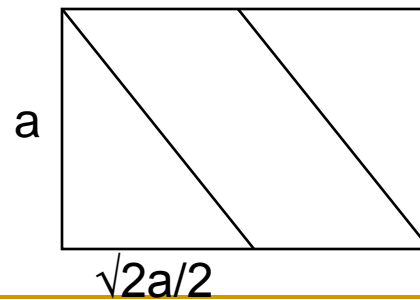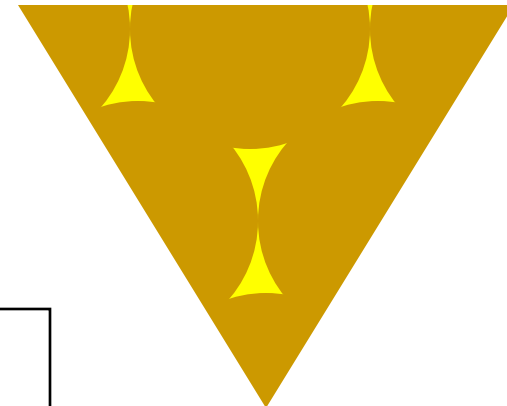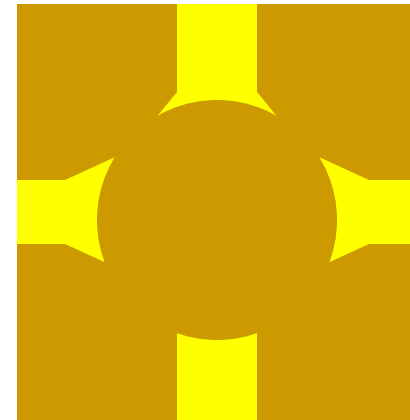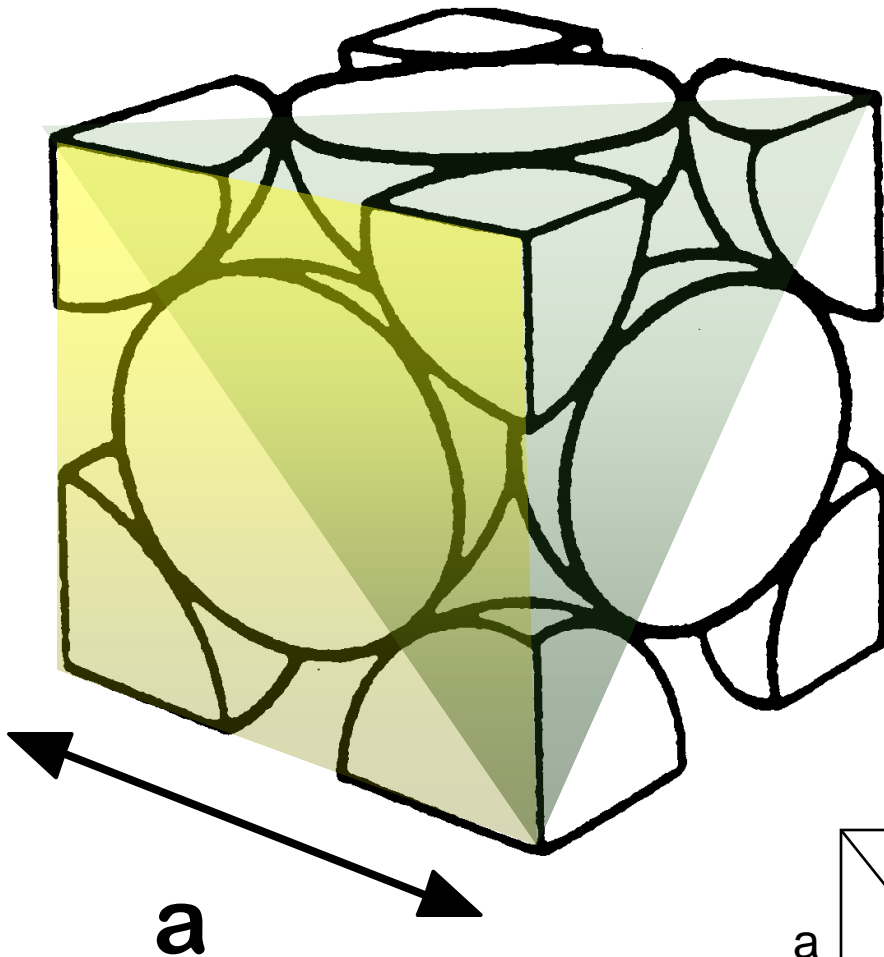# Neutron and X-ray Scattering Studies of Glass-The Experiments and Data Mining

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Outline

- Planar Density from Monday
- Review intensity to correlation function for neutrons
- X-rays
- Experimental layouts
- Interpreting the correlation functions

Planes in crystals

a

√2a/2

Basic Properties of X-rays and Neutrons

Property	X-rays	Neutrons
Wavelength	Ag-Kα to Cr-Kα ,0.56-2.29Å Synchotron tune 0.01Å-123Å	0.8-10Å
Energy at 1Å	≈12.4keV not likely to initiate atomic vibreations	80meV similar to typical phonon energy
Production	X-ray tube, synchotron or X-ray laser	Reactor or pulsed accelerator
Detection	Proportional counters or scintillators	Gas counters or scintillators
Angular dependence	Form factor f(Q)	No Q dependence if non magnetic
Isotopic variation	None	b varies irregularly with Z
Phase change on scattering	180	180 or 0
Magnetic	None	Magnetic form factor

Real Space Correlation Function

Older papers present data as the radial distribution function, whereas modern studies employ the differential correlation function, $d(r)$, or the total correlation function, $t(r)$.

Differential Correlation Function
$$d(r) = 4\pi r \, [\rho(r) - \rho^\circ]$$

$-4\pi r \rho^\circ$

Radial Distribution Function
$$g(r) = 4\pi r^2 \rho(r)$$

$4\pi r^2 \rho^\circ$

Total Correlation Function
$$t(r) = 4\pi r \rho(r)$$

$4\pi r \rho^\circ$
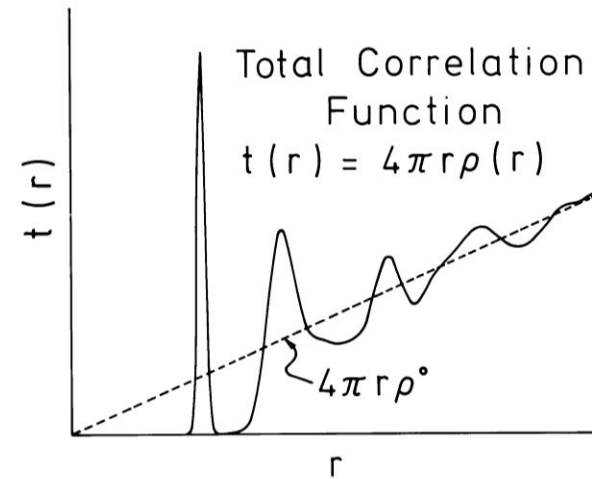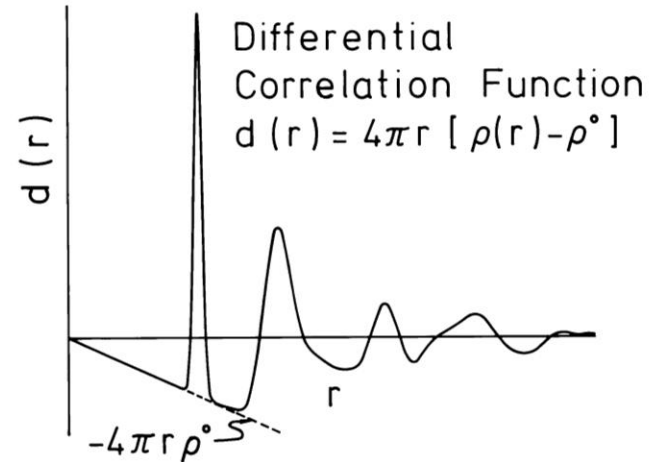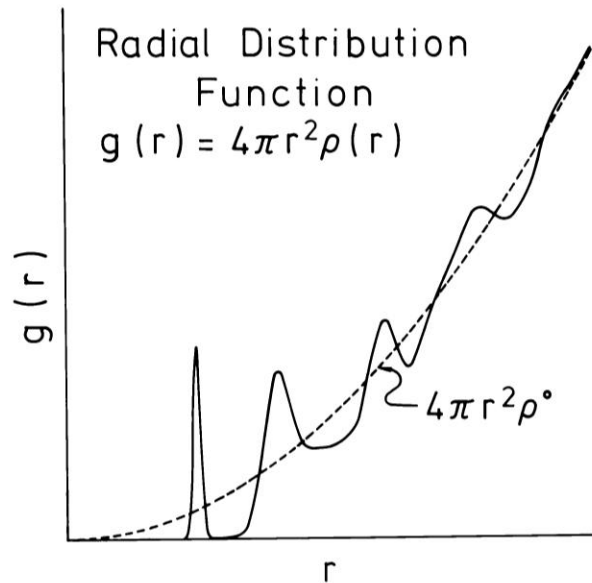
You can't get to Infinity from Here Either

- Why do we Fourier Transform $Qi(Q)$?
- Truncation of the Fourier Integral
- How the way you truncate affects your real space correlation function
- How high should you go in Q anyway?

Truncation of the Fourier Integral

FIGURE 6.7 The Dependence of T(r) Upon Truncation of the Scattering
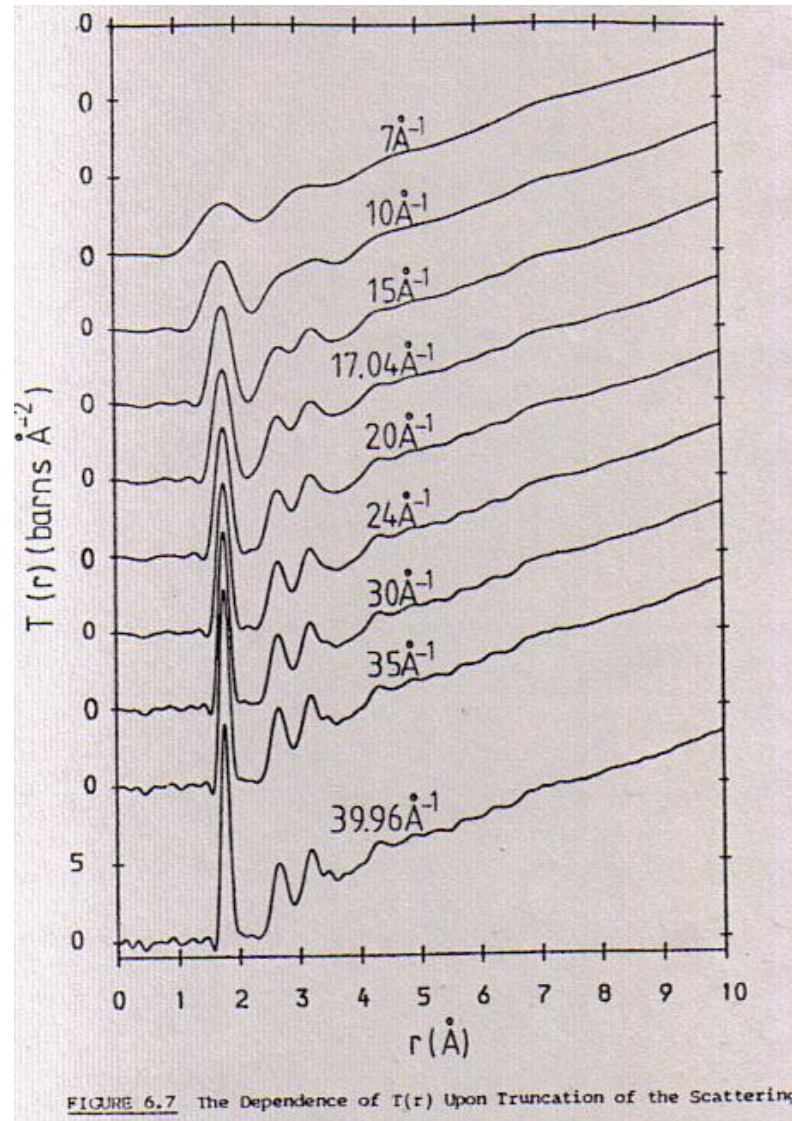
Termination of Fourier Integral

- Data collection cannot go to infinite Q
- A bigger Q gives you better resolution in real space
- Step function termination introduces high frequency ripples in the real space correlation function so use artificial temperature function or Lorch function

$$\exp(-BQ_0^2)$$

$$\text{where} \quad \exp(-BQ_{max}^2) = 0.1$$

$$M(Q_0) = \frac{\sin \Delta rQ_0}{\Delta rQ_0} \qquad Q_0 \leq Q_{max}$$

$$M(Q_0) = 0 \qquad\qquad Q_0 > Q_{max}$$
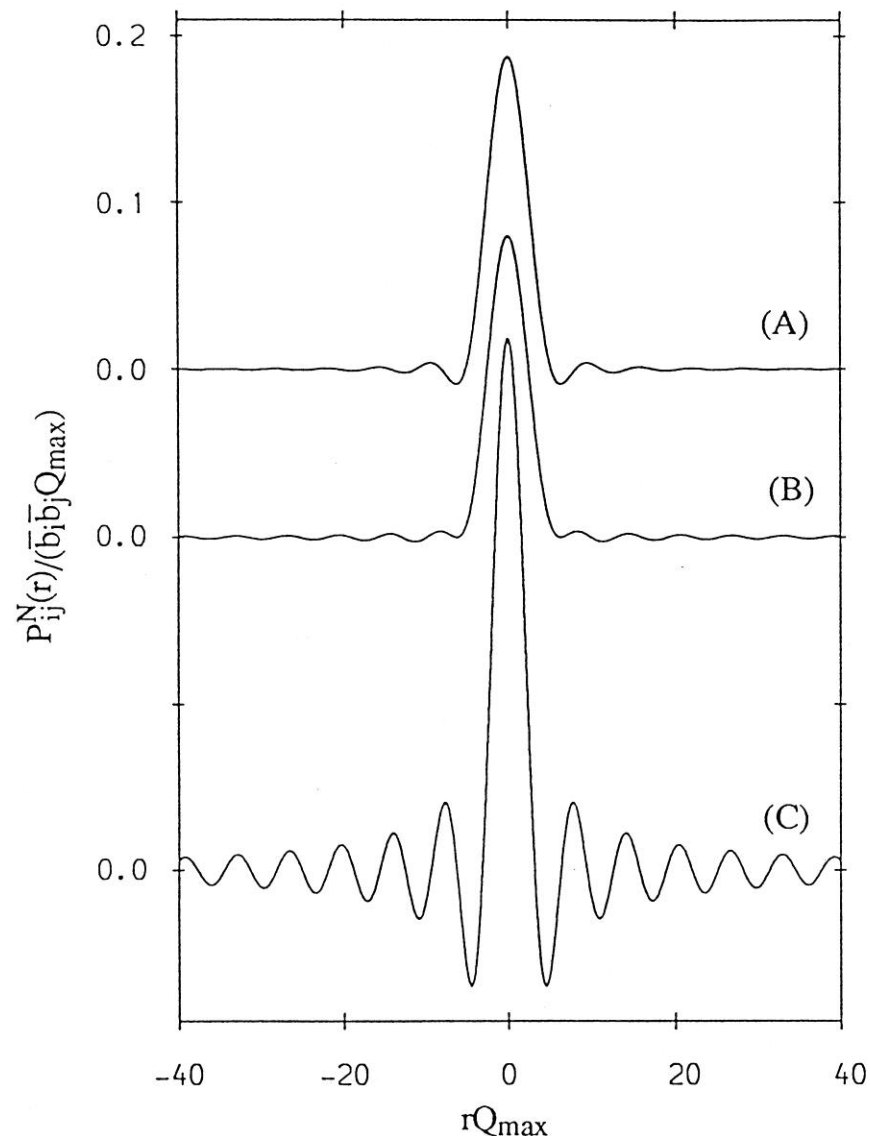
$$\Delta r = \frac{\pi}{Q_{max}}$$

Neutron Peak Function

The termination of the Fourier integral at a finite value of Q, Q_{max}, means that the correlation function is broadened by the real space peak function, $P(r)$. The form of $P(r)$ depends on the modification function, $M(Q)$:

A: Lorch function.

B: Artificial temperature factor.

C: Step function.

Detail on the math etc.

- The Structure of Amorphous Solids by X-ray and Neutron Diffraction

A.C.Wright

Advances in Structure Research by Diffraction Methods 5 (1974) Pergamon Press ISBN 0 08 017287 3

Coherent Scattering in X-rays

- For no change in quantum state you can integrate the scattering over all ω to give

$$\frac{1}{N_u}\frac{d\sigma}{d\Omega} == I_N^{coh}\left(Q_0\right)$$

$$= \sum_j f_j^2\left(Q_0\right) + \sum_j \sum_k f_j\left(Q_0\right)f_k\left(Q_0\right)\int_o^\infty 4\pi r^2 \rho_{jk}\left(r\right)\frac{\sin Q_0 r}{Q_0 r}dr$$

When Fourier Transforme d this will give....

$$d_{jk}\left(r\right) = \frac{2}{\pi}\int_0^\infty \frac{Q_0 i_{jk}^x\left(Q_0\right)}{f_j\left(Q_0\right)f_k\left(Q_0\right)}\sin rQ_0 dQ_0$$

What about Compton

- ## It is difficult to account for the Compton Scattering because
    - ### It is usually really big
    - ### It interferes with the elastic peak

Q_0

I

Q

Energy Analysis
At one value of Q_0
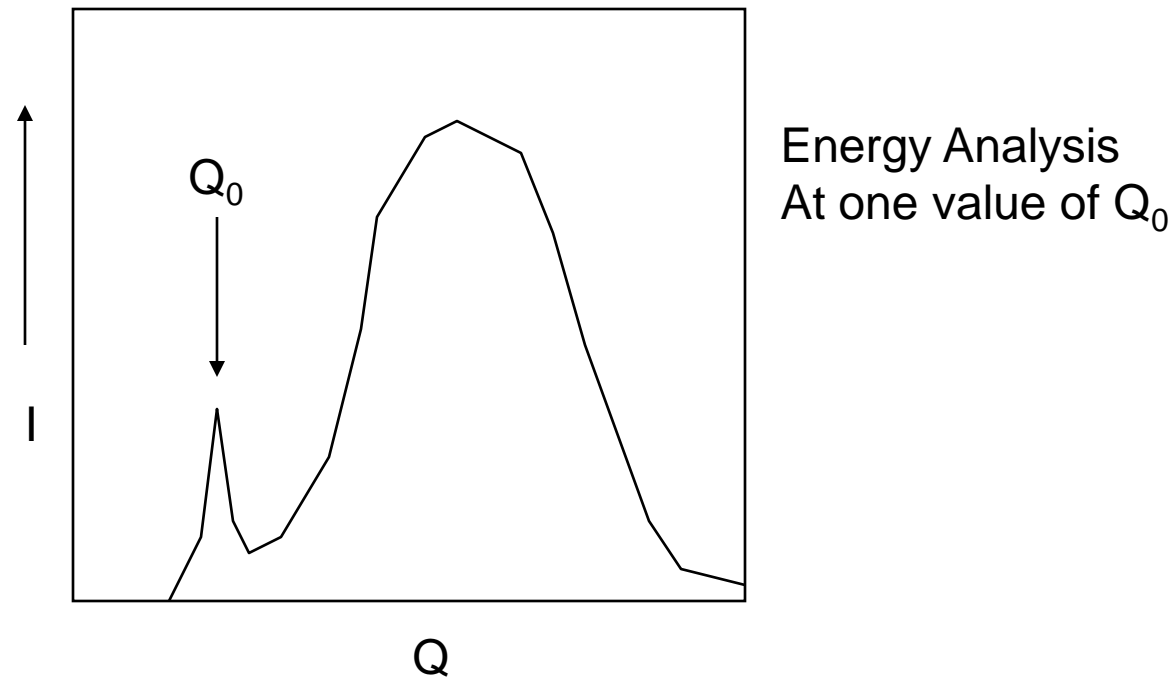
Experimental Arrangements X-rays

Source
X-ray Tube (Ag)

2θ

Energy Analyzer
SiLi or GeLi
Detector + Pulse
Height Analyzer
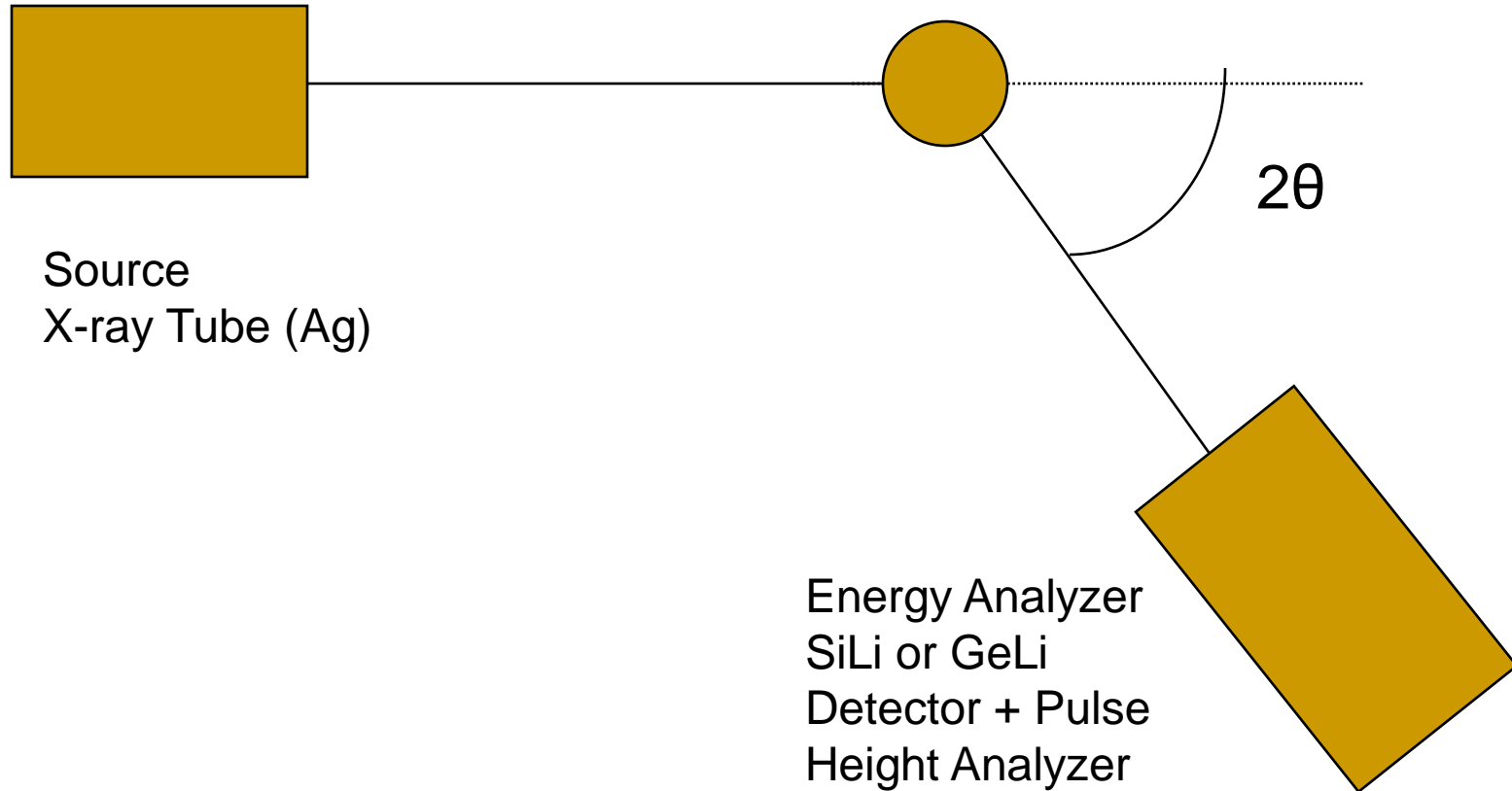
Neutron Diffraction Techniques

STEADY STATE REACTOR

PULSED ACCELERATOR SOURCE

$$Q_e = \frac{4\pi}{\lambda_0} \sin \theta$$
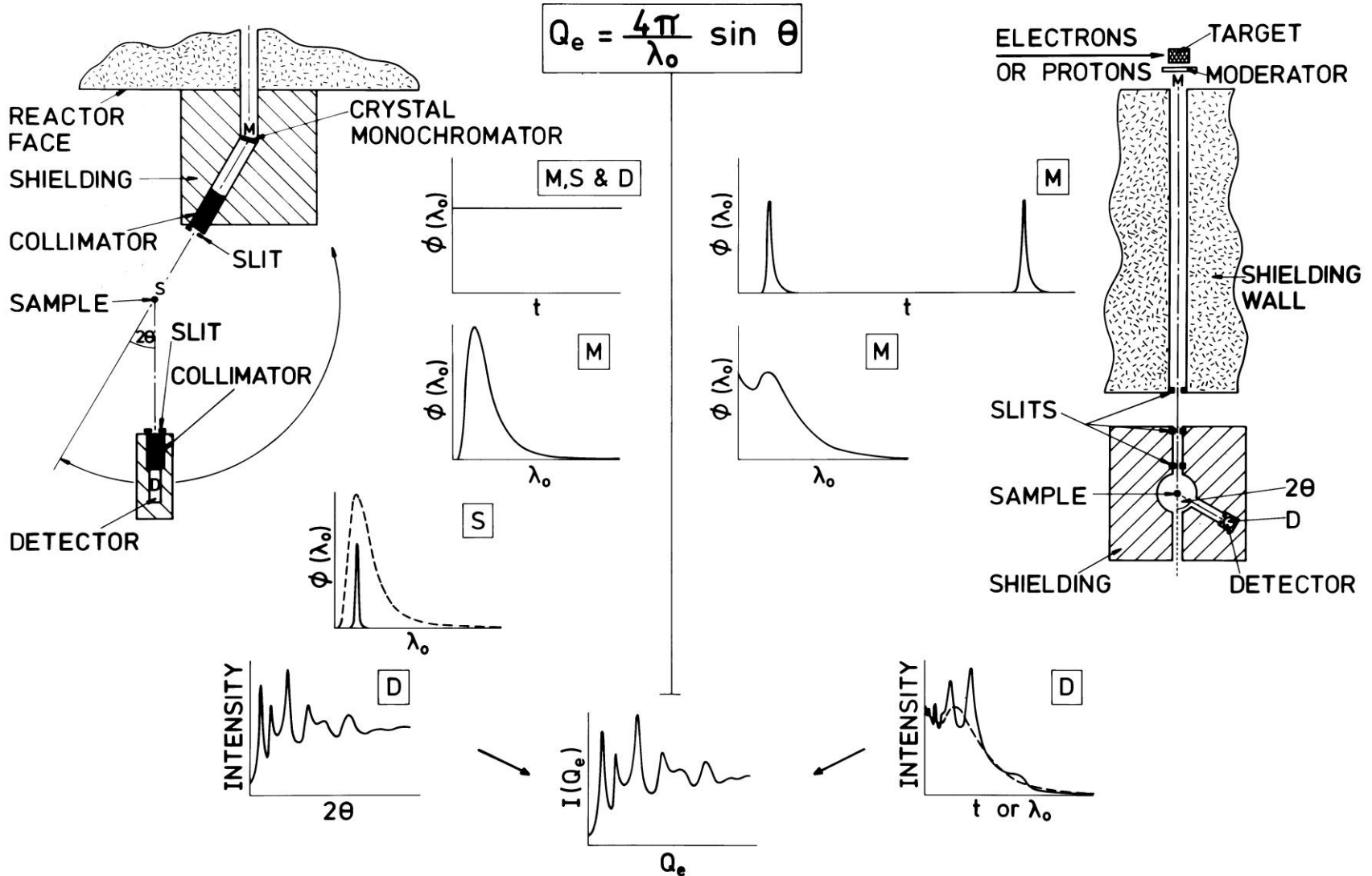
ILL D4c Amorphous Materials Diffractometer

Array of 9 Microstrip Detectors

Detection Plane

8°   7°

0 5 10 20   40   60   80   100 cm

120°

Detector 9

Shielding

Collimation Tubes

15°

2θ

Monochromator

4 Slits

Detector 1

Primary Shutter

Beamstop "Cloche"

Beamstop "Detector"

Vertical Slits

Evacuated Sample Bell Jar

Neutron Beam

Monitor   Turbo Pump

Sample

Shielding

Secondary Shutter

Movement Limits

Gabriel Cuello
www.ill.fr/YellowBook/D4/

ISIS GEM Spectrometer

GEM

Sample Tank

Banks 6 & 7
142° – 171°

Incident Beam

Bank0
1° – 3°

To Beam Stop

Bank1	Bank2	Bank3	Bank4	Bank5	Bank5X
5° – 12°	13° – 21°	24° – 45°	50° – 74°	79° – 106°	106° – 114°

A.C. Hannon, *Nucl. Instrum. Meth. Phys. Res.* **A551** (2005), 88-107.

Stay Awake Question

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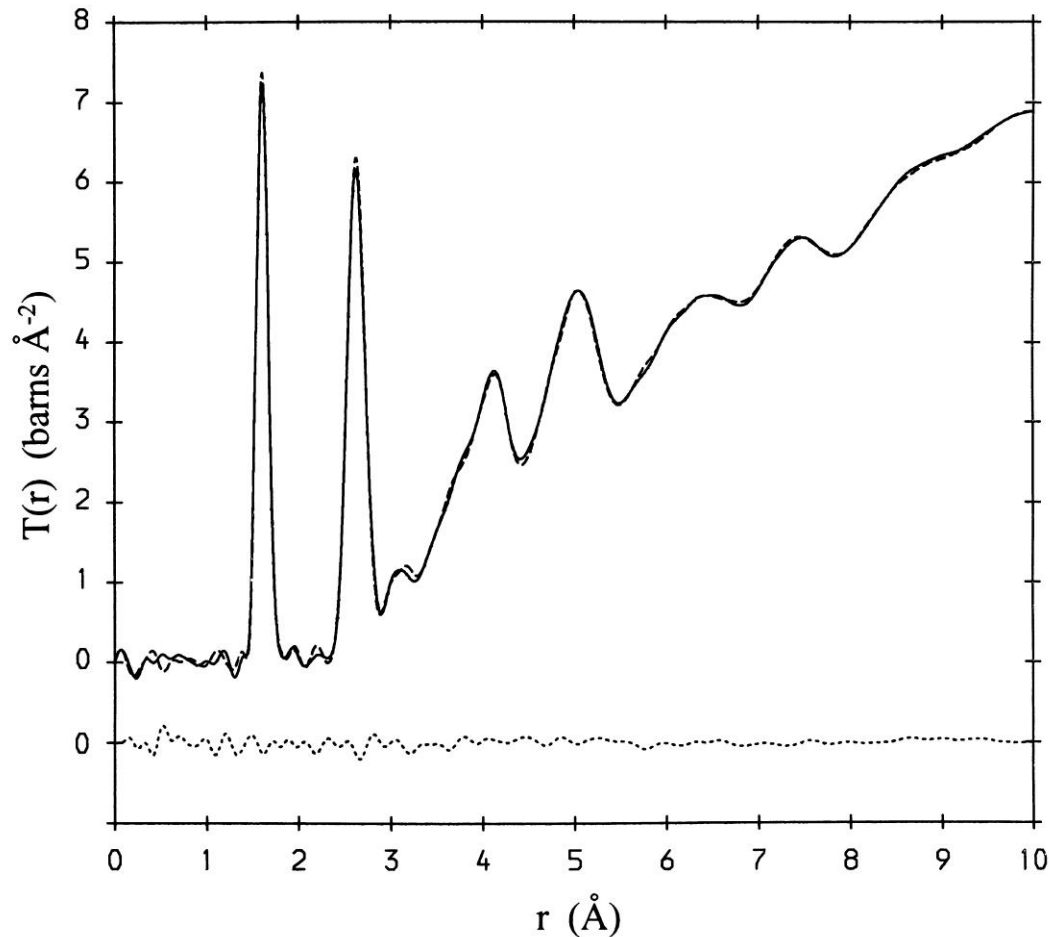
The solid and dashed lines represent two data sets for vitreous silica, obtained with different combinations of instrument and approximately 10 years apart. The dotted line gives the difference between the two data sets.
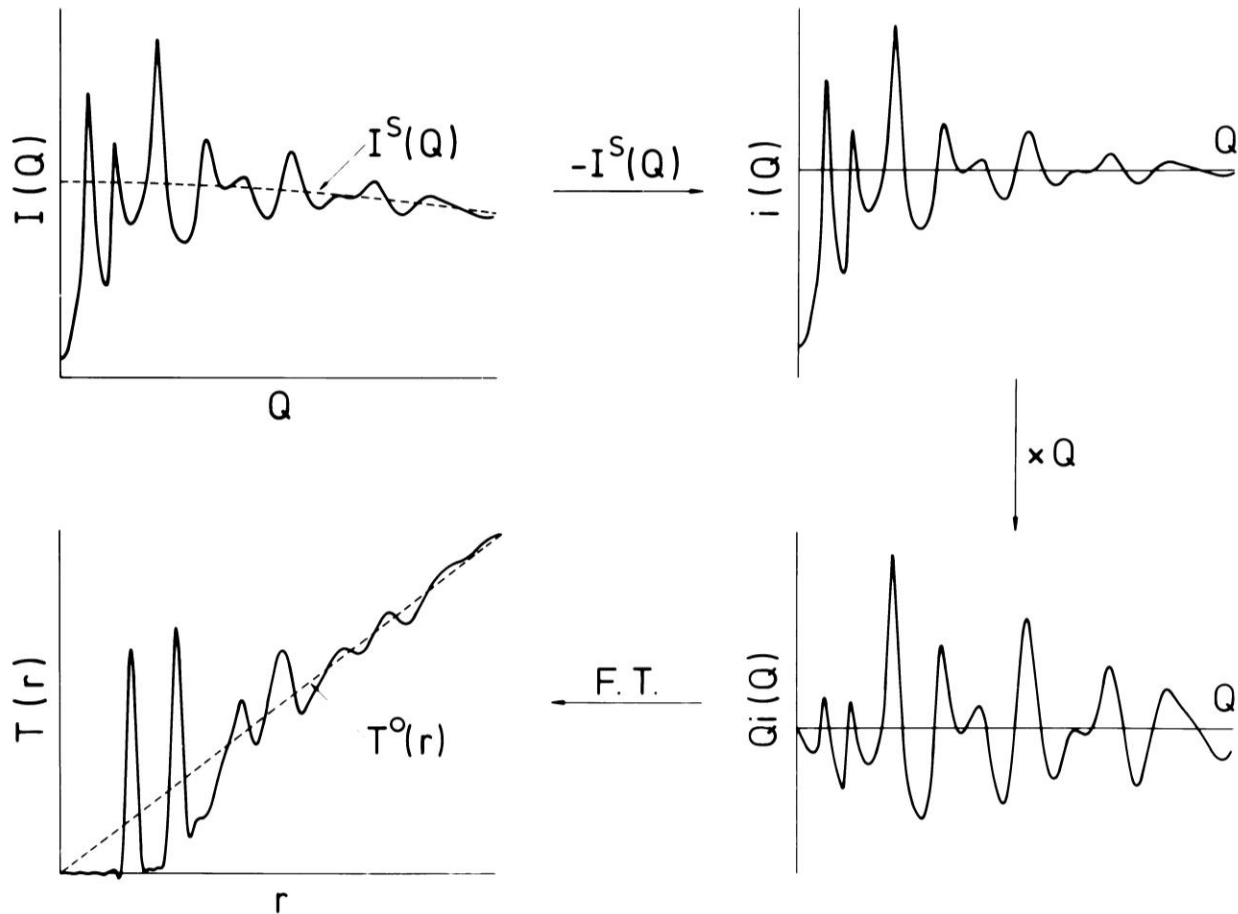
Mining the Data

- 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
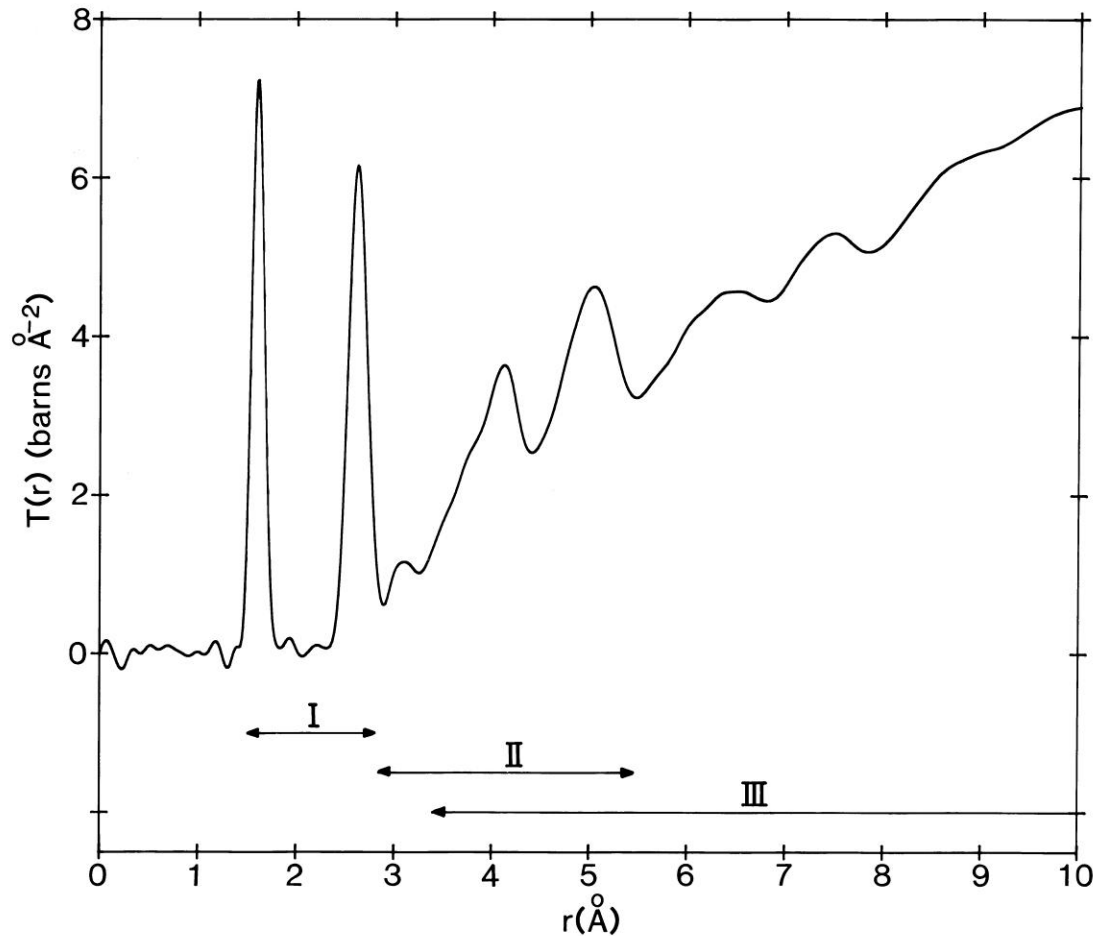
T(*r*) from a Neutron Diffraction Experiment

$$I(Q) = I^S(Q) + i(Q)$$
$$\text{self} \quad \text{distinct}$$

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

# 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.
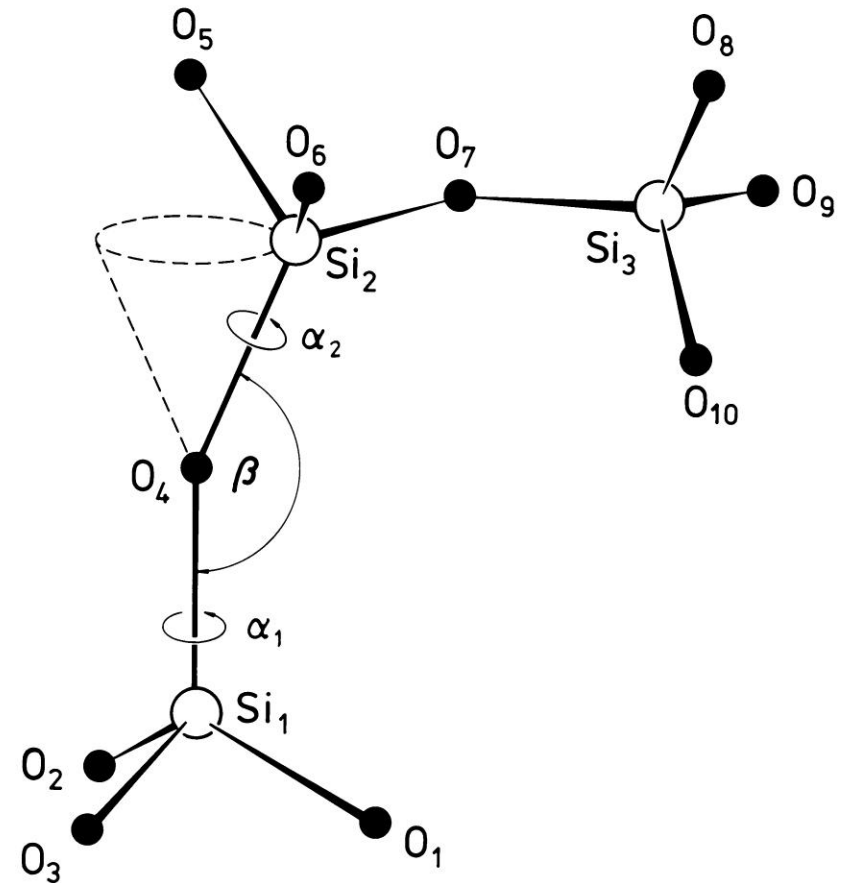
Structural Models of Amorphous Solids

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.
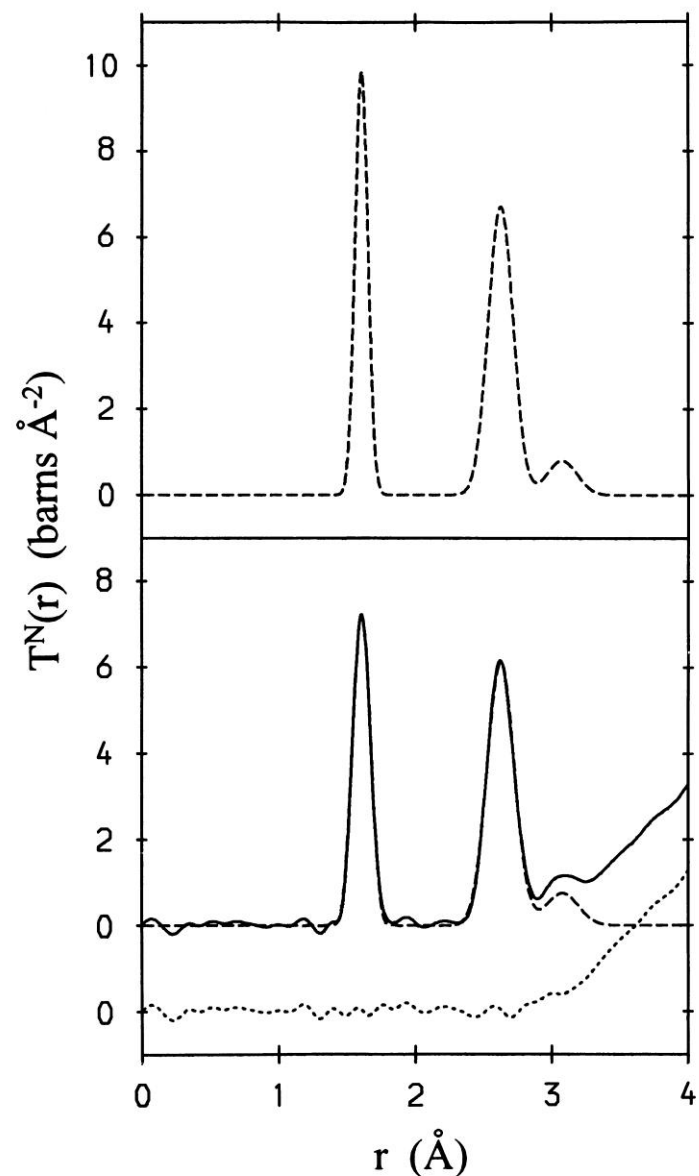
Vitreous Silica

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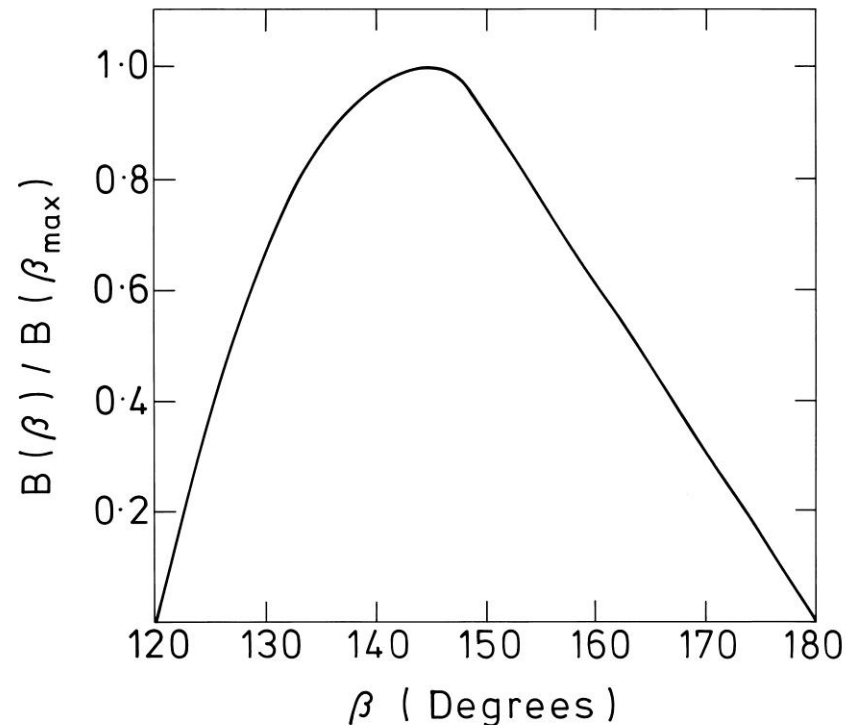
The accuracy of fit is given by the rms R-factor

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

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.

Component Correlation Functions

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, $P(r)$)

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.