Structure of glasses and melts

Martin Wilding
Institute of Mathematical and Physical Sciences, University of Wales, Aberystwyth, Ceredigion, SY23 3BZ

Chris Benmore,
Intense Pulsed Neutron Source and the Advanced Photon Source, 9700 Cass Avenue, Argonne, IL 60439

11 December, 2006
Outline

- The Liquid State
- Neutron Scattering theory
- Instrumentation and sample environment
- Interpretation of glass structure
- Studies of liquids and amorphous materials
- Summary and future directions
The Liquid State

- Liquids lack long-range order
  - Pair distribution function shows Short range order
- Glasses formed by super-cooling a liquid.
  - Show a glass transition
- Amorphous materials by other routes
  - Inherent polyamorphism
The pair distribution function

- Average separation of atom pairs
- Region where $g(r)$ is zero
- Pronounced first peak
- Series of smaller peaks
- $g(r)=1$ mean density of the system
Glasses and amorphous materials

- Super-cooling
  - Ergodicity
  - Non-ergodicity

- Configurational entropy and fragility

- Pressure-induced amorphisation
Neutron diffraction: Scattering theory

- Double differential cross section
- Coherent scattering law
- Static approximation

\[ I = I_0 \frac{d^2 \sigma}{d \Omega dE_1} d \Omega dE_1 \]

\[ S(Q, \omega) = \frac{1}{N} \frac{k_{\text{incident}}}{k_{\text{scattered}}} \frac{4\pi}{\sigma_{\text{coh}}} \frac{d^2 \sigma}{d \Omega dE_1_{\text{coh}}} \]

\[ Q^2 \approx 2k_{\text{incident}}^2 (1 - \cos 2\theta) \]
Neutron diffraction: Scattering in multi-component systems

- Scattering:
  - Sum of several atom-pairs
  - Partial contributions

- Faber-Ziman formalism

\[ \frac{1}{N} \left[ \frac{d\sigma}{d\Omega} (Q) \right] = F(Q) + \sum_{\alpha} c_{\alpha} b_{\alpha,\text{inc}}^2 \]

\[ F(Q) = \sum_{\alpha,\beta} c_{\alpha} c_{\beta} \overline{b_{\alpha} b_{\beta}} [S_{\alpha,\beta}(Q) - 1] \]
Neutron diffraction: the differential cross section

\[ \frac{d\sigma_N}{d\Omega} = \sum_{\alpha} c_{\alpha} b_{\alpha,\text{inc}}^2 + P(\theta) + F_N(Q) \]
Neutron diffraction: the pair correlation function

- Sine Fourier transform of the $S_{\alpha,\beta}(Q)$:
  - Total number density is $\rho_0$
  - $G_{\alpha,\beta}(r)$ is the probability of finding atom $\beta$ at distance $r$ from atom $\alpha$.

- Fourier transform of the total $F(Q)$ is the weighted sum of all partial values.

- Total correlation function, $T(r)$.
  - Highlights correlation at high $r$

- Differential distribution function $D(r)$.
  - Bulk density removed.

\[
g_{\alpha,\beta}(r) = 1 - \frac{1}{2\pi^2 r \rho_0} \int_0^\infty Q [S_{\alpha,\beta}(Q) - 1] \sin(Qr) dQ
\]

\[
G(r) = \frac{1}{2\pi^2 r \rho_0} \int_0^\infty Q F(Q) \sin(Qr) dQ = \sum_{\alpha,\beta} c_{\alpha} c_{\beta} \bar{b}_{\alpha} \bar{b}_{\beta} [g_{\alpha,\beta}(r) - 1]
\]

\[
T(r) = 4\pi r \rho_0 \left[ G(r) + \sum_{\alpha,\beta} c_{\alpha} c_{\beta} \bar{b}_{\alpha} \bar{b}_{\beta} \right]
\]

\[
D(r) = 4\pi r \rho_0 \left[ G(r) + \sum_{\alpha,\beta} c_{\alpha} c_{\beta} \bar{b}_{\alpha} \bar{b}_{\beta} \right] - 1
\]
Neutron instrumentation

- Steady state (reactor type)
- Beam of wavelength $\lambda$ is scattered though angle $2\theta$.
Neutron instrumentation

- Time-of-flight (spallation type) glass/liquid diffractometer
- Detectors at fixed angle record different wavelengths (Q)

- Soller collimator
- Position sensitive detectors
- Beam gate
- Monitor
- White neutron beam
- Sample
- Scattering angle $2\theta$
- Beam stop
- $I$ vs $\lambda$
- $2\theta_1$, $2\theta_2$, $2\theta_n$
Neutron diffraction: correction procedures

Structural information is in elastic, single scattering events.
Sample environments

Pressure cells

Type V3b Paris-Edinburgh Cell

Encapsulated gasket

Standard gasket

Standard anvil & gasket configuration
Sample environments

Containerless levitation

11 December, 2006 Neutron Scattering in Earth Sciences
Interpretation of glass structure

- Based on the pair distribution function (PDF)
- Continuous random networks (CRN)
- Characteristic distance ranges
Interpretation of glass structure

- Short-range order and connectivity
- Intermediate range Order
- The first sharp diffraction peak (FSDP)

\[
S(Q) \rightarrow T(r) = 4\pi r \rho \cdot g(r)
\]
Partial structure factor determination

Isotopic substitution, e.g. H/D

\[
G_{\text{H}_2\text{O}}(r) = \frac{c_h^2 b_h^2}{A} g_{\text{HH}}(r) + \frac{2c_h c_0 b_h b_0}{A} g_{\text{OH}}(r) + \frac{c_0^2 b_0^2}{A} g_{\text{OO}}(r)
\]

\[
A = c_h^2 b_h^2 + 2c_h c_0 b_h b_0 + c_0^2 b_0^2
\]

\[
G_{\text{H}_2\text{O}}(r) = 0.318 g_{\text{HH}}(r) - 0.492 g_{\text{OH}}(r) + 0.190 g_{\text{OO}}(r)
\]

\[
G_{\text{H}_2\text{O}}(r) = 0.486 g_{\text{HH}}(r) + 0.23 g_{\text{OH}}(r) + 0.091 g_{\text{OO}}(r)
\]

\[
G_{\text{H}_2\text{O}}(r) = 0.113 g_{\text{HH}}(r) + 0.446 g_{\text{OH}}(r) + 0.441 g_{\text{OO}}(r)
\]
Partial structure factor determination

Combined neutron and X-ray data

$$\Delta S(Q) = \frac{[S_N(Q) - 1] - \frac{W_N}{W_X(Q)}[S_X(Q) - 1]}{1 - \left[\frac{W_N}{W_X(Q)}\right]}$$
Partial structure factor determination

Reverse Monte Carlo and empirical structural refinement

Reverse Monte Carlo Modeling of Neutron and X-ray data
Studies of liquids and amorphous materials: Simple oxides

- Confined to simple systems:
  - SiO$_2$
  - Li$_2$O-SiO$_2$
  - K$_2$O-SiO$_2$
  - Na$_2$O-SiO$_2$
  - CaO-Al$_2$O$_3$-SiO$_2$
Studies of liquids and amorphous materials: Simple oxides

- **MgO-SiO$_2$ glasses**

![Graph showing S(Q) and T(r) for different MgO-SiO$_2$ compositions](image)

*Graph showing the structure factors S(Q) and the radial distribution functions T(r) for MgO-SiO$_2$ glasses with different compositions.*

- 67% MgO 33% SiO$_2$ (forsterite)
- 62% MgO 38% SiO$_2$
- 58% MgO 42% SiO$_2$
- 54% MgO 46% SiO$_2$
- 50% MgO 50% SiO$_2$ (enstatite)

*Composition and corresponding S(Q) and T(r) profiles.*

**Momentum transfer (Angstrom$^{-1}$)**

**Radial distance (Angstrom)**
Studies of liquids and amorphous materials: amorphous ices

- Low and high-density forms of amorphous ice
- Demonstration of LDA-HDA transitions
- Fully hydrogen-bonded tetrahedral networks
- Interstitial water molecule
- Related to the high pressure structure of liquid water
Studies of liquids and amorphous materials: amorphous ices

- Changes in the first peak in the diffraction pattern
- Changes in the O-O partial in real space
- Change in O-O, moves to greater radial distance with HDA-LDA
Studies of liquids and amorphous materials: high pressure studies

- Amorphous forms of GeO₂
- Classic “strong” network-forming glass
- Tetrahedral-octahedral coordination change
- Changes in height and position of FSDP
- Shrinkage and collapse of open network structures
- Intermediate 5-coordinate Ge-O stabilised
MgO-SiO$_2$ glasses: Neutron diffraction

Abrupt changes in the S(Q) between 6 and 8 GPa
Studies of liquids and amorphous materials: high pressure studies

- Change in first peaks
  - Si-O
  - Mg-O

- Increasing distortion of the Mg-O polyhedron?

- Non-linear change in structure

- Is it polyamorphic?
Neutrons offer the opportunity to determine the structure of liquids directly by diffraction.

- Total structure factor related to the PDF by Fourier transform.
- Combined techniques can be used to extract partial $S(Q)$'s.
- Developments in sample environment:
  - Levitation studies
  - High pressure studies
- New neutron sources
- More challenging experiments