From Structure Factor to Pair Distribution Functions and the Fundamental Information these Functions Contain

Principles

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Science & Technology Facilities Council
ISIS

My Background

- I study structure of glass and disordered crystals
- See http://alexhannon.co.uk for…
- more scientific information
- software
- experimental data

5

NEUTRON DIFFRACTION TECHNIQUES FOR STRUCTURAL STUDIES OF GLASSES

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5.1 INTRODUCTION

Neutron diffraction (ND) is an important experimental technique for the investigation of the structure of glasses. It can be used to study oxide glasses, chalcogenide glasses, metallic glasses, amorphous semiconductors, molecular glasses, amorphous polymers, organic glasses, and so on. An ND experiment yields a measurement of the distribution of interatomic distances that can be more accurate than for any other experimental method. The shortest distances in the glass (the short range order, SRO) can be characterized in terms of coordination numbers, bond lengths, and other short distances. These can be measured very accurately by ND, and used to determine the coordination polyhedra that form the basis of the glass structure. The way in which these units connect together (the intermediate range order, IRO) is also probed by ND, although in a more subtle way, and its investigation usually requires some kind of modeling of the ND results. The results of an ND experiment can be predicted exactly for a structural model, and hence ND provides a rigorous test of structural models.

The main aim of this chapter is to provide empirical information to enable a new researcher, such as a research student, to plan and perform an ND investigation of the structure of glass samples, to analyze the experimental data, and to begin to interpret

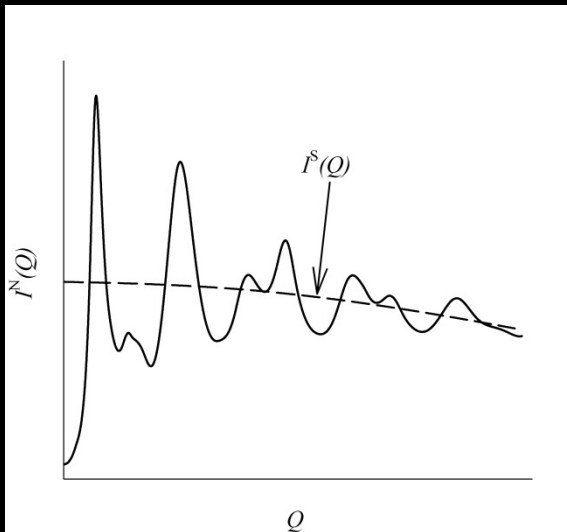Please also see this long (83 pages) book chapter
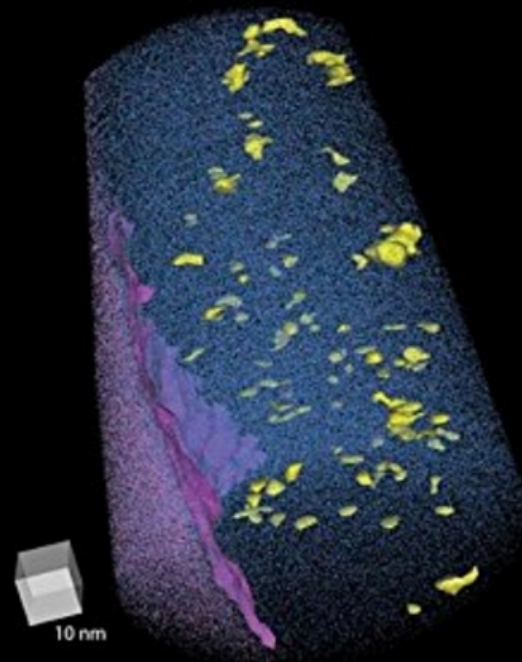
Modern Glass
Characterization

EDITED BY **MARIO AFFATIGATO**

WILEY

The Fourier Transform

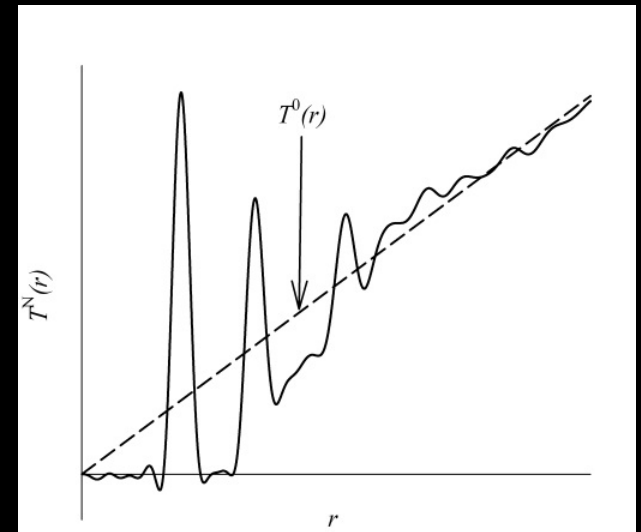- Fourier transform from reciprocal-space (Q) to real-space (r)

$$T^{\mathrm{N}}(r) = T^0(r) + \frac{2}{\pi} \int_0^\infty Q i^N(Q) \sin rQ \, dQ$$

"Structure factor"

Fourier transform
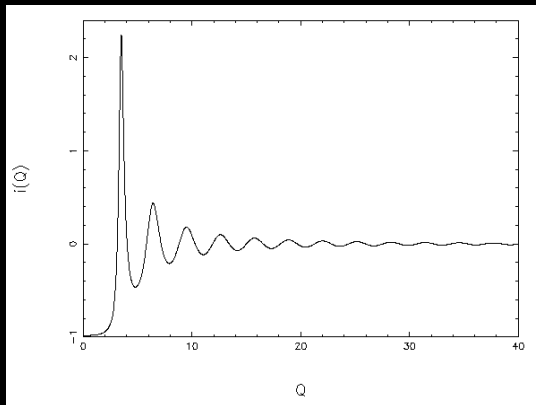
(B$_2$O$_3$ glass)

PDF "pair distribution function"

simple Fourier transform software

- A simple standalone Fourier transform program I2T is available here http://alexhannon.co.uk

(Percus-Yevick hard sphere liquid)

Fourier transform

Diffraction pattern $i(Q)$
Reciprocal-space
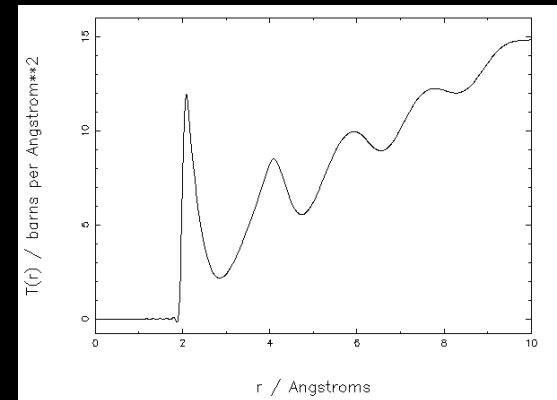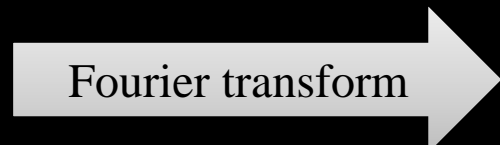
Correlation function $T(r)$
Real-space
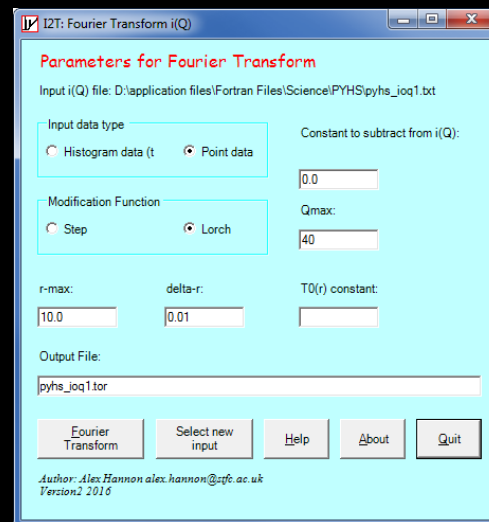
"the fundamental information"

- Fundamentally, the structure factor and the PDF contain information on the <u>distances between pairs of atoms</u>.

- Full theory involves quantum mechanics, but static approximation theory is enough for basic understanding.

- For full theory see:
  G.L.Squires *Introduction to the Theory of Thermal Neutron Scattering*, Cambridge University Press, 2012.
  D.L.Price & K.Sköld *Introduction to Neutron Scattering*, in: Neutron Scattering Part A, Academic Press, 1986
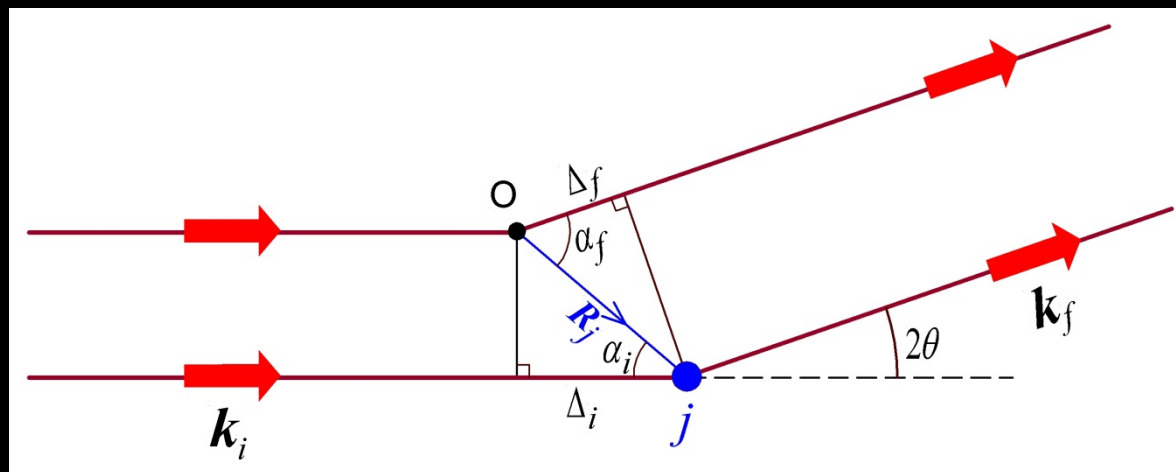
The Interaction

- Incident neutron wave, wavelength $\lambda \sim 1\text{Å} = 10^{-10}\text{m}$
  $$\psi = \exp ikz$$
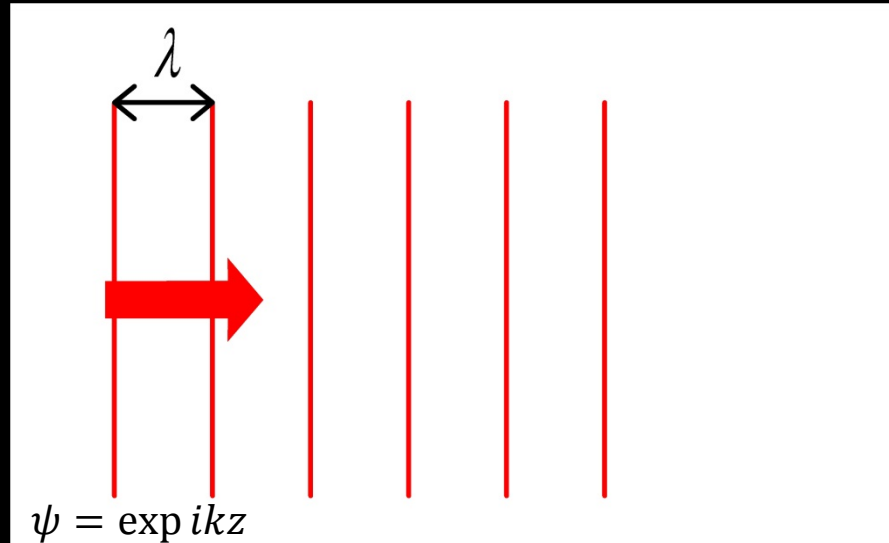
The Interaction

- Incident neutron wave, wavelength $\lambda \sim 1\text{Å} = 10^{-10}$m

  $\psi = \exp ikz$

- Wave is scattered by a <u>nucleus</u>, diameter $\sim 10^{-15}$m

  $\psi = -\dfrac{b}{r}\exp ikr$

- Scattering length b is a <u>constant</u>

"the fundamental information"

- Incident neutron beam has wavevector $\boldsymbol{k}_i$

- Final scattered neutron beam has wavevector $\boldsymbol{k}_f$ (scattering angle is 2θ)
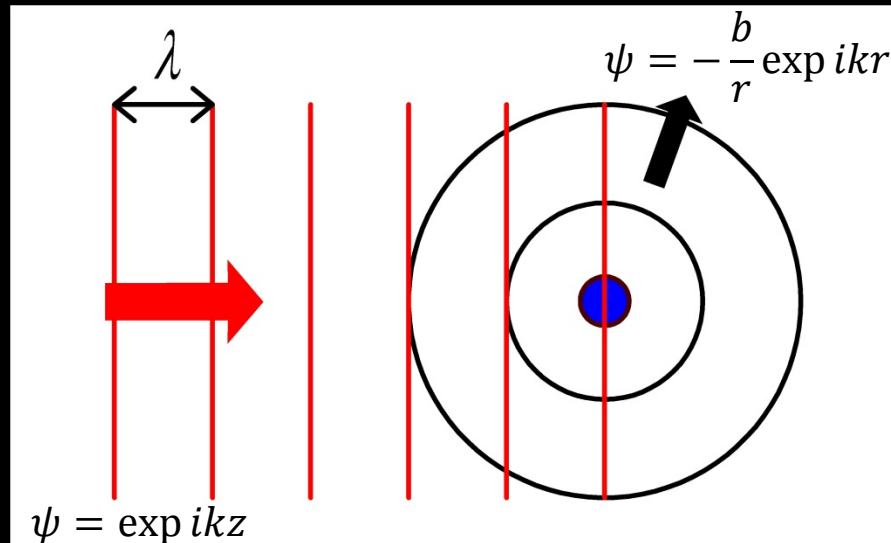
- Momentum transfer is $\boldsymbol{Q} = \boldsymbol{k}_i - \boldsymbol{k}_f$

Bold letters are vectors:
$\boldsymbol{k}_i, \boldsymbol{k}_f, \boldsymbol{Q}$

scattering triangle

Neutron beam
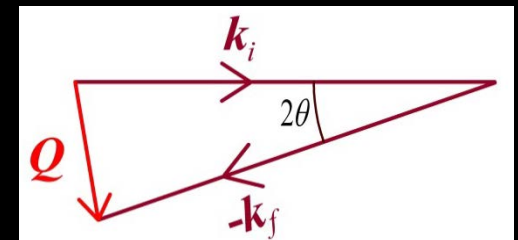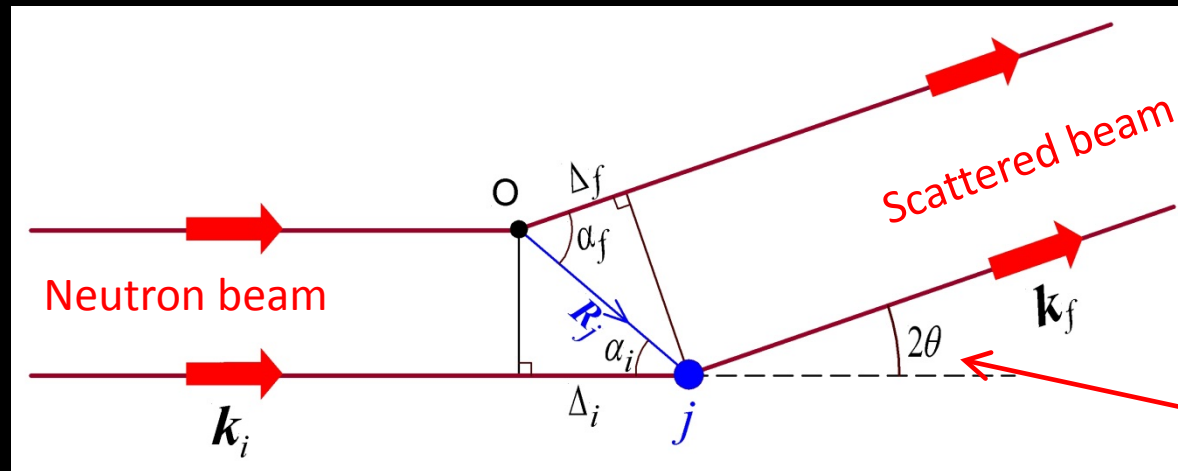
Scattered beam

Scattering angle

"the fundamental information"

- Nucleus j, at vector position $\boldsymbol{R}_j$ relative to origin O
- For the scattered wave, the path difference relative to the origin is $\left(\Delta_i - \Delta_f \right)$
- This is a phase difference $\left(\boldsymbol{Q} . \boldsymbol{R}_j \right)$
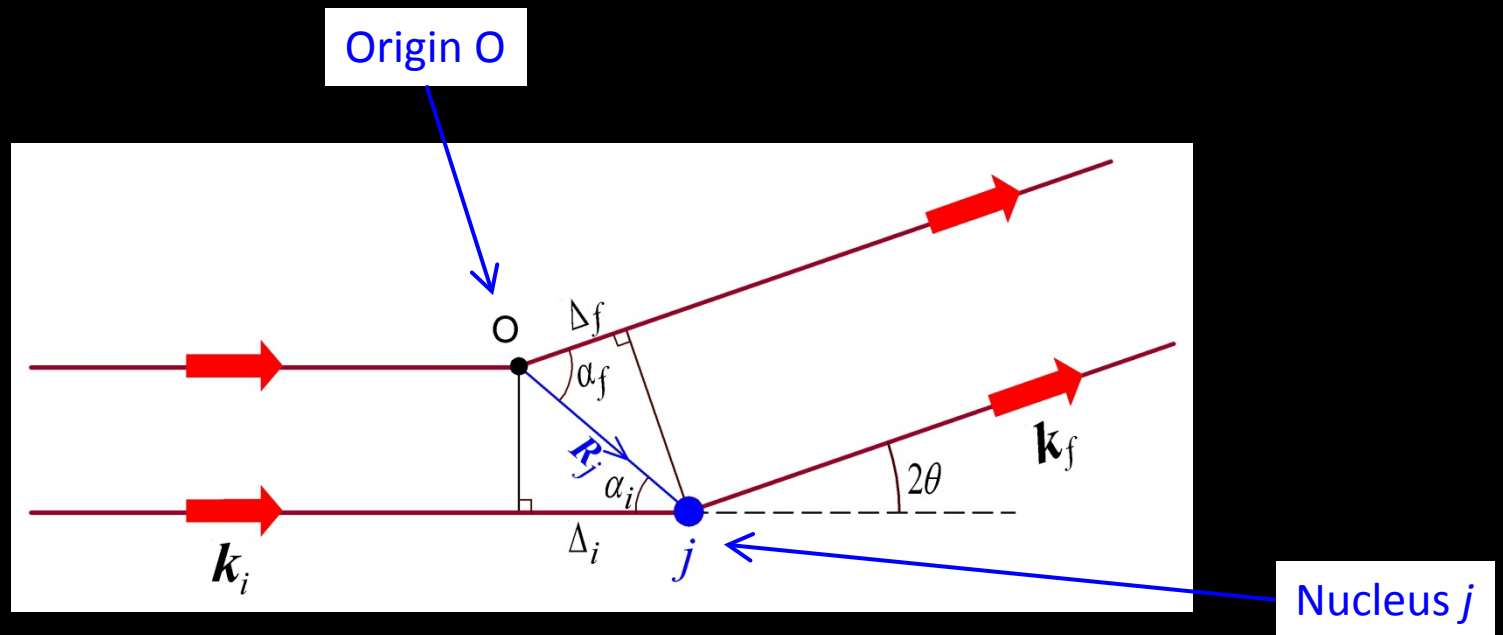
Origin O

Nucleus j

"the fundamental information"

- For N nuclei the scattered wavefunction is a sum of the phase factors $\psi_f = \sum_{j=1}^{N} -\frac{b_j}{r} \exp i\boldsymbol{Q}.\boldsymbol{R}_j$

- The differential cross-section measured in an experiment is

$$I^{\text{N}}(Q) = \frac{r^2}{N}\left|\psi_f\right|^2 = \frac{1}{N}\sum_j \sum_k b_j b_k \sin i\boldsymbol{Q}.\left(\boldsymbol{R}_j - \boldsymbol{R}_k\right)$$
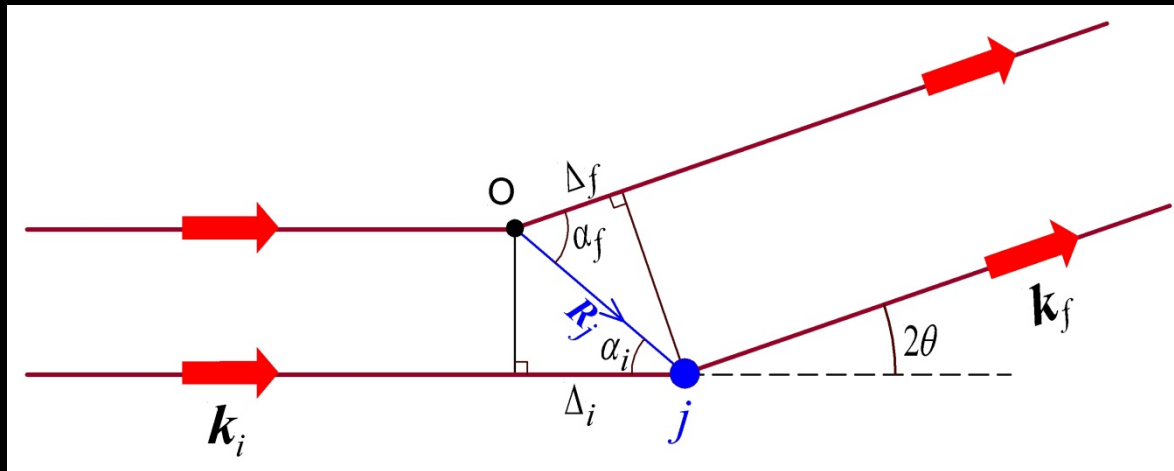
"the fundamental information"

- For *N* nuclei the scattered wavefunction is a sum of the phase factors $\psi_f = \sum_{j=1}^{N} -\frac{b_j}{r} \exp i\boldsymbol{Q}.\boldsymbol{R}_j$

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$$I^{\mathrm{N}}(Q) = \frac{r^2}{N}\left|\psi_f\right|^2 = \frac{1}{N}\sum_j \sum_k b_j b_k \sin i\boldsymbol{Q}.\left(\boldsymbol{R}_j - \boldsymbol{R}_k\right)$$

Sum over all atom pairs

"the fundamental information"

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- The differential cross-section measured in an experiment is

$$I^N(Q) = \frac{r^2}{N}\left|\psi_f\right|^2 = \frac{1}{N}\sum_j \sum_k b_j b_k \sin i\boldsymbol{Q}.\left(\boldsymbol{R}_j - \boldsymbol{R}_k\right)$$
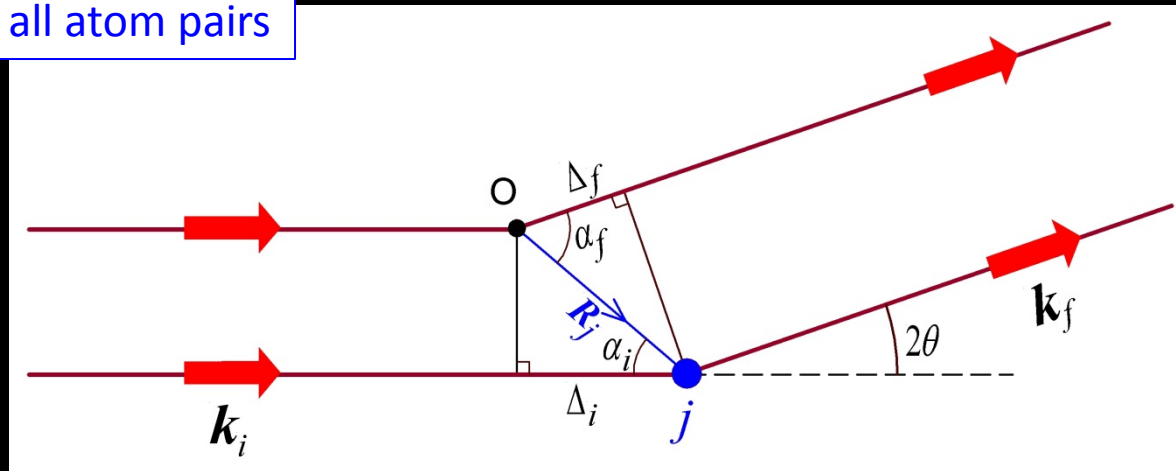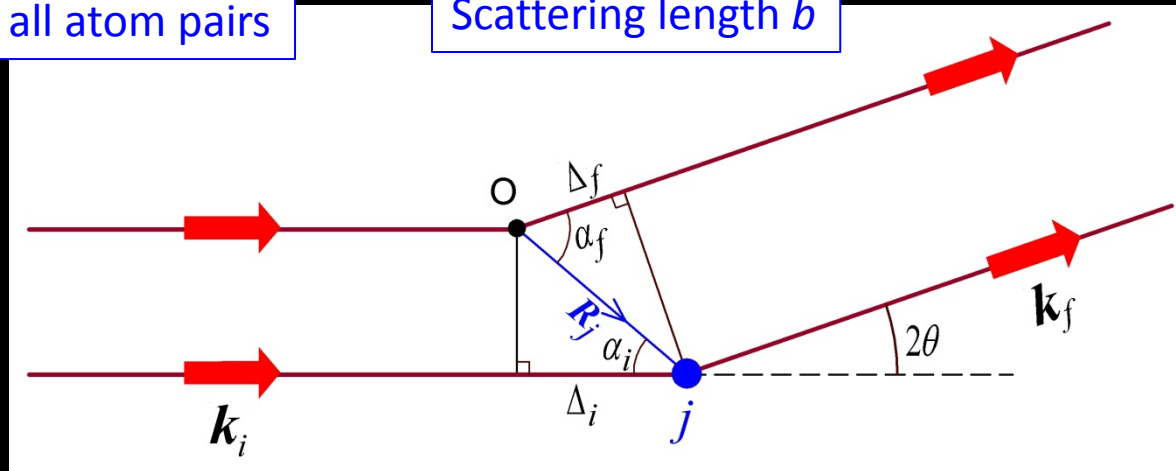
Sum over all atom pairs

Scattering length *b*

"the fundamental information"
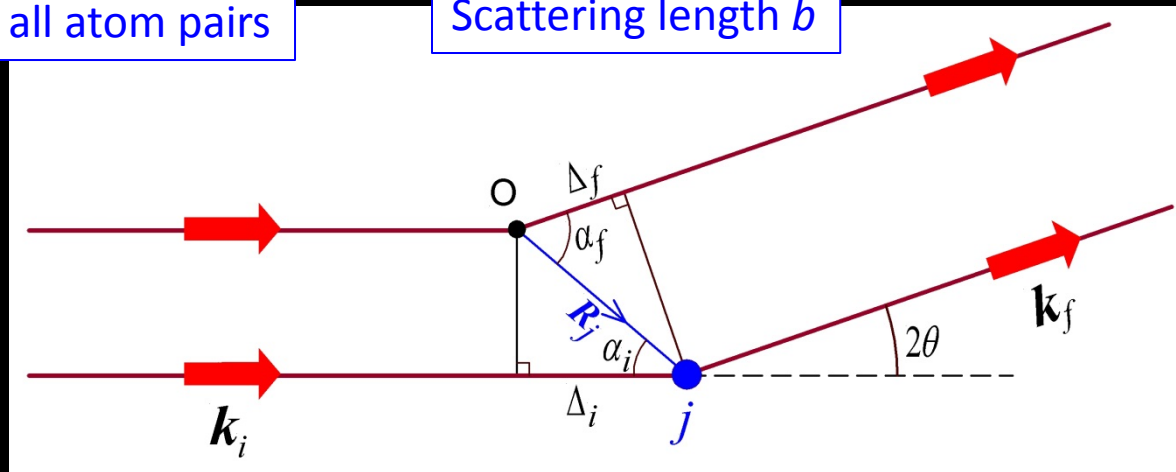
- For *N* nuclei the scattered wavefunction is a sum of the phase factors $\psi_f = \sum_{j=1}^{N} -\frac{b_j}{r} \exp iQ.R_j$

- The differential cross-section measured in an experiment is
$$I^{N}(Q) = \frac{r^2}{N}|\psi_f|^2 = \frac{1}{N}\sum_j \sum_k b_j b_k \sin iQ.(R_j - R_k)$$

Sum over all atom pairs

Scattering length *b*

Vector between atoms

Debye Equation

- For an <u>isotropic</u> sample, $Q = |\boldsymbol{Q}|$

- directional averaging gives the Debye equation

$$I^{\mathrm{N}}(Q) = \frac{1}{N}\sum_{j=1}^{N}\sum_{k=1}^{N} b_j b_k \frac{\sin QR_{jk}}{QR_{jk}}$$
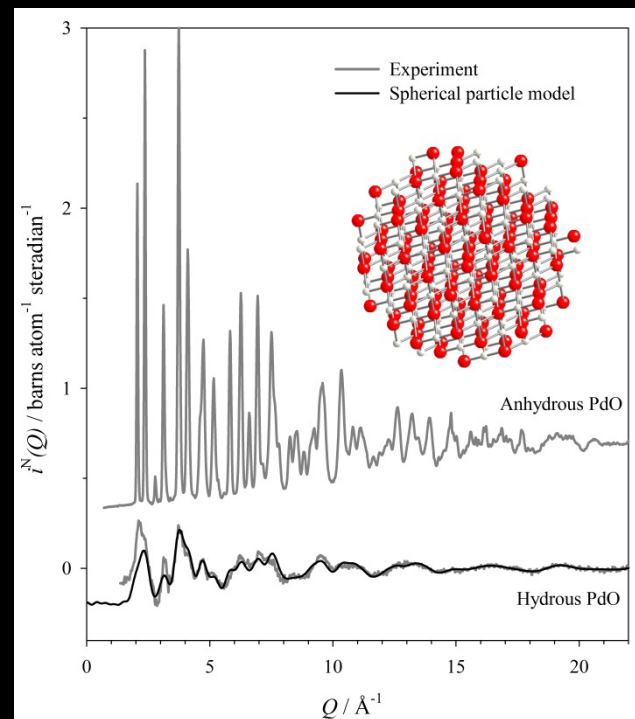
Distance between atoms

Sum over all atom pairs

- A useful equation, e.g. for modelling the diffraction pattern of small particles

18Å particles of PdO

$\frac{\sin x}{x}$ *is very important for diffraction*
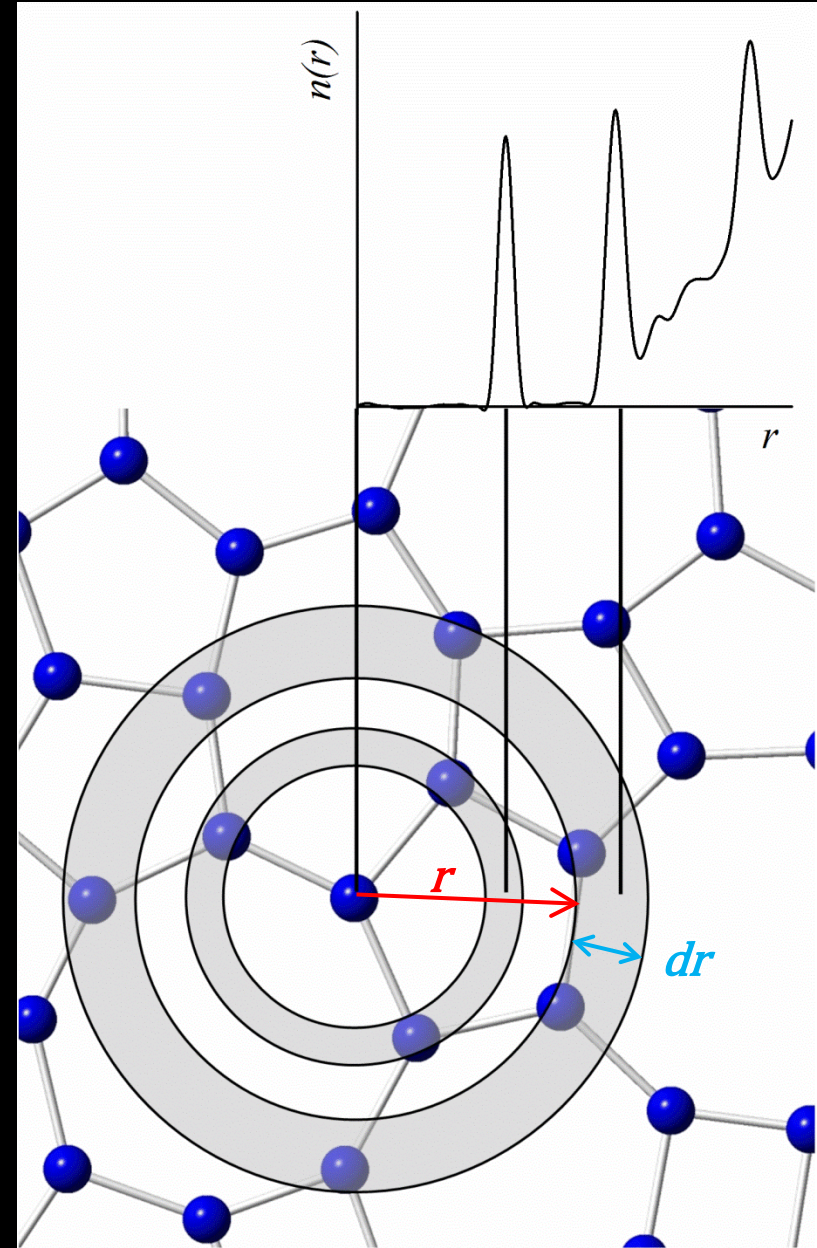

(Parker et al, J Phys Chem C 2010)

Real-space: The RDF

- The Radial Distribution Function (RDF), $n(r)$

- $n(r)dr$ is the number of atoms in a spherical shell with radii r and $r + dr$

- The RDF depends on <u>number</u> of atoms

- If r is large, then
  $n(r) = 4\pi r^2 g^0$
  (g^0 = atom number density)
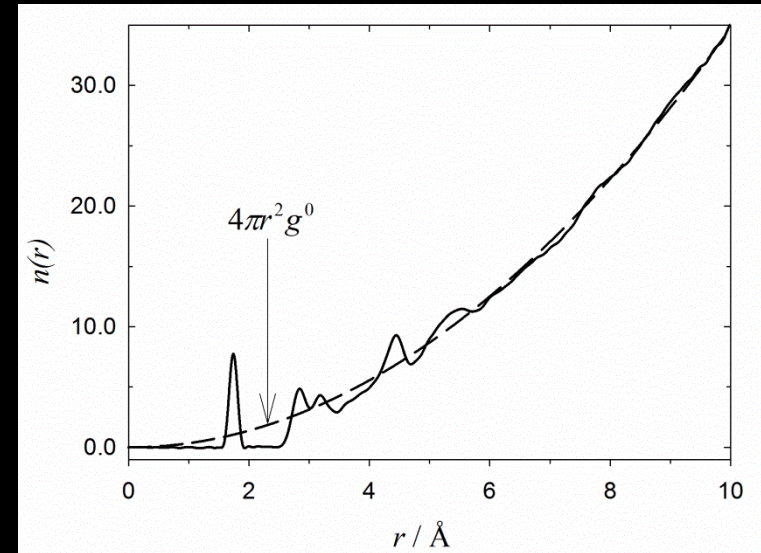
(monatomic sample)

RDF

- RDF $n(r)$ was popular in early X-ray studies of glass

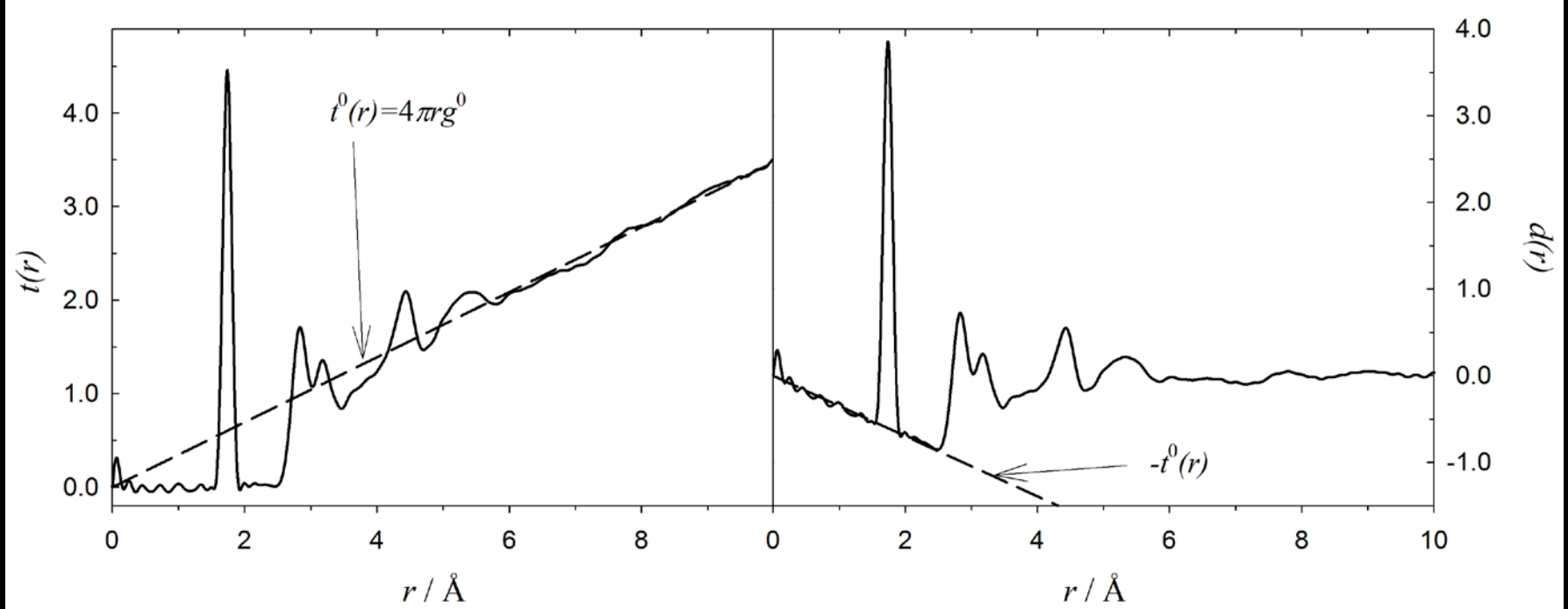 (e.g. Warren et al, J Am Ceram Soc 1936)

(*GeO$_2$ glass*)

- The RDF depends on <u>number</u> of atoms

- RDF is rarely used now

- If r is large, then
  $$n(r) = 4\pi r^2 g^0$$
  (g^0 = atom number density)

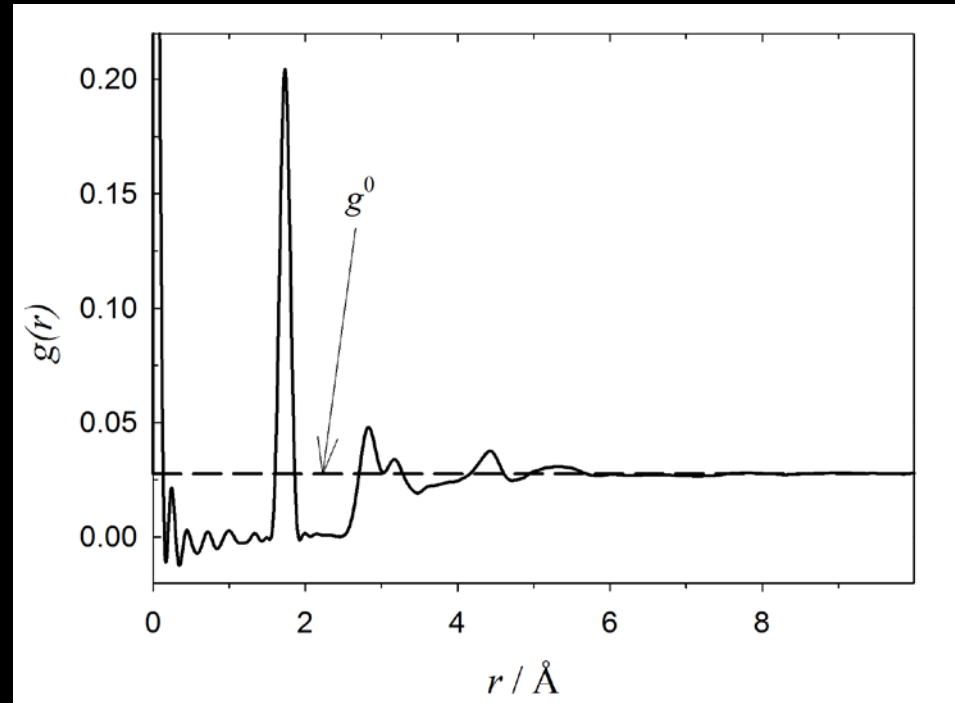# Total Correlation Function

(GeO$_2$ glass)

- Total correlation function $t(r)$ is commonly used for studies of glass: $n(r) = rt(r)$

- Differential correlation function (or PDF) is commonly used for studies of crystals: $t(r) = d(r) + 4\pi r g^0$

A comparison of various commonly used correlation functions for describing total scattering, Keen, J Appl Cryst 2001

Large r limit
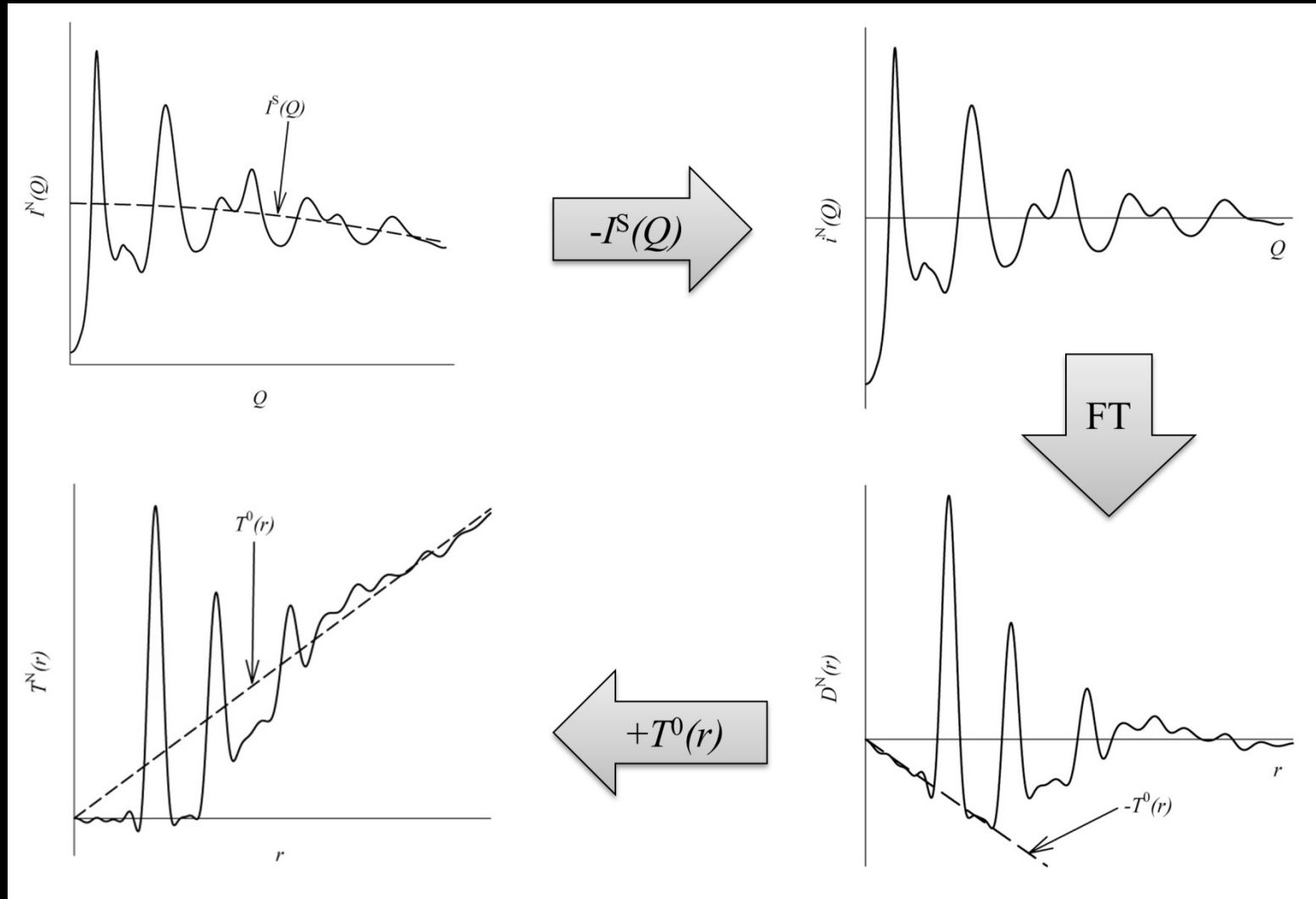
Pair Correlation Function

- Pair correlation function $g(r)$ is commonly used for studies of liquids:
  $$n(r) = 4\pi r^2 g(r)$$

- $g(r)$ depends on <u>atom number density</u>

- If r is large, then $g(r) = g^0$ atom number density

(*GeO$_2$ glass*)

A comparison of various commonly used correlation functions for describing total scattering, Keen, J Appl Cryst 2001

How to Measure the Correlation Function

- A Fourier transform of the total scattering
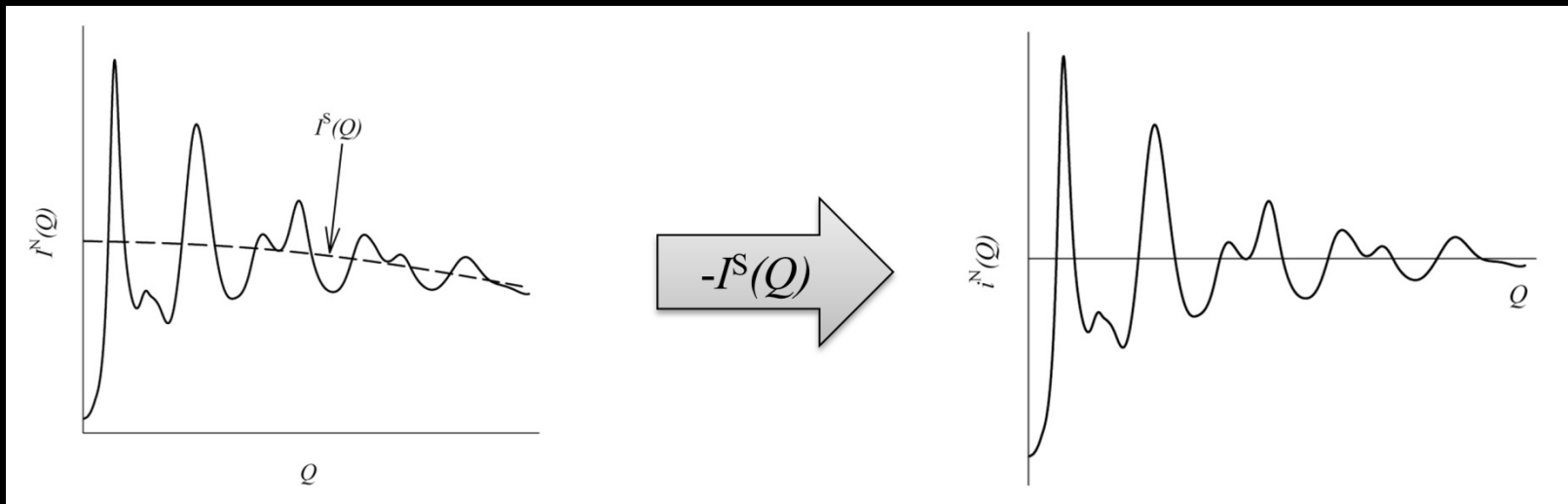

$(B_2O_3\ glass)$

How to Measure the Correlation Function

- Total scattering $I^N(Q)$ has 2 parts, self and distinct

- Self scattering $I^S(Q)$ is 'background'

- Distinct scattering $i^N(Q)$ oscillates around zero

- Self scattering must be <u>subtracted</u>

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

$$t(r) = t^0(r) + \frac{2}{\pi \bar{b}^2} \int_0^\infty Q i^N(Q) \sin rQ \, dQ$$

$$t^0(r) = 4\pi r g^0 \qquad (\textit{monatomic sample})$$
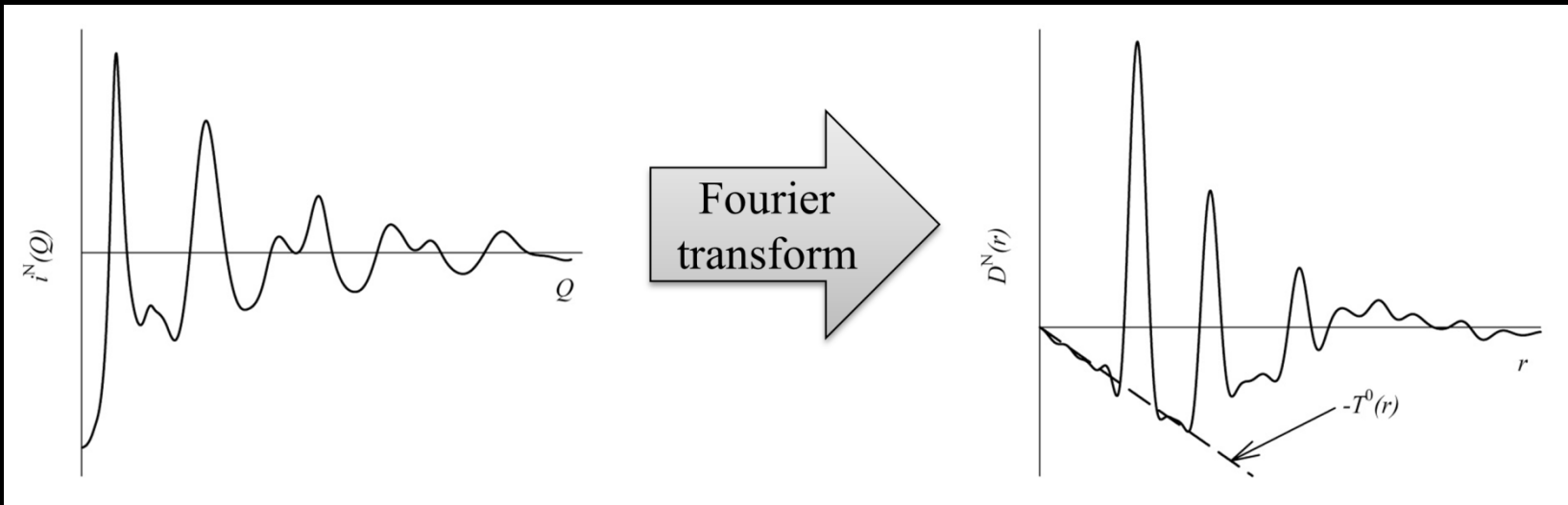

$-I^S(Q)$

(B_2O_3 glass)

How to Measure the Correlation Function

- Distinct scattering $i^N(Q)$ oscillates around zero

- The distinct scattering must be <u>Fourier transformed</u>

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

$$t(r) = t^0(r) + \frac{2}{\pi \bar{b}^2} \int_0^\infty Q i^N(Q) \sin rQ \, dQ$$

$$t^0(r) = 4\pi r g^0 \qquad \textit{(monatomic sample)}$$

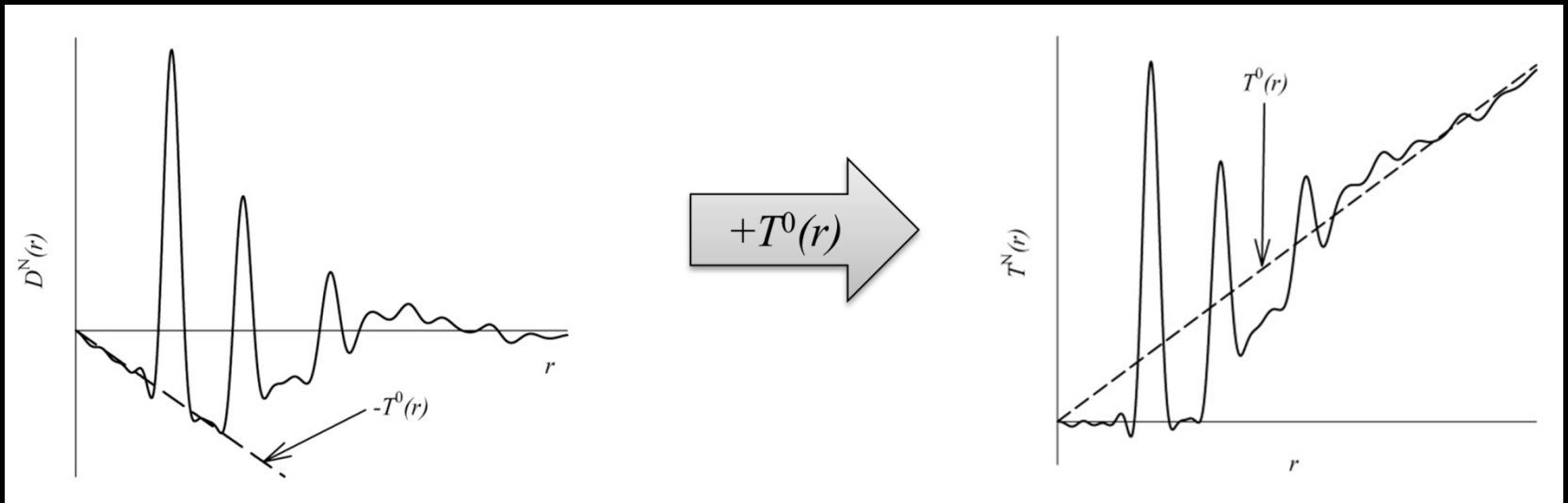*Fourier transform*

(B_2O_3 *glass*)

How to Measure the Correlation Function

- The average density contribution $t^0(r)$ must be <u>added</u>

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

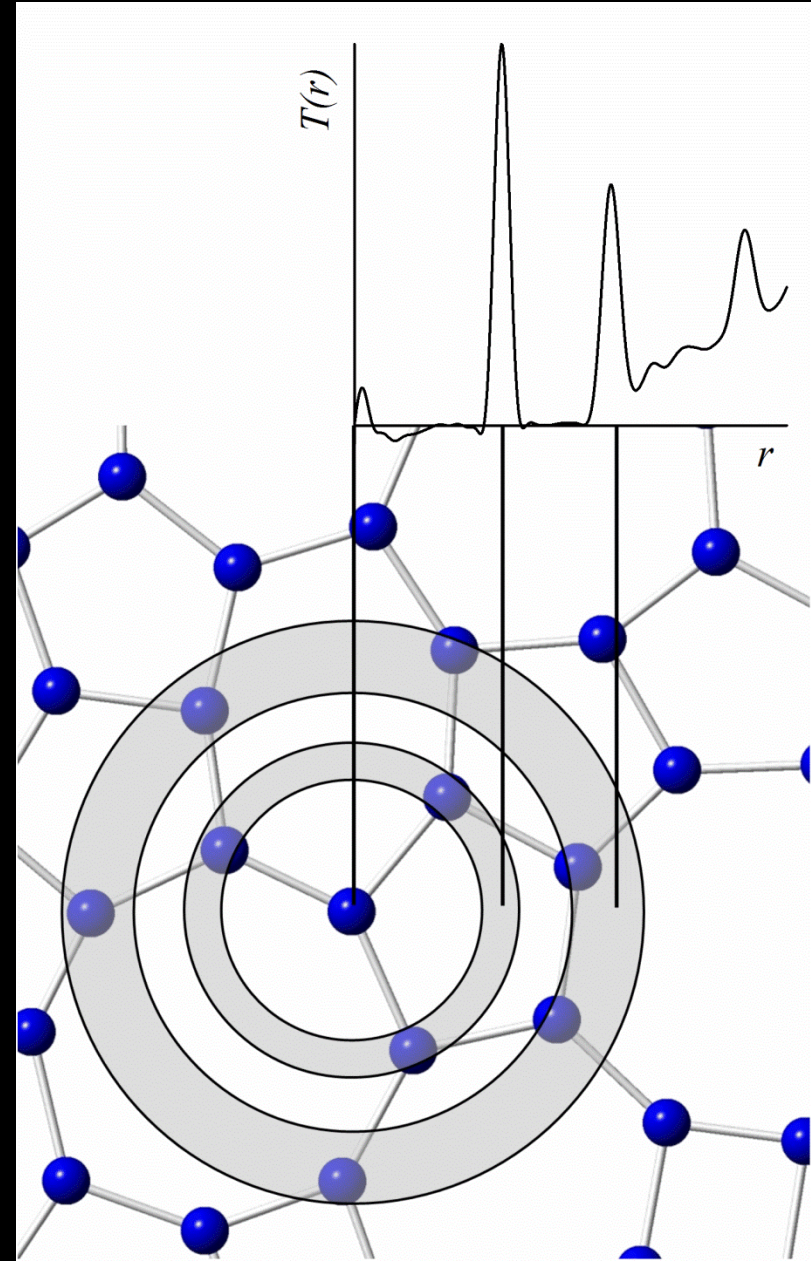$$t(r) = t^0(r) + \frac{2}{\pi \bar{b}^2} \int_0^\infty Q i^N(Q) \sin rQ \, dQ$$

$$t^0(r) = 4\pi r g^0 \qquad \text{(monatomic sample)}$$

$+T^0(r)$

(B_2O_3 glass)

What does the correlation function mean?

- A peak in $T^{\mathrm{N}}(r)$ indicates an interatomic distance that occurs frequently in the sample

- Peak area gives the coordination number n_{jk}

- Peak width/shape gives distribution of distances

What does the correlation function mean?

- A peak in $T^{\mathrm{N}}(r)$ indicates an interatomic distance that occurs frequently in the sample

- Peak area gives the coordination number n_{jk}

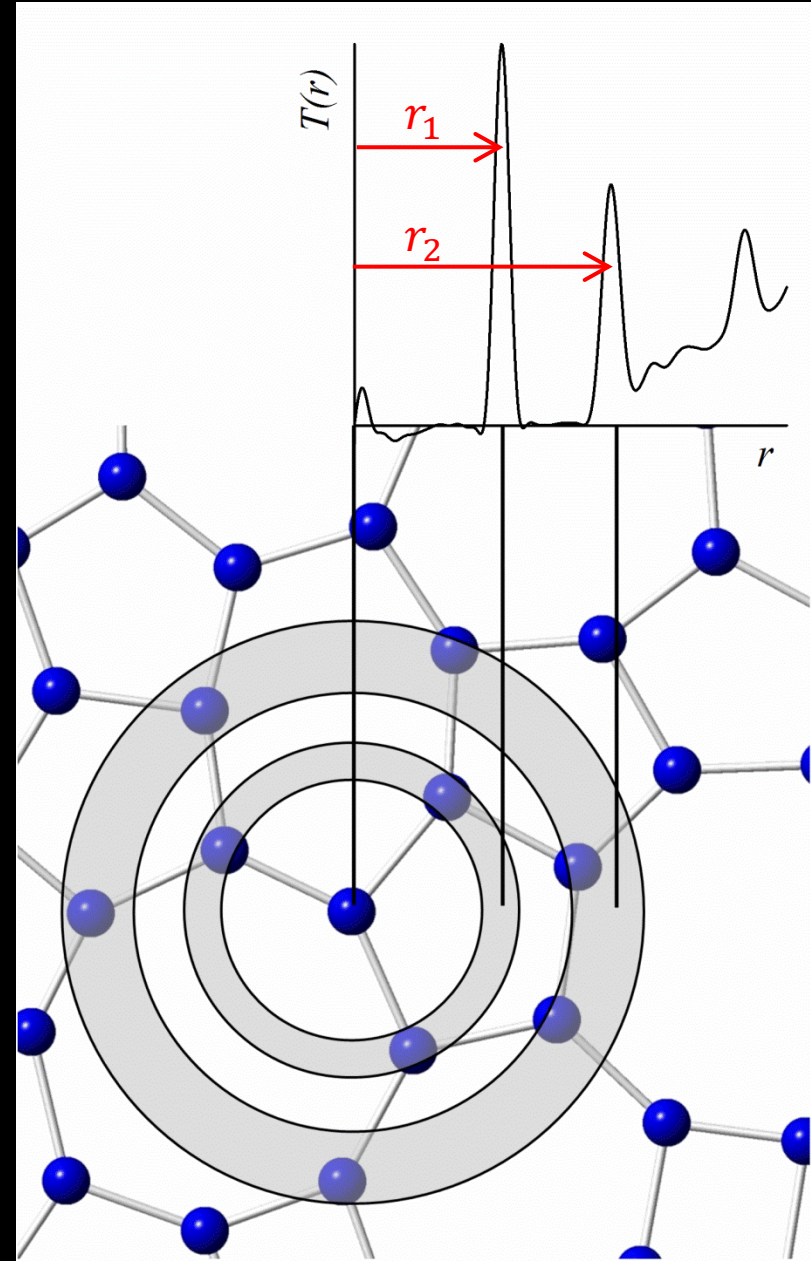- Peak width/shape gives distribution of distances

2D example

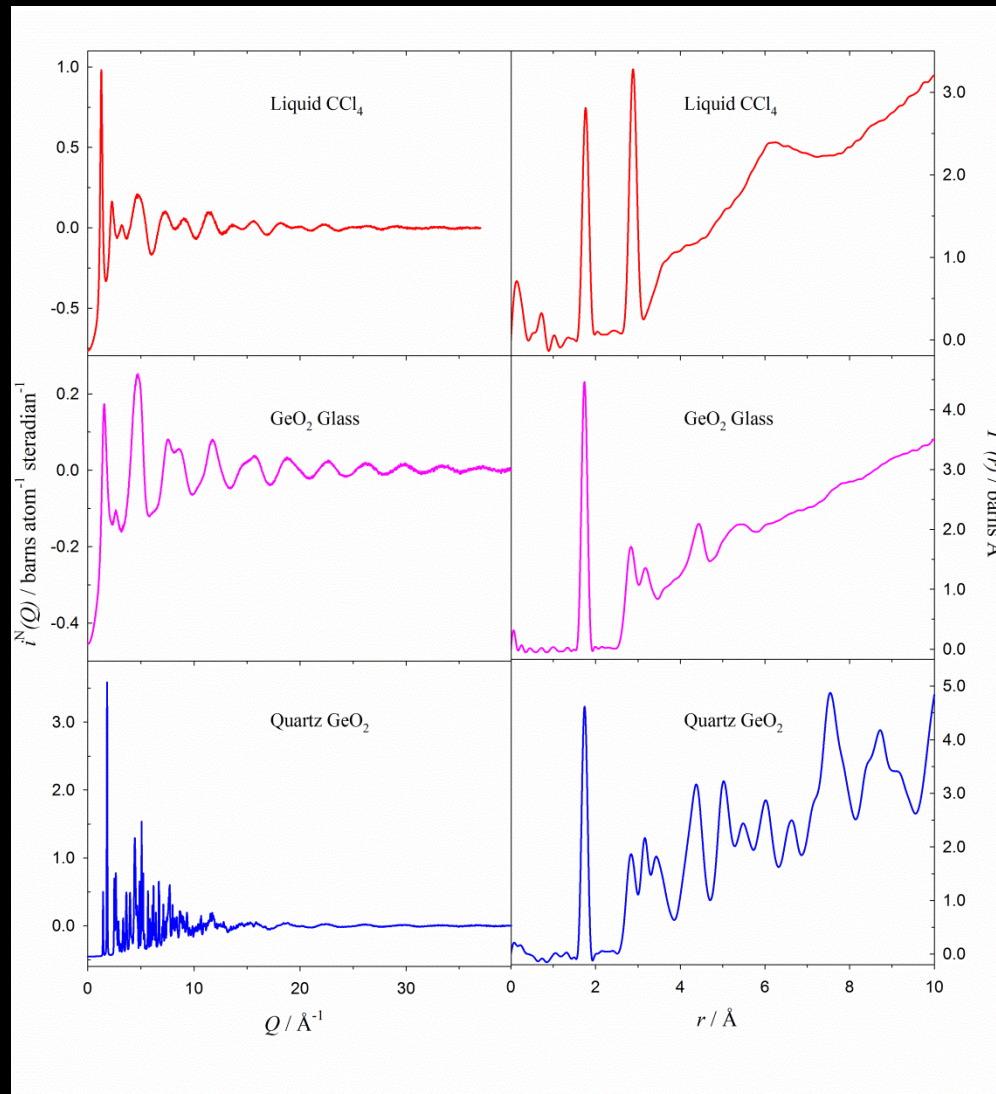r_1 is the bond length

$n_1 = 3$

r_2/r_1 gives the bond angle 120°
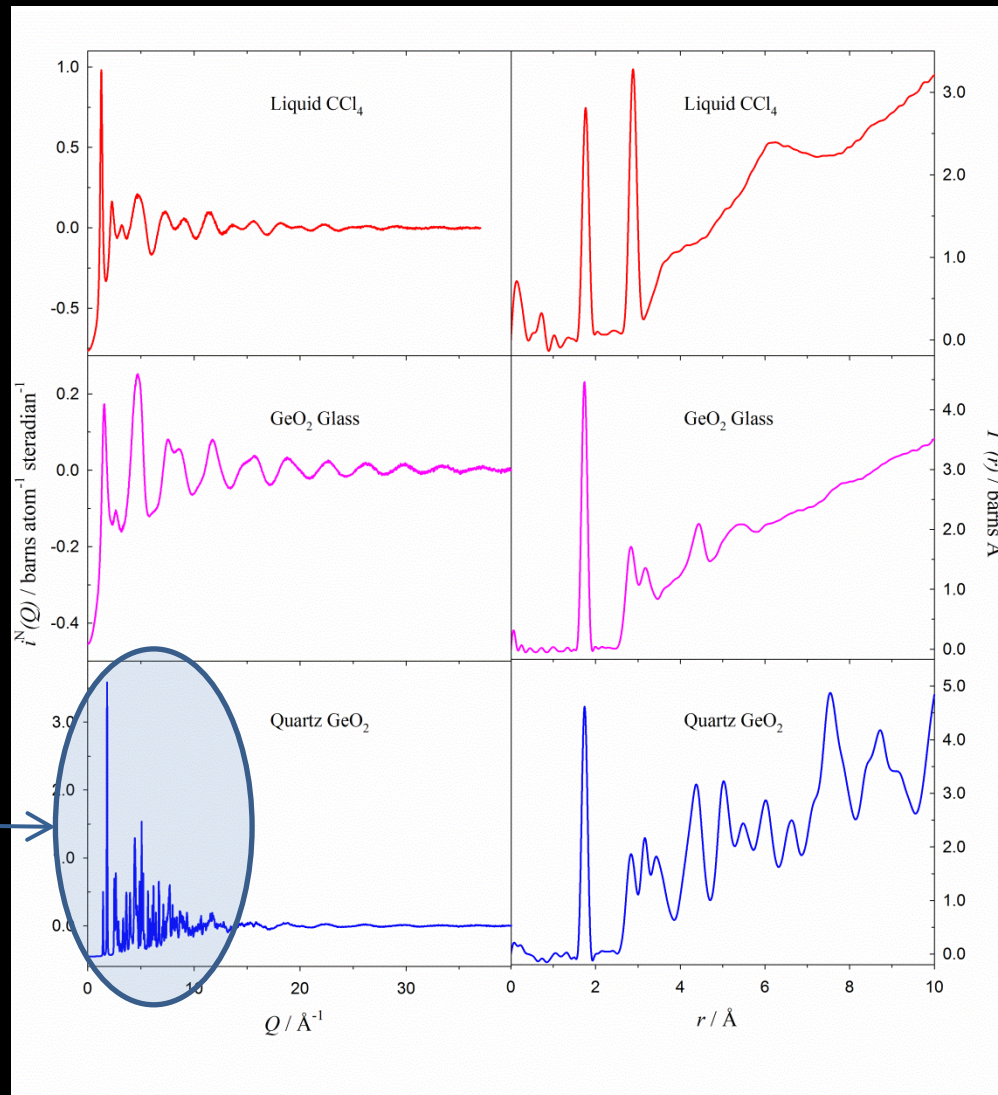
$n_2 = 6$

$T(r)$ for Different Phases of Matter

$T(r)$ for Different Phases of Matter

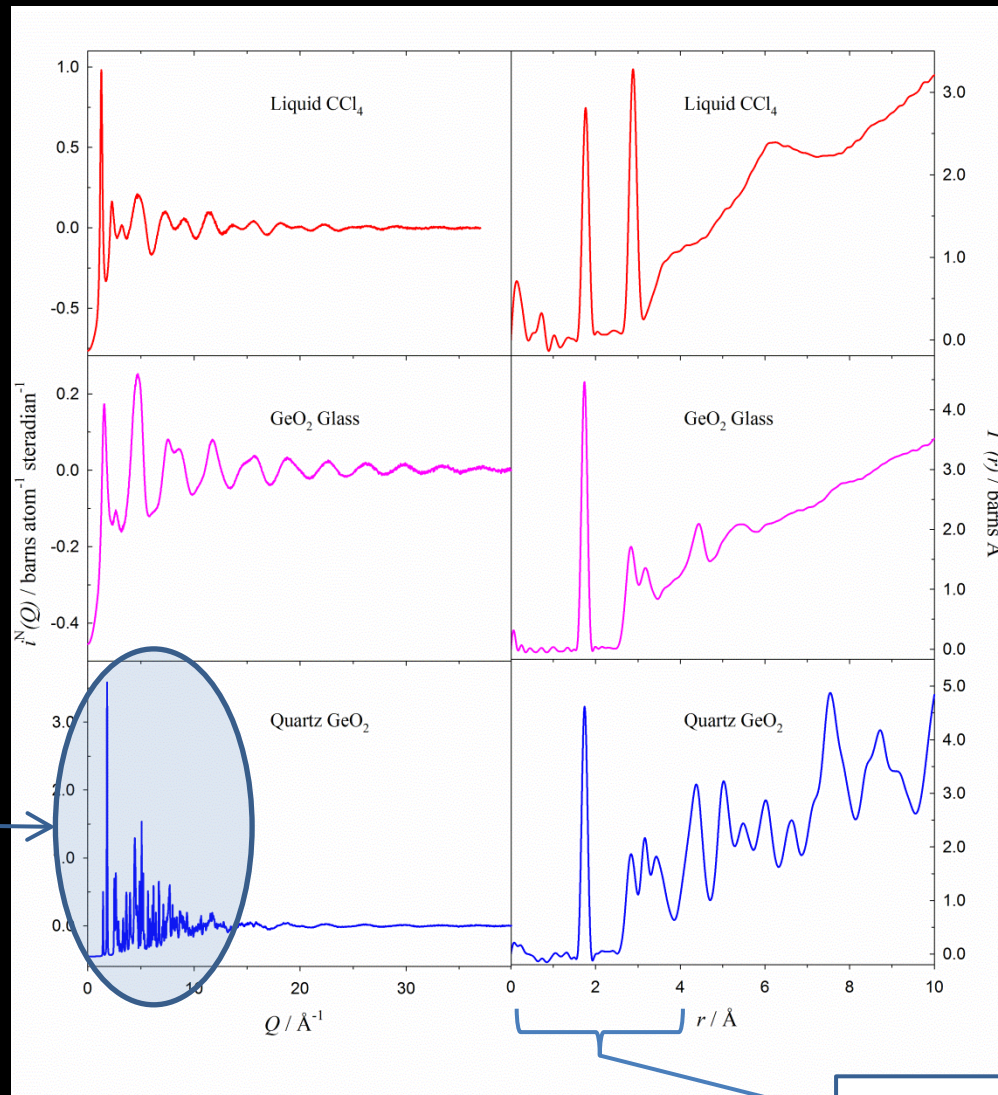Q-space r-space

Liquid

Glass

Crystal
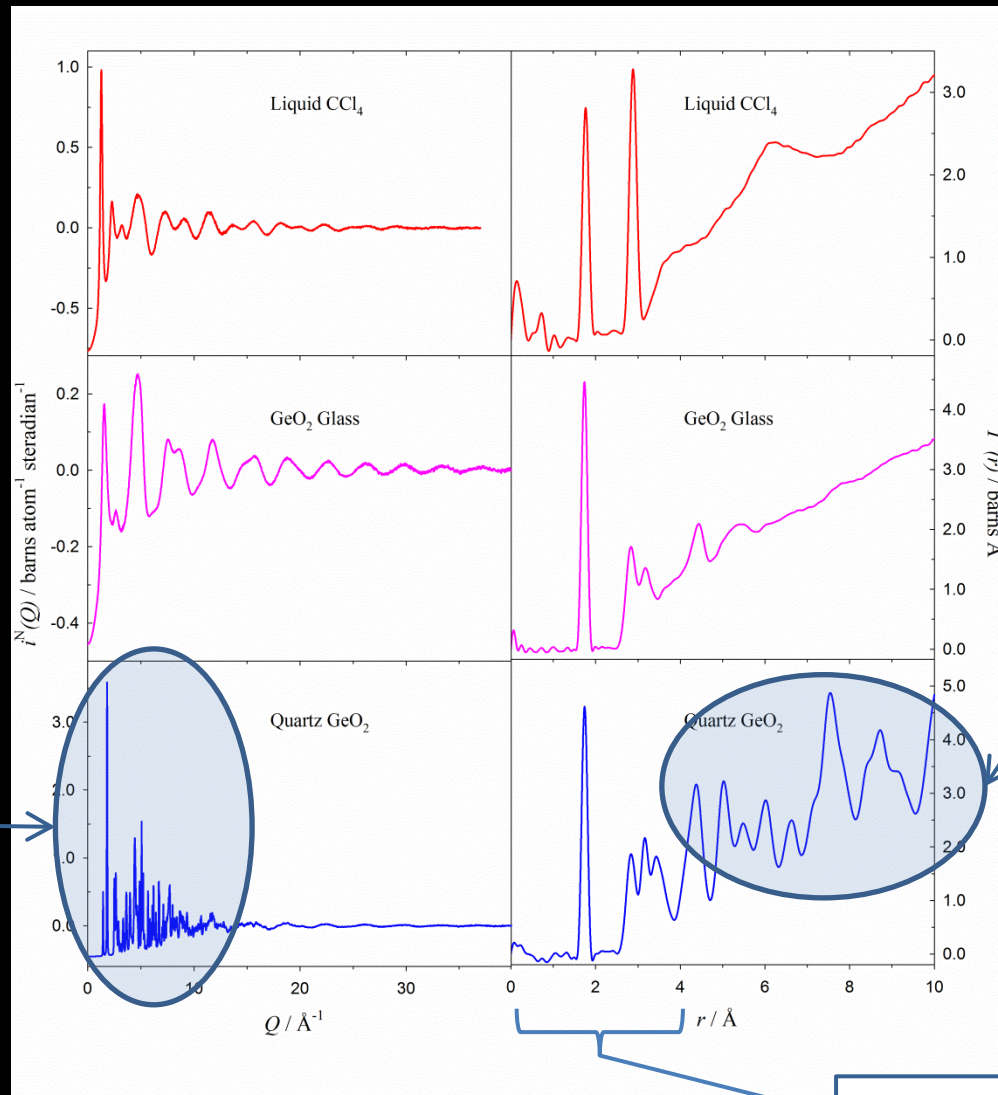
Bragg peaks

$T(r)$ for Different Phases of Matter

Q-space r-space

Liquid

Glass

Crystal

Bragg peaks

Short range order

$T(r)$ for Different Phases of Matter
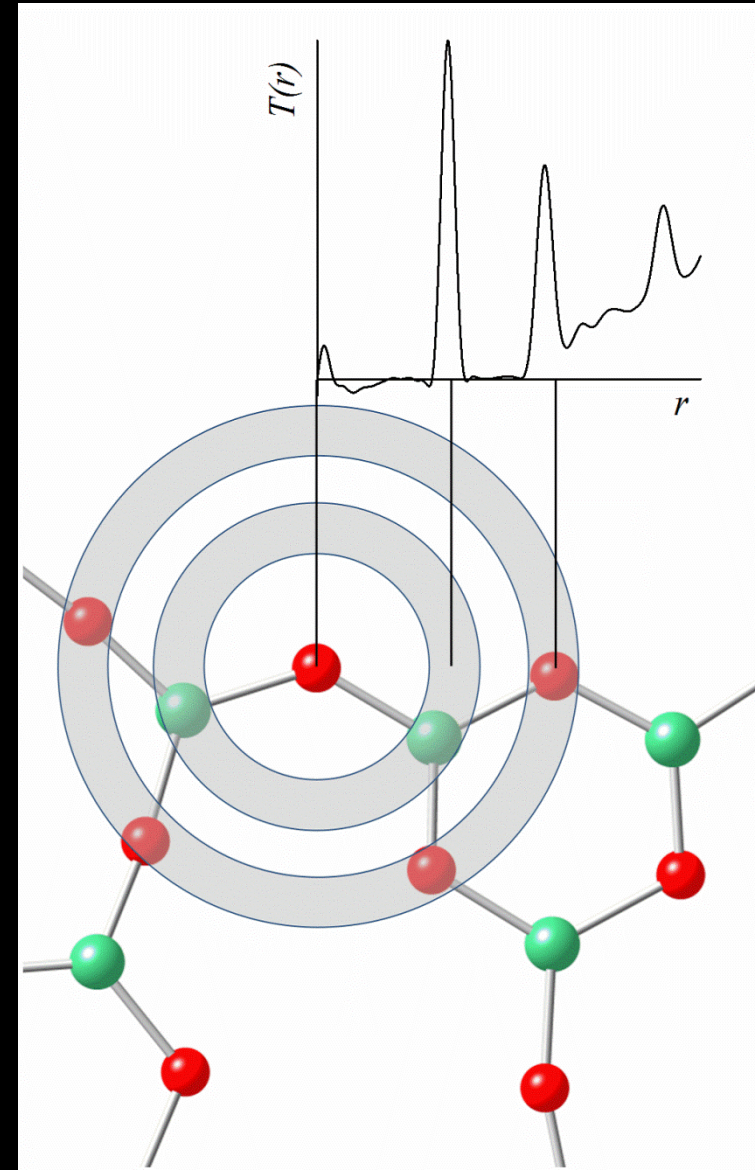
Polyatomic Samples: Partial Correlation Functions

- Most samples have more than one element...

  ...partial correlation functions

$$T^{\mathrm{N}}(r) = \sum_{l,m} c_l \bar{b}_l \bar{b}_m t_{lm}(r)$$

Polyatomic Samples: Partial Correlation Functions

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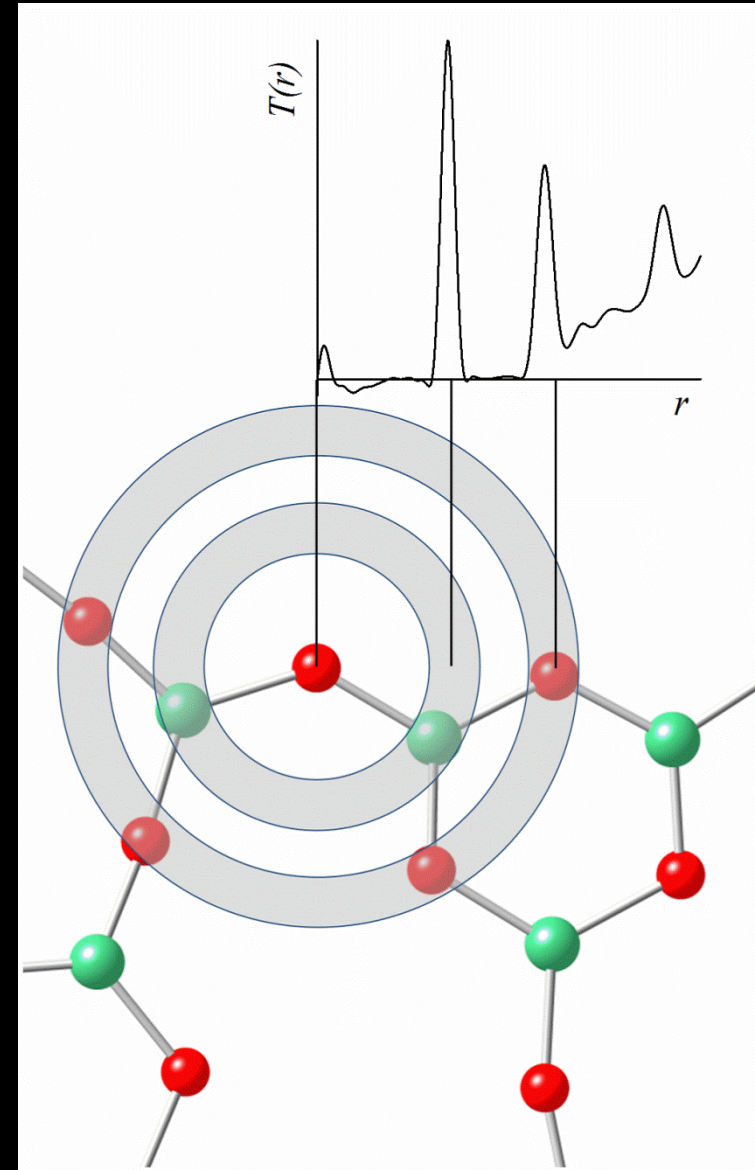$$T^{\mathrm{N}}(r) = \sum_{l,m} c_l \bar{b}_l \bar{b}_m t_{lm}(r)$$

Sum over atom pairs
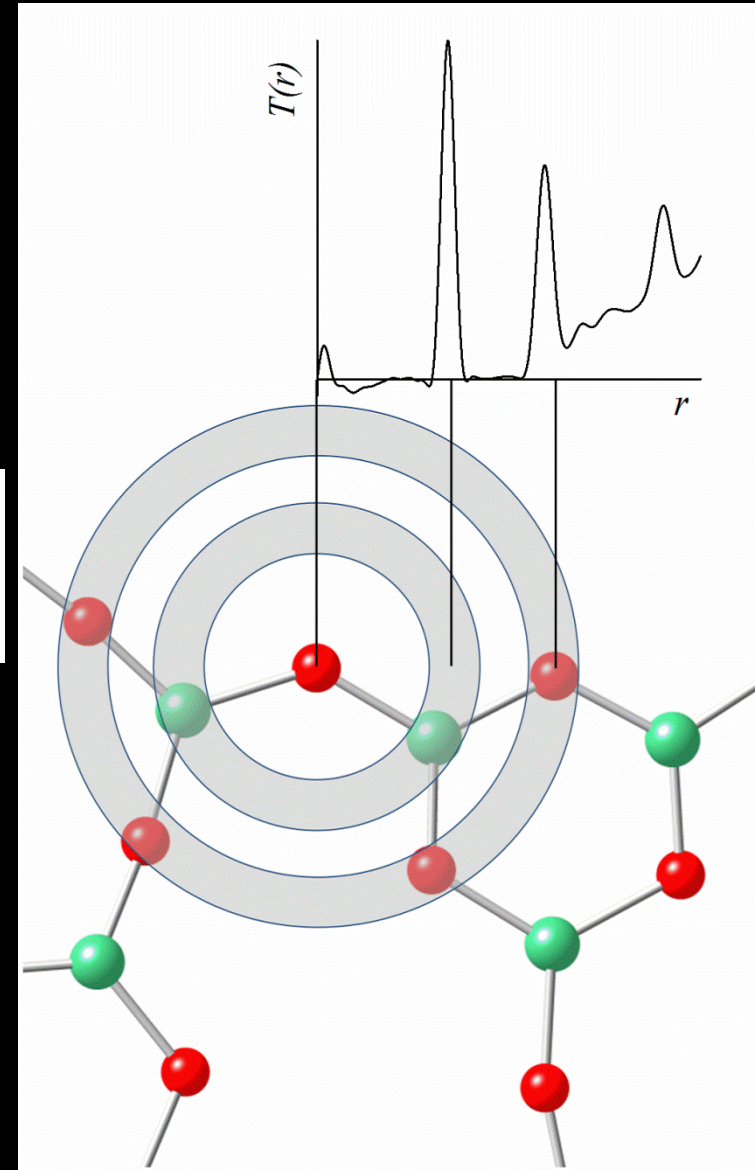
Polyatomic Samples: Partial Correlation Functions

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  …partial correlation functions

$$T^N(r) = \sum_{l,m} c_l \bar{b}_l \bar{b}_m t_{lm}(r)$$

Sum over atom pairs

Atomic fraction,
Scattering length,
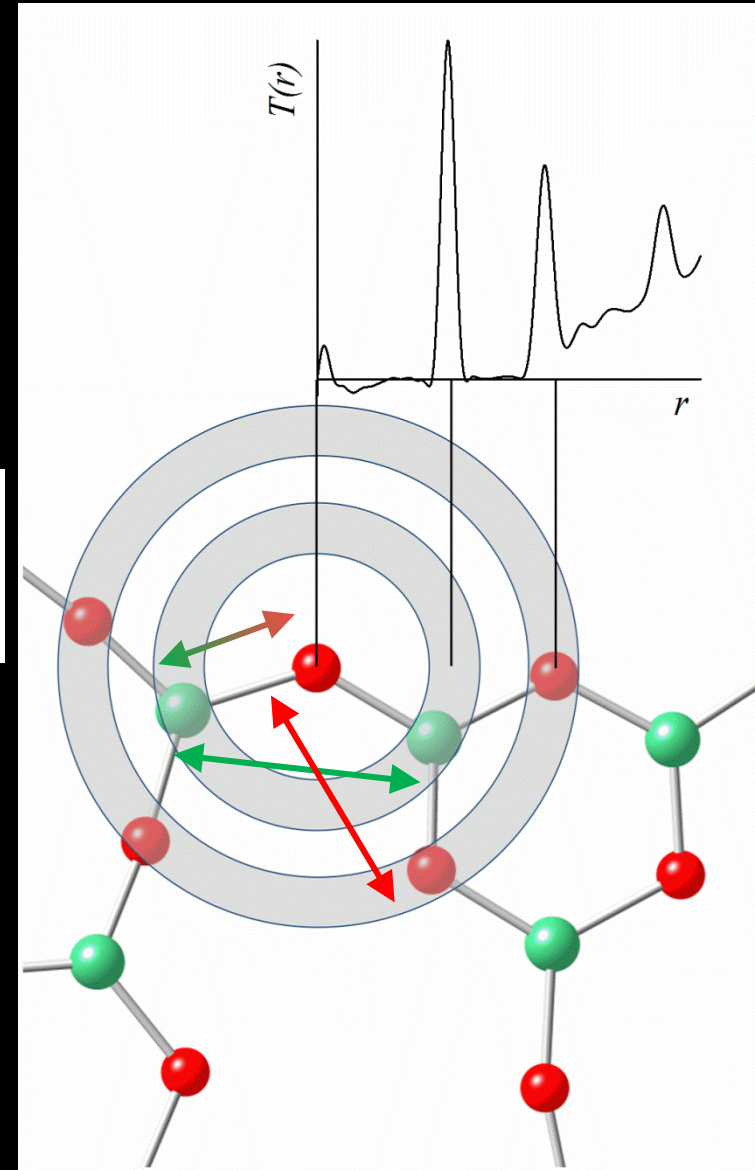Partial correlation function

Polyatomic Samples: Partial Correlation Functions

- Most samples have more than one element…

  …partial correlation functions

$$T^{\mathrm{N}}(r) = \sum_{l,m} c_l \bar{b}_l \bar{b}_m t_{lm}(r)$$

Sum over atom pairs

Atomic fraction,
Scattering length,
Partial correlation function

- For example, B_2O_3 :

  B-B　　　B-O　　　O-O

$$T^{\mathrm{N}}(r) = \tfrac{2}{5}\bar{b}_{\mathrm{B}}^2 t_{\mathrm{BB}}(r) + \tfrac{4}{5}\bar{b}_{\mathrm{B}}\bar{b}_{\mathrm{O}} t_{\mathrm{BO}}(r) + \tfrac{3}{5}\bar{b}_{\mathrm{O}}^2 t_{\mathrm{OO}}(r)$$
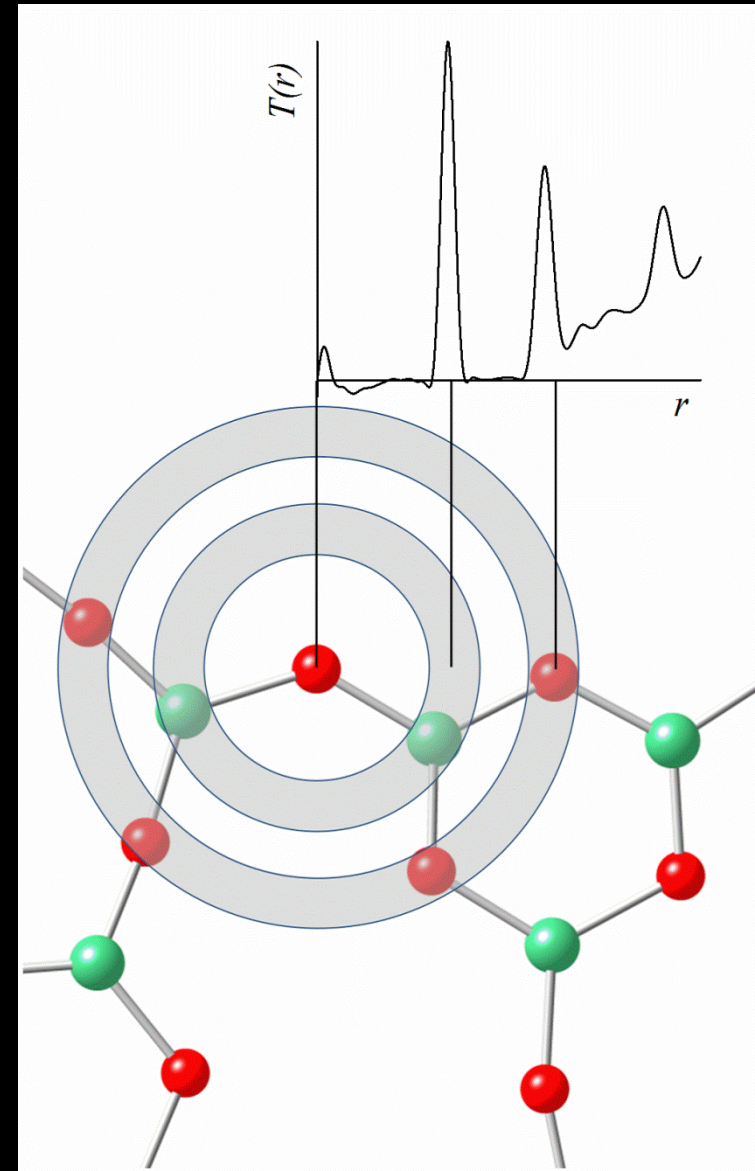
Dependent Partial Correlations

- l-m and m-l functions are not independent
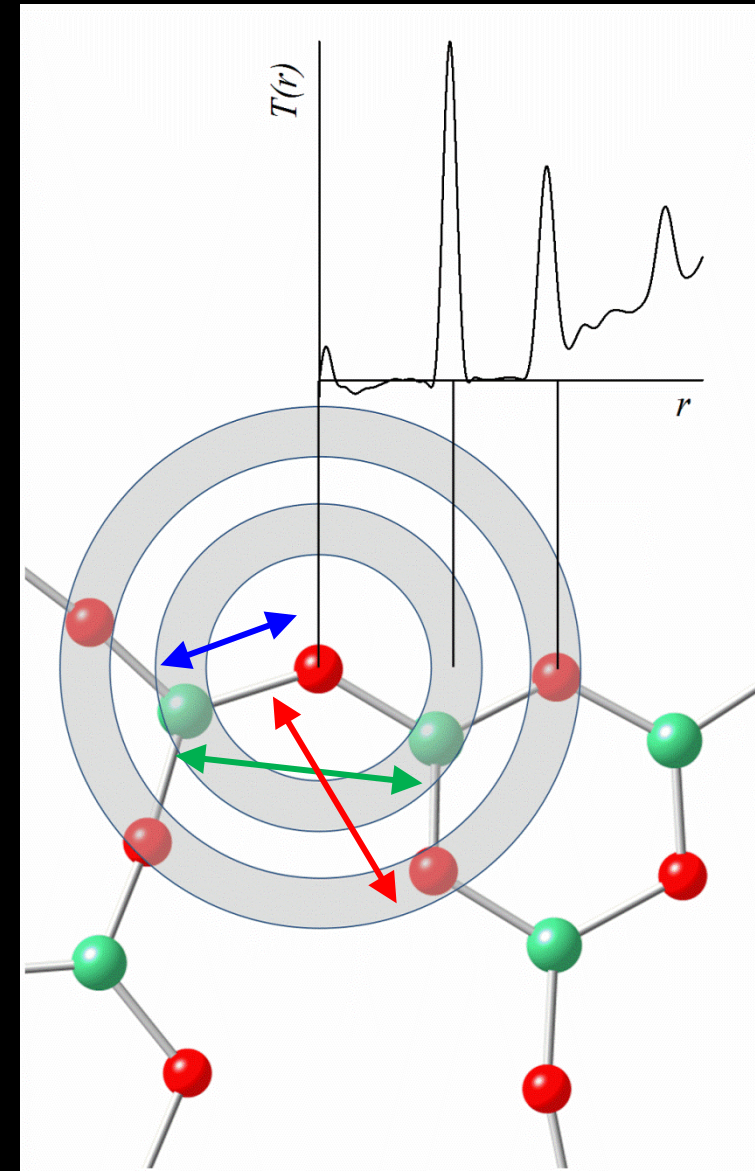
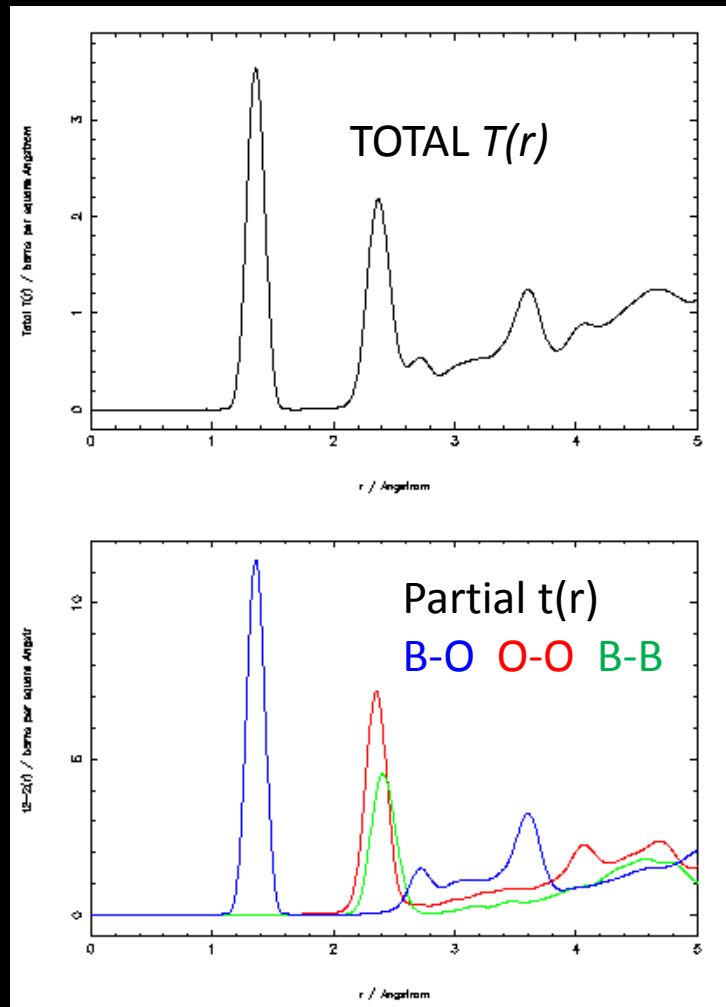$$c_m t_{ml}(r) = c_l t_{lm}(r)$$

  (*unlike atoms, $l \neq m$*)

- For example, in B_2O_3 the number of B-O bonds equals the number of O-B bonds

Partial correlations for B$_2$O$_3$ glass

- Partial correlation functions for model of B$_2$O$_3$ glass

van Hove correlation functions

- A full quantum mechanical theory shows that the pair correlation function is a distinct van Hove correlation function, $g_{lm}(r) = G_{lm}^D(r, 0)$

- This gives the <u>exact interpretation</u> of total diffraction…
  …total diffraction is an instantaneous "snapshot" of the interatomic distances

$$G_{lm}^D(\boldsymbol{r}, t) = \sum_{\substack{j=1,k=1 \\ j \neq k}}^{N_l, N_m} \langle \int \delta\left(\boldsymbol{r}' - \boldsymbol{R}_j(0)\right) \delta\left(\boldsymbol{r}' + \boldsymbol{r} - \boldsymbol{R}_k(t)\right) \rangle \, d\boldsymbol{r}'$$

Van Hove correlation function

Key points

1. Total diffraction depends on distances between atoms.

2. Correlation functions are measured by Fourier transform of diffraction data, from reciprocal-space to real-space.

Thanks for listening!
Any questions?