delocalization function. The delocalization size is typically a factor \(~2–4\) greater than the voxel size. This computed concentration space can then be used to draw three-dimensional surfaces of constant composition within the data set, or so-called isoconcentration surfaces. Assuming that two phases are present in the data set with well-defined and different composition, the interface of the two phases can be defined as an isoconcentration surface half-way between the compositions of each phase.

Local elemental concentrations and concentration gradients can be calculated by binning the APT in various ways into small, spatially resolved volumes of material and counting the
atoms. The simplest example of this is the one-dimensional concentration profile. A region from which the profile will be extracted is first defined by positioning a cylindrical or other sampling volume perpendicular to some ROI (typically an interface). The cylindrical volume is then subdivided along its axis into many subvolumes. The size of each subvolume can be adjusted, but it is typically ~0.1–1 nm in length along the cylinder. Therefore each bin measures a volume of material equal to the cross-sectional area of the cylinder multiplied by the sampling step size, which enables tremendous flexibility in balancing statistical sampling noise with spatial resolution (smaller volume → better spatial resolution but higher noise). The concentration profile is then a compilation of concentrations measurements along the length of the cylinder. Importantly, the concentration is measured by counting atoms and not by using the concentration space calculation described above, which avoids unintentional smoothing of data.

Combining the ideas of isoconcentration surfaces and one-dimensional concentration profiles, it is also possible to derive a one-dimensional concentration profile that accounts for the inherent three-dimensional shape of a phase or precipitate in APT data using the proximity histogram method [42, 43]. The proximity histogram is arguably the greatest advantage APT can offer over other high resolution analytical techniques. Briefly, this method removes the convolution of physical roughness or precipitate/interface morphology with the compositional gradient across the interface. This results in the sharpest possible profile of the composition across an interface with optimal counting statistics. A representative analysis is presented in Figure 10.9 of an irregularly shaped B-rich Ni-Fe oxide within a matrix of a different Ni-Fe oxide. The proximity histogram method begins by defining an interface with an isoconcentration surface (2.5 at. % B). Using this surface as a reference shape, a shell volume is defined around this shape by incrementing some distance (typically ~0.1 nm), shown schematically as a dark-shaded region. The local concentration is then calculated by counting the atoms present within this shell volume. This process occurs in both the inward (toward a higher concentration of B, white arrows) and outward (toward a lower concentration of B, black arrows) directions. The proximity histogram is thus compiled by measuring the concentration within each of these shells to either some threshold distance or until the shape collapses to a point. This method has tremendous advantages over conventional one-dimensional concentration profiles in both spatial resolution and counting error, which is very apparent when comparing the resulting concentration profiles in Figure 10.9. Therefore the proximity histogram method is generally the preferred concentration profile in APT data whenever an interface of interest can be well-defined by an isoconcentration surface. This process works equally well for the analysis of planar interfaces, such as thin films or corrosion fronts (as discussed in the case study later in this chapter) or three-dimensional precipitates.
Figure 10.9 Representative analysis of a B-rich oxide precipitate (dark dots—outlined by a 2.5 at. % B isoconcentration surface) within a Ni-Fe oxide using a one-dimensional concentration profile (left) and a proximity histogram (right). The resulting concentration profiles across the interface are depicted below each image. The red region schematically depicts the area from which an individual concentration measurement is calculated in each case. The one-dimensional concentration profile proceeds linearly along the length of the analysis cylinder, while the proximity histogram follows the contours defined by the isoconcentration surface. The error bars represent one standard deviation ($\sigma$) as defined by Eq. 1.8.

APT data can also be utilized to determine the roughness of buried interfaces in complex heterostructures [44, 45]. This is done by first defining the interface between two materials as an isoconcentration surface. The root-mean-squared (RMS) roughness of this interface can then be calculated using the following equation:
where $S_q$ is the RMS roughness value, $M$ and $N$ are the total number of $x$ and $y$ coordinate points defining the interface, $z(x,y)$ is the height of any given point on the isoconcentration surface, and $\mu$ is the mean height of the isosurface, defined as $\mu = \frac{1}{MN} \sum_{k=0}^{M-1} \sum_{l=0}^{N-1} z(x_k, y_l)$. Of course, such analysis must be done with knowledge of its limitations. The layer targeted for analysis must not be too thin, or the sampling and counting errors will produce erroneous results. A minimum layer thickness of approximately the delocalization distance is required to measure reliably and independently the roughness of both the top and bottom interfaces of a single layer. Increasing the delocalization distance to values of greater than two times the voxel size leads to excessive interfacial smoothing and unrealistically small roughness values. Too small of a delocalization leads to numerical noise in roughness measurements. Therefore the interfacial roughness of layers less than approximately 1.5 nm thick cannot be reliably analyzed with this method.

A final analysis method that is sometimes applied to APT data is the nearest-neighbor analysis. The nearest-neighbor analysis proceeds by interrogating directly the local distribution of individual atoms within a data set. This can be performed on the basis of all atoms to each other, or specific combinations of atoms. By comparing the measured nearest-neighbor distribution with a randomized distribution it is possible to identify atomic clustering or precipitate formation. This is a classic APT interrogation method that is covered in significant detail in other texts [13, 15]. However, the method suffers when applied to oxides or other materials that exhibit significant molecular evaporation in the mass spectrum. In these materials systems, it is no longer possible to probe single-atom distributions reliably as the individual data points are a convolution of single-atom and multi-atom ions. At the current time there has not been, to our knowledge, a reliable method established for nearest neighbor analysis in this more complicated scenario. As this could potentially be a very useful analysis tool for glass scientists, this appears to be an area that should receive significant attention in the coming years as further experience is gained on glass investigations utilizing APT.

### 10.4.1 Estimating Error

#### 10.4.1.1 Compositional Error

The compositional error associated with APT analysis is typically considered in two categories: the inherent statistical error with the quantification and the variability of the measured composition. In most cases, the statistical error is easily estimated using counting statistics. For any given composition measurement, whether it is the bulk composition or a local measurement of one data point in a linear profile, the statistical counting error can be estimated as:
where $\sigma$ is one standard deviation of the counting error, $C_i$ is the measured concentration of the elemental species of interest in the volume of interest, and $N_T$ is the total number of ions in the volume of interest. This is the standard counting error that is most often reported for APT data, in particular the error bar most often depicted in concentration profiles. This error, however, is the absolute minimum error associated with the data and oftentimes other forms of error are more dominant.

The variability of concentration measurements between APT data sets is sometimes more relevant to quantitative uncertainty than the counting error within one measurement. For example, varying experimental parameters such as laser pulse energy or voltage pulse fraction can slightly or dramatically alter the measured composition. Ideally these parameters are optimized for a material system with a known stoichiometry. Realistically, such experimental standardization to a known stoichiometry is impractical. Instead, the variability of the measured composition across a range of experimental parameters or samples is used to establish the composition variability/uncertainty.

A related final concern for compositional accuracy is the preferential evaporation or retention of species. In complex materials systems, it is sometimes the case that a specific element is either significantly easier (e.g., Li, Mg, P, N, or O) or more difficult (e.g., B, C, W, or Ta) to evaporate than the other major constituent elements. The more easily ionized species can be preferentially lost between pulses via dc ionization and do not appear as timed events in the time-of-flight mass spectrum, degrading the compositional accuracy of the resulting APT reconstruction. This problem can be overcome in most cases by optimizing experimental parameters, usually by either increasing the pulse fraction in voltage mode or decreasing the laser pulse energy in laser mode. Increasing the pulse fraction decreases the standing voltage on the APT specimen, thereby decreasing the probability of ionization between pulses. On the other hand, decreasing the pulse energy in laser mode actually increases the voltage applied to the specimen, which has a somewhat counterintuitive beneficial effect. It has been observed in several materials systems that are routinely analyzed in laser-pulsing mode that off-stoichiometric composition measurements can be improved by decreasing the pulse energy, particularly for oxide- and nitride-based systems (e.g., GaN and MgO) which commonly exhibit molecular peaks in the mass spectrum. It has been suggested that decreasing the pulse energy, and thus peak temperature of the APT specimen, reduces the probability of neutral $O_2$ or $N_2$ gas from forming at the elevated temperatures during the laser pulse. Therefore, decreasing the pulse energy results in more measured O and N and improved measurements of the stoichiometry. It could, however, also be argued that the increased dc field applied to the specimen to compensate for the decreased pulse energy results in increased loss of other species (Ga or Mg in the given examples) between pulses, which artificially improves the measured stoichiometry. Further studies are needed to prove one hypothesis over the other, but for now it is generally believed that higher voltage pulse fractions and smaller laser pulse
energies generally improve the compositional accuracy of APT measurements. These improvements do, however, come at the price of increased probability of tip fracture as both methods result in a greater overall stress being applied to the specimen.

### 10.4.1.2 Spatial Resolution

In ordered materials, it is readily possible to estimate the spatial resolution of APT by its ability to discriminate individual atomic planes in an ordered lattice. With this method it has been possible to establish its spatial resolution for ordered metallic specimens to be ~0.1 nm in the z-direction of the reconstruction and ~0.2–0.4 nm in the lateral directions. Recently, atomic planes have also been visualized in bulk magnetite and Ni-Fe spinel oxides formed as a result of corrosion in high temperature water. An example of the appearance of atomic planes in a Ni-Fe spinel is exhibited in Figure 10.10, which firmly establishes the spatial resolution of oxide-based materials by APT to be better than 1 nm in ideal analysis circumstances (i.e., a homogeneous material with good evaporation control). Conceptually, this resolution should also extend to amorphous oxides, although internal scale markers (atomic planes) are not available to confirm such a supposition.

![Figure 10.10](image)

**Figure 10.10** APT reconstruction of a Ni-Fe spinel oxide that exhibits ordered atomic planes, demonstrating the sub-nm spatial resolution of APT in ordered oxide structures. While the atomic planes are only apparent along the crystallographic pole, crystalline planar faults that incorporate hydrogen (OH) are apparent across the entire tip diameter.

In more complicated materials systems, the spatial resolution can be expected to be substantially degraded. One common spatial aberration is called the local magnification effect,
which occurs when analyzing a heterogeneous material [46–48]. Two different scenarios are depicted schematically in Figure 10.11. In the first case, a small particle of a material requiring a higher evaporation field protrudes from the surface of the surrounding matrix. This specimen geometry forms naturally during the field evaporation of such a materials system and is generally unavoidable. This small protrusion results in the spreading of the ion trajectories (local magnification) from the high field phase material and a local decrease in the apparent atomic density on the sample detector and a lower local atomic density in the resulting reconstruction of the small particle. The opposite scenario of a low field precipitate is depicted in the bottom panel. In this case the small particle causes a local indentation on the APT specimen surface, causing the ion trajectories to collapse together. This results in a local demagnification of the specimen and apparent higher local atomic density in the subsequent reconstruction. It is difficult to estimate quantitatively how strongly these spatial aberrations can affect the spatial resolution of the APT reconstruction, but they are believed to be on the order of 1–3 nm. More importantly, these aberrations affect the local composition as the ion trajectories of the precipitate particle can overlap with those of the surrounding matrix, resulting in a mixed composition of matrix and precipitate. Currently there are ongoing efforts to improve the APT reconstruction algorithm to account for these well-known artifacts [35, 36, 40]. However, until those improvements can be achieved, great care must be taken when analyzing heterogeneous materials systems and any APT reconstruction that exhibits significant local atomic density variations, which oftentimes reveal local magnification artifacts and degraded local spatial resolution.
Figure 10.11 Schematic illustrating local magnification artifacts associated with field evaporation of heterogeneous materials. (a) A high field material exhibits local magnification (trajectory spreading) resulting in an apparent lower atomic density at the detector than the surrounding matrix. (b) A low field material exhibits local demagnification (trajectory overlap) resulting in an apparent higher atomic density than the surrounding matrix.

10.4.1.3 Common Errors

At its best, APT provides revealing three-dimensional compositional information with sub-nanometer spatial resolution. Its combination of spatial resolution and composition sensitivity is unrivaled by any other experimental technique. This is a compelling picture of the local microstructure that can oftentimes lead to novel observations. It is important, however, that the researcher is mindful of possible errors in both the raw three-dimensional data and sampling methods to avoid erroneous data interpretation.

First, APT does not provide any information on chemical bonding. Despite the observation of molecular ions in the time-of-flight mass spectra, these molecular species should not be used to make any determinations of the local bonding environment in the material. These molecular
bonds may have existed in the native material, or they could have formed by surface diffusion before ionization, or as a result of the extreme environment present at the specimen apex, or actually formed post-ionization. Suffice to say, it is not currently possible to discern which scenario may be correct and therefore the analysis of chemical bonding is not possible.

Improper or inaccurate data reconstruction is the most prominent error experienced by both advanced and novice APT researchers. The APT data reconstruction method is simple and largely automated. It does, however, rely on several assumptions and user-entered information. Entry of an incorrect parameter (e.g., errant tip diameter, evaporation field, peak identification) or failed assumption (e.g., hemispherical apex, equal detection efficiency of all elements) can cause massive errors in the resulting data set in both spatial and compositional accuracy. Therefore, it is often beneficial to assume each APT dataset, in particular of a new materials system, exhibits some errors that must be identified and mitigated. Local density variations, uncontrolled evaporation events, sudden voltage changes, unidentified peaks in the mass spectrum, and unexpected spatial dimensions should all alert the researcher to potential errors. Unexpected errors are most prevalent in materials systems new to APT analysis. This is therefore very pertinent to the analysis of insulating glass materials which are still very new to APT analysis. Unfortunately it is not always obvious when erroneous data are present in the final reconstruction. Complementary observations from other analytical techniques should be used whenever possible to identify and mitigate these errors.

One of the easiest of these “checks” to implement is confirmation against the glass composition. When the material composition is well-known, errors in compositional accuracy can oftentimes be overcome through optimization of analysis parameters (pulse energy and detection rate in particular) or sometimes through improved peak identification in the mass spectrum. Effectively, poorly constrained parameters can be found through fitting to known atomic ratios. Peak identifications can also sometimes be aided by altering the isotopic abundance of some elements in the material to be analyzed to avoid suspected or apparent peak convolution problems. Indeed, well-known isotopic ratios can help to resolve peak overlaps and deconvolute the relative contributions of overlapping species. Errors in spatial dimensionality can typically be corrected through optimization of the various reconstruction parameters. In extreme cases where strong evaporation field differences are present in heterogeneous materials, the resulting aberrations can be minimized by using a smaller field of view during the data reconstruction. Generally speaking, whenever possible, electron microscopy should be performed on a specimen prior to and after APT analysis to establish a baseline estimate of the field evaporation and reconstruction parameters for a new materials system. These experiments are becoming more common in the APT community and most groups have established standard methods for accomplishing this with equipment available at their facility or through collaborations.

10.5 CASE STUDIES

The strength of atom probe tomography is its unique combination of spatial and compositional information. This ability has been utilized for several decades in electrically conductive
the discussion of metallic glasses to other reviewers [41, 49–55]. Conversely, only recently has APT been able to probe reliably insulating materials such as oxide-containing materials. Because of this, relevant case studies are extremely limited and we focus our attention on these new applications. Specifically, we endeavor to demonstrate the capabilities of APT in the broader field of glass science in the hopes to inspire others to pursue this new form of characterization.

The most successful glass research to date utilizing APT involves the study of the corrosion layers on multicomponent boroaluminosilicate glasses produced by exposure to water. While extremely challenging, this study represents an excellent example of both strengths and weaknesses of APT and warrants a detailed discussion. The study focused on a persistent question: what mechanisms control the long-term durability of glass?

Boroaluminosilicate glasses corroded in static (near equilibrium) conditions produces several structural layers during corrosion [56, 57]. In sequence starting from the solution toward the pristine glass, the following layers are commonly observed:

1. crystalline byproducts,
2. an amorphous gel layer composed primarily of a nanoporous aluminosilicate network (possibly with nuclei forming within) and depleted of B, Na, and Li,
3. a poorly understood hydrated glass/ion exchange layer (hydrated layer (HL)), and
4. the homogenous pristine glass that contains the nominal concentrations of all elements

Two pieces of SON68 borosilicate glass, a non-radioactive surrogate glass for the French vitrified nuclear waste R7T7 glass [58], were analyzed. Sample 1 was exposed to simulated groundwater at 90°C for ~26 years. Sample 2 was corroded in 90°C deionized water for just over 1 year and consisted of artificially enriched abundances for $^6$Li, $^{10}$B, $^{29}$Si, $^{44}$Ca, $^{57}$Fe, and $^{68}$Zn. This study focused specifically on the buried interface between the hydrated glass layer and the pristine glass, as it has been theorized to control the residual rate of glass dissolution during corrosion [56].

10.5.1 Composition

Collected mass spectra from Samples 1 and 2 from both pristine and hydrated (corroded) regions are shown in Figure 10.12. SON68 consists of $>$20 individual component oxides resulting in substantial peak interpretation challenges in the APT mass spectra. As is the case with field ionization of most oxide-based materials, the mass spectra exhibited both elemental peaks and molecular oxide complexes [59, 60]. Hydroxide peaks present throughout the spectra, particularly in the hydrated glass, further complicated the analysis and generally prevented the use of natural isotopic abundances for peak deconvolution. Comparison and careful analysis of these spectra, however, enabled the identification of all major peaks and elements of interest. Note that Sample 2 contained enriched isotopic abundances of several key species: $^6$Li, $^{10}$B, $^{29}$Si, $^{44}$Ca, $^{57}$Fe, and $^{68}$Zn. Thus comparison of the pristine glass in Samples 1
and 2 enabled the identification of the major peaks of each isotopically tagged element (labeled in bold font in Figure 10.12). It was known from previous observations that the hydrated glass layer was enriched in H and depleted of B, Li, and Na [56, 58, 61, 62]. Peaks that were apparent in the hydrated glass and absent in the pristine glass (i.e., products of the dissolution process) are labeled in italics font, while peaks that were apparent in the pristine glass and absent in the hydrated glass (i.e., elements leached out of the glass during corrosion) are labeled in bold italics font. As expected, the hydrated layer was strongly depleted of B, Li, and Na and simultaneously enriched in H, as indicated by the appearance of several hydroxide peaks (OH$_x$ and SiO$_y$H$_x$ in particular). Note that the chemical state of the hydrogen cannot be determined by APT, and thus the question of whether the H is in the form of hydroxide terminal groups, molecular water, or some other species is unanswerable.
Figure 10.12 Representative mass spectra from SON68 glass in (a) pristine glass of Sample 2 (loaded isotopes); (b) pristine glass of Sample 1 (natural isotopes); and (c) hydrated glass of Sample 1. Peaks unique to (a) and (c) are denoted by different font styles, with bold corresponding to intentionally enriched isotopes in Sample 2, and bold italics denoting peaks absent in the hydrated glass, and non-bold italics denoting peaks found only in the hydrated glass. The vertical axis has been normalized in each spectrum to the maximum of the 16 a.m.u. ($^{16}$O$^+$) peak for more direct comparisons.

Careful analysis revealed the presence of other significant peak overlaps within the mass spectra, including $^{16}$O$_2^+$/64Zn$^{2+}$, 28Si$^+$/56Fe$^{2+}$, and $^{11}$B$^{16}$O$_{(x+1)}^+$/$^{27}$Al$^{16}$O$_x^{y+}$. Many peak overlaps can be accounted for using the natural isotopic abundances to ratio peaks, but some uncertainties remain. Most important among these was the overlap of $^{11}$B$^{16}$O$_{(x+1)}^+$ with $^{27}$Al$^{16}$O$_x^{y+}$ as one of the primary interests in these analyses was the distribution of B. These overlaps occurred in three key peaks: 13.5 a.m.u., 27 a.m.u., and 43 a.m.u. The overlap in the 27 a.m.u. range is highlighted in Figure 10.13. The clear asymmetry at 26 a.m.u. shown in Figure 10.13 can be attributed to the <1 a.m.u. mass difference between $^{10.01}$B$^{15.99}$O$^+$ and
51.94 Cr$^{2+}$. This asymmetry is absent in the hydrated glass of Sample 1 (bottom panel). The 51.94 Cr$^{2+}$ peak is sharp, likely because the hydrated glass is boron-free and thus does not exhibit a 10.01 B$^{15,99}$O$^+$ peak. One way to decompose these overlapping peaks is to use the natural isotopic abundance of $^{10}$B (19.9%) and $^{11}$B (80.1%) within Sample 1 to subtract the contribution of $^{11}$B$^{16}$O$_{(x+1)}^{y+}$ from each peak. This method, however, overestimates the contribution of $^{11}$B$^{16}$O$^+$ as a result of the $^{10}$B$^{16}$O$^+$ overlap with $^{52}$Cr$^{2+}$ and $^{10}$B$^{16}$O$_2^+$ with $^{52}$CrO$_2^{2+}$. Thus this method was expected to overestimate the contribution of B and underestimate the contribution of Al. This problem was mitigated in Sample 2 by the artificial enrichment of $^{10}$B to approximately 99.6%, which largely eliminated the Al overlap and resulted in more reliable quantitative measurements. The complexity of the SON68 glass composition, prevalence of peak overlaps, and strong presence of oxide and hydroxide ion complexes highlight the challenges inherent in quantitative compositional analysis with APT, in particular for minor species in the oxide glass. Such ambiguities could be reduced through increased mass resolution, but the longer flight paths to enable improved resolution would increase substantially the data collection times. The current APT design is therefore a compromise of mass resolving power and data collection speed.
Figure 10.13 A small region of the TOF mass spectra comparing the various samples highlighting the peak overlap for Cr$^{2+}$, BO$^{+}$ and Al$^{+}$. The colored vertical lines indicate the precise atomic mass of each species, which gives a slight asymmetry to the peak shape for overlapping species.

Table 10.2 presents a comparison of the nominal SON68 glass composition with the APT measurements. Considering the complexity of the mass spectra, the composition measurements are quite reasonable. The quoted measurement error is based on counting statistics (Eq. 10.8) as it is a reliable minimum error value. As mentioned previously, however, the true error is likely substantially larger due to other sources of error. We believe the error is ~1 at. % or less for each element. The largest discrepancies from the nominal glass composition appear to be for Al, B, and O. The apparent O deficiency is typical for APT analysis of oxide samples [60, 63, 64]. The apparent enrichment of Si in the HL is believed to be a result of depletion of the other species (B, Li, and Na) and not indicative of enrichment via influx of Si from water during corrosion. C and K were also apparent in the hydrated glass, likely from the corroding water environment since they were not native to the glass.
Table 10.2 Nominal composition of SON68 glass and that measured experimentally by APT within the pristine glass and hydrated corrosion layer of Samples 1 and 2 in atomic percent.

<table>
<thead>
<tr>
<th>Element</th>
<th>Nominal</th>
<th>Sample 1 –</th>
<th>Sample 2 –</th>
<th>Sample 1 –</th>
<th>Sample 2 –</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>2.01</td>
<td>4.93 ± 0.02</td>
<td>3.05 ± 0.004</td>
<td>3.21 ± 0.02</td>
<td>4.57 ± 0.07</td>
</tr>
<tr>
<td>B</td>
<td>8.41</td>
<td>9.40 ± 0.03</td>
<td>2.72 ± 0.004</td>
<td>5.87 ± 0.02</td>
<td>0.79 ± 0.04</td>
</tr>
<tr>
<td>Ca</td>
<td>1.50</td>
<td>1.68 ± 0.01</td>
<td>2.48 ± 0.004</td>
<td>2.09 ± 0.01</td>
<td>2.86 ± 0.06</td>
</tr>
<tr>
<td>Fe</td>
<td>0.76</td>
<td>1.25 ± 0.01</td>
<td>1.53 ± 0.003</td>
<td>2.60 ± 0.01</td>
<td>1.81 ± 0.04</td>
</tr>
<tr>
<td>H</td>
<td>0.00</td>
<td>2.12 ± 0.01</td>
<td>12.62 ± 0.008</td>
<td>1.75 ± 0.01</td>
<td>10.13 ± 0.10</td>
</tr>
<tr>
<td>Li</td>
<td>2.77</td>
<td>2.32 ± 0.02</td>
<td>0.09 ± 0.001</td>
<td>2.60 ± 0.02</td>
<td>0.27 ± 0.03</td>
</tr>
<tr>
<td>Mo</td>
<td>0.25</td>
<td>0.59 ± 0.01</td>
<td>0.67 ± 0.002</td>
<td>N/D</td>
<td>N/D</td>
</tr>
<tr>
<td>Na</td>
<td>6.64</td>
<td>4.61 ± 0.02</td>
<td>0.42 ± 0.002</td>
<td>6.53 ± 0.02</td>
<td>1.95 ± 0.06</td>
</tr>
<tr>
<td>O</td>
<td>59.13</td>
<td>51.86 ± 0.05</td>
<td>51.36 ± 0.012</td>
<td>51.92 ± 0.04</td>
<td>51.75 ± 0.16</td>
</tr>
<tr>
<td>Si</td>
<td>15.81</td>
<td>16.47 ± 0.04</td>
<td>19.54 ± 0.009</td>
<td>17.24 ± 0.03</td>
<td>22.27 ± 0.13</td>
</tr>
<tr>
<td>Zr</td>
<td>0.45</td>
<td>0.97 ± 0.01</td>
<td>1.22 ± 0.003</td>
<td>0.91 ± 0.01</td>
<td>0.97 ± 0.03</td>
</tr>
</tbody>
</table>

The indicated uncertainty only represents counting errors (two standard deviations). The true error is expected to be larger and element dependent.

10.5.2 Interfaces

The interrogation of buried interfaces is a unique strength of APT. The corrosion layers mentioned earlier are an excellent example of this. An atom probe reconstruction of the interface between pristine glass and hydrated glass in Sample 1 is exhibited in Figure 10.14. The element-specific atom maps (20 nm image depth) clearly mark a sharp delineation between the H- and K-rich hydrated glass (lower left) and Li-, B-, and Na-rich pristine glass. A proximity histogram [42] of the composition changes across the interface is depicted in Figure 10.14b. This concentration profile was centered at a 6 at.% B isoconcentration surface, which defined an abrupt three-dimensional interface separating pristine glass from the hydrated layer. The interfacial width, measured as the distance between 10% and 90% of the difference between the minimum and maximum in the measured concentration, was extremely sharp for B (3.4 nm) and Na (5.2 nm) and much broader for Li (12.4 nm) and H (10.4 nm). The interfacial width measured by APT was substantially sharper than measured previously in the same material by NanoSIMS (70–300 nm, depending on the primary ion beam) [58], highlighting the ability of APT to determine nanoscopic profiles with supreme spatial resolution.
Figure 10.14 (a) Element-specific ion maps of the pristine glass / hydrated glass interface from Sample 1 (20 nm image depth). (b) Proximity histogram extracted across the same interface. The interfacial width seems quite different for different species, with H and Li being much broader (10–15 nm) than B and Na (3–5 nm).

A similar analysis of the comparable interface in Sample 2 is presented in Figure 10.15. Because this sample was corroded for only one year, as opposed to the 25.75-years of corrosion in Sample 1, a single APT reconstruction easily contained all of the corrosion layers (~100 nm corrosion depth). Additionally, it is important to highlight that the evaporation sequence is reversed between Sample 1 and Sample 2. Whenever possible, it is important to analyze similar interfaces in the opposite evaporation order to eliminate possible biases in the interfacial measurements that result from preferential retention/evaporation of specific elements. From the elemental maps and concentration profile, four distinct zones of glass were apparent: the gel layer (I); the hydrated corrosion layer (II); a hydrated “pristine” layer (III); and the pristine glass (IV). The interfacial widths of several species were again quantified across the pristine glass/hydrated layer interface. The interfacial width based on B was again extremely sharp (1.5 nm), while that of Na (20.7 nm) was broader but still sharper than either Li (25.5 nm) or H (27.0 nm). The repeatability of these profiles in both sample orientations, and with the added quantitative accuracy of the isotopic tagging in Sample 2, definitively confirmed the similar observations in the 26-year corrosion front in Sample 1.
Figure 10.15 (a) Element specific atom maps and (b) corresponding concentration profiles of the corrosion layer in the 1-year corroded SON68 specimen (Sample 2). The regions labeled I-IV in (a) correspond to the gel layer, hydrated corroded layer, hydrated pristine glass, and pristine glass, respectively. The B profile is again extremely sharp (1.5 nm) while the other elemental profiles are substantially broader.

These experiments have shown that APT can provide unique insights into buried gradated interfaces, in this case for simulated vitrified nuclear waste glass. In most respects the results are in very good agreement with previous observations of the alteration layers using other experimental techniques. In particular, the depletion of B, Na, and Li and ingress of H and K within the hydrated glass layer is in excellent agreement with observations by TEM, SIMS, and NanoSIMS [58, 62]. APT has added greatly to the picture of the corrosion front by improving the resolution of the interfacial width measurements between the hydrated glass layer and pristine glass for various elements. This is a critical consideration when evaluating the mechanism by which the corrosion front is advancing and the rate-limiting mechanism of corrosion/dissolution of the glass [57].

From a microscopy standpoint, the success of these experiments is, perhaps, surprising. Previous analyses of (insulating) glass and of general corrosion by APT have been very limited [21, 65–67] but these results indicate that APT analysis of complicated, insulating glass structures has a potential which has not yet been fully realized. We note, however, that attempts to analyze the corrosion of other (generally simpler) glass compositions have been
more challenging and further development is necessary to understand these limitations. APT analysis inherently exposes a nanoscopic piece of material to an extreme environment of temperature and stress, the combination of which can cause the sample to break. Intriguingly, it may actually be the complexity of the SON68 itself that lends itself to reliable APT analysis.

It is important to discuss possible artifacts that could affect the scientific interpretation of these results. The hydrated glass exhibited an evaporation field approximately 20% smaller than the pristine glass. Additionally, the known difference in average atomic density of the hydrated (~2 g/cm$^3$) than pristine glass (~2.7 g/cm$^3$) cannot be directly utilized in the APT reconstruction (see details in Section 10.3.3), which will likely degrade the accuracy of the tomographic scaling [68]. Significantly different evaporation fields can lead to element-specific differences in the interfacial width and elemental distribution of multilayer specimens [69–71]. This possibility was disproven in the current study by inverting the sample geometry between Sample 1 and Sample 2. The fact that the same features (sharp B and Na profiles and broader Li and H profiles) were repeatable in both specimen orientations implies that preferential evaporation did not significantly affect the measured interfacial width. It is therefore reasonable to determine that these profiles are indeed representative of the real microstructure and not strongly affected by field evaporation artifacts, but other materials systems with comparable compositional and evaporation field differences may not be so fortunate [69].

A second major concern in the analysis of these glass specimens was the quantitative accuracy of the compositional measurements. The limited mass resolving power of APT prohibited the separation of peak overlaps in the time-of-flight mass spectra based on mass deficiency. Furthermore the complexity of the SON68 glass prohibited the commonplace deconvolution of peaks based on natural isotopic abundances. Considering these two fundamental limitations it is likely that quantitative errors exist and are most problematic for peaks with significant peak overlaps. Therefore the current analyses should be considered largely qualitative in nature until further work can be performed to quantify the error. Efforts are currently underway to quantify these errors through isotopic loading of key species, as was done in Sample 2 of this study, and simplified glass compositions, but uncertainty persists in this area and will likely occur in other complicated glasses.

10.5.3 Conclusions

The above examples have briefly illustrated the capabilities and challenges associated with APT analysis of bulk insulating glasses. To date, these are the best examples available (excluding bulk metallic glass) of APT applied to what is broadly characterized as glass science. The recent advancements in both FIB-based sample preparation and pulsed laser APT systems has opened to door to many other areas of glass science which have yet to be explored in earnest. Looking forward, it seems very likely that APT will continue to expand into glass science, likely in the areas of clustering, phase separation, and nucleation formation.

It has been estimated that in the past 10 years (2002–2012), which coincides with the introduction of the commercially available local-electrode atom probe instruments by Imago Scientific / Cameca Instruments, the number of active atom-probe users has quadrupled [72].
This tremendous influx of users, and also atom-probe instruments, reflects the so-called “renaissance” and “second revolution” of APT [25, 73]. Several user facilities, some of which are free to use through competitive user proposal systems [74–76], are available throughout the United States and around the world [77–79]. Cameca, which is currently the sole producer of commercial atom-probe tomographs in the world, maintains a partial list of atom-probe groups around the globe: http://www.atomprobe.com/2ndlinks/MainLinks.aspx

At the time of this writing there are more than 50 publicly acknowledged commercial atom-probe tomographs operating in 11 different countries around the globe, and this list is growing substantially each year. Looking forward, it seems very likely that APT will continue to expand into glass science, likely in the areas of nucleation, clustering, and phase separation (as shown on the cover of this book).

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REFERENCES


INDEX

*Ab initio* molecular dynamics
Absolute shielding
Absorbance
Absorption coefficient (\(\mu\))
Accelerator-based neutron sources
Acetone
Adiabatic modulus
Aerodynamic levitation technique
AgI (silver iodide)
Aging of gels
Airy function
Alkali borates
Alkali incorporation in silicate glasses, structural effects of
Alkali metal halide salts, as matrix materials
Alkaline borates
Alkali
Aluminosilicate glasses
American Society for Testing and Materials (ASTM) methods, for density determination
Anisotropy
Anomalous dispersion technique
Anomalous X-ray scattering (AXS) technique
Anti-Stokes Raman scattering
APT. See Atom probe tomography (APT)
Archimedes' principle, and density determination
  - sink-float method
  - wet/dry weighing
Argon laser, for Raman spectroscopy
As-cast glass
Asymmetry parameter (η)
Atomic-force microscopy (AFM)
Atomic vibrations, effect of, on diffraction,
Atom probe tomography (APT)
  advancements in
  analysis methods,
  background and theory
  case studies
    composition
    interfaces
data reconstruction
  mass-spectra analysis
  tomographic reconstruction
error estimation
  common errors
  compositional error
  spatial resolution
experimental procedure and parameters
field-ion microscopy (FIM) and
instrumentation
limitations of
local electrode atom probe (LEAP)
nearest-neighbor analysis
proximity histogram method
roughness of buried interfaces, determination of
specimen preparation
unique feature of
voltage-pulsed
Attenuation coefficient
Auger electron yield
AX$_2$ glasses

Background subtraction. See also XAFS (X-ray absorption fine structure) spectroscopy
post-edge
pre-edge
Backscattering
Ball and spoke models of glass structure
Ball-and-stick model
Barium borosilicate glasses, glass transition temperature of
Bas protocol
Beamstop alignment
Beer–Lambert law
Berreman effect
Bhatia–Thornton formalism
Boltzmann distribution
Bond-valence (BV), concept of
Bora (B$_2$O$_3$
Borate glasses, infrared spectroscopy and
   borate network structure
   metal ion-site interactions
Boron anomaly
Boron, as shielding material in neutron diffractometers
Borophosphate glasses
   NMR spectroscopy and
   speciations and connectivity distributions in
Borosilicate glasses
  barium
  calcium
  glass transition temperature
  lithium
  NMR spectroscopy
Boroxol groups
Bose–Einstein thermal phonon population factor
Boson peak
Bragg–Brentano reflection geometry
  and synchrotron high energy X-ray
Bragg's law
Bridging angle
Bridging oxygen (BO)
Brillouin light scattering
background and theory
  dielectric permittivity/dielectric constant
  dielectric susceptibility of scattering medium
  dynamic structure factor
  intensity of scattered light
  isothermal compressibility of scattering medium
  magnitude of electric field
  Pockels coefficient
  scattering volume
  strength of induced polarization density
  total dipole moment
  wavelengths and propagation direction of phonon
Brillouin spectra, information from case studies
  mechanically fragile systems
  room-temperature glass
  systems under pressure
  temperature dependence, glass transition, and visco-elasticity
  thin films
challenge with data analysis and information
instrumentation for loss modulus from scattering geometries for bulk samples
Brillouin peaks
Bruker Vertex 80v vacuum spectrometer
Bulk modulus
Bulk viscosity
Carr-Purcell-Meiboom-Gill (CPMG) pulse
CCDs. See Charge coupled devices (CCDs)
Central transition
Cesium borate glass system, density of
Chalcogenide glasses
  covalently bonded
  Raman spectroscopy of
  X-ray diffraction and
Charge coupled devices (CCDs)
Chemical shielding anisotropy
Chemical shift
Classical dispersion theory
Coefficient of finesse
Coherent anti-Stokes Raman spectroscopy (CARS)
Coherent scattering
Coherent scattering length
Complex modulus
Compositional error
Concentration profile
Contrast matching
Convolution model
Coordination number
  for glass
Coordination polyhedra, for glasses
Coordination shell
Copper molybdo-phosphates
Correlation function, in real space
Corrosion interface
Cristobalite
Critical cooling rates
Cross-polarization
Cross-section (neutron scattering). See also Neutron diffraction (ND)

Cryogen-free magnets

Crystal contamination, neutron diffraction and

Crystallite models

Cubic spline procedure

Cumulants method

Curl-of-curl identity

Dark currents
de Broglie wavelength

Debye equation

Debye–Waller factor

Deconvolution

Density

of alkali borates glasses
data analysis and useful information

extraction of atomic level volumes directly from density

molar volume

packing fraction

volume per mole glass former

defined
determination of
direct determination of mass and volume

general considerations in

gradient density column

instrumentation for

pycnometry

sink-float method

wet/dry weighing

of lithium silicate glasses

overview
Density functional theory (DFT)
Depolarization, of Raman lines
Depolarization ratio (DR)
Detector efficiency
Detector memory effects
2D flat plate area detectors
Diborate
Dielectric constant
Dielectric filter
Dielectric function
Dielectric permittivity
Differential pair distribution function
Differential scanning calorimetry (DSC)
  modulated
  and practical considerations
  TA® modulated DSC
  thermogram from
Differential thermal analysis (DTA)
Diffraction grating
Diffractometer. *See also* Neutron diffraction (ND)
Diiodomethane
Diode lasers, for Raman systems
Dipolar interactions
Dipolar recoupling techniques
Dipolar solid state NMR spectroscopy, advanced case studies
  borophosphate and thioborophosphate glasses
  connectivity distribution in $70\text{SiO}_2$-$30\left[(\text{Al}_2\text{O}_3)_x\text{P}_2\text{O}_5_{1-x}\right]$ glasses
  spatial distributions of mobile ions in alkali silicate and borate glasses
heteronuclear experiments
cross-polarization
indirect spin–spin interactions, connectivity studies on
instrumental considerations and caveats
rotational echo adiabatic passage double resonance
rotational echo double resonance
spin echo double resonance
homonuclear experiments
dipolar recoupling experiments
indirect spin–spin interactions, recovery of
instrumental considerations and caveats
second moment measurements
static spin echo decay spectroscopy
two-dimensional correlation methods
for medium-range glass structure
spatial correlations in network glasses
theory related to
direct magnetic dipole–dipole coupling
indirect spin–spin coupling
total spin Hamiltonian
Dipole-dipole interactions
Dipole moment
Direct dipolar coupling
Dispersion analysis
Dispersive spectrometer
Distinct scattering
DL_POLY package
Double-null isotopic substitution technique
Double-quantum (DQ) coherences
DQ-DRENAR (double-quantum-based dipolar recoupling effects nuclear alignment reduction)
DR. See Depolarization ratio (DR)
DSC. See Differential scanning calorimetry (DSC)
DTA. See Differential thermal analysis (DTA)
Dynamic structure factor
Dynamic viscosity
Dy$_7$Ni$_3$

EBS. See Electrostatic bond strength (EBS)
Edge filters
Eight minus $n$-rule
Elastic scattering
Elastic storage modulus
Elasto-optic coefficients
Electric susceptibility tensor
Electrostatic bond strength (EBS)
Empirical potential structure refinement (EPSR)
Energy discriminating solid state detectors
Epoxy cure
Equation of continuity
EXAFS. See Extended X-ray absorption fine structure (EXAFS)
Excitation wavelength
Extended range ordering
Extended X-ray absorption fine structure (EXAFS). See also XAFS (X-ray absorption fine structure) spectroscopy
Faber–Ziman formalism
Faber–Ziman partial structure factors
Fabry-Perot cavity
Fabry-Perot interferometer
Fast-ion-conducting glasses
FDMNES (Finite Difference Method Near-Edge Simulation) software
Fermi’s Golden rule
Fictive temperature
Field desorption
Field-ion microscopy (FIM). See also Atom probe tomography (APT)
Filon's quadrature
Finesse
First difference, isotopic substitution
First sharp diffraction peak (FSDP)
Fitting procedure
Focused ion beam (FIB)
Focus software, for curve-fitting
Form factor
Four-coordinated boron (N4; f2)
Fourier artifacts
Fourier noise
Fourier's second law
Fourier-transform infrared (FT-IR) spectrometer. See also Infrared (IR) spectroscopy
Fourier-transform (FT) Raman spectrometer
Free-induction decay (FID)
Fresnel formulae
FSDP. See First sharp diffraction peak (FSDP)
FT-IR spectrometer. See Fourier-transform infrared (FT-IR) spectrometer
Full width at half maximum (FWHM)
Gas ionization chambers
Gas lasers, for Raman spectroscopy
Gas pycnometry
Gaussian broadening
Gaussian dispersion analysis
Gels
Generalized hydrodynamic approach
GEneral Materials diffractometer (GEM)
Germania (GeO$_2$)
Germanosilicate glasses, Raman study of
GeSe$_2$
GeS$_2$-Sb$_2$S$_3$
Glass ceramics
Glass-in-glass phase separation phenomena. See also Raman spectroscopy
  nucleation phenomenon
  spinodal decomposition
Glass stability parameters
Glass transition temperature
  of barium borosilicate glasses
  determination of, (see also Thermal properties)
Glitches
Goldschmidt radii
Gradient density column method, for density determination
Group theory
Hamiltonian
Hartmann–Hahn matching condition
Heteronuclear correlation experiments
Hooke's law
Hydrogen contamination, neutron diffraction and
Image compression factor
INADEQUATE experiment
Incoherent scattering
Indirect spin–spin coupling
indirect spin–spin coupling tensor
Inelastic neutron scattering
Inelastic scattering
Infrared (IR) spectroscopy
applications in glasses
assessment of glass films by
bulk materials, reflectance spectroscopy of
dispersion analysis
Kramers–Krönig transformation
case studies
bulk glasses
glass thin films
data analysis
bulk glasses
thin films of amorphous materials
instrumentation for
refractive index and dielectric function
short-range order structure and
thin films, infrared spectra of
Institut Laue-Langevin (ILL)
Instrumental errors
Interference fringes
Interferograms
Intermediate range order (IRO)
Inverse methods
Ion-conducting channels
Ion coordination
Ionization
Isoconcentration surfaces
Isomorphic substitution
Isomorphous substitution
Isothermal modulus
Isotopic incoherence
Isotopic substitution
Jahn–Teller effect
J-resolved spectroscopy
Kinematic viscosity
Klein-Nishina formula
Kramers–Krönig transformation
Krogh-Moe/Norman technique
Kronecker delta
k-space
Lambert's law
Lamb modes
Landau–Placzek ratio
Larmor frequency
Laser monochromator
Lasers, for Raman spectroscopy
Lever rule
Lift out methods
Light scattering. See also Brillouin light scattering
thermal phonons and
Light sources, for Raman spectroscopy
Linear elasticity, constants of
Lithium borate glasses
density of
stability parameters in
Lithium borates
Lithium diborate (Li$_2$O-2B$_2$O$_3$)
Lithium silicate glasses
  density of
  lever rule
  $Q^i$ structural units
  sink-float method
  volume per mole silica
  volumes of silicate units
Lithium silicates
Local electrode atom probe (LEAP)
Local magnification effect
Longitudinal modulus
Longitudinal optical (LO)
Longitudinal viscosity
Lorch function
LTCP glass, phase transformations in
Lyddane–Sachs–Teller relationship
Magic-angle spinning (MAS). See also Nuclear magnetic resonance (NMR) spectroscopy
Magnet
Magnetic shielding
Magnetization
Magnetogyric ratio
Magnification, of point projection
MAS. See Magic-angle spinning (MAS)
Mass spectrum
Maxwell's equations
Maxwell's relation
Mean free path (MFP), of photoelectron
Measurement uncertainties, in NMR spectroscopy
Mechanical loss modulus
Medium range structure
Mesostructure
Michelson interferometer. See also Infrared (IR) spectroscopy
Microchannel plate (MCP) detector
Micro-Raman spectrometers
Mode coupling theory
Modeling techniques
Moderator
Modification function
Modified Atomic Form Factor (MAFF)
Modifier cations, in alkali borate glasses
Modulated differential scanning calorimetry (MDSC)
Molar volumes
  of alkali and alkaline-earth borate glass system
  of alkali borates
  stiffness and
Molecular dynamics (MD)
Momentum transfer
Monochromator
Mott–Bethe formula
Multi-channel detectors
Multiple quantum magic angle spinning (MQMAS)
Multiple scattering (MS)
Nanostructure. See also Dipolar solid state NMR spectroscopy, advanced
Navier–Stokes equation
NBO. See Non-bridging oxygen (NBO)
ND. See Neutron diffraction (ND)
Near and Intermediate Range Order Diffractometer (NIMROD)
Nearest-neighbor analysis
Network-modifying cations
Neutron diffraction (ND)

- assembly of nuclei, scattering from atomic vibrations and diffraction
- effect of inelasticity on self scattering
- coherent and incoherent scattering
- experimental corrections
- inelastic scattering processes
- interactions between neutron and sample
- intermediate range order (IRO) and isotropic samples
- modeling techniques
- neutron diffractometer
  - general principles
  - pulsed source diffractometers
  - reactor source diffractometers
- neutrons and normalization of data
- partial correlation functions
  - isotopic substitution
  - other methods
- PDF (pair distribution function) method
- peak fitting and integration
- real-space correlation functions
- real-space resolution
- reciprocal-space resolution
results, interpretation of
bonding and bond lengths
comparison with crystalline structures
coordination polyhedra
crystallite models
first sharp diffraction peak
sample-related difficulties
crystal contamination
hydrogen contamination
nuclear resonances
scattering at low $Q$
homogeneous samples
inhomogeneous samples
short range order (SRO) and
single nucleus, scattering from
sources of neutron
accelerator sources
reactor sources
static approximation
for structural studies of glasses
and x-ray diffraction
Neutron diffractometer. See also Neutron diffraction (ND)
Niobium germanosilicate glasses, Raman study of
NMR spectroscopy. See Nuclear magnetic resonance (NMR) spectroscopy
Non-bridging oxygen (NBO)
alkali incorporation in silicate glasses and
Raman spectroscopy for
Normalization
Notch filters
Nuclear fission
Nuclear magnetic resonance (NMR) spectroscopy

background and theory
- dipolar interactions
- high resolution methodologies
- magnetic shielding
- quadrupolar interaction
- Zeeman effect

case studies
- aluminosilicate glasses
- borophosphate glasses
- borosilicate glasses
- modifier cations in alkali borate glasses

data analysis and structural interpretation
- chemical shift assignments
- low-$\gamma$ nuclei
- paramagnetic effects
- quadrupolar effects

instrumentation
- computer control
- magnet
- measurement uncertainty
- probe
- radiofrequency transmitter and receiver

nuclear properties of selected nuclides
spin description of NMR experiment

Nuclear resonances
Null technique
Nutation frequencies
Nyquist sampling theorem
Packing fraction
of alkali and alkaline-earth borates
ion coordination and size
Pair distribution function (PDF)
Paramagnetic effect
Paramagnetic ions
Partial correlation function
PDFfit program
Peak fitting
Percus–Yevick equation
Percus–Yevick model
Phase separation mechanisms, in phosphate glasses
Phonons
Phosphate glasses
Photoluminescence yield mode (PLY)
Photomultiplier tube (PMT)
Placzek correction
PLAP. See Pulsed laser atom probe (PLAP)
Platelet scattering geometry
PMT. See Photomultiplier tube (PMT)
Pockels elasto-optic coefficients
Poisson ratio
Polarizability
Polymer-cellulose
Porod approximation
Potassium diborate (K_2O-2B_2O_3)
Potassium silicates
Potassium tellurites
Powder pattern
π pulse
Pressure
Pressure-induced amorphization
Probe, NMR
Proximity histogram
Pulsed laser atom probe (PLAP)
Pulsed laser deposition (PLD)
Pulsed source diffractometers
Pulse fraction
Pycnometry, for density determination
  advantages of
  disadvantages of
  helium, use of
  instrumentation for
Quadrupolar asymmetry parameter
Quadrupolar coupling constant
Quadrupolar interactions
Quadrupolar product
Quadrupole moment
Quantachrome® manual pycnometer
Q units
Q-value
Radial distribution function
Radial distribution function (RDF)
  of monatomic system
Radio frequency driven recoupling (RFDR)
Raman effect,76. See also Raman spectroscopy
Raman lines, depolarization of
Raman shift
Raman spectroscopy
  anti-Stokes Raman effect
  Boson peak
  case studies on
    alkali incorporation in silicate glasses, structural effects of
    germanosilicate glasses and glass ceramics
    phase separation mechanisms in phosphate glasses
    Raman study of chalcogenide glasses
  data analysis
  depolarization of Raman lines
  elastic Rayleigh scattering
  electric susceptibility tensor
  instrumentation
    detector
    light sources
    micro-Raman spectrometers
  resolution
  sample compartment
  spectrometers
  laser beam for
  linearly induced polarization
  Raman effect
  Raman shift
  selection rules for
  spontaneous, mechanisms of
  theory
  use of
Random network theory, of glasses
  Zachariasen–Wright network model of glass
Range File
Rare earths
Rayleigh scattering
Reactor neutron sources
Reactor source diffractometers
Real-space correlation functions
Real-space resolution
REAPDOR. See Rotational echo adiabatic passage double resonance (REAPDOR)
Reciprocal-space resolution
REDOR. See Rotational echo double resonance (REDOR)
Reflectance spectroscopy, of bulk materials
Refocused INADEQUATE method
Refractive index
Region of interest (ROI)
Relaxational modulus
Renishaw Raman Imaging Microprobe System
Resolution, neutron scattering
Resolution, of Raman system
Retardation
Reverse Monte Carlo (RMC) method
Root-mean-squared (RMS) roughness
Rotational echo adiabatic passage double resonance (REAPDOR)
Rotational echo double resonance (REDOR)
    constant time (CT-REDOR)
R-space
R7T7 glass
SANS. See Small angle neutron scattering (SANS)
Satellite transitions
90°-scattering
Scattering length of nucleus
Scherrer equation
Secondary ion mass spectrometry (SIMS)
Second difference, isotopic substitution
Second moment
SEDOR. See Spin echo double resonance (SEDOR)
Selection rules, for Raman spectroscopy of glasses
Self scattering
  effect of inelasticity on
Shear modulus
Short range order (SRO). See also Nuclear magnetic resonance (NMR) spectroscopy
Silica (SiO$_2$)
Silica alumino-phosphates
Silicate glasses, alkali incorporation in, structural effects of
Silver borates
SIMPSON program
Single-mode diode lasers
Single scattering (SS)
Sink-float method, for density determination
  acetone-diodomethane solution, use of
  advantages of
  disadvantages of
  instrumentation for
  lithium silicate glasses and
Small Angle Neutron Diffractometer for Amorphous and Liquid Samples (SANDALS)
Small angle neutron scattering (SANS)
Small angle X-ray scattering (SAXS)
Snell's law
Soda lime silicates
Sodium borates
Sodium-calcium silicates
Sodium metasilicate glass, polarized Raman spectra of
Sodium phosphate
Sodium silicates
Sodium tetrasilicate glass, Raman spectra of
SON68 glass
Soper's GudrunN program
Spallation
Spatial resolution
  of APT
  of Raman spectrometers
Spectrometers
  dispersive
    Fourier-transform
Spin echo decay method
Spin echo double resonance (SEDOR)
Spin incoherence
Spin–lattice relaxation times
Spinning sidebands
Splat-quenched glass samples
Splice method
Spontaneous Raman effect. See also Raman spectroscopy
Static approximation
Static spin echo decay spectroscopy
Stiffness, and molar volumes
Stimulated Raman scattering (SRS)
Stokes effect. See also Brillouin light scattering; Raman spectroscopy
Structure factor
Superionic conducting glasses, ionic conductivity in, doped with AgI
Surface-enhanced Raman spectroscopy (SERS)
Tandem Fabry–Pérot interferometer
Tandem interferometry
Terbium phospho-aluminate
Terminal oxygens (TOs)
Thermal diffusivity
Thermal properties. See also Glass transition temperature
data analysis and useful information
experimental methods and theory
calorimetry
differential thermal analysis
instrumentation used
stability parameters in lithium borate glasses
Thin films
of amorphous materials
Brillouin light scattering and
infrared spectra of
infrared spectroscopy and
Thioborophosphate glasses, speciations and connectivity distributions in
Time-of-flight mass spectrometry (TOF-MS). See also Atom probe tomography (APT)
Time-of-flight neutron diffractometer
Time-of-flight (T-O-F) technique
Tin borate glass
Tip-enhanced Raman spectroscopy (TERS)
Ti$_{62}$Zr$_{38}$ alloy
Tomographic reconstruction
Total electron yield (TEY)
Total pair distribution function
Transition energy
Transmission electron microscopy (TEM)
Transmittance
Transverse optical (TO)
Triborate
Turing's number

Ultralow frequency filters

Uniqueness problem

$UO_2$

$U_4O_9$

Vanadium, role in neutron scattering

Van Vleck formulae

Vibrational density of states (VDOS)

Vibrational spectroscopy. See also Infrared (IR) spectroscopy

Virtual image phased array (VIPA) spectrometer

Vitreous silica

Voigt model

Volume per mole glass former

- in lithium borate glass system
- in lithium germanate glass system
- in lithium silicate glass system

Wavefunction

Waveguides

Wet/dry weighing method, for density determination

- advantages of
- disadvantages of
- instrumentation for

Wide angle neutron scattering (WANS)

Wide angle X-ray scattering (WAXS)

Wideband uniform rate smooth truncation (WURST) pulse

XAFS (X-ray absorption fine structure) spectroscopy
data analysis

conversion to \( k \)-space, threshold energy and weighting corrections for instrumental errors
fitting procedures
Fourier filtering
log amplitude ratio and phases difference method
normalization
post-edge background subtraction
pre-edge background subtraction
transformation from \( k \)-space to \( R \)-space

EXAFS

accuracy and limitations
cumulants
effective distribution
formula for glasses
radial distribution function
single-shell EXAFS

for glass structure investigations

Ag nanoparticles in soda-lime silicate glasses
ionic conductivity in superionic glasses doped with AgI
nanoparticles embedded in glasses
rare-earth impurities dispersed in glassy matrices
silica and germania glasses under high pressure
silica at high temperature
silica glass
silicate glasses
instrumentation

apparatus for transmission measurements
detection modes
direct measurements
duration of measurements
Energy Dispersive-XAFS spectrometers
fluorescence detection mode
indirect measurements
Quick-XAFS apparatuses
scanning transmission mode
synchrotron beamline for XAFS measurements
total electron yield detection mode (TEY)

physical mechanism of
multiple scattering
single scattering
theory

XANES
X-ray absorption spectra, origins of
XANES. See X-ray absorption near edge structure (XANES)
X-ray Absorption Fine Structure (XAFS)
X-ray absorption near edge structure (XANES). See also XAFS (X-ray absorption fine structure) spectroscopy
X-ray absorption spectroscopy (XAS). See also XAFS (X-ray absorption fine structure) spectroscopy
X-ray diffraction
background and theory
  average scattering
  Bhatia–Thornton formalism
  differential pair distribution function
  electron distribution function
  electron form factors
  Modified Atomic Form Factor
  pseudo-atomic function
  pseudo-nuclear function
  radial distribution function
  sharpening function
  total pair distribution function
  X-ray form factors

case studies
  amorphous materials, gels, foams and fibers
  chalcogenide glasses
  SiO₂ and oxide glasses

data analysis and useful information
  beam polarization effects
  bond angle information
  consistency checks
  detector corrections
  first sharp diffraction peak (FSDP)
  orientational correlation functions
  Q-dependent corrections
  ring size distribution
  sample-dependent absorption corrections
  X-ray PDF function

future perspective
instrumentation
and neutron diffraction
X-ray pair distribution function
X-ray PDF technique
X-ray diffraction (XRD)
X-ray excited optical luminescence (XEOL) spectra
X-ray fluorescence yield (FLY)
X-ray free electron lasers (X-FEL)
X-ray photoemission spectroscopy (XPS)
XTAL (computer program)

Young's modulus
Yttria (Y$_2$O$_3$)

Zeeman effect
Zero-quantum (ZQ) coherences
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