Neutron and X-ray Scattering Studies

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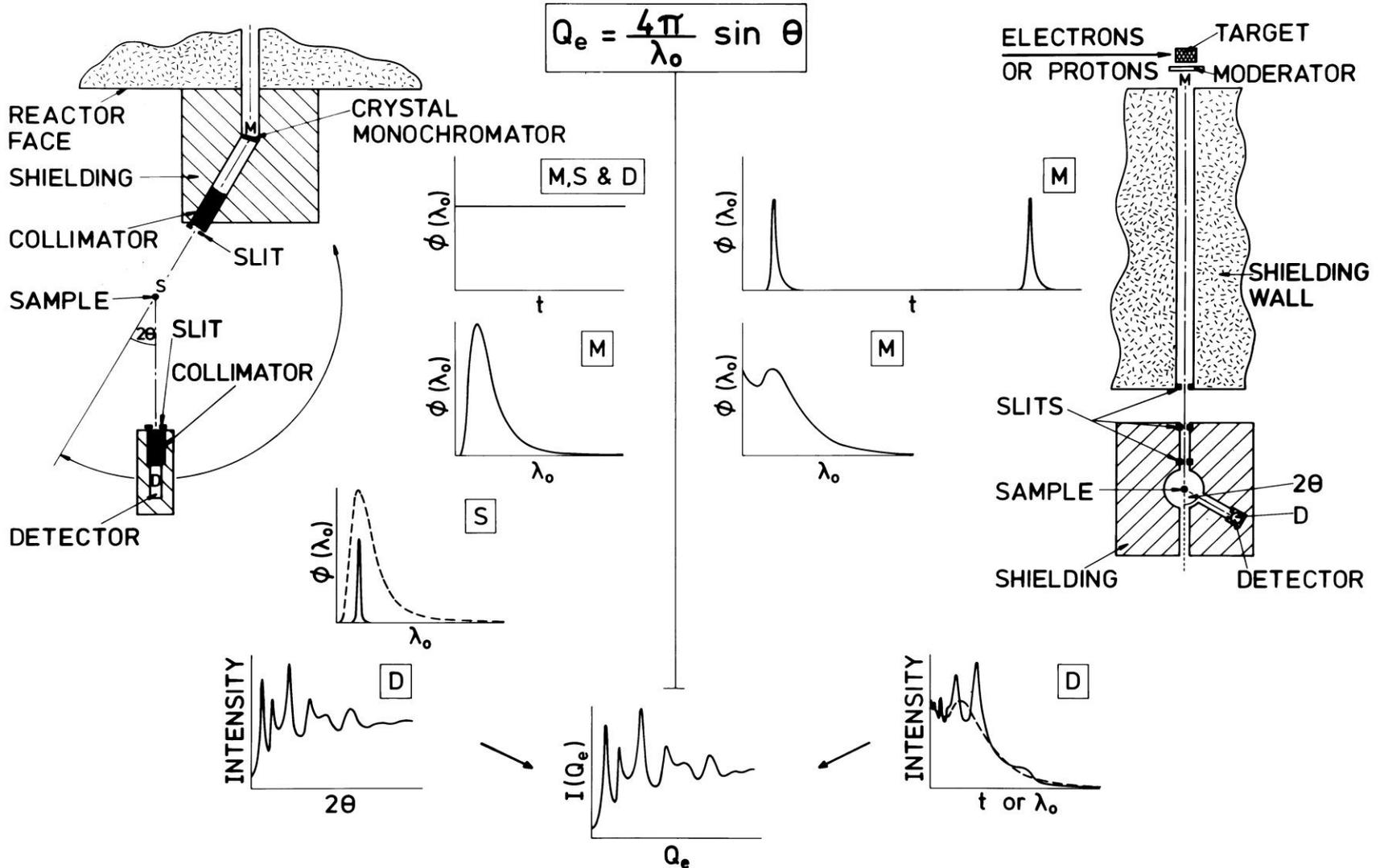
Outline

- Review of experimental layouts and corrections

- Normalization and reproducibility

- Interpreting the correlation functions

Neutron Diffraction Techniques

STEADY STATE REACTOR

PULSED ACCELERATOR SOURCE

$$Q_e = \frac{4\pi}{\lambda_0} \sin \theta$$

Corrections

- ## Background:
    - cosmic and instrumental
    - cylinder is complicated; plane is easy
    - Instrumental eliminated by evacuation or helium

- ## Absorption and multiple scattering

$$I(Q_0) = [1 - A_1(Q_0)]\sum_{i=1}^{\infty} I_i(Q_0)$$

Where A_1 is the absorption after one scattering event and $I_i(Q_0)$ is the true intensity

- ## X-rays absorption>> multiple scattering

- ## Neutrons easy if σ^A is small and sample is not in a can

Corrections

- ## Neutron multiple scattering:
  - If multiple scattering <10% it is isotropic can be subtracted

- ## Anomalous Dispersion if wavelength is close to an absorption edge f or b can become complex

Corrections

- ## X-ray
  - Polarization: unpolarized light is assumed but this is not realistic
  - Residual Compton from the monochromator

- ## Neutron
  - Departure from static approximation (that we integrate along ω-Q_0 space and is corrected for by an expansion of the self scattering
 - The bottom line is that if your Placzek corrections don't work you get a droopy i(Q)

- ## Other Corrections
  - Beam Fluctuations
  - Detector/electronic dead time
  - Extrapolation to Q=0

Normalization

- Intensity is arbitrary units until you normalize

- We know that as r goes to 0 $\rho_{jk}(r)$ should go to zero so I can be scaled this only works for fixed wavelength

- OR for neutrons vanadium scatters incoherently so if you have a piece of vanadium equal in size to your sample it will give you the incident beam spectrum at each angle.

# Experimental Uncertainty in *T*(*r*)
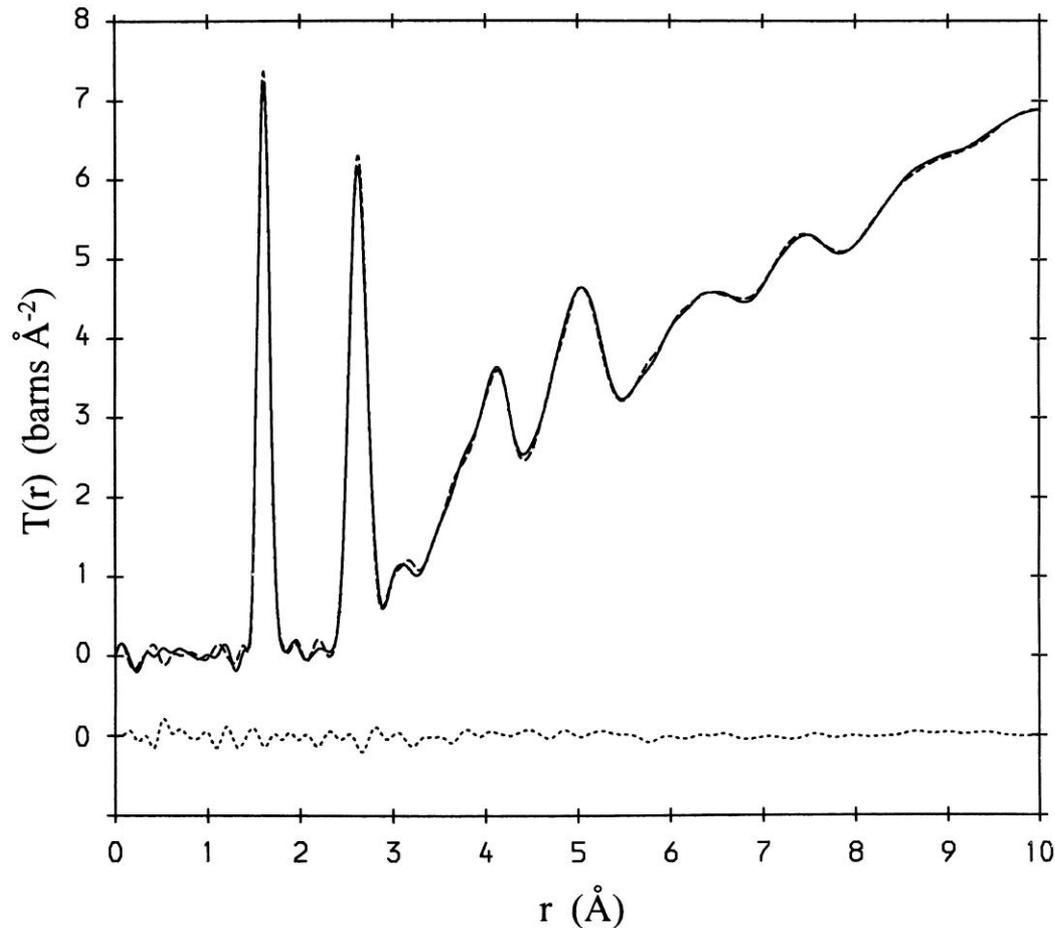
The solid and dashed lines represent two data sets for vitreous silica, obtained with different combinations of instrument and approximately 10 years apart. The dotted line gives the difference between the two data sets.

Mining the Data

- So we take the Intensity data remove background correct and normalize it.

- We calculate the interference function then Fourier Transform that (using computational techniques) to the correlation functions……………………………………….then what????

- Lets start with something really simple
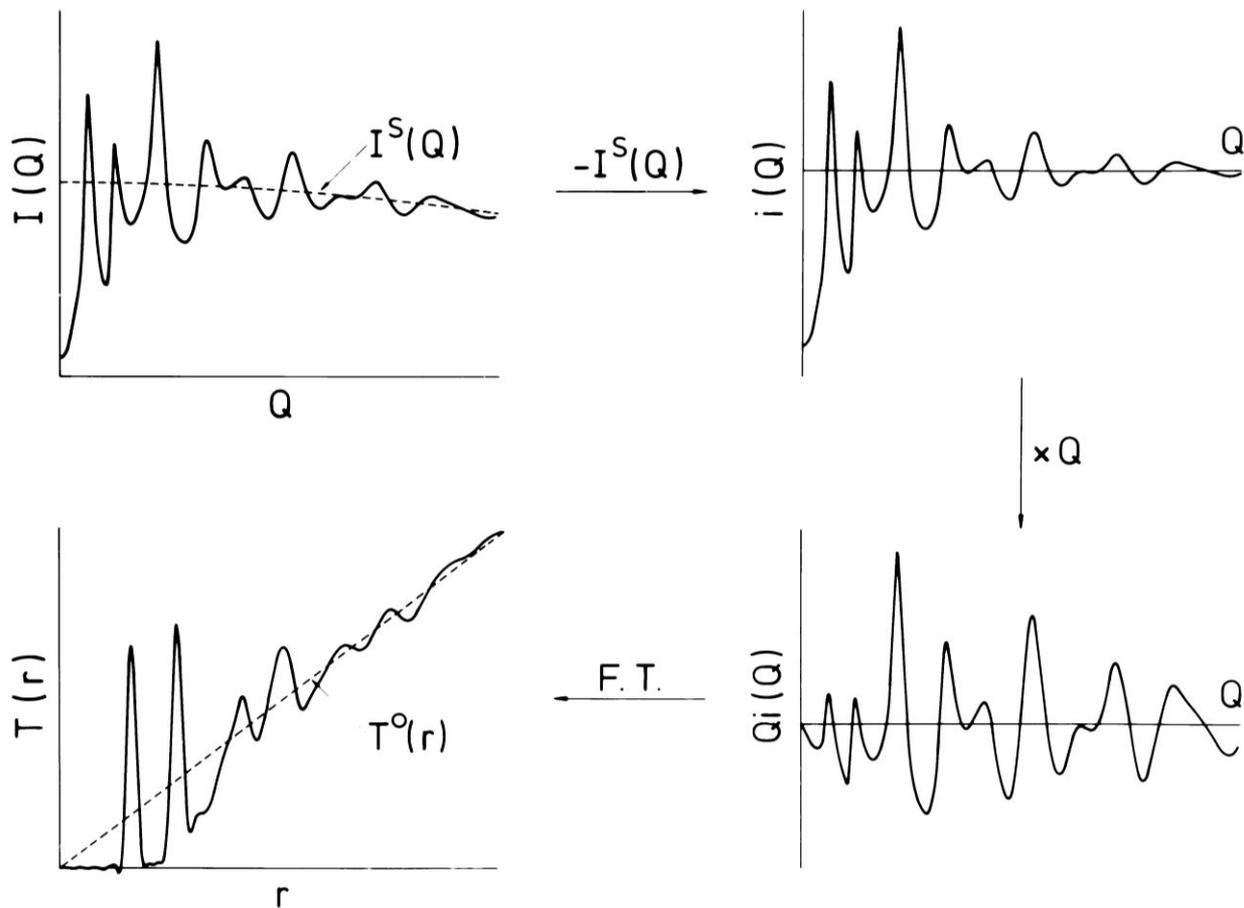
Neutron Correlation Function for Vitreous SiO$_2$
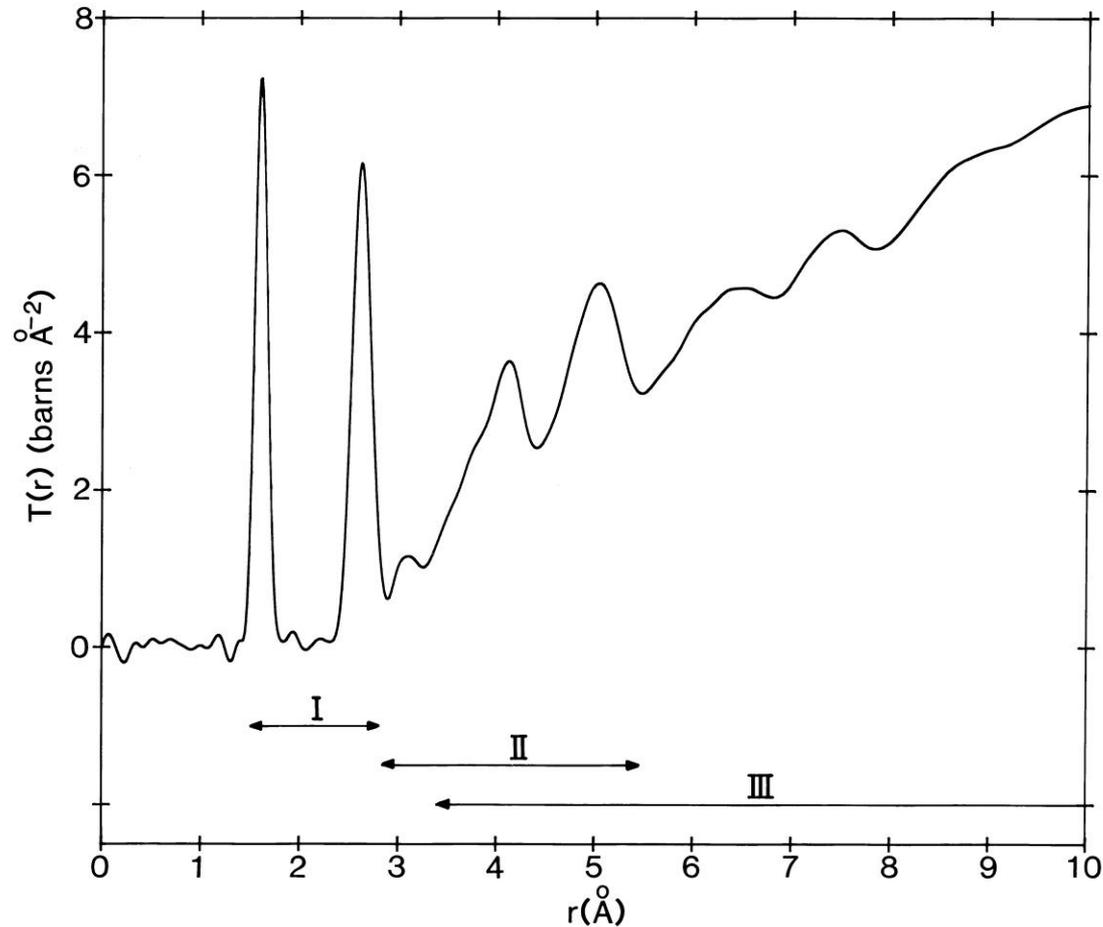
The neutron correlation function, *T*(*r*), for vitreous silica, showing the extent of the contributions from the order in ranges I, II and III.

T(*r*) from a Neutron Diffraction Experiment

$$I(Q) = I^S(Q) + i(Q)$$

self   distinct

$$T(r) = T^\circ(r) + \frac{2}{\pi} \int_0^\infty Qi(Q) M(Q) \sin rQ \, dQ$$

Structural Models of Amorphous Solids

1. Random Network.
    (a) Hand built.
    (b) Computer generated.
    (c) Geometric transformation.
2. Random Coil.
3. Random Sphere Packing.
    (a) Hand generated.
    (b) Computer generated.
4. Molecular Model.
5. Crystal Based Models.
    (a) Limited range of order (finite size).
    (b) Strained crystal models.
6. Layer model.
7. Amorphous Cluster.
8. Monte Carlo Techniques.
    (a) Conventional (energy minimisation).
    (b) Reverse (minimisation of difference from experiment).
9. Molecular Dynamics Simulation.

OK but before we go that far can we mine the data for as much information as possible without inferring a structural model?

Neutron Correlation Function for Vitreous SiO_2
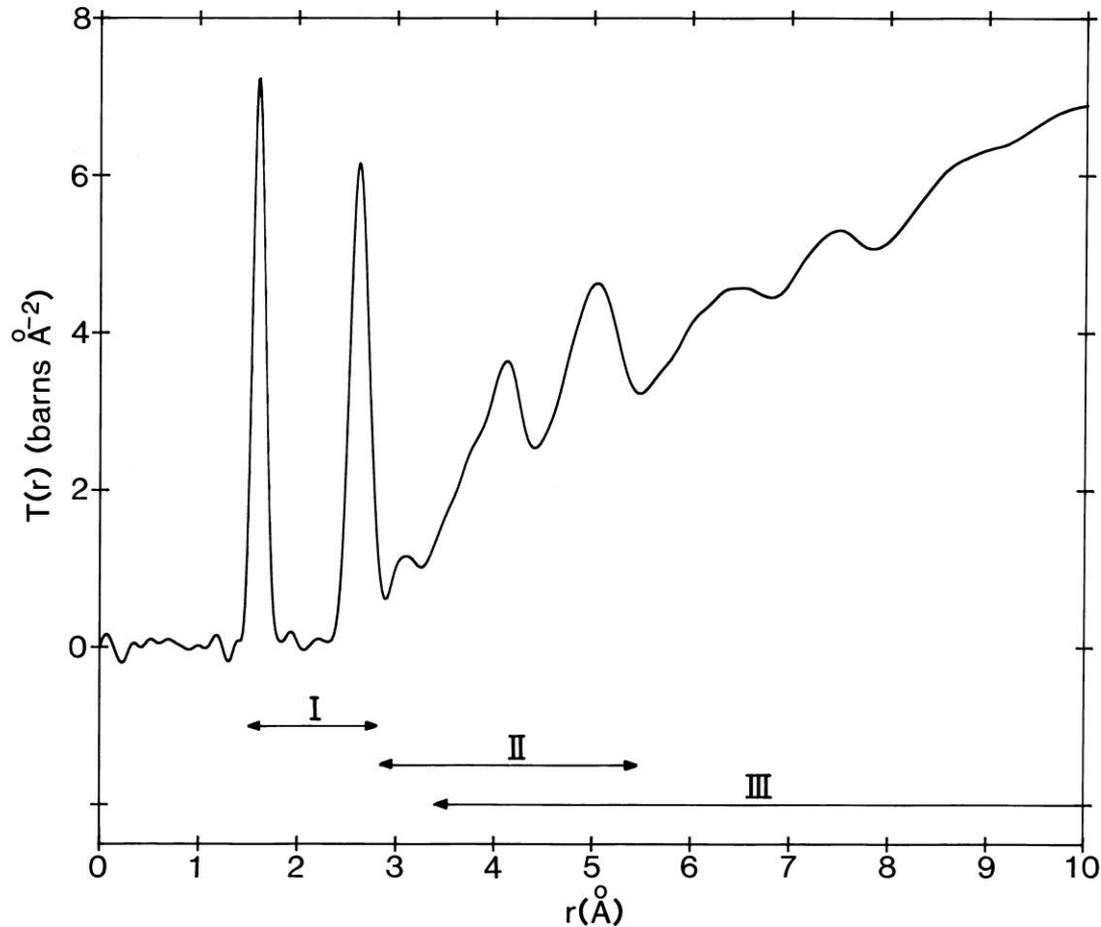
The neutron correlation function, *T(r)*, for vitreous silica, showing the extent of the contributions from the order in ranges I, II and III.

Range I – parameters include the internal co-ordination number and the distribution of bond lengths and angles.

Range II – parameters include the connection mode (corner, edge or face sharing) the connectivity (number of connected structural units) and the distribution of bond and torsion angles. It is in range II that the glass first differs from the crystal.
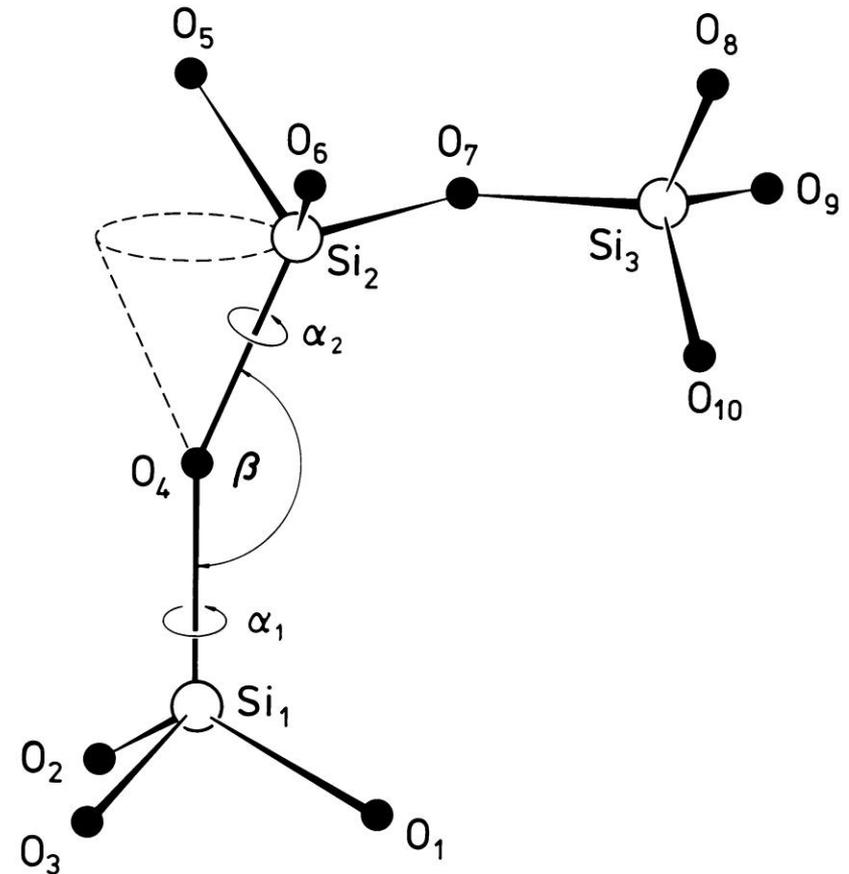
Neutron Peak Fit: Get the Bond length, Distribution and Coordination Number

A fit (dashed lines) to the first two peaks in the neutron correlation function, $T(r)$, for vitreous silica (solid line). The dotted line is the residual and the upper curve is the unbroadened fit. The mean Si–O bond length is 1.608 ± 0.004 Å, with an rms deviation of 0.047 ± 0.004 Å, and the mean O-O distance is 2.626 ± 0.006 Å, with an rms deviation of 0.091 ± 0.005 Å. The Si(O) co-ordination number is 4 and the Si-Si contribution is obtained from the corresponding X-ray data.

The accuracy of fit is given by the rms R-factor

$$R_\chi = \{\Sigma_i[T_{exp}(r_i) - T_{fit}(r_i)]^2/\Sigma_i T_{exp}{}^2(r_i)\}^{\frac{1}{2}},$$

which is equal to 0.038.
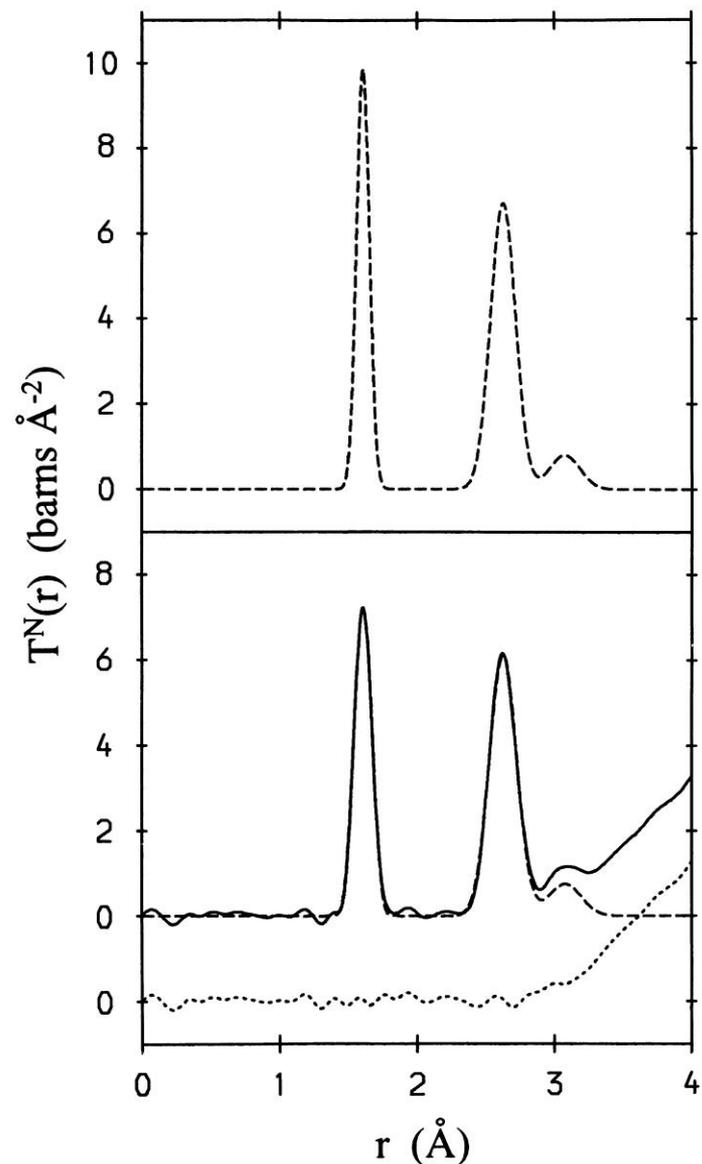
Bond Angle Distribution for Vitreous SiO$_2$
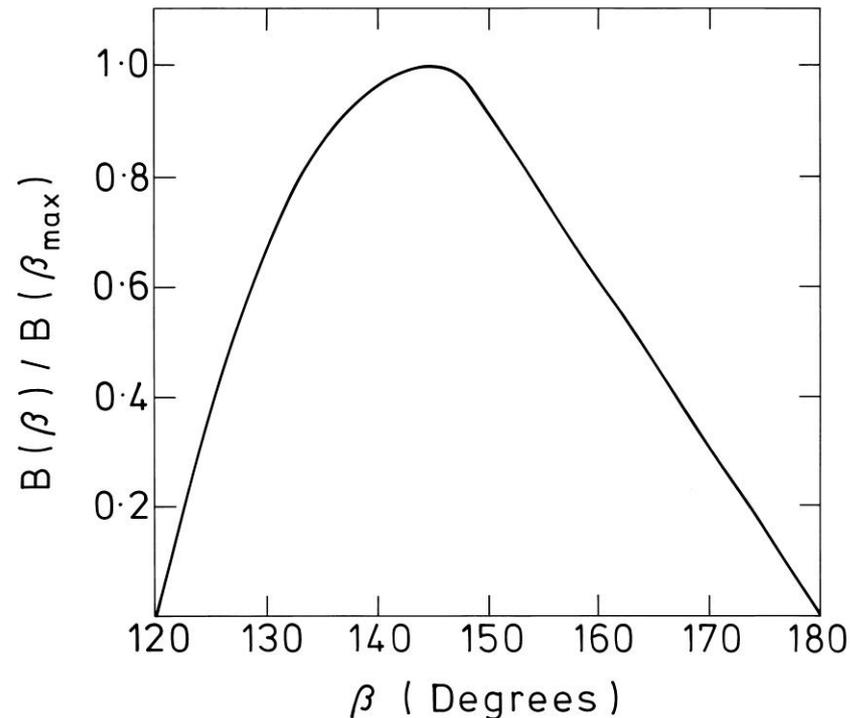
The bond angle distribution, $B(\beta)$, for vitreous silica obtained by Mozzi and Warren, assuming a random distribution of torsion angles and no correlation between bond and torsion angles.

Even in the Simple Case Component Correlation Functions are Complicated

For a sample with n elements there are $n(n+1)/2$ independent component correlation functions,

$$t_{ij}(r) \; = \; 4\pi r \rho_{ij}(r);$$

e.g. for vitreous SiO_2, the components are Si-Si, Si-O and O-O (O-Si is simply related to Si-O). A single diffraction experiment measures a weighted sum of these components,

$$T(r) \; = \; \sum_i \sum_j w_i w_j t_{ij}'(r),$$

where the i summation is taken over the atoms in the composition unit and that for j over atomic species (elements). For X-rays, the weighting factors, w, are equal to the number of electrons in the given atom/ion, Z_i, whereas, for neutrons, w is equal to the neutron scattering length, b_i. (The prime on $t_{ij}'(r)$ indicates that it is broadened by the peak function, $P(r)$)

So how can we sort out the contributions from the various pair correlations?

Compare Neutron and X-Ray Data for Vitreous As$_2$O$_3$

In the case of vitreous arsenic oxide, the neutron scattering lengths for As and O are very similar (b_{As} = 0.658×10^{-14} m; b_O = 0.5803 × 10^{-14} m), whereas arsenic scatters X-rays very much more strongly than oxygen (Z_{As} = 33; Z_O = 8). Hence, for X-rays, the O-O peak is insignificant and the As-As peak is very strong.
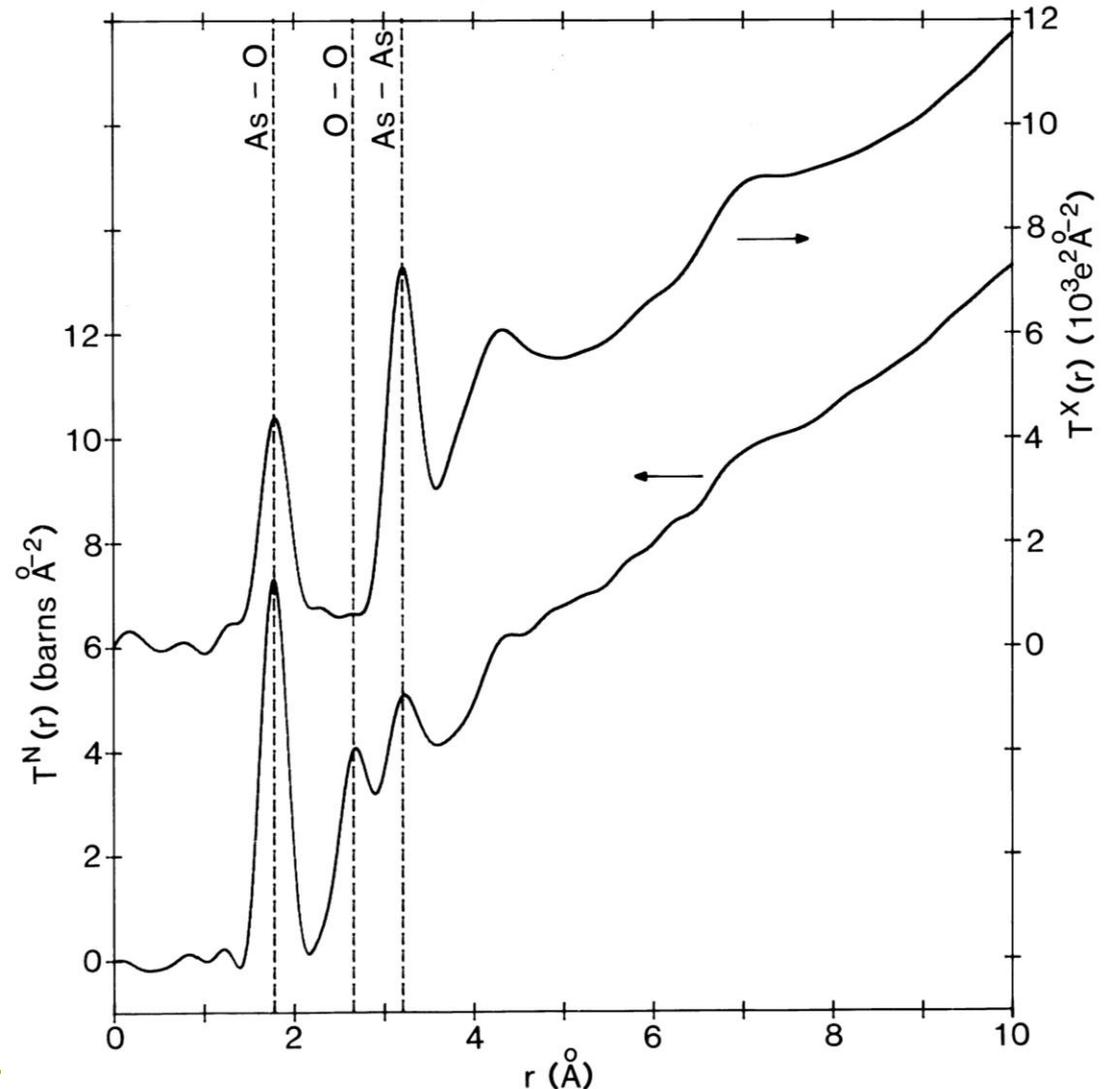
Stay Awake Question

For a sample containing *n* atomic species, there are *n*(*n*+1)/2 component correlation functions and various techniques exist that allow their complete or partial separation:

1. **Isotopic Substitution** (neutron diffraction).
   Since neutrons are scattered by the nucleus, the isotopes of a given element have different scattering amplitudes (lengths).

2. **Anomalous Dispersion** (neutron and X-ray diffraction).
   The scattering amplitude (X-ray form factor) becomes complex and wavelength dependent in the region of an absorption resonance (edge).

3. **Magnetic Neutron Diffraction.**
   The magnetic correlation function can be used to infer the inter-atomic distances between the magnetic atoms/ions.

4. **EXAFS Spectroscopy.**

Isotopic Substitution

An investigation of the structure of melt-spun Dy_7Ni_3, using the isotopic substitution double-null technique in which first the Ni scattering length was set to zero (Dy-Dy component correlation function) and then that of Dy (Ni-Ni component). A measurement for a sample containing natural Dy and Ni then allowed extraction of the Dy-Ni component correlation function. The dashed lines give the component correlation functions for a binary Percus-Yevick hard-sphere liquid.
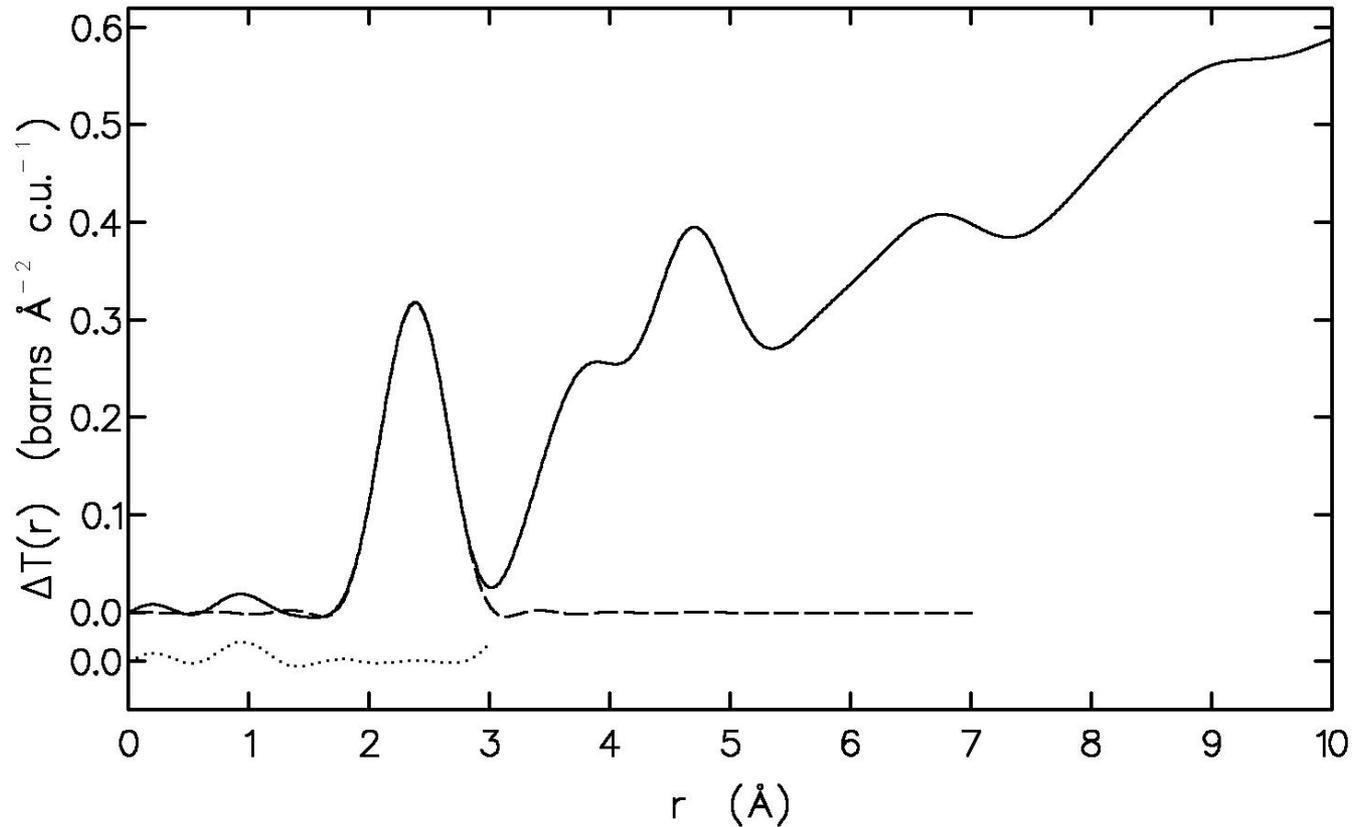
Structure of Glass
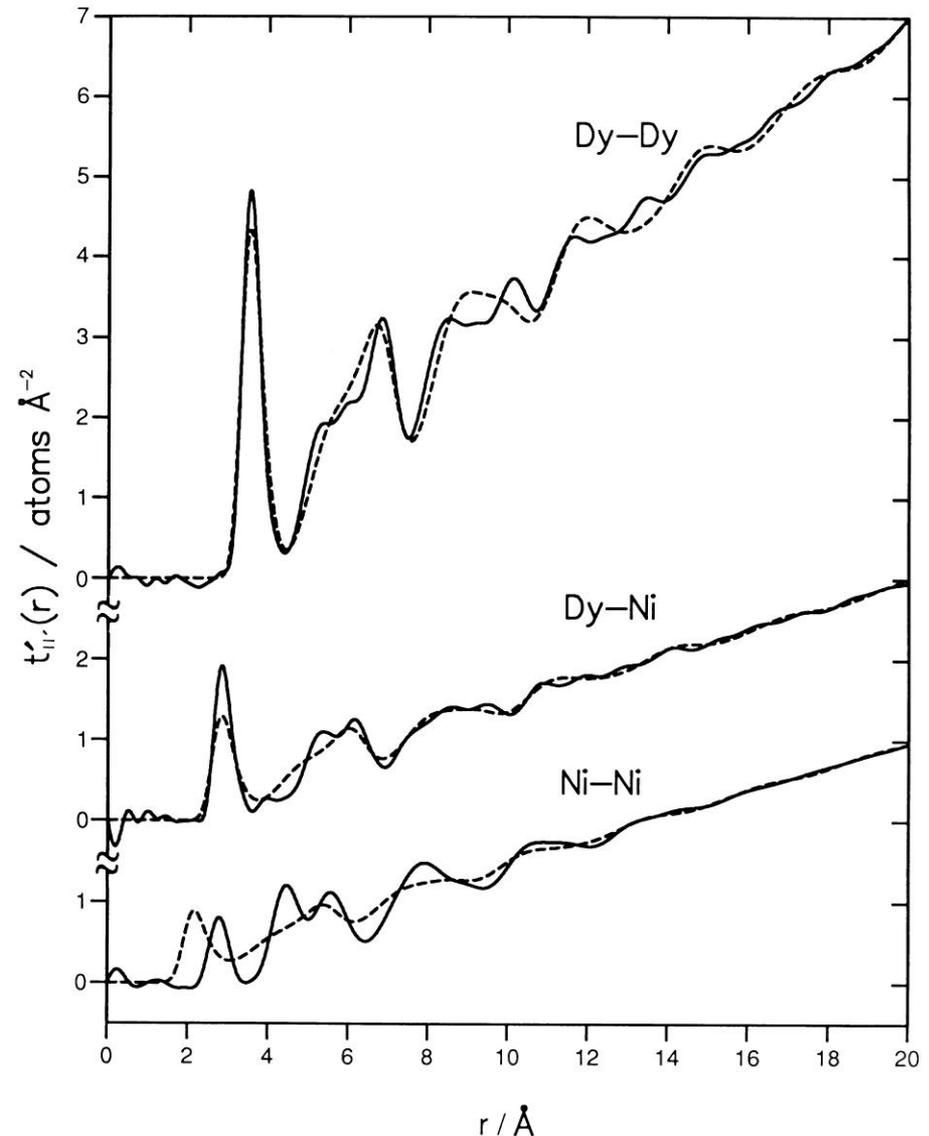
Anomalous Dispersion
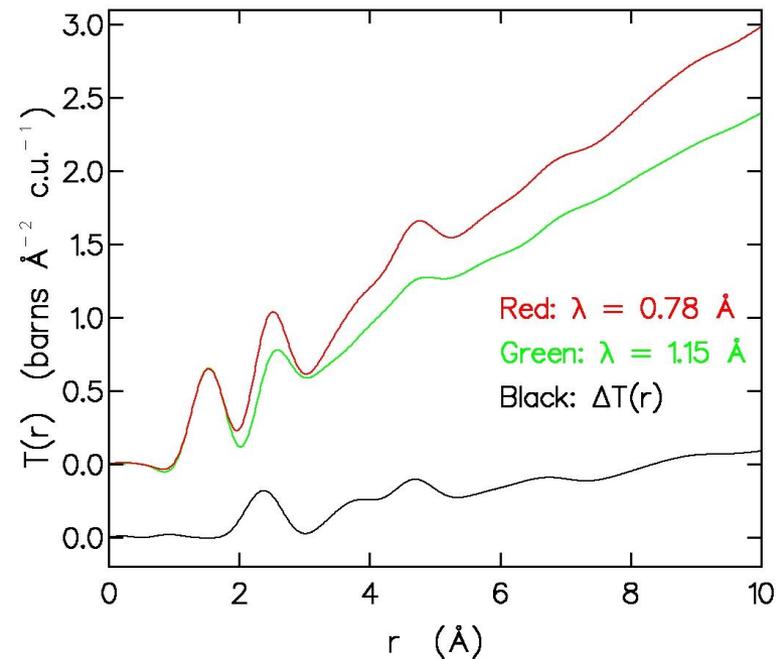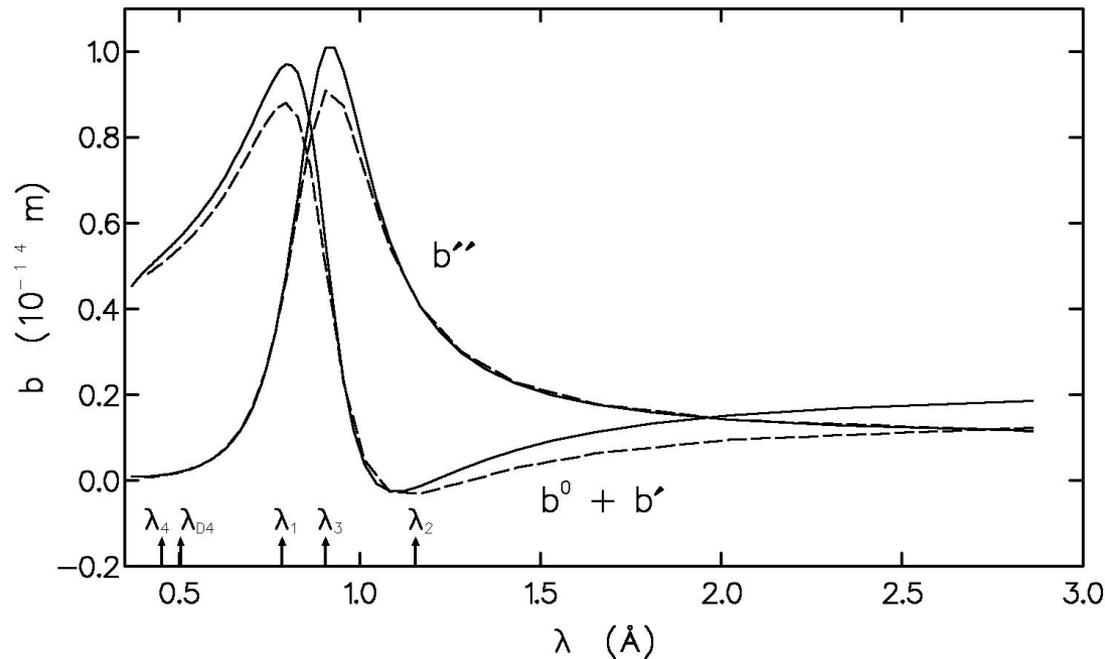
Anomalous dispersion data for vitreous Sm_2O_3-P_2O_5. Data were recorded at two wavelengths on either side of the [149]Sm absorption resonance and so the difference function shown relates to the Sm atom environment.

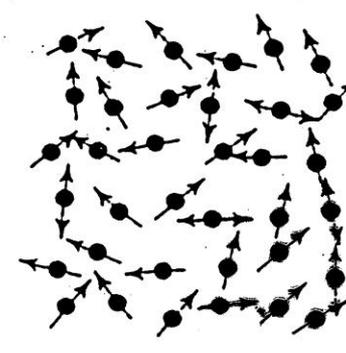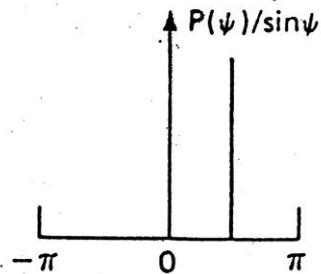The fit yields a mean bond length of 2.375 ± 0.005 Å, with a root mean square variation of 0.146 ± 0.010 Å and an average co-ordination number of 6.9 ± 0.2.
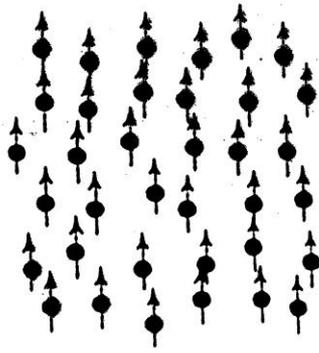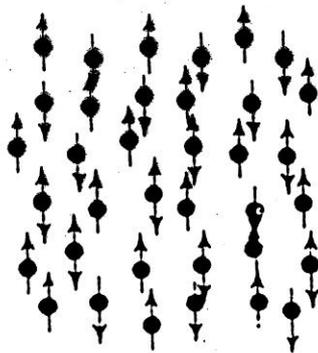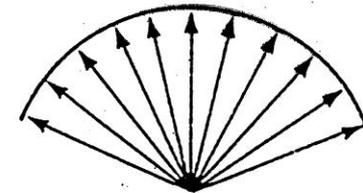
Ferromagnet   Antiferromagnet   Speromagnet   Asperomagnet
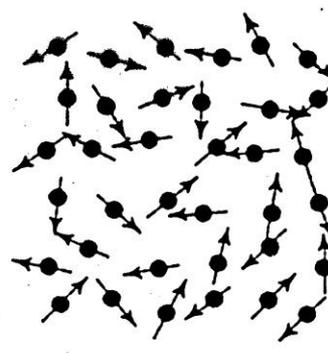
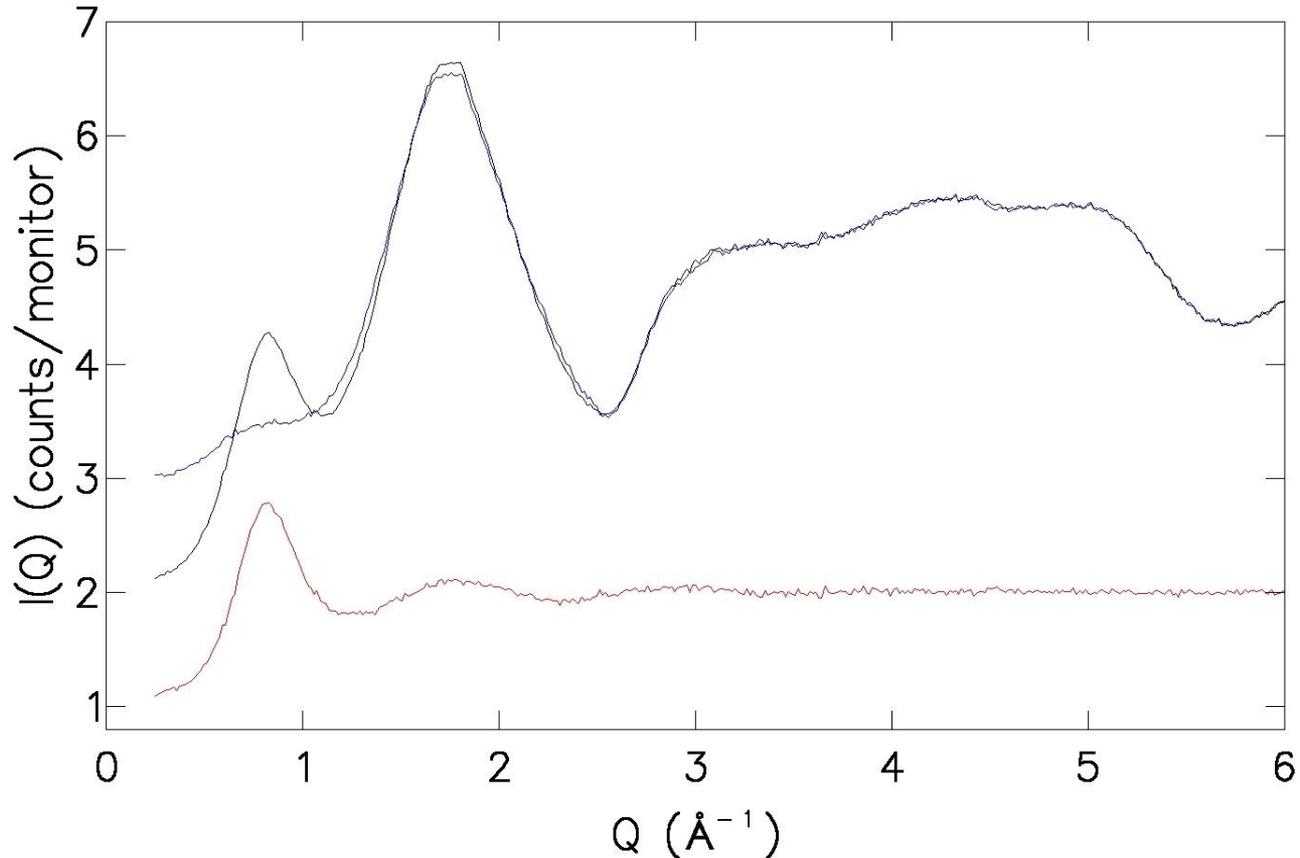$P(\psi)/\sin\psi$ $P(\psi)/\sin\psi$ $P(\psi)/\sin\psi$ $P(\psi)/\sin\psi$

$-\pi$ 0 π $-\pi$ 0 π $-\pi$ 0 π $-\pi$ 0 π
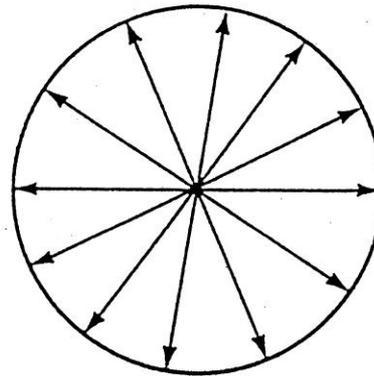
(a)   (b)   (c)   (d)
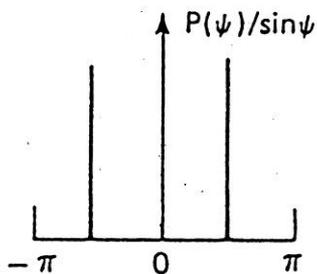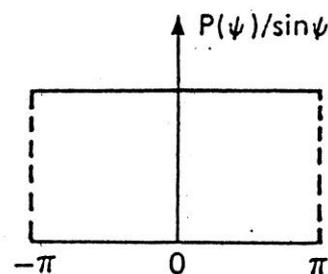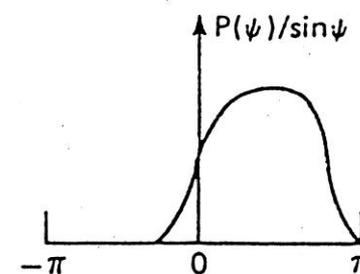
$44Fe_2O_3.56P_2O_5$ $I(Q)$ and $i^M(Q)$ $(2K - 80K)$

Fe_2O_3-P_2O_5 glasses exhibit speromagnetic (short-range antiferromagnetic) ordering at low temperatures, leading to an extra (magnetic) peak at low Q in the diffraction pattern. The magnetic scattering, $i^M(Q)$, is obtained from the difference between diffraction patterns measured above and below the magnetic ordering transition.

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The magnetic correlation function, $d^M(r)$, for vitreous $0.79Fe_2O_3 \cdot P_2O_5$, obtained from the Fourier transformation of $i^M(Q)$. That the ordering is speromagnetic (short-range antiferromagnetic) is indicated by the fact that the first peak in $d^M(r)$ is negative. The vertical lines indicate the Fe-Fe distances in crystalline $FePO_4$.
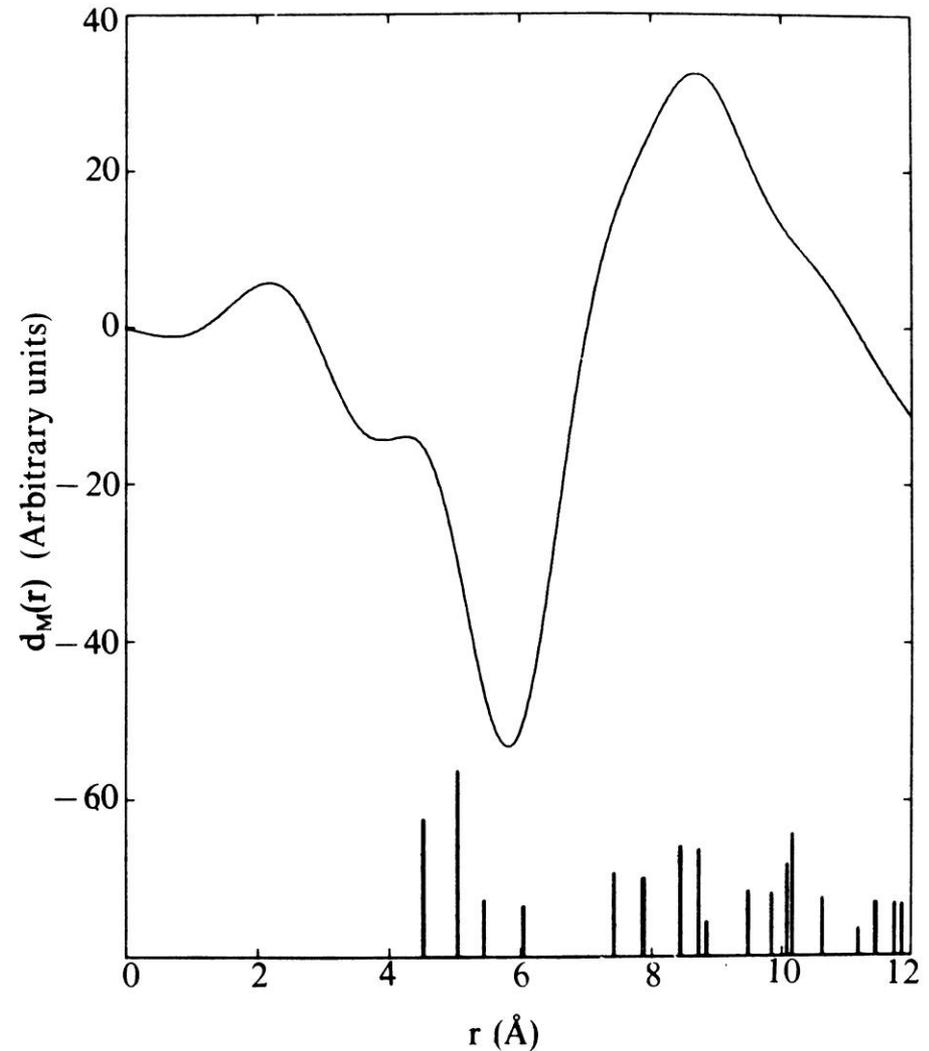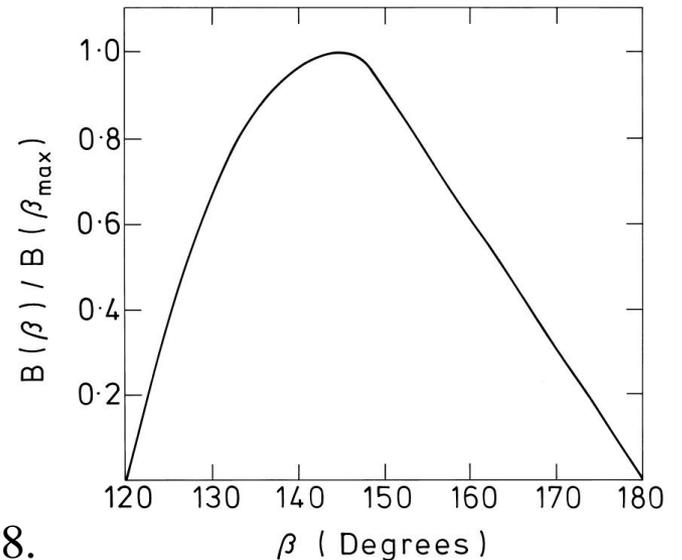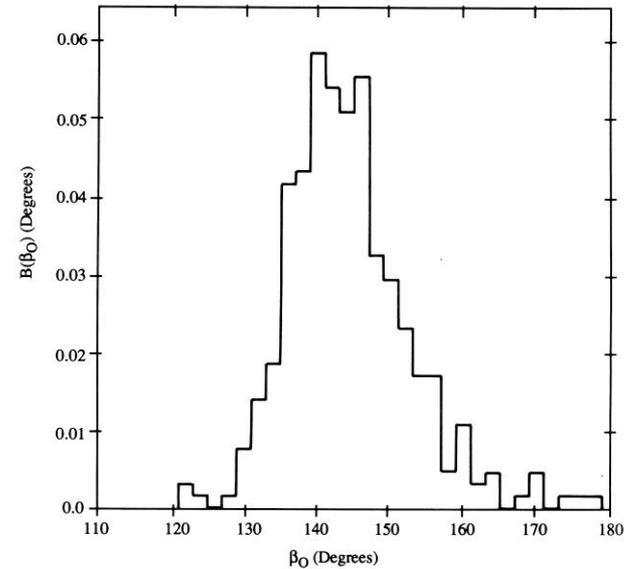
So what sort of models are for the glasses that can further the mining of the data?

Bell & Dean Model for Vitreous SiO$_2$
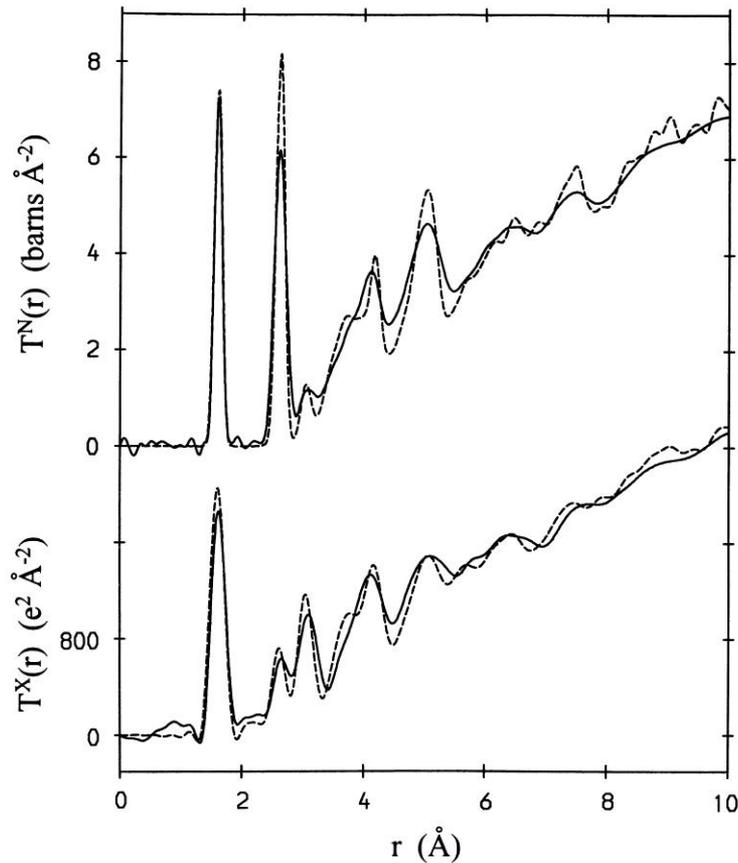
The Bell & Dean model (dashed lines) compared to experiment (solid lines). The model bond angle distribution is too narrow.

R.J. Bell and P. Dean, *Philos. Mag.* **25** (1972), 1381-1398.
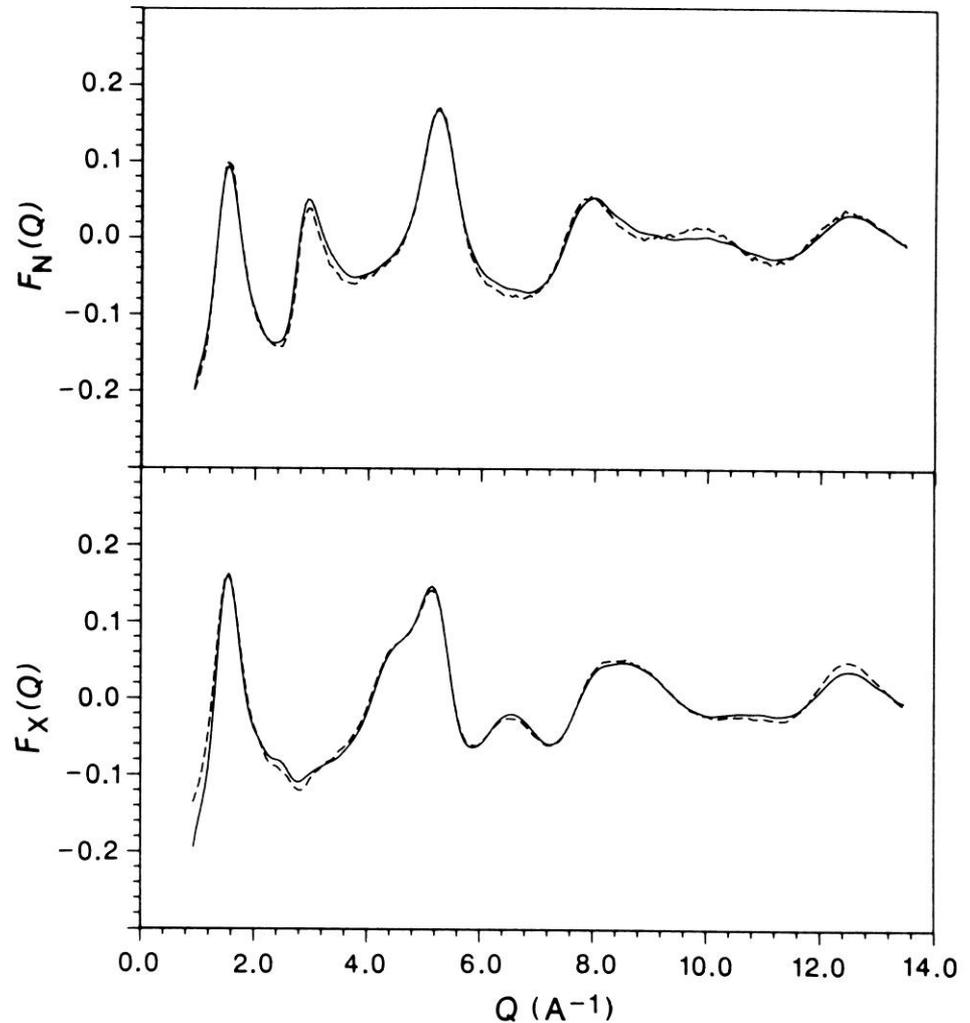
Vitreous Silica

Reverse Monte Carlo (RMC) Modelling

In reverse Monte Carlo (RMC) modelling, several thousand atoms are put into a box, with periodic boundary conditions, and the moved at random until the best fit is obtained with experiment. A problem is that the number of degrees of freedom is extremely high (3 times the number of atoms), which means that it is essential to check whether the model generated is chemically reasonable. For example, the model of vitreous silica shown at the right has too many 5-fold co-ordinated silicon atoms.

D.A. Keen and R.L. McGreevy, *Nature* **344** (1990), 423-425.

Gladden Model of Vitreous SiO$_2$

An alternative approach is to employ the reverse Monte Carlo technique to optimise a model generated using another method, as in the case of the Gladden model of vitreous silica. This is a computer generated random network, optimised using RMC techniques.
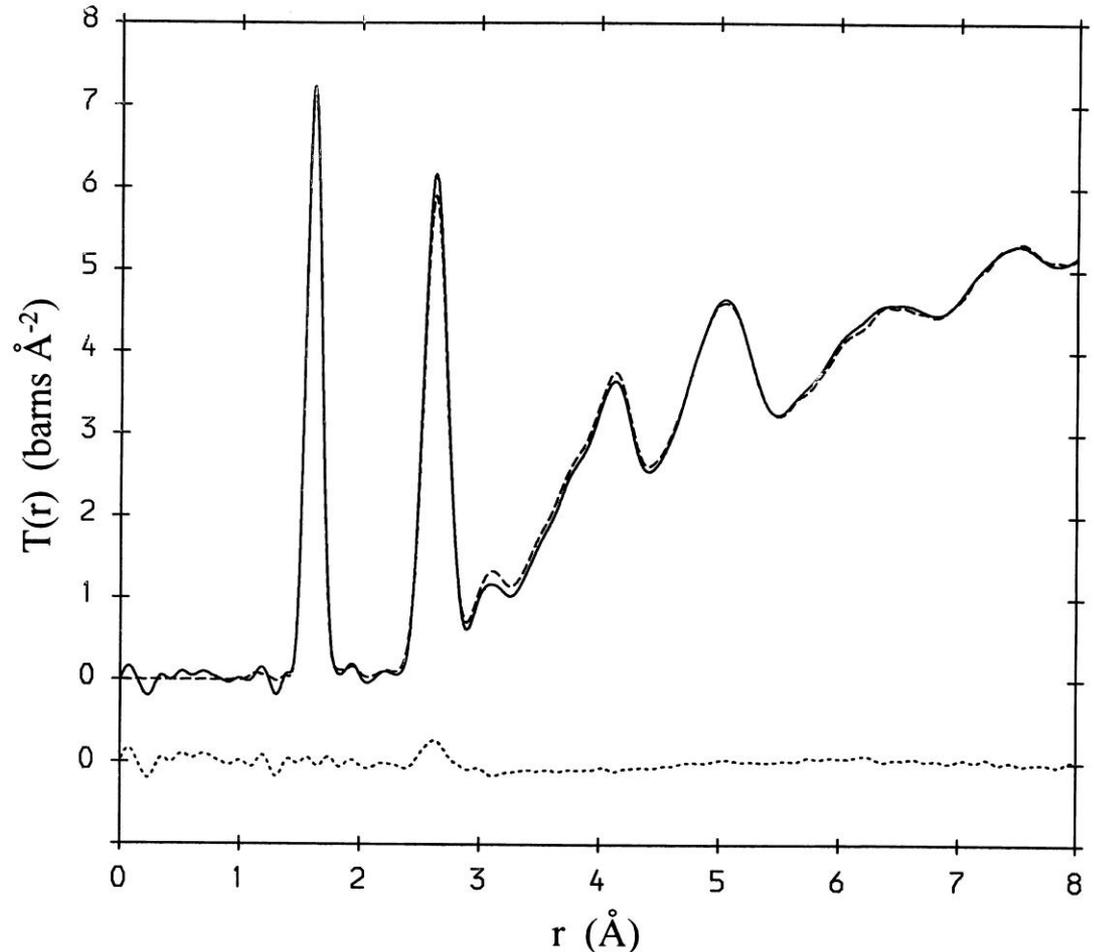

L.F. Gladden, in: *The Physics of Non-Crystalline Solids,* eds L.D. Pye, W.C. La Course and H.J. Stevens (Taylor & Francis, London, 1992), pp. 91-95.

Molecular Dynamics Simulation
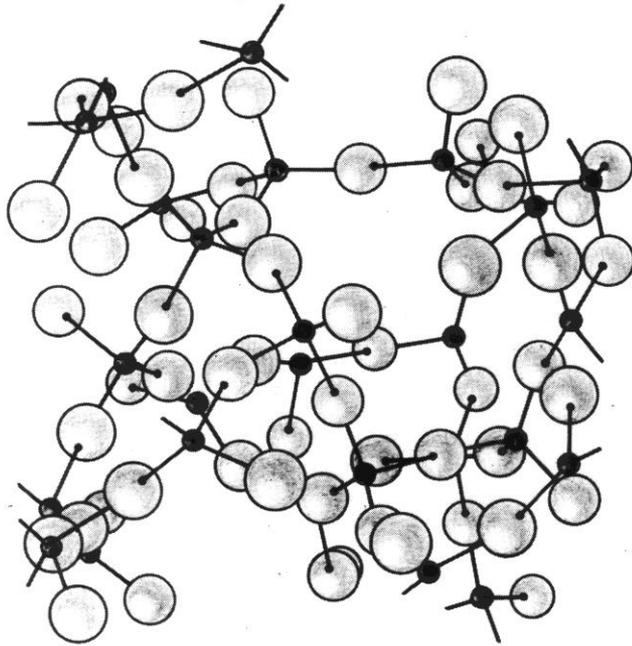
Models of melt-quenched glasses can also be generated by molecular dynamics simulation. In general, the extremely rapid quenching and the imposition of periodic boundary conditions yield structural units (*e.g.* SiO$_4$ tetrahedra) that are too distorted.

B. Vessal, M. Amini and C.R.A. Catlow, *J. Non-Cryst. Solids* **159** (1993), 184.
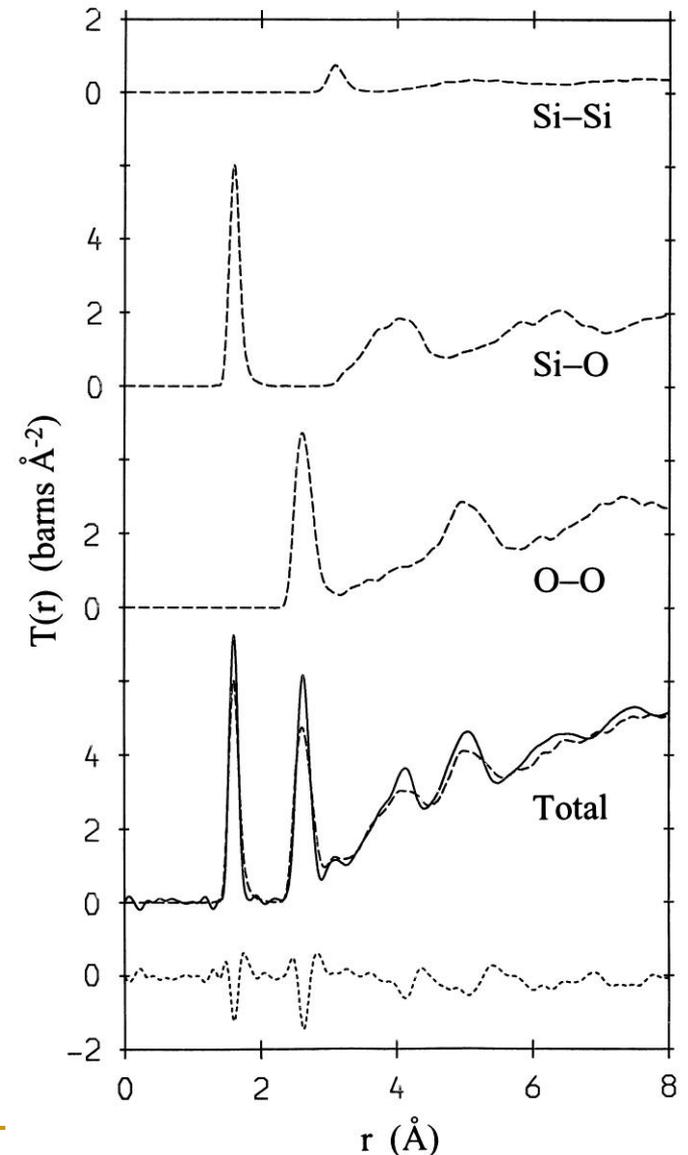
Most glasses are not as simple as silica though…..

Complex Systems

The figure shows a molecular dynamics simulation of a fluoroberyllate glass (NaF-DyF_3-BeF_2), including the contributions from all 10 individual components, and it can be seen that interpretation of the structure in $T(r)$ is extremely difficult, except for the first (Be–F) peak. The interest in this particular glass concerns the detailed environment of the Dy atoms, which can be studied using isotopic substitution.
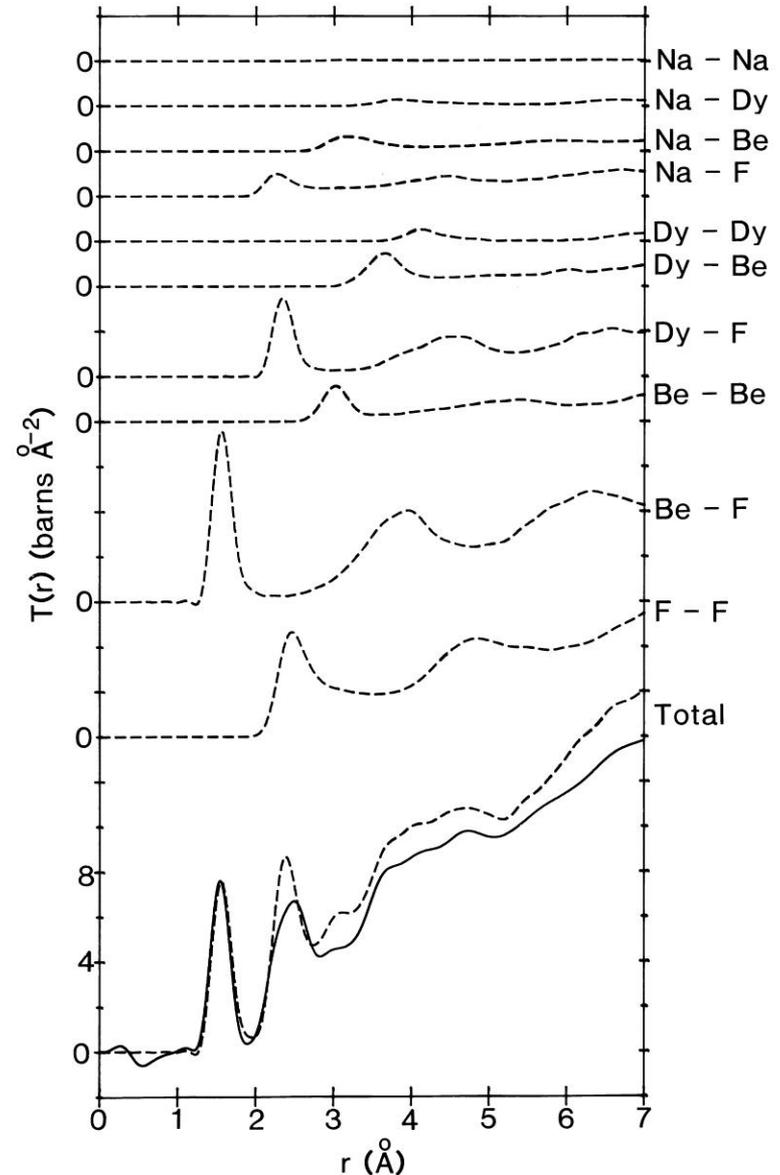
Dy Atom Environment
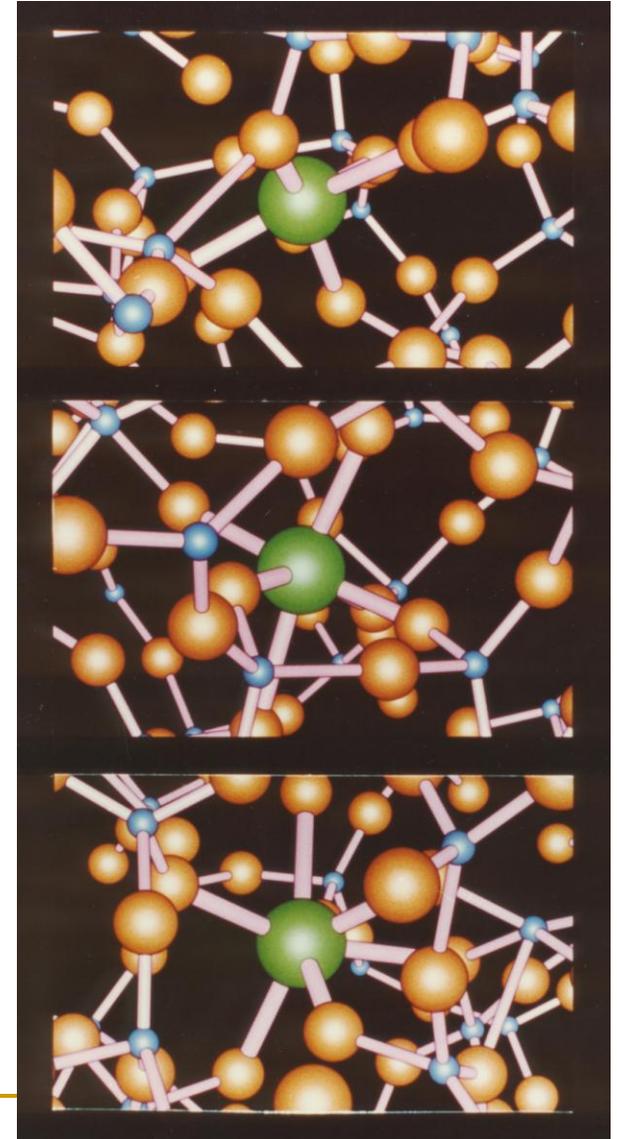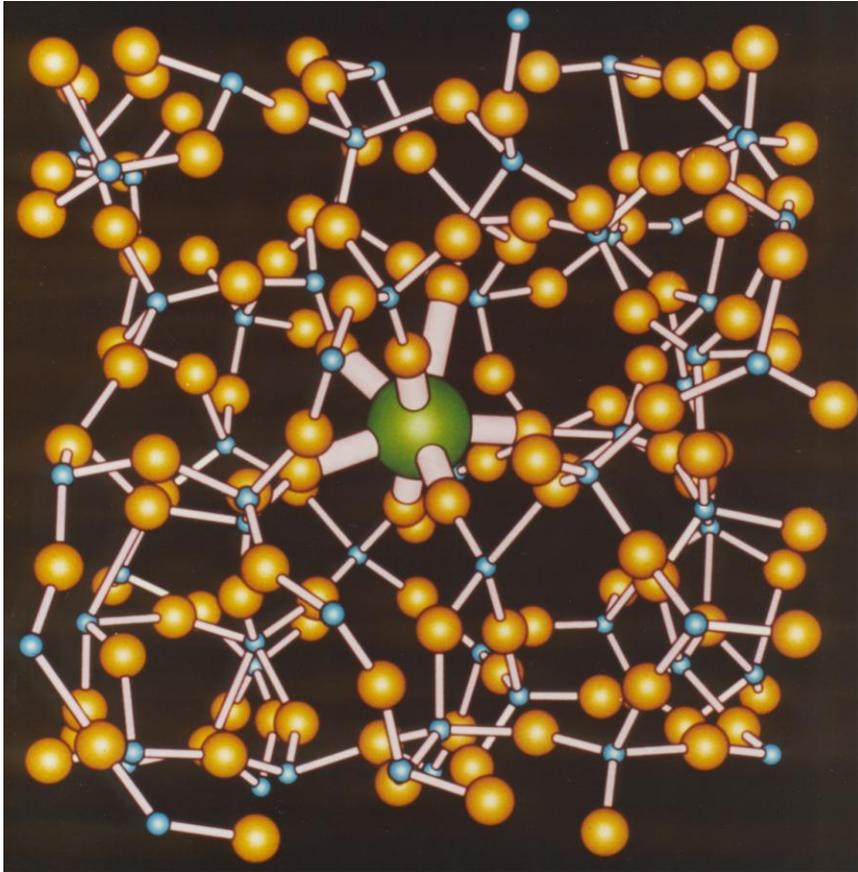
The insertion of one DyF_3 formula unit into vitreous BeF_2 shows the varying Dy environment as the simulation proceeds.
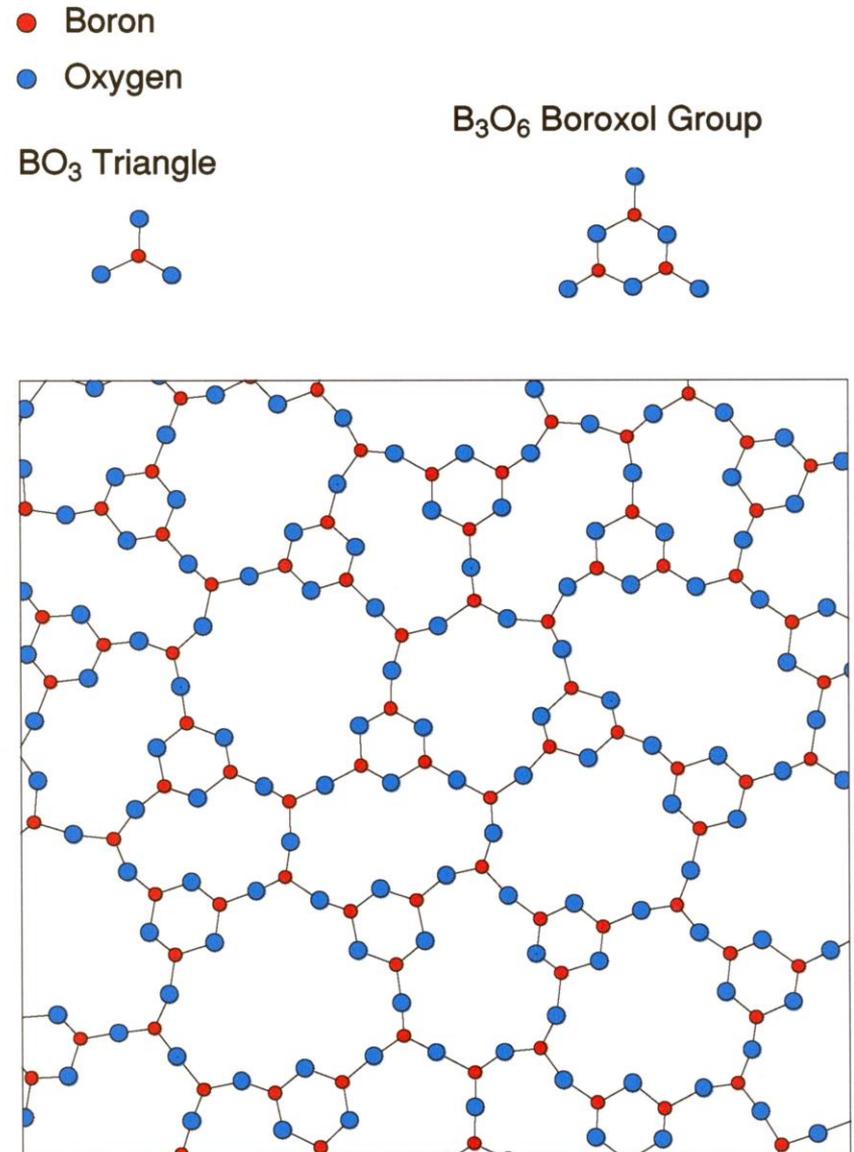
Dy Isotopic Difference Correlation Function

The isotopic difference correlation function, $\Delta T(r)$, shows that the Dy-atom environment predicted by the molecular dynamics simulation is qualitatively correct but that the simulated structure is too distorted.
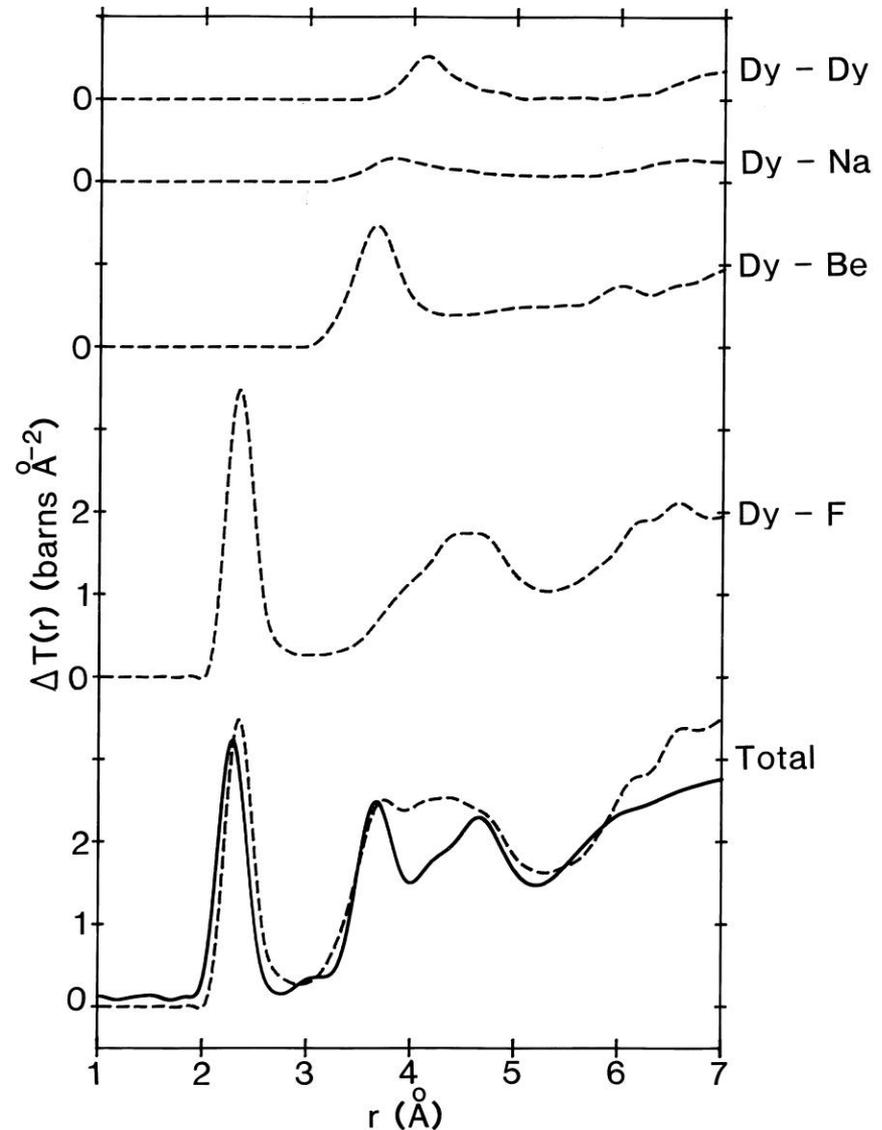
The structure of vitreous B_2O_3 thus comprises a mixture of $B\emptyset_3$ triangles and $B_3\emptyset_6$ boroxol groups. Neutron diffraction and NMR data indicate that 70-80% of the boron atoms are in boroxol groups [Figure: A.C. Hannon].

The presence of boroxol groups explains both the low density of the glass (71% of crystal density) and the fact that a crystal seeded into the anhydrous supercooled melt does not grow, even over a period of several months.

- Boron
- Oxygen

BO_3 Triangle
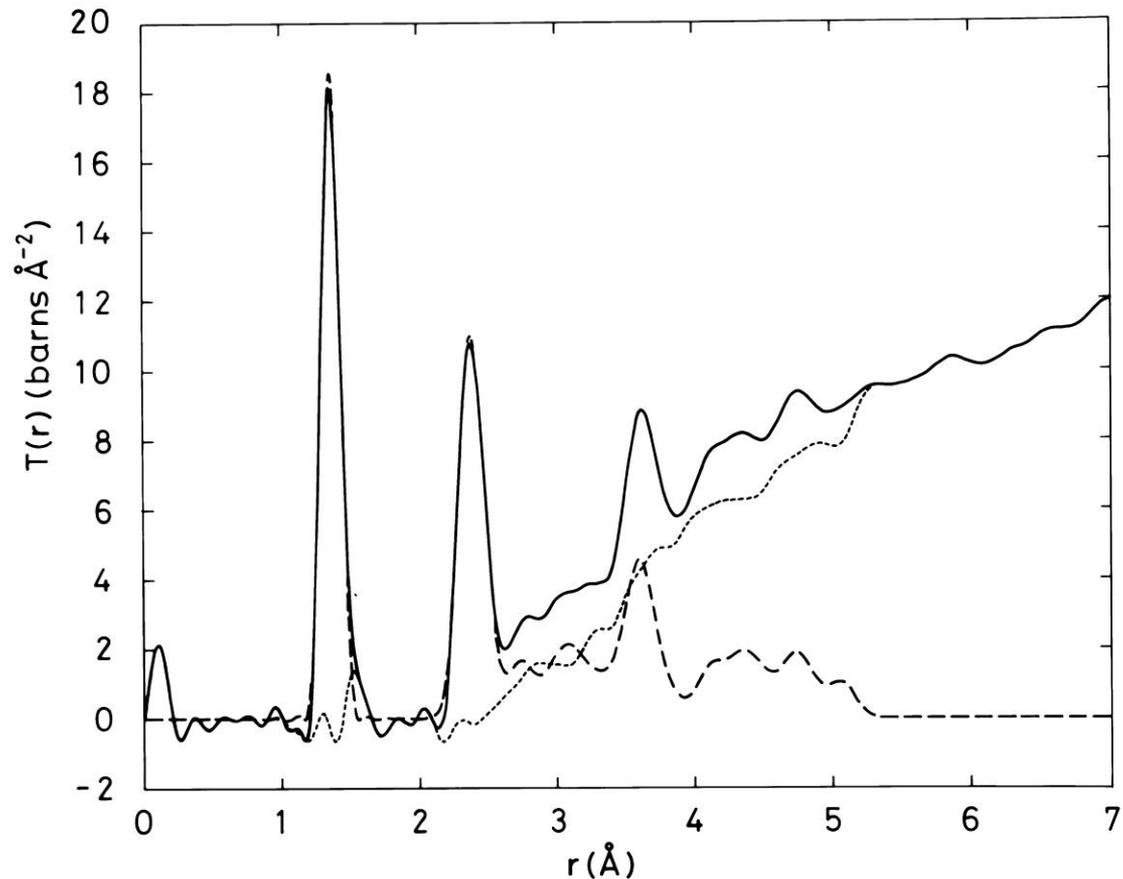
B_3O_6 Boroxol Group

The correlation function for vitreous B_2O_3. A fit to the first two peaks indicates that the basic structural units are $B\emptyset_3$ triangles (Ø represents a non-bridging oxygen atom). However, the sharp peak at 3.6 Å reveals the presence of boroxol groups. A fit to extract the fraction of the boron atoms, f, in boroxol groups yields $f = 0.8 \pm 0.05$. Solid line, experiment; dashed line, fit and dotted line, residual.