Lecture 4, Part 1: Glass: Structure determination by synchrotron based scattering and spectroscopic techniques

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Glass Structure by Synchrotron Techniques

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Glass Structure by Synchrotron Techniques

- Knowledge of structure is important in glass science and technology in:
  - Understanding and controlling physical and chemical properties
  - Leads to optimization of processing

- Practically all atomic-scale structural characterization techniques are based on:
  - Elastic scattering (e.g. neutron scattering, SAXS, WAXS, AXS)
  - Spectroscopy (XAS, magnetic resonance, Raman/IR, UV/VIS, XPS, QENS, XPCS, IXS etc.)
How do synchrotrons work?

• A Synchrotron accelerates electrons using magnets and RF waves, into an orbit at almost the speed of light. When electrons are deflected through magnetic fields they emit extremely bright light, million times brighter than sunlight.

• Basic parts of synchrotron
  – 1. Electron gun
  – 2. LINAC
  – 3. Booster Ring
  – 4. Storage Ring
  – 5. & 6. Beamline- End Station
Why Synchrotron?

Brilliance / Intensity

Up to 12 orders of magnitude
Brighter than laboratory source

45 synchrotron sources worldwide

11 in the USA

SPRING8 in Japan is the brightest
Neutron Sources

• **Reactor sources**

Neutrons produced from fission of $^{235}\text{U}$. Moderated to thermal energies (5 to 100 meV corresponding to wavelengths of 1 to 4 Å) e.g. with $\text{D}_2\text{O}$. These are continuous sources.

• **Spallation sources**

Proton accelerator and heavy metal target (e.g. W or U) Higher energy neutrons, comes in pulses, wider range of incident neutron energies
# Neutron vs. x-ray: properties

## Neutron
- Mass = $1.675 \times 10^{-27}$ kg
- Charge = 0; spin = $\frac{1}{2}$
- Has magnetic dipole moment
- Wavelength can vary over a wide range (e.g. 1 to 30 Å)

## Photon
- Mass = 0
- Spin = 1
- Charge = 0
- Magnetic Moment = 0
- High-energy x-ray (40 to 100 keV) provides wavelength range of 0.125 to 0.3 Å
Neutron vs. x-ray: advantages & disadvantages

**Neutron**

λ = inter-atomic spacing  
Penetrates bulk matter  
Strong isotopic contrast possible  
Magnetic order can be probed  
Low brilliance, needs large sample  
Not suitable for some elements e.g. B (needs isotopic replacement)

**X-ray**

λ = inter-atomic spacing  
High brilliance. High resolution  
Needs small sample  
Weak scattering from light elements  
No isotopic contrast  
Radiation damage to samples
Scattering Techniques

X-ray and Neutron Scattering
Theory of elastic x-ray (and neutron) scattering

Elastic (Thomson) scattering of photon by one electron:

\[ \frac{d\sigma}{d\Omega} = \frac{\# \text{ of scattered photons into unit solid angle}}{\# \text{ of incident photons per unit time}} \]

\[ \frac{d\sigma}{d\Omega} = \left( \frac{e^2}{mc^2} \right)^2 \left[ \frac{1 + \cos^2 \theta}{2} P \right] = r_0^2 P \]

\[ r_0 = 2.82 \text{ fm} \] is the Thomson scattering length, \( P \) is the polarization factor.

Atom has many electrons in the form of an electron cloud around the nucleus.
Theory of elastic scattering (contd.)

Atomic form factor or scattering factor $f$ is the ratio of amplitude of wave scattered by an atom to that by an electron

$$f (Q) = \int_{0}^{\infty} \rho (r) e^{iQr} \, dr$$

FT of the spatial distribution of electron cloud, considered to spherically symmetric.

A wave has a momentum $p = \hbar k$. Momentum transfer due to scattering is $Q = k_f - k_i$.

** Neutrons are scattered by nuclei; \( \frac{d\sigma}{d\Omega} = b^2 \) for single atom

$b = \text{nuclear scattering cross section (Q-independent !)}$
X-ray and Neutron scattering lengths

Figure 20. Coherent scattering lengths for x-rays ($r_e f$) and neutrons ($b$) as a function of atomic number. Note the dependence on $q \propto \sin \theta / \lambda_c$ for x-rays but not for neutrons. Figure after Bacon (1975).

X-ray and neutron form factor

- The form factor is related to the scattering density distribution in an atom.
  - It is the Fourier transform of the scattering density.
  - Neutrons are scattered by the nucleus not electrons and as the nucleus is very small, the neutron form factor shows no angular dependence.
Theory of elastic scattering (contd.)

For many atoms with spherical electron clouds centered around each atom: add up phases of the wavelets scattered from all the electron clouds (atoms) in the sample.
Theory of elastic scattering (contd.)

\[
\frac{d\sigma}{d\Omega} (\text{elastic}) = \sum_{\alpha} c_{\alpha} f_{\alpha}^2 (Q) + I_x (Q)
\]

Measured experimentally (plus inelastic/Compton scattering)
Distinct scattering contains structural information !!
It is related to structure factor \( S(Q) \), the FT of the pair distribution function \( g(r) \):

\[
S (Q) = V \int dr dr \quad e^{-iQ \cdot (r-r')} \left\langle \rho_N (r) \rho_N (r') \right\rangle
\]

positional correlation of atoms
Theory of elastic scattering (contd.)

**Neutron**

\[
\frac{d\sigma}{d\Omega} = \frac{d\sigma}{d\Omega}_{self} + \frac{d\sigma}{d\Omega}_{\text{Inelastic}} + \frac{d\sigma}{d\Omega}_{\text{Distinct}} = \sum c_\alpha b_\alpha^2 + P(\theta) + F_N(Q)
\]

- Self scattering
- Inelastic scattering "Plazeck"
- Distinct scattering

**X-ray**

\[
\frac{d\sigma}{d\Omega} = \frac{d\sigma}{d\Omega}_{self} + \frac{d\sigma}{d\Omega}_{\text{Compton}} + \frac{d\sigma}{d\Omega}_{\text{Distinct}} = \sum c_\alpha f_\alpha^2(Q) + C_X(Q) + I_X(Q)
\]

- Self scattering
- Compton scattering
- Distinct scattering
Theory of elastic scattering (contd.)

Static structure factor

**Neutron Nuclear function**

\[
S_N(Q) - 1 = \frac{F_N(Q)}{\left(\sum_\alpha c_\alpha b_\alpha\right)^2}
\]

\[
= \frac{1}{\left(\sum_\alpha c_\alpha b_\alpha\right)^2} \sum_\alpha c_\alpha b_\alpha c_\beta b_\beta (S_{\alpha\beta}(Q) - 1)
\]

**Distinct scattering**

**X-ray pseudo-nuclear function**

\[
S_X(Q) - 1 = \frac{I_X(Q)}{\left(\sum_\alpha c_\alpha f_\alpha(Q)\right)^2}
\]

\[
= \frac{1}{\left(\sum_\alpha c_\alpha f_\alpha(Q)\right)^2} \sum_\alpha c_\alpha f_\alpha(Q) c_\beta f_\beta(Q) (S_{\alpha\beta}(Q) - 1)
\]

**Coherent neutron scattering length**

**X-ray form factor**

**De-convolute electron cloud**
Theory of elastic scattering (contd.)

\[ \frac{d\sigma^N}{d\Omega} = \sum_{\alpha} c_{\alpha} b_{\alpha}^2 + P(\theta) - F_N(Q) \]

\[ \frac{d\sigma^X}{d\Omega} = \sum_{\alpha} c_{\alpha} f_{\alpha}^2(Q) + C_X(Q) - I_X(Q) \]

\[ \sum_{\alpha} c_{\alpha} b_{\alpha}^2 \]

\[ P(\theta) + \sum_{\alpha} c_{\alpha} b_{\alpha}^2 \]

\[ \sum_{\alpha} c_{\alpha} f_{\alpha}^2(Q) + C_X(Q) \]

\[ C_X(Q) \]
How to obtain $G(r)$ from $I(Q)$?
How to obtain DFs from \( I(Q) \) ?

\[
g(r) = 1 + \frac{1}{2\pi^2 \rho r} \int Q i(Q) M(Q) \sin(Qr) dQ
\]

Total: \( T(r) = 4\pi \rho r g(r) \)

Differential: \( D(r) = [4\pi \rho r g(r) - 1] \)
Effect of cutoff on resolution

As$_4$O$_6$ molecule

Physical meaning of RDF
Types of Disorder

Orientational Disorder

Plastic Crystals  
Defects  
Perfect Crystals  
Nanoparticles

Translational Disorder

Dense fluid  
Liquids  
Glasses  
Quasicrystals

Translational Disorder
Glass structure at various length scales

Bond lengths and Coordination numbers

\[ n^\alpha_\beta(r) = c_\alpha \int_1^2 T_{\alpha\beta}(r) r dr \]

A formation of skydivers illustrates order on an intermediate length scale.

P.S. Salmon Nature Materials
1, 87–88 (2002)
Glass structure at various length scales

'Second sharp diffraction peak'

Sine Fourier Transformation

\[ S(Q) \rightarrow T(r) = 4\pi r g(r) \]
Intermediate-range order

A case study of molecular Ge-doped As-S glasses:

S. Soyer-Uzun et al., 2009, JPC-C
Intermediate-range order - contd.

A case study of molecular Ge-doped As-S glasses:

S. Soyer-Uzun et al., 2009, JPC-C
Intermediate-range order contd.

A case study of molecular Ge-doped As-S glasses:

S. Soyer-Uzun et al., 2009, JPC-C
For a material with \( n \) different types of atoms there are \( n(n+1)/2 \) partial structure factors \( S_{\alpha\beta}(Q) \) and hence, that many partial pair distribution functions \( g_{\alpha\beta}(r) \).

A complete structural description at the short-range requires this information.

Need to vary the weighting factors of \( S_{\alpha\beta}(Q) \) in the above equation: combined neutron & x-ray, isotope substitution for neutron and anomalous x-ray scattering (AXS).
Partial Structure Factors: vitreous GeO$_2$

Total Structure Factor, $S(Q)$ = Weighting factors, $W_{\alpha\beta}(Q)$ \times Partial Structure Factors, $S_{\alpha\beta}(Q)$

Neutron

X-ray

Vitreous Germania.
Partial Pair Distribution Functions: vitreous SiO$_2$

\[
\begin{bmatrix}
I_{Nat}^N (Q) \\
I_{29}^N (Q) \\
I_X^X (Q)
\end{bmatrix} =
\begin{bmatrix}
\frac{Nat}{c_{Si}^2 b_{Si}^2} & 2c_{Si} c_{O} b_{Si} b_{O} & c_{O}^2 b_{O}^2 \\
\frac{29}{c_{Si}^2 b_{Si}^2} & 2c_{Si} c_{O} b_{Si} b_{O} & c_{O}^2 b_{O}^2 \\
c_{Si}^2 f_{Si}^2 (Q) & 2c_{Si} c_{O} f_{Si} (Q) f_{O} (Q) & c_{O}^2 f_{O}^2 (Q)
\end{bmatrix}
\begin{bmatrix}
S_{SiSi} (Q) - 1 \\
S_{SiO} (Q) - 1 \\
S_{OO} (Q) - 1
\end{bmatrix}
\]
Anomalous x-ray scattering (AXS)

Marked change in atomic form factor near absorption edge:

\[ f(Q, E) = f_0(Q) + f'(E) + if''(E), \quad f''(E) \propto \mu(E) \]

Kramers-Kröning Dispersion Relation

\[ f'(E) = \frac{2}{\pi} \int_0^\infty \frac{f''(E') E'}{E^2 - E'^2} dE' \]
Anomalous x-ray scattering (AXS): contd.

- Limited applicability but powerful technique
- Good for heavy elements
- Longer range than EXAFS
- Depends on very small differences between S(Q) collected near and away from the absorption edge: hence requires sufficient statistics and careful data processing
- Absorption and fluorescence corrections are critical
AXS on Rb$_2$O-GeO$_2$ glasses

D.L. Price et al., PRB, 55, 11249 (1997)

Ge-Rb third neighbor
Diffraction + Simulation (MD/RMC)

- Often a combined analysis is the best way to obtain structural information

- Most useful for multi-component systems (will discuss later)

- Use SRO as constraint and investigate IRO (will discuss later)

Grandinetti and coworkers PRB, 70, 064202, 2004
Small-Angle X-ray Scattering (SAXS)

- X-rays (and neutrons) are also scattered at very small angles (0.001 to 0.5 Å⁻¹) from large scale (bigger than individual atoms- e.g. 1-100 nm) fluctuations in electron/nuclear density
- For glasses small-angle scattering originates typically from density and/or concentration fluctuations related or unrelated to phase separation
- For glass-ceramics the coexistence of glass and crystal with different densities is important
- Particle shape, size distribution, crystallinity
SAXS-Fundamentals

Differential Scattering Cross-section \( \frac{d\sigma}{d\Omega}(Q) = \Phi_1 - \rho_2 \sqrt{V_1^2 nP(Q) S(Q)} \)

\[ \rho = N_A d \left( \sum b_i / \sum M_i \right) \]

\( V_1 = \) scattering particle volume
\( n = \) concentration of particles
\( d = \) density of particles
\( b_i, M_i = \) scattering length and atomic weights of elements in the particle
\( N_A = \) Avogadro’s number
\( \rho_1, \rho_2 = \) scattering length density of particle and matrix
\( P(Q) = \) form factor (intra-particle atomic arrangement)
\( S(Q) = \) structure factor (inter-particle correlations)
Guinier (low Q) region, single particle scattering approximation holds

\[ I(Q) = I(0)e^{-R_{g}^{2} Q^2 / 3} \]

\( R_g \) = radius of gyration, related to overall particle dimension

- Looking at scattering in the low-Q regime, where \( Q_{\text{max}} R_g \leq 1.0 \)
  - The range can extend up to \( \leq 1.2 \) to 1.3 for ellipsoidal particles
- Plot the data as \( \ln[I(Q)] vs Q^2 \)
  - The data lie on a straight line and the gradient is \( -R_{g}^{2/3} \)
  - The intercept is proportional to the molecular mass of the particles
Porod limit, large Q

\[ Q . R_g \gg 1 \]

\[ \lim_{Q \to \infty} I(Q) = \frac{2 \pi S_v}{\Delta \rho^2} Q^{-4} \]

Spherical particles:
\[ I(Q) \sim Q^{-4} \]

Rod-shaped particles:
\[ I(Q) \sim Q^{-1} \]

Disk-shaped particles:
\[ I(Q) \sim Q^{-2} \]
Hierarchical structures—many length scales


Bimodal size distribution

Schaefer, U. Cinn

(NaO)(SiO$_2$)$_{3.3}$

polymerization

85G/L
SAXS Invariant

The scattered intensity from above systems are different.

For an incompressible two-phase system

$$\int_0^\infty Q^2 I(Q) dQ = 2\pi^2 V_v (1-V_v) |\Delta \rho|^2$$

$$\text{Invariant} = 2\pi^2 \phi_{\text{black}} (1-\phi_{\text{black}}) (\rho_{\text{white}} - \rho_{\text{black}})^2$$

Guinier and Fournet, pp. 75 - 81
SAXS Invariant: Contd.

- \( \frac{S}{V} = \text{specific surface area of sample} \)

\[
\lim_{Q \to \infty} I(Q) = 2\pi S \rho \Delta \rho^2 Q^{-4}
\]

\[
\frac{S_A}{V_A} > \frac{S_b}{V_B}
\]

\[
\frac{S}{V} = \frac{\pi \cdot \lim I(Q) \cdot Q^4}{\int I(Q) Q^2 dQ}
\]

Specific surface area can be determined from scattering data even without absolute scaling.
I(Q) ~ P(Q), the form factor that represents interference between radiation scattered by different parts of the same scattering body/particle

Provides information on particle morphology or shape

\[ P(Q) = |F(Q)|^2 \]

Scattered intensity:

\[
I(Q) = |\Delta \rho|^2 \left| \int dr \ e^{-iQ \cdot r} \right|^2 = |\Delta \rho|^2 |F(Q)|^2
\]

where \( F(Q) \) represents the shape of the particle

For a sphere where \( V = 4(\pi R^3)/3 \)

\[
F(Q) = 3 \left[ \frac{\sin(QR) - QR \cos(QR)}{(QR)^3} \right]
\]
Alkali silicate glasses - density and concentration fluctuations

Alkali Percolation Network Dimensionality

SAXS and dimensionality and ionic diffusion

Long range fluctuation near glass transition: OTP

Ornstein-Zernike approximation


\[ I(Q) = \frac{I_0}{1 + Q^2 \xi^2} \]

\[ \xi \text{ correlation length} \]

\[ 1/R_{iso} \]

\[ \text{linear fit, slope=2.24} \]

A. Patkowski et al., PRE, 61, 6909, 2000
X-ray Absorption Spectroscopy

EXAFS & XANES
X-ray Absorption Process

Beer’s Law: $I = I_0 e^{-\mu t}$

At most x-ray energies $\mu$ is a smooth function of x-ray energy $E$

$$\mu = \frac{\rho Z^4}{AE^3}$$

$\rho$ : density, $Z$ : atomic number, $A$ : atomic mass
X-ray Photoelectric effect

When the incident x-ray energy is equal to or higher than the binding energy of a core K, L or M electron there is a sharp rise in absorption: this is Absorption Edge

The absorption edge energy scales with Z as $Z^2$
X-ray photon is absorbed by a core-level electron which is excited to an unoccupied state above the Fermi level, the core hole that is left behind gets filled up within a few femtoseconds by a higher-lying electron emitting fluorescence or Auger electron.
Absorption coefficient above edge

Fermi’s Golden Rule

\[ \mu(E) \propto \left| \left\langle i \left| H \right| f \right\rangle \right|^2 \]

For a bare atom: NO EXAFS, smooth drop in \( \mu(E) \) above absorption edge
Effect of neighboring atoms

The ejected photoelectron is scattered by the neighboring atoms. This results in interference between outgoing and backscattered waves.

\( \mu(E) \) depends on density of final states at energy \( E-E_0 \) that is modulated by the interference at the absorbing atom: EXAFS

**THE EXAFS FUNCTION**

\[
\chi(E) = \frac{\mu(E) - \mu_0(E)}{\Delta \mu_0(E)}
\]

Usually represented in terms of wavevector \( k \)

\[
k = \sqrt{\frac{2m(E - E_0)}{\hbar^2}}
\]
The EXAFS Equation

\[ \chi(k) = \sum_j N_j f_j(k) e^{-\frac{2k^2 \sigma_j^2}{R_j}} e^{-\frac{2R_j}{\lambda(k)}} \sin \left( \frac{2kR_j + \delta_j(k)}{R_j} \right) \]

- \( N \) = coordination number
- \( \sigma \) = mean square variation in distance (Debye-Waller factor)
- \( R \) = inter-atomic distance
- \( f(k), \delta(k) \) are scattering properties of the neighboring atoms
- \( \lambda(k) \) = mean free path of photoelectron

Typically \( N, \sigma \) and \( R \) are fitted to the \( \chi(k) \) data
\( f(k), \delta(k) \) and \( \lambda(k) \) are theoretically calculated
EXAFS Data Reduction Steps

Experimentally $\mu(E) \propto \log(I_0/I)$ or $I/I_0$

Subtract a smooth pre-edge function to get rid of instrumental background and absorption from other edges

Identify $E_0$, energy of the maximum derivative of $\mu(E)$

Normalize $\mu(E)$ to go from 0 to 1

Remove a smooth post-edge background function to approximate $\mu_0(E)$

Isolate the EXAFS: $\chi(k)$

Fourier Transform to get real space pair-correlation function

Fit $k^2$ or $k^3$ –weighted $\chi(k)$ data to the EXAFS equation to get coordination environment
EXAFS Data Reduction Steps - I

Fitting of backgrounds

Isolation of XANES
EXAFS Data Reduction Steps - II

Experiment

Simulation
Although physically and theoretically XANES is not well understood, it is used as a fingerprint technique for determination of
1. Valence state
2. Phase identification
3. Coordination number/chemistry
4. Hybridization, band structure etc.
Nature of intermediate-range order in Ge-As sulfide glasses: A case study employing a combination of EXAFS, Neutron & x-ray scattering, SANS, RMC

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Background and Motivation

- Complex glasses with wide compositional range of glass formation
- Technologically important: passive and active photonic devices
- Model system for testing structure-property models based on average coordination numbers
Short-range order from Ge and As K-edge EXAFS

Ge K-edge EXAFS

$k^2 \chi(k)$

Wavenumber $k$ (angstrom $^{-1}$)

Radial Distance (angstrom)

Fourier Transform (arb. units)

FT

+57.1%
+6.1%
0.0%
-14.3%
-30.2%
-42.9%
-53.3%
-61.9%
-69.2%
Short-range order from Ge and As K-edge EXAFS

- Ge and As are always 4 and 3 coordinated
- As-As homopolar bonding takes up initial S-deficiency
- Ge takes part in homopolar bonding when all As is used up in As-As bonding

Sen et al. PRB, 64, 104202 (2001); JNCS, 293-295, 204 (2001).
How to study IRO?

• Compositional evolution of RDF in real space

• Behavior of First Sharp Diffraction Peak (FSDP) parameters

• Combine RMC simulation with diffraction to build large-scale structural models
Experimental Methods

• Sample synthesis
  – Ge-As-S glasses with Ge=As and 33.3 ≤ S ≤ 70.0
  – melting of constituent elements (≥99.9995% purity) in evacuated (10^{-6} Torr) fused silica ampoule at 1200 K for 24 h, quenched in water, annealed at Tg

• Neutron and high-energy x-ray diffraction
  – GLAD Diffractometer at IPNS
  – Sector 11-IDC at Advanced Photon Source, ANL (115.47 keV)
Why combine neutron & x-ray?

- structural interpretation of RDF for multi-component glasses becomes non-unique due to the convolution of a large number of pair-correlation functions

- neutrons and X-rays often weigh pair-correlations differently

- For example in stoichiometric and S-excess glasses the first peak at 2.24 Å in RDF corresponds to Ge-S and As-S correlations:
  \[ C^N = N \cdot W_{AsS} C_{As}(S) + N \cdot W_{GeS} C_{Ge}(S) \]
  \[ C^X = x \cdot W_{AsS} C_{As}(S) + x \cdot W_{GeS} C_{Ge}(S) \]
Neutron and x-ray structure factors
Neutron and x-ray RDFs

(a) 

N(r) 

0 1 2 3 4 5 6 7 8 

r (Å) 

~2.2 Å ~3.4 Å ~3.8 Å ~2.5 Å 

Ge\text{33.3A533.3S33.3} 
Ge\text{32.5A532.5S35} 
Ge\text{30A530S40} 
Ge\text{17.5A527.5S45} 
Ge\text{15A525S50} 
Ge\text{12.5A522.5S55} 
Ge\text{10A520S60} 
Ge\text{8A518S65} 
Ge\text{6A516S70} 
Ge\text{4A514S75} 
Ge\text{2A512S80} 
Ge\text{1A510S85} 
Ge\text{0A508S90} 

\( x = 33.3 \) 
\( x = 32.5 \) 
\( x = 30 \) 
\( x = 27.5 \) 
\( x = 25 \) 
\( x = 22.5 \) 
\( x = 20 \) 
\( x = 15 \) 
\( x = 12.5 \) 

UCDAVIS UNIVERSITY OF CALIFORNIA
Short-range atomic correlations

~2.2 Å : Ge-S and As-S nearest neighbors

~2.5 Å : Ge-Ge, As-As and Ge-As nearest neighbors

~3.4 Å : Ge/As – S – Ge/As next-nearest neighbors

~3.6 Å : S – S nearest neighbors

~3.8 Å : Ge/As – Ge/As – Ge/As next-nearest neighbors
FSDP parameters: intensity & position
FSDP parameters: intensity & position

Graph showing the relationship between Molar Volume (cm$^3$ mol$^{-1}$) and Atom % Ge (or As), x.
FSDP parameters: width
Small-angle neutron scattering

![Graph showing the relationship between \( S_N(0.2 \text{ Å}^{-1}) - S_N(0.5 \text{ Å}^{-1}) \) and Atom % Ge (or As), x.]
Nature of Intermediate-Range Order

- FSDP intensity shows reversal around $x=25$ where Ge starts participating in Ge-Ge/As bonding

- Metal-metal correlations in GeS$_2$ and As$_2$S$_3$ networks - Additional IRO from As-As correlations in As-rich clusters - increase in coherence length

- Strong density fluctuation from coexistence of heteropolar and homopolar bonded regions: increasing SAS

- For $x>25$: loss of GeS$_2$ network, structure dominated by metal-metal bonded network, decrease in SAS and coherence length
1. 1700-1800 atom simulation (box size ~ 3.6 nm)

2. Initial configuration was setup using short-range order constraints from EXAFS and diffraction

3. X-ray and neutron S(Q) were fitted simultaneously using the code RMCA

(McGreevy and Pusztai; J. Phys.: Cond. Matter 13, R877-R913, 2001)
Stoichiometric glass
S-deficient glass
Most S-deficient glass
New Techniques
(with a lot of future potential for glasses & liquids)

IXS & XPCS
Inelastic x-ray scattering

- Involves energy loss of x-ray photon associated with bound-state electronic transitions of core-level electrons
- Especially useful for low-Z atoms (e.g. B, C, Li) where absorption techniques are not practical due to low energies of absorption
- Use monochromatic high-energy x-ray and look at energy loss spectrum (sort of like the difference between IR and Raman spectroscopy)
- Can be done in resonance to get element-specific and amplify the effect (RIXS)
- More conventional application is in studying fast dynamics (ps), sound velocity, elastic properties (x-ray Brillouin spectroscopy)
Inelastic x-ray scattering

IXS of borate glasses: pressure effect on B coordination

Dynamics in Al₂O₃ liquid

IXS spectra at 1.8 meV resolution (APS 3-ID) from liquid aluminum oxide at 2323K

S.K. Lee et al. PRL, 2007

X-ray photon correlation spectroscopy

• PCS probes slow dynamics (mHz to MHz) by analyzing temporal correlation among scattered photons

• Visible light PCS is an important technique for studying the long wavelength dynamics in glass-forming liquids.

• XPCS offers unprecedented opportunity in probing slow dynamics at very short wavelengths: x-ray speckle spectroscopy
X-ray photon correlation spectroscopy

- XPCS study of suspended nanoparticles in a supercooled glass-forming liquid

- At $T >> T_g$ the particles undergo Brownian motion; measurements closer to glass transition ($T \sim 1.2 T_g$) indicate hyperdiffusive behavior

*Caronno, et al., PRL 100, 055702 (2008)*
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