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**
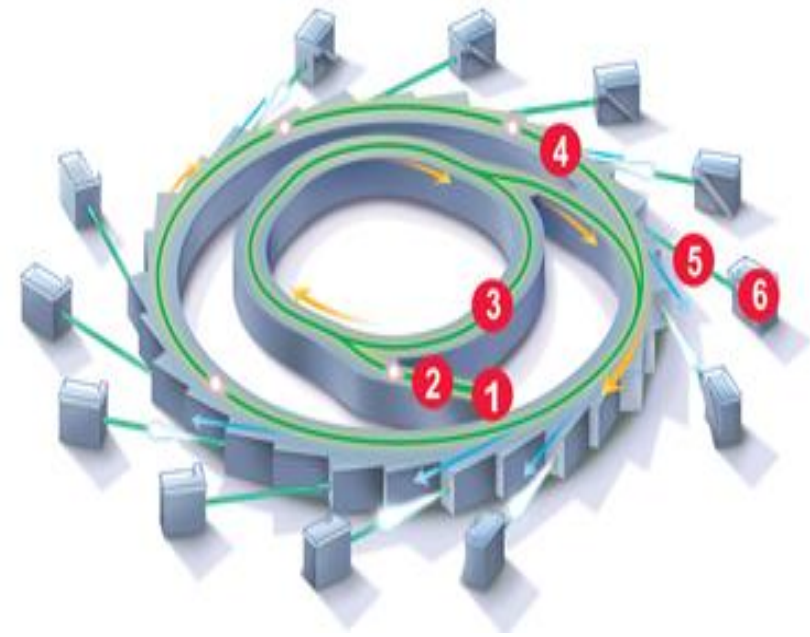
Why Synchrotron ?

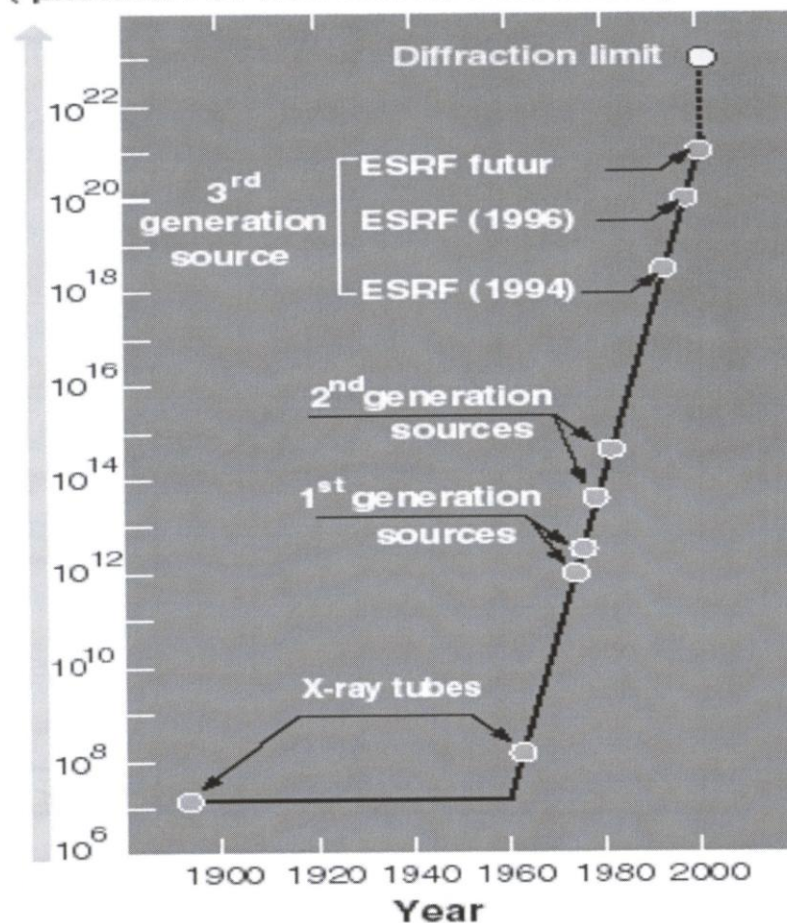## Brilliance / Intensity

Up to 12 orders of magnitude
Brighter than laboratory source

45 synchrotron sources
    worldwide

11 in the USA

SPRING8 in Japan is the
    brightest

Brilliance of the X-ray beams
(photons / s / mm^2 / mrad^2 / 0.1% BW)

Diffraction limit

10^{22}

3rd generation source — ESRF futur / ESRF (1996) / ESRF (1994)

10^{20}

10^{18}

10^{16}

2nd generation sources

10^{14}

1st generation sources

10^{12}

10^{10}

X-ray tubes

10^8

10^6

1900 1920 1940 1960 1980 2000
Year

Neutron Sources

- ## Reactor sources

Neutrons produced from fission of ^{235}U. Moderated to thermal energies (5 to 100 meV corresponding to wavelengths of 1 to 4 Å) e.g. with D_2O. These are continuous sources.

- ## Spallation sources

Proton acclerator 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 = 1.675×10^{-27} kg
- Charge = 0; spin = ½
- 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:

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

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

r_0 = 2.82 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

$$f(Q) = \int_0^\infty \rho_{(r)} e^{iQ.r} \, dr$$

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

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

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

b= nuclear scattering cross section (Q-independent !)

X-ray and Neutron scattering lengths
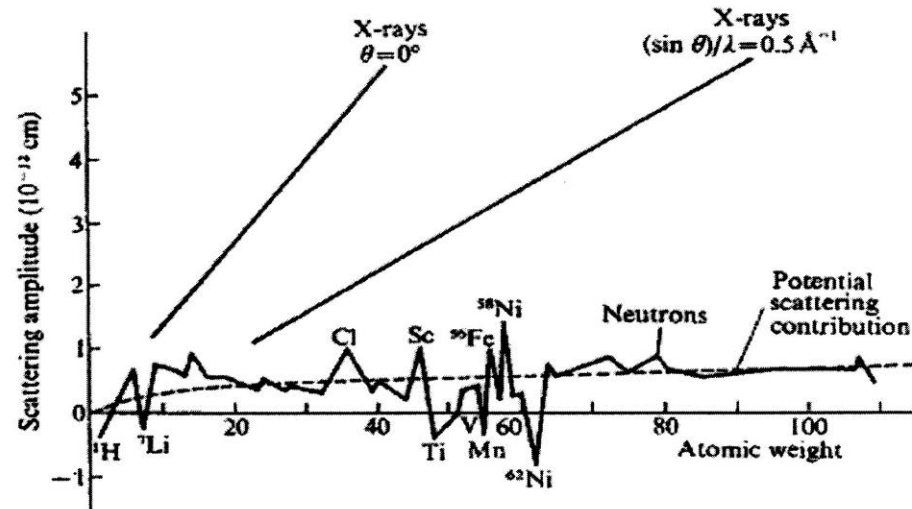
Figure 20. Coherent scattering lengths for x-rays ($r_e f$) and neutrons (b) as a function of atomic number. Note the dependence on $q \propto \sin\theta/\lambda_0$ for x-rays but not for neutrons. Figure after Bacon (1975).

X-ray and neutron form factor

◆ The form factor is related to the scattering density distribution in an atoms

- 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
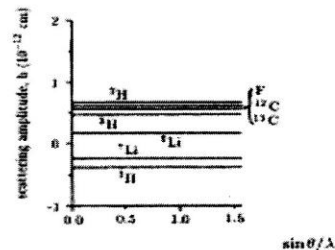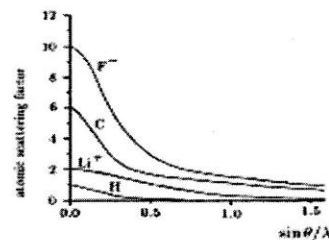
Theory of elastic scattering (contd.)

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.
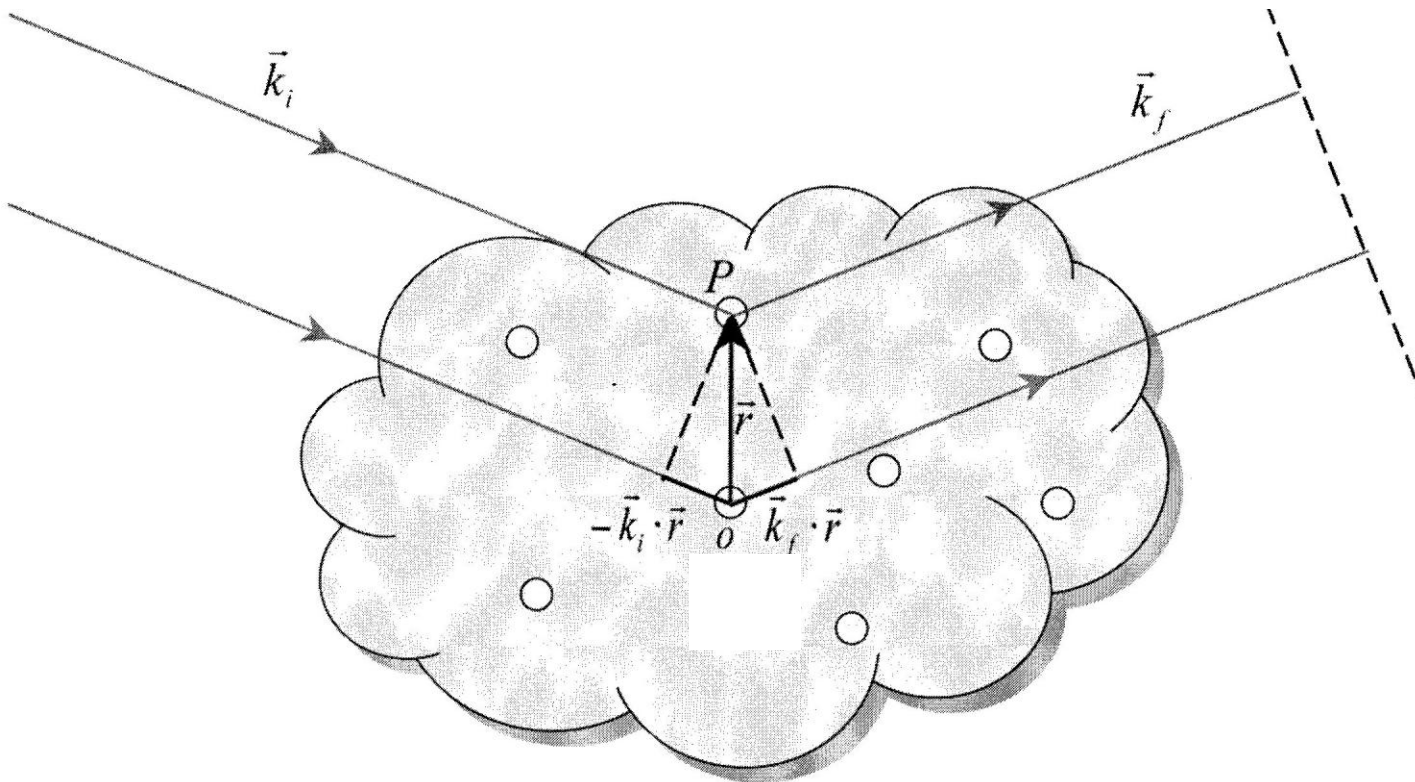
Theory of elastic scattering (contd.)

$$\frac{d\sigma}{d\Omega}(elastic) = \sum_{\alpha} \underbrace{c_{\alpha} f_{\alpha}^{2}(Q)}_{\text{Self}} + \underbrace{I_{x}(Q)}_{\text{Distinct}}$$

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):

$$S(Q) = V \int dr dr' e^{-iQ\cdot(r-r')} \underbrace{\left\langle \rho_{N}(r) \rho_{N}(r') \right\rangle}_{\text{positional correlation of atoms}}$$

Theory of elastic scattering (contd.)

Neutron

$$\frac{d\sigma}{d\Omega} = \frac{d\sigma}{d\Omega}_{self} + \frac{d\sigma}{d\Omega}_{Inelastic} + \frac{d\sigma}{d\Omega}_{distinct}$$

$$= \sum_{\alpha} c_{\alpha} b_{\alpha}^2 + P(\theta) + \boxed{F_N(Q)}$$

Self scattering

Distinct scattering

Inelastic scattering "Plazeck"

X-ray

$$\frac{d\sigma}{d\Omega} = \frac{d\sigma}{d\Omega}_{self} + \frac{d\sigma}{d\Omega}_{Compton} + \frac{d\sigma}{d\Omega}_{distinct}$$

$$= \sum_{\alpha} c_{\alpha} f_{\alpha}^{2}(Q) + C_X(Q) + \boxed{I_X(Q)}$$

Self scattering

Distinct scattering

Compton scattering

Theory of elastic scattering (contd.)

Static structure factor

Neutron Nuclear function

Distinct scattering

X-ray pseudo-nuclear function

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

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

De-convolute electron cloud

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

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

Coherent neutron scattering length

X-ray form factor

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Theory of elastic scattering (contd.)

Neutron

$$\frac{d\sigma_N}{d\Omega} = \sum_\alpha c_\alpha b_\alpha^2 + P(\theta) + F_N(Q)$$

$$\sum_\alpha c_\alpha b_\alpha^2$$

$$P(\theta) + \sum_\alpha c_\alpha b_\alpha^2$$
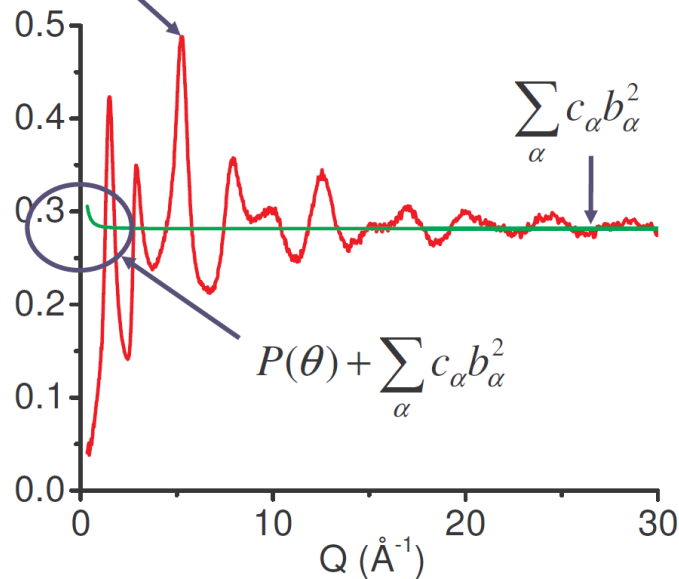
X-ray

$$\frac{d\sigma_X}{d\Omega} = \sum_\alpha c_\alpha f_\alpha^{\,2}(Q) + C_X(Q) + I_X(Q)$$

$$\sum_\alpha c_\alpha f_\alpha^{\,2}(Q) + C_X(Q)$$

$$C_X(Q)$$

Q (Å⁻¹)
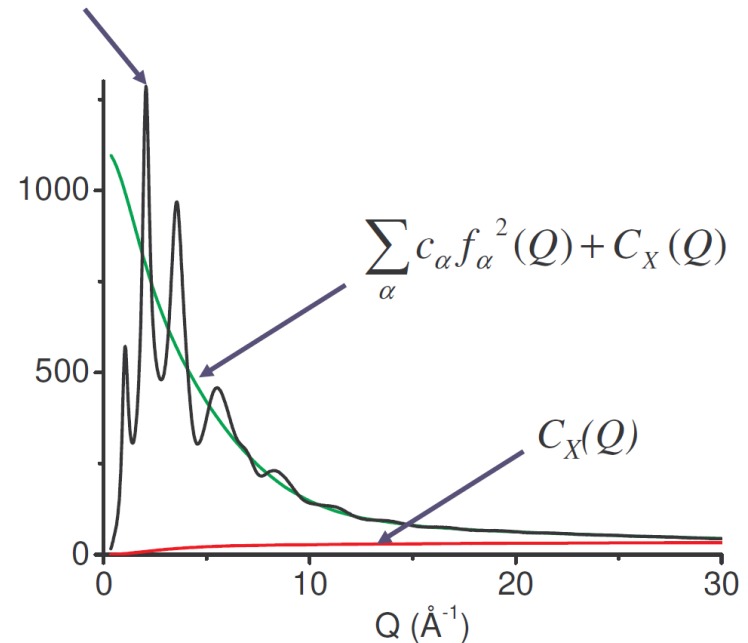
How to obtain G(r) from I(Q) ?

High energy X-ray diffraction corrections

HEXRD Technique developed in mid-1990's by J. Neuefeind and H. Poulsen 'Neutron like high energy Photon Diffraction'.

Detector slit

Incident beam slit

IS to S distance

incident beam polarized 91% in plane

2θ

SAMPLE

Si diode

Ge detector

S to DS distance

beam stop

Detector deadtime

$$I_c = I_0 \exp(-I_0 \tau)$$

Beam polarization

$$P = \frac{1}{F_{ver} + F_{hor} \cos^2(2\theta)}$$

Geometric correction

$$g_k = \left(\frac{[D_{SD}/\cos(2\theta_m)] - D_{SS}}{[D_{SD}/\cos(2\theta_m + 2\theta)] - D_{SS}} \right)^2$$
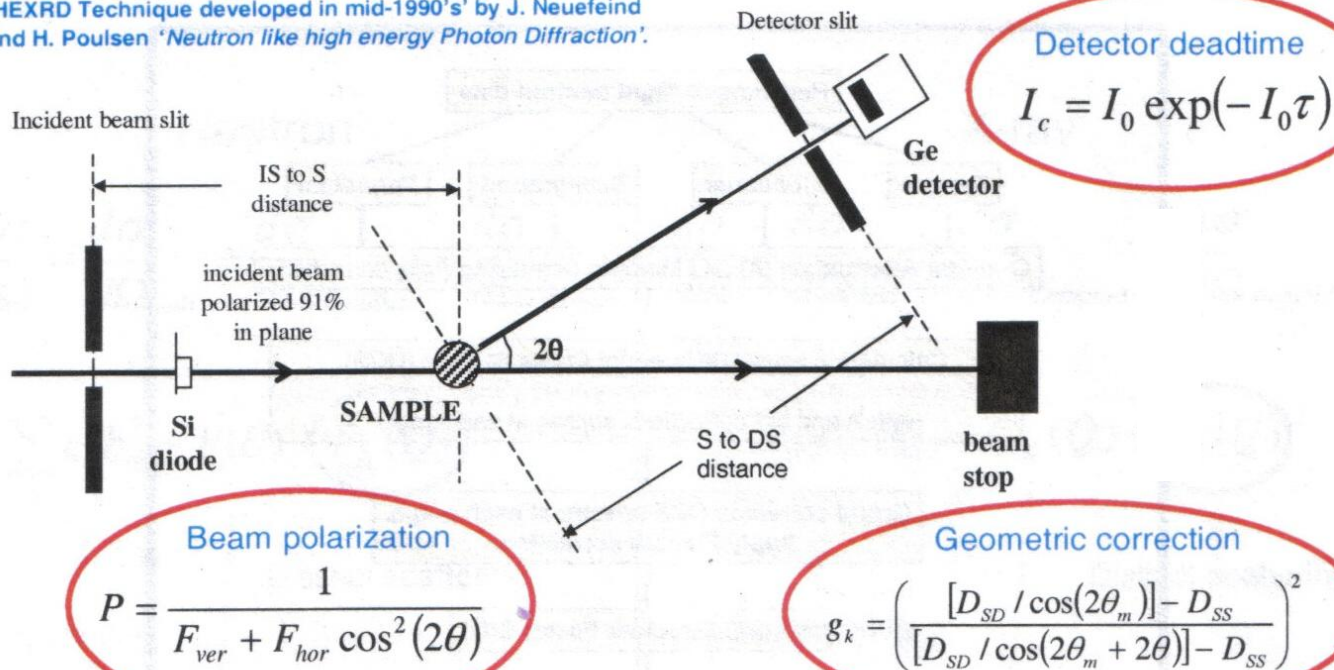
For conventional laboratory x-ray, attenuation and multiple scattering effects can be >30%.
At a high energy synchrotron X-ray instrument (~100KeV) these effects are only a few percent.

How to obtain DFs from I(Q) ?

Measured Diffraction Intensity
$I(Q) \rightarrow\rightarrow S(Q)$
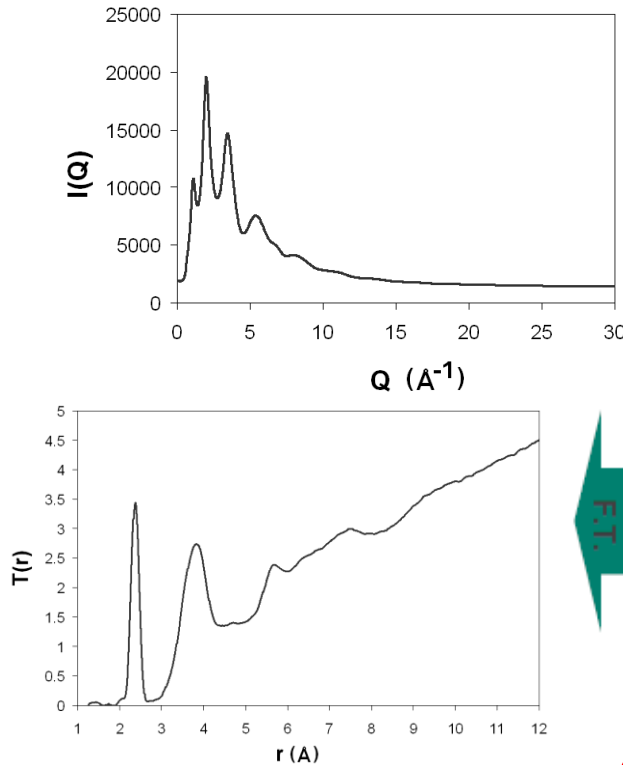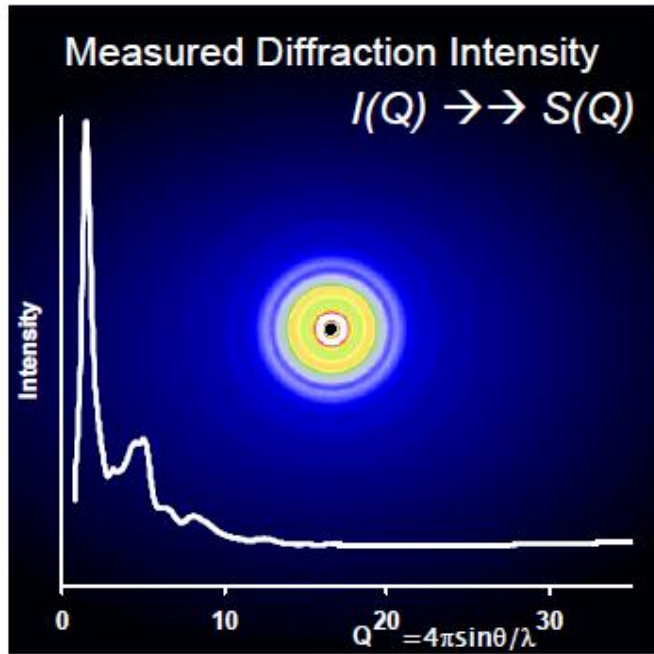
corrections
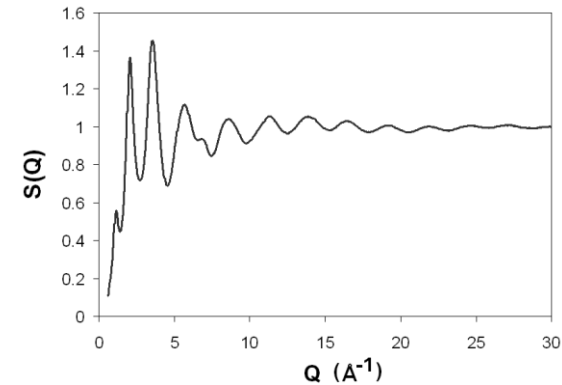
F.T.

F.T.
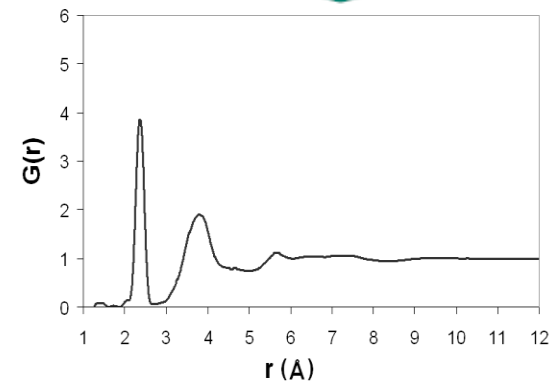
$$g(r) = 1 + \frac{1}{2\pi^2 \rho r} \int Q\, i(Q) M(Q) \sin(Qr)\, dQ$$

Fourier Transformation

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

Differential : $D(r) = [4\pi\rho r.g(r) - 1]$

Effect of cutoff on resolution
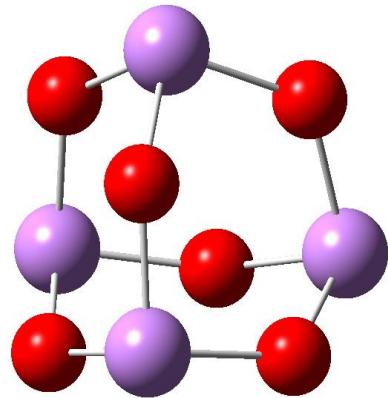
As_4O_6 molecule
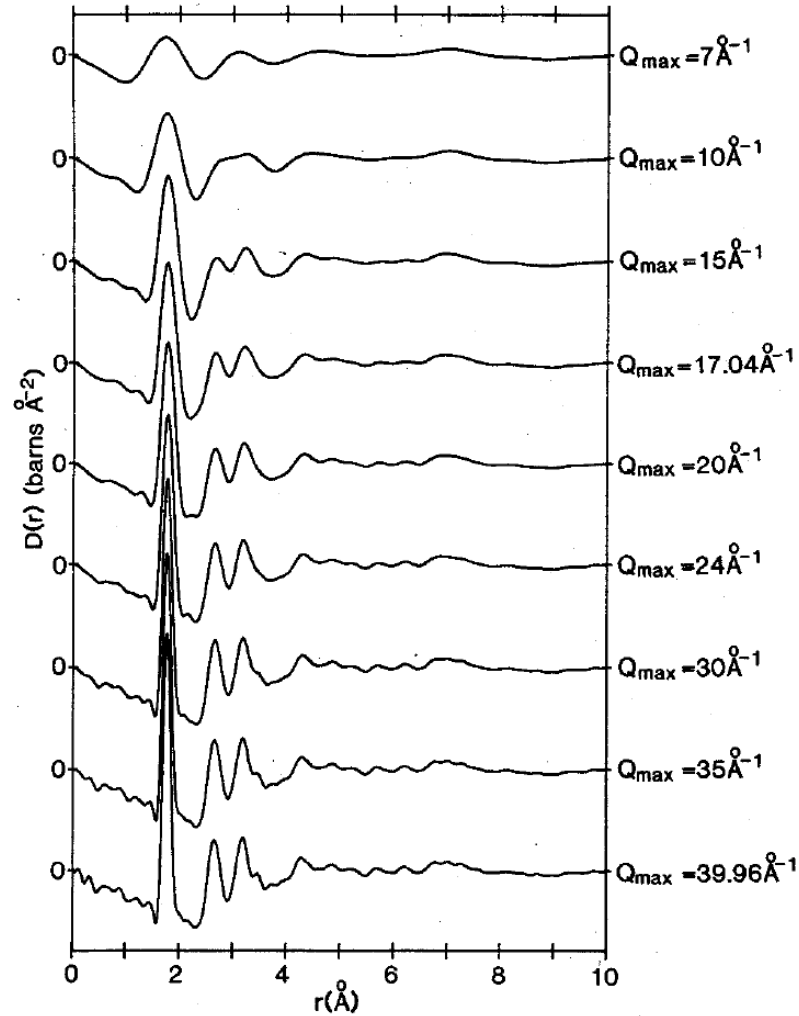
J. Non-Cryst. Sol 111 (1989) 123.

Physical meaning of RDF

First Coordination shell

Second Coordination shell

σ

$g(r)$

1.0

0   σ 2σ 3σ

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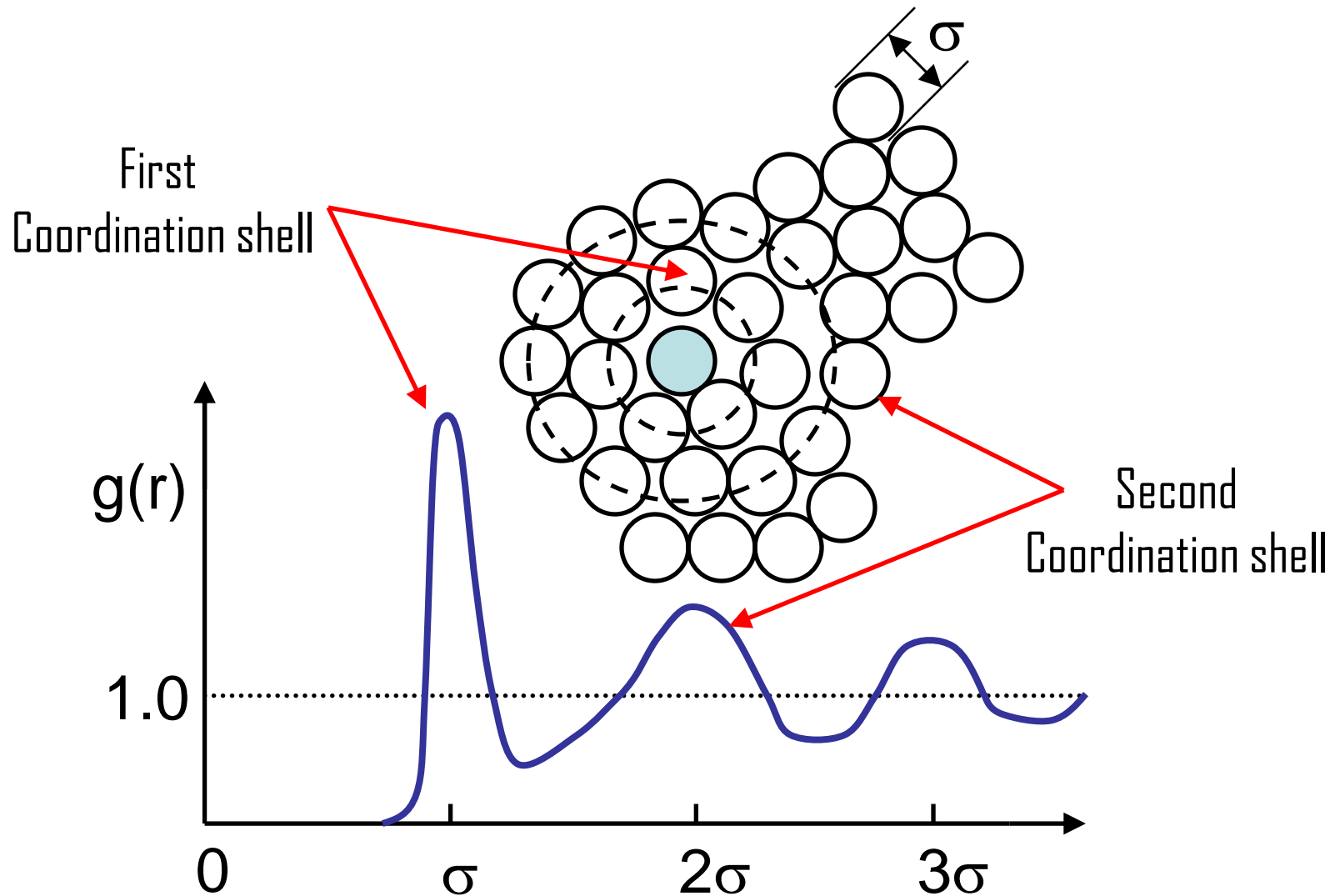
Types of Disorder
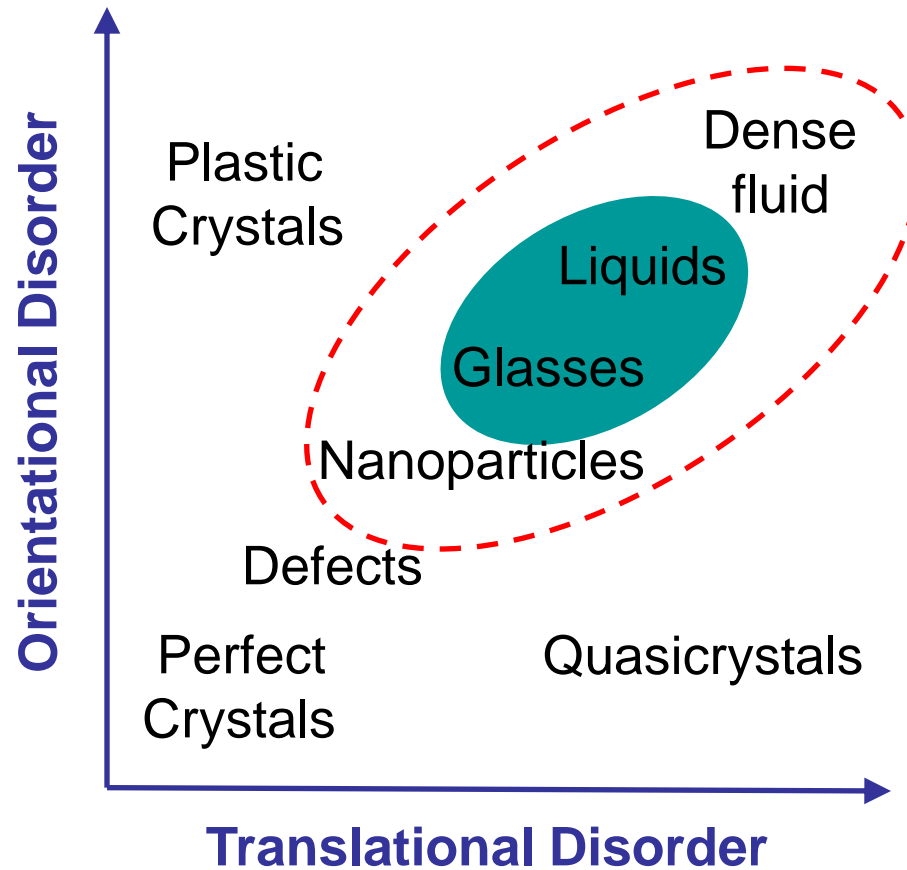
Glass structure at various length scales

Bond lengths and Coordination numbers
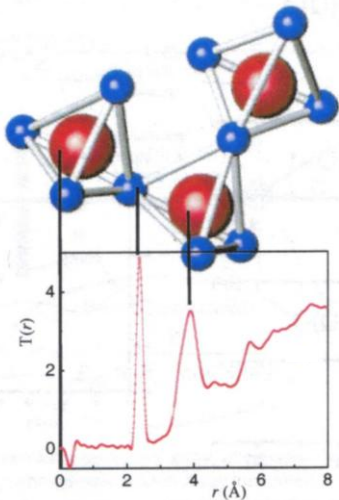
$$n_\beta^\alpha(r) = c_\alpha \int_{r_1}^{r_2} T_{\alpha\beta}(r) r \, dr$$
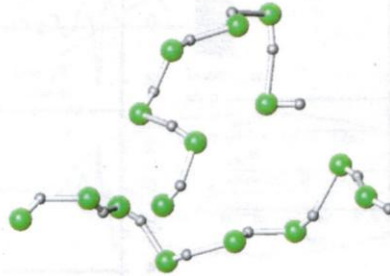
A formation of skydivers illustrates order on an intermediate length scale.

P.S. Salmon *Nature Materials* 1, 87–88 (2002)

Glass structure at various length scales

'First sharp diffraction peak'
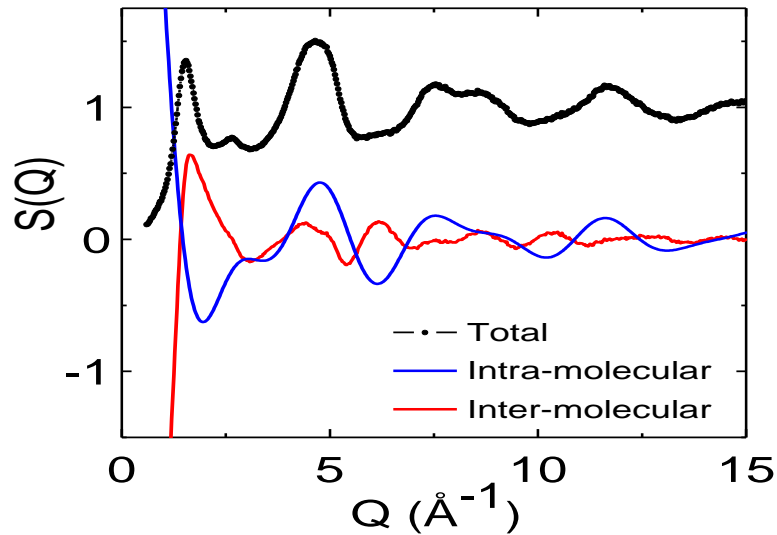
Sine Fourier
Transformation
$$S(Q) \rightarrow T(r) = 4\pi\rho r.g(r)$$
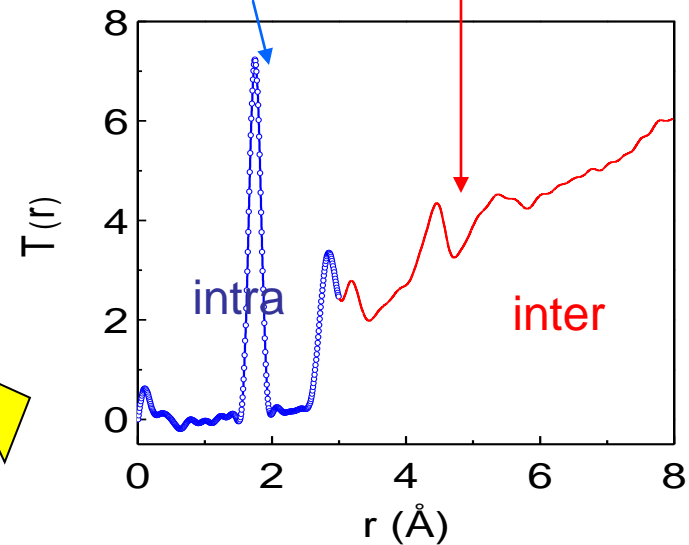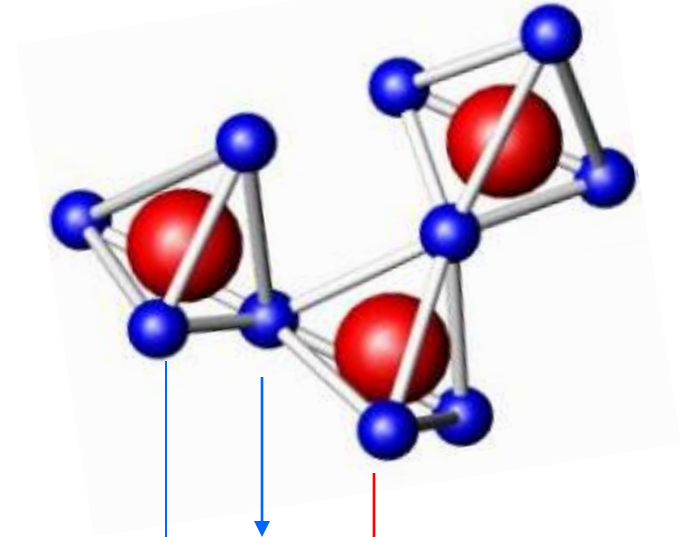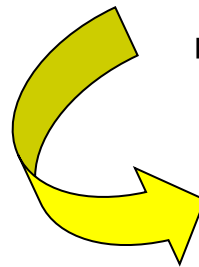
Intermediate-range order

A case study of molecular Ge-doped As-S glasses:
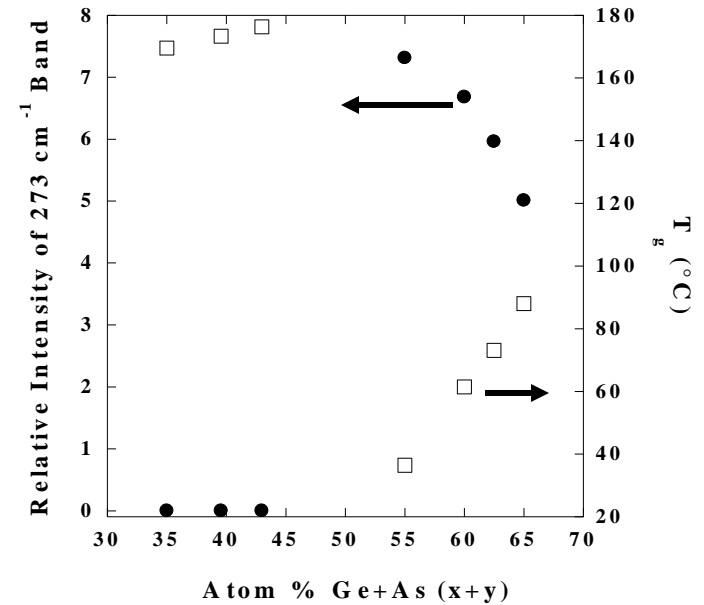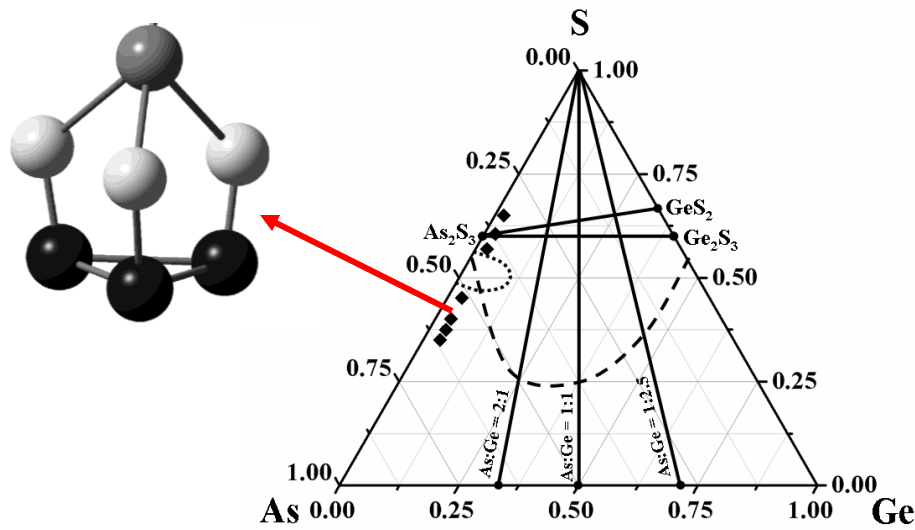
S. Soyer-Uzun et al. , 2009, JPC-C

Intermediate-range order-contd.

A case study of molecular Ge-doped As-S glasses:
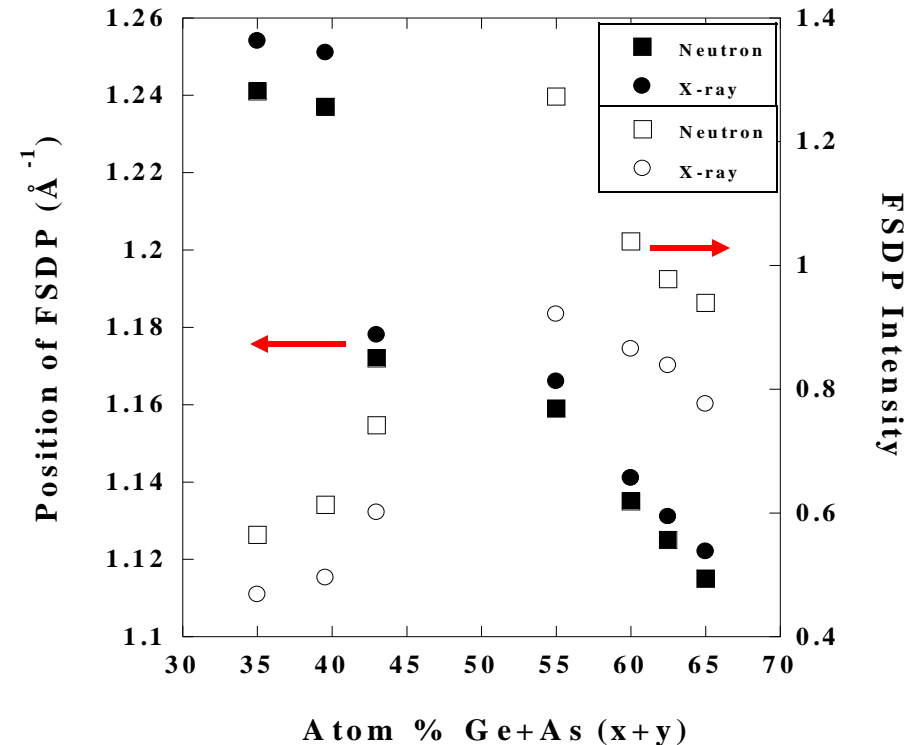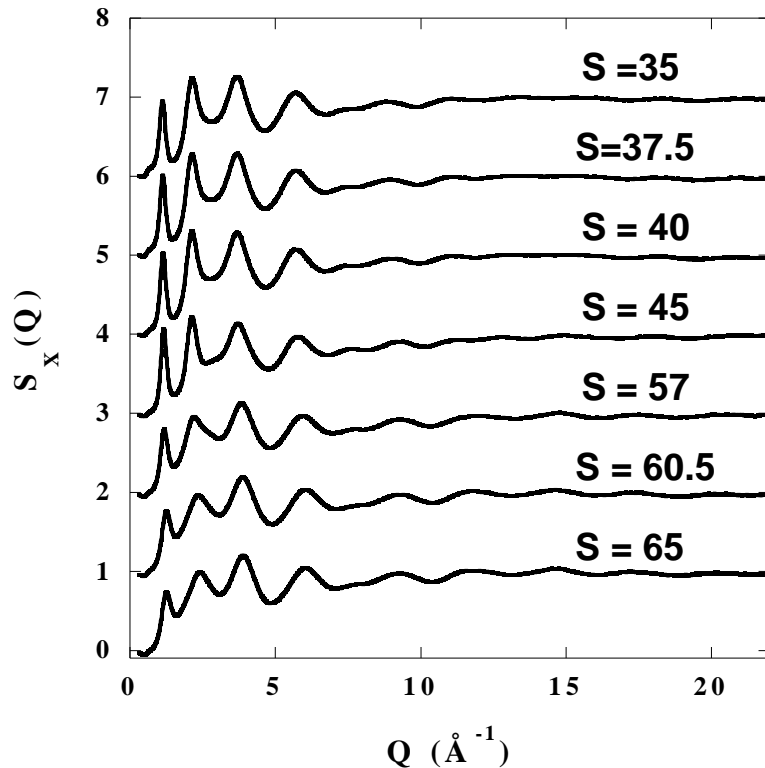
S. Soyer-Uzun et al. , 2009, JPC-C

Intermediate-range order-contd.

A case study of molecular Ge-doped As-S glasses:
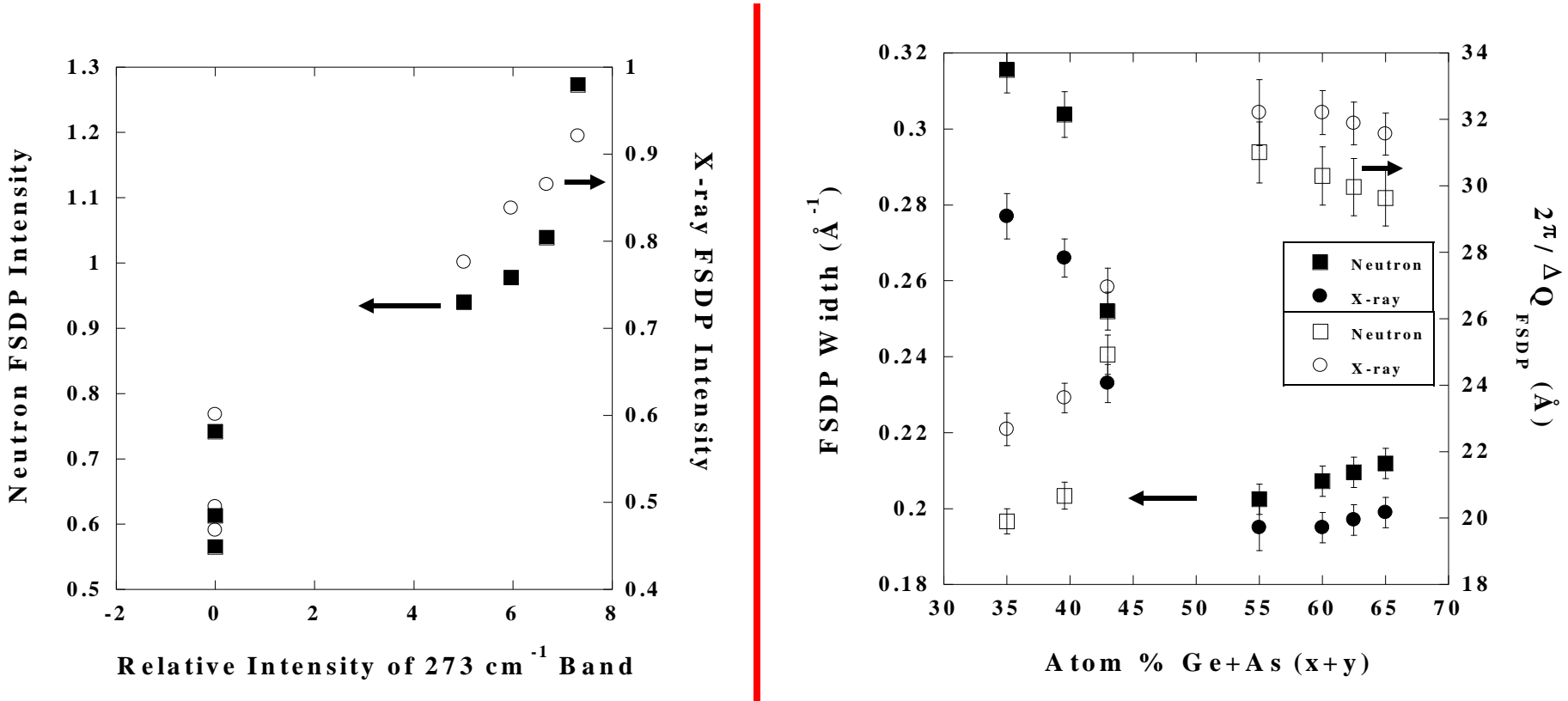
S. Soyer-Uzun et al. , 2009, JPC-C

Partial Pair Distribution Functions: The Holy Grail

Remember : $$S(Q) - 1 = \frac{1}{\left(\sum\limits_{\alpha} c_{\alpha} f_{\alpha}(Q) \right)^2} \sum\limits_{\alpha, \beta} c_{\alpha} f_{\alpha}(Q) c_{\beta} f_{\beta}(Q) \left[S_{\alpha\beta}(Q) - 1 \right]$$

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, $W_{\alpha\beta}(Q)$ | X | Partial Structure Factors, $S_{\alpha\beta}(Q)$ |

Neutron

X-ray

w_{OO}
w_{GeO}
w_{GeGe}

$W_{GeGe}(Q)$
$W_{GeO}(Q)$
$W_{OO}(Q)$

$S_{GeGe}(Q)-1$
$S_{GeO}(Q)-1$
$S_{OO}(Q)-1$

Vitreous Germania.
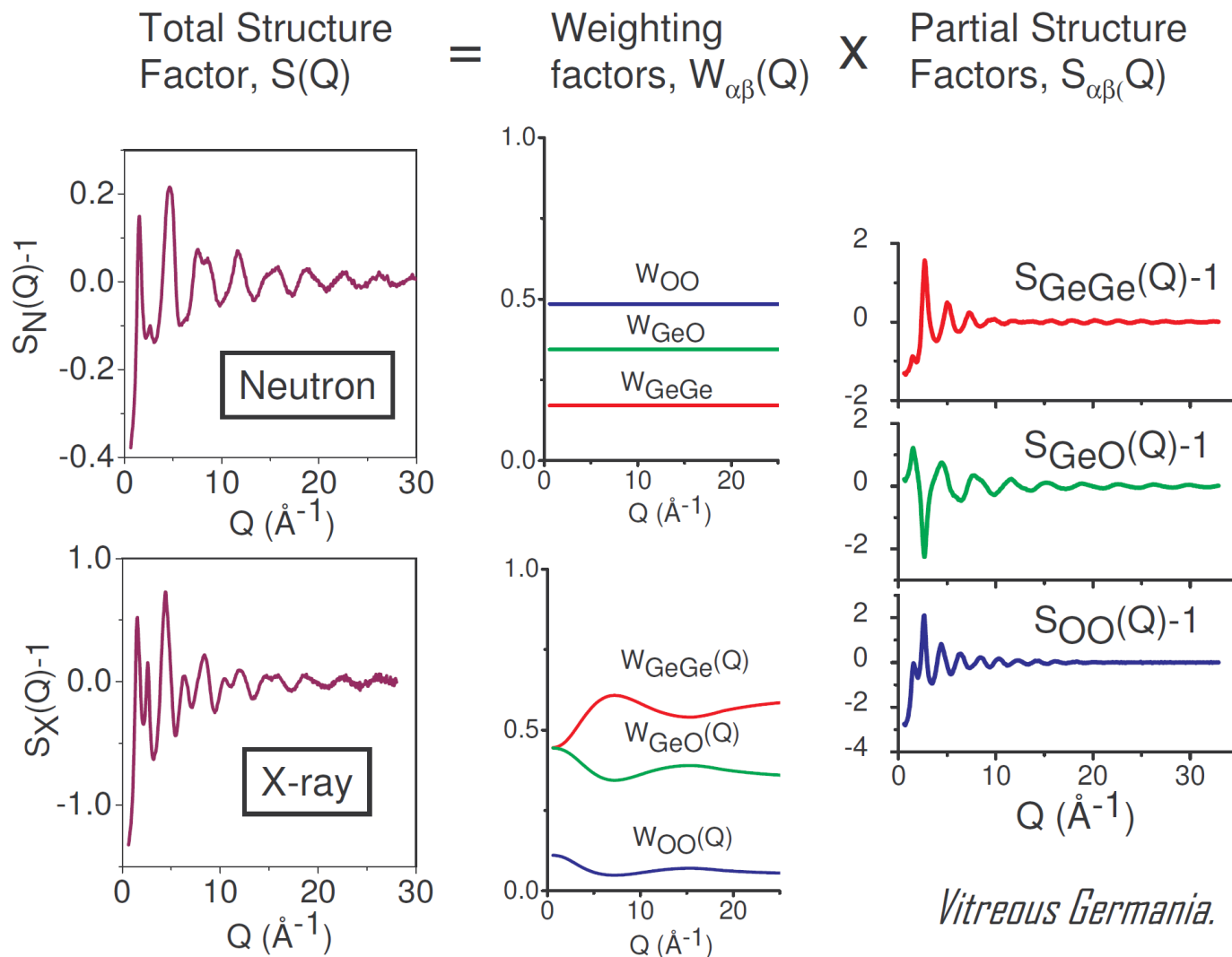
Partial Pair Distribution Functions: vitreous SiO_2

- Vitreous Silica

$g_{SiSi}(r)$

$g_{SiO}(r)$

$g_{OO}(r)$
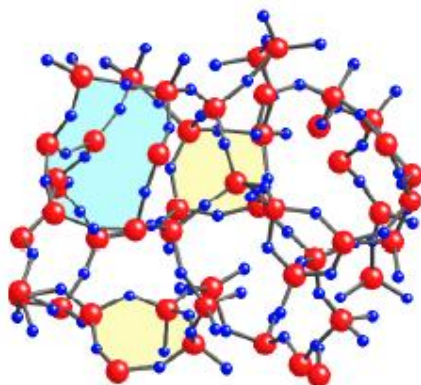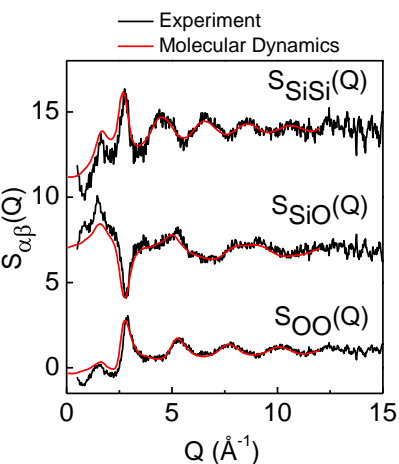
Courtesy of Shinji Kohara

Intermediate range order in vitreous silica from a partial structure factor analysis.
Q. Mei, C.J. Benmore, S. Sen, R. Sharma and J.L. Yarger. .PRB 78 (2008) 144204.
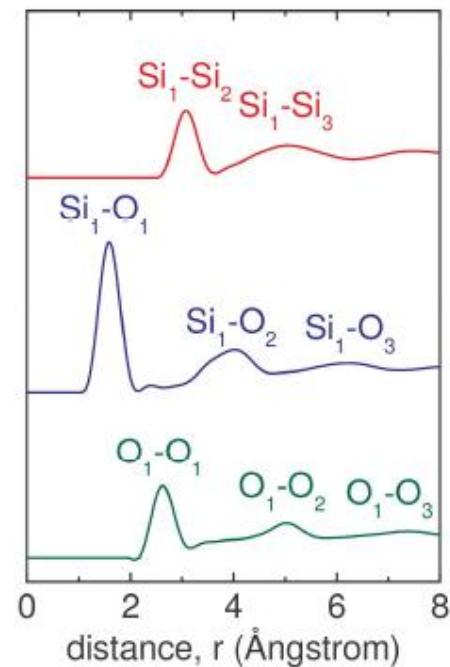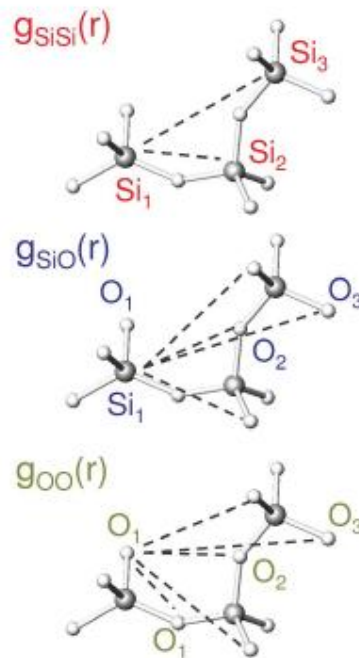
$$
\begin{bmatrix}
^{Nat}I_N(Q) \\
^{29}I_N(Q) \\
I_X(Q)
\end{bmatrix}
=
\begin{bmatrix}
c_{Si}^2 \, _{Nat}b_{Si}^2 & 2c_{Si}c_O \, _{Nat}b_{Si}b_O & c_O^2 b_O^2 \\
c_{Si}^2 \, _{29}b_{Si}^2 & 2c_{Si}c_O \, _{29}b_{Si}b_O & c_O^2 b_O^2 \\
c_{Si}^2 f_{Si}^2(Q) & 2c_{Si}c_O f_{Si}(Q)f_O(Q) & c_O^2 f_O^2(Q)
\end{bmatrix}
\cdot
\begin{bmatrix}
S_{SiSi}(Q)-1 \\
S_{SiO}(Q)-1 \\
S_{OO}(Q)-1
\end{bmatrix}
$$

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-Krönig Dispersion Relation

$$f'(E) = \frac{2}{\pi} \int_0^\infty \frac{f''(E')E'}{E^2 - E'^2} dE'$$

f''   E (keV)   *f'*   E (keV)
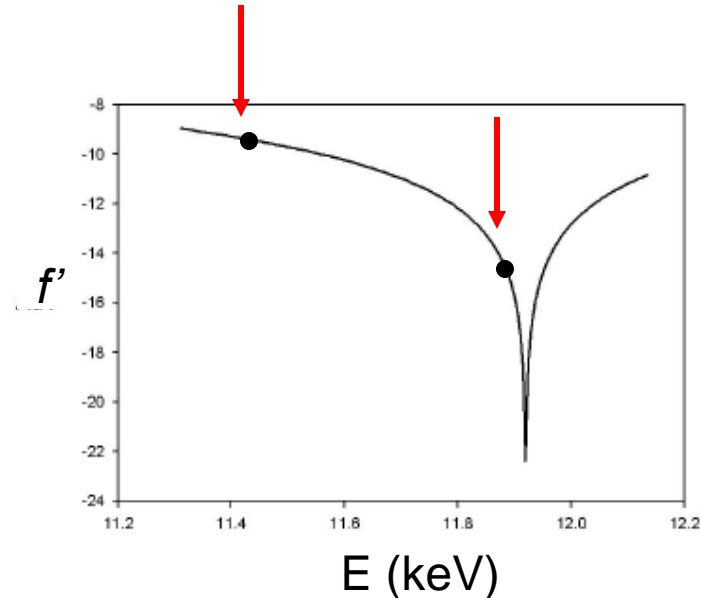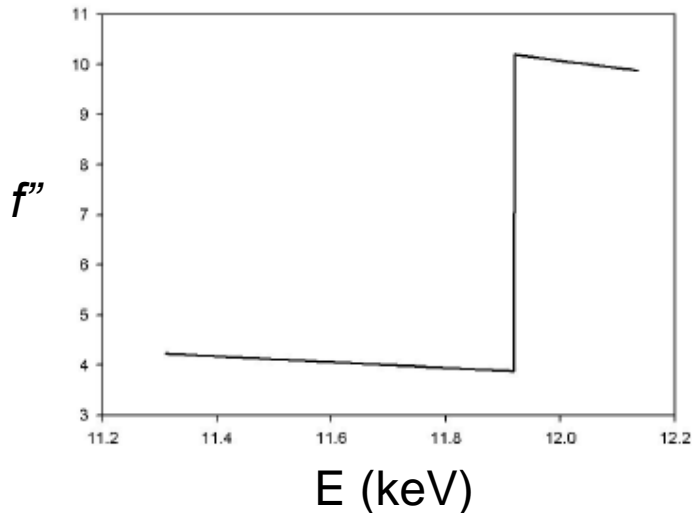
Anomalous x-ray scattering (AXS): contd.

- 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_2O-GeO_2 glasses
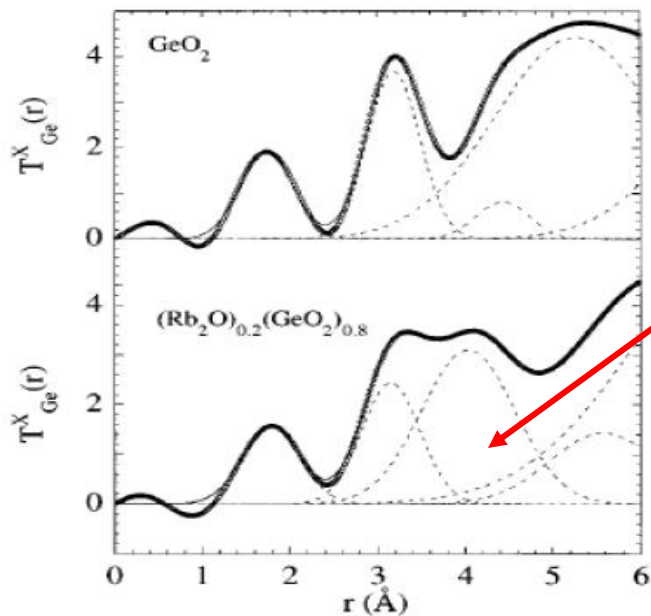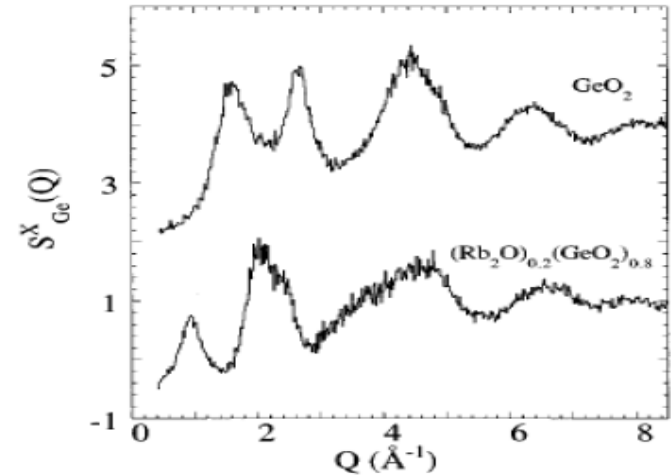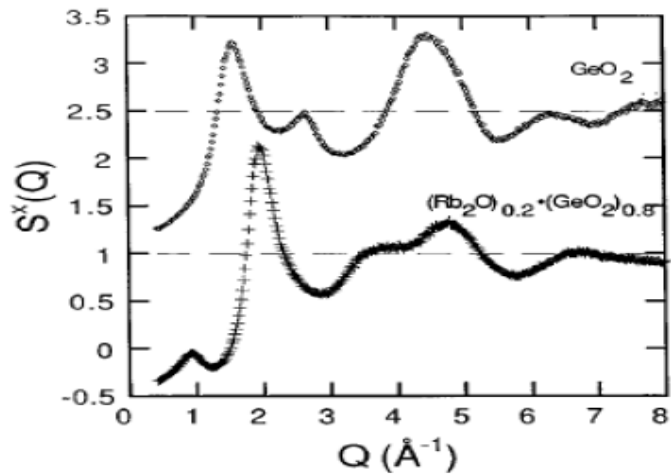
Ge-Rb third neighbor

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

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)
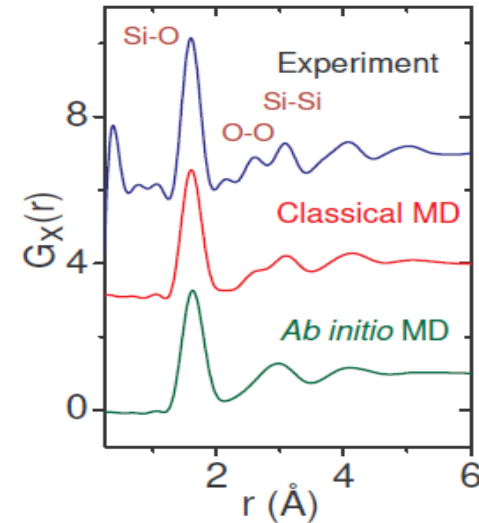
The structure of Liquid SiO_2
Q. Mei, C.J. Benmore and J. Weber. PRL 98 (2007) 057802.
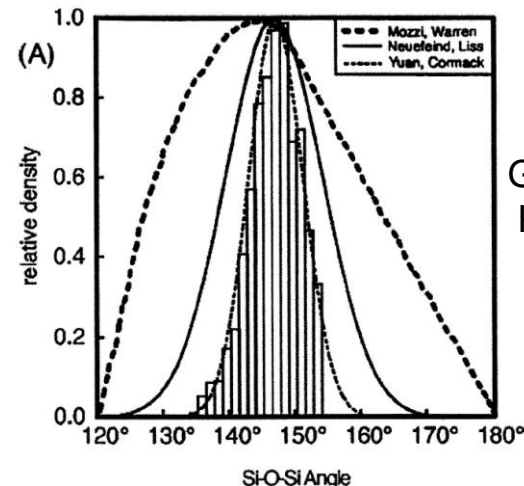
Grandinetti and coworkers
PRB, 70, 064202, 2004

Small-Angle X-ray Scattering (SAXS)

- X-rays (and neutrons) are also scattered at very small angles (0.001 to 0.5 $\mathring{A}^{-1}$) 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 $= \dfrac{d\sigma}{d\Omega}(Q) = (\rho_1 - \rho_2)^2 V_1^2 n P(Q) S(Q)$

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

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

ρ_1,ρ_2 = scattering length density of particle and matrix

P(Q) = form factor (intra-particle atomic arrangement)

S(Q)= structure factor (inter-particle correlations)

SAXS-Fundamentals: Contd.

Guinier (low Q) region, single particle scattering approximation holds $\quad I(Q) = I(0)e^{-R_{R_g}^2 Q^2/3}$

R_g= radius of gyration, related to overall particle dimension

- Looking at scattering in the low-Q regime, where $Q_{max}R_g \leq 1.0$
  The range can extend up to ≤ 1.2 to 1.3 for ellipsodal 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
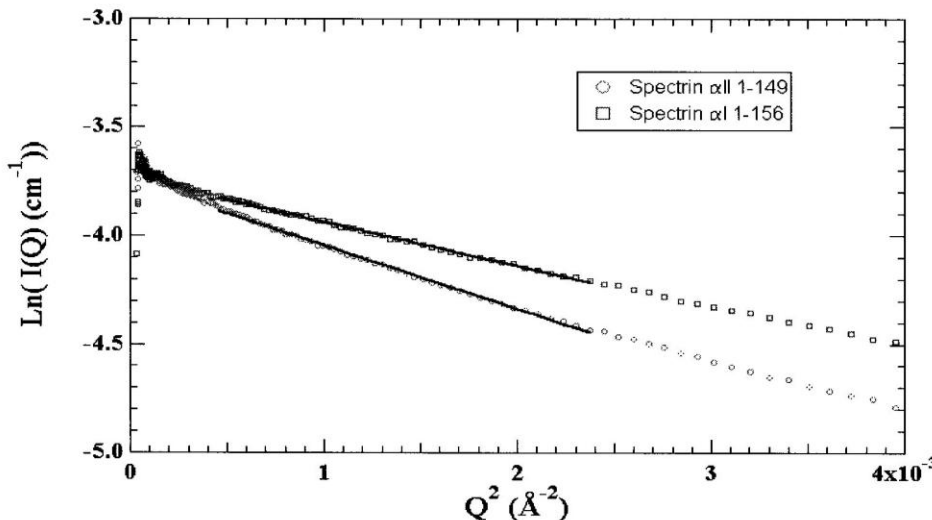
SAXS-Fundamentals: Contd.

Porod limit, large Q

$$Q \cdot R_g \gg 1$$

$$\lim_{Q \to \infty} I(Q) = 2\pi S_v \left| \Delta \rho^2 \right| Q^{-4}$$

Spherical particles:

$I(Q) \sim Q^{-4}$

Rod-shaped particles:

$I(Q) \sim Q^{-1}$

Disk-shaped particles:

$I(Q) \sim Q^{-2}$

Sphere (a/b=1)
Rod (a/b=30)
Disk (a/b=1/30)
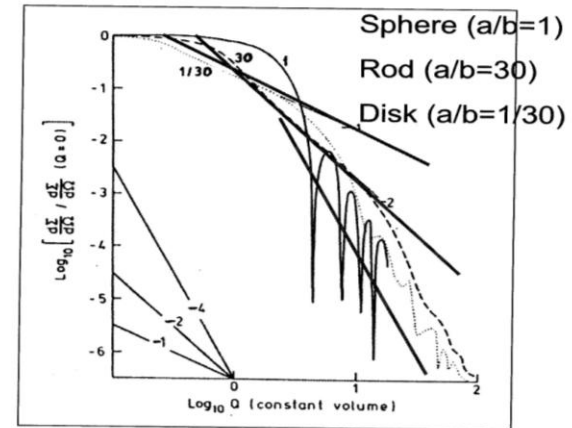
C. Windsor, *J. Appl. Cryst.* (1987)

Guinier

bulk dimensionality
2<p,3

Porod

interface
roughness/overlap
3.5<p<4.5

$$I(Q) = K_1 + \frac{K_2}{Q^p} \quad Q > \frac{1}{R_g}$$

16
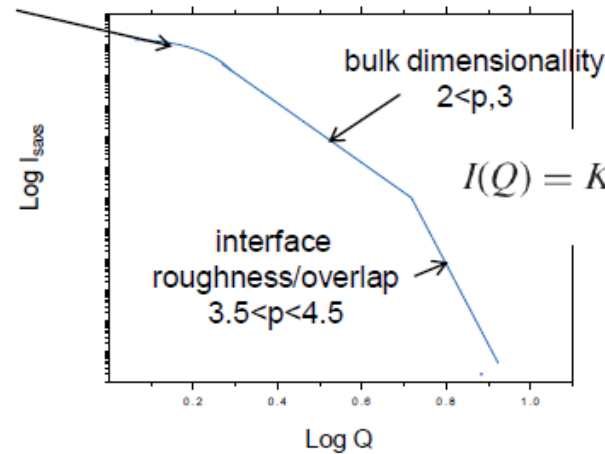
Hierarchical structures-many length scales

Schaefer, U. Cinn
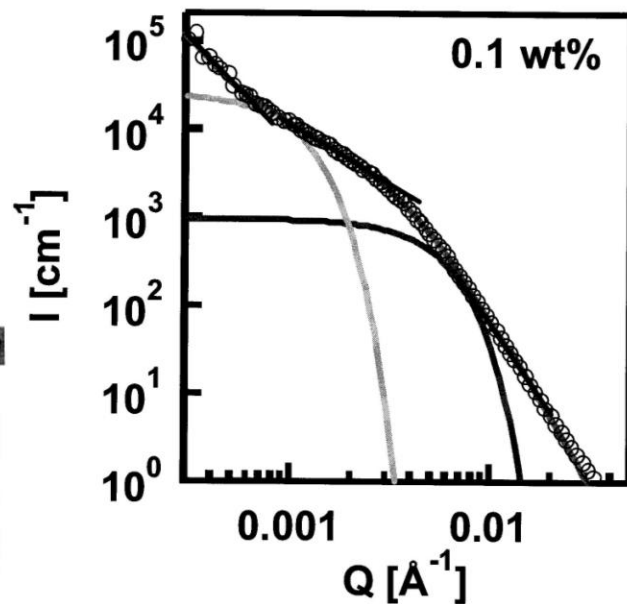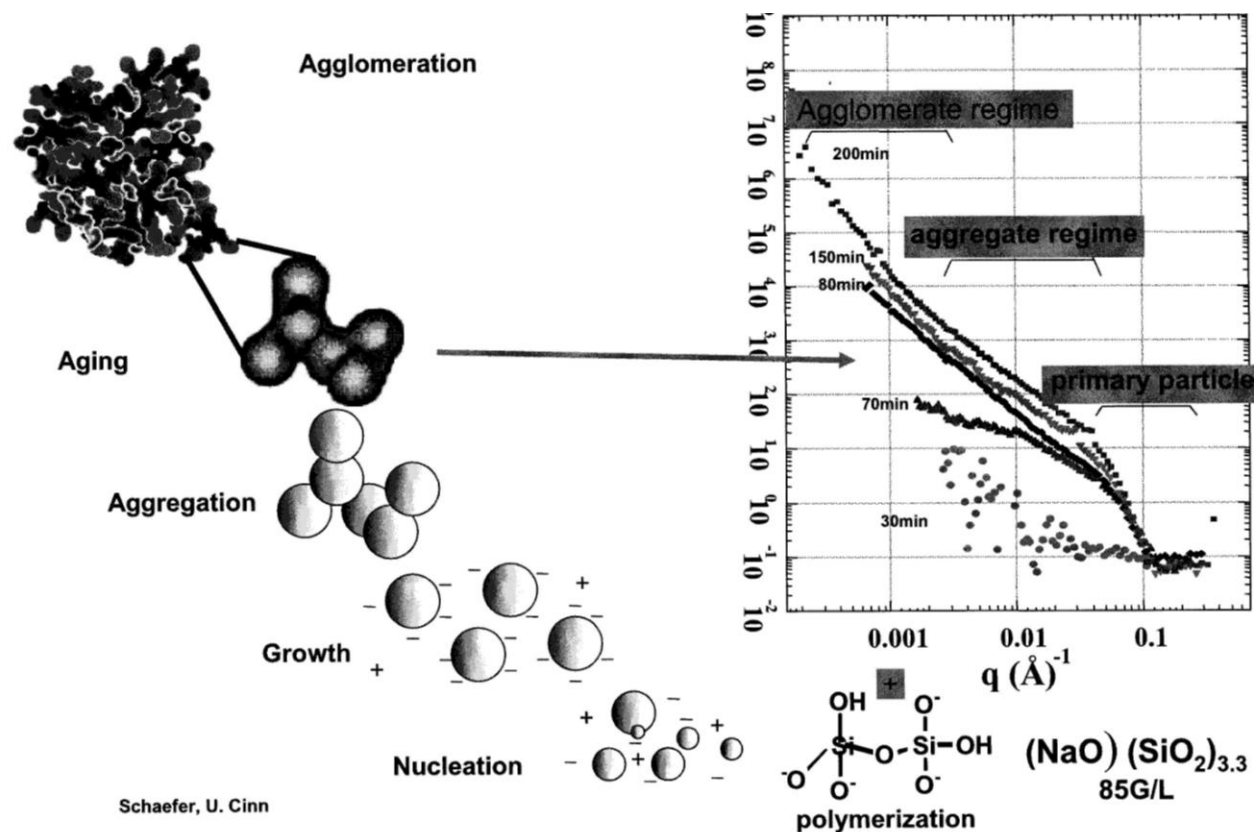
Bimodal size distribution

G. Beaucage, J.Appl. Cryst., 28, 717, 1995

SAXS Invariant
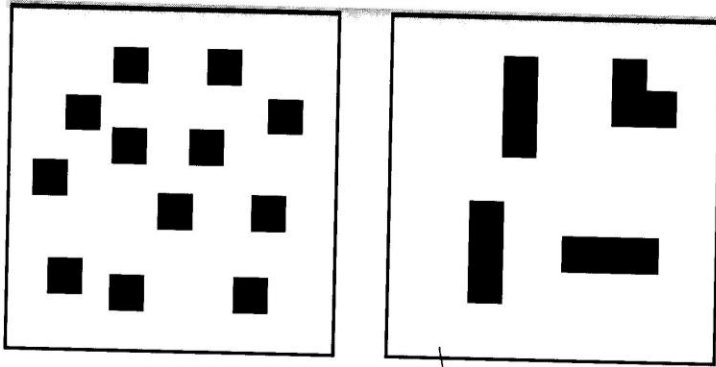
Direct measure of mean square fluctuation of electron (SAXS) or nuclear density (SANS)

The scattered intensity from above systems are different

For an incompressible two-phase system

$$\int_0^\infty Q^2 I(Q)\, dQ = 2\pi^2 V_V \left(1 - V_V\right)|\Delta\rho|^2$$

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

Guinier and Fournet, pp. 75 - 81

SAXS Invariant: Contd.

- S/V = specific surface area of sample

$$\frac{S_A}{V_A} > \frac{S_b}{V_B}$$

$$\lim_{Q \to \infty} I(Q) = 2\pi\, S_V\, |\varDelta\rho|^2\, Q^{-4}$$
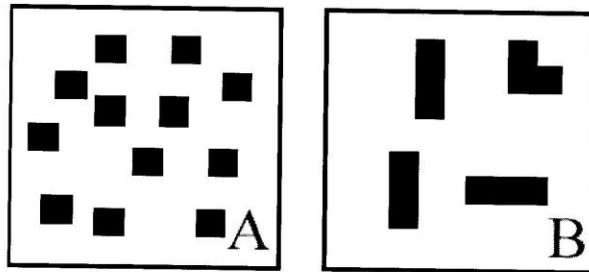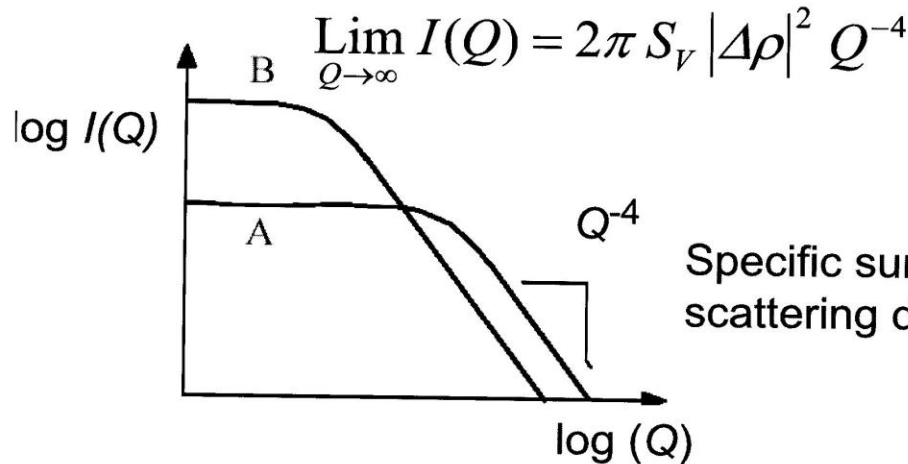
$$\frac{S}{V} = \frac{\pi \cdot \lim I(Q) \cdot Q^4}{\int I(Q) Q^2 dQ}$$

Specific surface area can be determined from scattering data even without absolute scaling

SAXS – Form Factor

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:

$$I(Q) = |\Delta\rho|^2 \, |\int dr \, e^{-iQ \cdot r}|^2 = |\Delta\rho|^2 \, |F(Q)|^2$$

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

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

$$F(Q) = 3\left[\frac{\sin(QR) - QR\cos(QR)}{(QR)^3}\right]$$
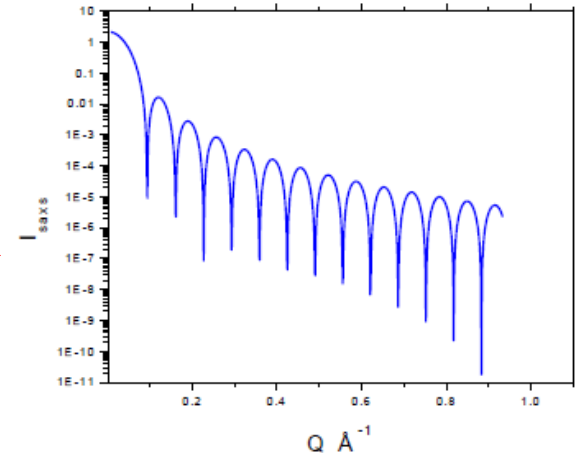
Alkali silicate glasses- density and concentration fluctuations
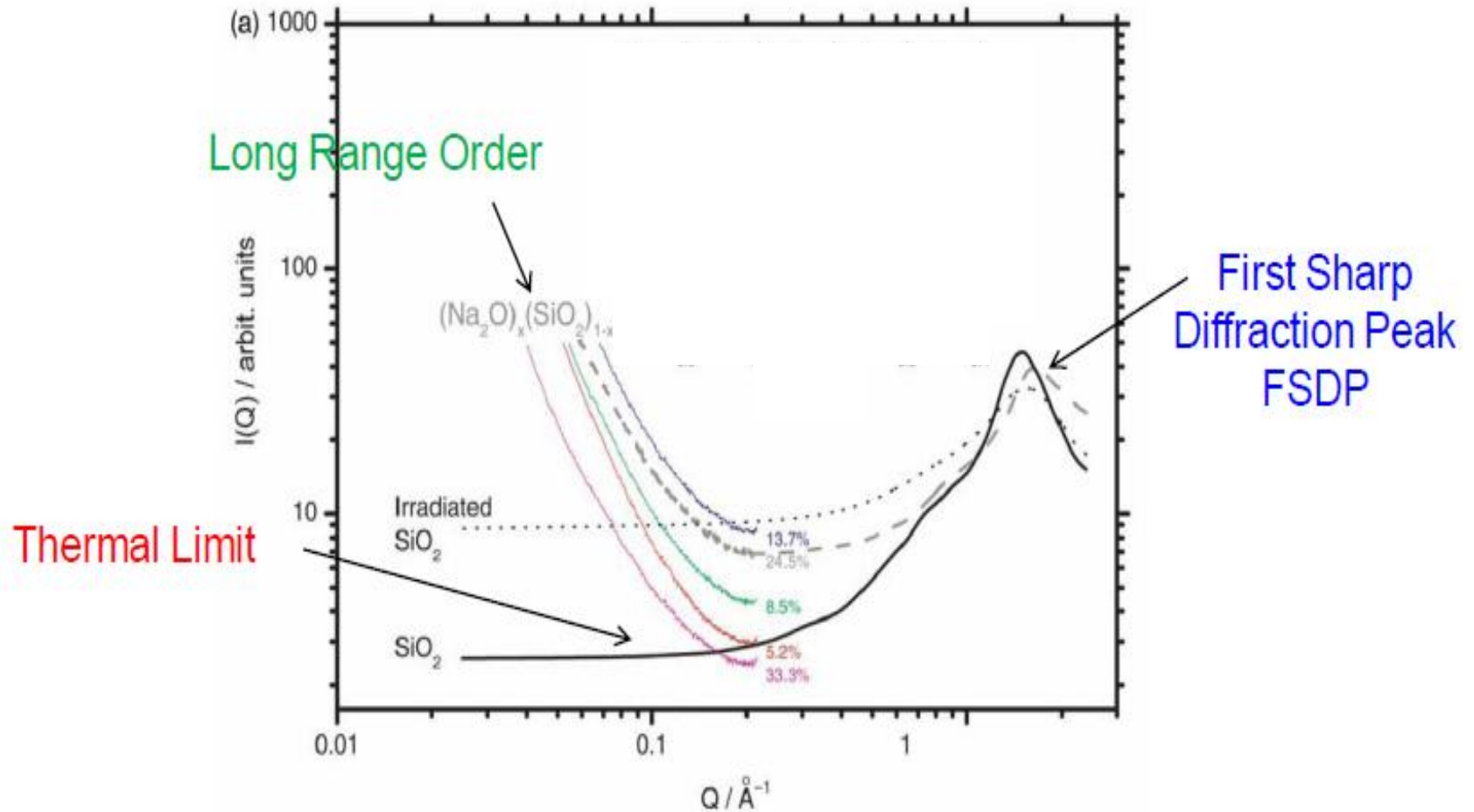
G.N. Greaves and S. Sen, Adv. Phys., 56, 1, 2007

Alkali Percolation Network Dimensionality

modified random network

SAXS and dimensionality and ionic diffusion

$(Na_2O)_x(SiO_2)_{1-x}$

G.N. Greaves and S. Sen, Adv. Phys., 56, 1, 2007
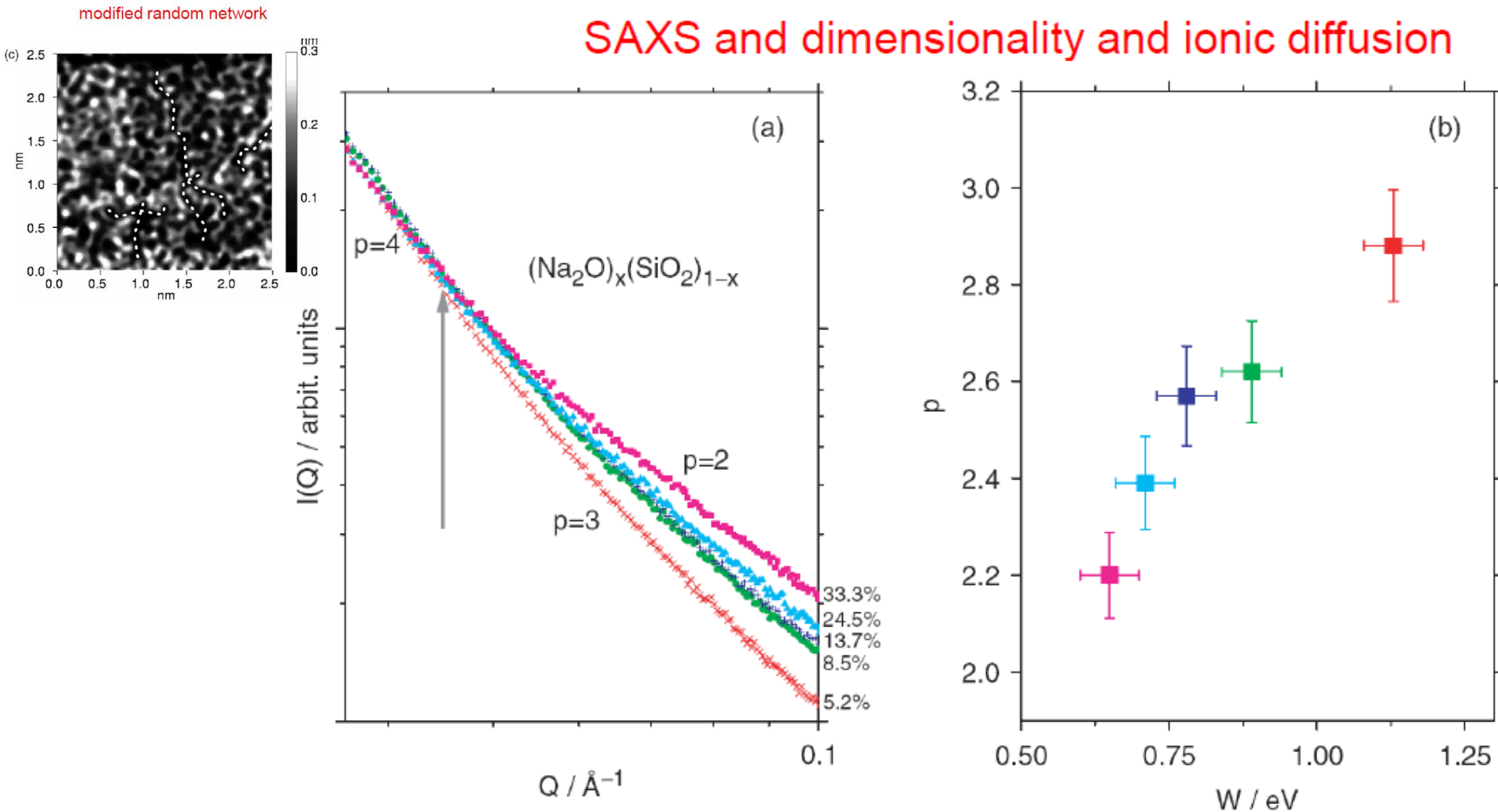
Long range fluctuation near glass transition: OTP

Ornstein-Zernike approximation

H.E. Stanley, Introduction to phase transitions and critical phenomena, Oxford University press Oxford, 1971

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

ξ correlation length

$\xi = 86$ nm
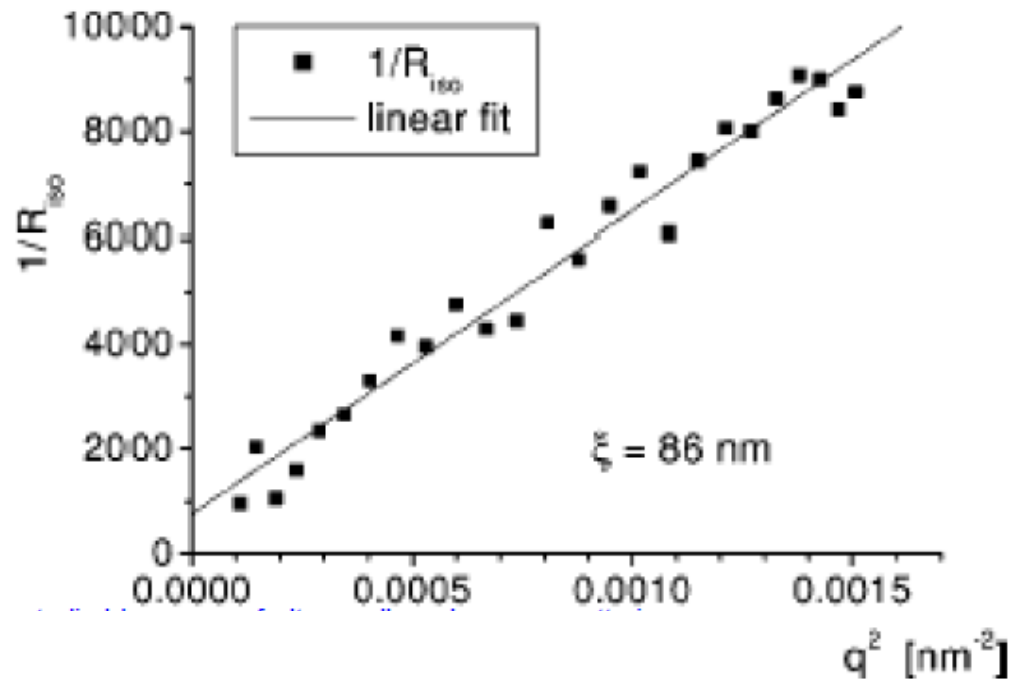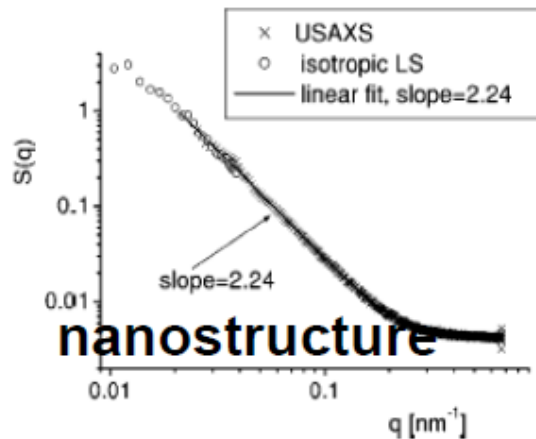
A. Patkowski et al., PRE, 61, 6909, 2000

X-ray Absorption Spectroscopy

EXAFS & XANES

X-ray Absorption Process

Beer's Law: $I = I_0 e^{-\mu t}$ μ is absorption coefficient

At most x-ray energies μ is a smooth function of x-ray energy E

$$\mu = \frac{\rho Z^4}{A E^3}$$ ρ : density, Z : atomic number, A : atomic mass
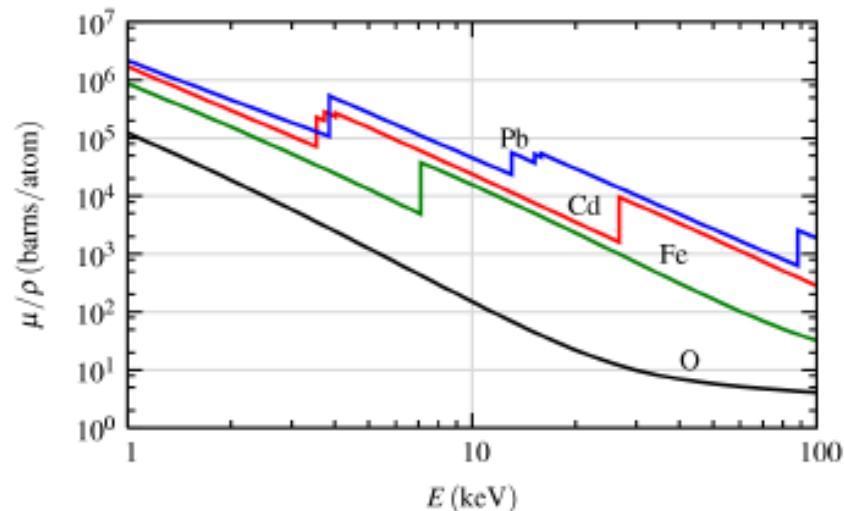
X-ray Photoelectric effect

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
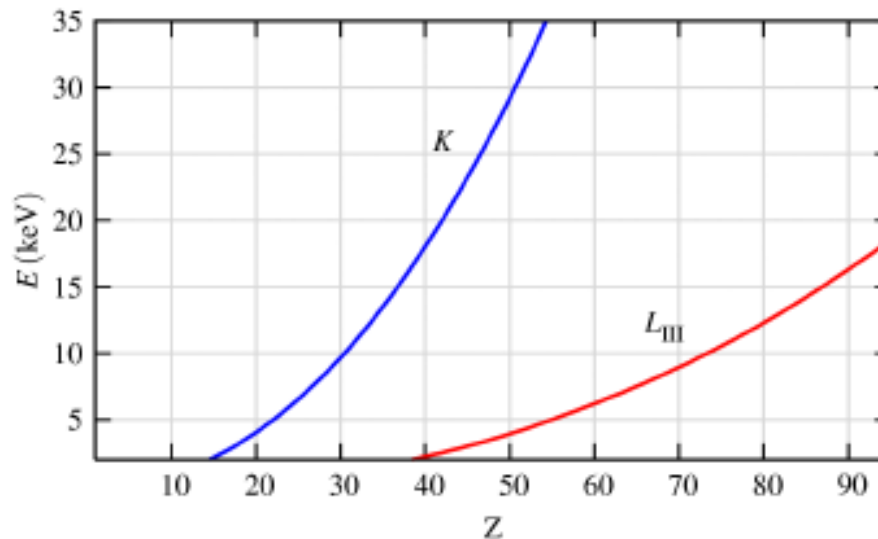
X-ray Photoelectric effect: Contd.

A few fs later
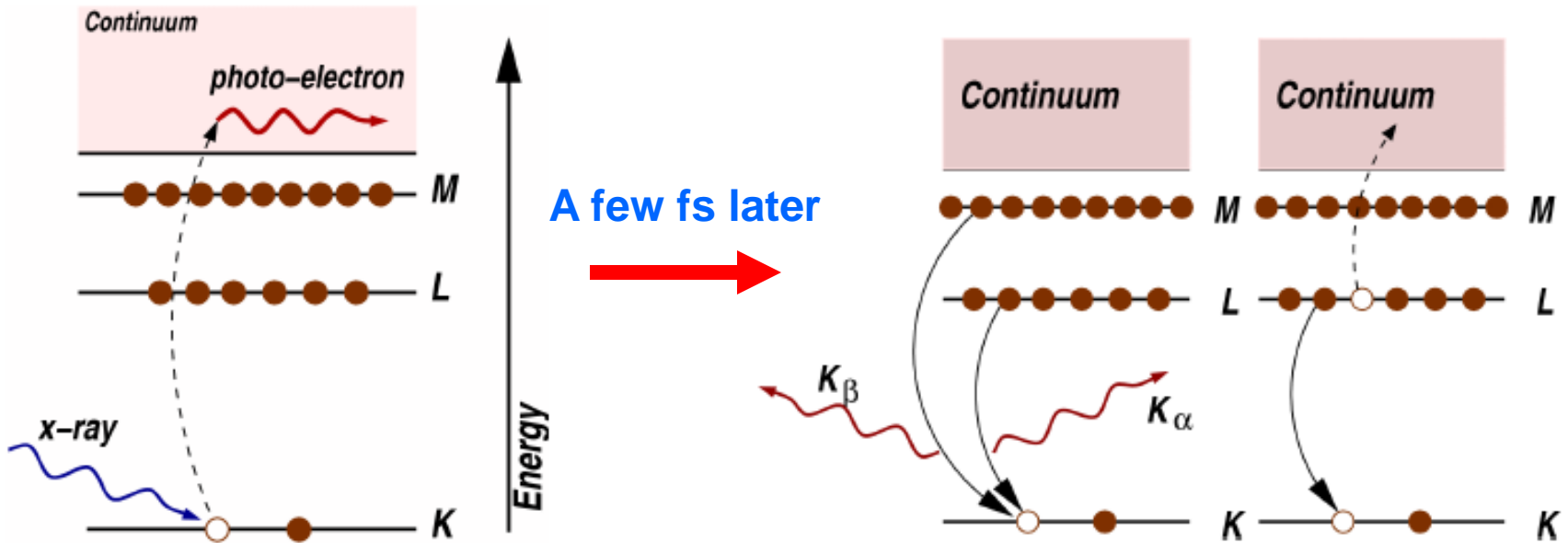
X-ray photon is absorbed by a core-level electron which is excited to an unoccupied

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 $\mu_{(E)} \propto \left| \left\langle i \left| \mathrm{H} \right| f \right\rangle \right|^2$

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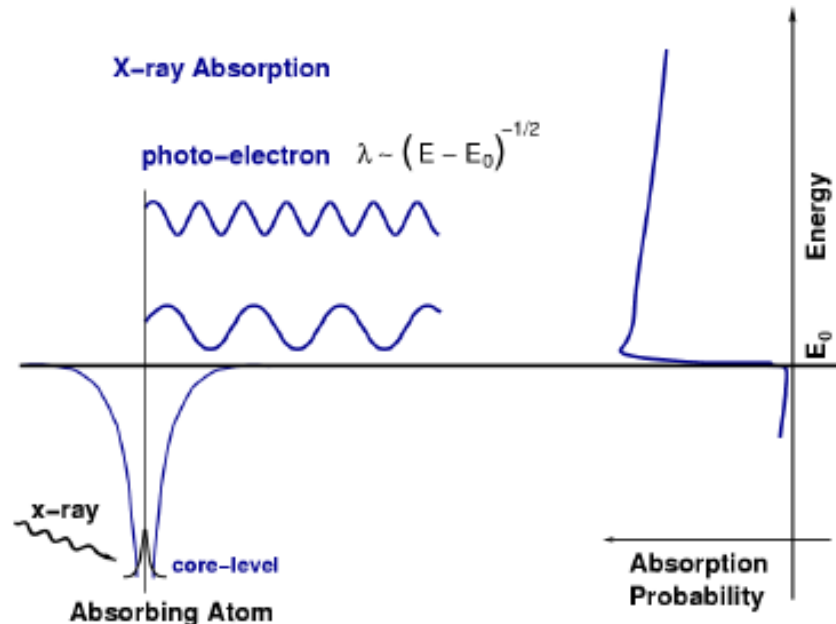
Effect of neighboring atoms

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

μ(E) depends on density of final states at energy E-E$_0$ that is modulated by the interference at the absorbing atom: EXAFS
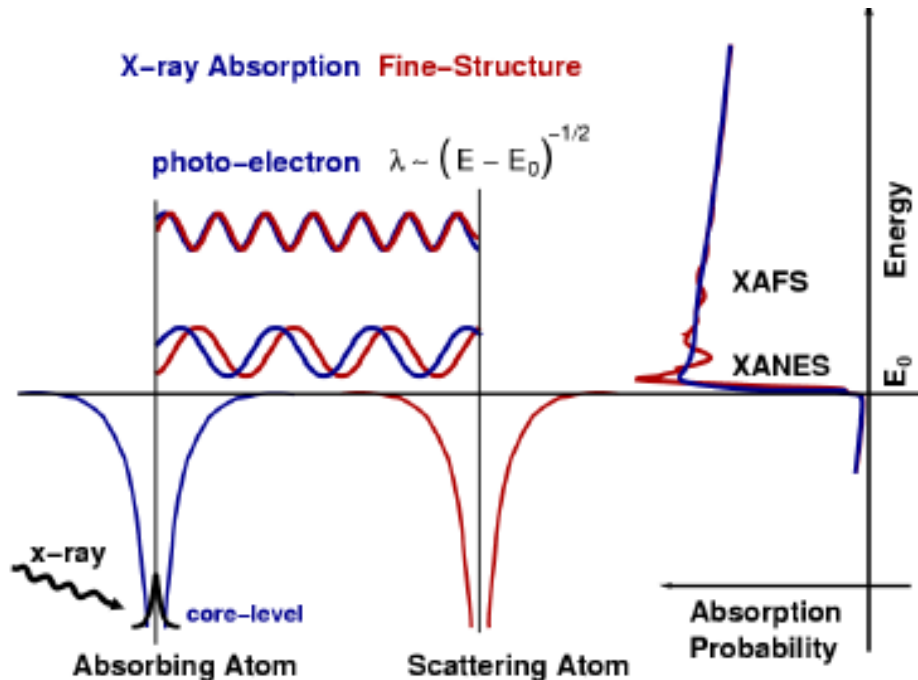
THE EXAFS FUNCTION

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

Usually represented in terms of wavevector k

$$k = \sqrt{\frac{2m(E - E_0)}{\hbar^2}}$$

The EXAFS Equation

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

N = coordination number

σ = mean square variation in distance (Debye-Waller factor)

R = inter-atomic distance

f(k), δ(k) are scattering properties of the neighboring atoms

λ(k) = mean free path of photoelectron

Typically N, σ and R are fitted to the χ(k) data
f(k) , δ(k) and λ(k) are theoretically calculated

EXAFS Data Reduction Steps

Experimentally $\mu(E) \propto \log(I_0/I)$ or I_f/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
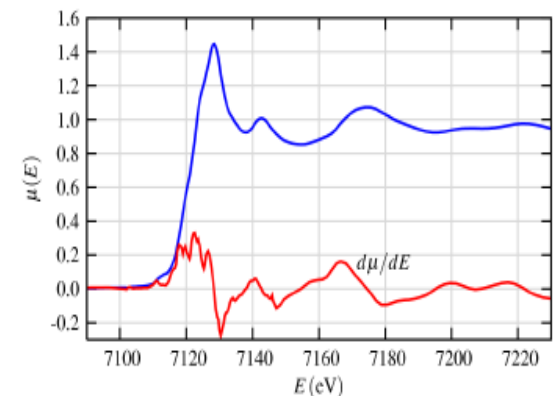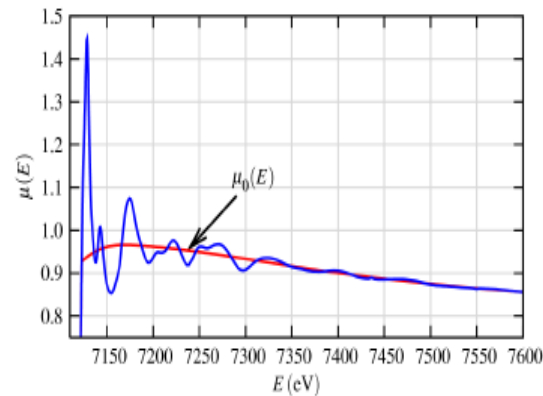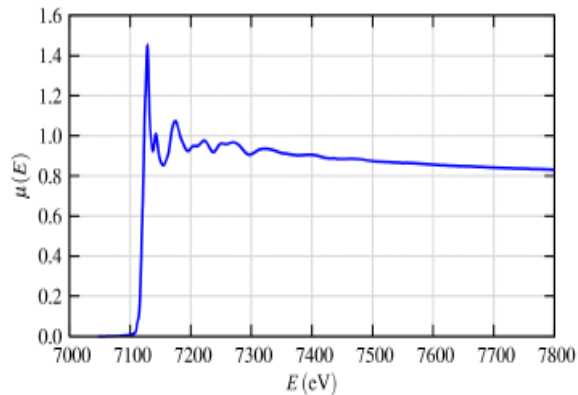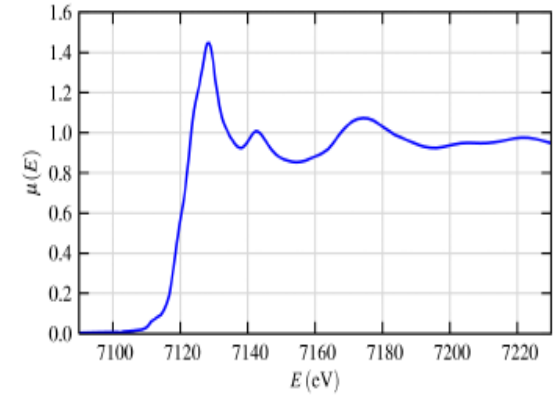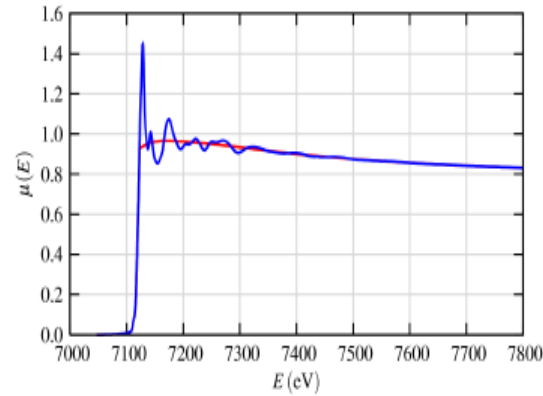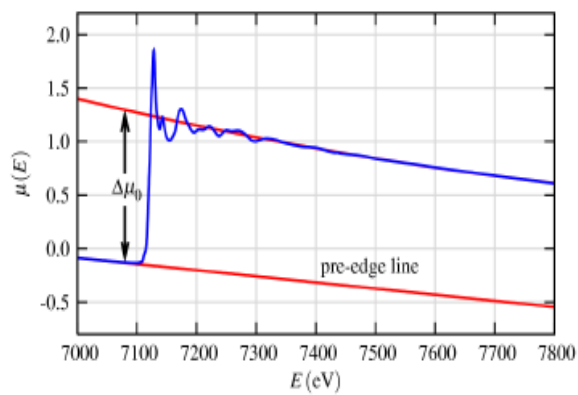
Fitting of backgrounds

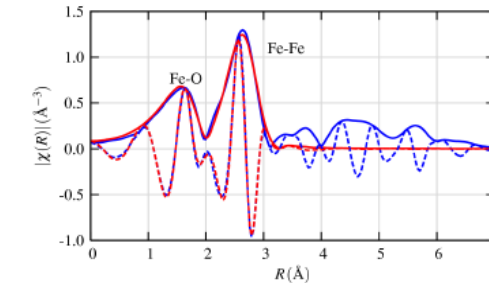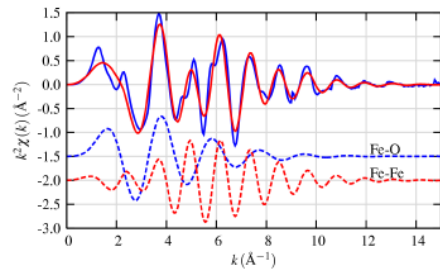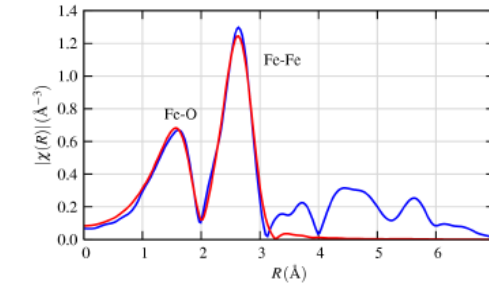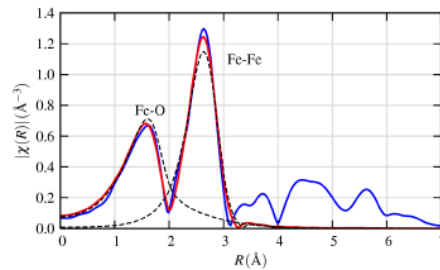Isolation of XANES

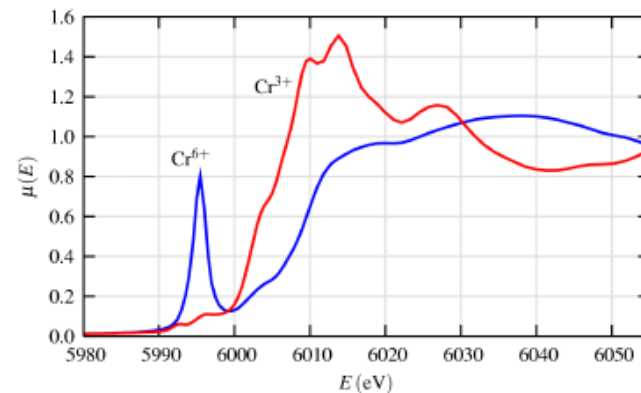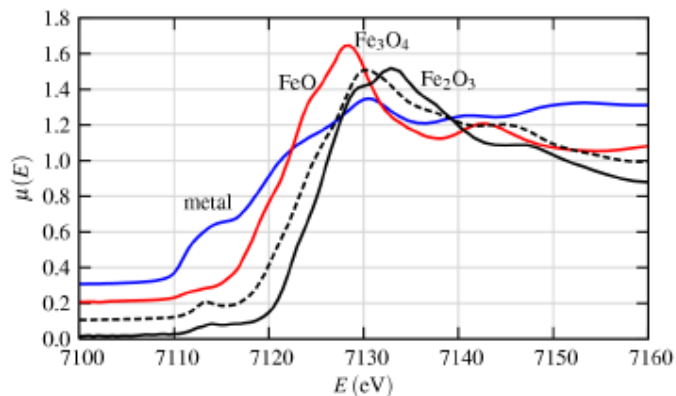# EXAFS Data Reduction Steps - II

Experiment
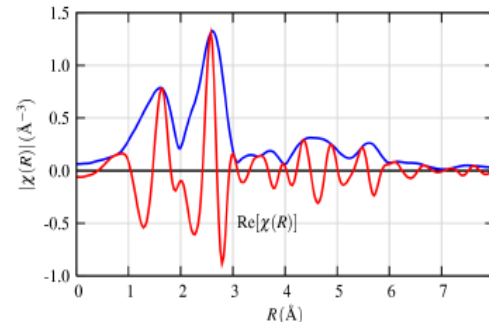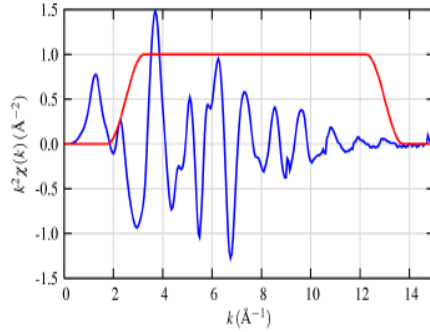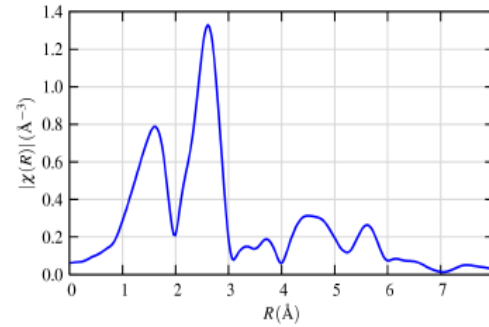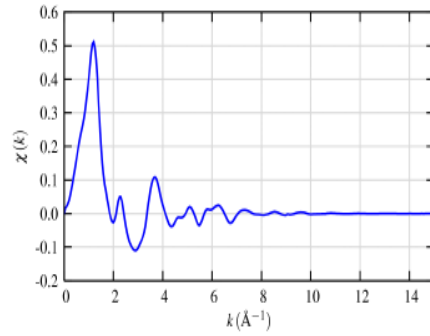
Simulation

XANES: Applications

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

S. Soyer Uzun*, S. Sen*, C.E. Benmore** and B.G. Aitken[†]

*Dept. of Materials Science, University of California at Davis
** Argonne National Laboratory
[†] Corning Incorporated
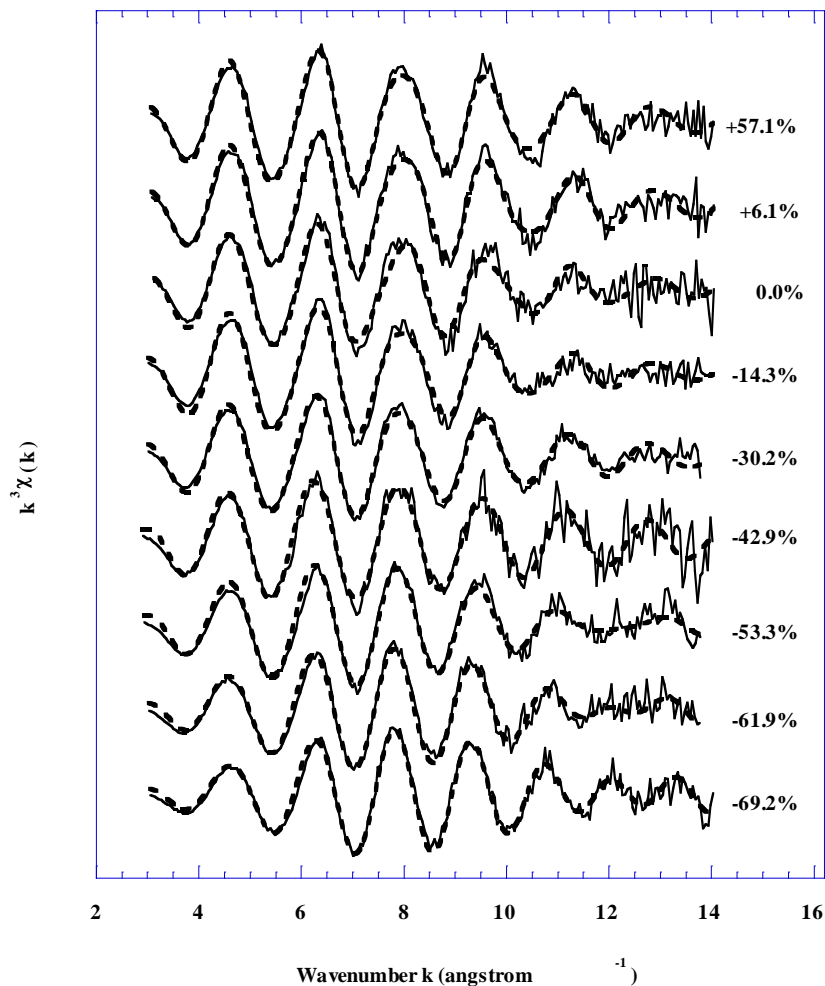
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Background and Motivation

- Complex glasses with wide compositional range of glass formation

- Technologically important: passive and active photonic devices

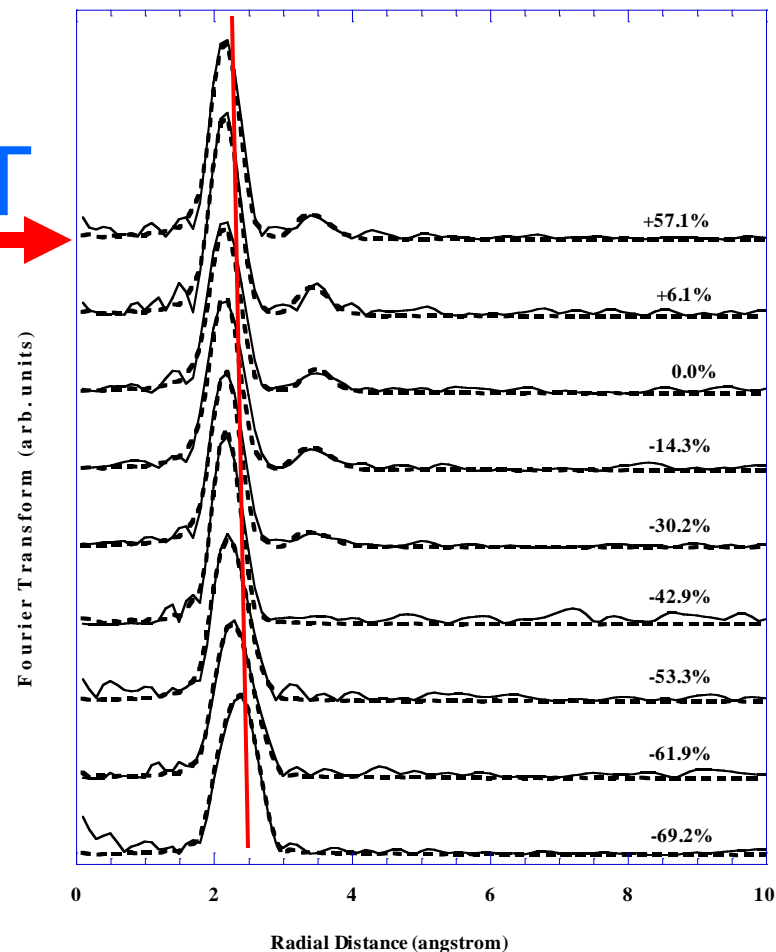- Model system for testing structure-property models based on average coordination numbers
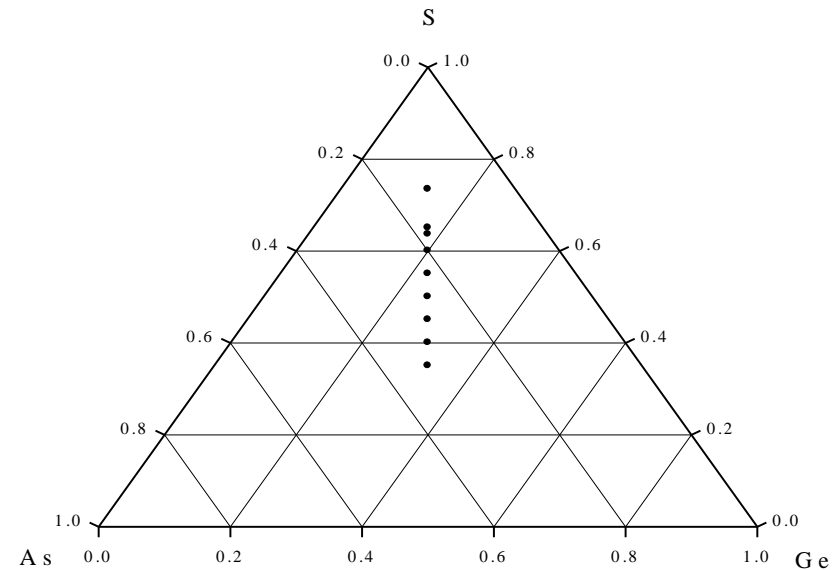
Short-range order from Ge and As K-edge EXAFS
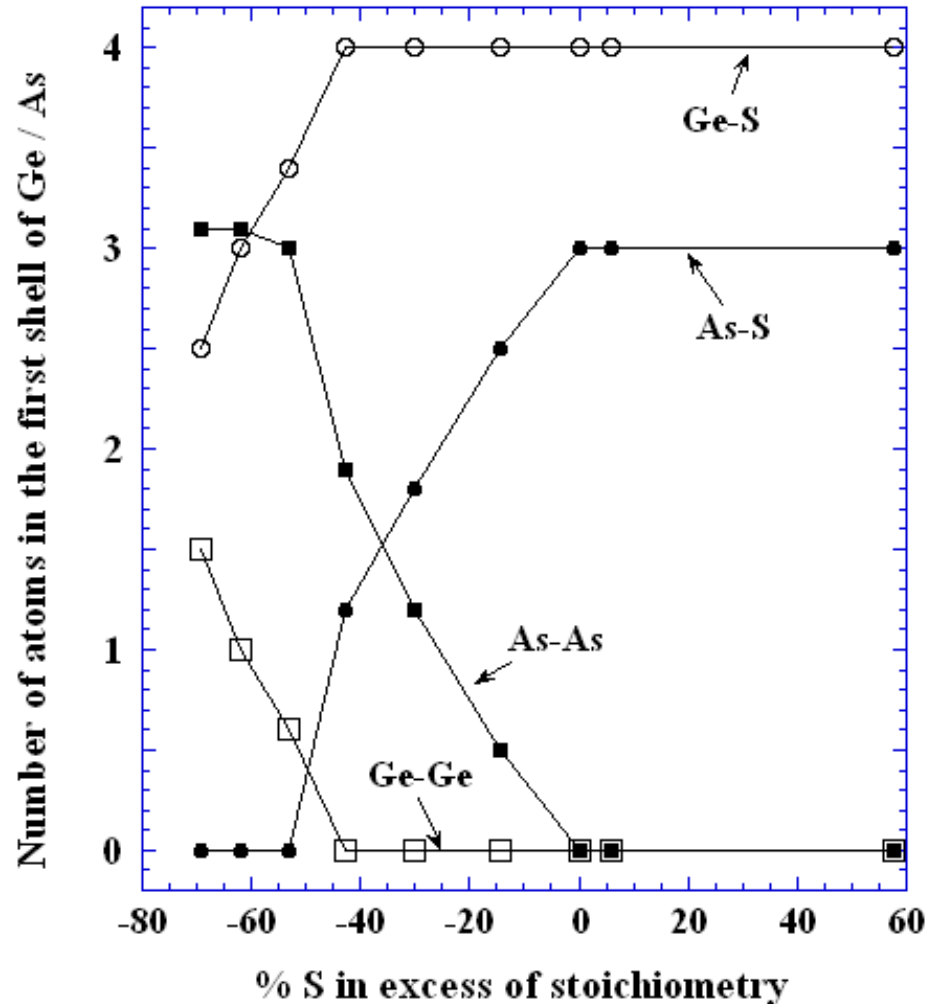
Ge K-edge EXAFS

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 $33.3 \leq S \leq 70.0$
  - melting of constituent elements ($\geq 99.9995\%$ 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:**

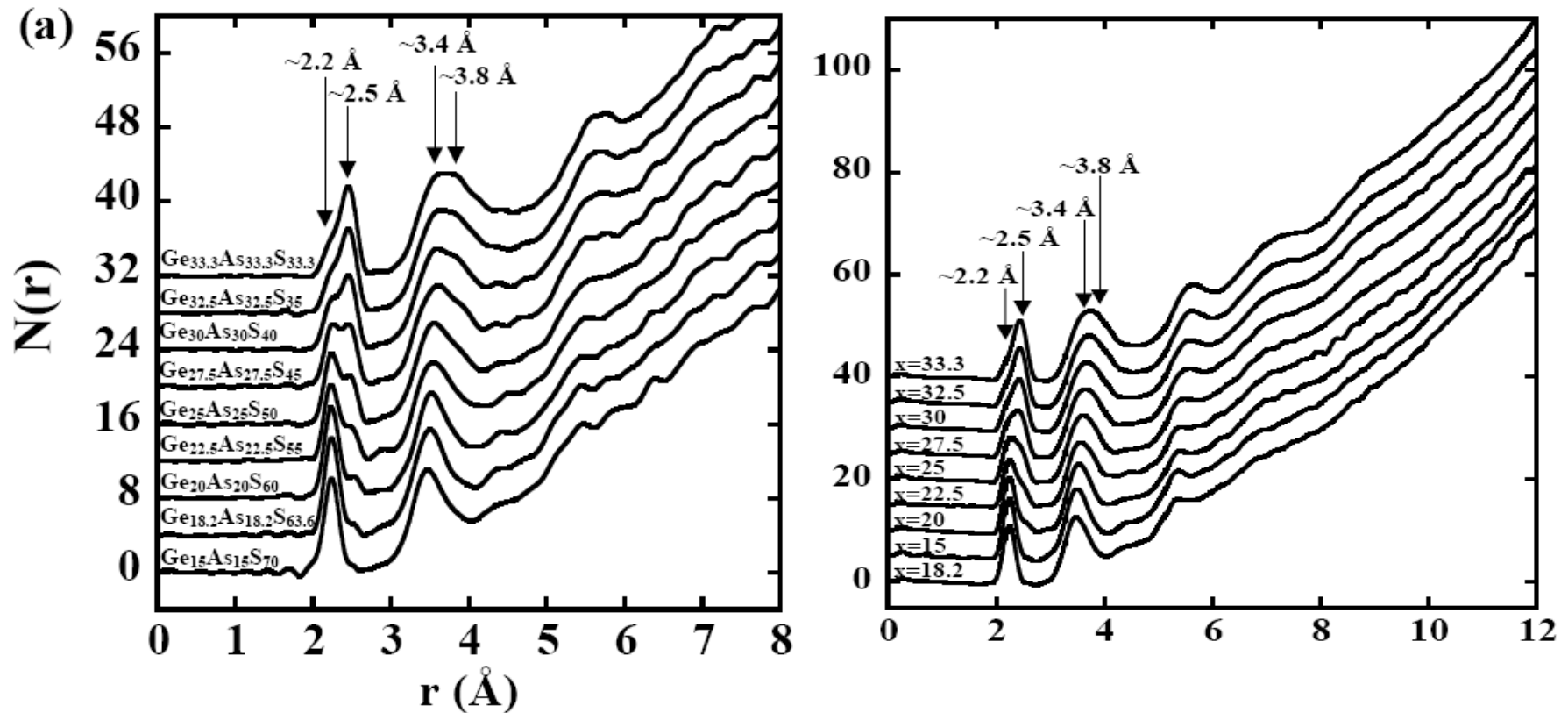$$C^N = {}^N W_{AsS} C_{As}(S) + {}^N W_{GeS} C_{Ge}(S)$$

$$C^X = {}^X W_{AsS} C_{As}(S) + {}^X W_{GeS} C_{Ge}(S)$$

Neutron and x-ray structure factors
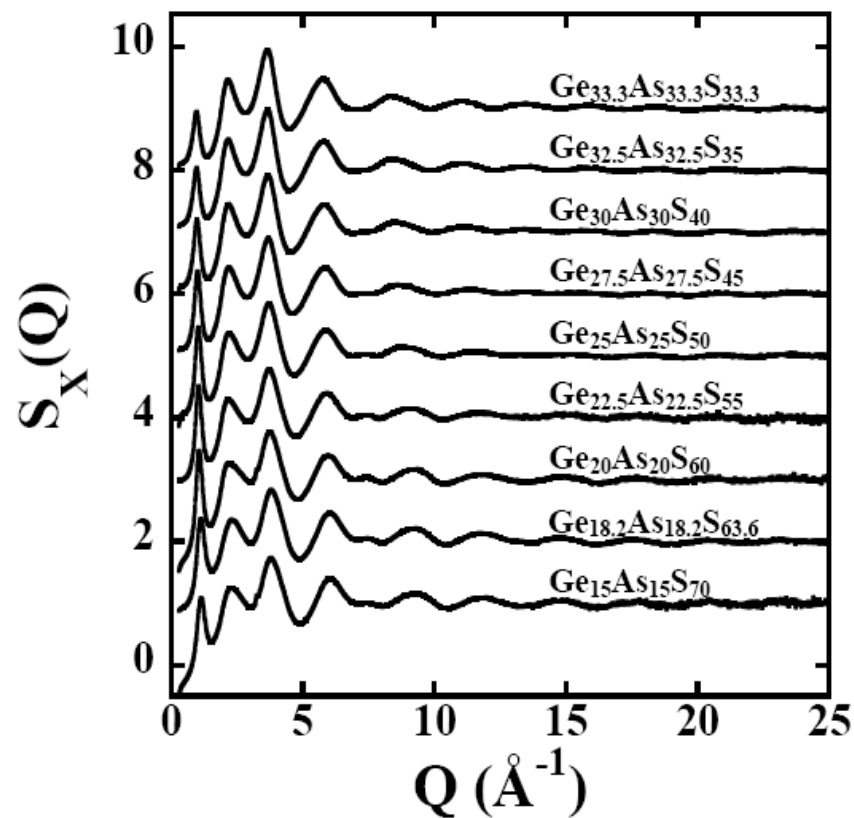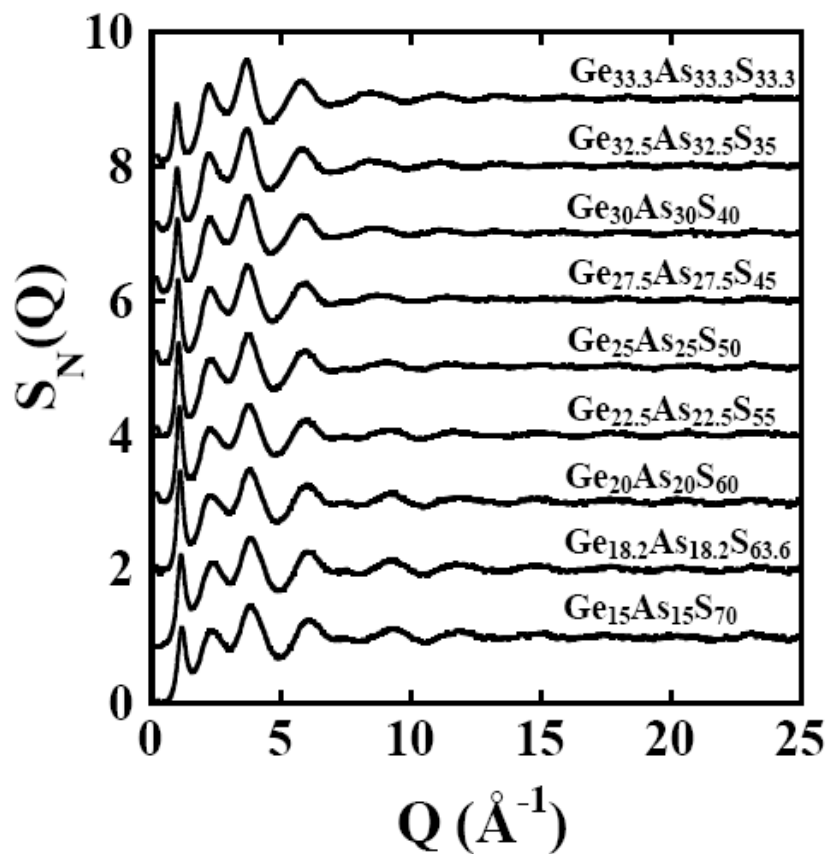
Neutron and x-ray RDFs

Short-range atomic correlations
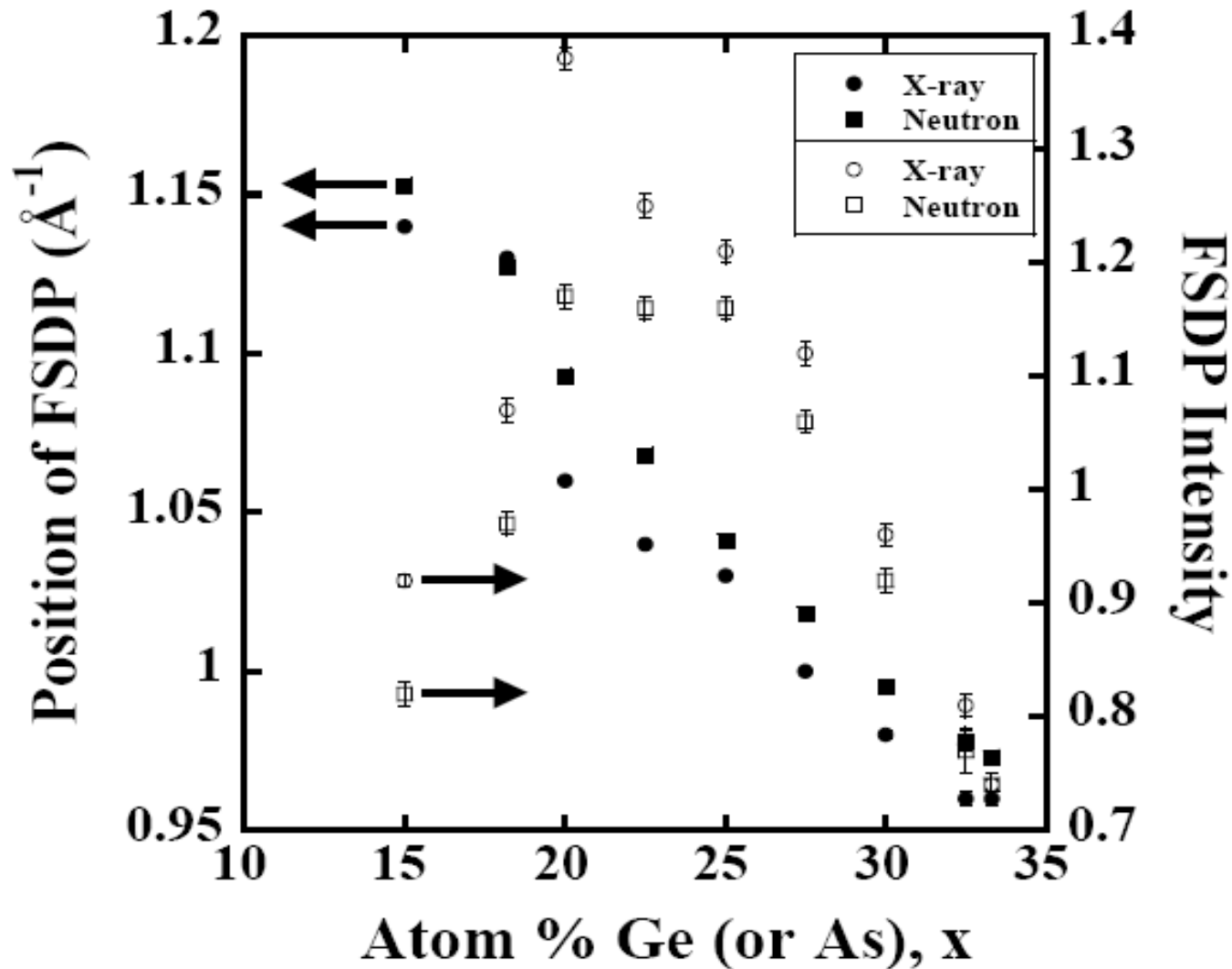
~2.2 Å : Ge-S and As-S nearest neighbors

~2.5 Å : Ge-Ge, As-As and Ge-As nearest neighbors
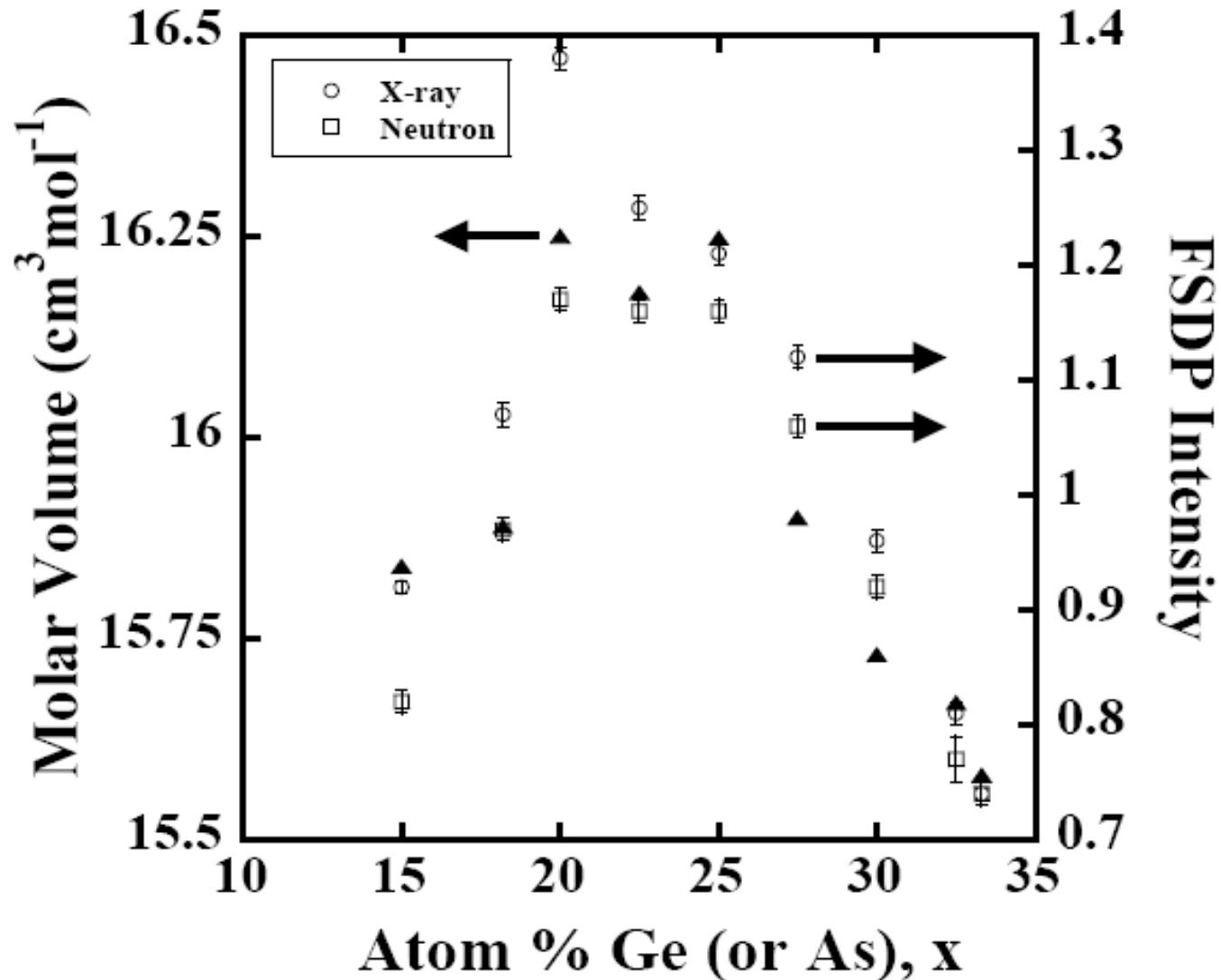
~3.4 Å : Ge/As – S – Ge/As next-nearest neighbors

~3.6 Å : S – S nearest neighbors

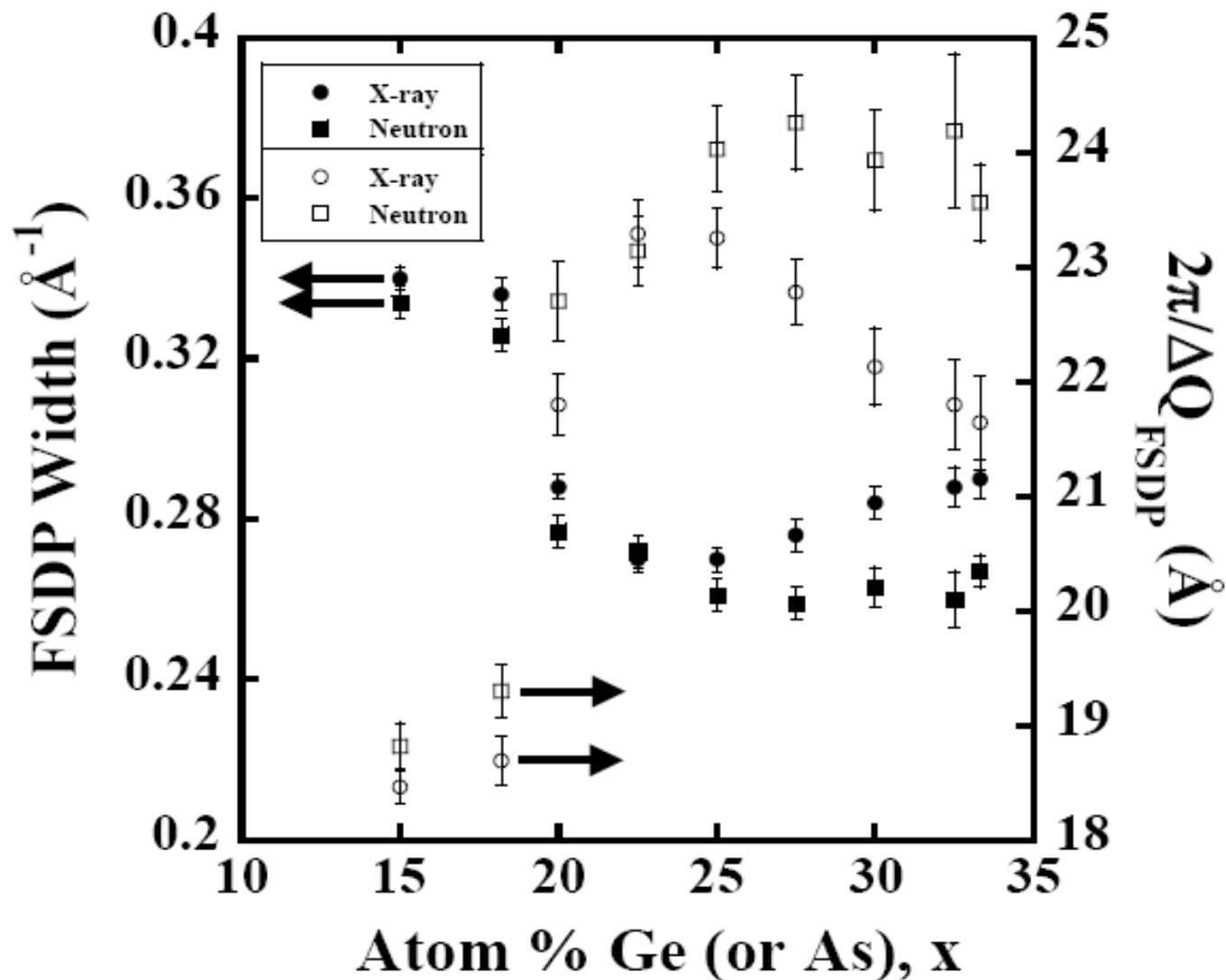~3.8 Å : Ge/As – Ge/As – Ge/As next-nearest neighbors
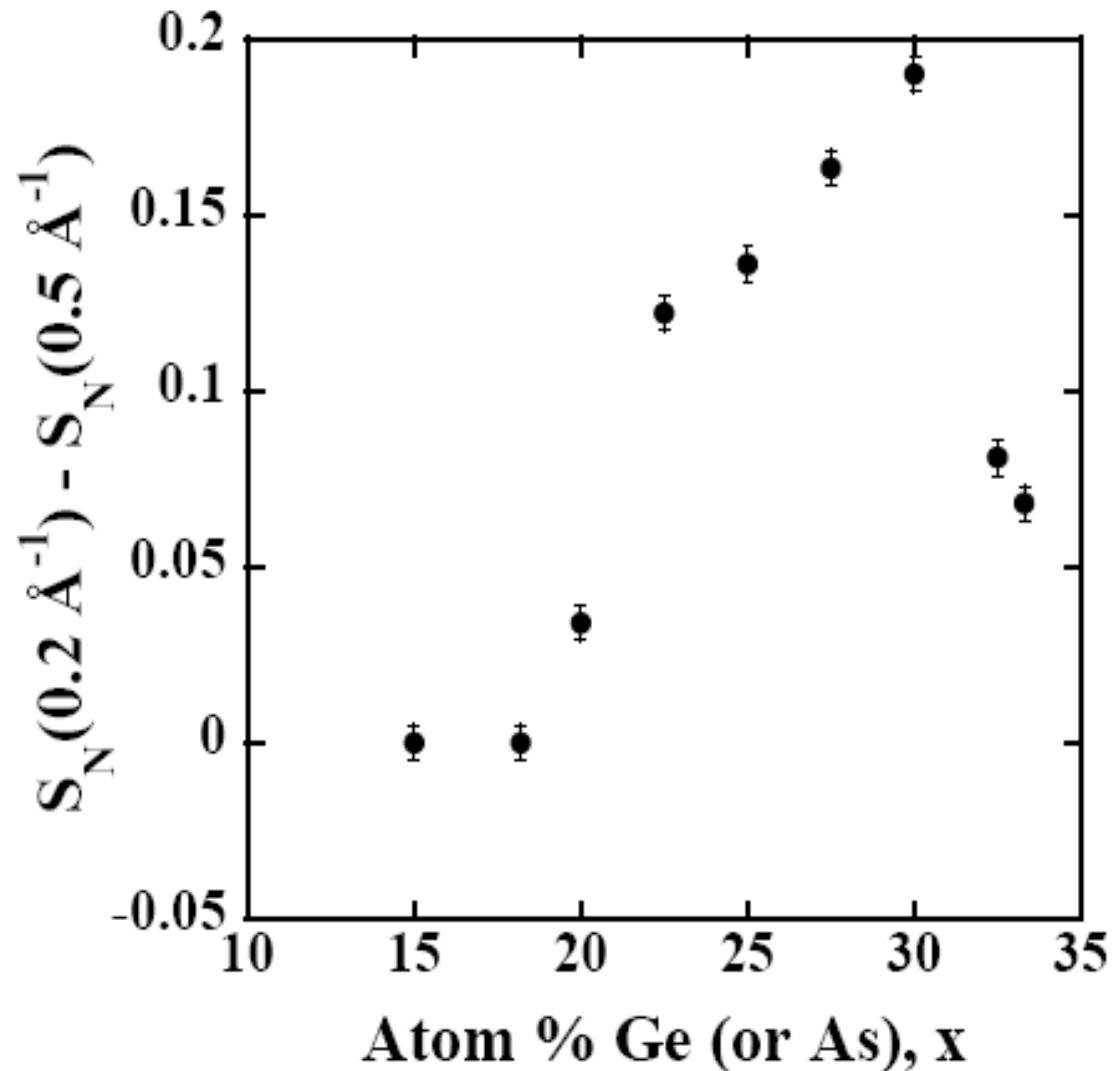
FSDP parameters: intensity & position

FSDP parameters: intensity & position

FSDP parameters: width

Small-angle neutron scattering

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_2S_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

Reverse Monte Carlo Simulation

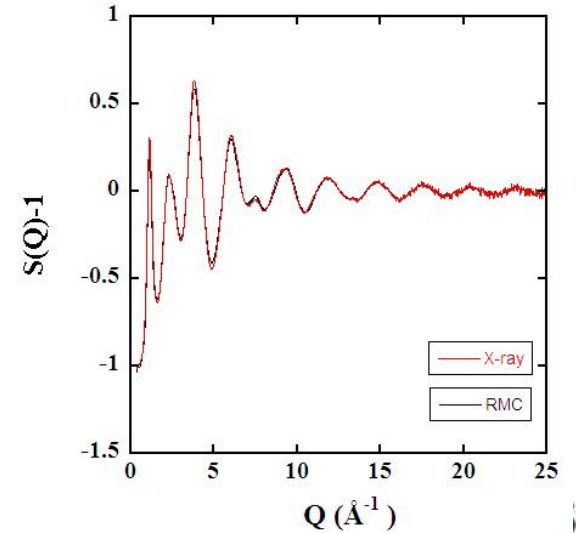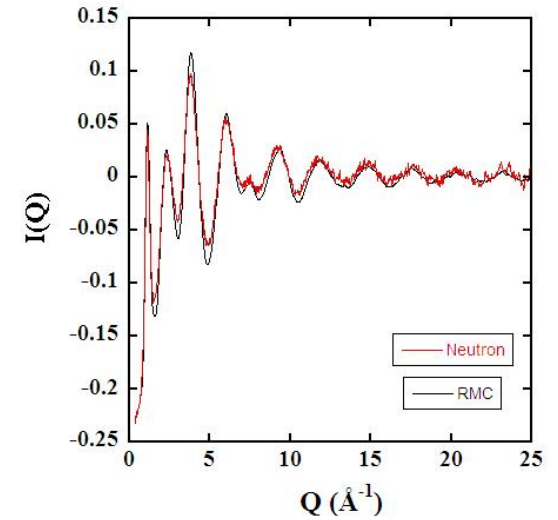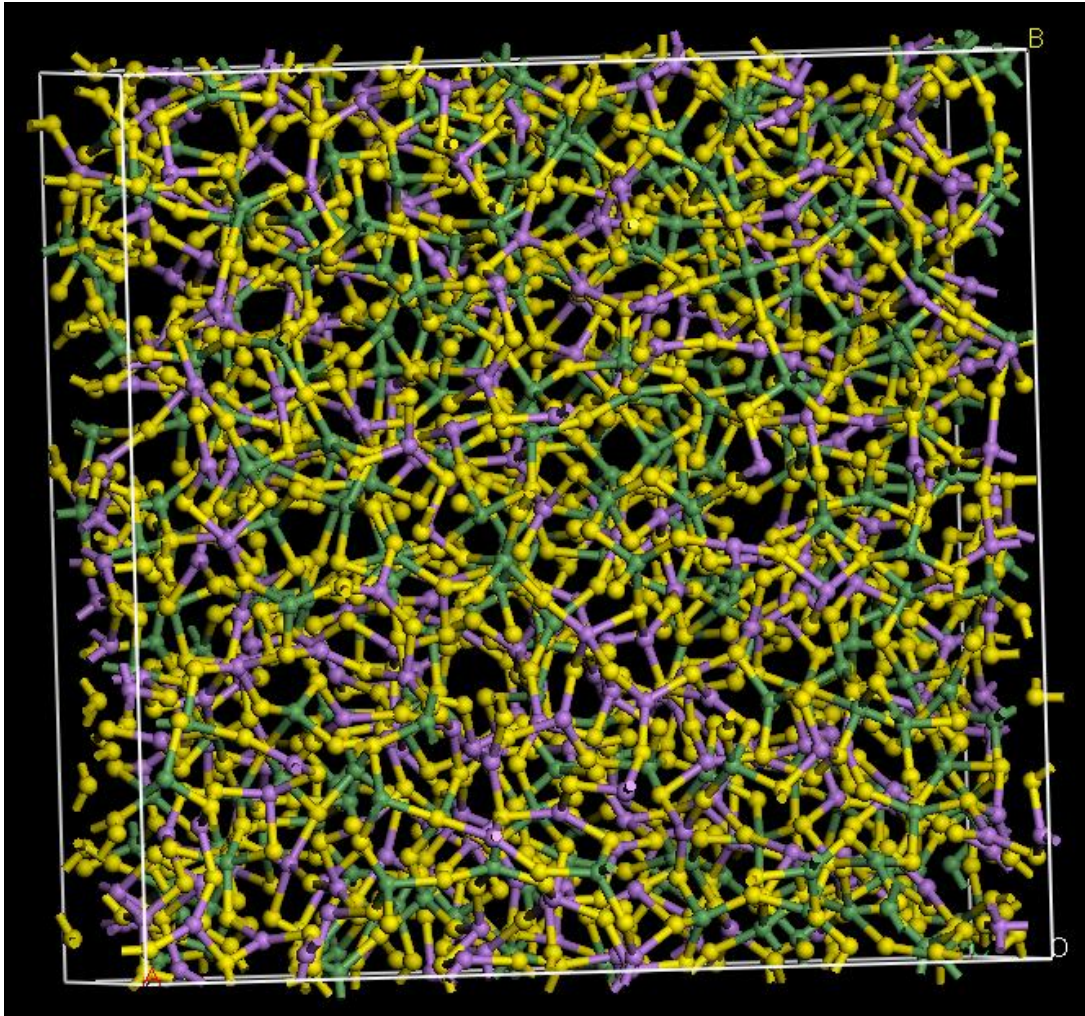1. **1700-1800 atom simulation (box size ~ 3.6 nm)**

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**

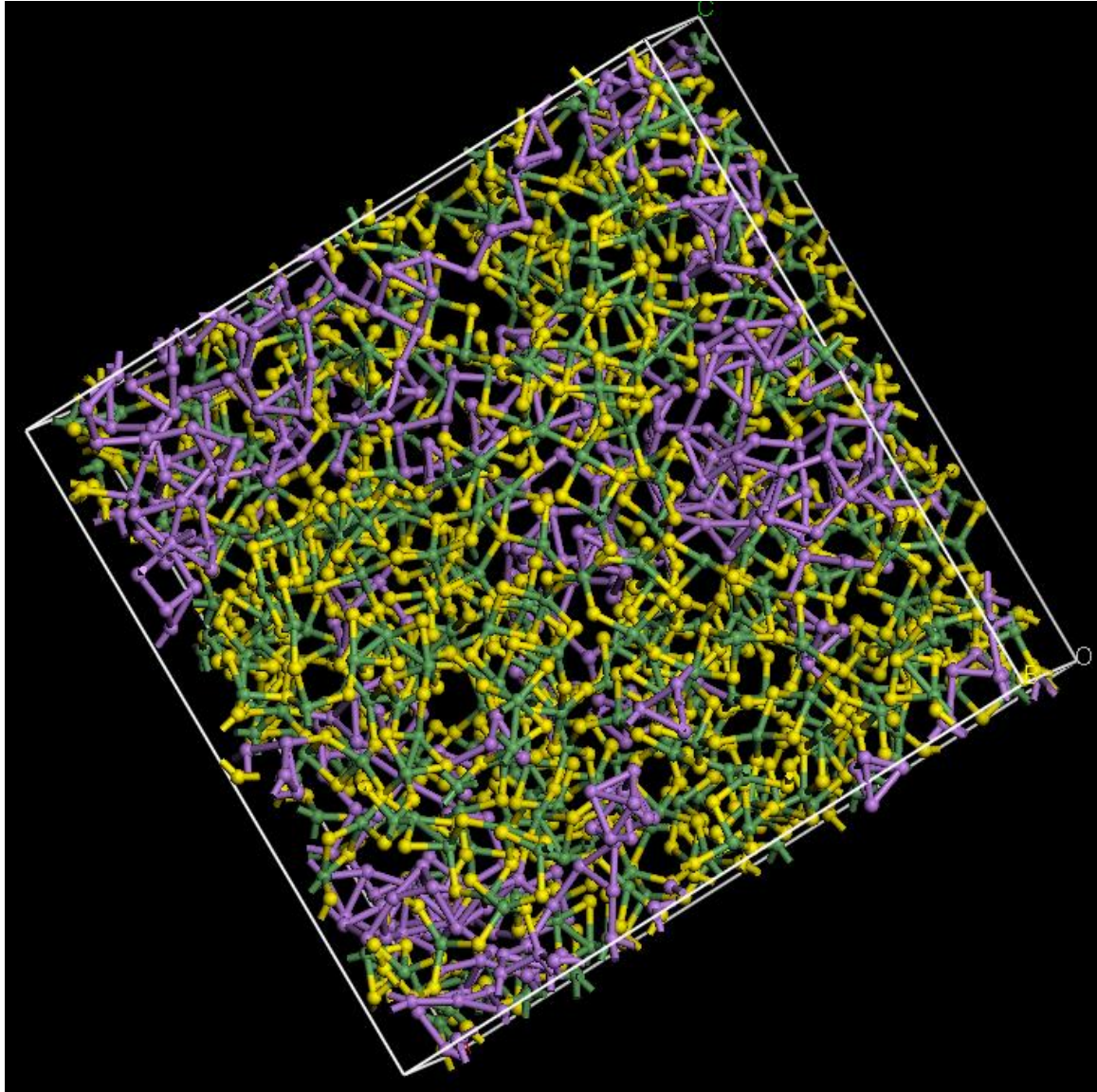   *(McGreevy and Pusztai; J. Phys.: Cond. Matter **13**, R877-R913, 2001)*
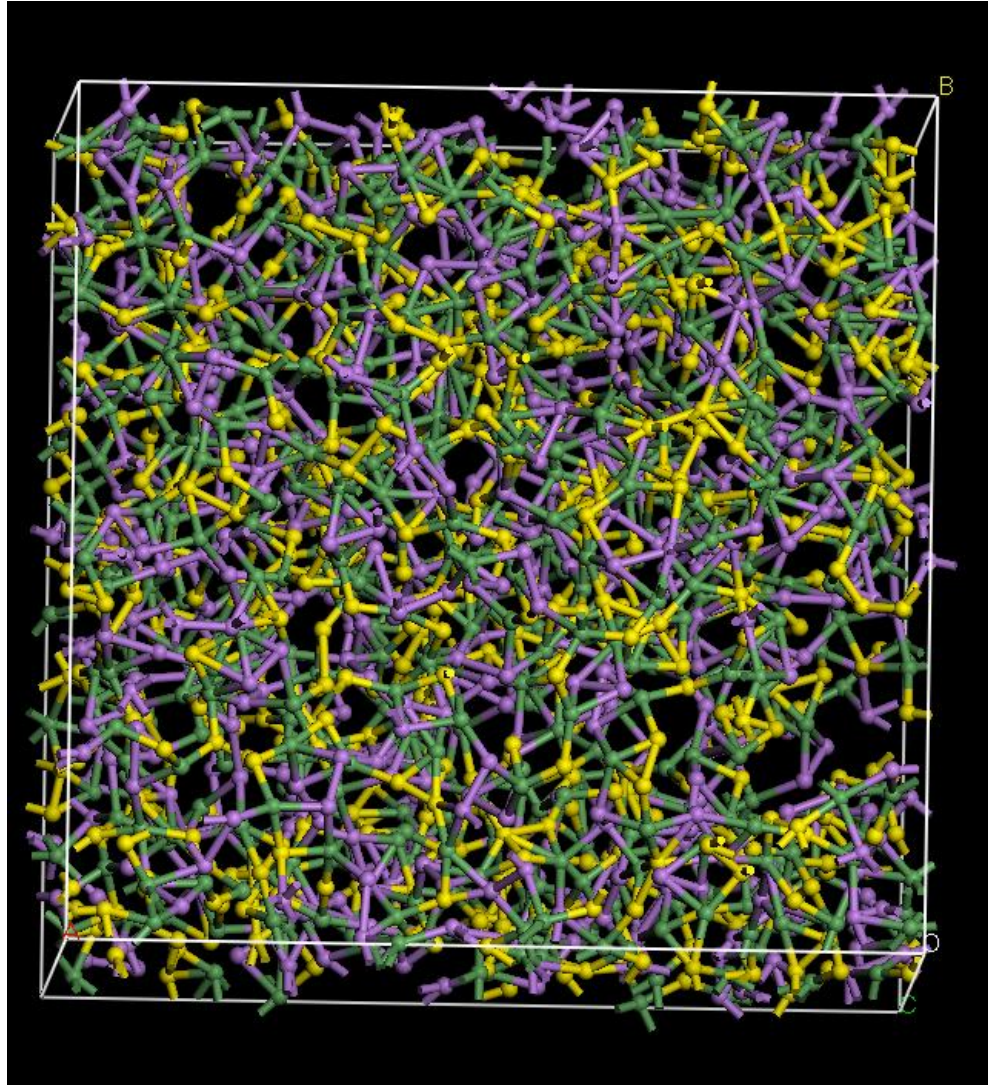
Stoichiometric glass

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)
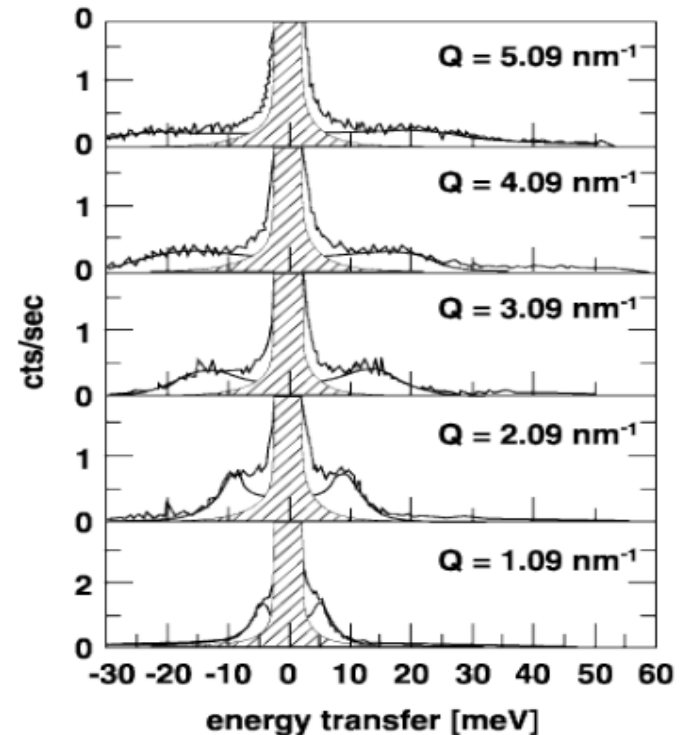
Inelastic x-ray scattering

IXS of borate glasses: pressure effect on B coordination

Dynamics in Al_2O_3 liquid
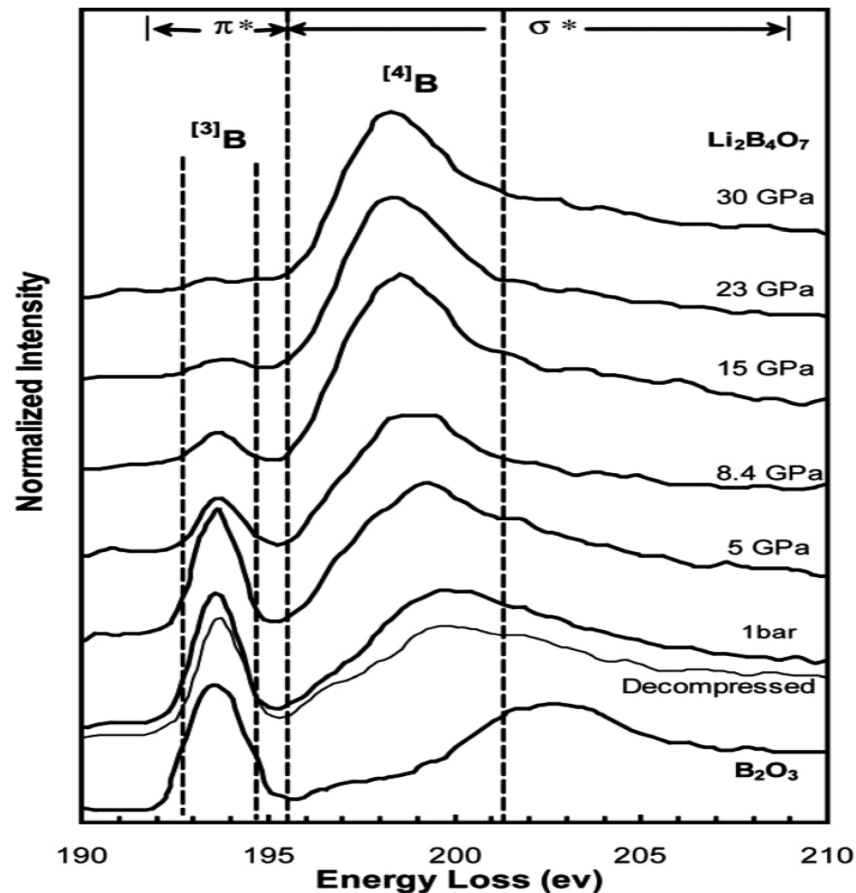
S.K. Lee et al. PRL, 2007

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

H. Sinn, et al, Science **299**, 2047 (2003).

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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 >> Tg the particles undergo Brownian motion; measurements closer to glass transition (T ~ 1.2 Tg) indicate hyperdiffusive behavior
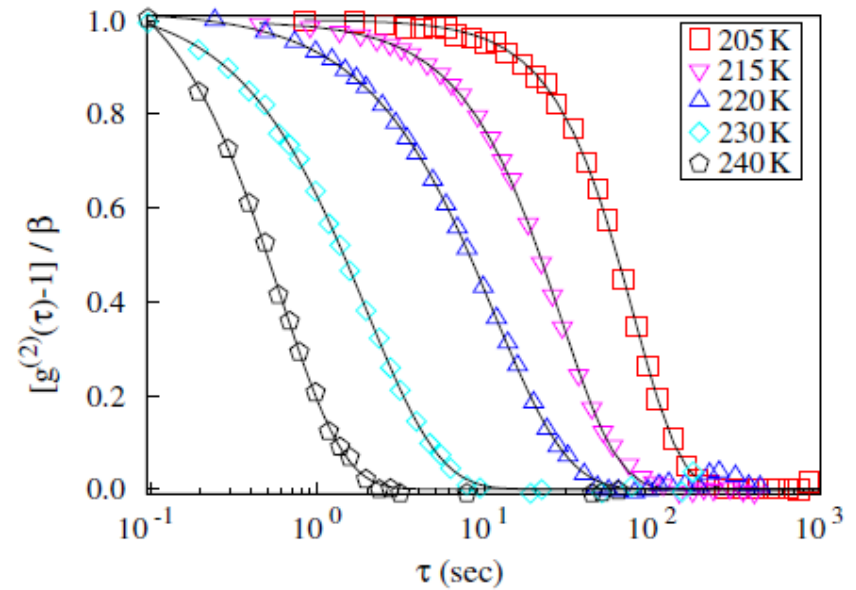
Caronna, et al., PRL 100, 055702 (2008)

Acknowledgments

National Science Foundation DMR grant

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