

Structure of glasses and melts

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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

The Liquid State

❖ Liquids lack long-range order

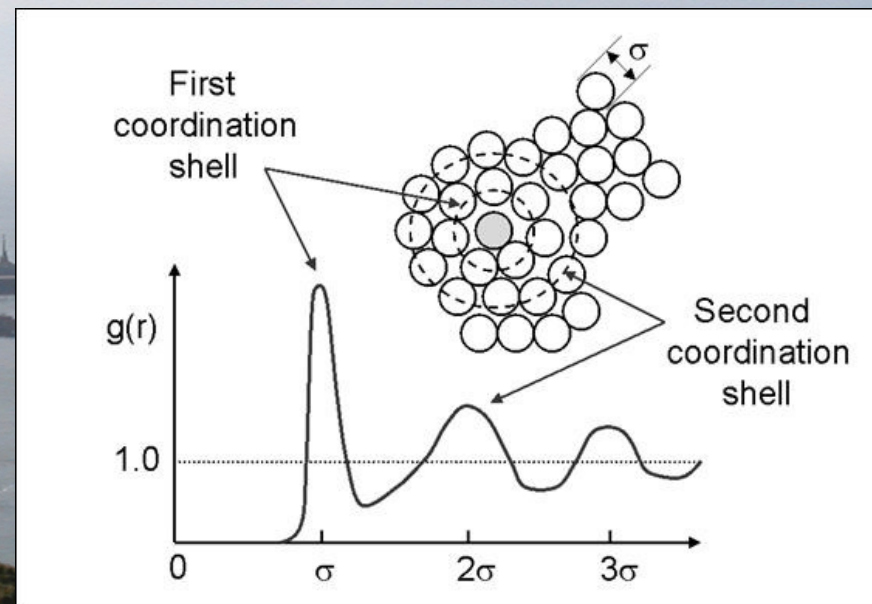
- Pair distribution function shows Short range order

❖ Glasses formed by super-cooling a liquid.

- Show a glass transition

❖ Amorphous materials by other routes

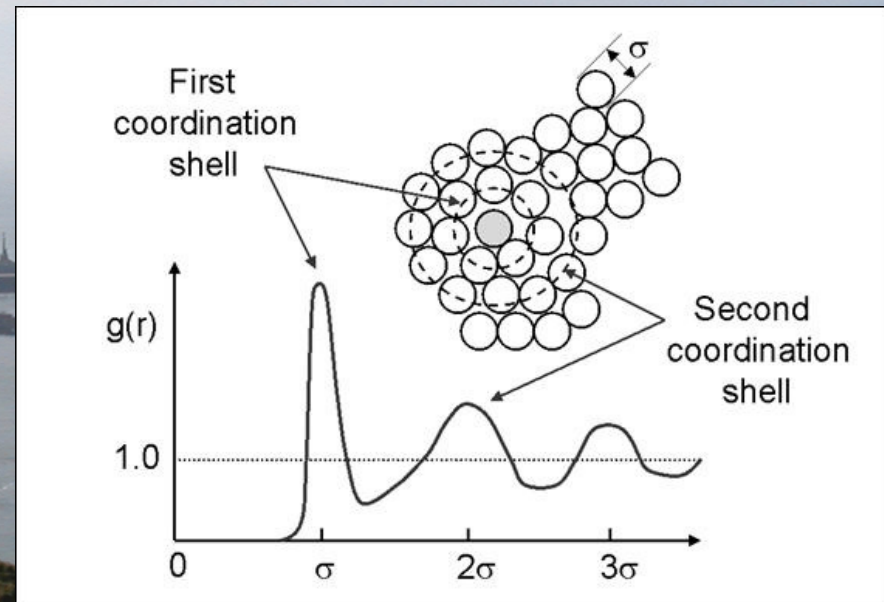
- Inherent polyamorphism





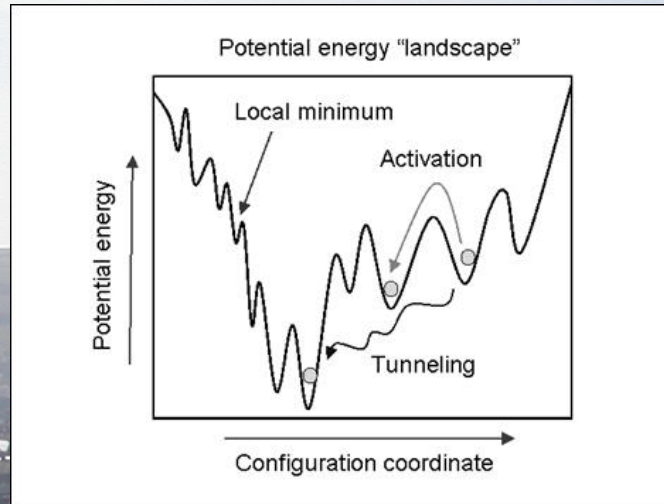
The pair distribution function

- ❖ 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

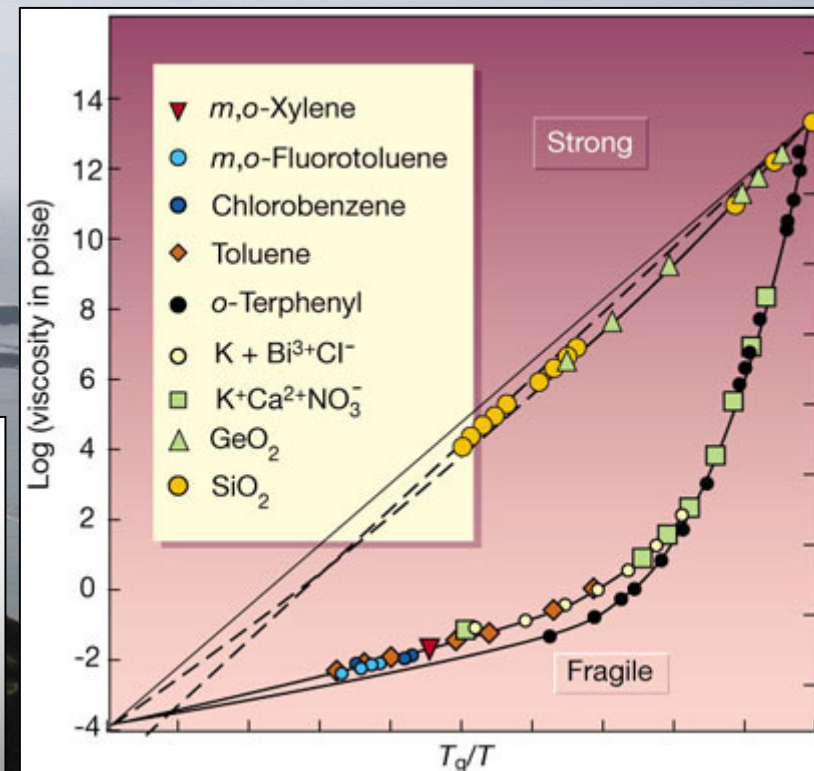


❖ Super-cooling

- Ergodicity
- Non-ergodicity

❖ Configurational entropy and fragility

❖ Pressure-induced amorphisation





Neutron diffraction: Scattering theory

❖ Double differential cross section

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

❖ Coherent scattering law

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

❖ Static approximation

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

Neutron diffraction: Scattering in multi-component systems

❖ Scattering:

- Sum of several atom-pairs
- Partial contributions

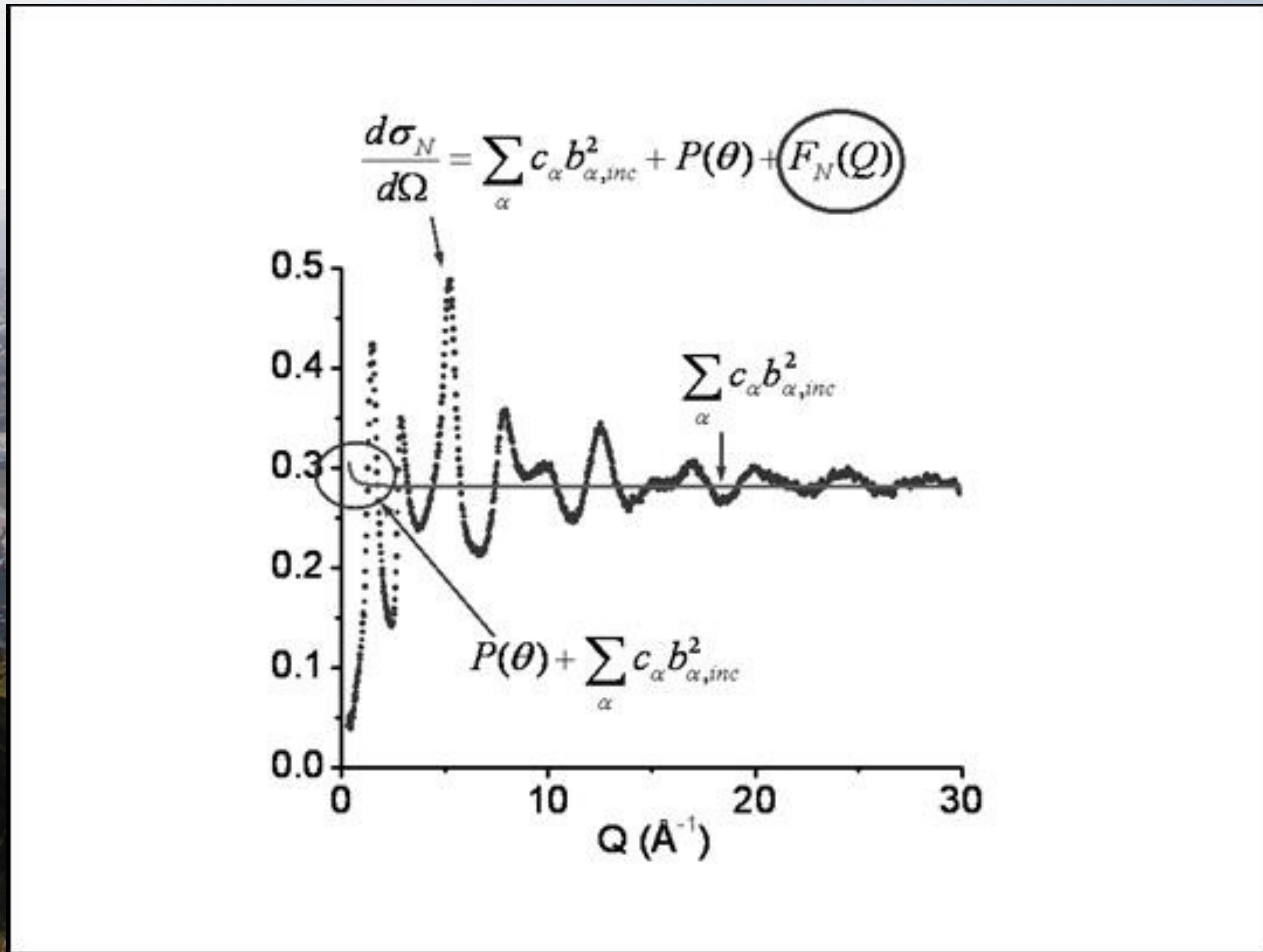
❖ Faber-Ziman formalism

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

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



Neutron diffraction: the differential cross section





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 finding 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.

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

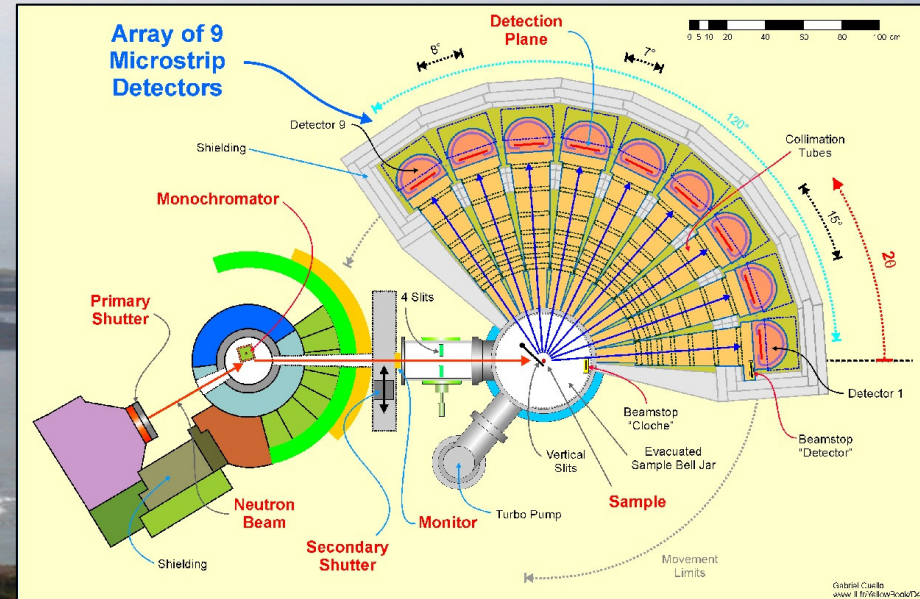
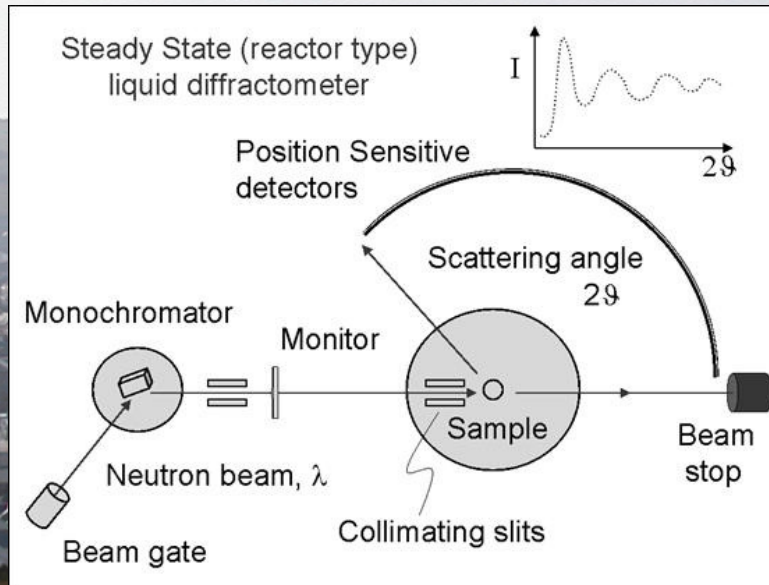
$$G(r) = \frac{1}{2\pi^2 r \rho_0} \int_0^\infty Q F(Q) \sin(Qr) dQ = \sum_{\alpha,\beta} c_\alpha c_\beta \bar{b}_\alpha \bar{b}_\beta [g_{\alpha,\beta}(r) - 1]$$

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

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



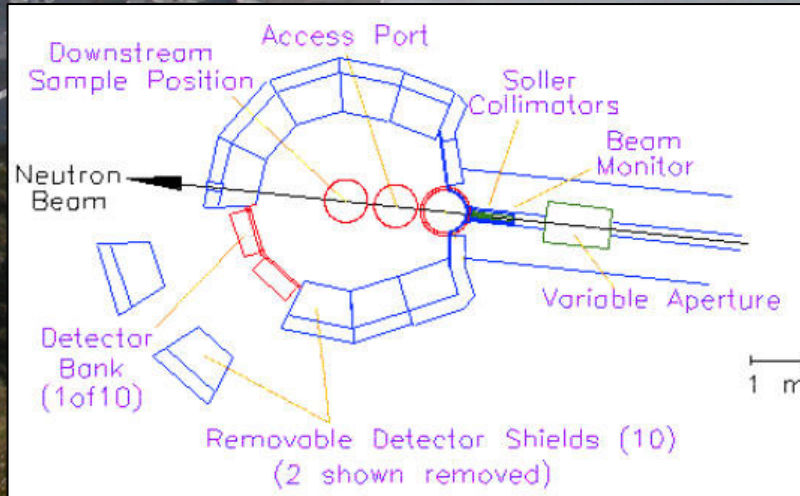
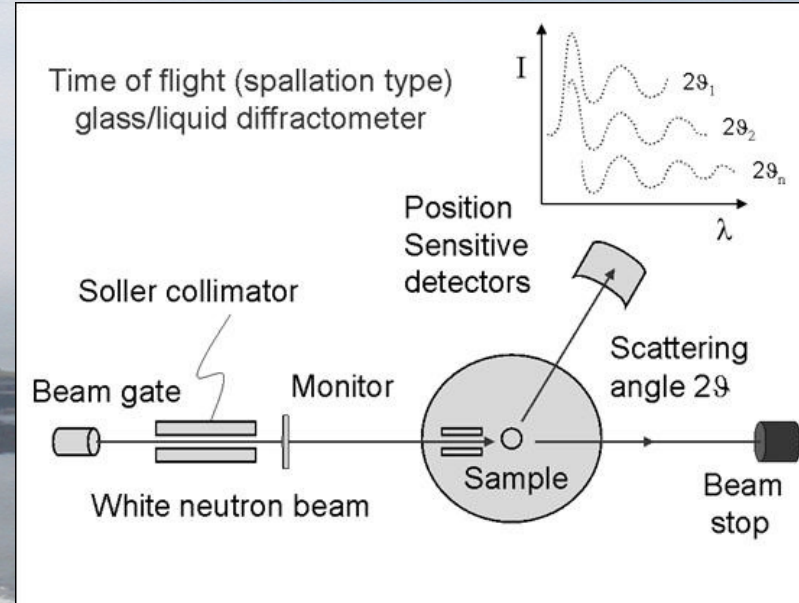
Neutron instrumentation



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



Neutron instrumentation

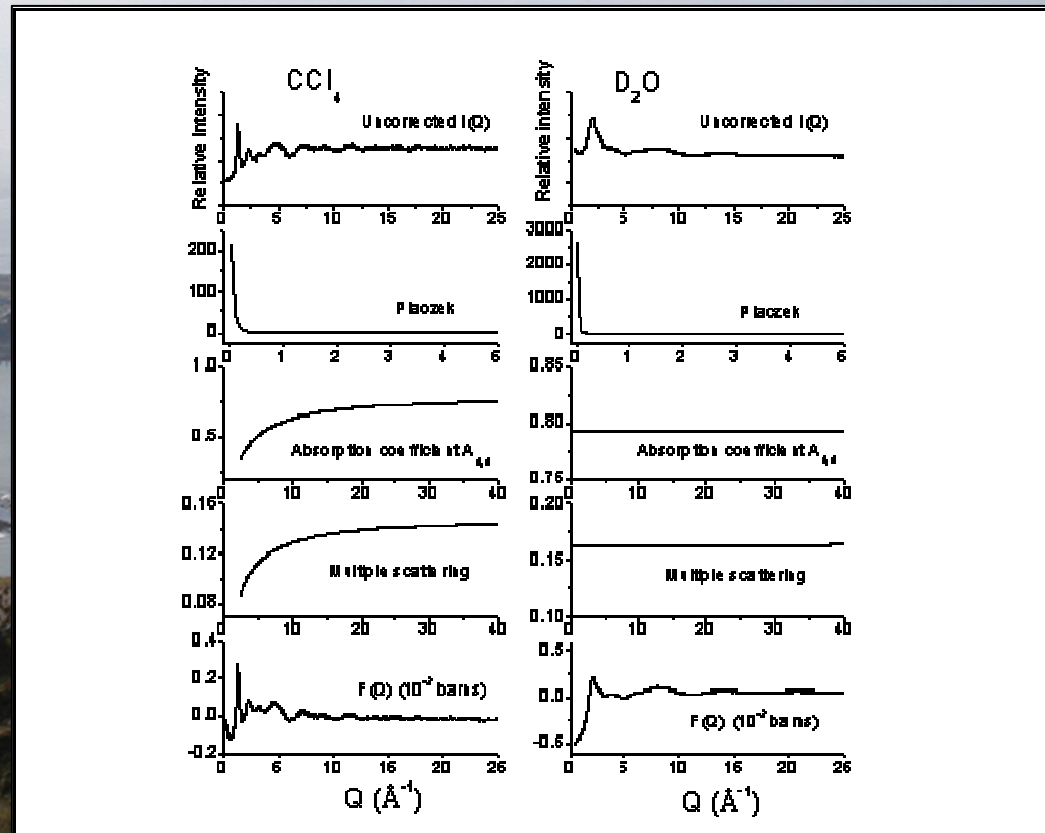
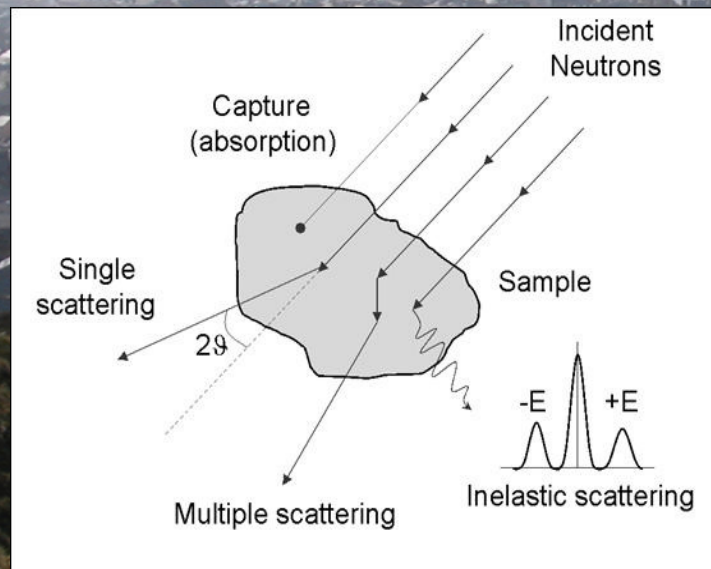


- ❖ Time-of-flight (spallation source)
- ❖ Detectors at fixed angle record different wavelengths (Q)



Neutron diffraction: correction procedures

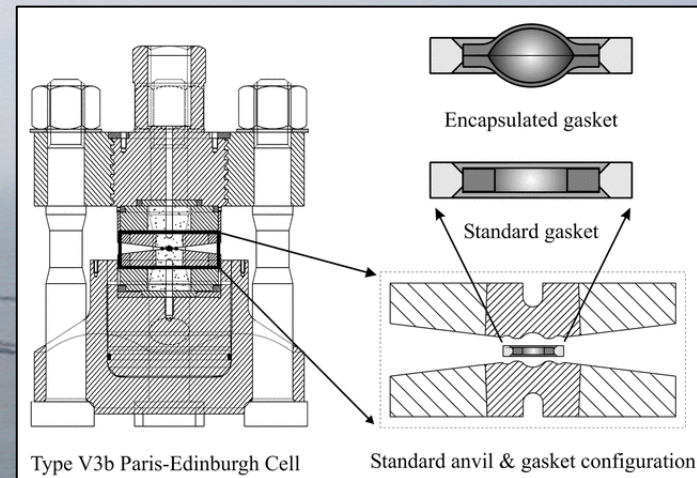
Structural information
 is in elastic, single
 scattering events.





Sample environments

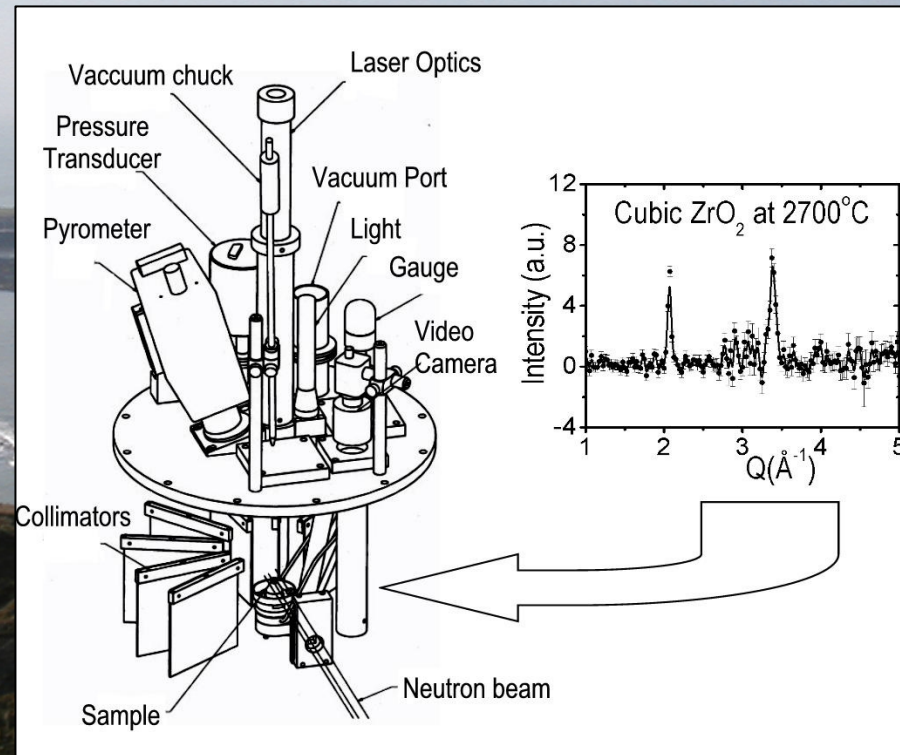
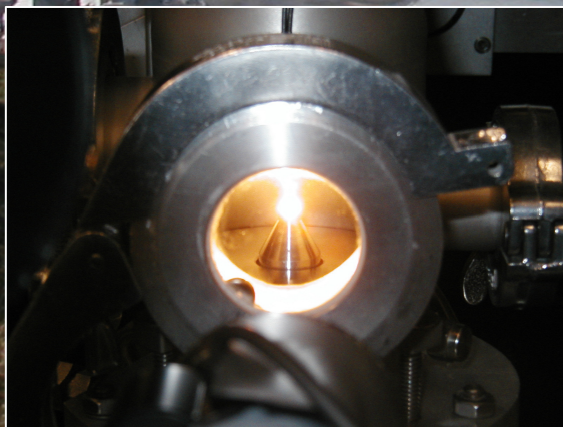
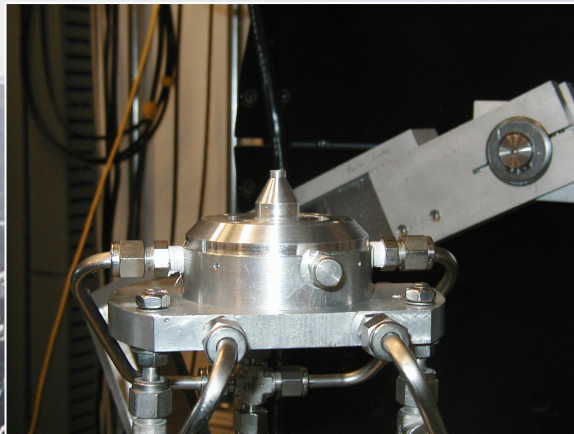
Pressure cells





Sample environments

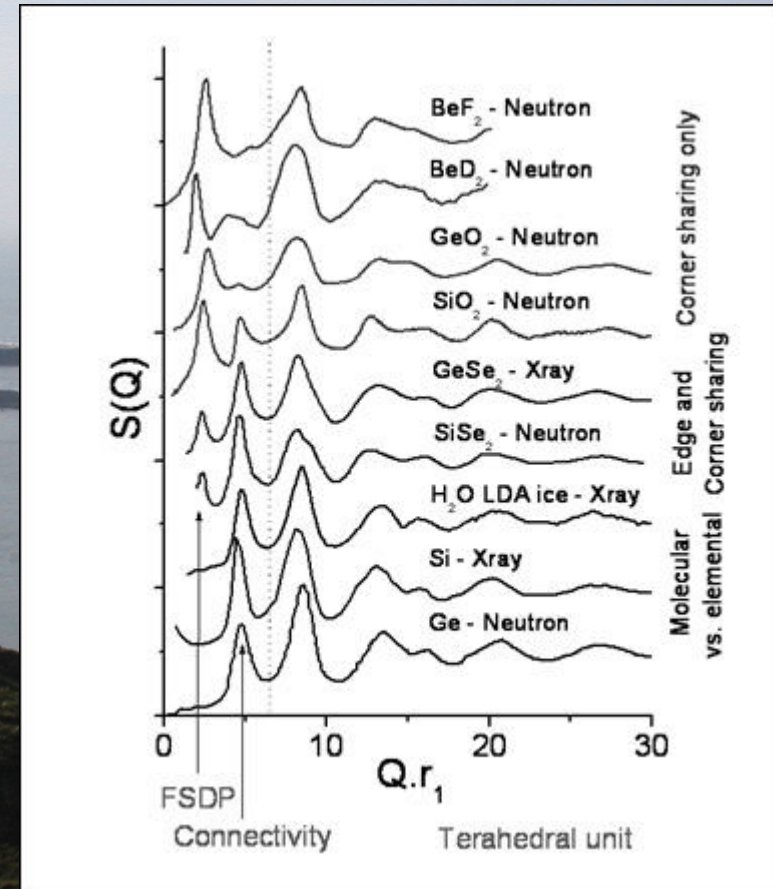
Containerless levitation





Interpretation of glass structure

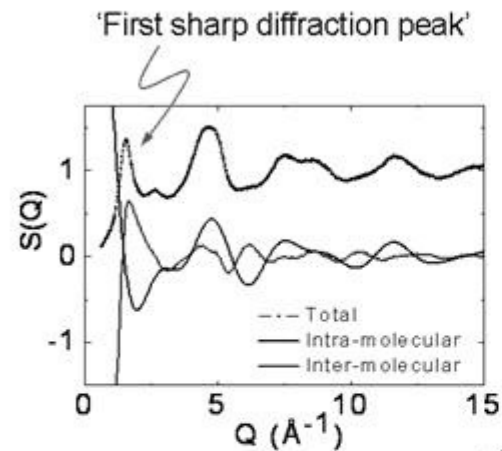
- ❖ Based on the pair distribution function (PDF)
- ❖ Continuous random networks (CRN)
- ❖ Characteristic distance ranges



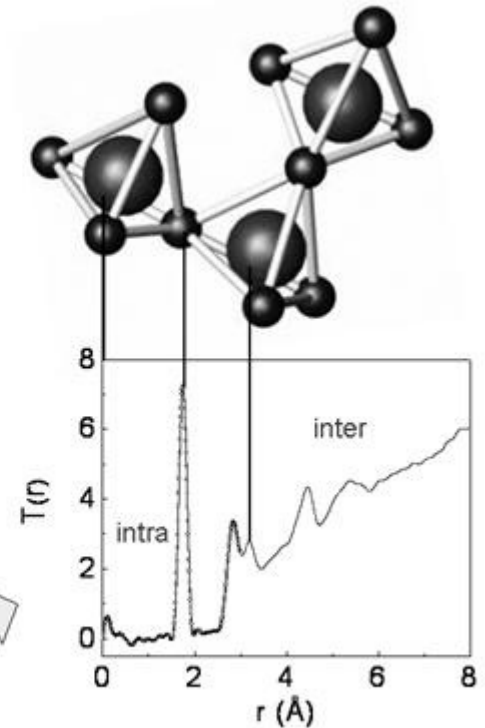


Interpretation of glass structure

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

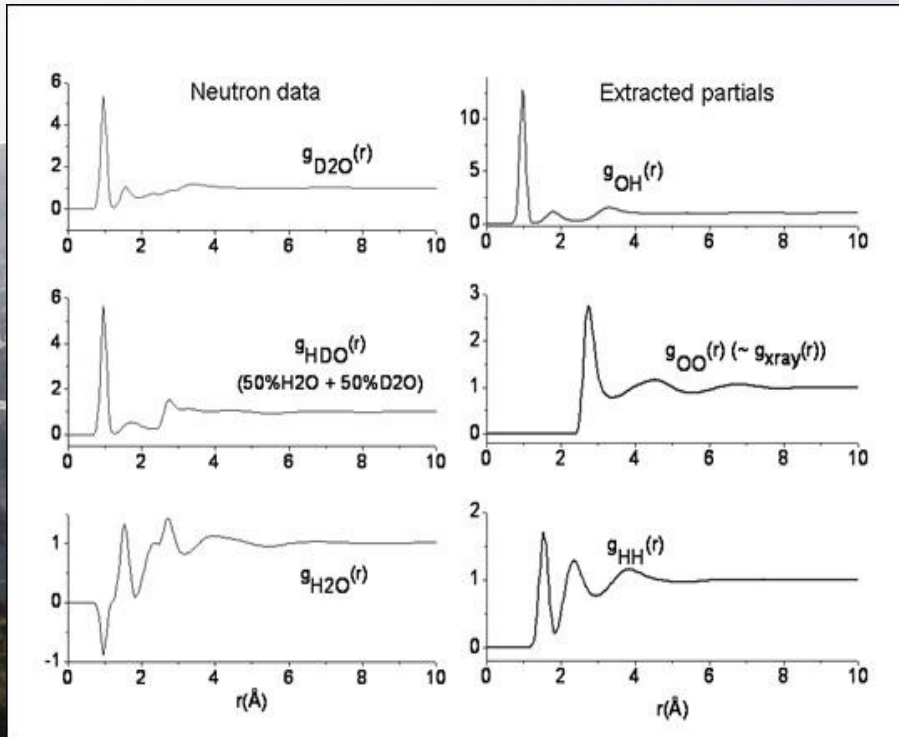


Sine Fourier Transformation
 $S(Q) \rightarrow T(r) = 4\pi r \cdot g(r)$





Partial structure factor determination



Isotopic substitution, e.g.
 H/D

$$G_{H_2O}(r) = \frac{c_H^2 b_H^2}{A} g_{HH}(r) + \frac{2c_H c_O b_H b_O}{A} g_{OH}(r) + \frac{c_O^2 b_O^2}{A} g_{OO}(r)$$

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

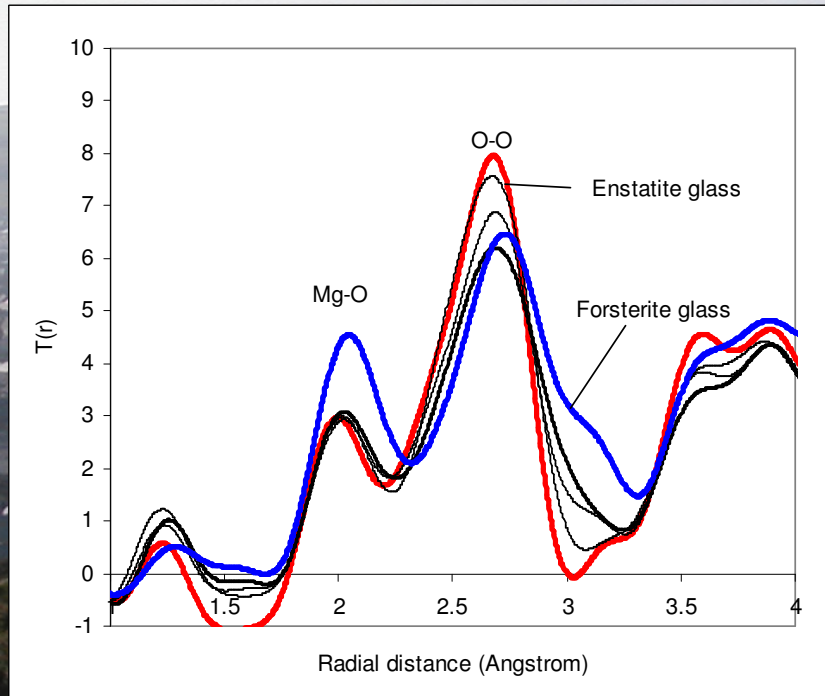
$$G_{H_2O}(r) = 0.318 g_{HH}(r) - 0.492 g_{OH}(r) + 0.190 g_{OO}(r)$$

$$G_{H_2O}(r) = 0.486 g_{HH}(r) + 0.423 g_{OH}(r) + 0.091 g_{OO}(r)$$

$$G_{H_2O}(r) = 0.113 g_{HH}(r) + 0.446 g_{OH}(r) + 0.441 g_{OO}(r)$$



Partial structure factor determination



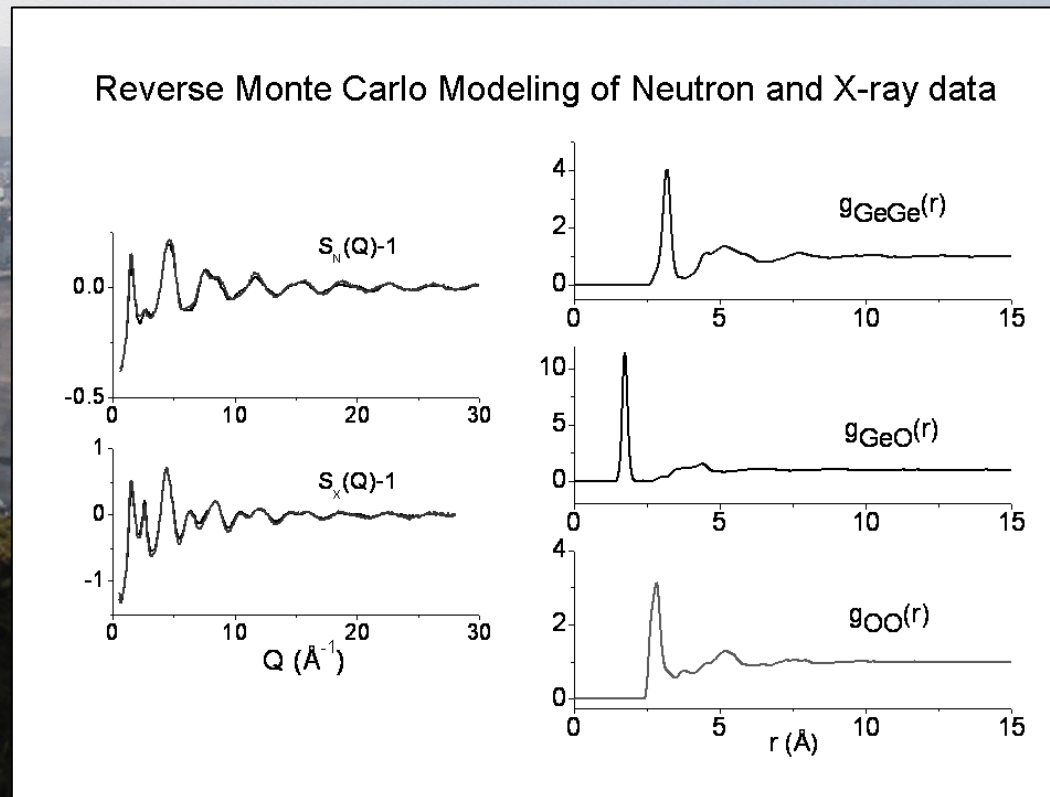
Combined neutron and X-ray data

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



Partial structure factor determination

Reverse Monte Carlo and empirical structural refinement

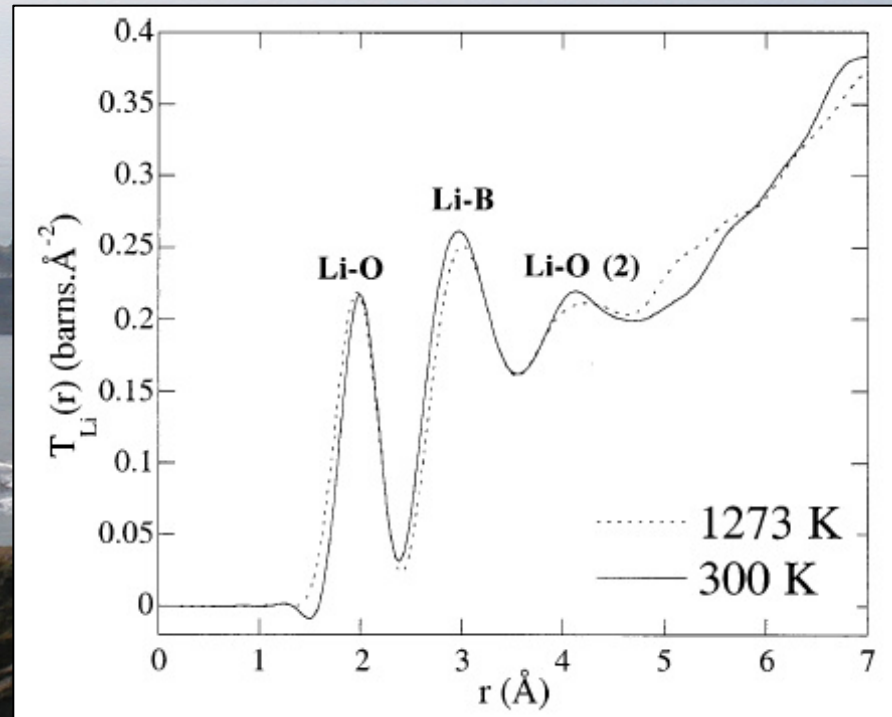




Studies of liquids and amorphous materials: Simple oxides

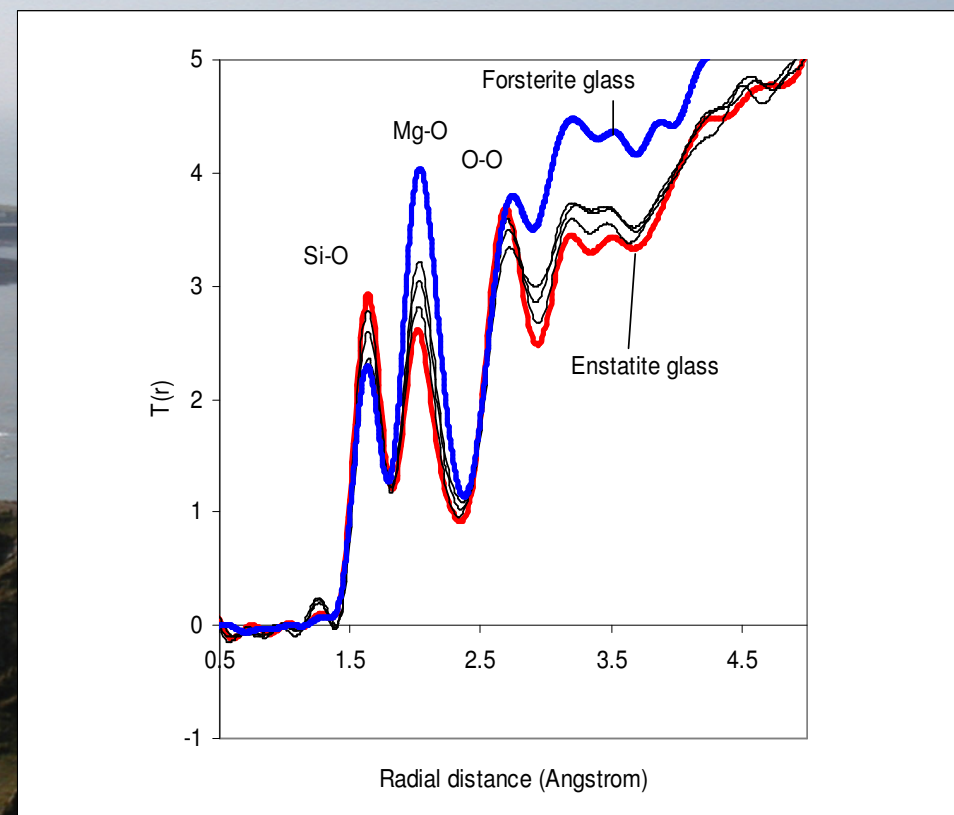
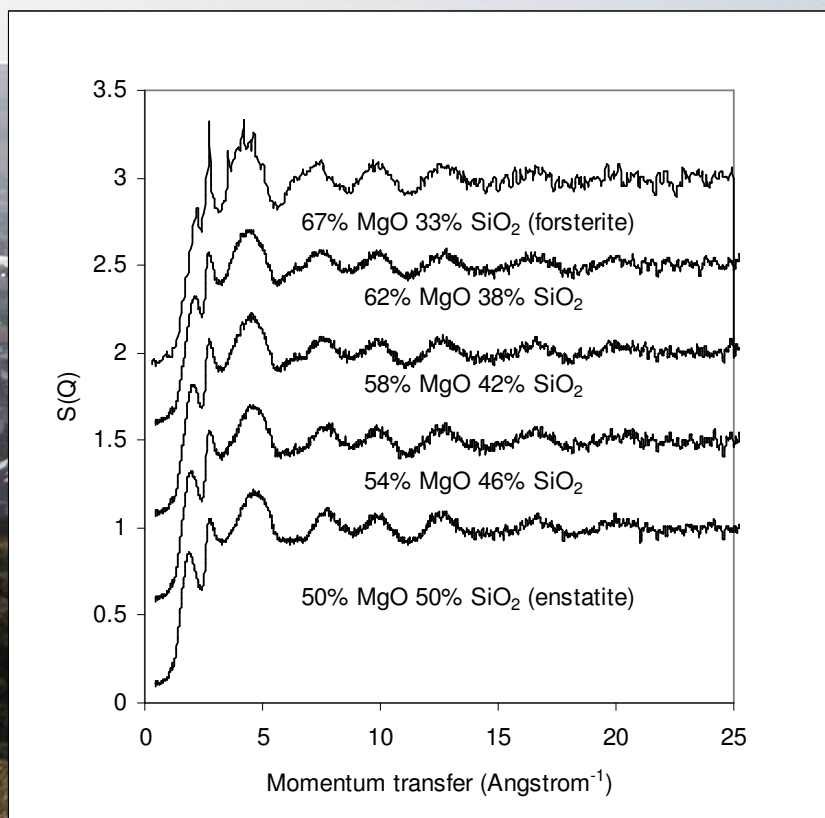
❖ Confined to simple systems:

- SiO_2
- $\text{Li}_2\text{O-SiO}_2$
- $\text{K}_2\text{O-SiO}_2$
- $\text{Na}_2\text{O-SiO}_2$
- $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$



Studies of liquids and amorphous materials: Simple oxides

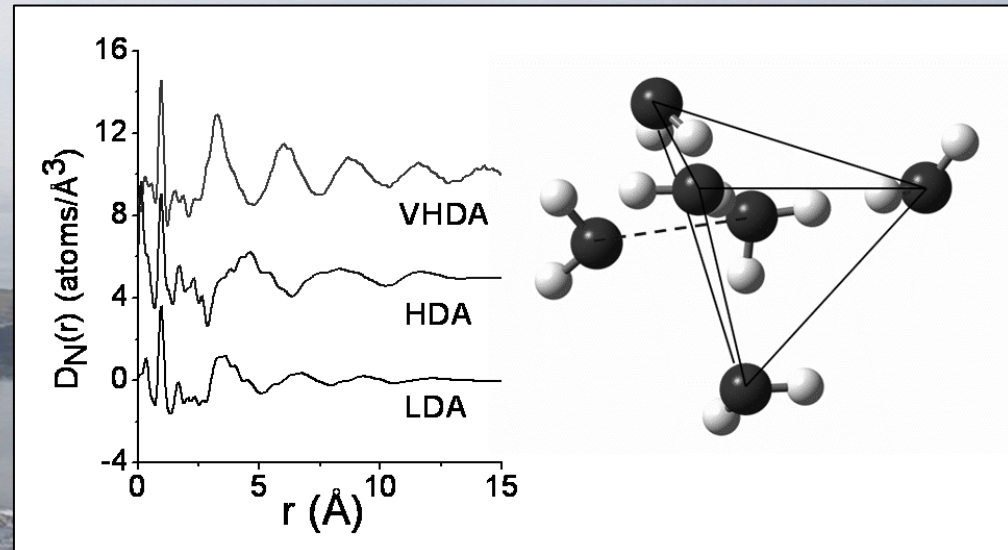
❖ MgO-SiO₂ glasses





Studies of liquids and amorphous materials: amorphous ices

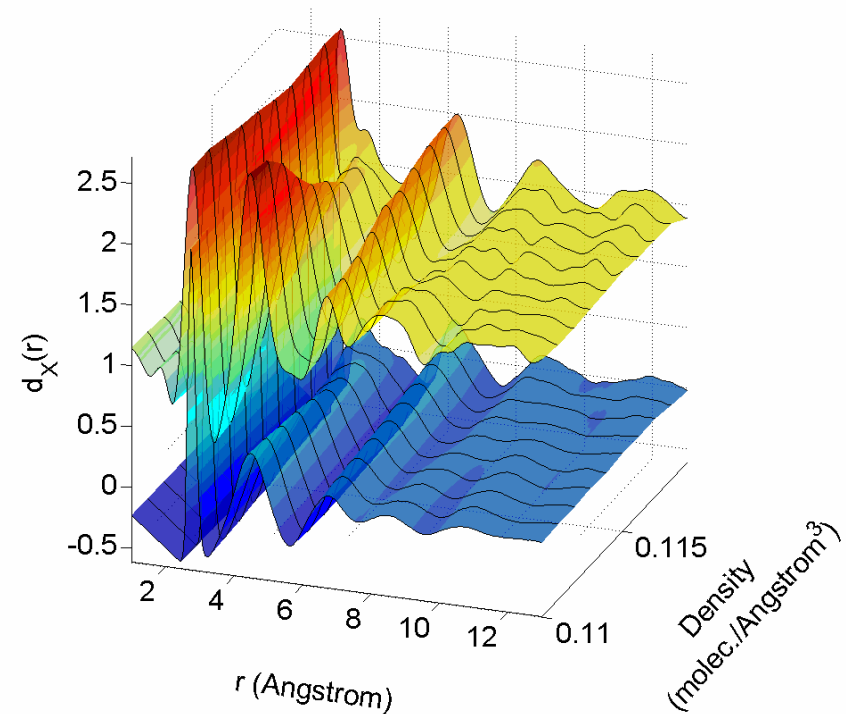
- Low and high-density forms of amorphous ice
- Demonstration of LDA-HDA transitions
- Fully hydrogen-bonded tetrahedral networks
- Interstitial water molecule
- Related to the high pressure structure of liquid water





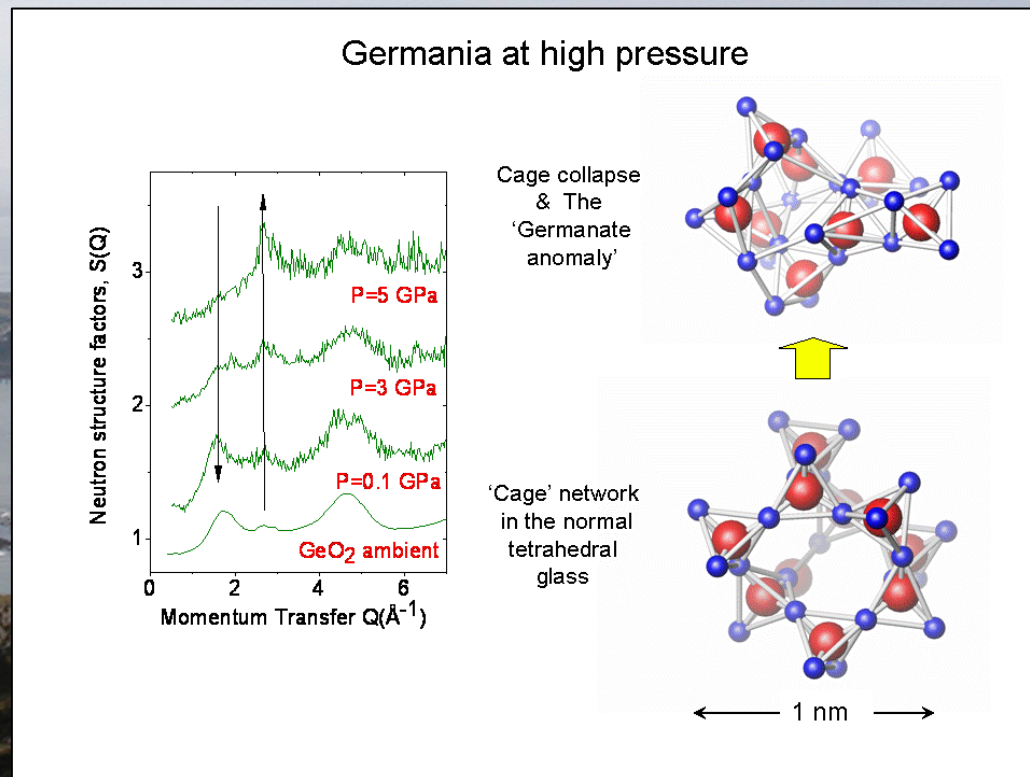
Studies of liquids and amorphous materials: amorphous ices

- ❖ 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



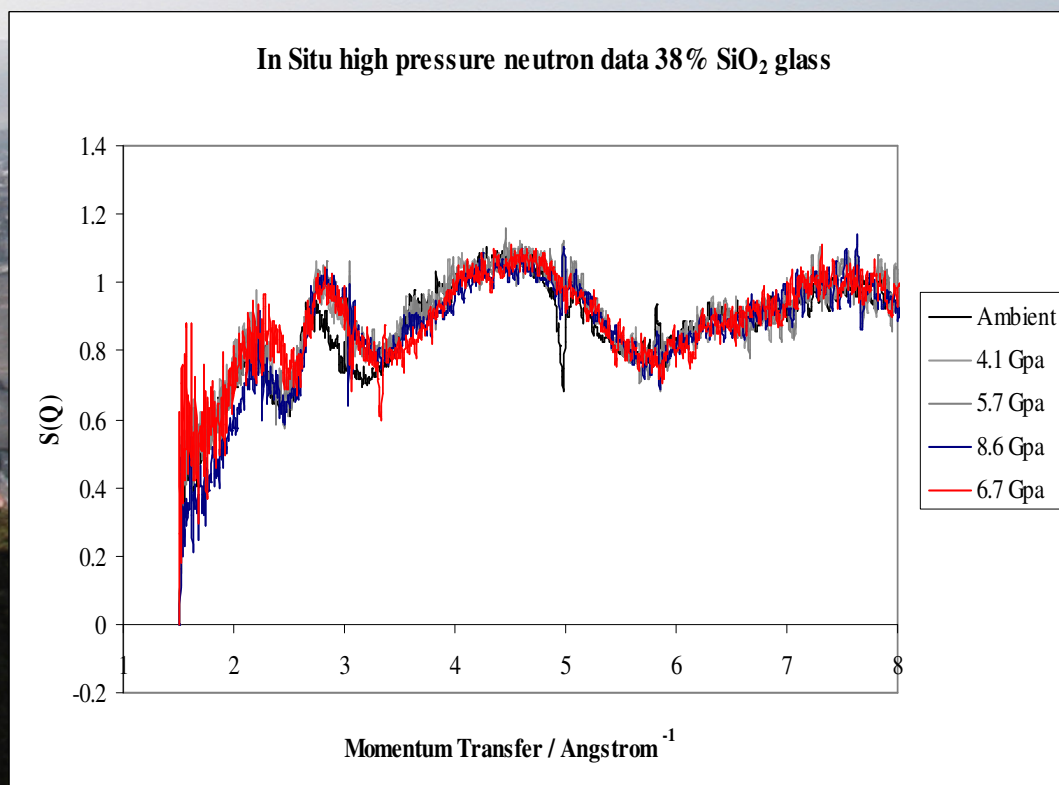
Studies of liquids and amorphous materials: high pressure studies

- ❖ 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-SiO₂ glasses: Neutron diffraction

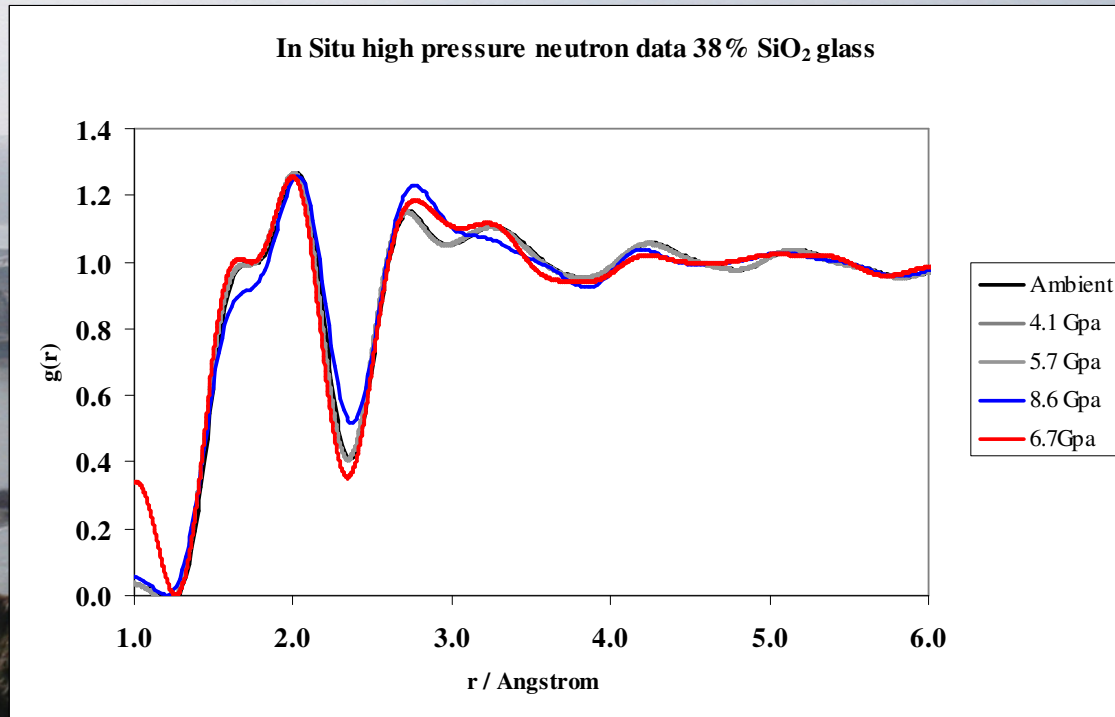
Abrupt changes in the S(Q) between 6 and 8 GPa





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?**



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