



# *Modern* Glass Characterization

EDITED BY **MARIO AFFATIGATO**



**WILEY**

# MODERN GLASS CHARACTERIZATION

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**Mario Affatigato**



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## Chapter 4

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**Figure 4.11** Longitudinal elastic moduli of sodium borate glasses and melts as a function of the  $\text{Na}_2\text{O}$  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  $1000^\circ\text{C}$ , respectively.

**Figure 4.12** Longitudinal and shear elastic moduli of three major glass formers,  $\text{SiO}_2$ ,  $\text{GeO}_2$ , and  $\text{B}_2\text{O}_3$ , 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  $\text{GeO}_2$  and  $\text{B}_2\text{O}_3$  at their glass transition temperature.

**Figure 4.13** Longitudinal elastic moduli of (a) potassium silicates; (b) potassium germanates; 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  $\text{B}_2\text{O}_3$  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  $\text{B}_2\text{O}_3$  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  $\text{B}_2\text{O}_3$  measured using Brillouin scattering; (d) real and imaginary components of the Poisson ratio as a function of temperature. Note the positive values of  $\text{Im}(n^*)$  in the temperature range in which the bulk viscosity dominates.

**Figure 4.15** Storage and loss moduli of (a)  $38\text{Na}_2\text{O}\cdot 62\text{B}_2\text{O}_3$  and (b)  $20\text{K}_2\text{O}\cdot 80\text{TeO}_2$  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  $B_2O_3$  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  $\mathbf{R}_j$  relative to an arbitrary origin O. For the wave scattered from the atom, there is a path length difference  $\Delta_i - \Delta_f = \mathbf{R}_j \cdot (\hat{\mathbf{k}}_i - \hat{\mathbf{k}}_f)$  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  $B_2O_3$  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  $B_2O_3$  glass on the GEM diffractometer. (b) The (corrected and normalized) differential cross-section of  $B_2O_3$  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  $SiO_2$  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.

**Figure 5.14** The neutron correlation function,  $T^N(r)$ , for  $B_2O_3$  glass [13], together with a fragment of a two-dimensional  $B_2O_3$ -like network, showing how the peaks in the correlation function arise from the interatomic distances.

**Figure 5.15** Neutron correlation functions for  $GeO_2$  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,  $GeO_2$  glass, and  $GeO_2$  in its quartz crystalline form [16].

**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.

**Figure 5.18** Neutron diffraction results for  $2\text{CaO}\cdot\text{Na}_2\text{O}\cdot 3\text{P}_2\text{O}_5$  glass [2, 42]. (a) The distinct scattering,  $i^{\text{N}}(Q)$ , with the high  $Q$  region shown in an inset. (b) The step and Lorch modification functions [37] for  $Q_{\text{max}} = 55\text{\AA}^{-1}$ . (c) The total neutron correlation function,  $T^{\text{N}}(r)$ , 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,  $T^{\text{N}}(r)$  (as obtained using the Lorch modification function [37]), for an ideal  $\text{GeO}_4$  tetrahedron, showing the effect of maximum momentum transfer,  $Q_{\text{max}}$ , on real-space resolution and termination ripples. (a)  $Q_{\text{max}} = 24\text{\AA}^{-1}$ , (b)  $Q_{\text{max}} = 40\text{\AA}^{-1}$ .

**Figure 5.20** The first peak region of the total neutron correlation function,  $T^{\text{N}}(r)$ , for (a)  $\text{GeO}_2$  glass [16] (thick grey line is experiment, thin black line is fit, dashed line is residual); (b)  $18\text{Cs}_2\text{O}\cdot 88\text{GeO}_2$  glass [16]; and (c)  $2\text{CaO}\cdot\text{Na}_2\text{O}\cdot 3\text{P}_2\text{O}_5$  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 5.21** 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)  $T^{\text{N}}(r)$  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  $20\text{\AA}$ , 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  $\text{Dy}_7\text{Ni}_3$ . 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  $10\text{K}_2\text{O}\cdot 90\text{TeO}_2$  glass,  $I^{\text{N}}(Q)$ , 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 ( $93^\circ$ ) of the GEM diffractometer [2] for amorphous zeolite precursor  $\text{LTA}_5$  [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).

**Figure 5.25** The distinct scattering,  $i^{\text{N}}(Q)$ , for a tin borate glass sample with nominal composition  $70\text{SnO}\cdot 30\text{B}_2\text{O}_3$  before and after removal of Bragg peaks (see text) [13]. Also shown is a simulation of the diffraction pattern for crystalline  $\text{SnO}_2$  and vertical tick marks indicate the positions of the Bragg peaks.

**Figure 5.26** The differential cross-section,  $I^{\text{N}}(Q)$ , of amorphous  $\text{Dy}_7\text{Ni}_3$  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  $\text{Dy}_7\text{Ni}_3$  [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  $\text{Dy}_3\text{Ni}_2$  [79] (large, translucent spheres are Dy, smaller, solid spheres are Ni).

**Figure 5.28** The differential cross-section for  $24.6\text{Tb}_2\text{O}_3 \cdot 72.2\text{P}_2\text{O}_5 \cdot 3.2\text{Al}_2\text{O}_3$  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  $24.6\text{Tb}_2\text{O}_3 \cdot 72.2\text{P}_2\text{O}_5 \cdot 3.2\text{Al}_2\text{O}_3$  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)  $\text{AX}_3$  triangle; (b)  $\text{AX}_3$  trigonal pyramid; (c)  $\text{AX}_4$  tetrahedron; (d)  $\text{AX}_4$  disphenoid; (e)  $\text{AX}_5$  trigonal bipyramid; (f)  $\text{AX}_5$  square pyramid-based unit; (g)  $\text{AX}_6$  octahedron; (h)  $\text{AX}_6$  trigonal prism; (i)  $\text{AX}_8$  Archimedean antiprism; (j)  $\text{AX}_{12}$  icosahedron.

**Figure 5.33** The total neutron correlation function,  $T^N(r)$ , of crystalline  $\text{U}_4\text{O}_9$ . (a) The experimental correlation function,  $T_{\text{exp}}(r)$ , compared with the U–O and U–U contributions,  $T_{\text{Con}}(r)$ , 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  $\text{U}_4\text{O}_9$  [160]. (c) The experimental correlation function, compared with the partial components of  $T_{\text{XTAL}}(r)$  [160].

## Chapter 6

**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<sub>2</sub>O [19].

**Figure 6.4** Measured X-ray intensity for GeSe<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> 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  $r$ .

**Figure 6.7** Photon scattering cross-sections for SiO<sub>2</sub> as a function of incident energy [34]. The photoelectric absorption cross-section (dash-dot line) dominates for energies below  $\sim 50$  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<sub>2</sub> [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<sub>2</sub>O<sub>5</sub> made with Ag K $\alpha$  X-rays  $\lambda = 0.561$  Å (open symbols) and

X-ray synchrotron radiation  $\lambda = 0.088 \text{ \AA}$  (filed circles). Digitized from Hoppe et al. [51]).

**Figure 6.11** The X-ray structure factor for glassy  $\text{SiO}_2$  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  $\text{SiO}_2$  (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 Neuefeind 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  $\text{SiO}_2$  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  $\text{SiO}_2$  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  $\text{SiO}_2$  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  $\text{GeSe}_2$  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).