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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

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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

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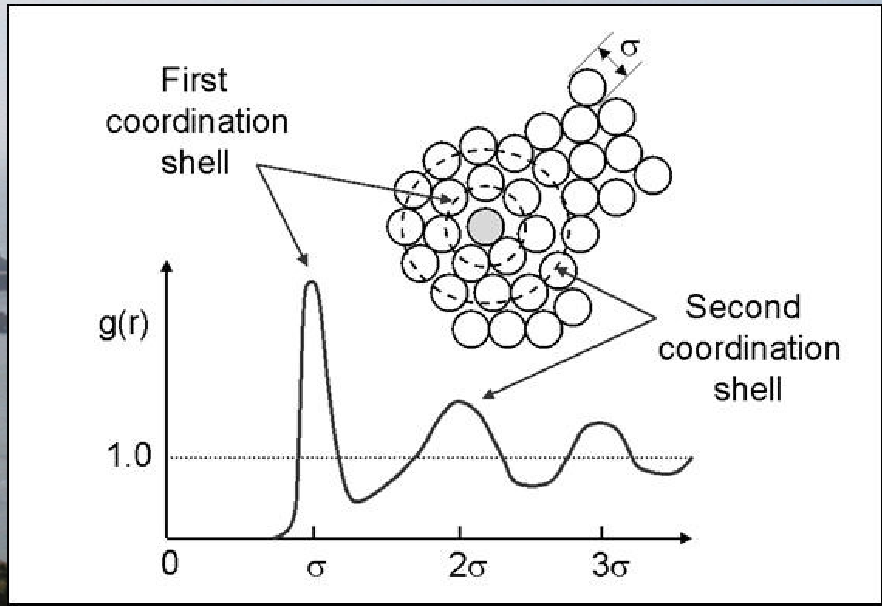
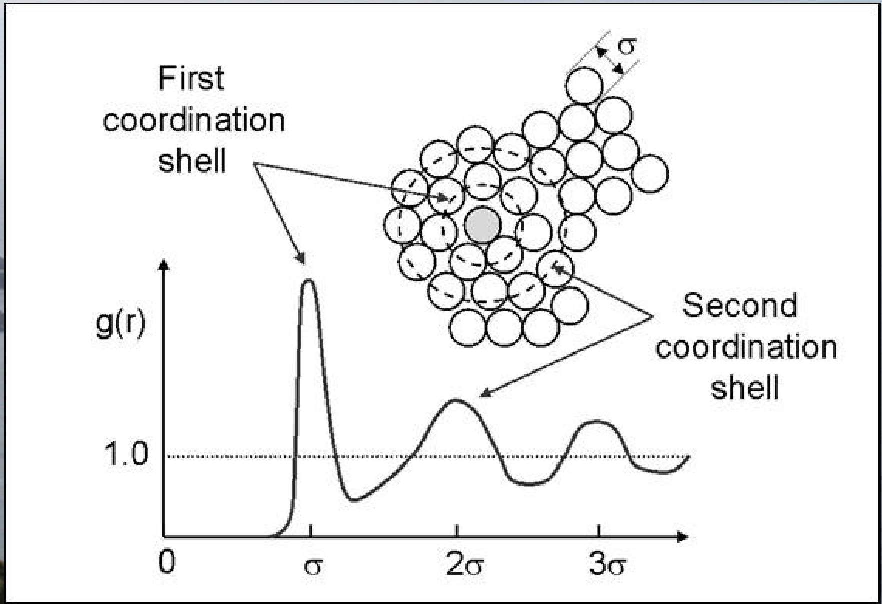
The Liquid State

- 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



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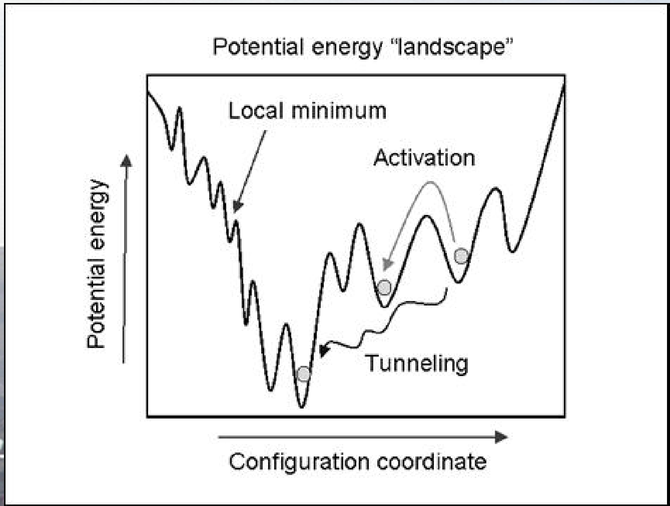
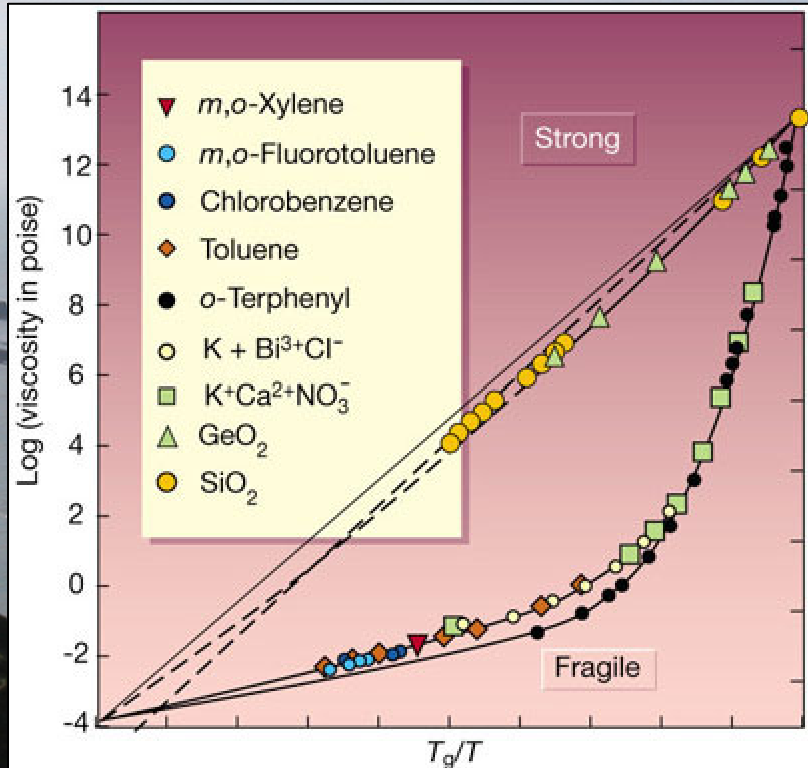
Glasses and amorphous materials





- Super-cooling
  - Ergodicty
  - Non-ergodicity
- Configurational entropy and fragility
- Pressure-induced amorphisation

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Neutron diffraction: Scattering theory

- Double differential cross section

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

- Coherent scattering law

$$S(Q,\omega) = \frac{1}{N} \frac{k_{incident} 4\pi}{k_{scattered} \sigma_{coh}} \frac{d^2\sigma}{d\Omega dE_1}\bigg|_{coh}$$

- Static approximation

$$Q^2 \approx 2k_{incident}^2 (1 - \cos 2\theta)$$

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Neutron diffraction: Scattering in multi-component systems

❖ Scattering:

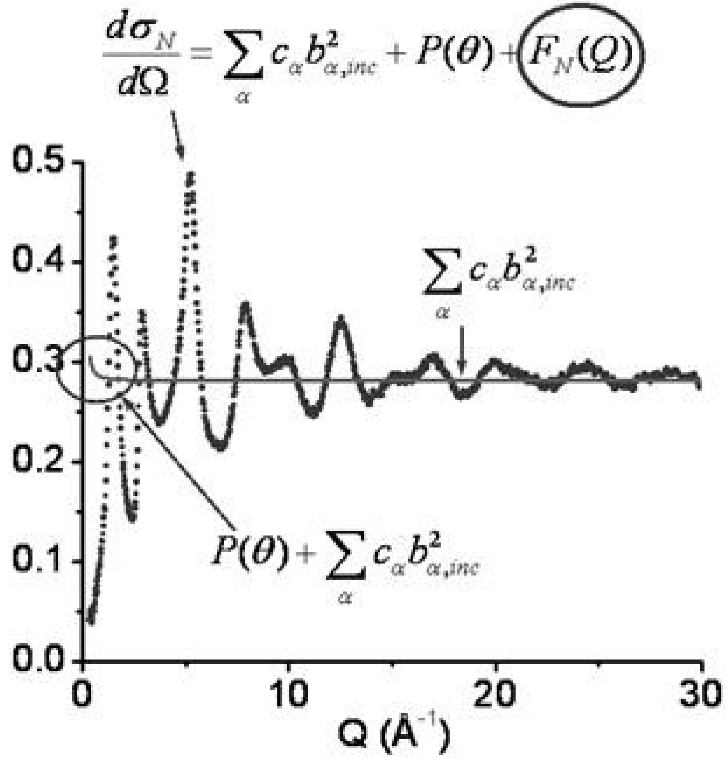
$$\frac{1}{N}\left[\frac{d\sigma}{d\Omega}(Q)\right] = F(Q) + \sum_{\alpha}^{n} c_\alpha \overline{b^2_{\alpha,inc}}$$

- Sum of several atom-pairs
- Partial contributions

❖ Faber-Ziman formalism

$$F(Q) = \sum_{\alpha,\beta}^{n} c_\alpha c_\beta \overline{b_\alpha}\,\overline{b_\beta}\left[S_{\alpha,\beta}(Q)-1\right]$$

Neutron diffraction: the differential cross section



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Neutron diffraction: the pair correlation function

- Sine Fourier transform of the $S_{\alpha,\beta}(Q)$:
  - Total number density is ρ_0
  - $G_{\alpha,\beta}(r)$ is the probability of funding atom β at distance r from atom α.
- 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.

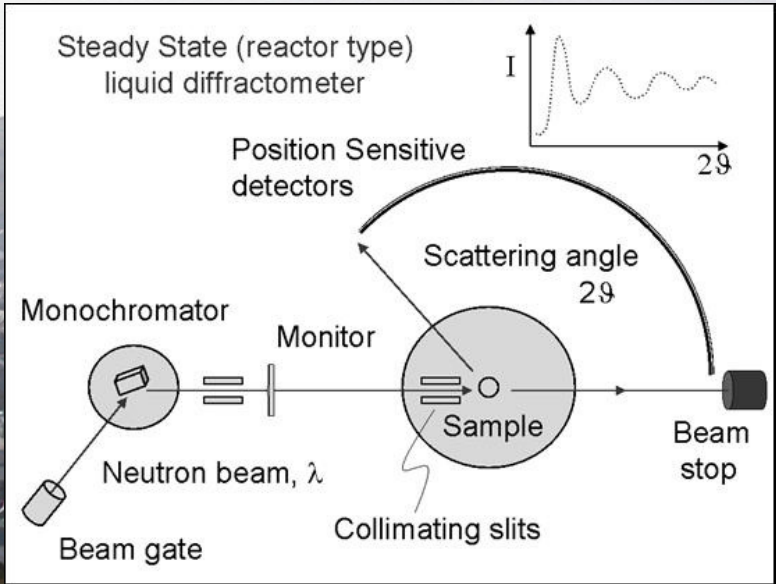
$$g_{\alpha,\beta}(r)-1=\frac{1}{2\pi^2 r\rho_0}\int_0^\infty Q\left[S_{\alpha,\beta}(Q)-1\right]\sin(Qr)\,dQ$$

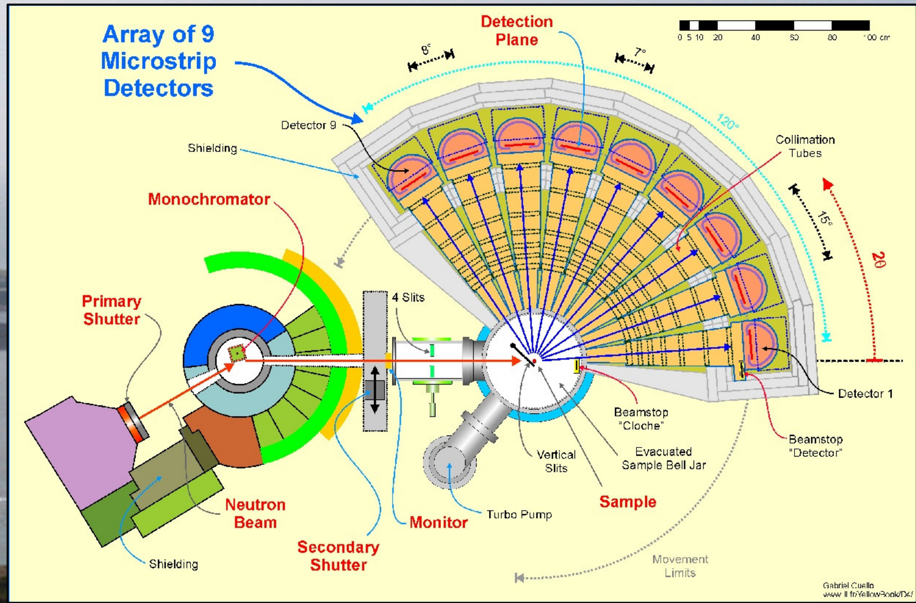
$$G(r)=\frac{1}{2\pi^2 r\rho_0}\int_0^\infty QF(Q)\sin(Qr)\,dQ=\sum_{\alpha,\beta}^{n} c_\alpha c_\beta \bar{b}_\alpha \bar{b}_\beta\left[g_{\alpha,\beta}(r)-1\right]$$

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

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

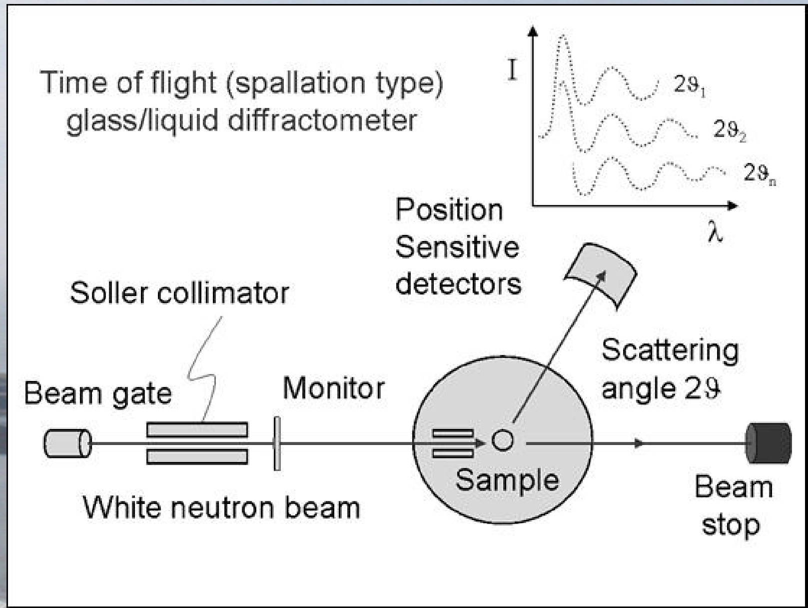
Neutron instrumentation

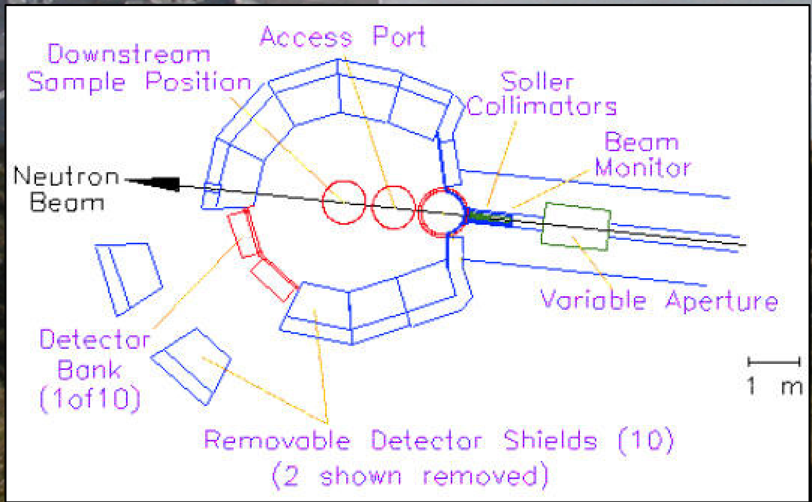




- Steady state (reactor type)
- Beam of wavelength λ is scattered though angle 2θ.

Neutron instrumentation





- Time-of-flight (spallation source)
- Detectors at fixed angle record different wavelengths (Q)

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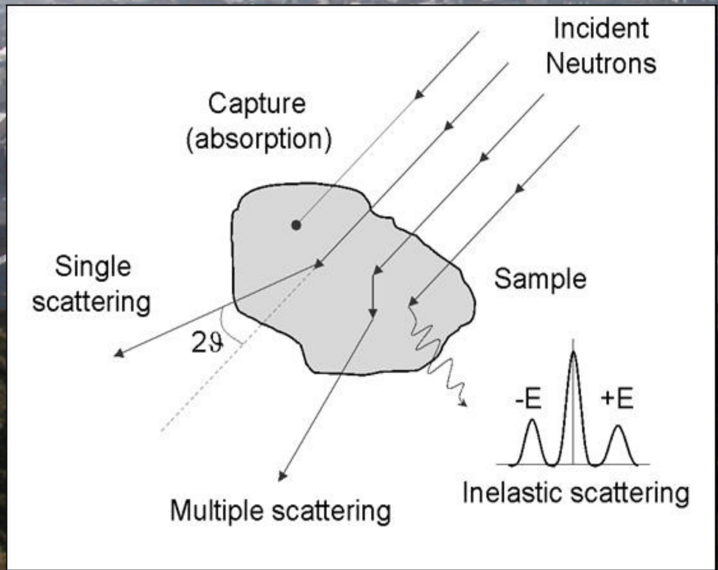
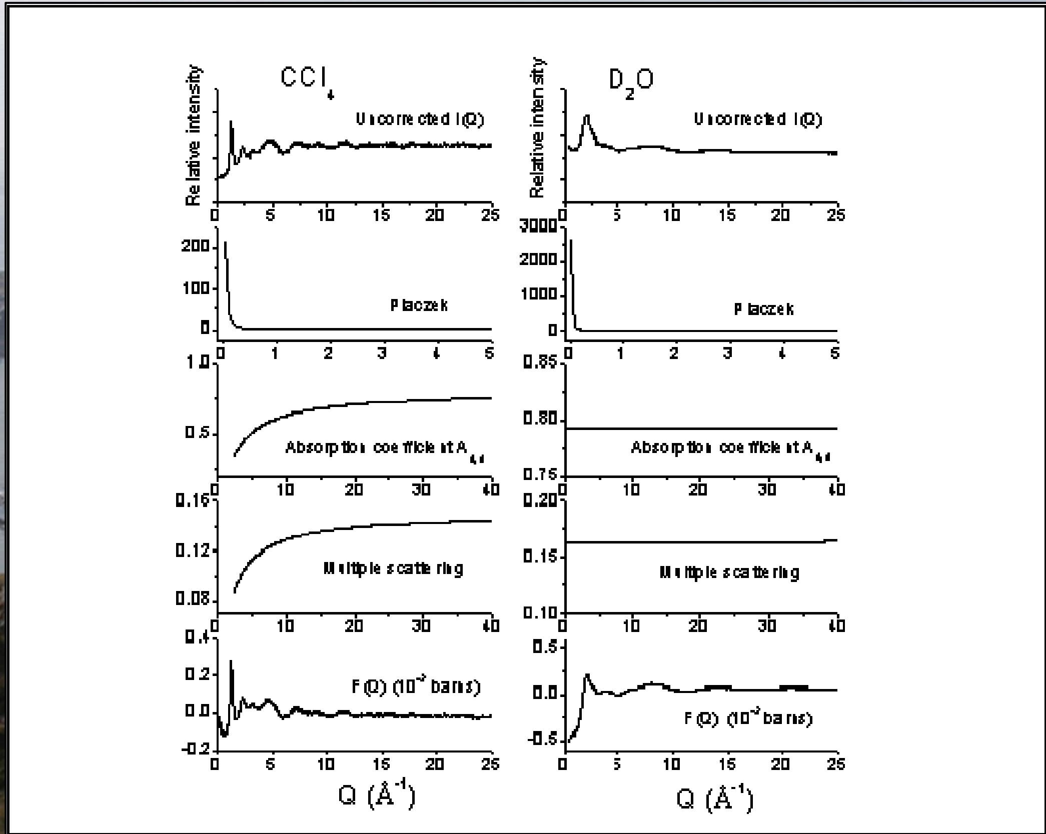
Neutron diffraction: correction procedures

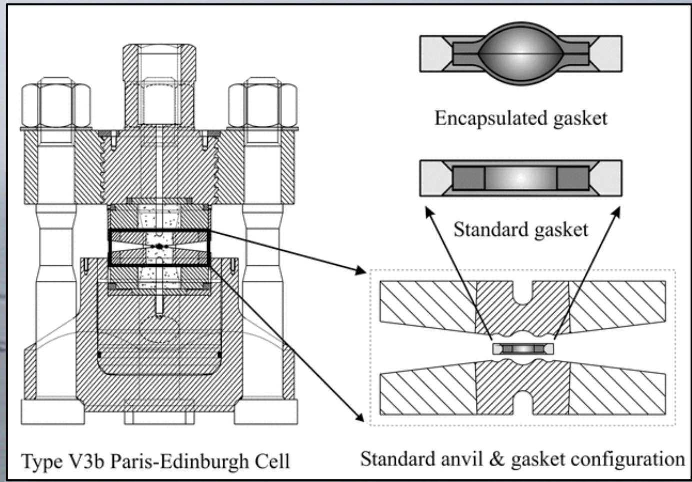
Structural information is in elastic, single scattering events.





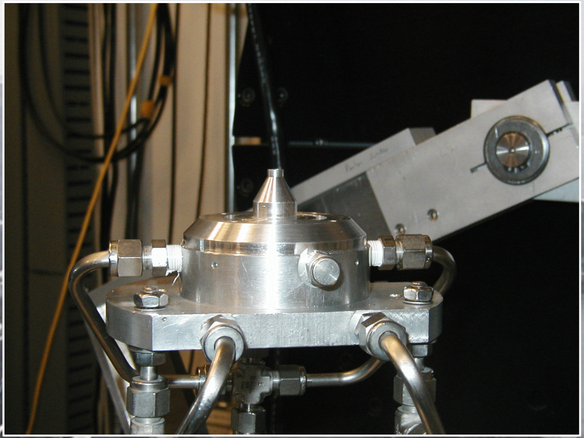
Sample environments

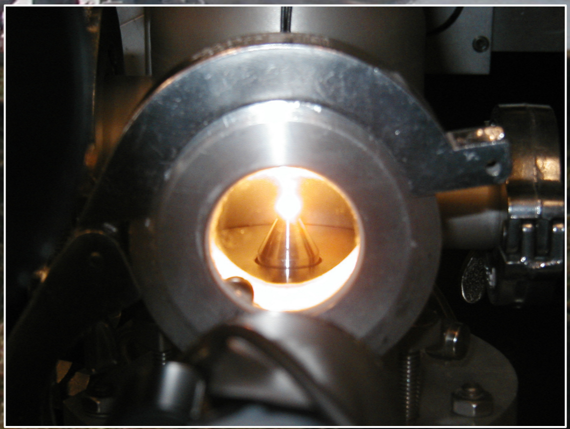
Pressure cells

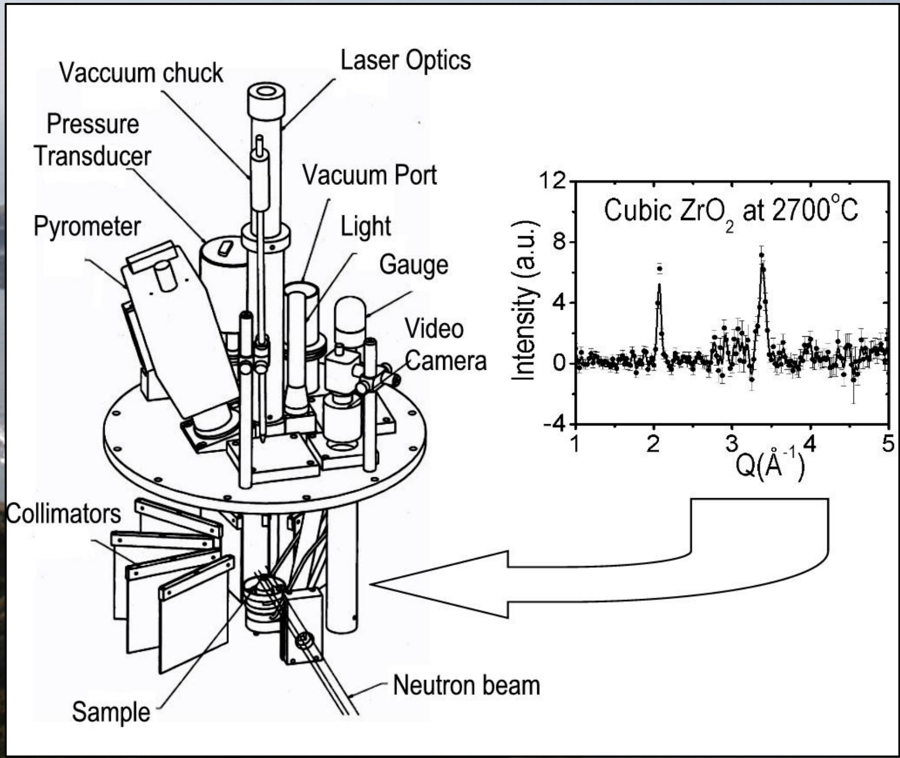


Sample environments

Containerless levitation

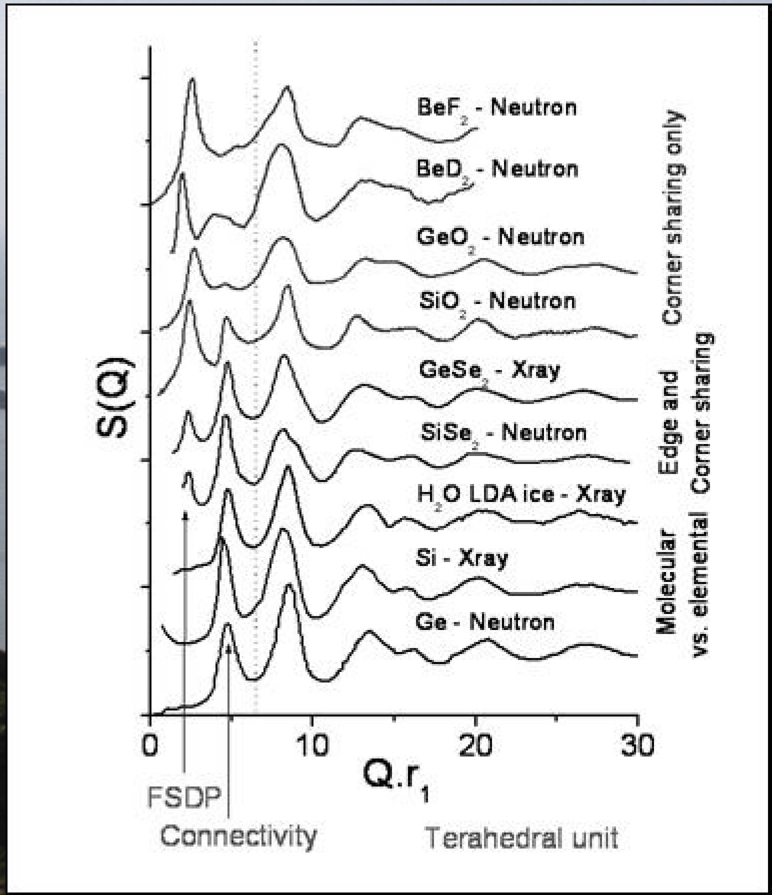


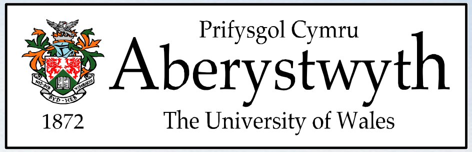




Interpretation of glass structure

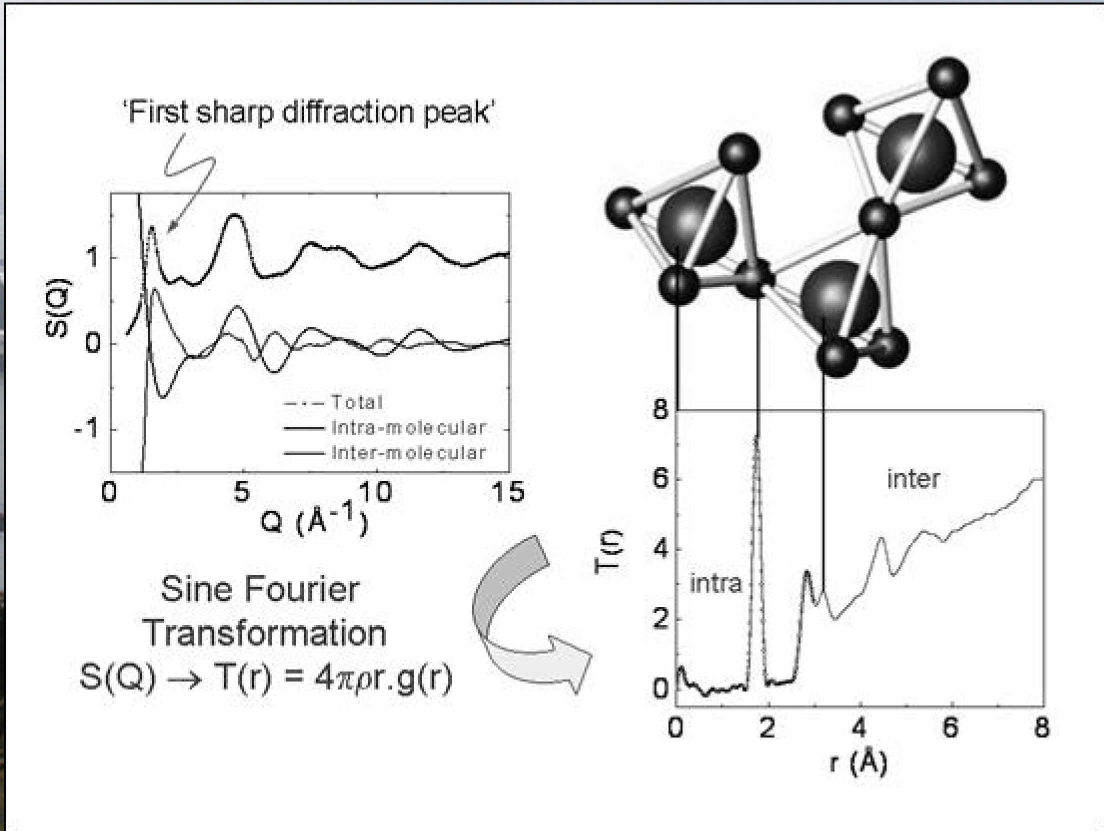
- Based on the pair distribution function (PDF)
- Continuous random networks (CRN)
- Characteristic distance ranges





Interpretation of glass structure

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



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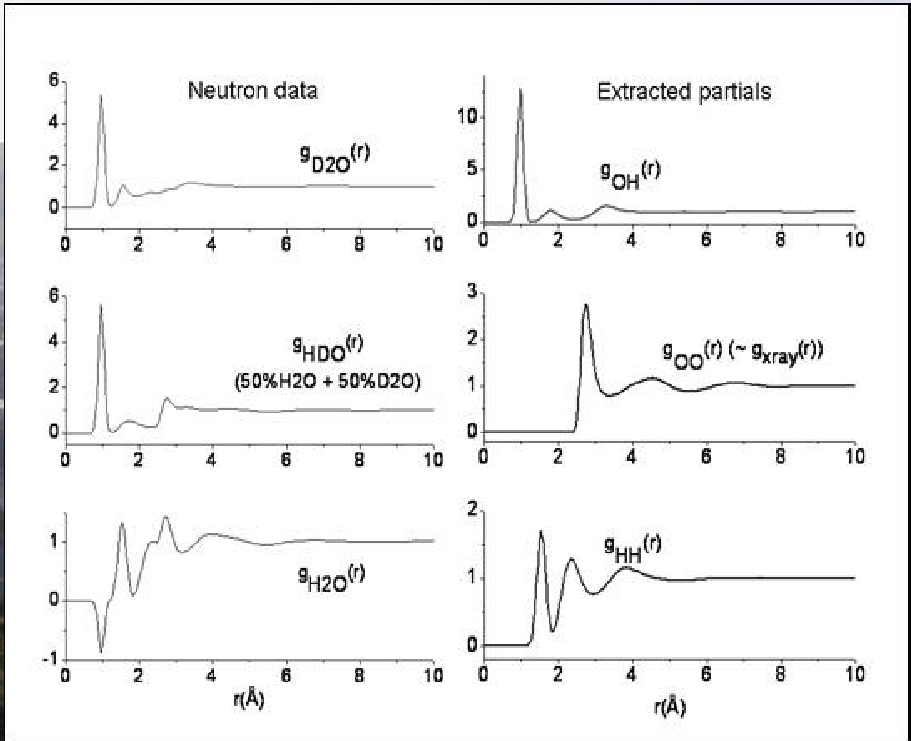
Partial structure factor determination



Isotopic substitution, e.g. H/D

$$G_{H2O}(r) = \frac{c_H^2 b_H^2}{A} g_{HH}(r) + \frac{2c_H c_O b_H b_O}{A} g_{OH}(r) + \frac{c_O^2 b_O^2}{A} g_{OO}(r)$$

$$A = c_H^2 b_H^2 + 2c_H c_O b_H b_O + c_O^2 b_O^2$$

$$G_{H2O}(r) = 0.318 g_{HH}(r) - 0.4.92 g_{OH}(r) + 0.190 g_{OO}(r)$$

$$G_{H2O}(r) = 0.486 g_{HH}(r) + 0.4.23 g_{OH}(r) + 0.091 g_{OO}(r)$$

$$G_{H2O}(r) = 0.113 g_{HH}(r) + 0.446 g_{OH}(r) + 0.441 g_{OO}(r)$$

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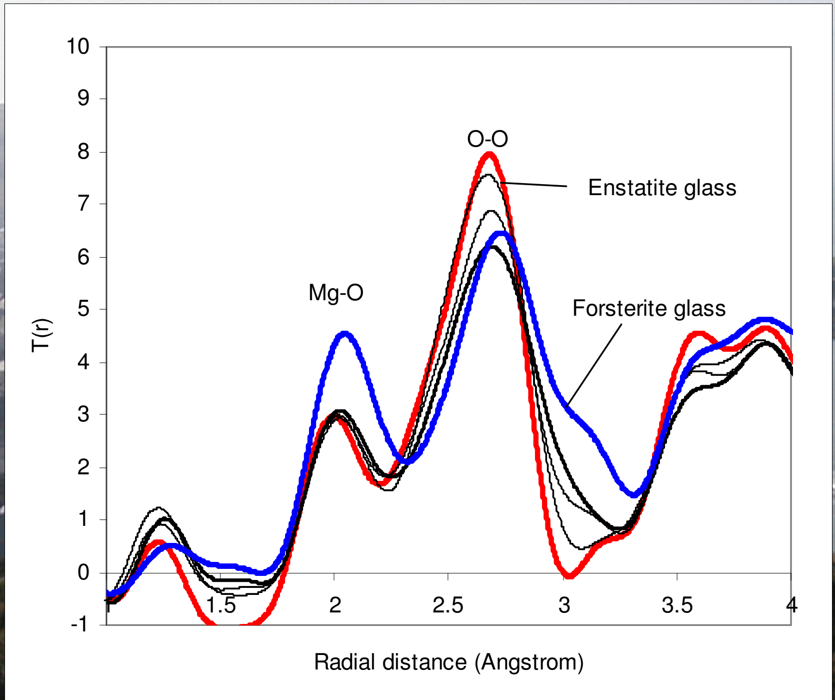
Partial structure factor determination

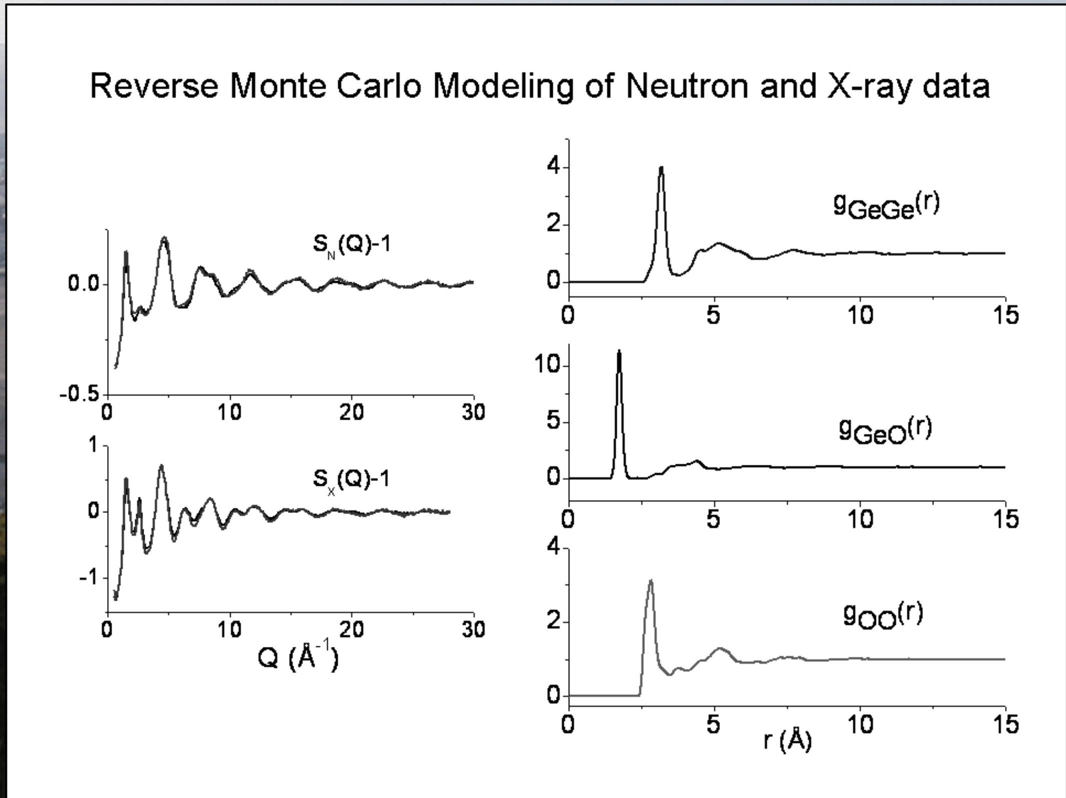


Combined neutron and X-ray data

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

Partial structure factor determination

Reverse Monte Carlo and empirical structural refinement



Studies of liquids and amorphous materials: Simple oxides

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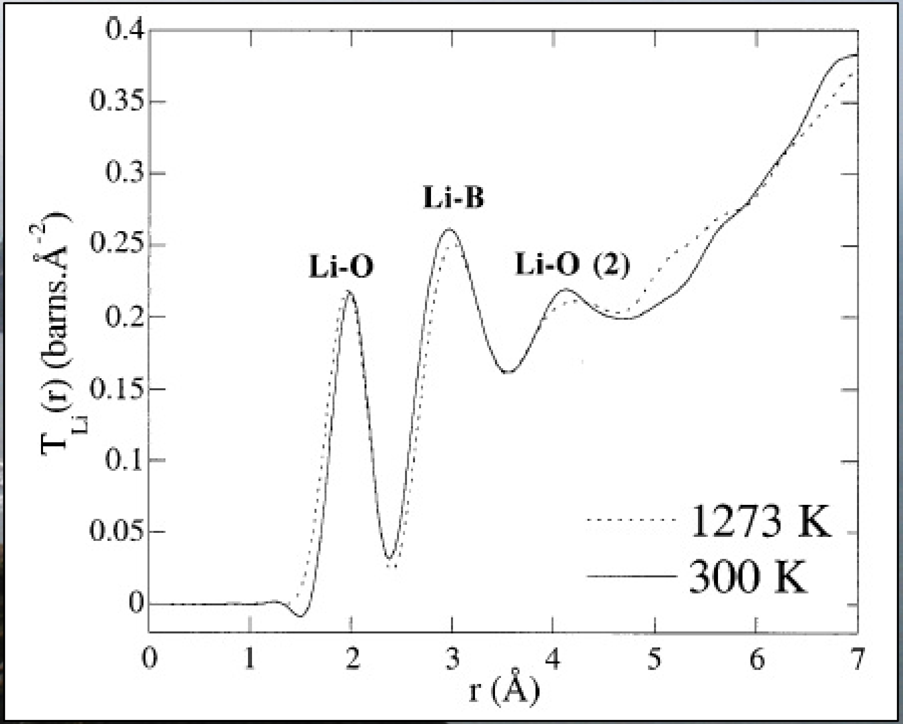
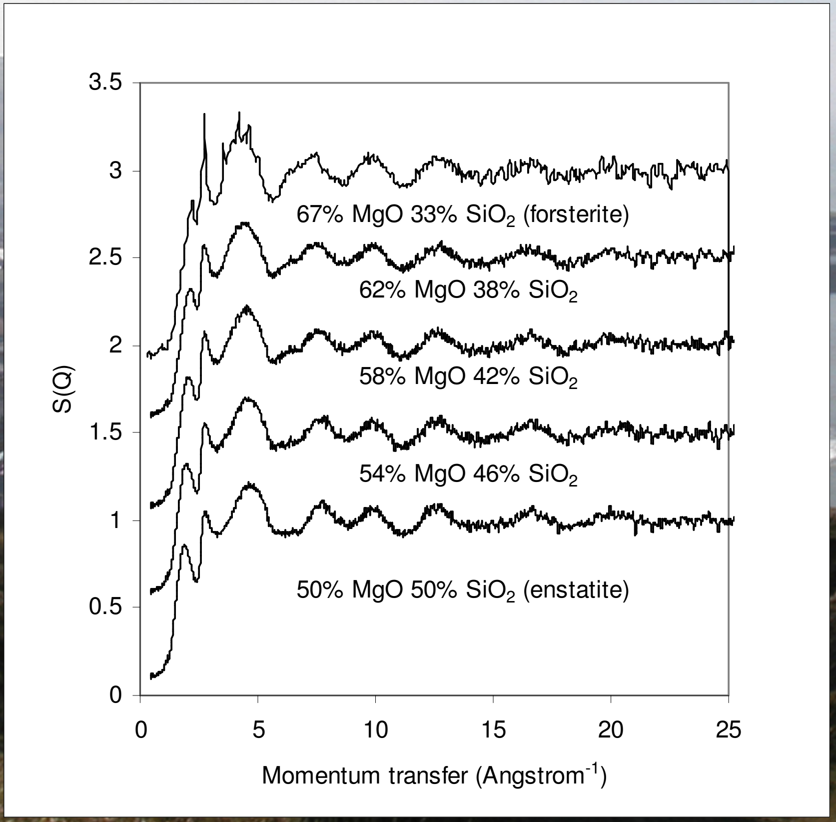
❖Confined to simple systems:

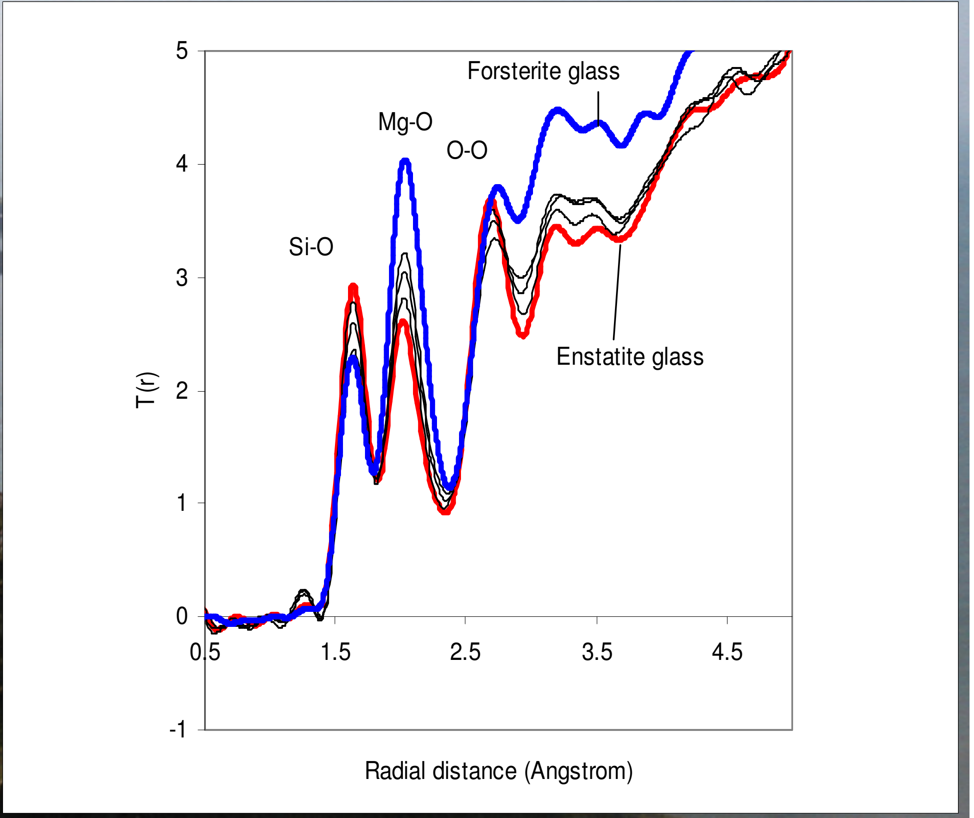
- SiO_2
- $Li_2O\text{-}SiO_2$
- $K_2O\text{-}SiO_2$
- $Na_2O\text{-}SiO_2$
- $CaO\text{-}Al_2O_3\text{-}SiO_2$



Studies of liquids and amorphous materials: Simple oxides

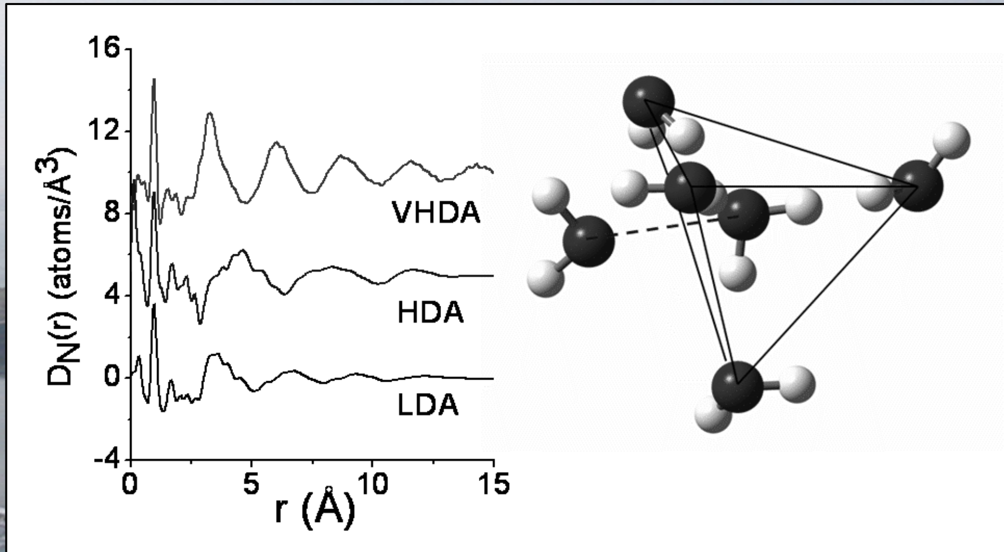
- $MgO-SiO_2$ glasses





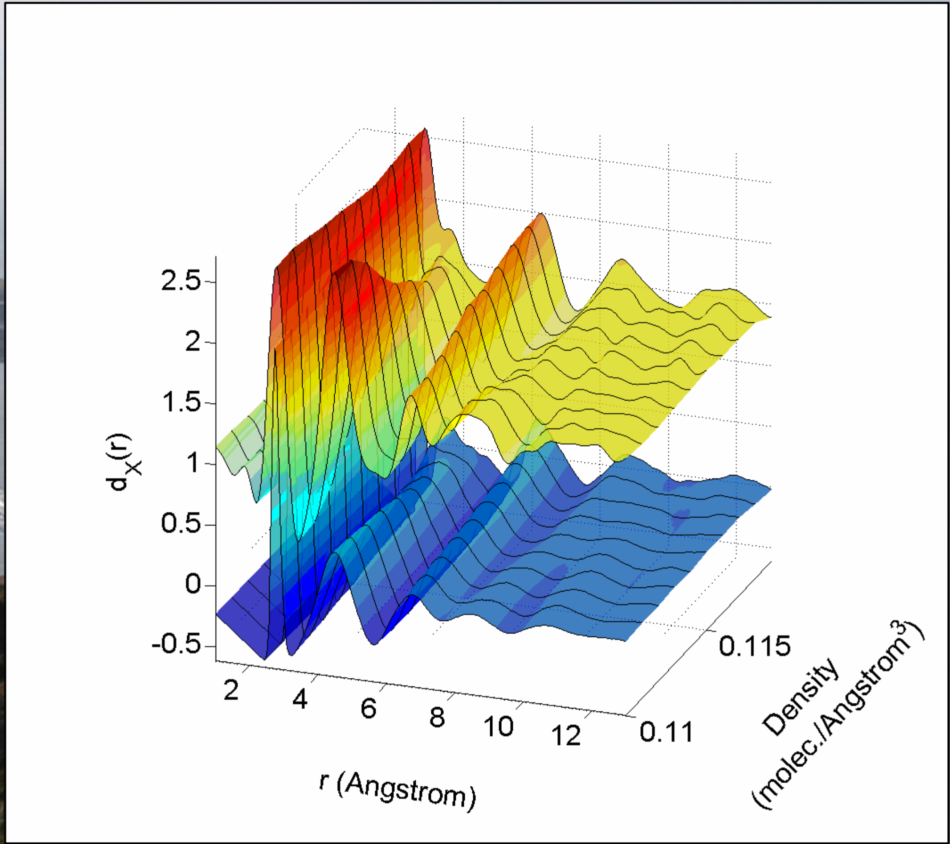
Studies of liquids and amorphous materials: amorphous ices

- 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



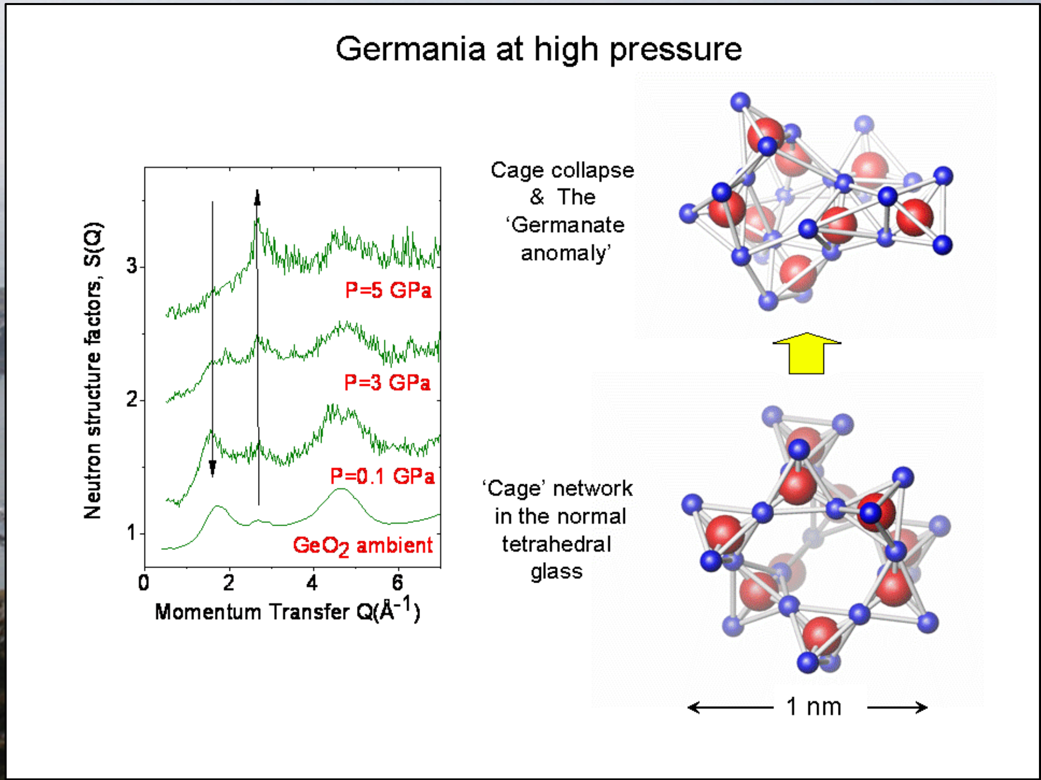
Studies of liquids and amorphous materials: amorphous ices

- ❖ 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



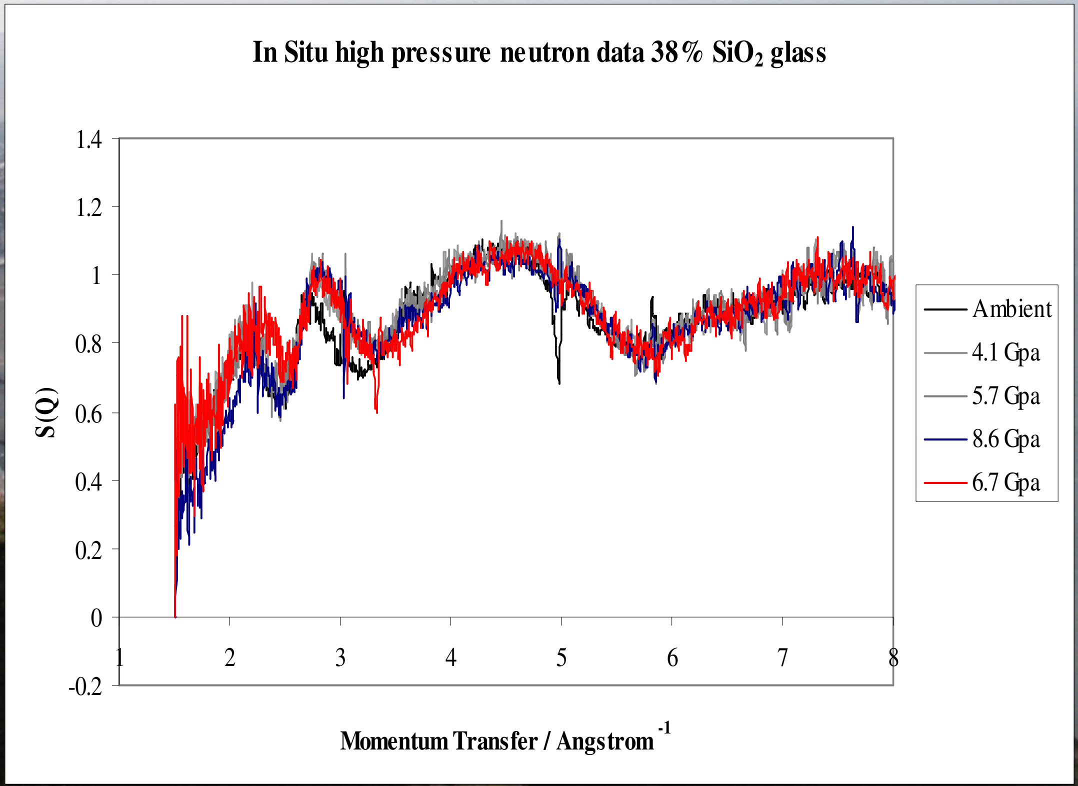
Studies of liquids and amorphous materials: high pressure studies

- Amorphous forms of GeO_2
- 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



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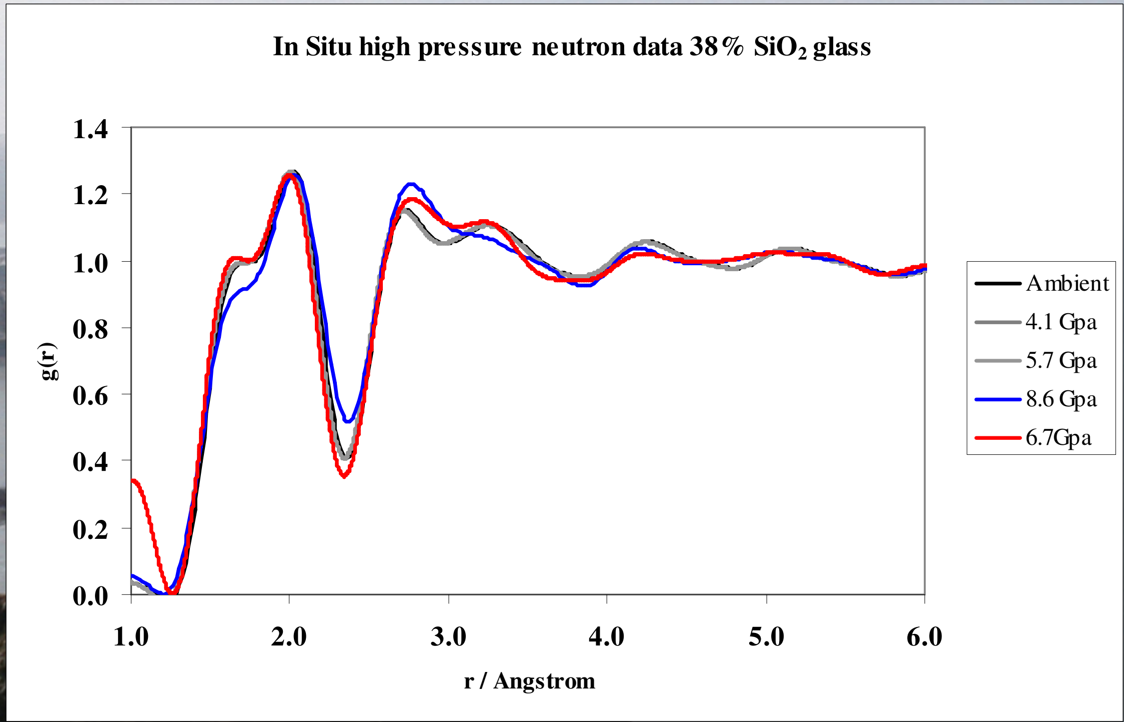
Studies of liquids and amorphous materials: high pressure studies

- **Change in first peaks**
  - **Si-O**
  - **Mg-O**
- **Increasing distortion of the Mg-O polyhedron?**
- **Non-linear change in structure**
- **Is it polyamorphic?**



Summary and future directions

- 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