Argonne NATIONAL LABORATORY

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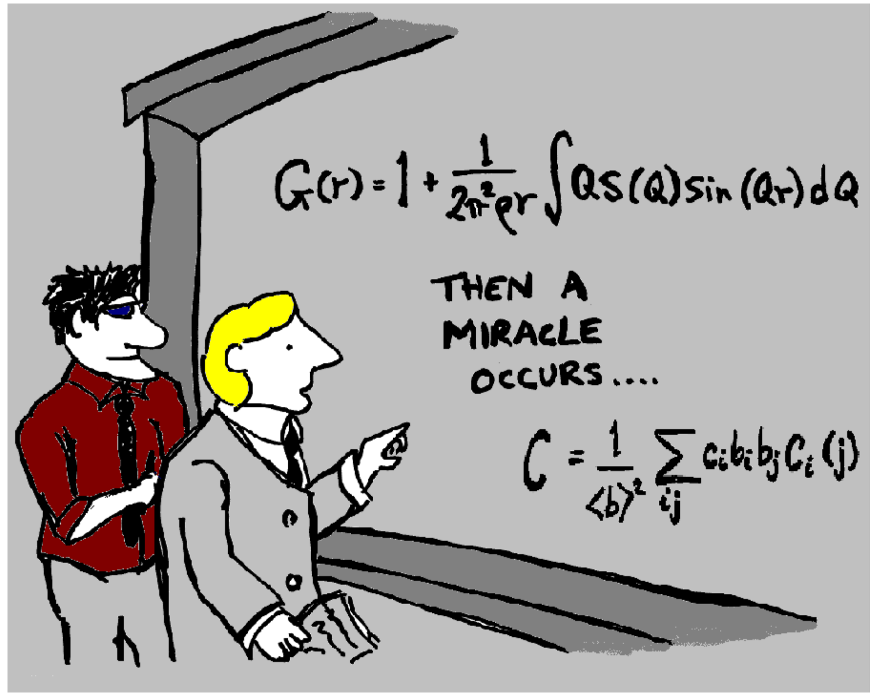

"I think you have to be a bit more explicit here in step two"

Pair Distribution Function Analysis

Chris Benmore
X-ray Science Division, Argonne National Lab.

U.S. Department of Energy

UChicago Argonne LLC

Office of Science U.S. DEPARTMENT OF ENERGY

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ASU

Pioneers in the history of PDF

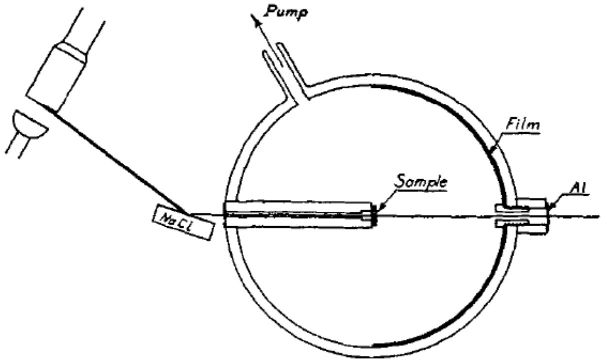


FIG. 1.—Vacuum camera with monochromator for making X-ray diffraction patterns of glass.

Bertram Warren

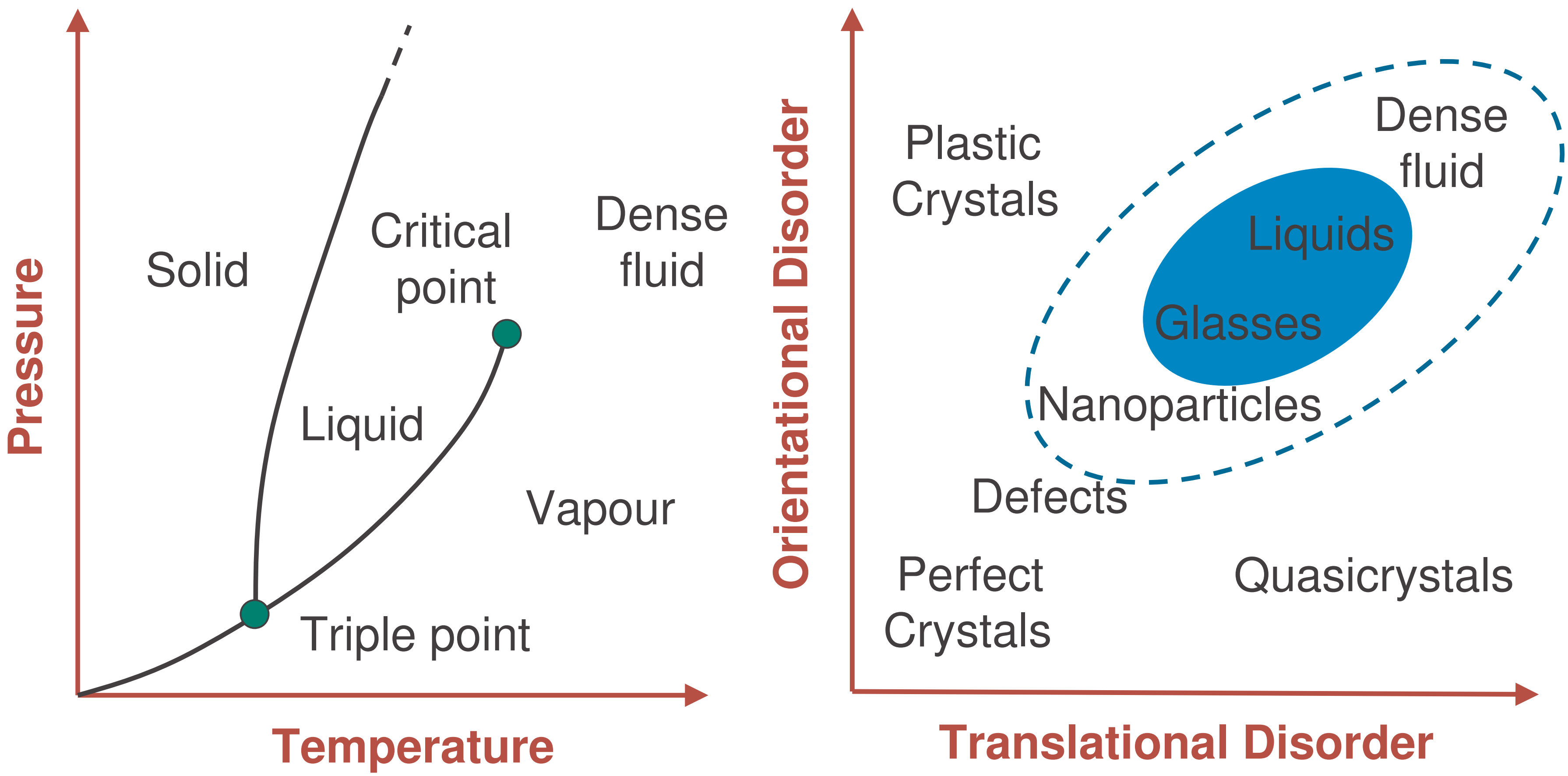
John Enderby

X-ray determination of the Structure of Glass
Warren BE. J. Am. Ceram. Soc. 17 (1934) 249.

The partial structure factors of liquid Cu-Sn
Enderby JE, North DM and Egelstaff PA.
Phil. Mag. 14 (1966) 961.

Peter Egelstaff

Types of Disorder



Order within Disorder

A formation of skydivers illustrates order on an intermediate length scale.

P.S. Salmon Nature Materials 1, 87–88 (2002)

"Each diver has a simple set of rules for bonding to the next, but there is sufficient flexibility for different patterns of ordering to be created on the scale of a few body lengths."

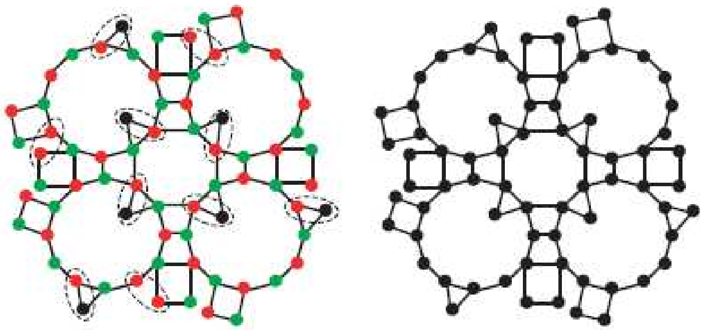
Faber-Ziman formalism – element specific

Phil. Mag 11 (1965) 153.

$S_{Red\text{-}Red}(Q)$

$S_{Red\text{-}Green}(Q)$

$S_{Green\text{-}Green}(Q)$



Bhatia-Thornton formalism

Phys. Rev. B 2 (1970) 3004.

$S_{Number\text{-}Number}(Q)$ - topology

$S_{Concentration\text{-}Concentration}(Q)$ - chemical ordering

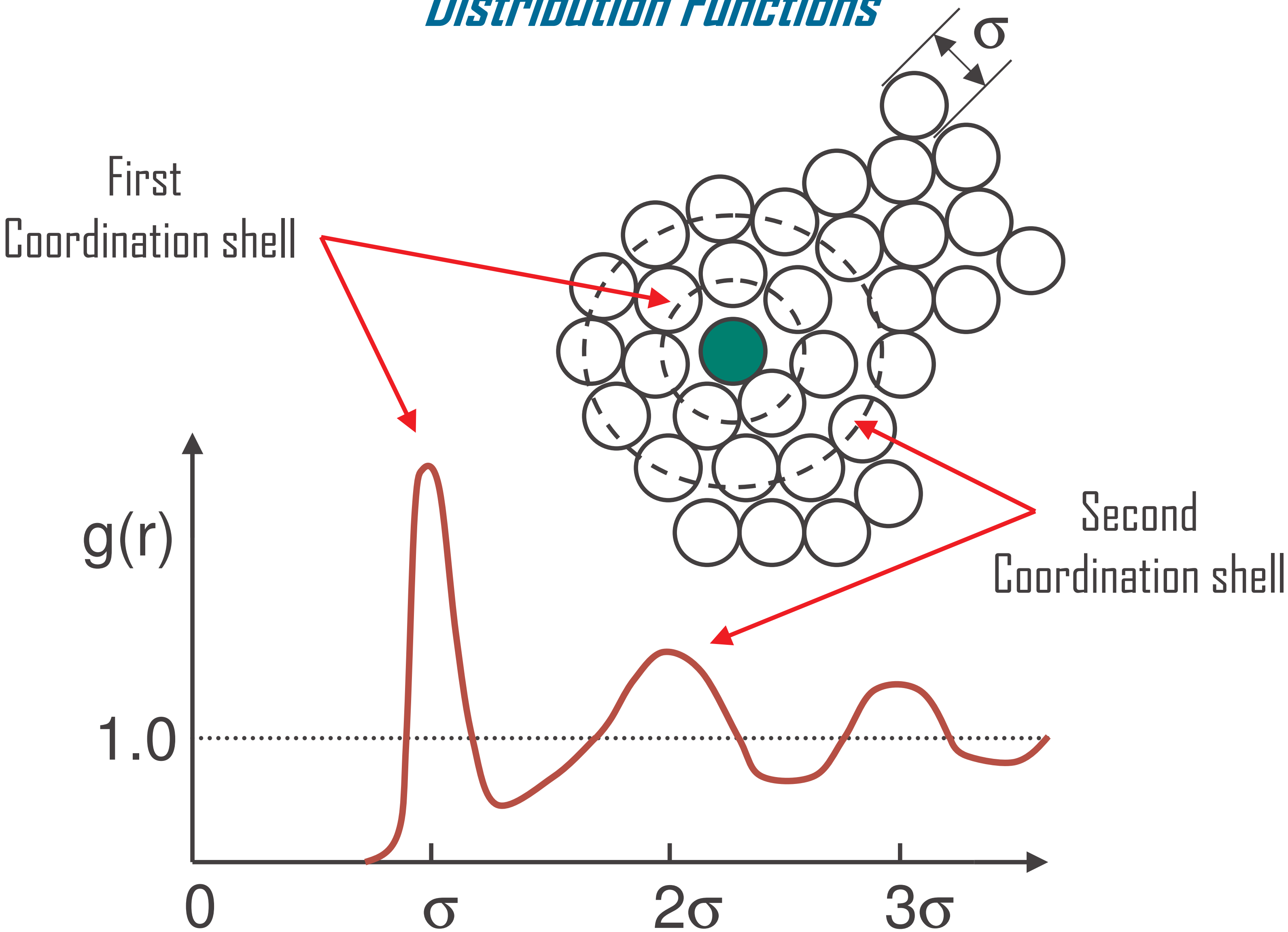
$S_{Number\text{-}Concentration}(Q)$

PDF in context with other common methods

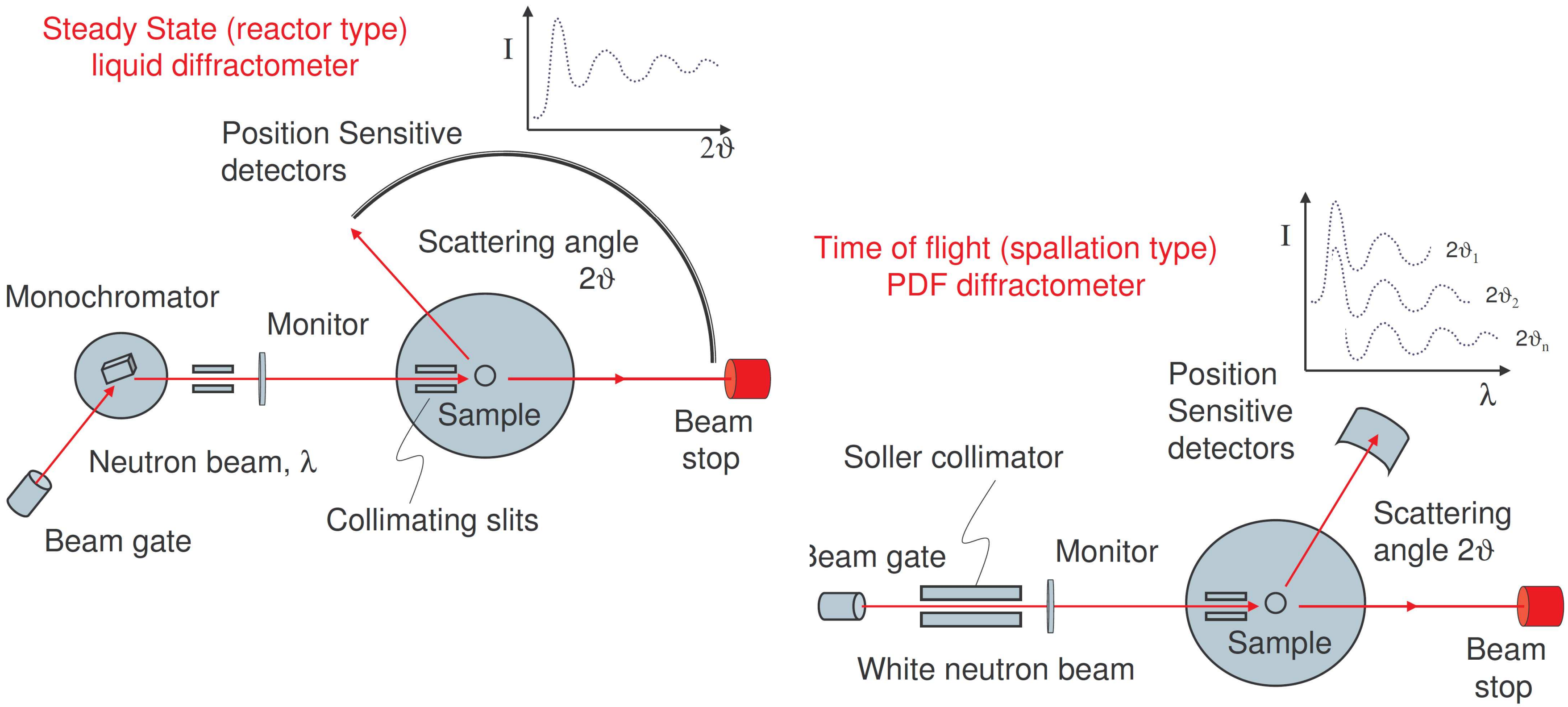
Experiment	
Neutrons/X-ray PDF	Good AVERAGE overview of structure Short range order (SRO) Medium range order (MRO) Neutron Diffraction Isotope Substitution
Crystallography	Long Range Order (LRO)
EXAFS, XANES	SRO, Element Specific, Small concs.
Anomalous x-ray	SRO, MRO. Element specific, Difficult to do accurately
Vibrational Spectroscopy	Inelastic N and X, Raman and Infrared. SRO, MRO. Need good structural model.
NMR	Isotope Specific. Speciation Q_n.
…..	

Simulation	
Inverse Methods:	Perfect fits to PDF data
Reverse Monte Carlo (RMC) Empirical Potential Structure Refinement (EPSR)	No predictive power Many constraints essential !
Classical Molecular Dynamics	Essential physics, trends Fit to PDF sometimes poor
Ab initio simulations Density Functional Theory (DFT)	Accurate predictions Box size limit ?
…..	

Distribution Functions

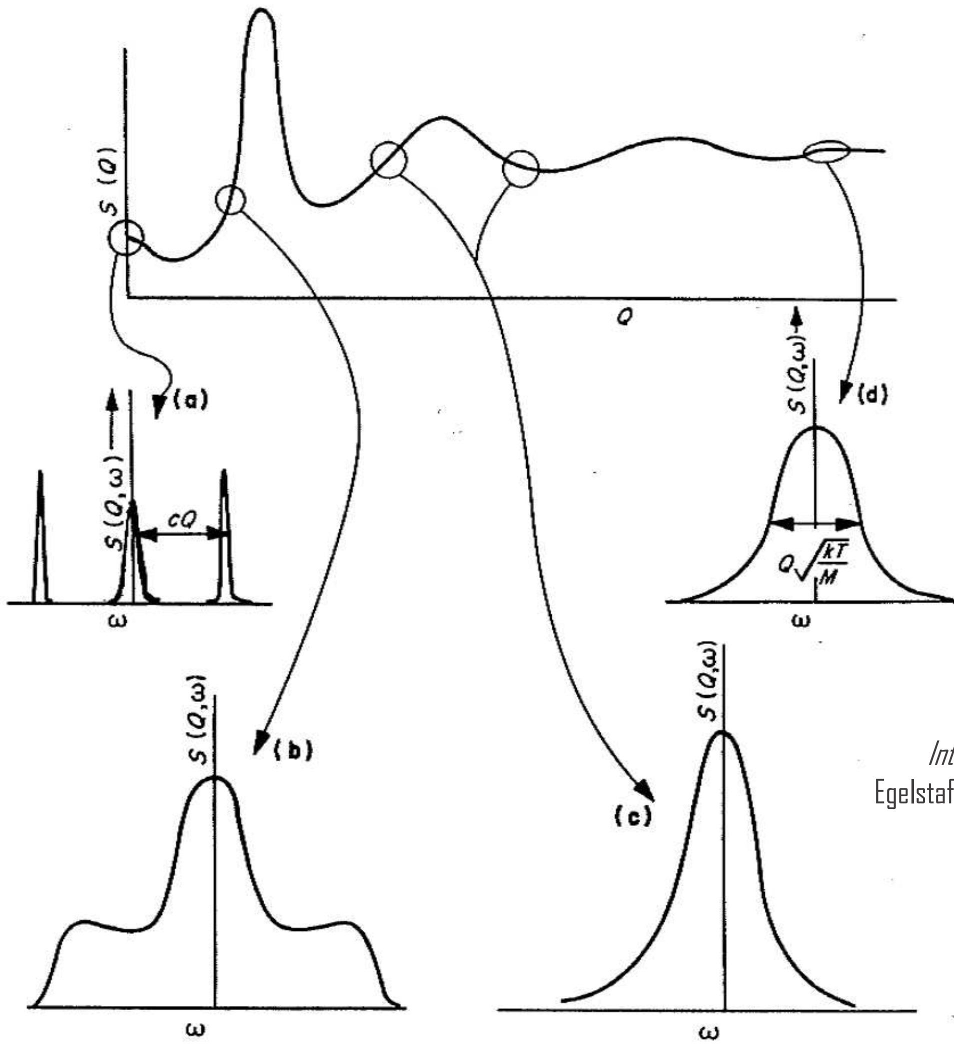


Monochromatic PDF versus time-of-flight PDF



Chapter 12: Structure of glasses and melts in "Neutron Scattering in Earth Sciences".
Reviews in Mineralogy and Geochemistry. 63 (2006) 375-311.

$S(Q,\omega)$ cuts along a liquid structure factor



Introduction to the Liquid State.
Egelstaff PA.Oxford University Press, 1994.

Neutron and X-ray differential cross sections

Neutron

$$\frac{d\sigma}{d\Omega} = \frac{d\sigma}{d\Omega}_{self} + \frac{d\sigma}{d\Omega}_{Inelastic} + \frac{d\sigma}{d\Omega}_{distinct}$$

$$= \sum_{\alpha} c_\alpha b_\alpha^2 + P(\theta) + F_N(Q)$$

Self scattering

Inelastic scattering
"Plazeck"

Distinct scattering

X-ray

$$\frac{d\sigma}{d\Omega} = \frac{d\sigma}{d\Omega}_{self} + \frac{d\sigma}{d\Omega}_{Compton} + \frac{d\sigma}{d\Omega}_{distinct}$$

$$= \sum_{\alpha} c_\alpha f_\alpha{}^2(Q) + C_X(Q) + I_X(Q)$$

Self scattering

Compton scattering

Distinct scattering

Neutron and X-ray Static Structure Factors

Neutron Nuclear function

Distinct scattering

X-ray pseudo-nuclear function

$$S_N(Q)-1=\frac{F_N(Q)}{\left(\sum_\alpha c_\alpha b_\alpha\right)^2}$$

$$=\frac{1}{\left(\sum_\alpha c_\alpha b_\alpha\right)^2}\sum_{\alpha,\beta}c_\alpha b_\alpha c_\beta b_\beta (S_{\alpha\beta}(Q)-1)$$

Coherent neutron scattering length

$$S_X(Q)-1=\frac{I_X(Q)}{\left(\sum_\alpha c_\alpha f_\alpha(Q)\right)^2}$$

De-convolute electron cloud

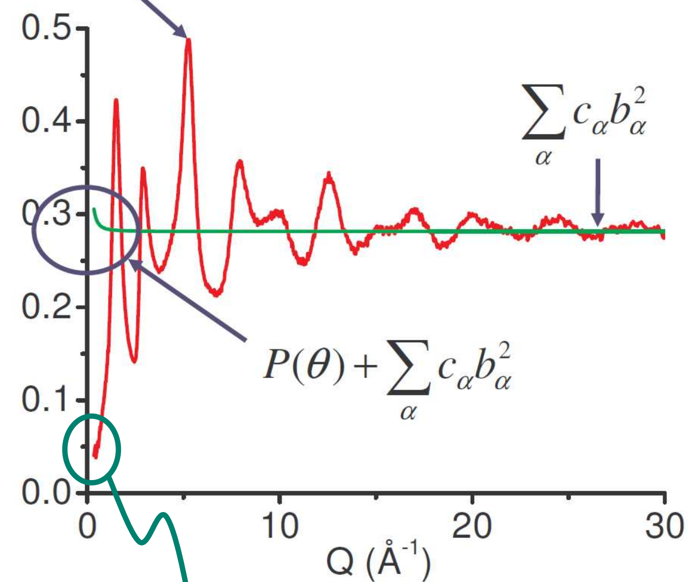
$$=\frac{1}{\left(\sum_\alpha c_\alpha f_\alpha(Q)\right)^2}\sum_{\alpha,\beta}c_\alpha f_\alpha(Q)c_\beta f_\beta(Q)(S_{\alpha\beta}(Q)-1)$$

X-ray form factor

Neutron and X-ray differential cross sections

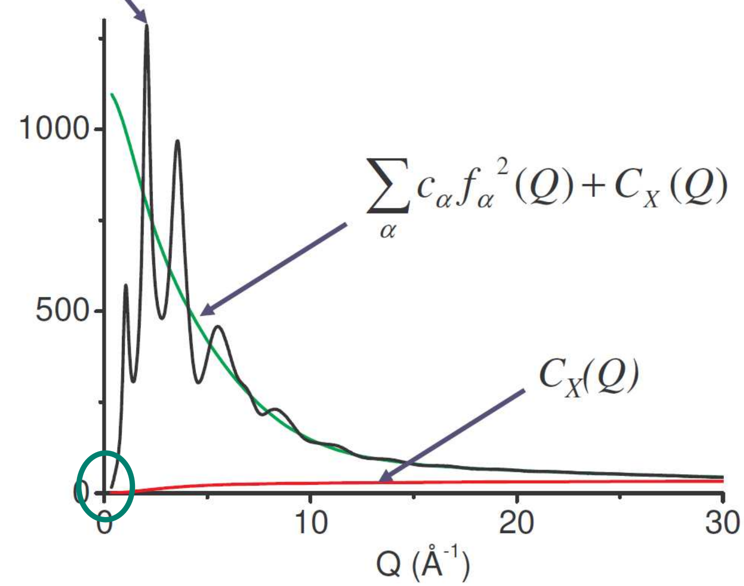
Neutron

$$\frac{d\sigma_N}{d\Omega} = \sum_\alpha c_\alpha b_\alpha^2 + P(\theta) + F_N(Q)$$



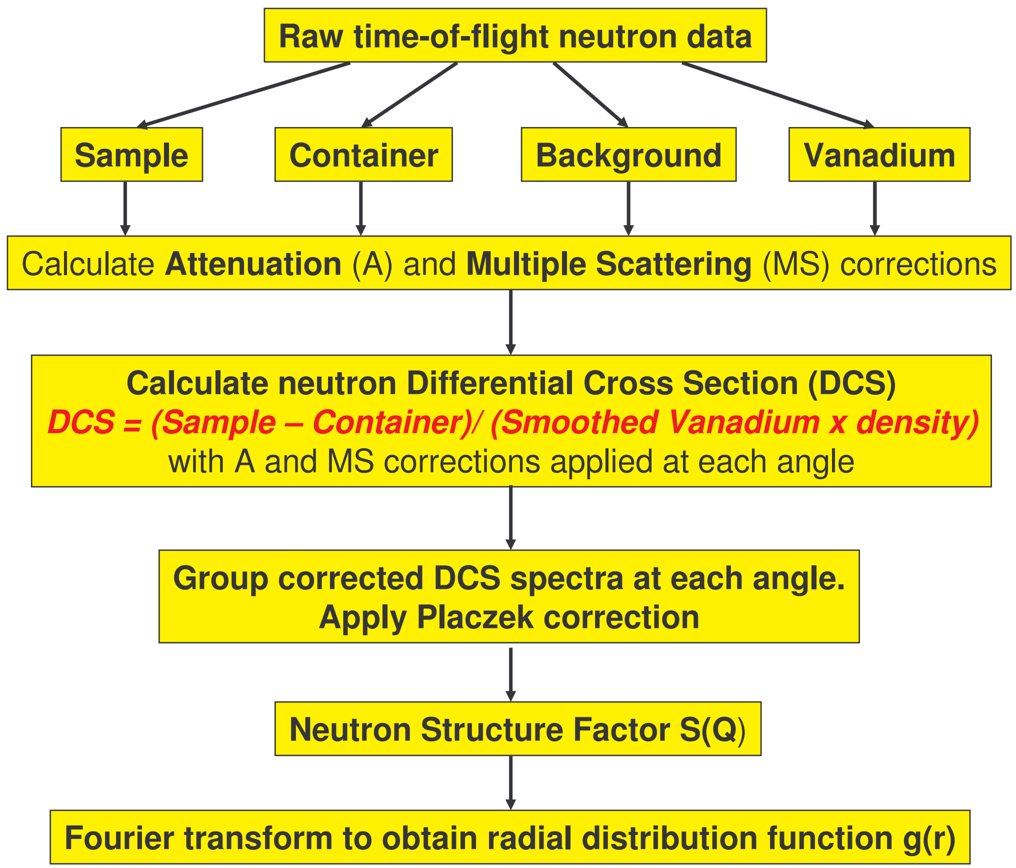
X-ray

$$\frac{d\sigma_X}{d\Omega} = \sum_\alpha c_\alpha f_\alpha{}^2(Q) + C_X(Q) + I_X(Q)$$

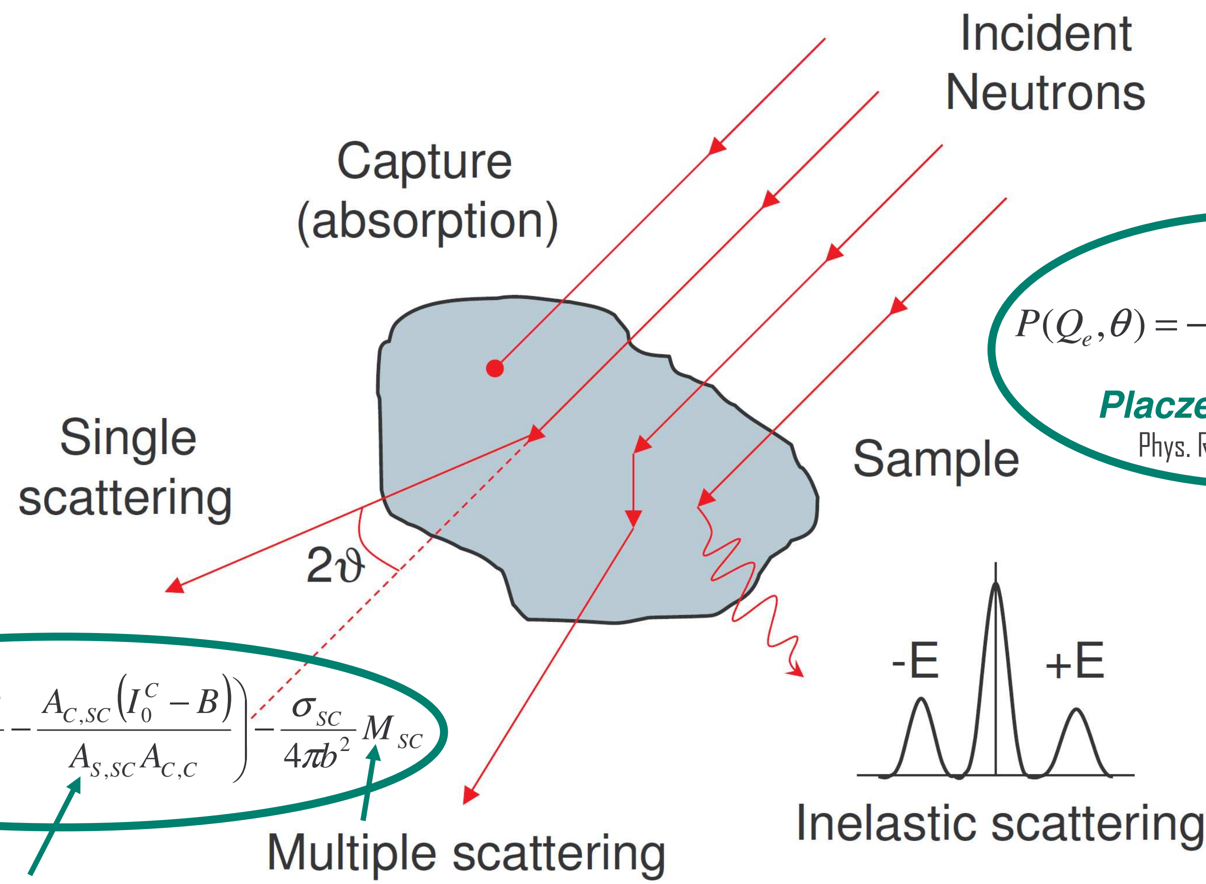


Related to isothermal compressibility for a liquid : $\frac{d\sigma}{d\Omega}(Q=0) = \rho K_B T \chi_T \sum_\alpha c_\alpha b_\alpha^2$

Outline of time-of-flight neutron analysis procedure



Neutron diffraction corrections



$$P(Q_e,\theta) = -\frac{2ym}{M}X + \frac{m}{M}\frac{k_B T}{2E_0}Y$$

Placzek correction

Phys. Rev. 86 (1952) 377

$$F_S(Q) = K\left(\frac{I_0^{SC} - B}{A_{S,SC}} - \frac{A_{C,SC}\left(I_0^{C} - B\right)}{A_{S,SC}A_{C,C}}\right) - \frac{\sigma_{SC}}{4\pi b^2}M_{SC}$$

Paalman and Pings attenuation factors

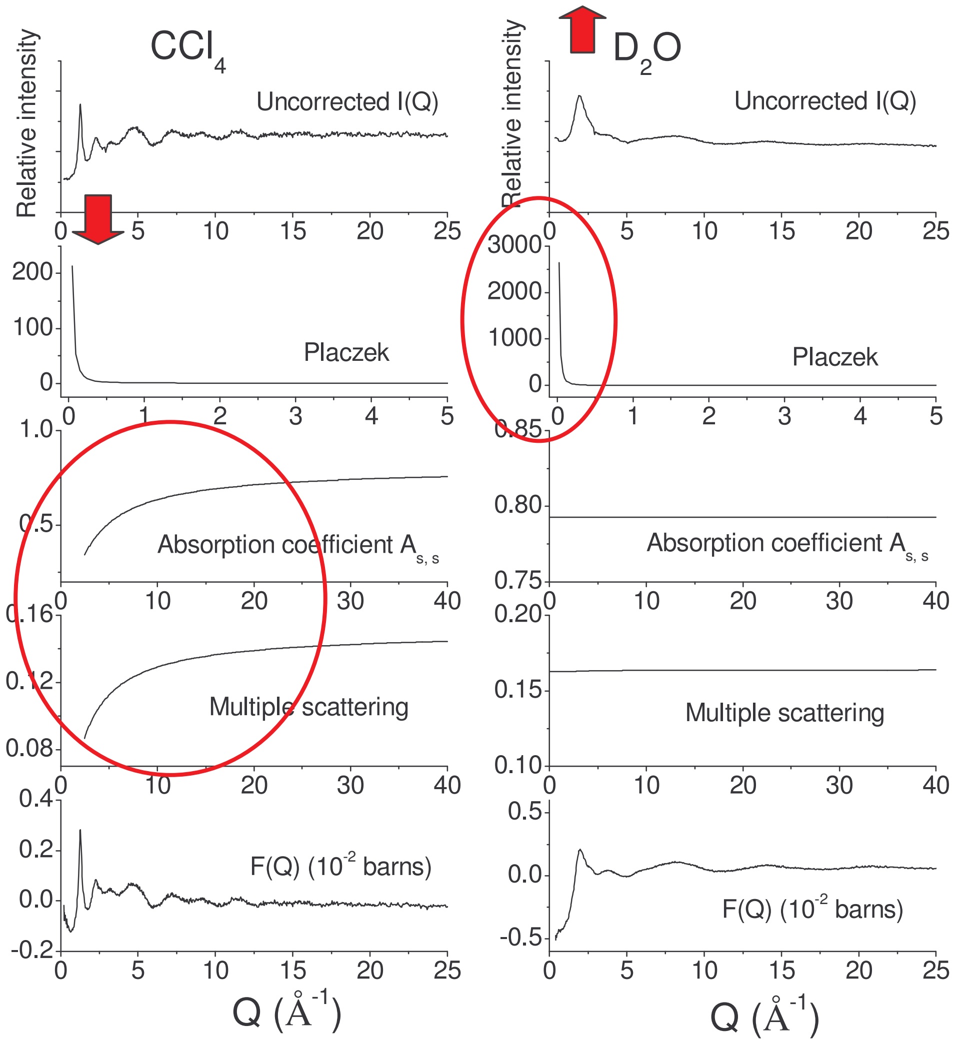
J. Appl. Phys. 33 (1962) 2635

Multiple scattering

Nuc. Instr. Meth. 178 (1980) 415

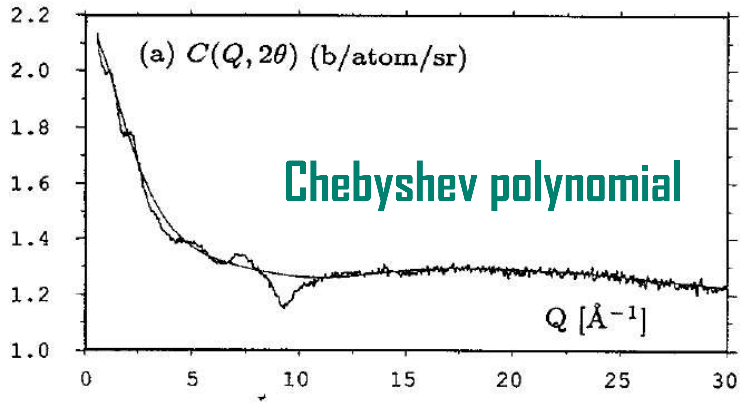
Ideal neutron PDF experiment designed so that attenuation and multiple scattering effects are ~10%

How do the corrections effect the measured data ?



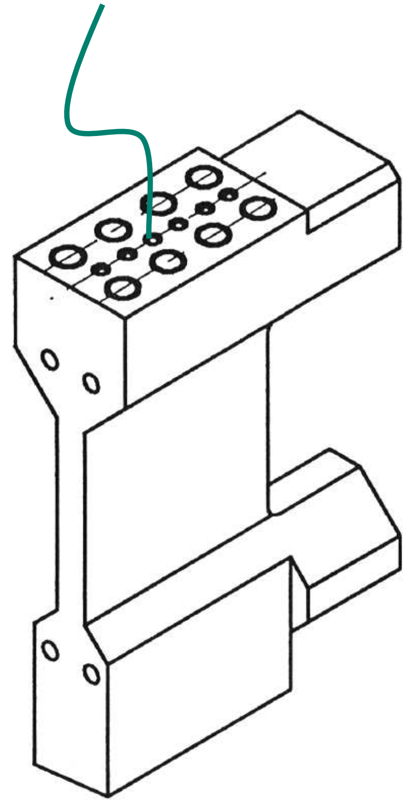
Time-of-Flight Neutron Total Scattering Data Analysis implemented in the software suite ISAW.
Nucl. Instrum. Methods. A 562 (2006) 422-432.

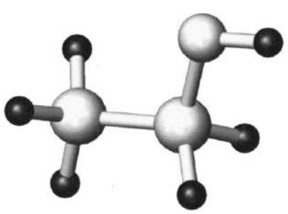
Proton recoil and Vanadium normalization

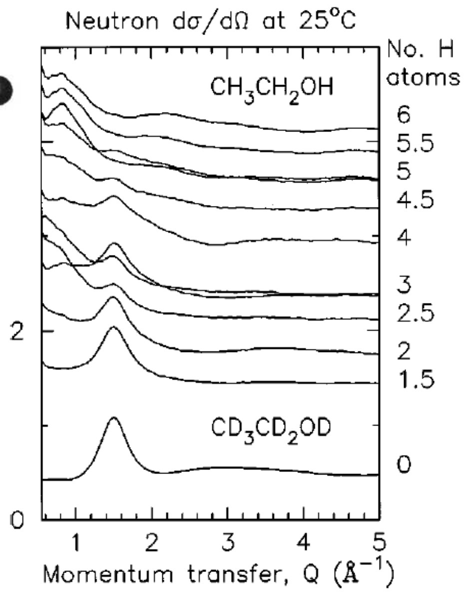


Vanadium rods

same geometry as sample







Hydrogen Placzek Correction

Check: cross-sections at all angles overlap

A.K. Soper

J. Chem. Phys. 97 (1992) 1320.

J. Chem. Phys. 106 (1997) 247.

J. Chem. Phys. 112 (2000) 5877.

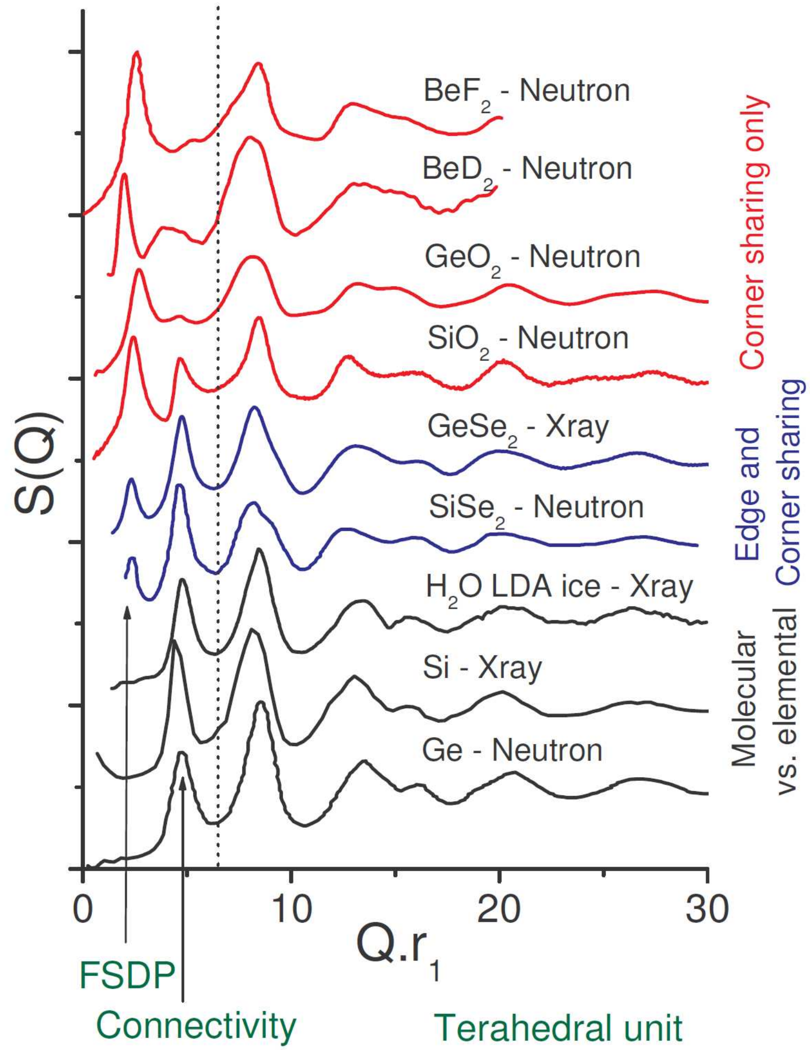
Interpreting Structure Factors

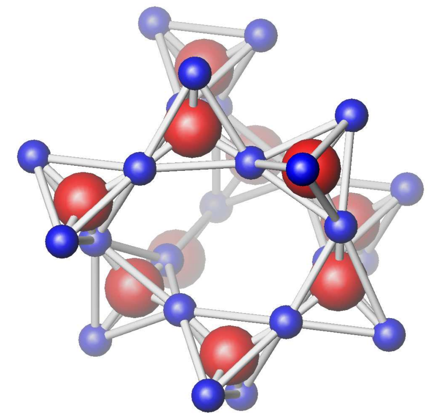
Tetrahedral glasses

r_1=first peak position in real space

FSDP – First Sharp Diffraction Peak : Intermediate Range Order

SSDP –Second Sharp Diffraction Peak : Extended Range Order

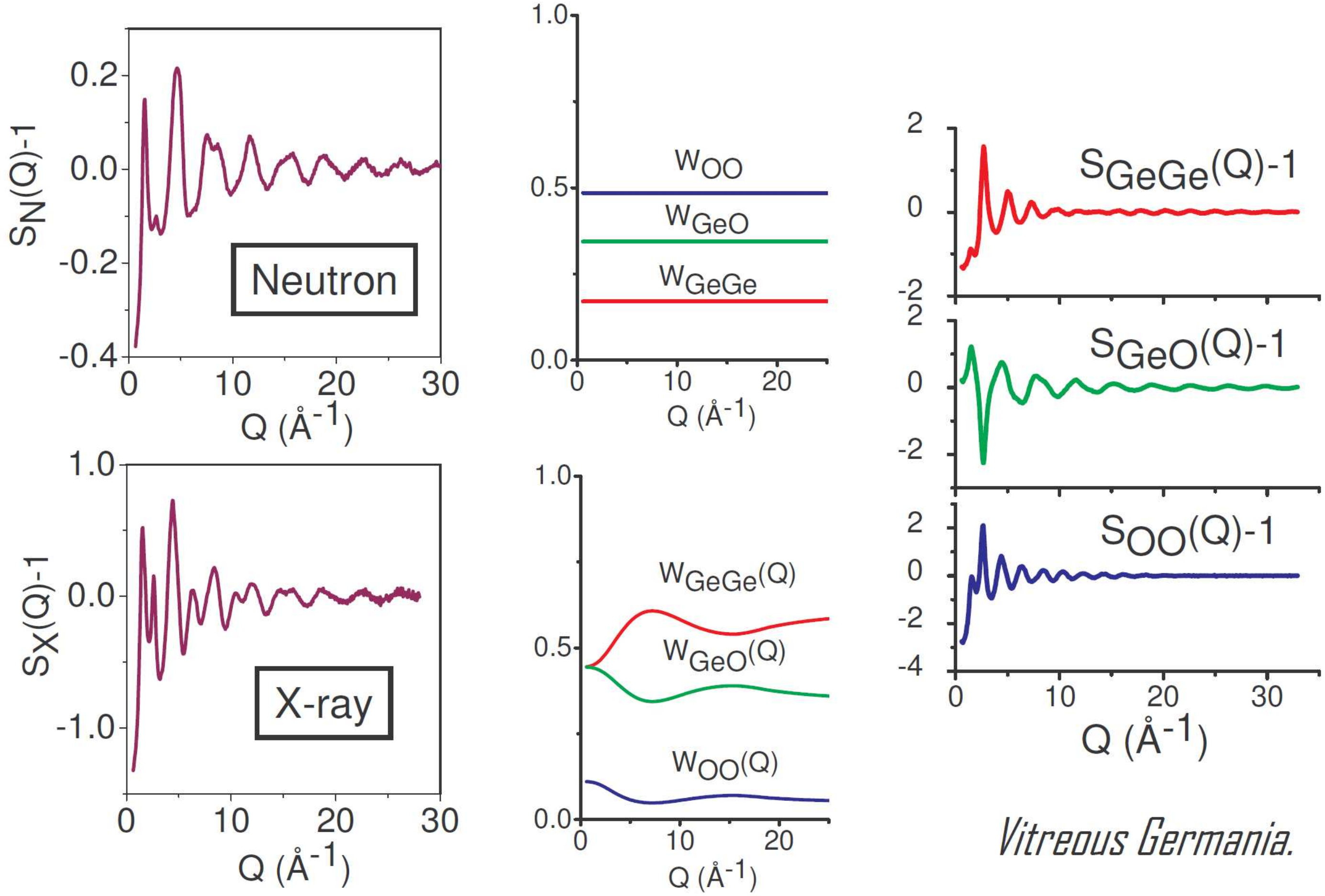




Phys. Rev. B. 72 (2005) 132201.

Weighted Partial Structure Factors

Total Structure Factor, $S(Q)$ = Weighting factors, $W_{\alpha\beta}(Q)$ X Partial Structure Factors, $S_{\alpha\beta(}Q)$



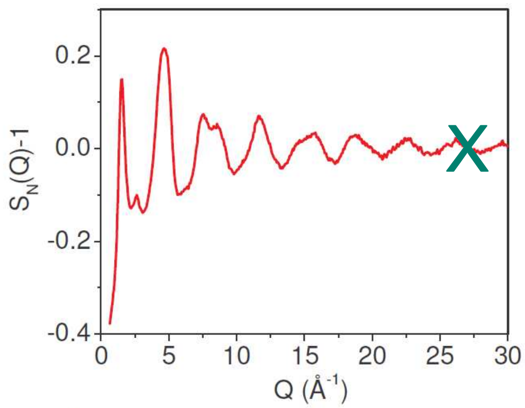
Vitreous Germania.

The Miracle step

Neutron

$$g(r)=1+\frac{1}{2\pi^2\rho r}\int Q\, i(Q)\sin(Qr)\,dQ$$

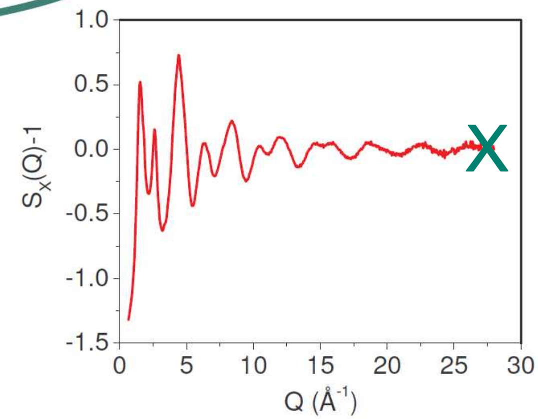
X-ray



$g(r) \rightarrow 0$ as $r \rightarrow 0$

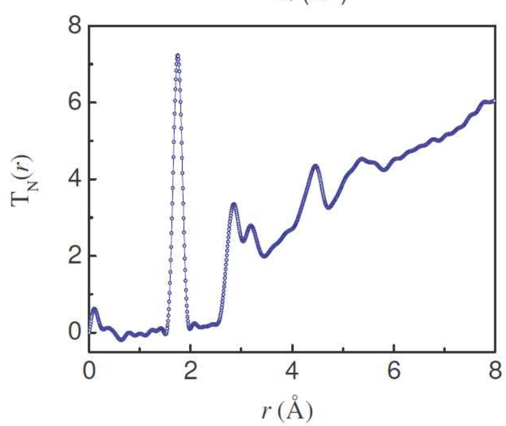
$g(r) \rightarrow 1$ as $r \rightarrow \infty$

Radial distribution function



$$T(r)=4\pi\rho r.g(r)$$

Total distribution function

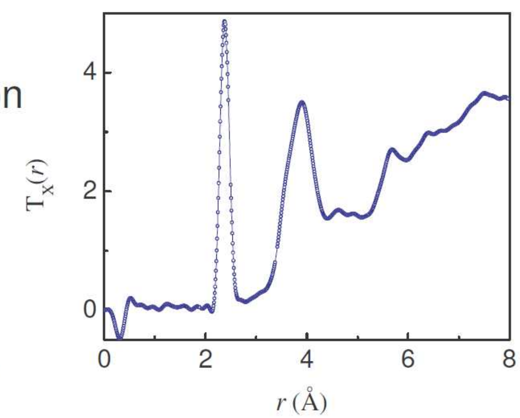


$$D(r)=4\pi\rho r.[g(r)-1]$$

Differential distribution function

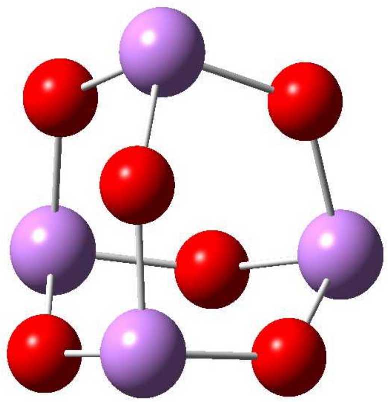
$$Sin\left(\frac{\pi Q}{Q_{max}}\right).\left(\frac{\pi Q}{Q_{max}}\right)^{-1}$$

Lorch modification function

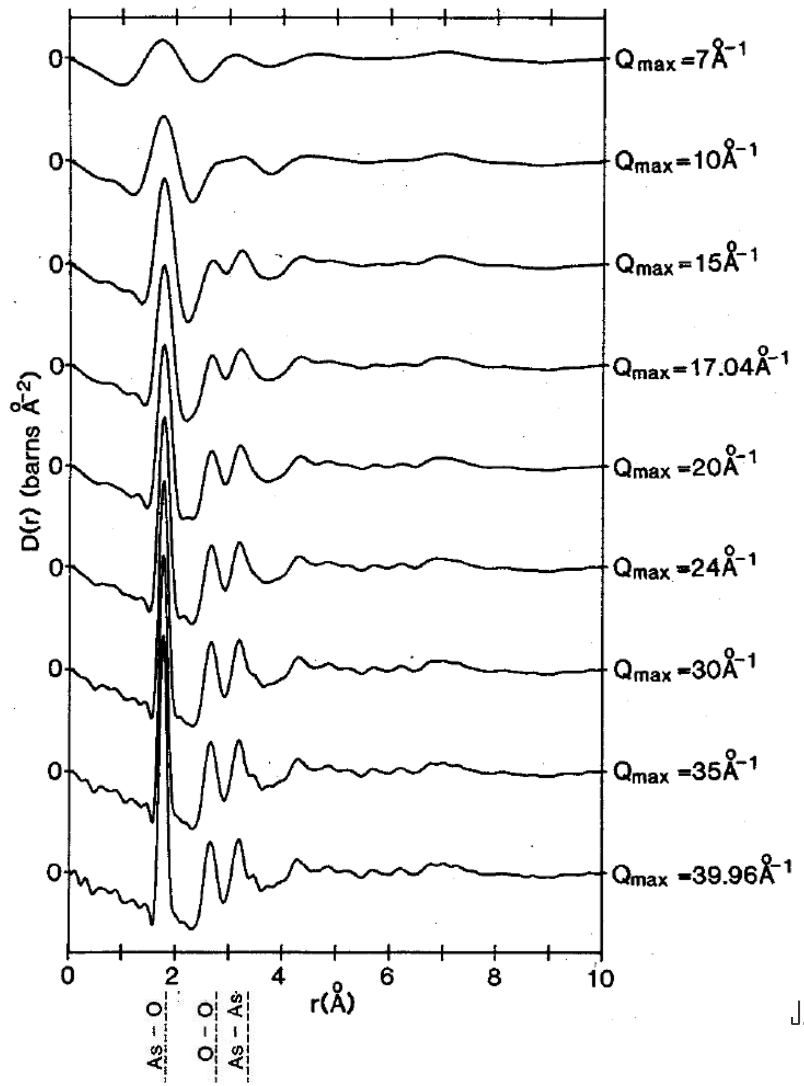


Truncate at a positive node to minimize Fourier artifacts

A question of resolution – the effect of Qmax



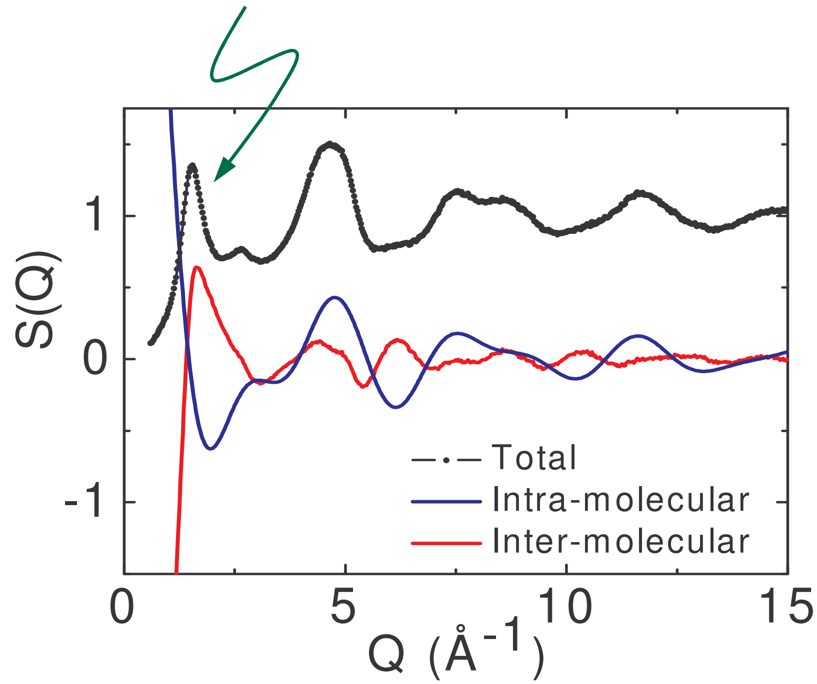
As_4O_6 molecule



J. Non-Cryst. Sol 111 (1989) 123.

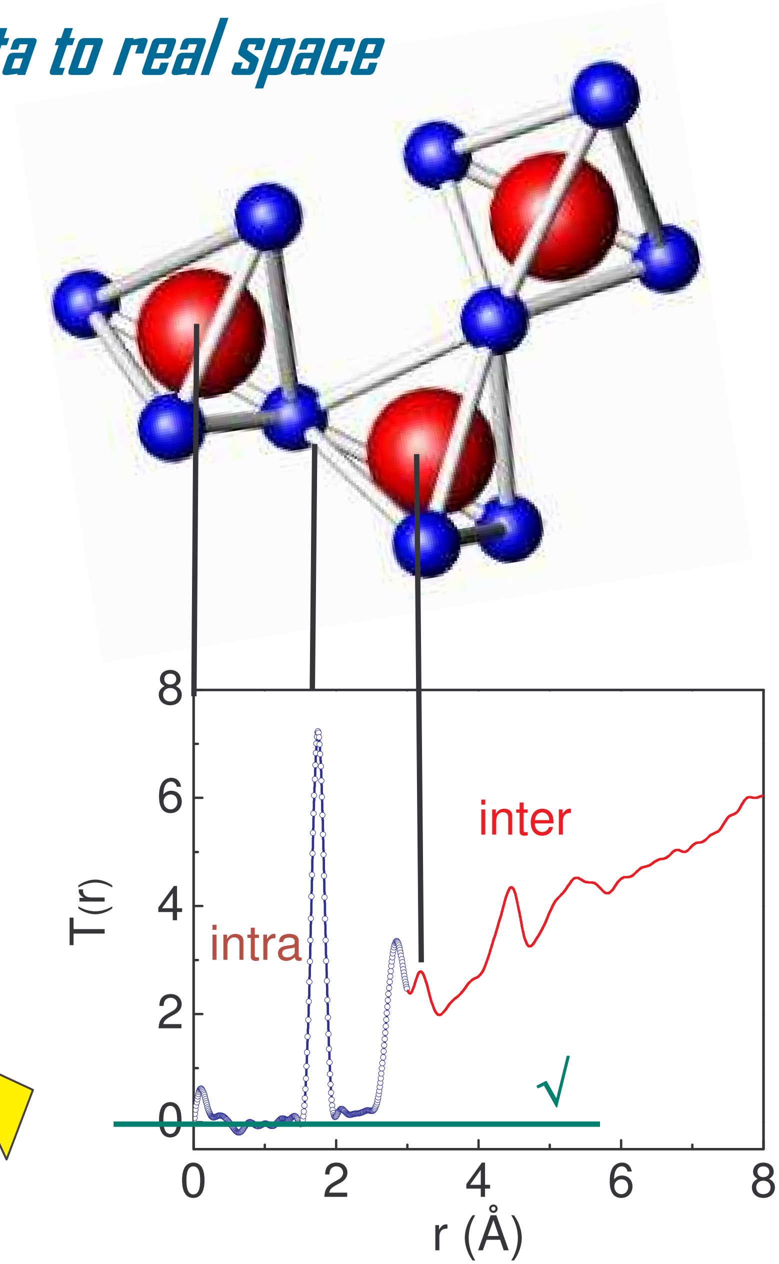
Inversion of data to real space

'First sharp diffraction peak'



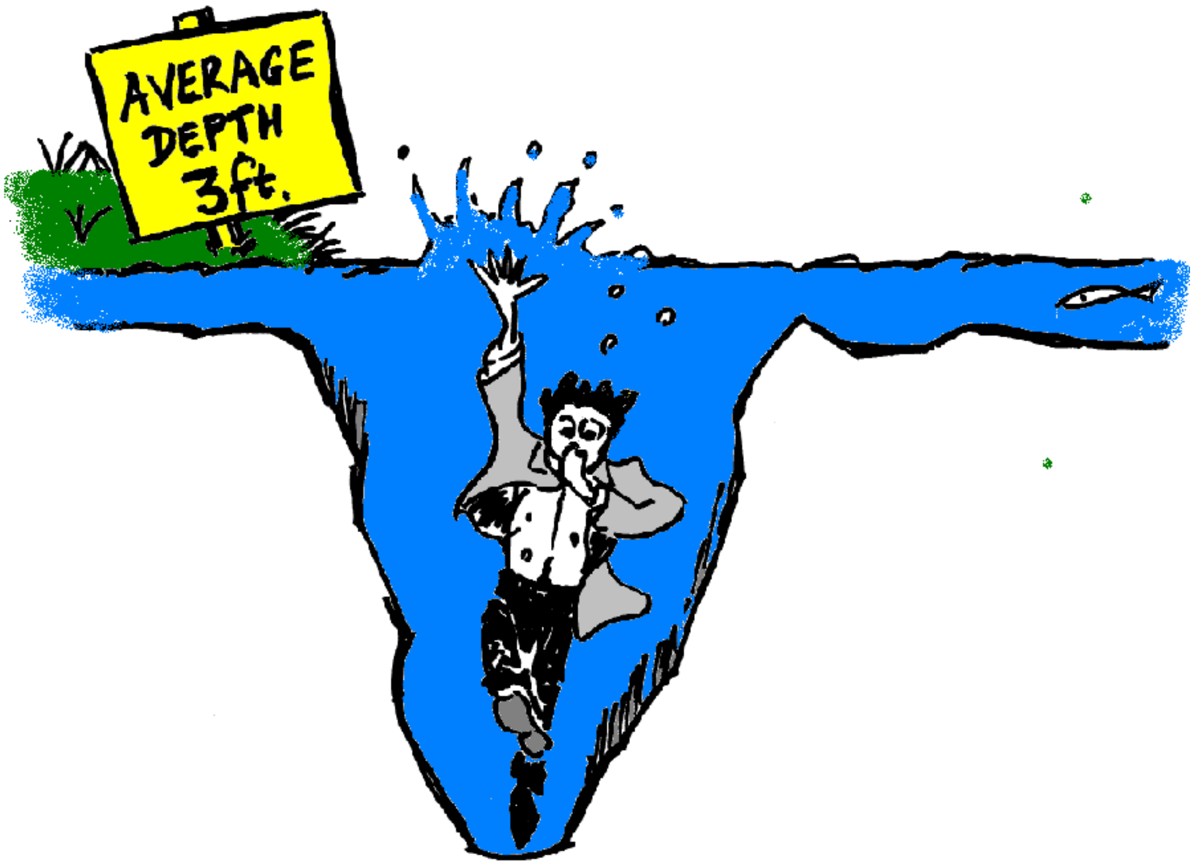
Sine Fourier Transformation

$S(Q) \rightarrow T(r) = 4\pi\rho r.g(r)$



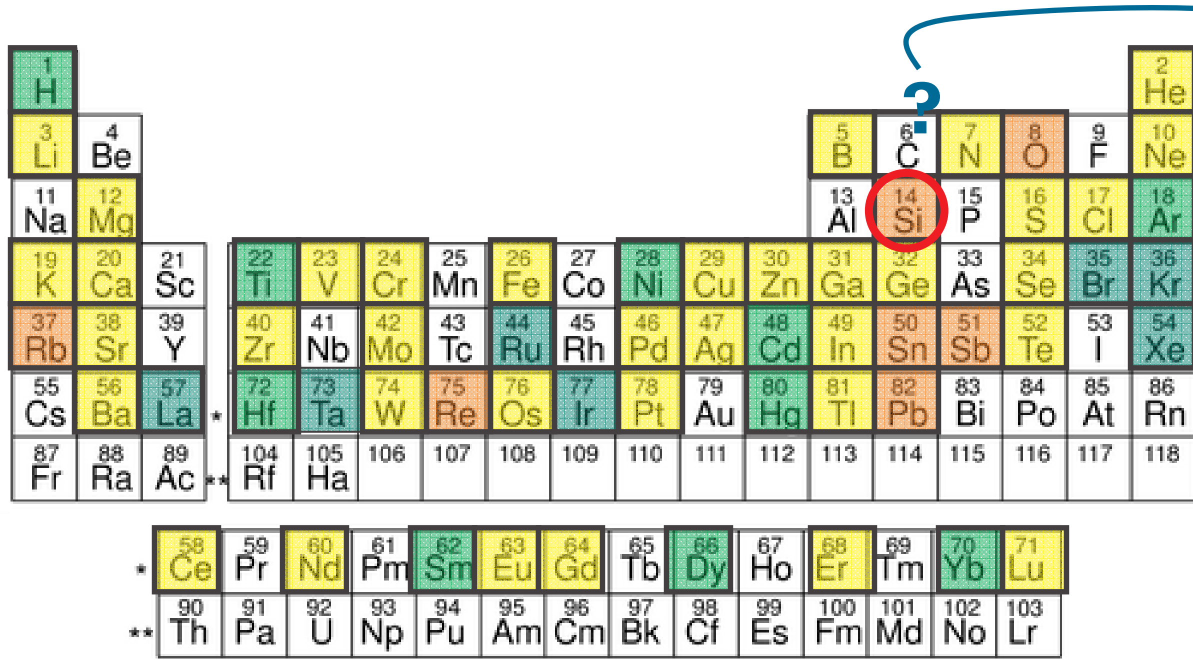
Flaw of Averages

PDF measures the AVERAGE structure i.e. coordination number



Naturally occurring nuclides for NDIS

Identified by feasibility of Neutron Diffraction Isotopic Substitution experiment



Δb = 0.10 fm
***NOT* 0.46 fm**
Scratched !

J. Phys. Condens. Matt. 20 (2008) 045221

- Second order difference Δb>10 fm
- First order difference Δb >1 fm
- Feasible using *NOMAD* at *SNS*
- Other

Isotopic Substitution and Partial Structure Factors
J. Enderby. World Scientific p16. ISBN 981-02-1463-4.

Partial Structure Factors for glassy SiO_2

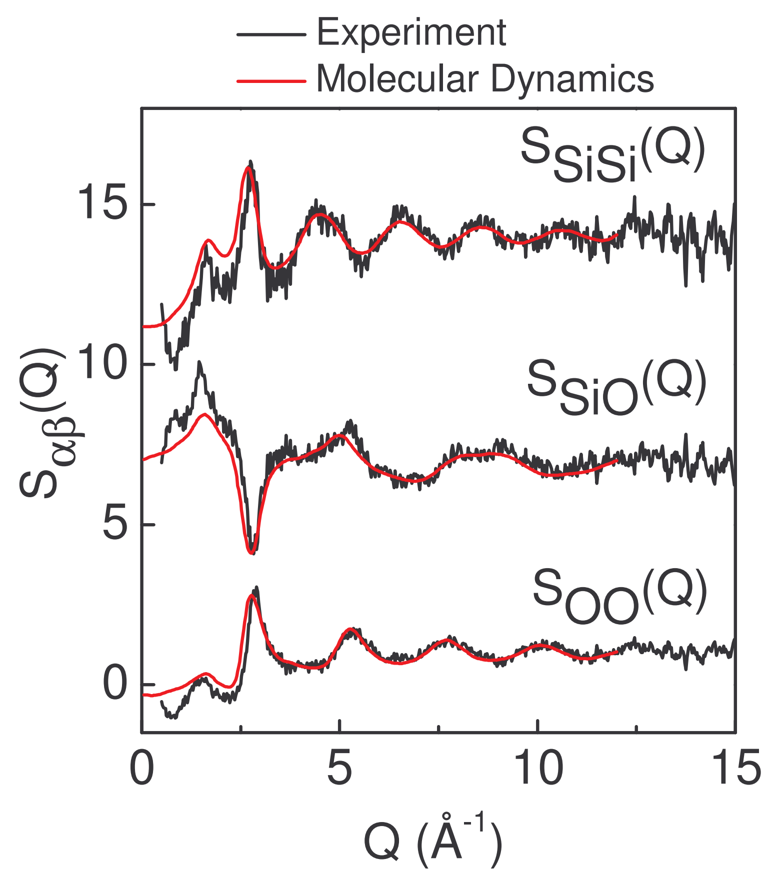
Matrix for extracting partial structure factors from two neutron ^{Nat}Si and ^{29}Si and one high energy x-ray experiment.

$$\begin{bmatrix} {}^{Nat}I_N(Q) \\ {}^{29}I_N(Q) \\ I_X(Q) \end{bmatrix} = \begin{bmatrix} c_{Si\,Nat}^2 b_{Si}^2 & 2c_{Si}c_{O\,Nat} b_{Si} b_O & c_O^2 b_O^2 \\ c_{Si\,29}^2 b_{Si}^2 & 2c_{Si}c_{O\,29} b_{Si} b_O & c_O^2 b_O^2 \\ c_{Si}^2 f_{Si}^2(Q) & 2c_{Si}c_O f_{Si}(Q) f_O(Q) & c_O^2 f_O^2(Q) \end{bmatrix} \cdot \begin{bmatrix} S_{SiSi}(Q)-1 \\ S_{SiO}(Q)-1 \\ S_{OO}(Q)-1 \end{bmatrix}$$

$$I_X(Q) = \langle F \rangle^2 . S_X(Q) = S_X(Q) \sum_{i,j=Si,O} c_i c_j f_i(Q) f_j(Q)$$

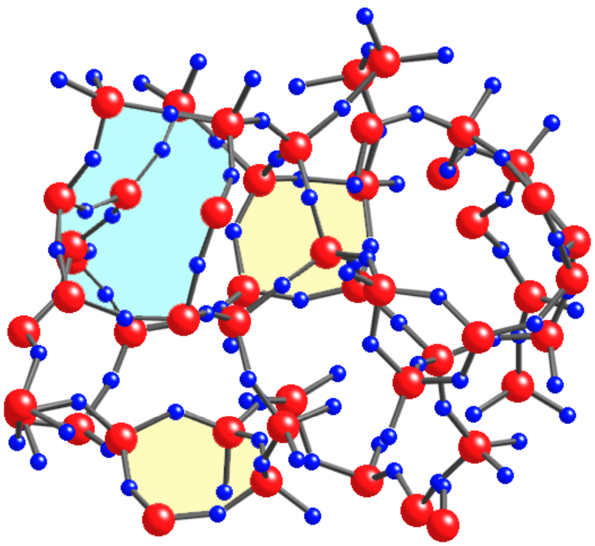
$$I_N(Q) = 4\pi \bar{b}^2 . S_N(Q)$$

$b(^{Nat}Si)$= 4.1491(10) fm and $b(^{29}Si)$=4.80(5) fm
Δb = 0.65 fm

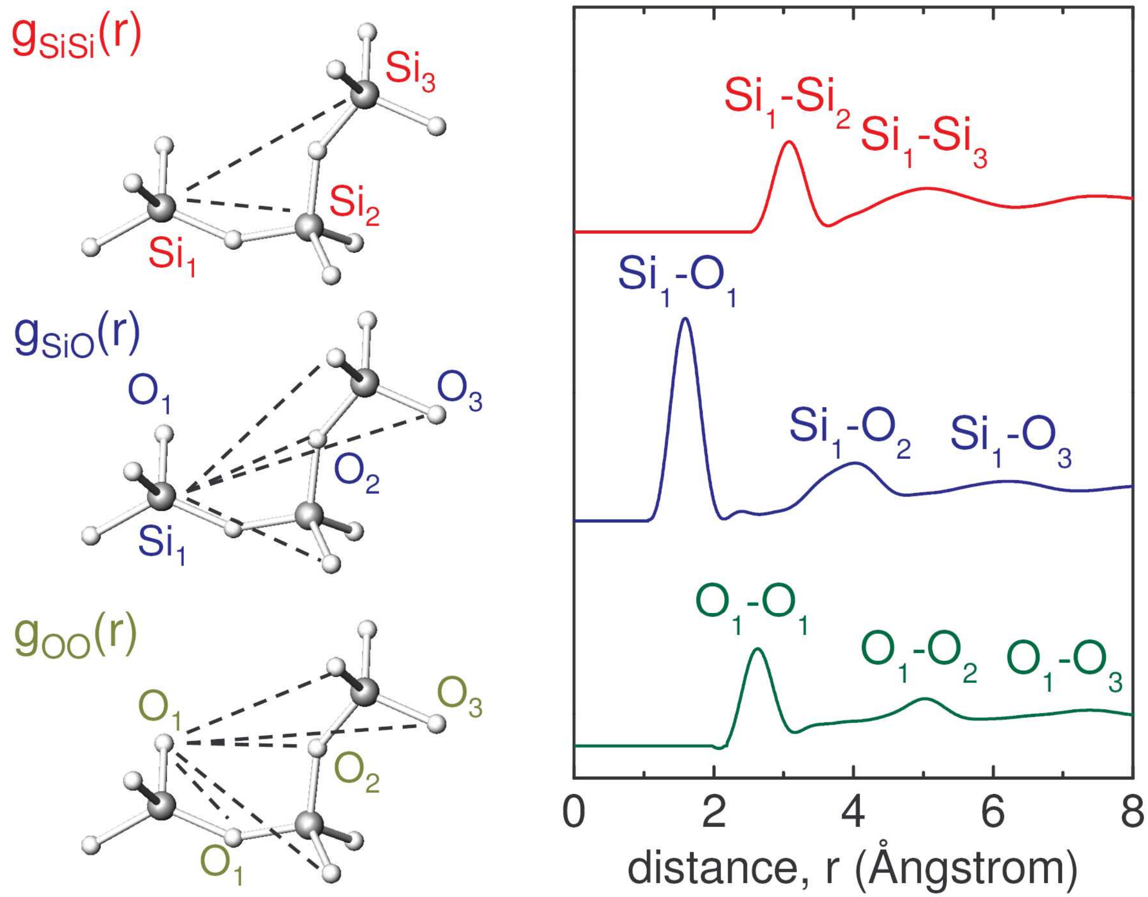


Phys. Rev. B. 78 (2008) 144204 .

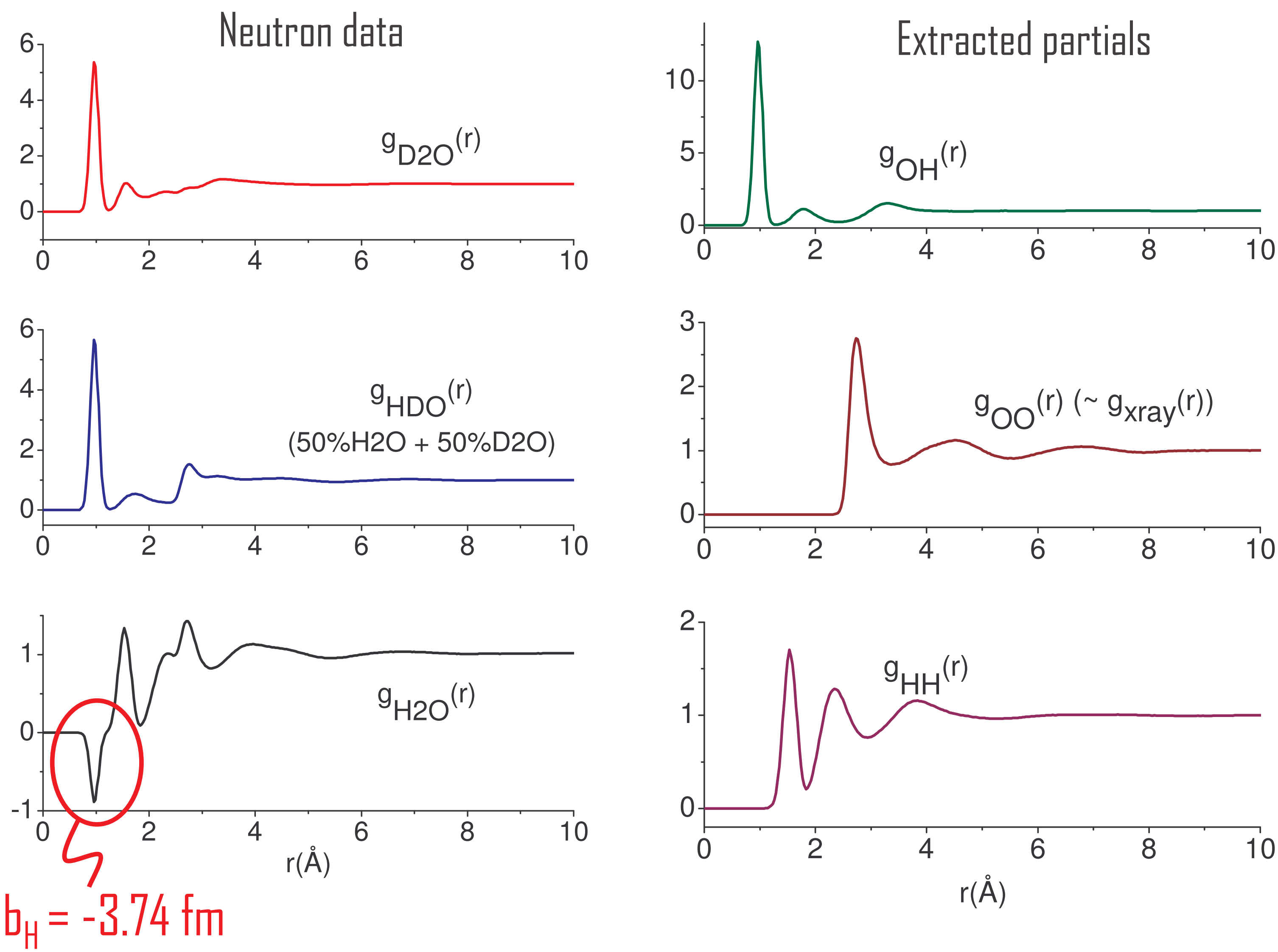
Partial Pair Distribution Functions of vitreous Silica



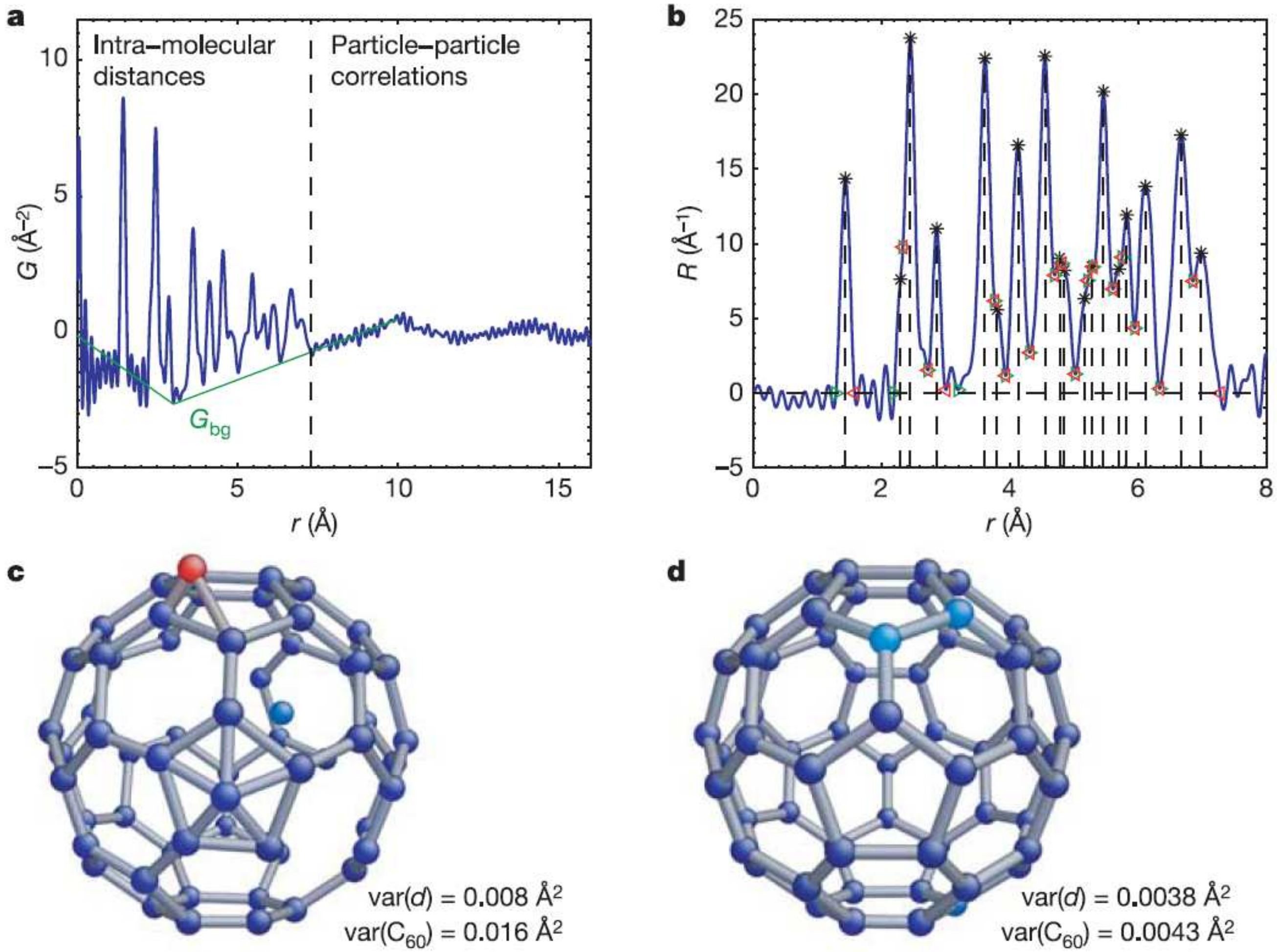
Courtesy of Shinji Kohara



H/D substitution : Partial Structure Factors for water



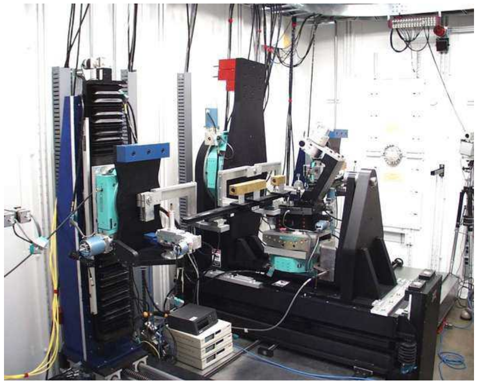
Solving the Nanoproblem

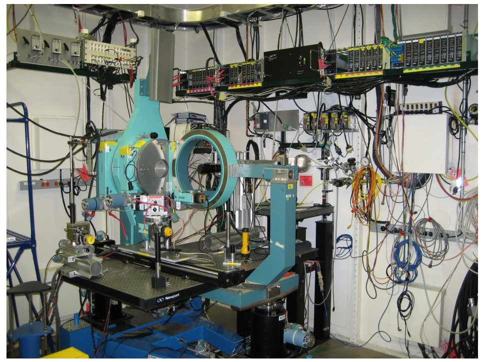


Nature 440 (2006) 655.

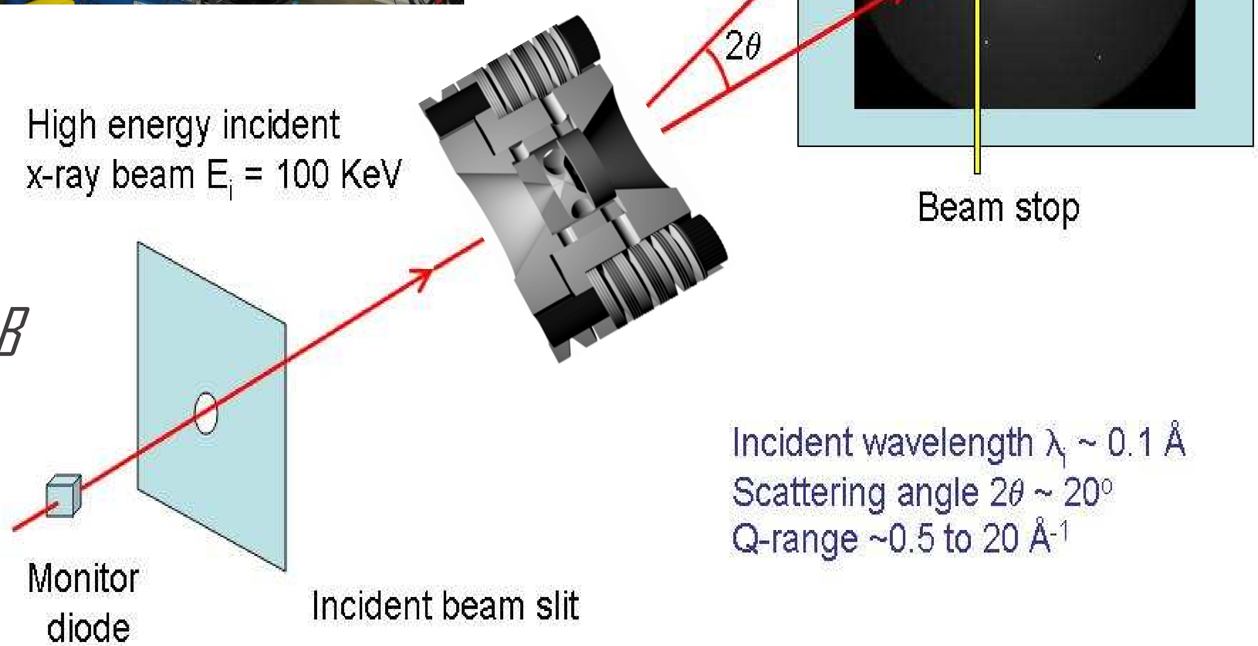
High energy x-ray beamlines at APS

11-ID-C

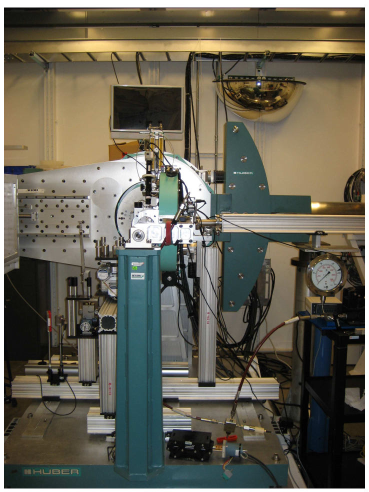




1-ID



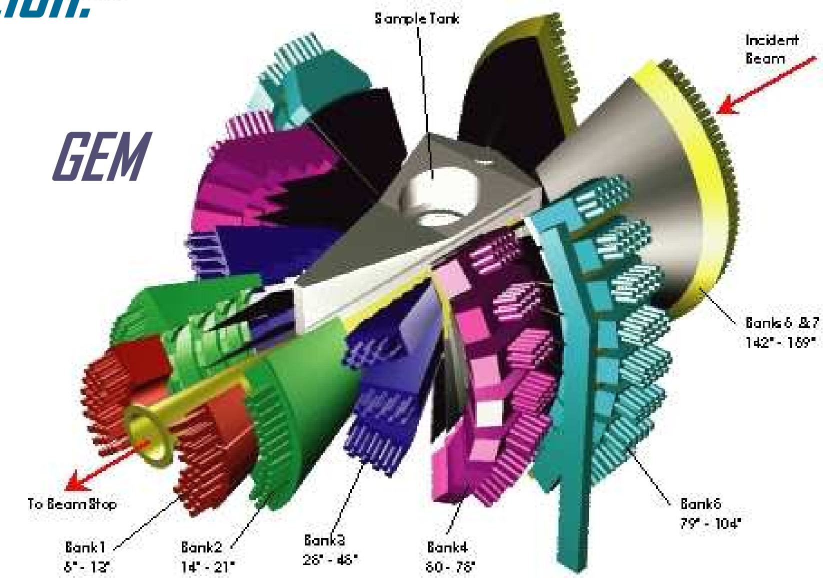
11-ID-B

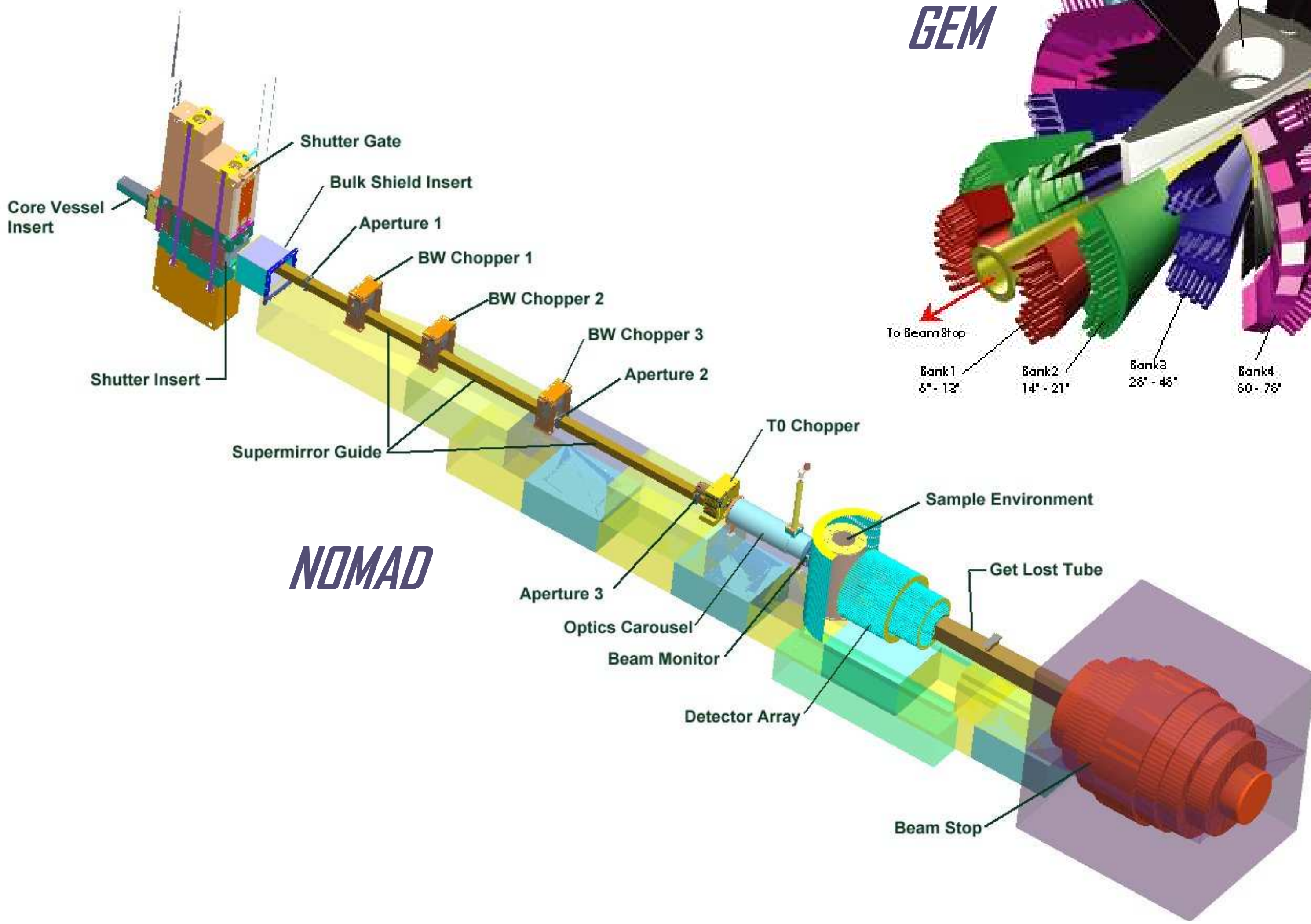


Incident wavelength λ_i ~ 0.1 Å
Scattering angle 2θ ~ 20°
Q-range ~0.5 to 20 $Å^{-1}$

State of the art neutron instrumentation.

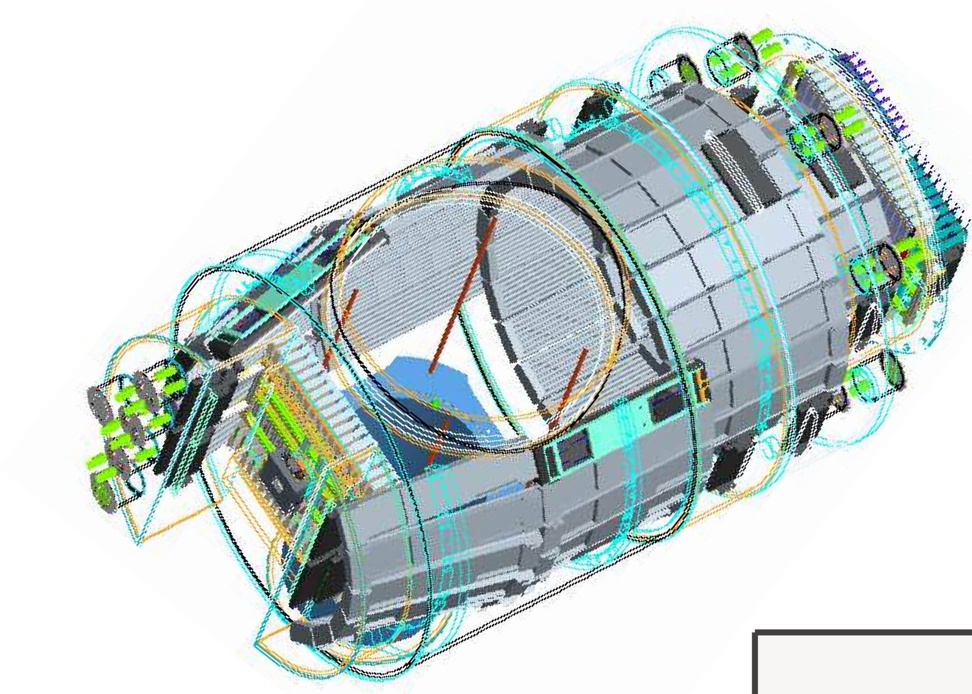
GEM



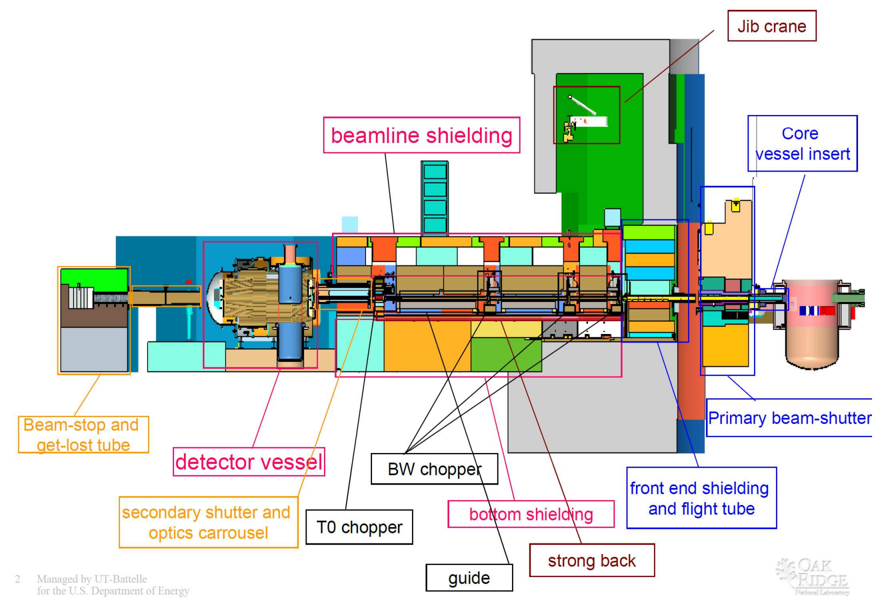


NOMAD

Nanoscale Ordered MAterials Diffractometer



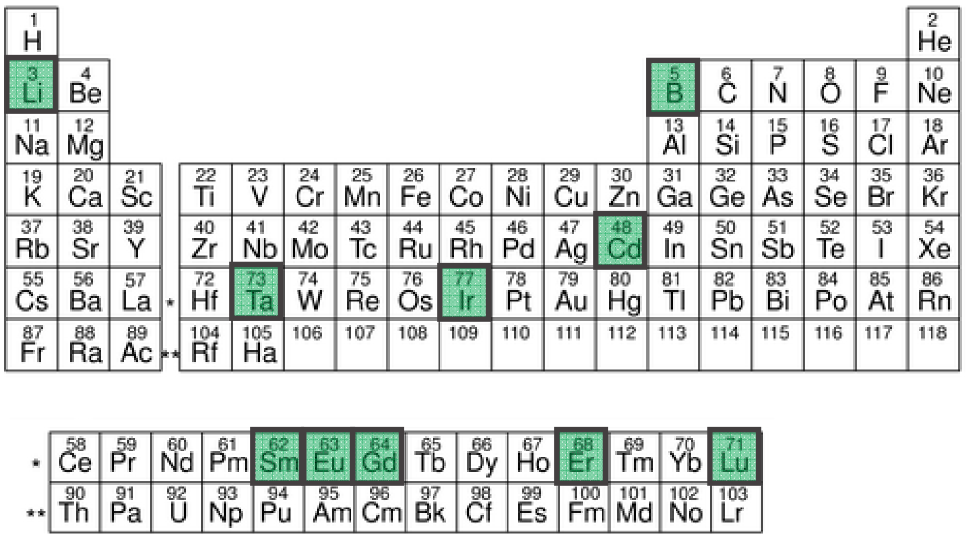
Courtesy of Joerg Neuefeind



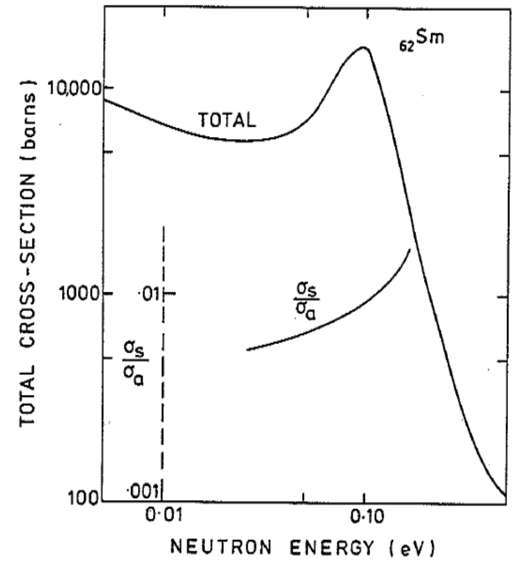
Online in 2011

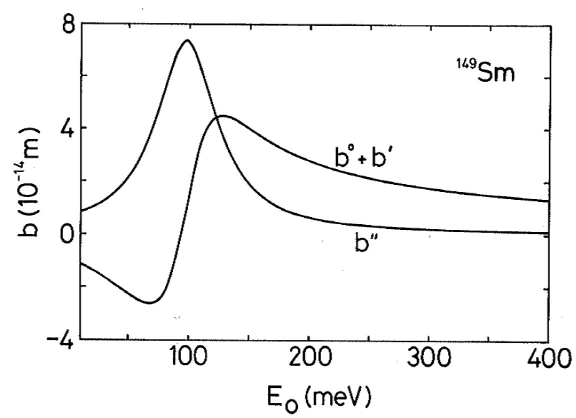
	D4c (ILL)	GEM (ISIS)	DRACULA (ILL Project)	NOMAD Project
Time averaged flux (10^8 n/cm^2)	0.4	~0.02	~1	~1.7 (1.4MW)
Detector coverage (strad)	0.11	4.0	1.5	~10
Product (10^6)	4.4	8	150	1700

Anomalous neutron diffraction - new possibilities at SNS

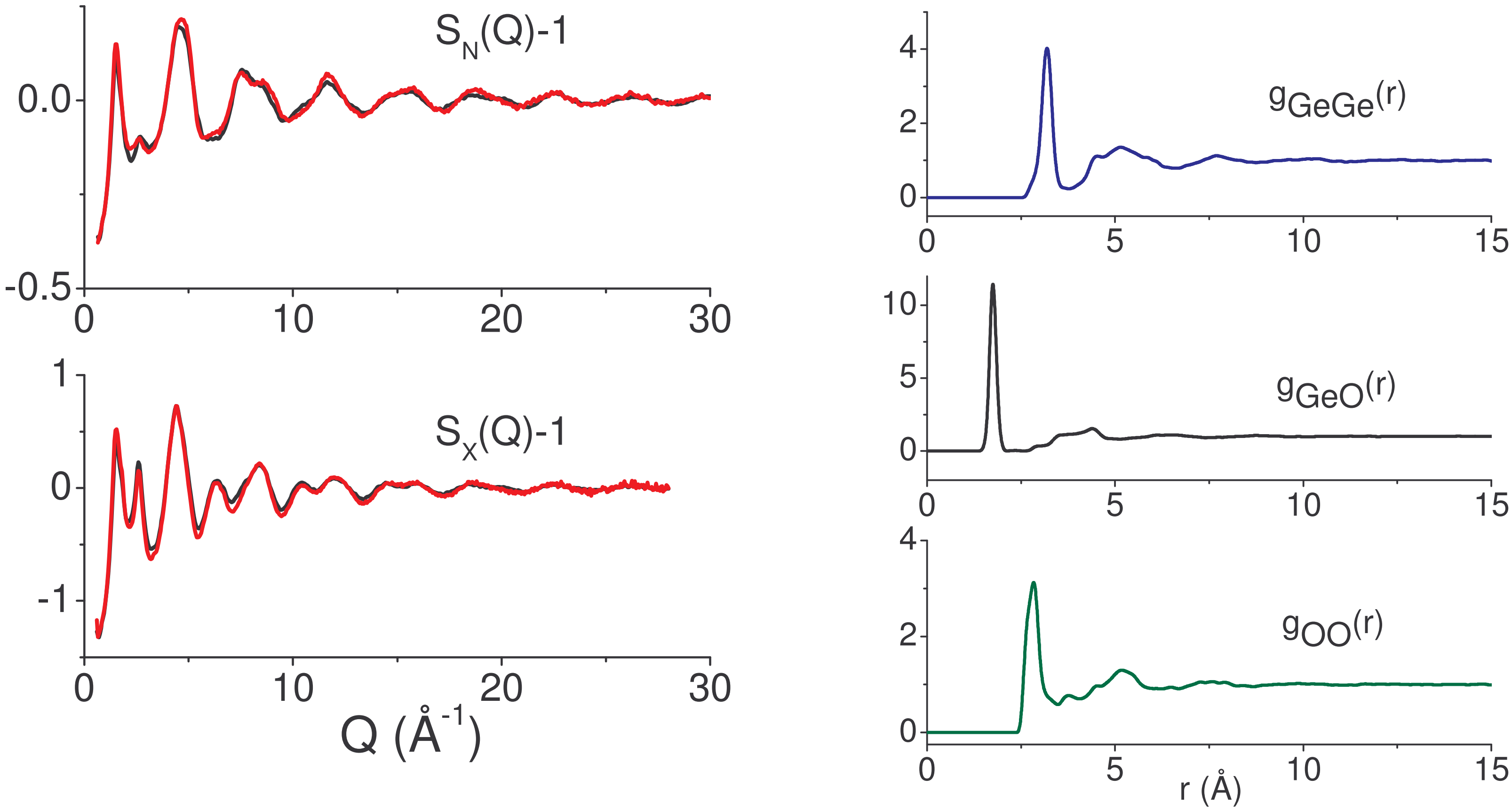


Anomalous Neutron Diffraction of Disordered Materials
R Sinclair. World Scientific p107. ISBN 981-02-1463-4.





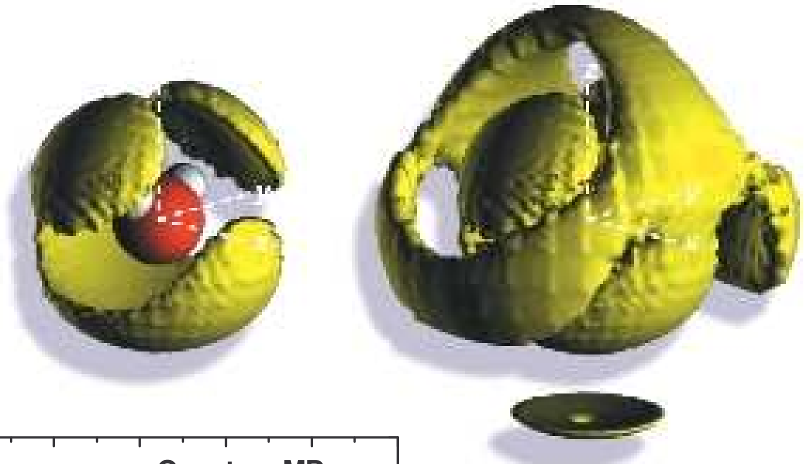
Reverse Monte Carlo Modeling of Neutron and X-ray data

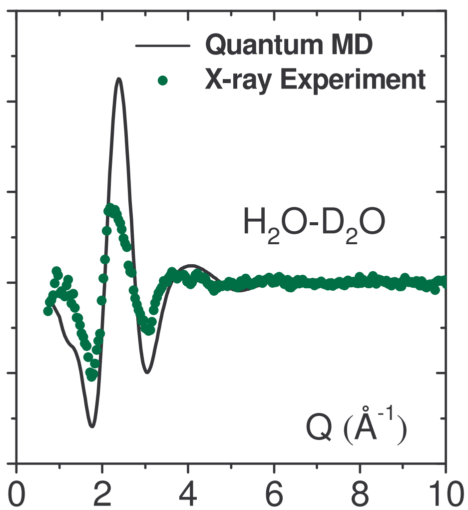


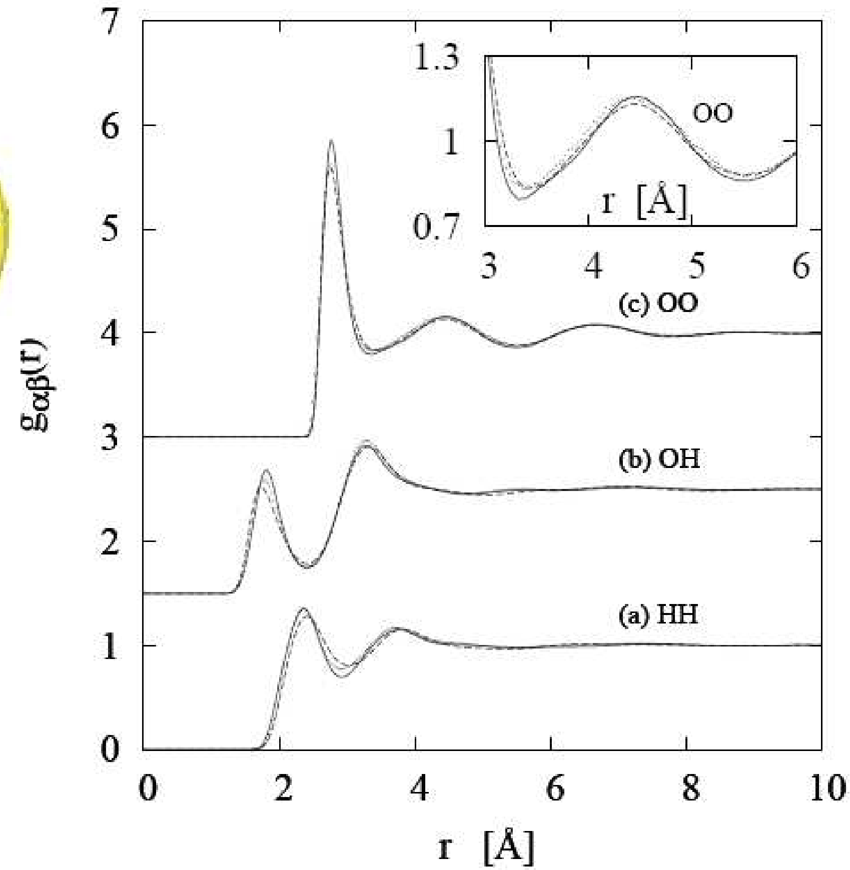
Best (essential ?) to use more than one structure factor plus chemical constraints

Empirical Potential Structure Refinement

Quantum isotope effects in water

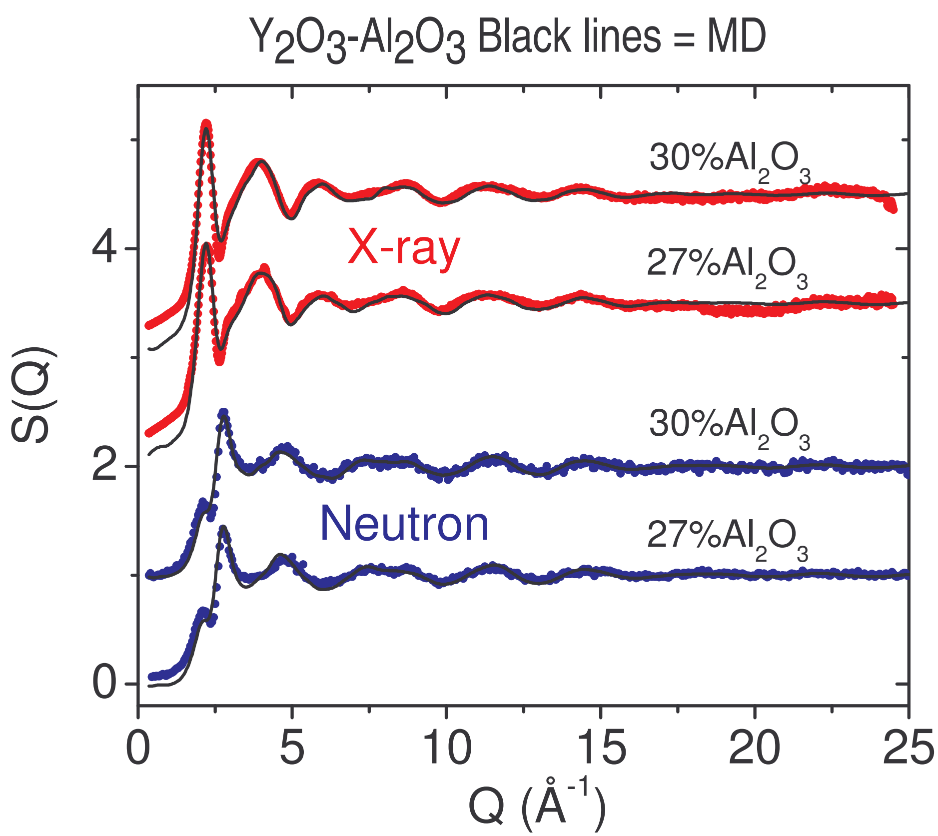


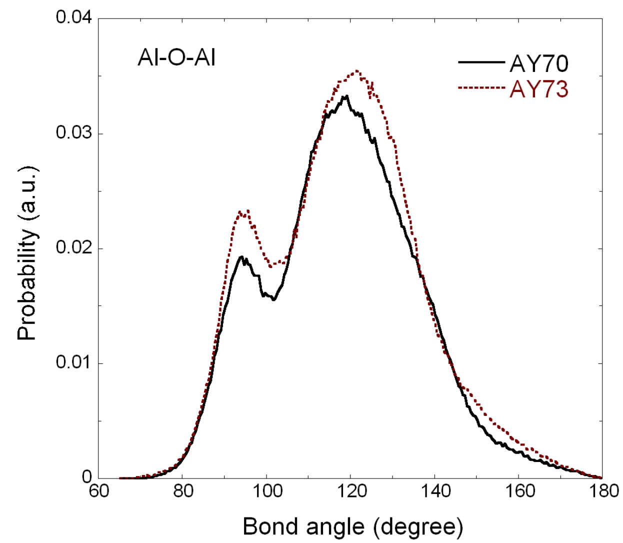


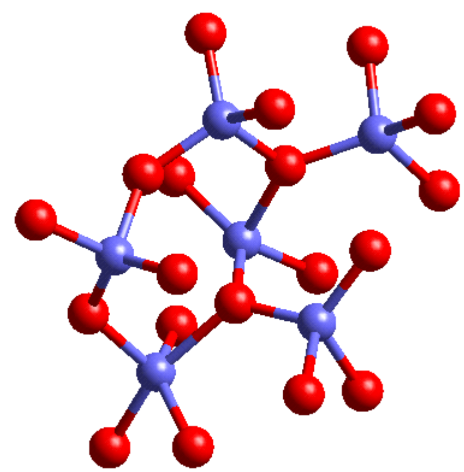


Phys. Rev. Lett., 101 (2008) 065502.

Molecular dynamics Simulations



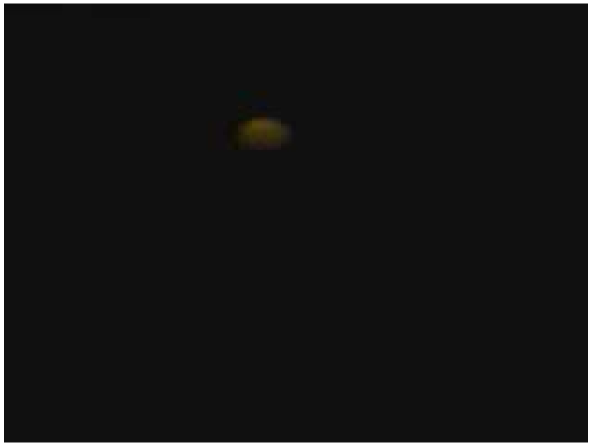




Tetrahedral oxygen triclusters in Yttria-Alumina glasses

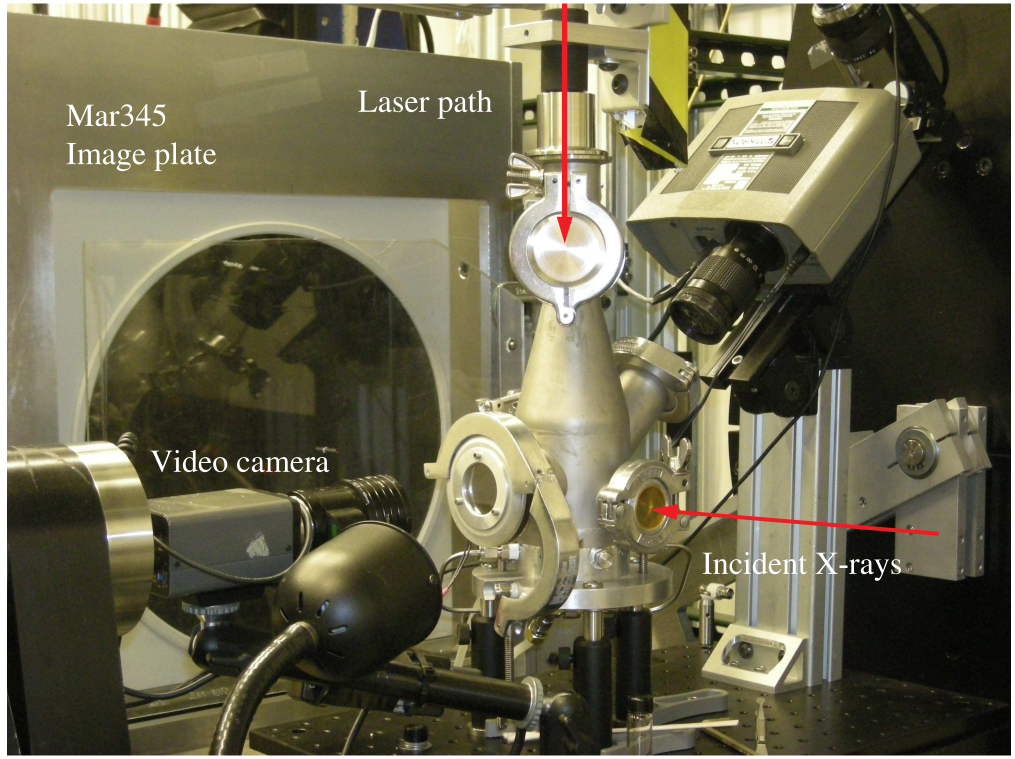
J. Phys.: Condens. Matter 21 (2009) 205102.

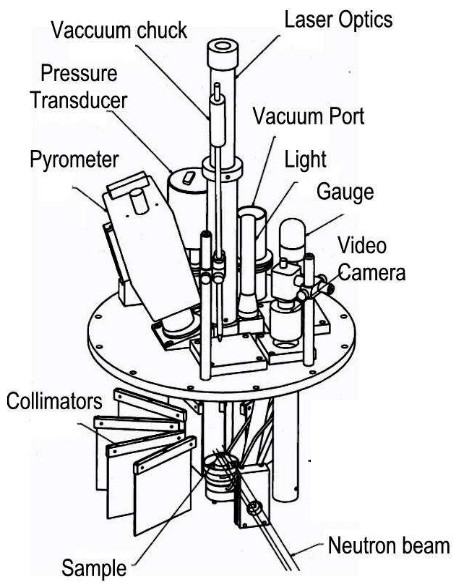
Specialized Sample Environments : Levitator



Tmax =300°C.

Supercool liquids several hundered degrees.

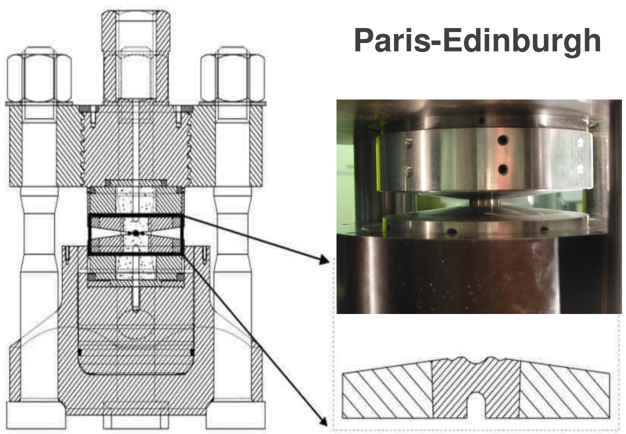


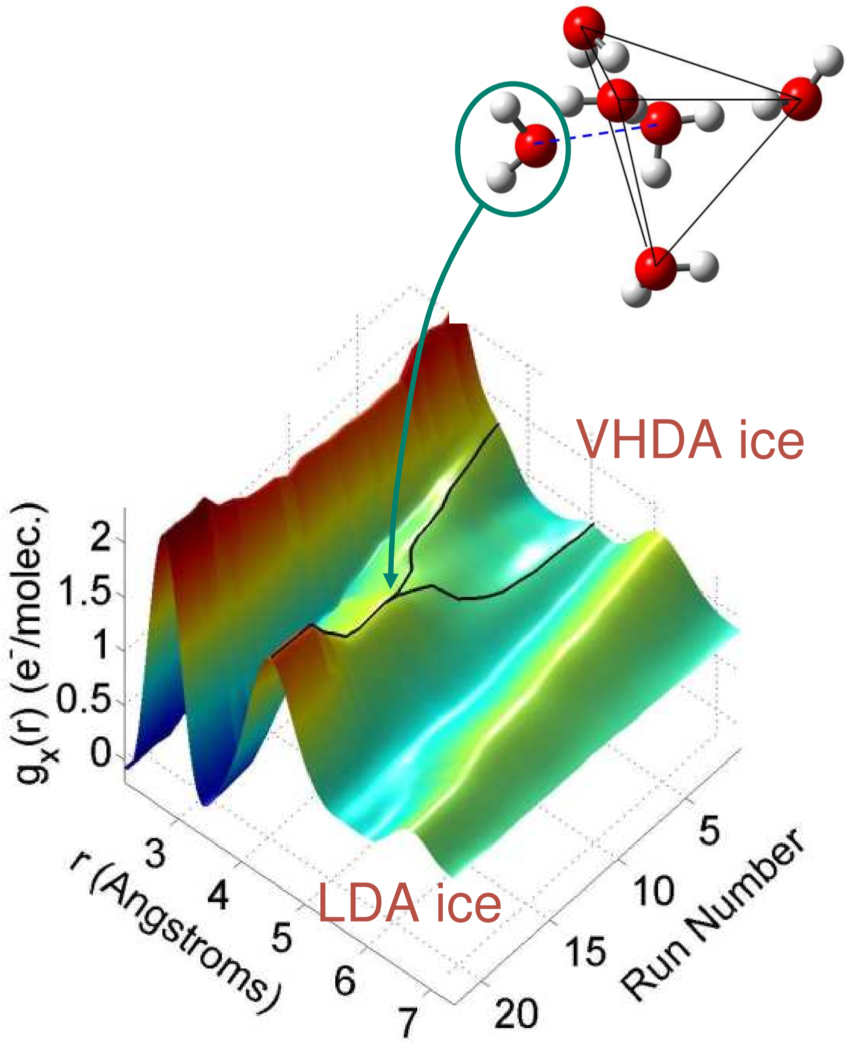


Phys. Rev. Lett., 98 (2007) 057802.

Specialized Sample Environments : High Pressure

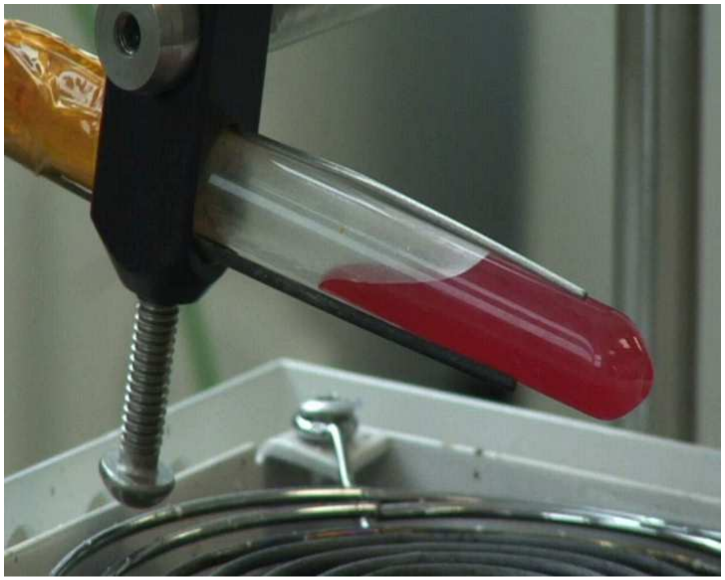
Paris-Edinburgh



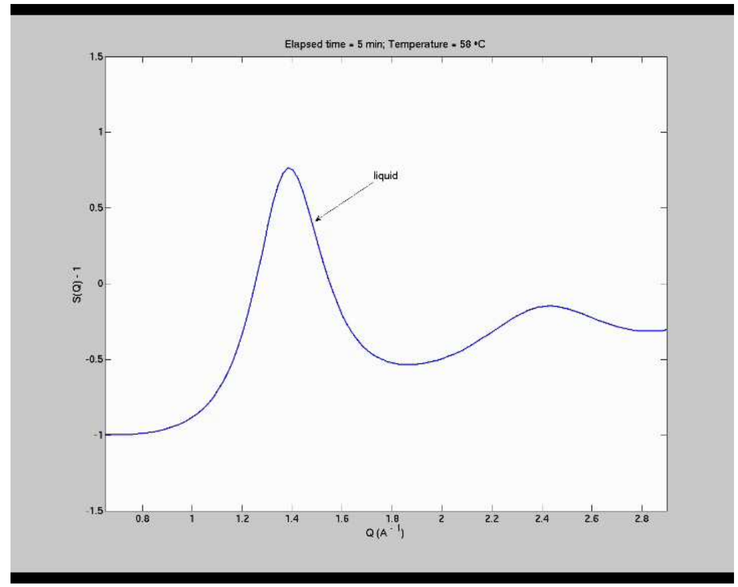


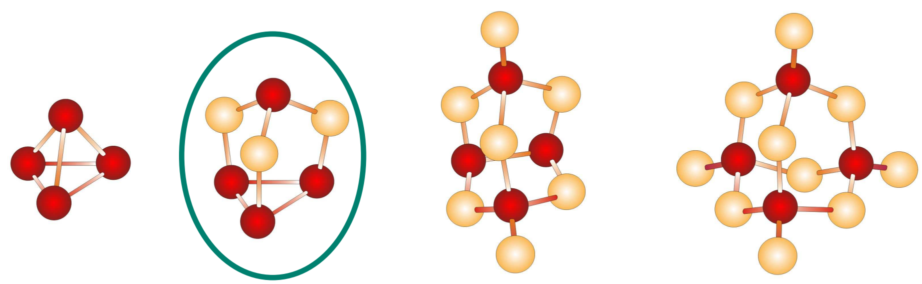
Phys. Rev. Lett., 97 (2006) 115503.
Science 297 (2002) 1320.

Time Resolved Measurements : Chemical Reactions



Courtesy of Eugene Bychkov





P_4 P_4S_3 P_4S_7 P_4S_{10}

Last slide

Chris's PDF guidelines

Real space peak position = bond length

Peak area α coordination number

Model disagrees with data = it's wrong!

No peaks = no atoms