Direct analysis of PDF data: Atomic pair correlations, coordination numbers, bond angles…

Practical aspects, Reality

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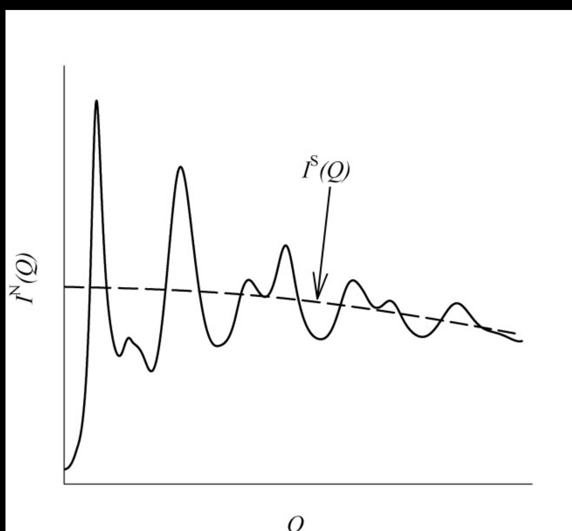
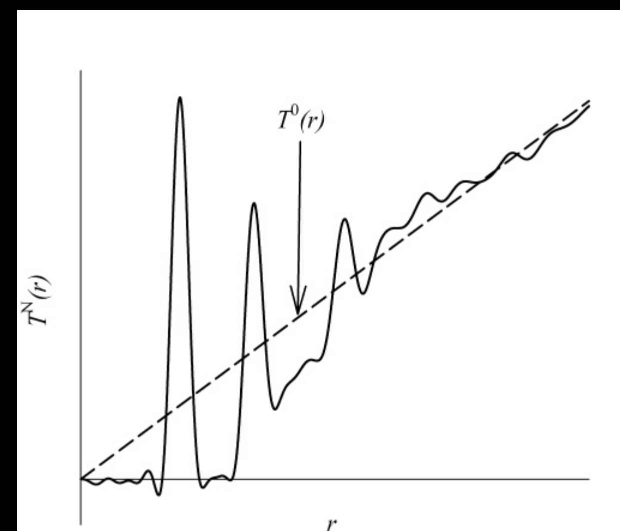
The Fourier Transform

- 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"

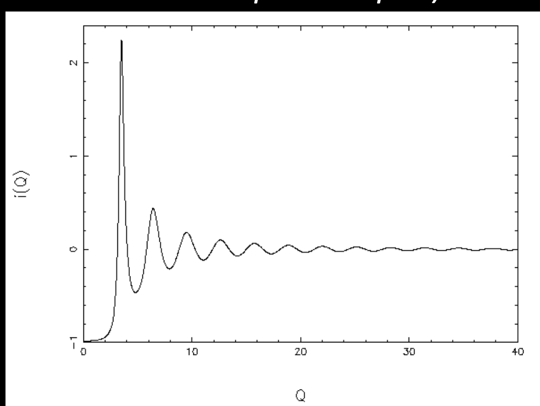
(B_2O_3 glass)

PDF "pair distribution function"

Calculation of the Fourier transform

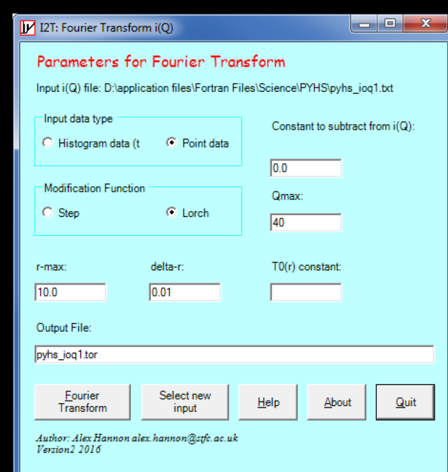
- The Fourier transform can be calculated by software, using numerical integration (Filon's quadrature), or a fast Fourier transform
- A simple standalone Fourier transform program I2T is available here http://alexhannon.co.uk

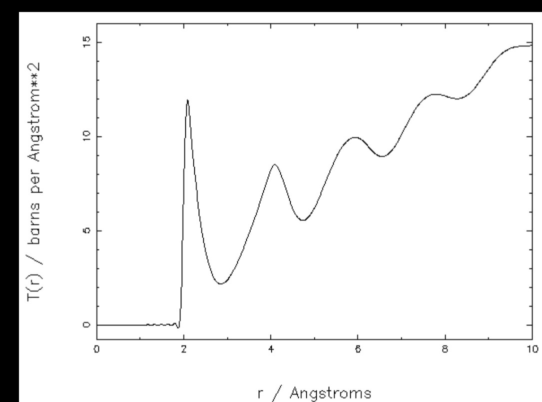
(Percus-Yevick hard sphere liquid)



Diffraction pattern $i(Q)$
Reciprocal-space

Fourier transform





Correlation function $T(r)$
Real-space

Q-range

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

- In theory the Fourier transform requires data with Q-values from zero to ∞ → impossible!
- Experimental data cover a limited range from Q_{min} to Q_{max}
- Typical values for the GEM diffractometer:
  Q_{min} = 0.58 Å^{-1} Q_{max} = 40 Å^{-1}

Q-range

Limits: 0, ∞

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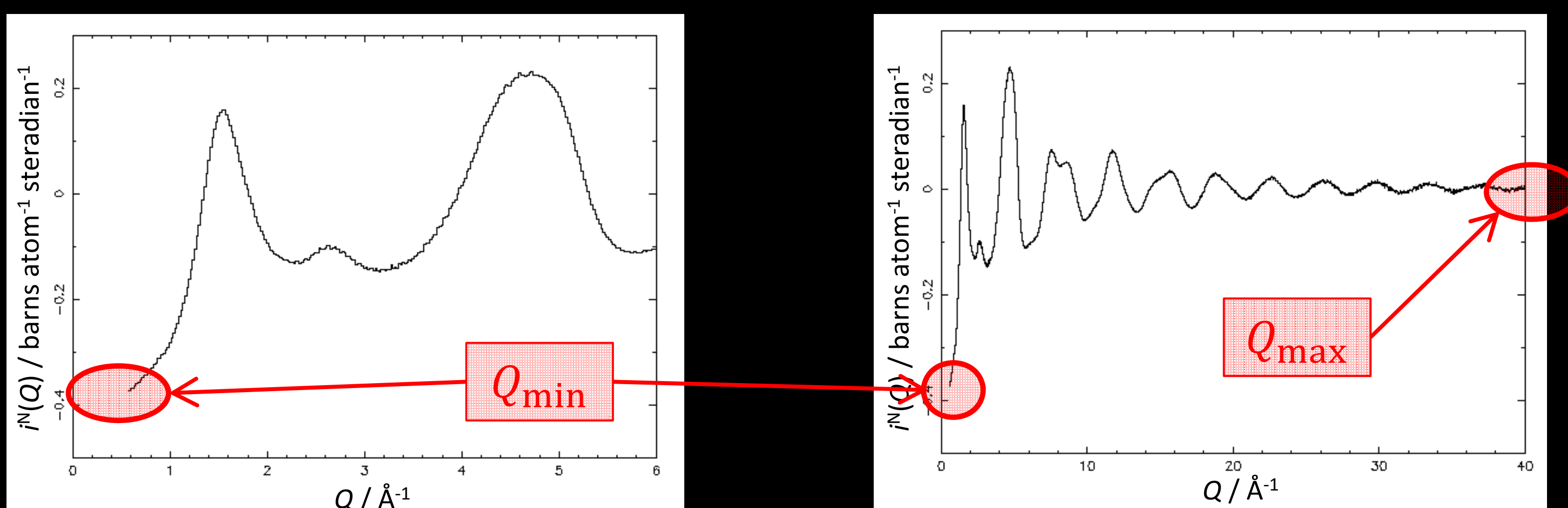
(GeO$_2$ glass)

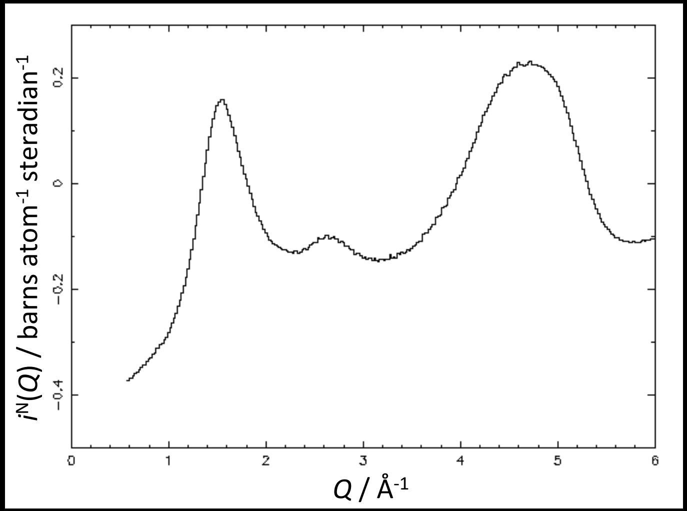


Low Q extrapolation

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

- Missing data in the Q-range 0 to Q_{min} can be estimated by extrapolation
- Use a constant, or better to fit $A + BQ^2$ ($i^{\mathrm{N}}(Q)$ is a symmetric function)
- A small effect, because integrand is $Qi^{\mathrm{N}}(Q)$ (multiply by Q)

(GeO_2 glass)



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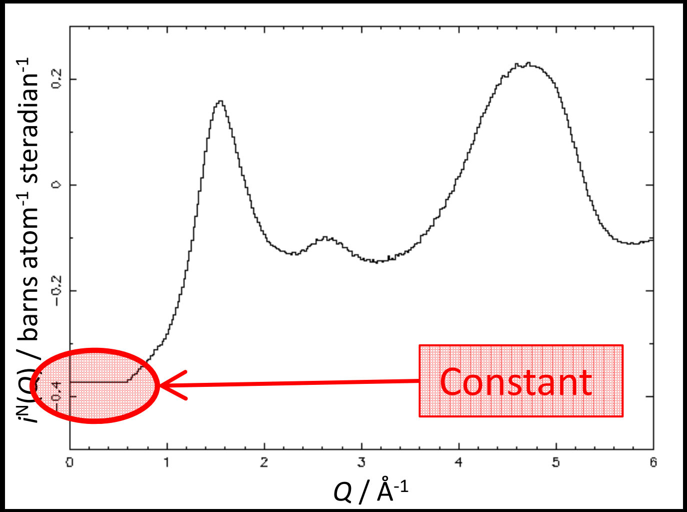

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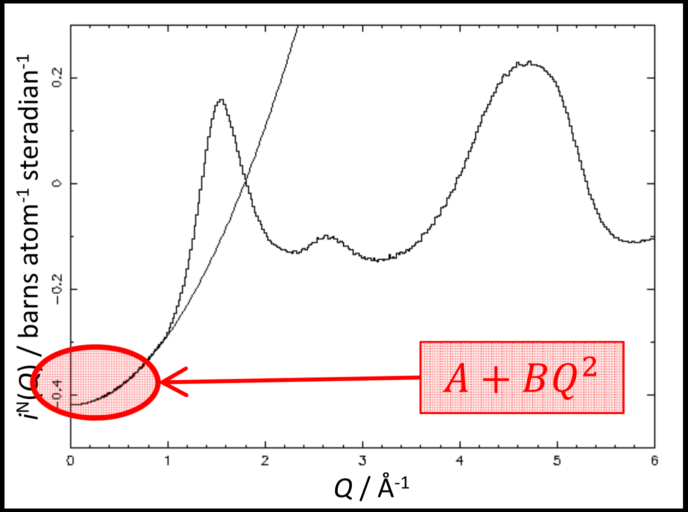

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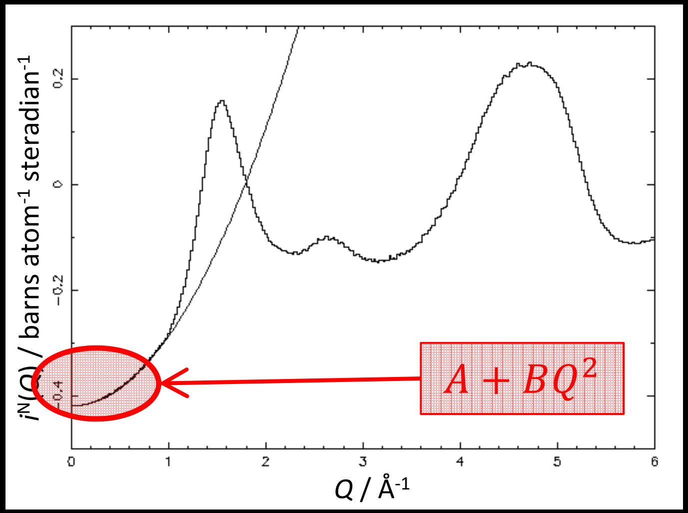

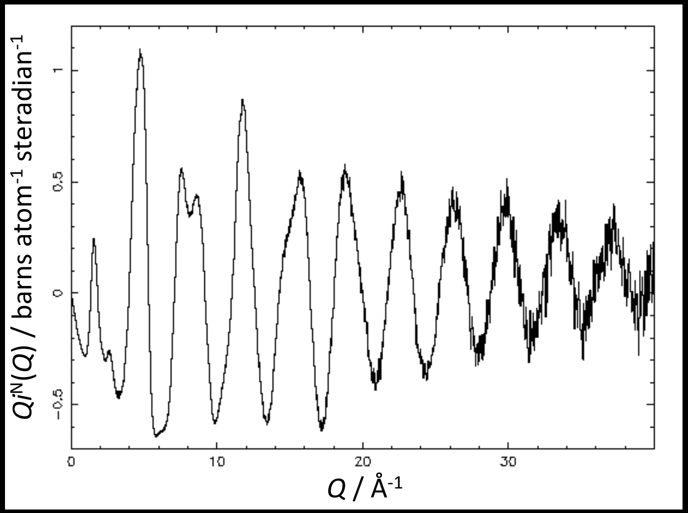

Termination at $Q_{\max}$

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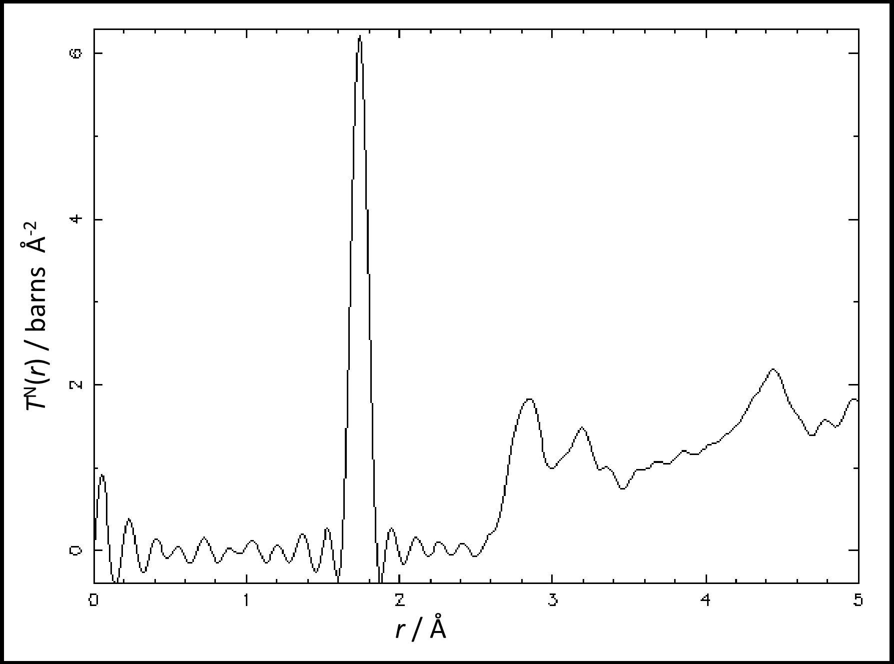

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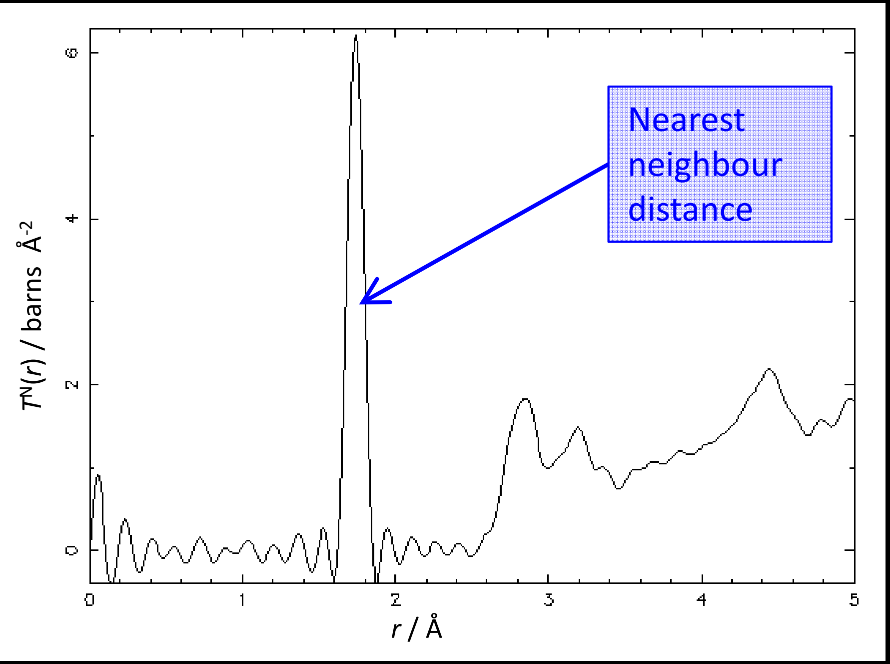
r_{GeO} = 1.7369(2) Å in GeO_2 glass

(Hannon et al, J Phys Chem B 2007)



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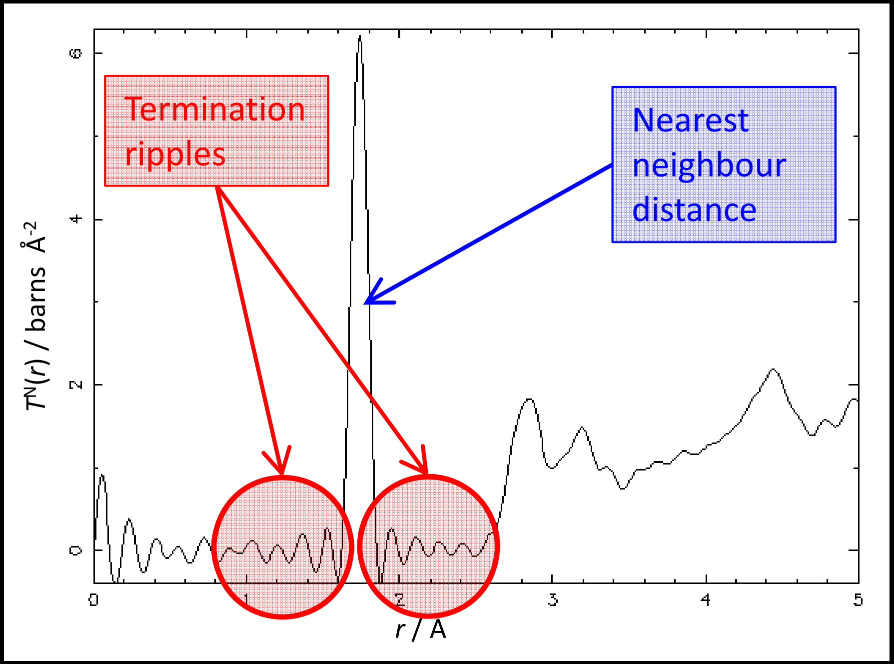

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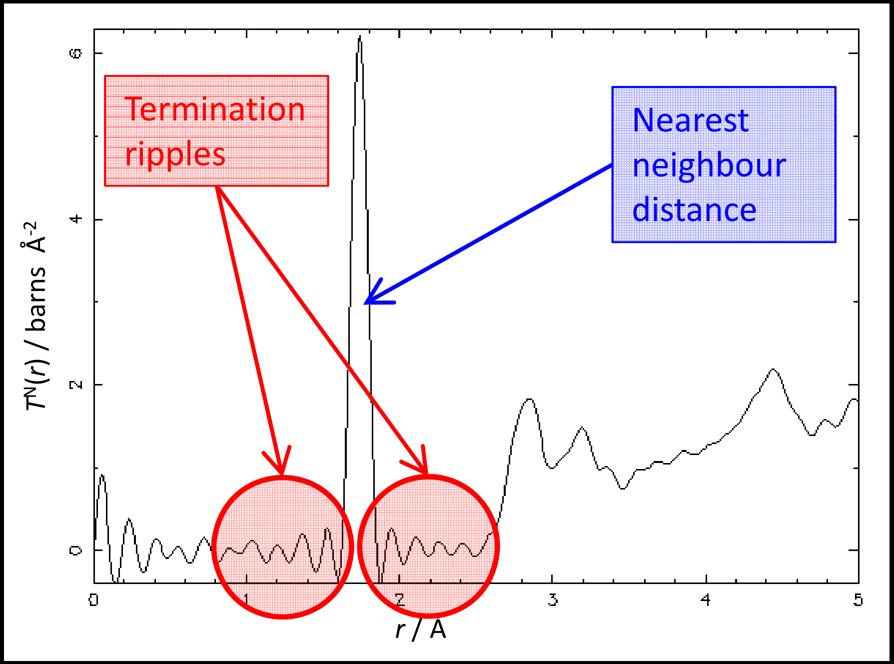


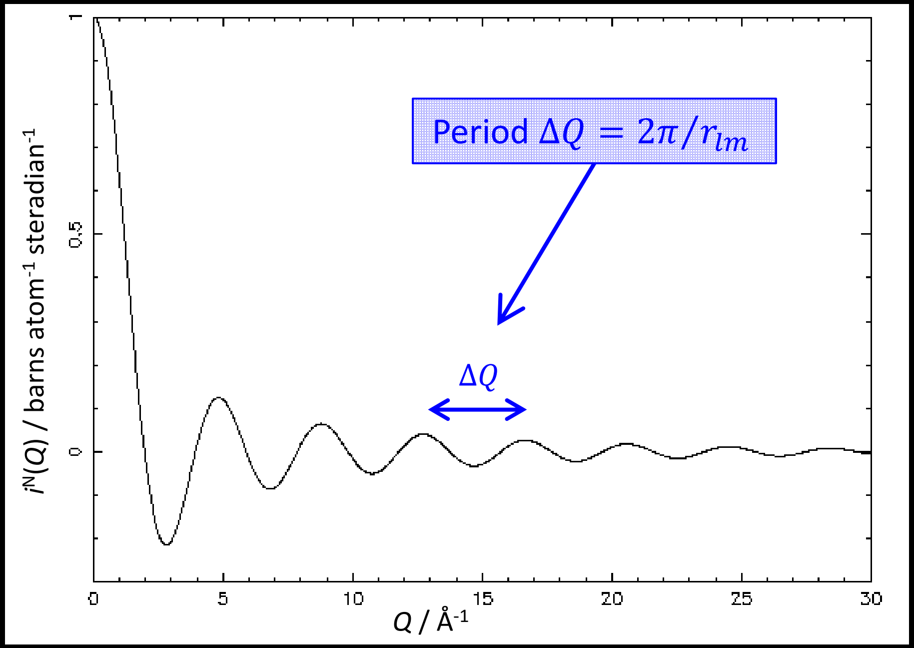
(GeO_2 glass)

Why are there termination ripples?

One distance

$$i_{lm}(Q) = n_{lm}\bar{b}_l\bar{b}_m \frac{\sin Qr_{lm}}{Qr_{lm}} \exp\left(-\frac{\langle u_{lm}^2\rangle Q^2}{2}\right)$$

- One interatomic distance r_{lm} gives damped sine wave contribution to $Qi^{\mathrm{N}}(Q)$
- Damping comes from the Debye-Waller factor
- $\langle u_{lm}^2\rangle$ is variance in distance r_{lm}



(*simulation*)

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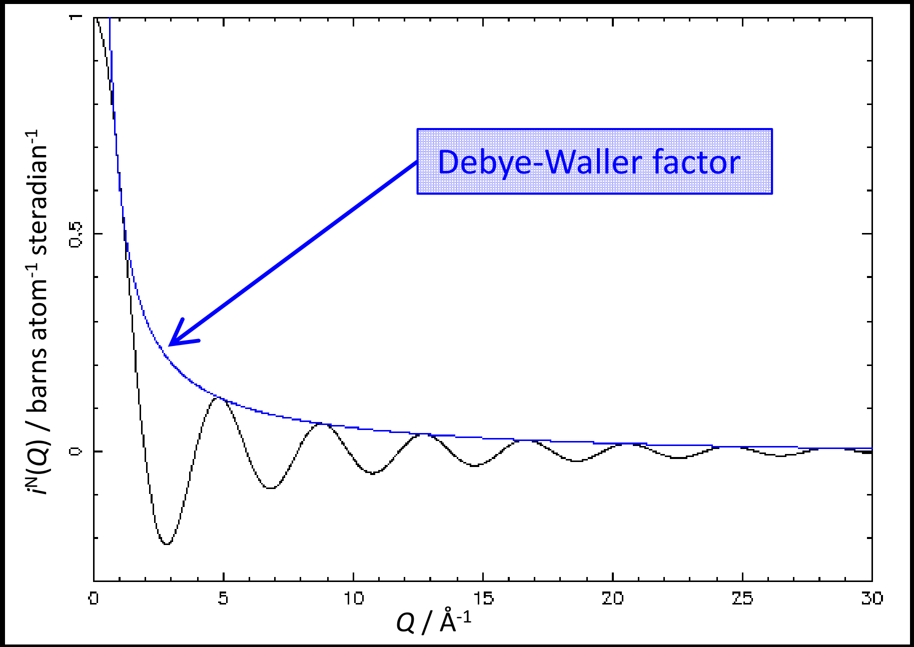

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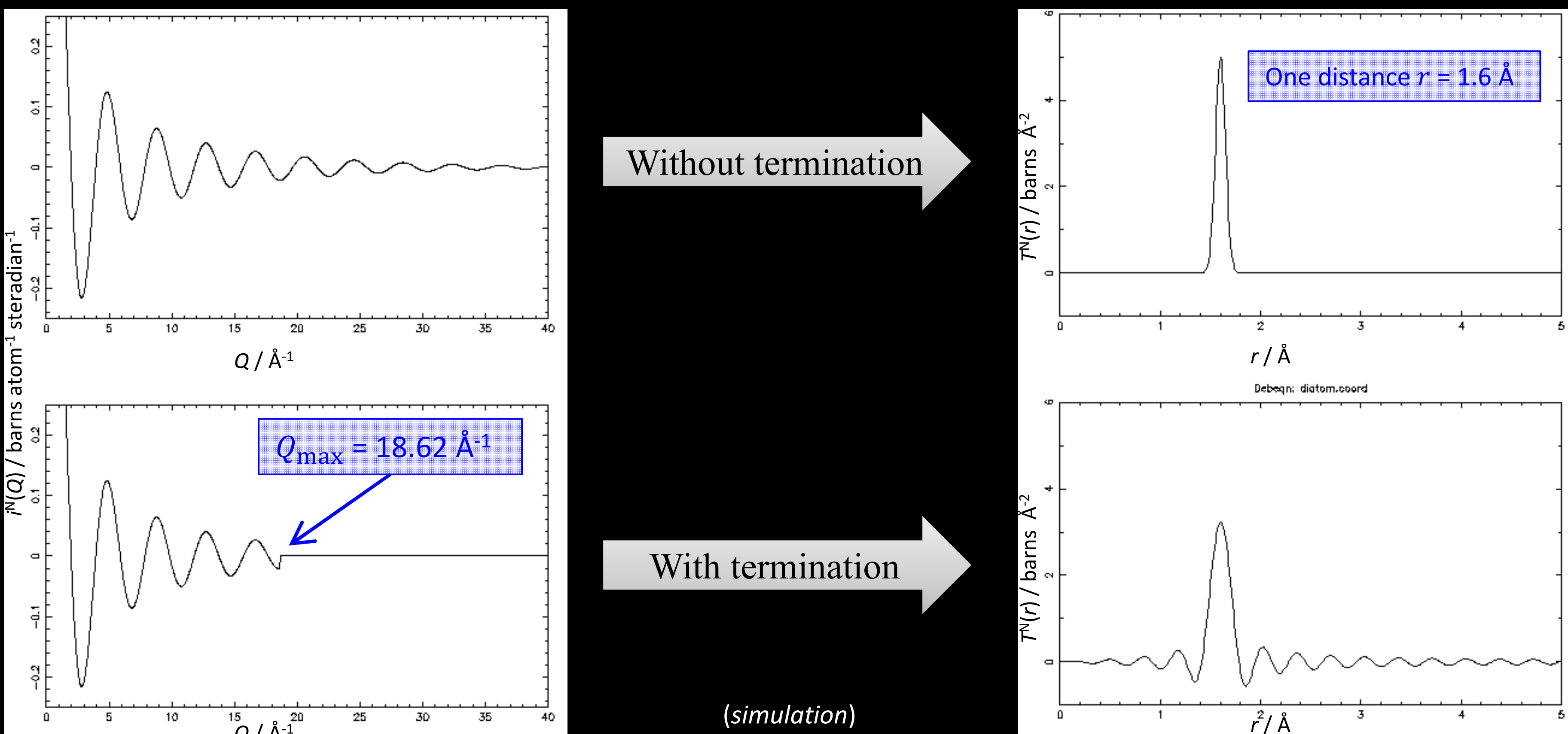
Why termination ripples?

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

- Without truncation: $T^{\mathrm{N}}(r)$ peak is narrow Gaussian
- With truncation: $T^{\mathrm{N}}(r)$ peak is broadened and there are <u>termination ripples</u>



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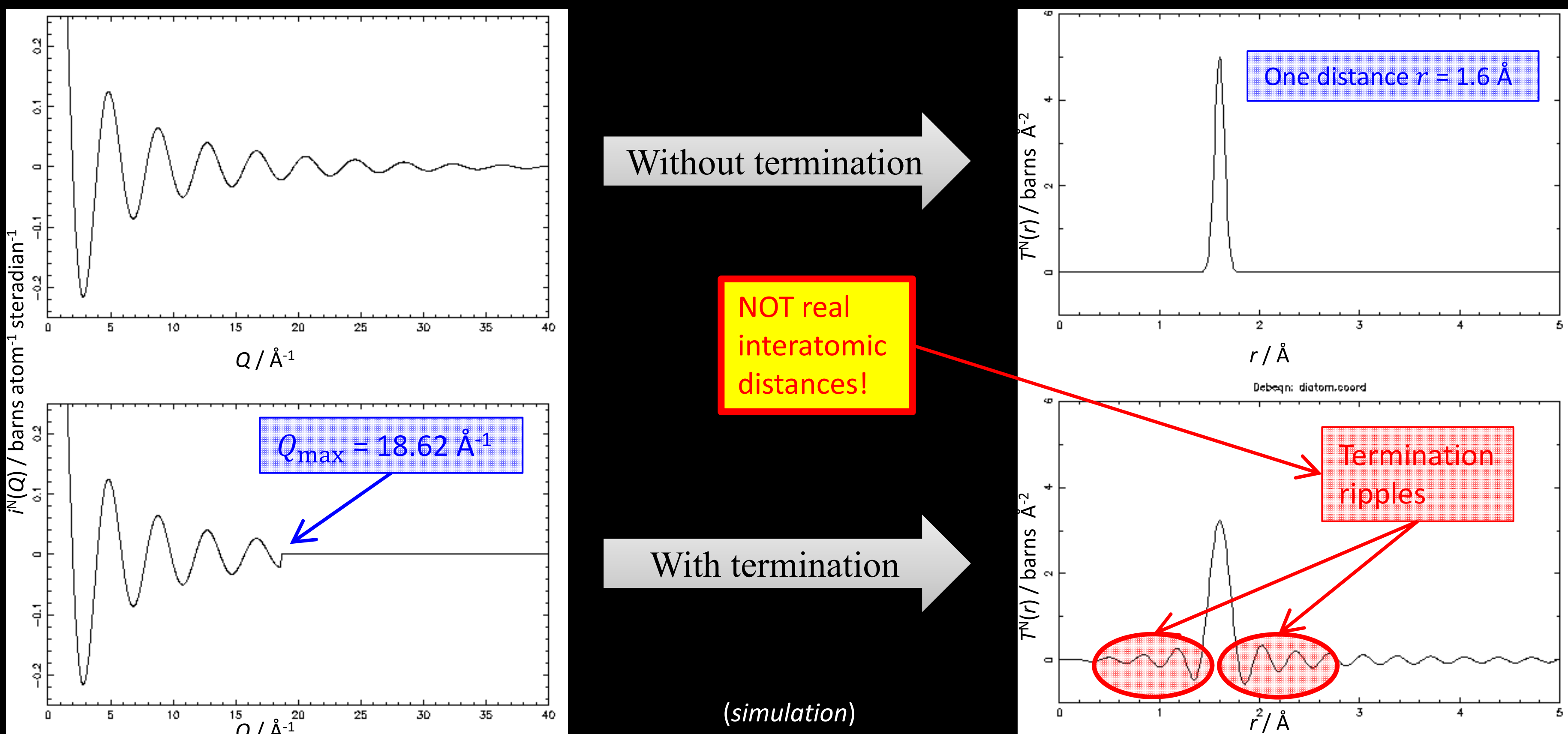

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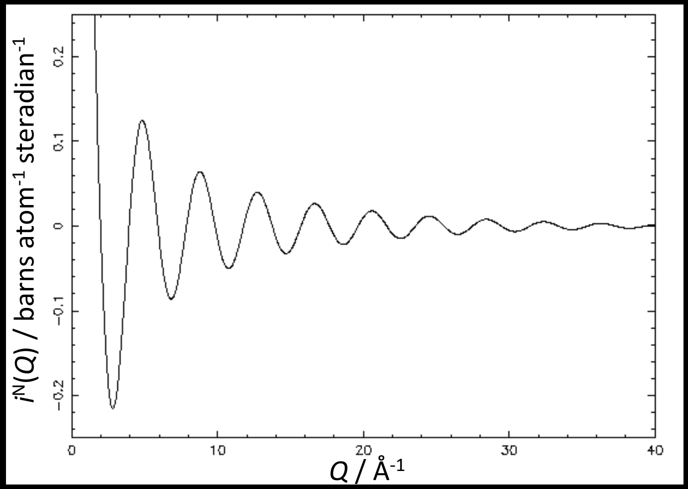
- Termination of $i^{\mathrm{N}}(Q)$ at $Q_{\max}$ is … the same as multiplication by a step function $M_{\mathrm{step}}(Q)$
- The sharp cutoff at $Q_{\max}$ causes termination ripples …and broadens $T^{\mathrm{N}}(r)$ with width $\Delta r_{\mathrm{step}} = 3.791/Q_{\max}$ (FWHM)
- Real-space resolution function is $\sin(Q_{\max}r)/(Q_{\max}r)$



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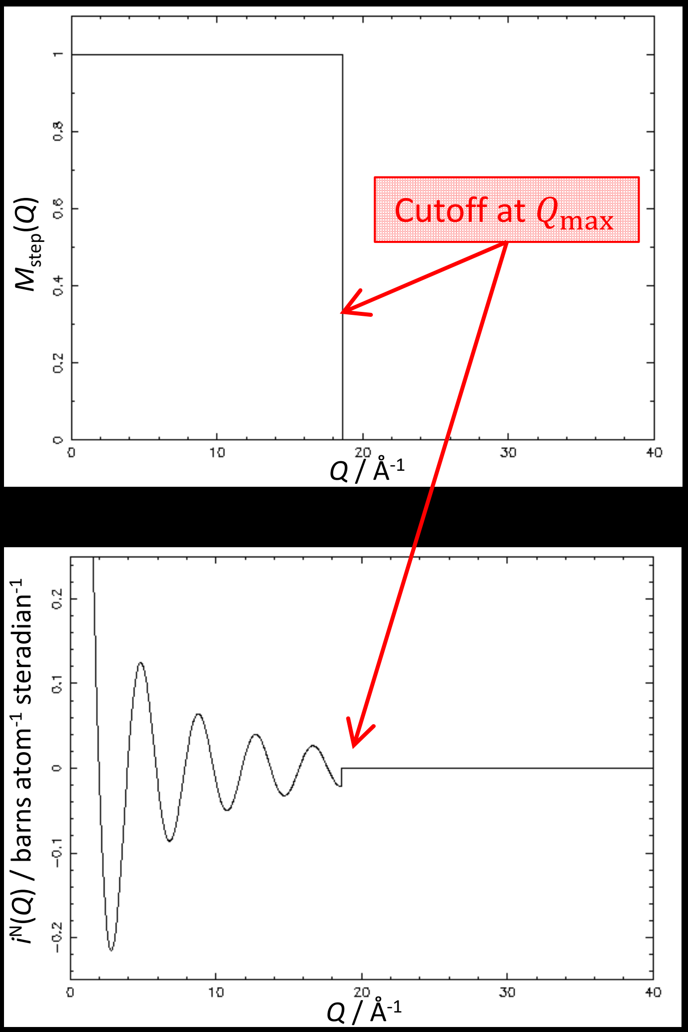
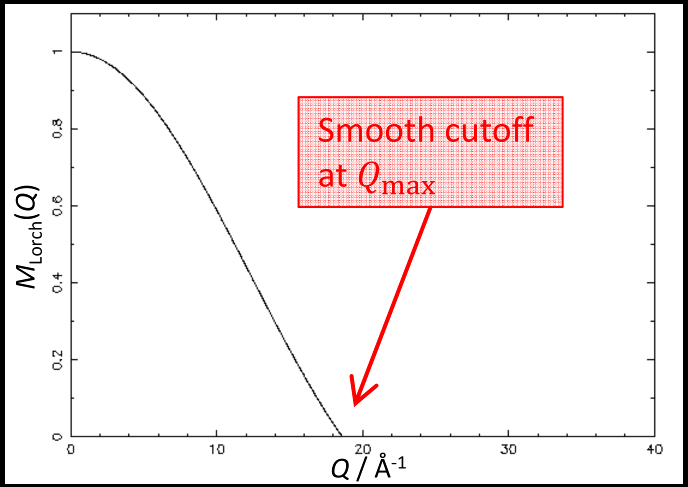


(simulation)

Modification function

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

- The step function has a sharp cutoff
- Instead multiply $i^{\mathrm{N}}(Q)$ by modification function with a smooth cutoff – then termination ripples are a lot smaller
- Most popular $M(Q)$ is the Lorch function



(*simulation*)

$$M_{\mathrm{Lorch}}(Q) = \frac{\sin(\Delta r Q)}{\Delta r Q} \quad Q \le Q_{\max}$$

$$M_{\mathrm{Lorch}}(Q) = 0 \quad Q > Q_{\max}$$

$$\Delta r = \pi / Q_{\max}$$

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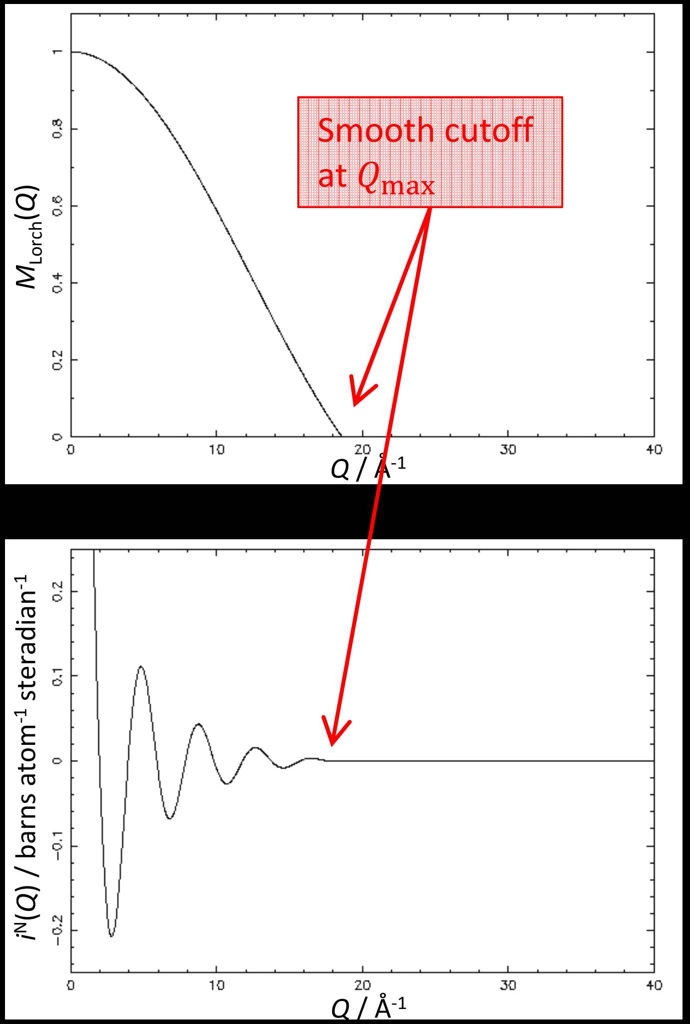

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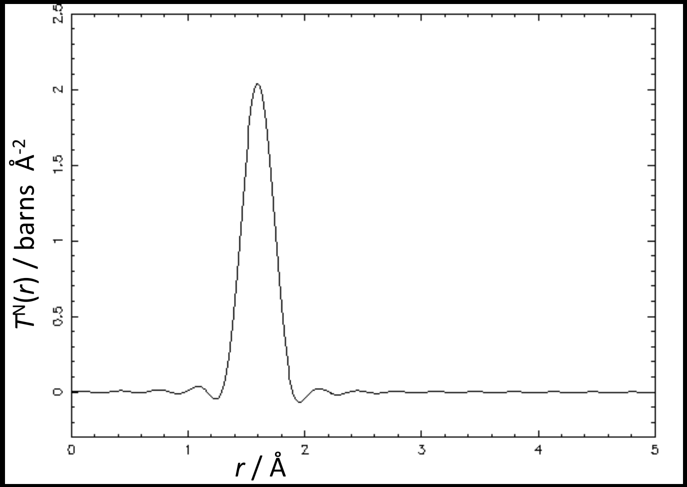
- With the Lorch function: termination ripples are a lot smaller

- Real-space resolution function is complicated

- $T^{\mathrm{N}}(r)$ is broadened more with width $\Delta r_{\mathrm{Lorch}} = 5.437/Q_{\max}$ (FWHM)



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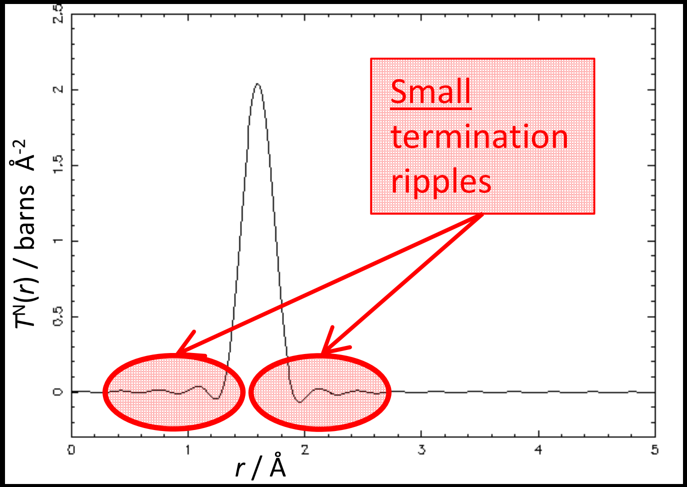

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Modification functions

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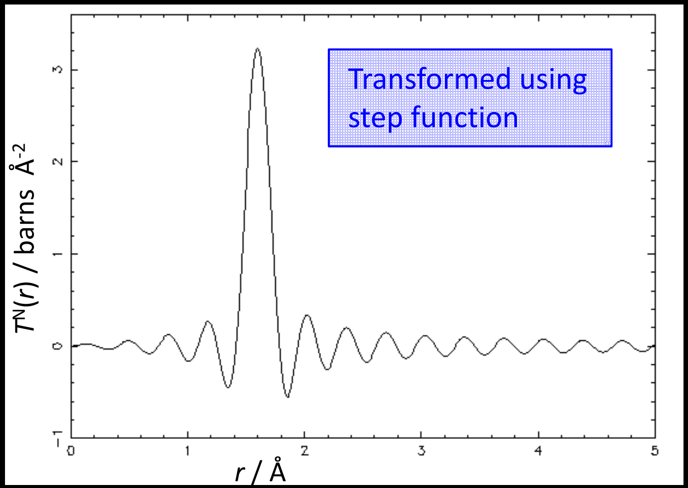

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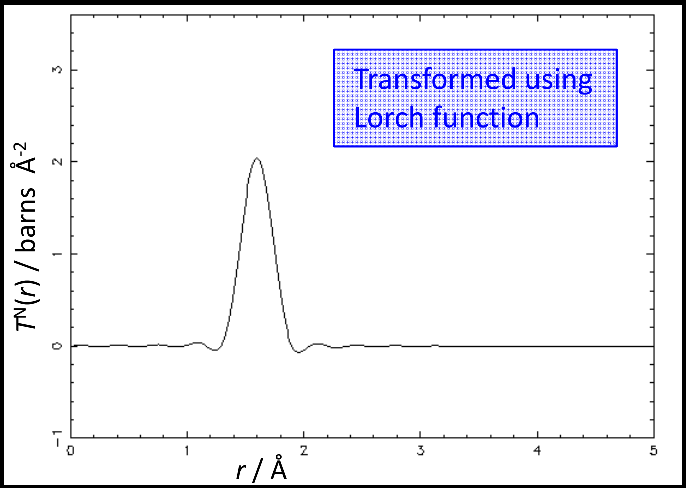


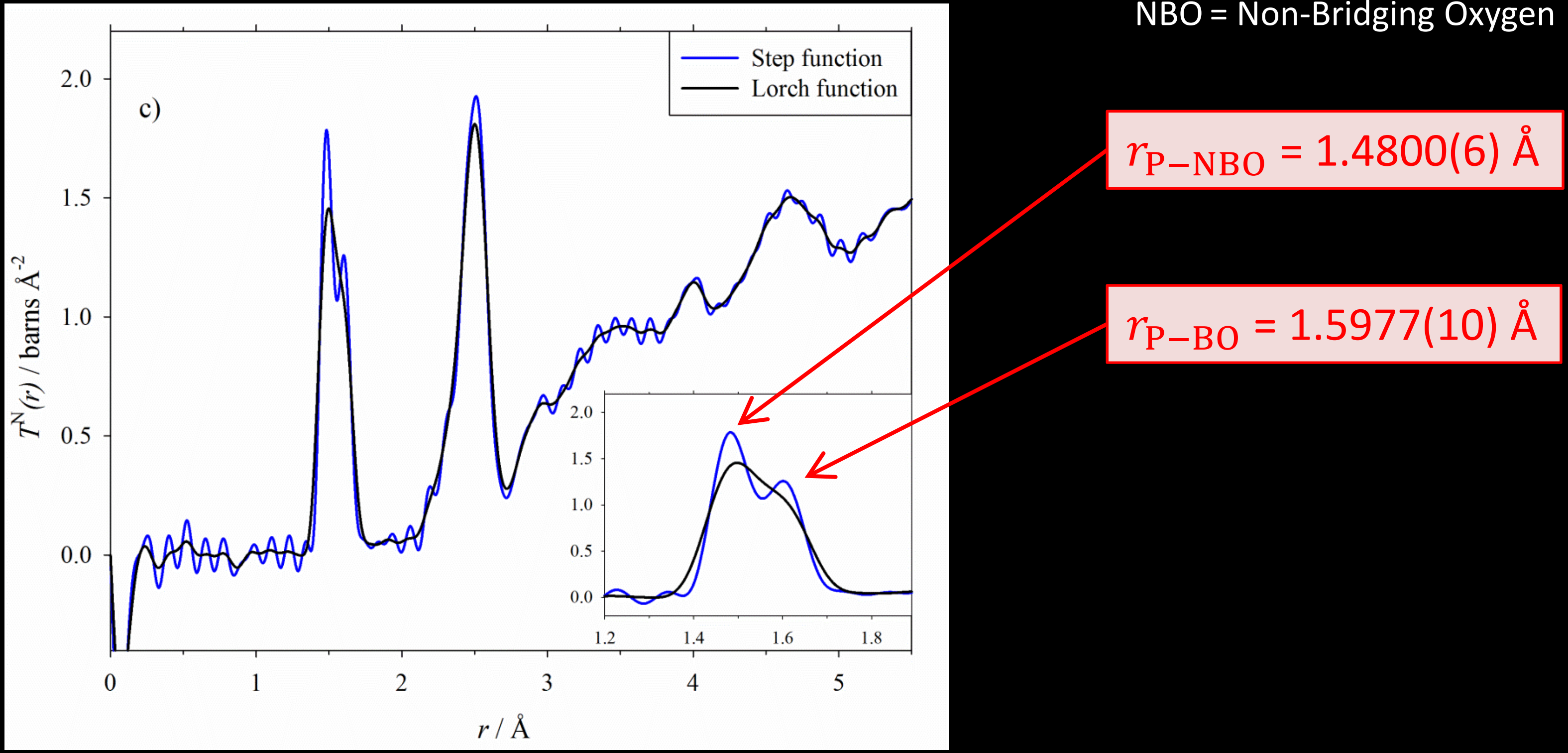
Function	Step	Lorch
Termination ripples	large	small
Peak shape	simple $\sin x/x$	complicated
Real-space resolution	narrower $\Delta r = 3.791/Q_{\max}$	broader $\Delta r = 5.437/Q_{\max}$

- Step function is better if resolution is most important
- Lorch function is better if clear determination of distance distribution is most important

Phosphate Glasses

- Phosphate glasses:
  2 different P-O bond lengths, P-NBO and P-BO
- Only high Q_{max} (55 Å^{-1}) and <u>step</u> modification function can resolve the bond lengths

BO = Bridging Oxygen
NBO = Non-Bridging Oxygen

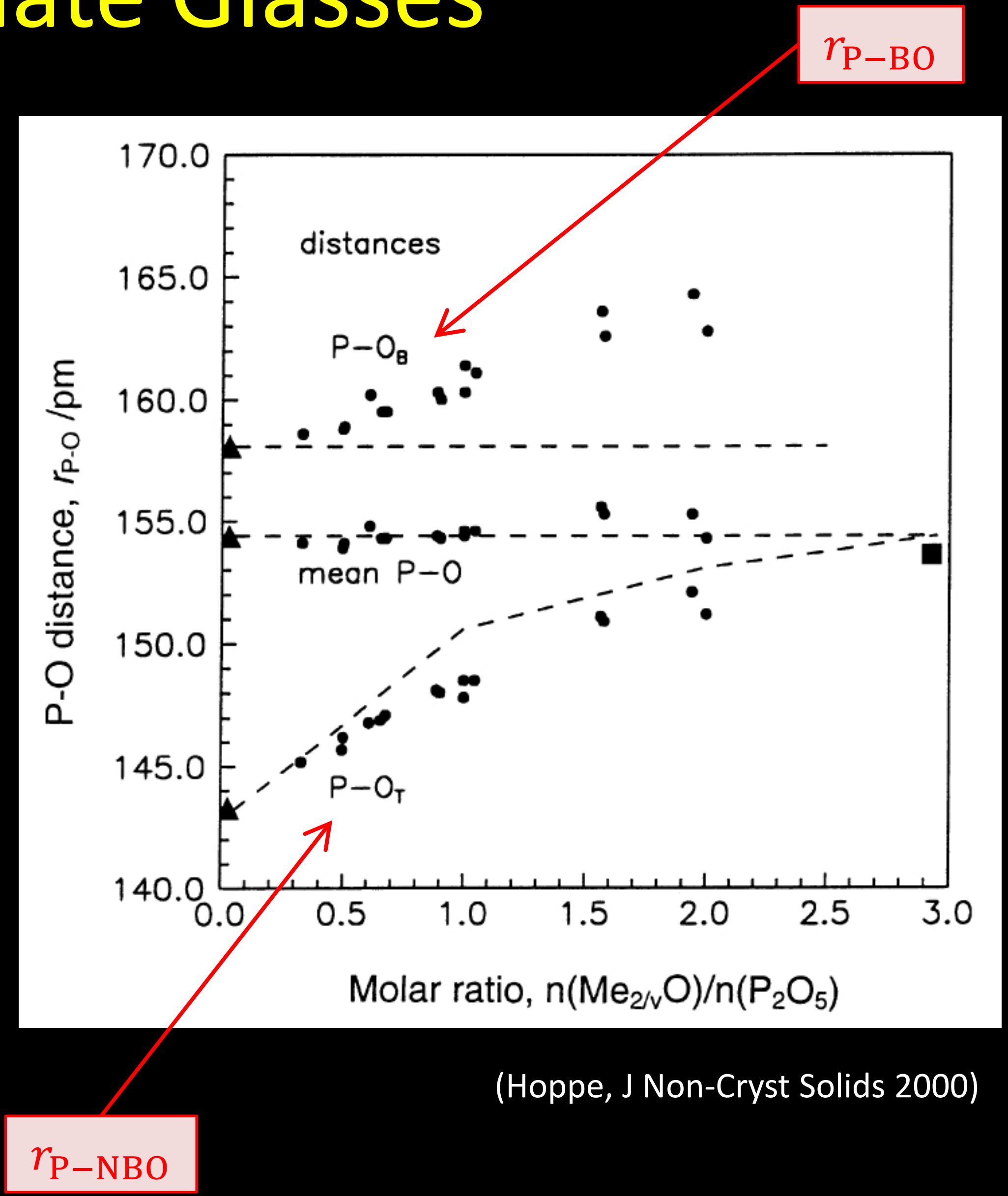


(2CaO·Na_2O·3P_2O_5 glass) (Hannon, Nucl Inst Meth A 2005)

Phosphate Glasses

- Only pulsed neutron diffraction can resolve the 2 different P-O bond lengths,
  P-NBO and P-BO

- Important for understanding structural behaviour



(Hoppe, J Non-Cryst Solids 2000)

BO = Bridging Oxygen
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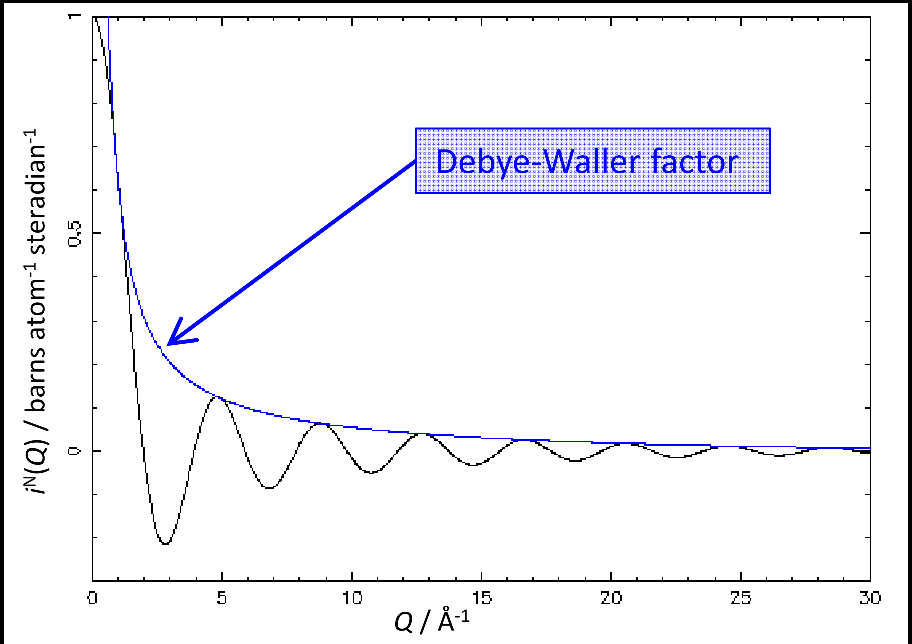
Real-space resolution

$\Delta r_{\text{step}} = 3.791/Q_{\max}$

- Narrow real-space resolution requires high $Q_{\max}$
- High $Q_{\max}$ requires high energy $(Q = 2k \sin\theta)$
- Only pulsed accelerator neutron sources (ISIS, China-SNS) have high energy 1 – 10 eV
- Achievable $Q_{\max}$ is limited by…
  - Debye-Waller factor



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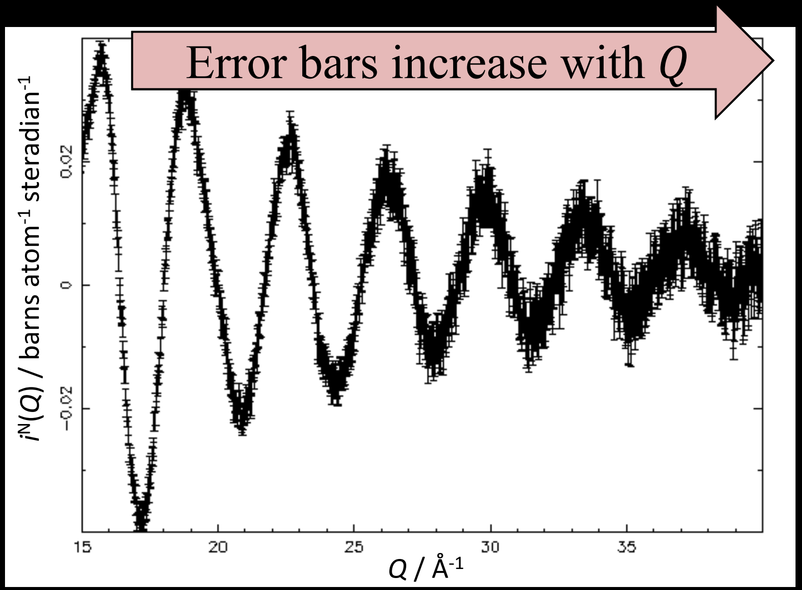

(*GeO_2 glass*)

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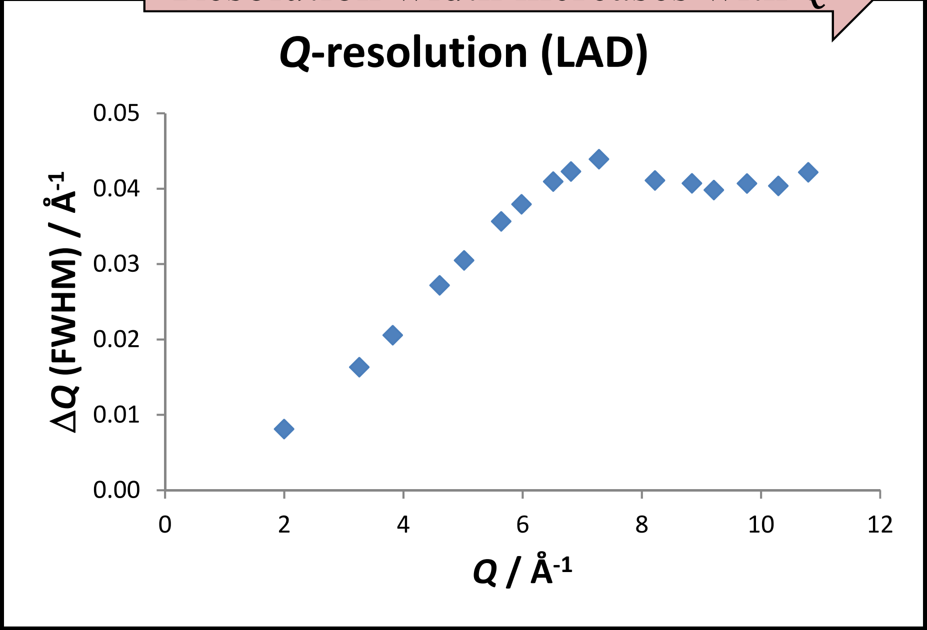
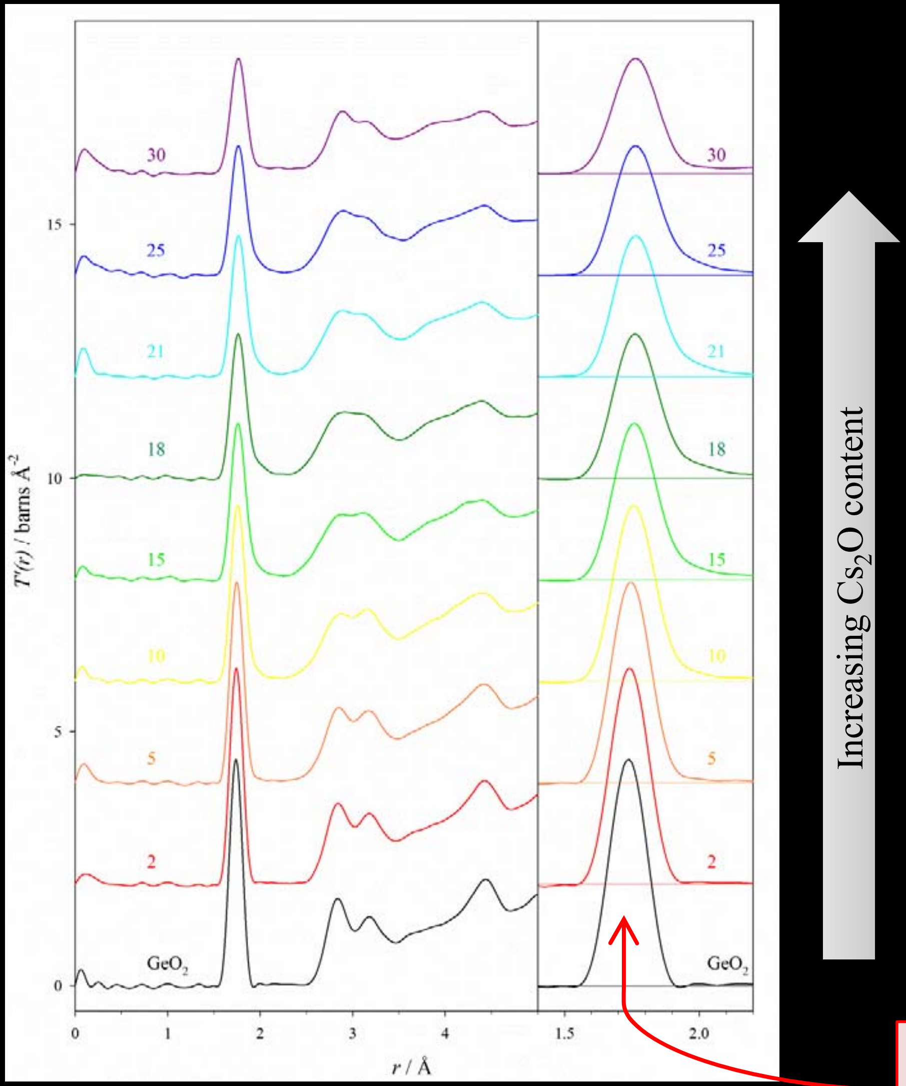
  - Debye-Waller factor
  - Neutron flux
  - Q-resolution

Resolution width increases with Q



Germanate Glasses

(Cs_2O-GeO_2 glasses)



(Hannon et al, J Phys Chem B 2007)

- Germanate glasses have a distribution of Ge-O bond lengths
- Use the Lorch function to observe the distribution clearly
- As Cs_2O is added, longer Ge-O bonds form, but then decline for high Cs_2O content

Ge-O peak moves to longer distance and a high-*r* shoulder develops

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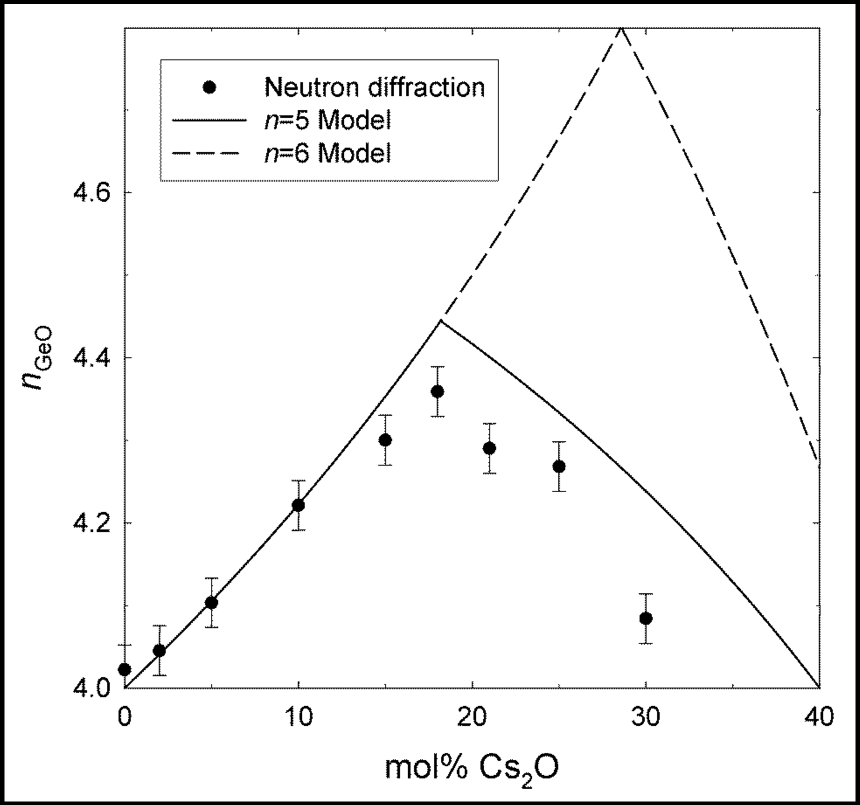
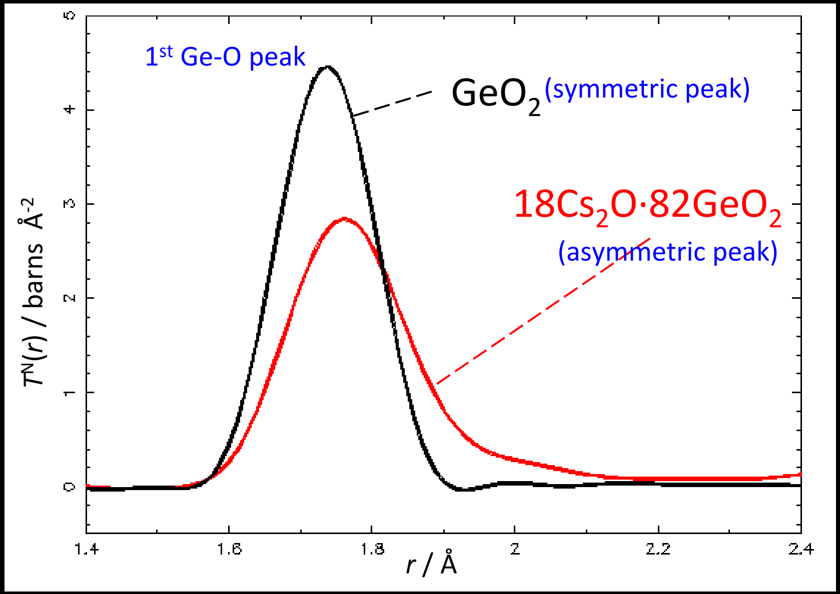


- Ge-O coordination number is obtained from the 1st Ge-O peak
- Pure GeO_2 is formed from GeO_4 tetrahedra
- As Cs_2O is added, GeO_5 units form, then decline

(Hannon et al, J Phys Chem B 2007)

Broadening of a $T^{\mathrm{N}}(r)$ peak

- A $T^{\mathrm{N}}(r)$ peak is broadened due to 3 factors:
  1. Real-space resolution (because Q_{max} is not ∞)
  2. Thermal motion of atoms (a Gaussian distribution)
  3. Static distribution of interatomic distances

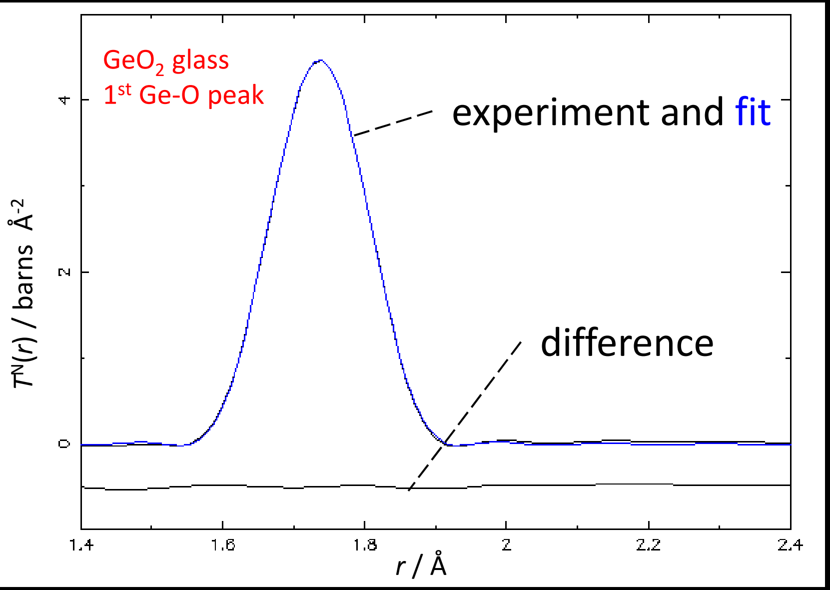


- If a $T^{\mathrm{N}}(r)$ peak is symmetric it can be fitted with a resolution-broadened Gaussian
- If a $T^{\mathrm{N}}(r)$ peak is not symmetric…
  – it can be fitted with multiple peaks
  – it can be integrated

Peak fitting

$$n_{lm} = \frac{r_{lm} A_{lm}}{(2 - \delta_{lm}) c_l \bar{b}_l \bar{b}_m}$$

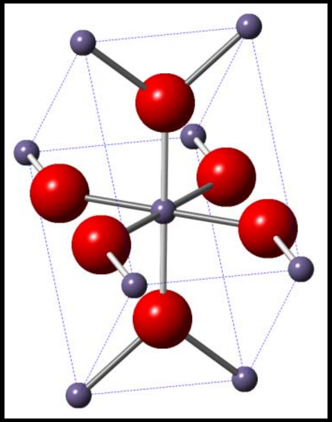
- The fit gives…
  - Accurate bond length $r_{\mathrm{GeO}} = 1.7369(2)$ Å
  - Distribution of bond lengths $\langle u_{\mathrm{GeO}}^2 \rangle^{½} = 0.0422(3)$ Å
  - Area A_{GeO} gives Ge-O coordination number…



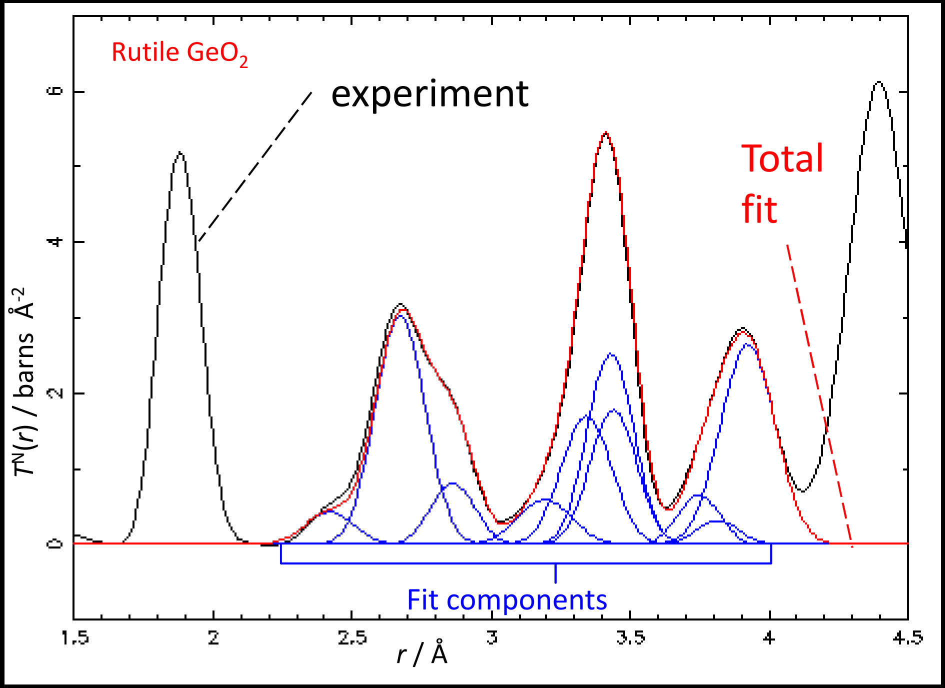
$$n_{\mathrm{GeO}} = \frac{r_{\mathrm{GeO}} A_{\mathrm{GeO}}}{2 c_{\mathrm{Ge}} \bar{b}_{\mathrm{Ge}} \bar{b}_{\mathrm{O}}} = 4.032(8)$$

Ideally we expect coordination number $n_{\mathrm{GeO}} = 4$ for a perfect network of GeO_4 tetrahedra

Peak fitting



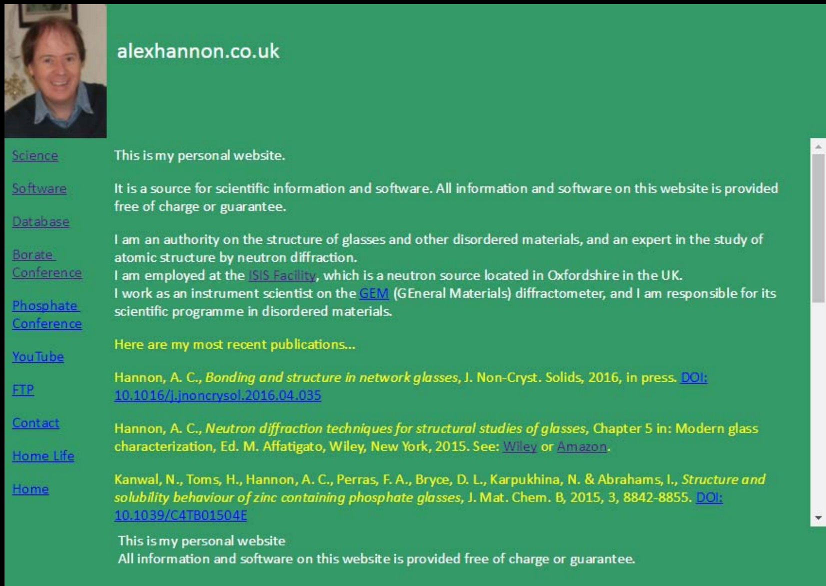
- GeO_2 glass is simple example, fitting one peak
- But many peaks can be fitted in the same way – example is rutile GeO_2



- For a glass, coordination numbers are not already known
- If a crystal structure is ordered then coordination numbers are already known, and are fixed in fitting

Software

- The Windows software used to make the plots in this presentation is available free at http://alexhannon.co.uk
- This includes fitting software *pfit* for fitting $T^{\mathrm{N}}(r)$

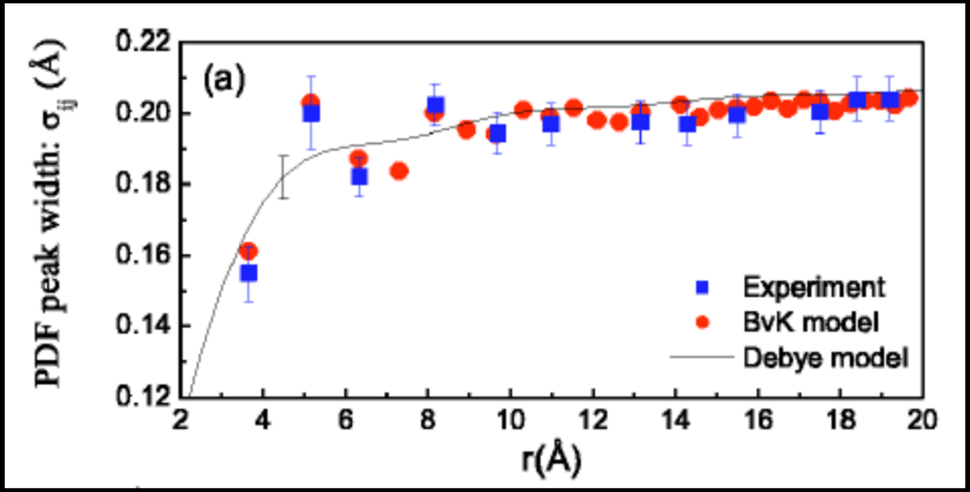


Correlated motion

- For $T^{\mathrm{N}}(r)$ thermal motion broadens each peak according to the variance $\langle u_{lm}^2 \rangle$ in the distance between atoms r_{lm}
- Crystallography is fundamentally different – it treats atoms as independent oscillators, with no dependence on distance between atoms

Correlated motion

- For $T^{\mathrm{N}}(r)$ thermal motion broadens each peak according to the variance $\langle u_{lm}^2 \rangle$ in the distance between atoms r_{lm}
- Correlations between motions of atoms cause $\langle u_{lm}^2 \rangle$ to be smaller for short distances, especially if atoms are bonded



(Jeong et al, Phys Rev B 2003)

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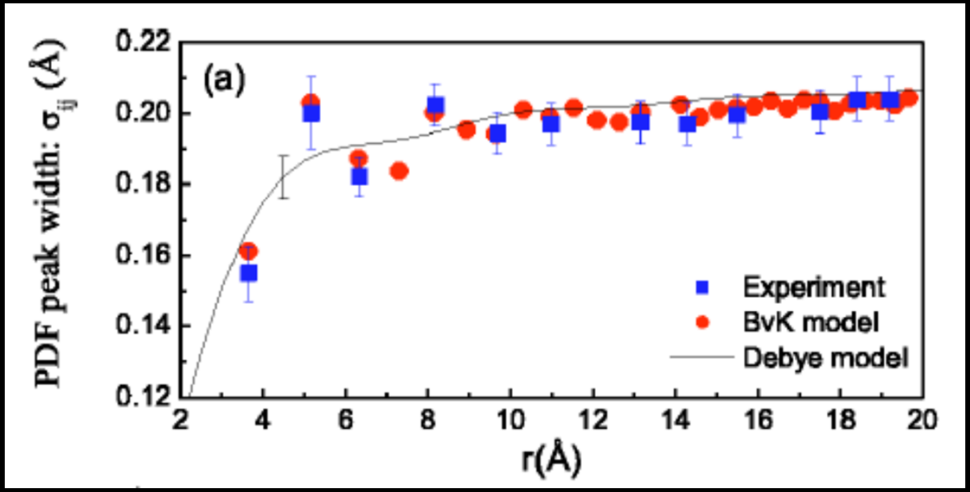


(Jeong et al, Phys Rev B 2003)

- A simple model for this behaviour is

$$\langle u^2 \rangle^{½} = \sqrt{\langle u^2 \rangle_0 - \frac{\delta_2}{r^2}}$$

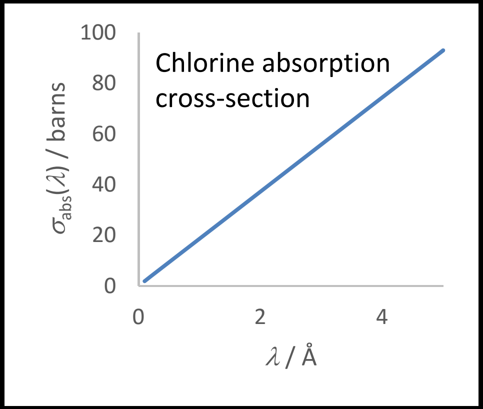
The error peak

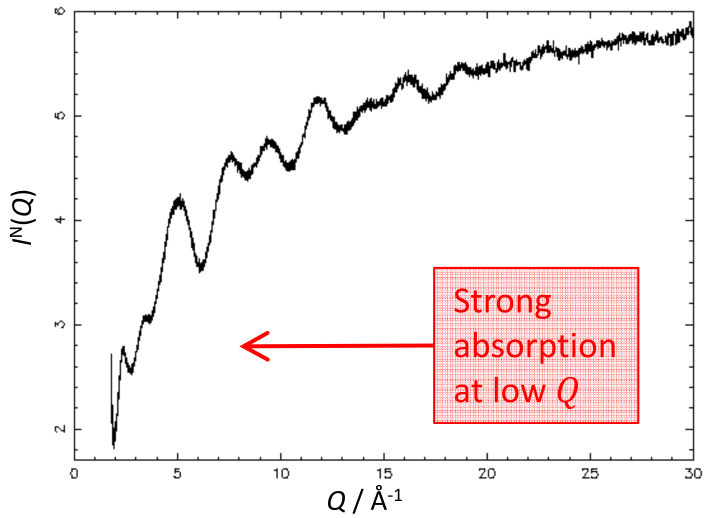
$$T^{\mathrm{N}}(r) = T^{0}(r) + \frac{2}{\pi}\int_{0}^{\infty} M(Q)Qi^{N}(Q)\sin rQ\, dQ$$

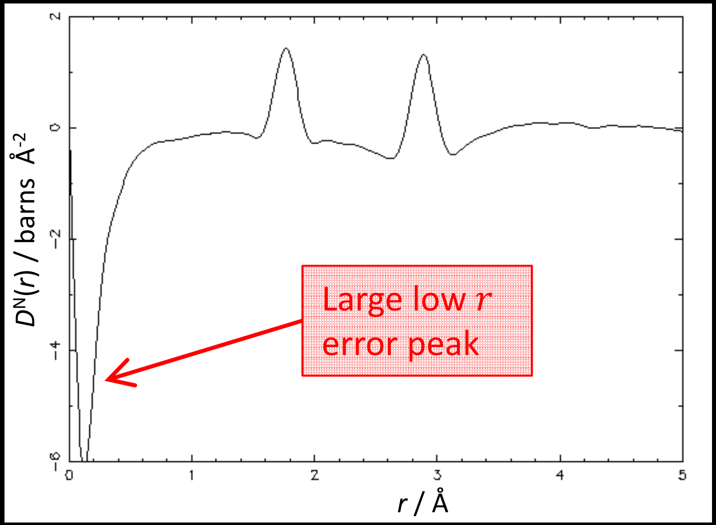
- Fourier transform requires integration of $i^{\mathrm{N}}(Q)$ over wide Q-range.
- For reliable results…
  - Normalisation must be consistent over full Q-range
  - Self scattering must be subtracted well
  - All corrections must be done as well as possible (attenuation, multiple scattering, backgrounds,…etc)
- But note, most corrections change slowly with Q
- Badly corrected data have large error peak at low r

Absorption

- Absorption cross-sections are usually proportional to wavelength λ
- Liquid CCl_4 uncorrected data show strong absorption at low Q
- This leads to large error peak at low r



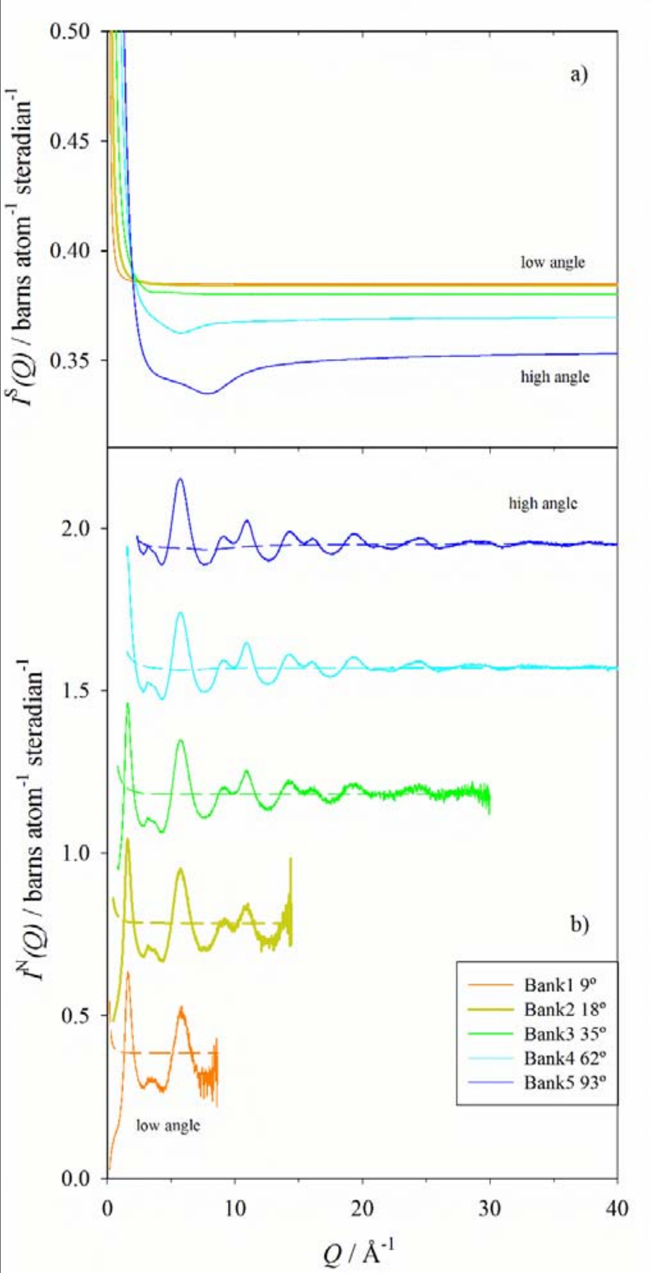




Self scattering

$$i(Q) = I(Q) - I^{\mathrm{Self}}(Q)$$

- The self scattering $I^{\mathrm{Self}}(Q)$ changes slowly with Q
- Before the Fourier transform, $I^{\mathrm{Self}}(Q)$ is subtracted from the total scattering $I(Q)$



(B_2O_3 glass)

Composition and Density

- For reliable results, such as coordination numbers, it is essential to know the composition and the density of the sample

$$T^{\mathrm{N}}(r) = T^0(r) + D^{\mathrm{N}}(r)$$
$$= 4\pi r g^0 \langle \bar{b} \rangle_{\mathrm{av}}^2 + D^{\mathrm{N}}(r)$$

average scattering length $\langle \bar{b} \rangle_{\mathrm{av}}$

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

$$n_{lm} = \frac{r_{lm} A_{lm}}{(2 - \delta_{lm}) c_l \bar{b}_l \bar{b}_m}$$

Low r correction

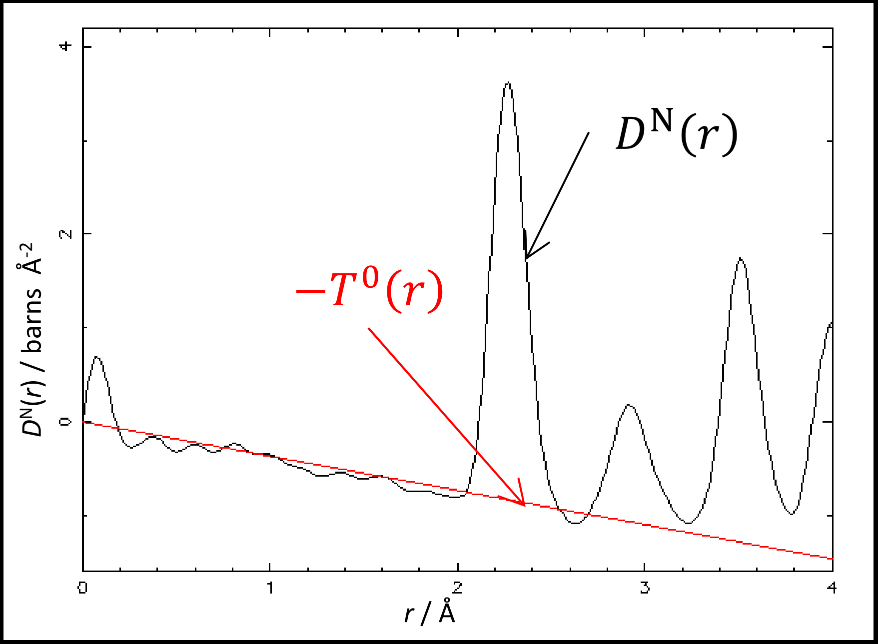
- For reliable results , such as coordination numbers, it is essential that $T^{\mathrm{N}}(r)$ is normalised correctly.
- Even after careful corrections, the normalisation may not be perfect for various possible reasons:
  - number of atoms in beam not known exactly
  - sample-dependent background, etcetera…
- The low r region of $T^{\mathrm{N}}(r)$ depends on only composition and density, and can be used to correct the normalisation

$$\begin{aligned} T^{\mathrm{N}}(r) &= T^{0}(r) + D^{\mathrm{N}}(r) \\ &= 4\pi r g^{0} \langle \bar{b} \rangle_{\mathrm{av}}^{2} + D^{\mathrm{N}}(r) \end{aligned}$$

Low r correction

$$T^{\mathrm{N}}(r) = T^{0}(r) + D^{\mathrm{N}}(r)$$
$$= 4\pi r g^{0} \langle \bar{b} \rangle_{\mathrm{av}}^{2} + D^{\mathrm{N}}(r)$$

- For example, crystalline Y_2O_3. Coordination number should be $n_{\mathrm{YO}} = 6$
- Without low r correction, $n_{\mathrm{YO}} = 6.53$ is obtained
- And at low r, $D^{\mathrm{N}}(r)$ is not consistent with the average density term $T^{0}(r)$



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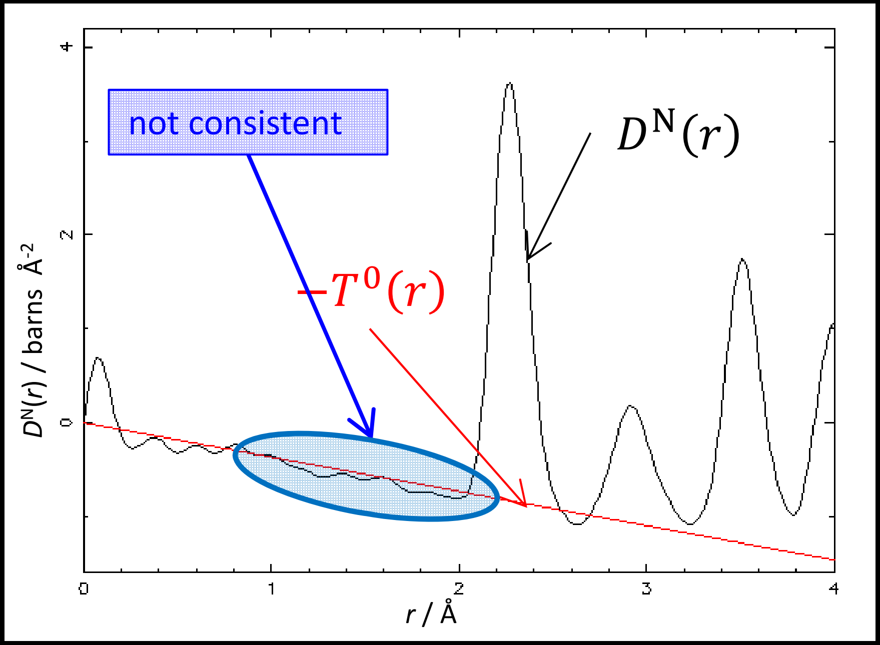
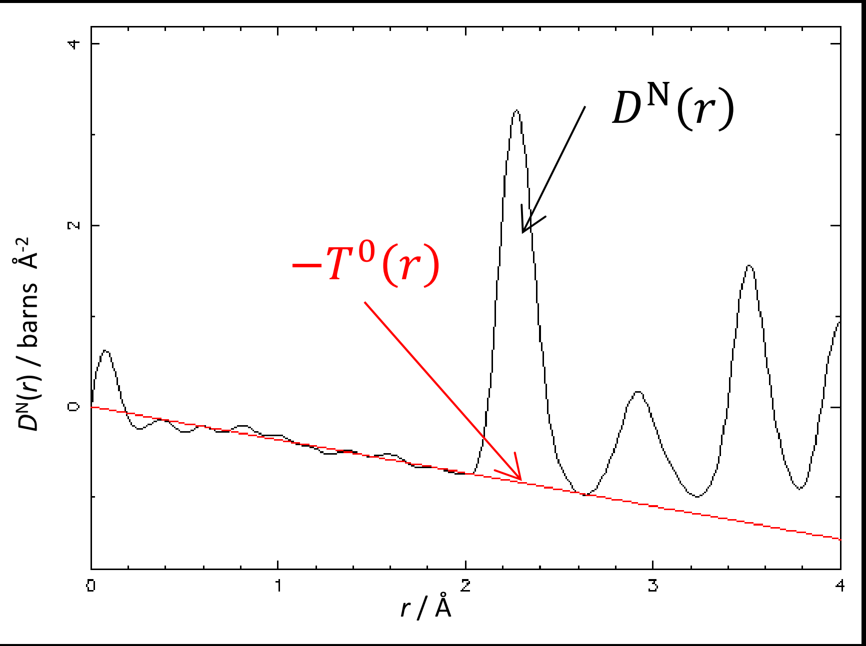


Low r correction

$$T^{\mathrm{N}}(r) = T^0(r) + D^{\mathrm{N}}(r)$$
$$= 4\pi r g^0 \langle \bar{b} \rangle_{\mathrm{av}}^2 + D^{\mathrm{N}}(r)$$

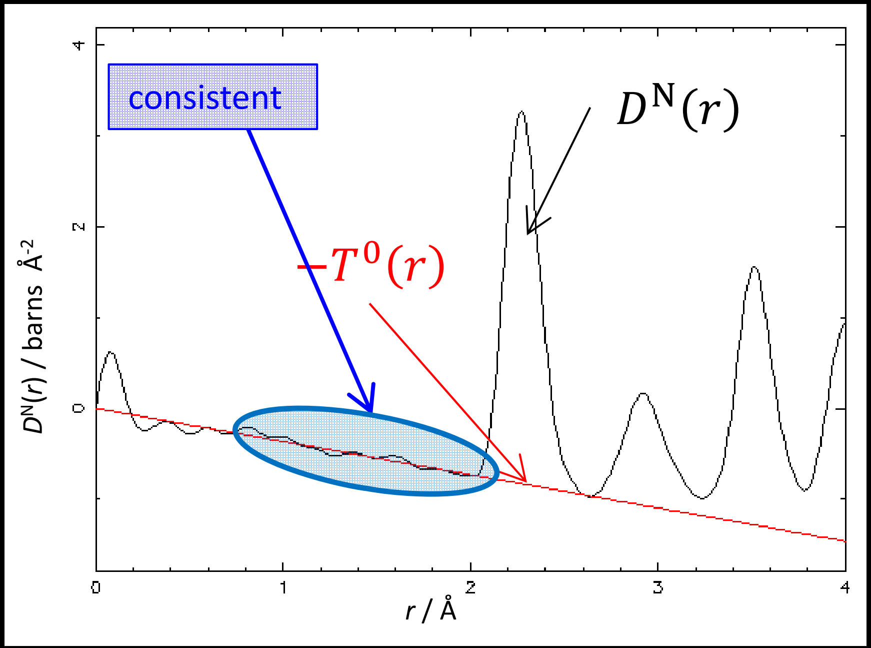
- Data were re-scaled so that at low r, $D^{\mathrm{N}}(r)$ is consistent with the average density term $T^0(r)$



Low r correction

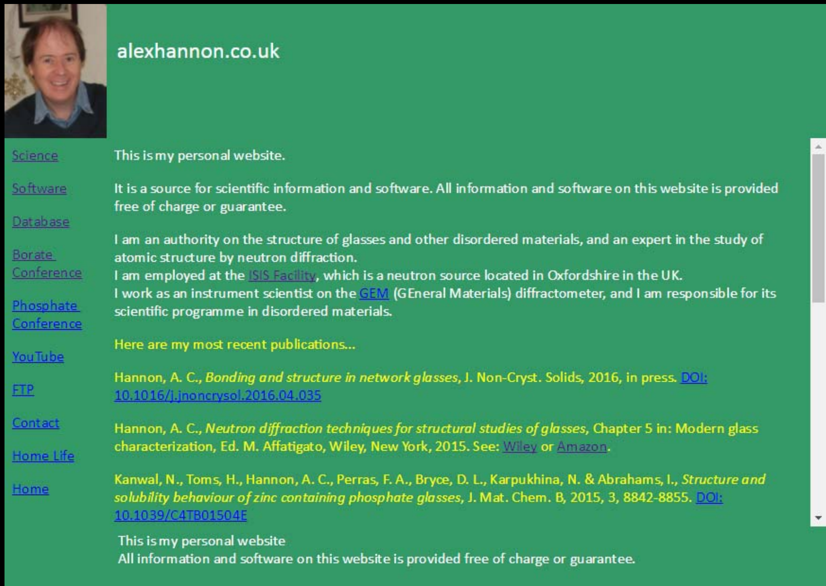
$$T^{\mathrm{N}}(r) = T^{0}(r) + D^{\mathrm{N}}(r)$$
$$= 4\pi r g^{0}\langle \bar{b} \rangle_{\mathrm{av}}^{2} + D^{\mathrm{N}}(r)$$

- Data were re-scaled so that at low r, $D^{\mathrm{N}}(r)$ is consistent with the average density term $T^{0}(r)$
- After this correction, $n_{\mathrm{YO}} = 5.93$ is obtained



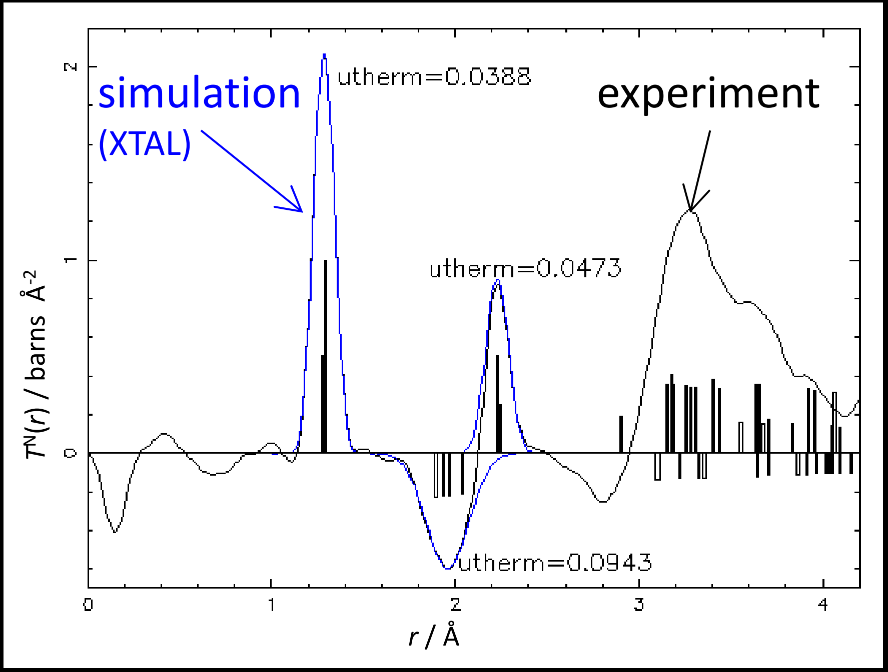
Software to simulate $T^{\mathrm{N}}(r)$ for crystals

- XTAL software to simulate $T^{\mathrm{N}}(r)$ for crystal structures is available free at http://alexhannon.co.uk
- The software includes detailed consideration of thermal broadening, including correlated motion



Crystal simulations

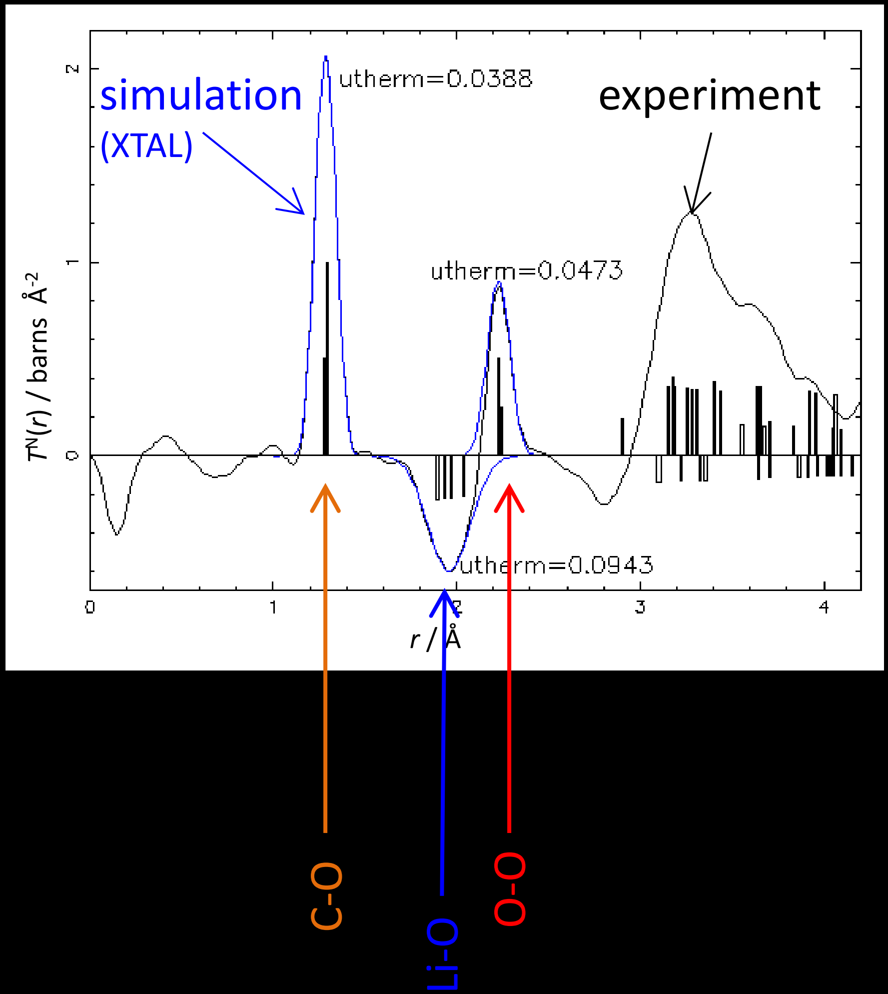
- $T^{\mathrm{N}}(r)$ was measured for $^{7}Li_2CO_3$ to investigate thermal displacement of Li.



Crystal simulations

- $T^{\mathrm{N}}(r)$ was measured for $^{7}Li_2CO_3$ to investigate thermal displacement of Li.

- Typical M-O thermal widths are $u{\sim}0.05$Å
- For Li_2CO_3 the thermal widths are…
  1. $u_{\mathrm{CO}} = 0.039$Å
  2. $u_{\mathrm{LiO}} = 0.094$Å
  3. $u_{\mathrm{OO}} = 0.047$Å
- The C-O and O-O widths in CO_3 groups are unusually small, due to the strong bonds
- The Li-O width is unusually large, due to the large thermal displacements of <u>light</u> Li



Key points

- Real-space resolution depends on value of Q_{max} (maximum momentum transfer)
- Termination ripples are minimised by Fourier transform with a modification function (e.g. Lorch function)
- Correlation function peaks are broadened for 3 reasons:
  1. Real-space resolution (because Q_{max} is not ∞)
  2. Thermal motion of atoms (a Gaussian distribution)
  3. Static distribution of interatomic distances
- $T^{\mathrm{N}}(r)$ peak area depends on coordination number
- Reliable results depend on good corrections and normalisation

Thanks for listening!
Any questions?