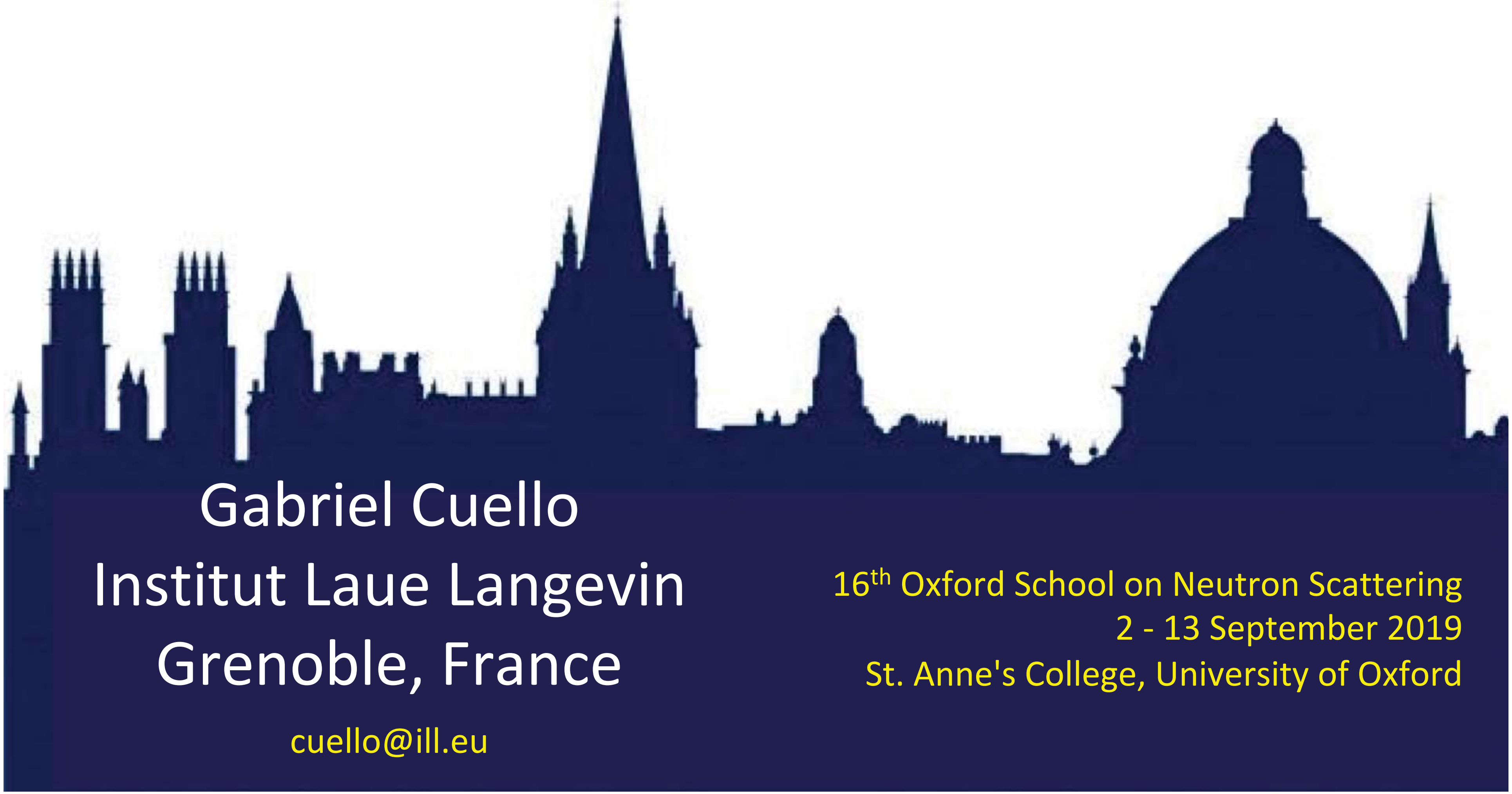
Structure of disordered materials

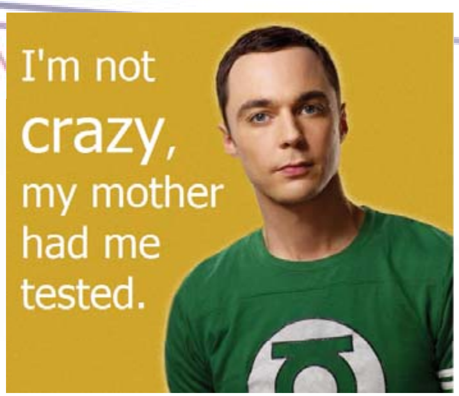


Gabriel Cuello
Institut Laue Langevin
Grenoble, France

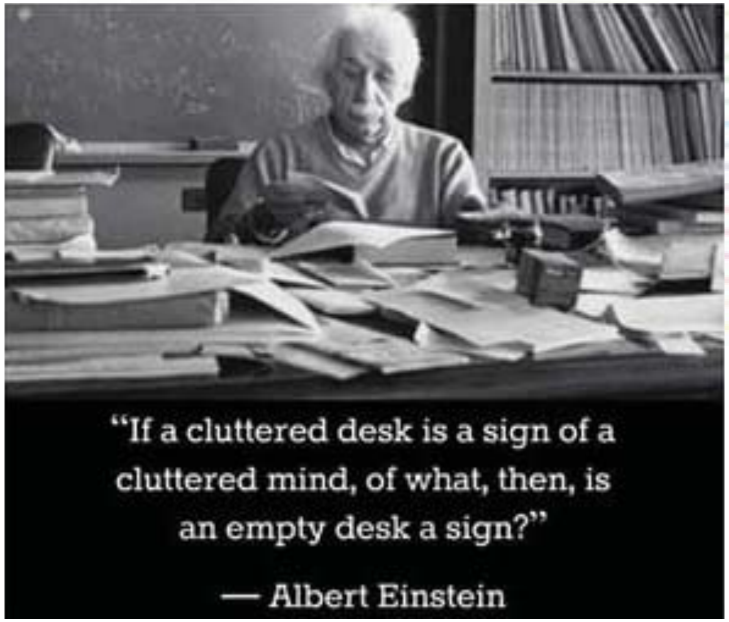
cuello@ill.eu

16th Oxford School on Neutron Scattering
2 - 13 September 2019
St. Anne's College, University of Oxford

Disorder

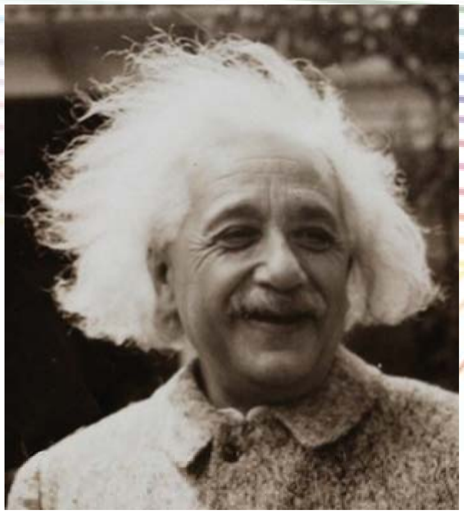


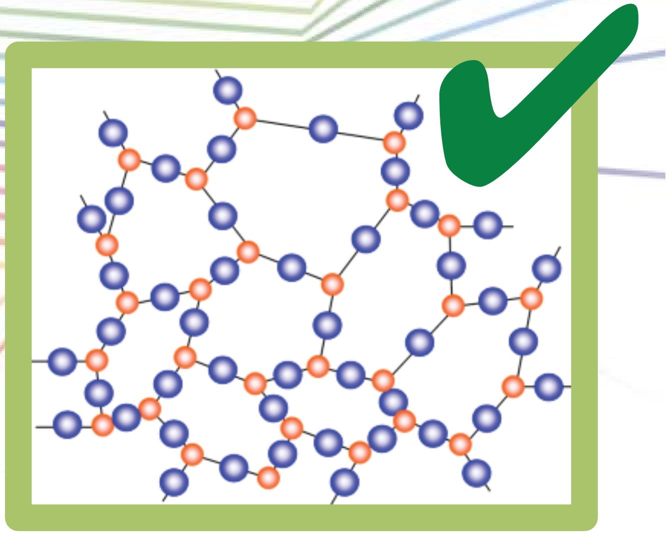
Disordered things



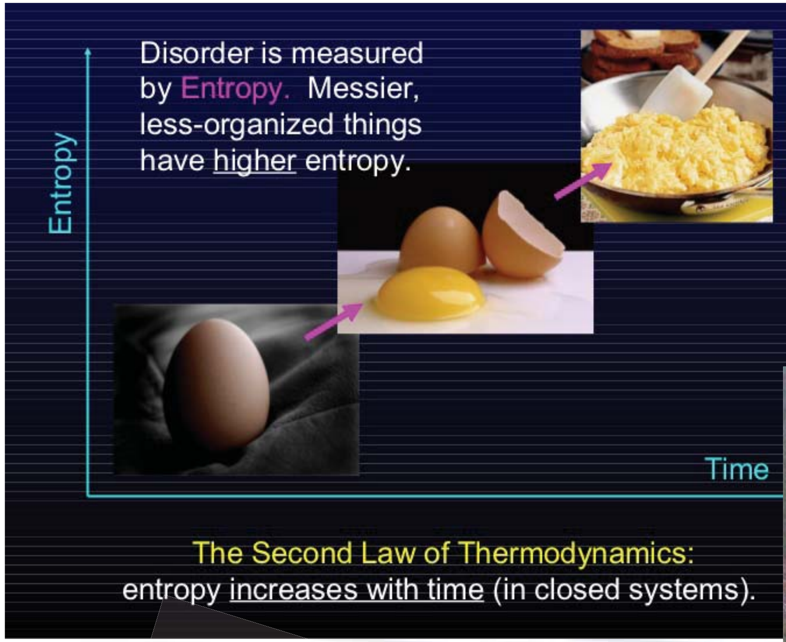
"If a cluttered desk is a sign of a cluttered mind, of what, then, is an empty desk a sign?"

— Albert Einstein





Disorder in Physics

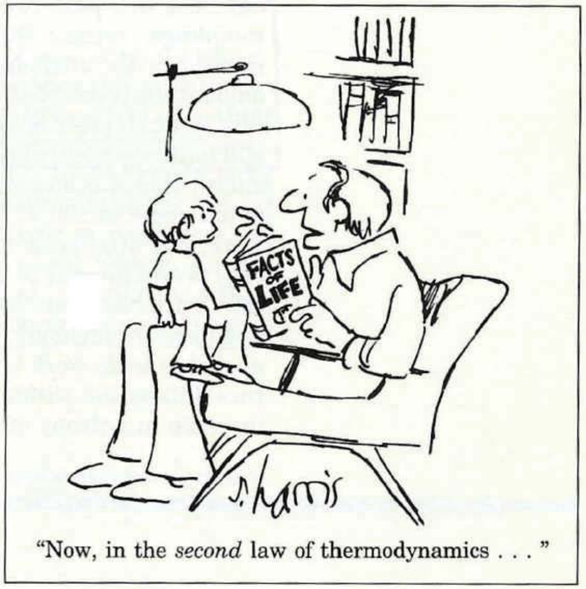


Disorder is measured by Entropy. Messier, less-organized things have higher entropy.

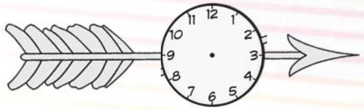
The Second Law of Thermodynamics:
entropy increases with time (in closed systems).

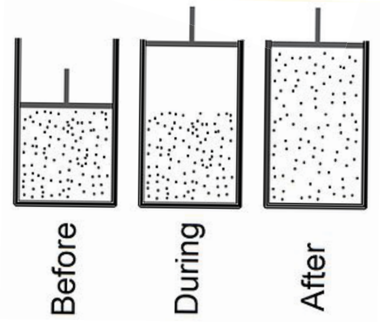
Entropy

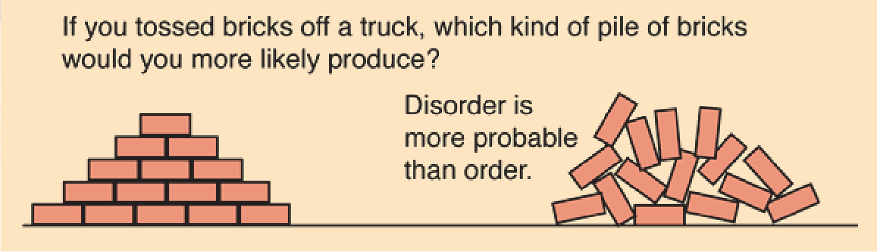
$$\frac{\mathrm{d}S}{\mathrm{d}t} > 0$$



“Now, in the *second* law of thermodynamics . . . ”







If you tossed bricks off a truck, which kind of pile of bricks would you more likely produce?

Disorder is more probable than order.

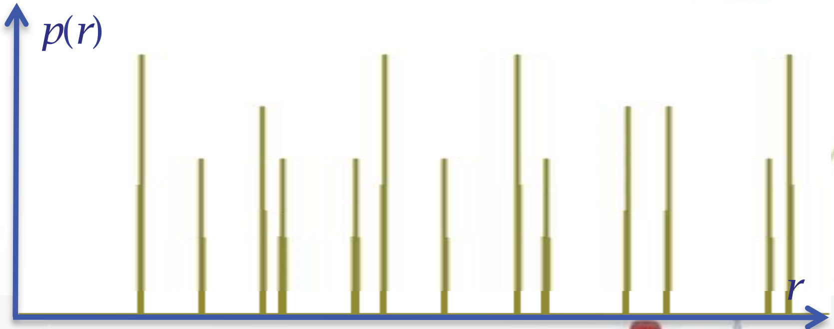
Order *vs* disorder

Disorder is fun

Creative clutter is better than idle neatness.

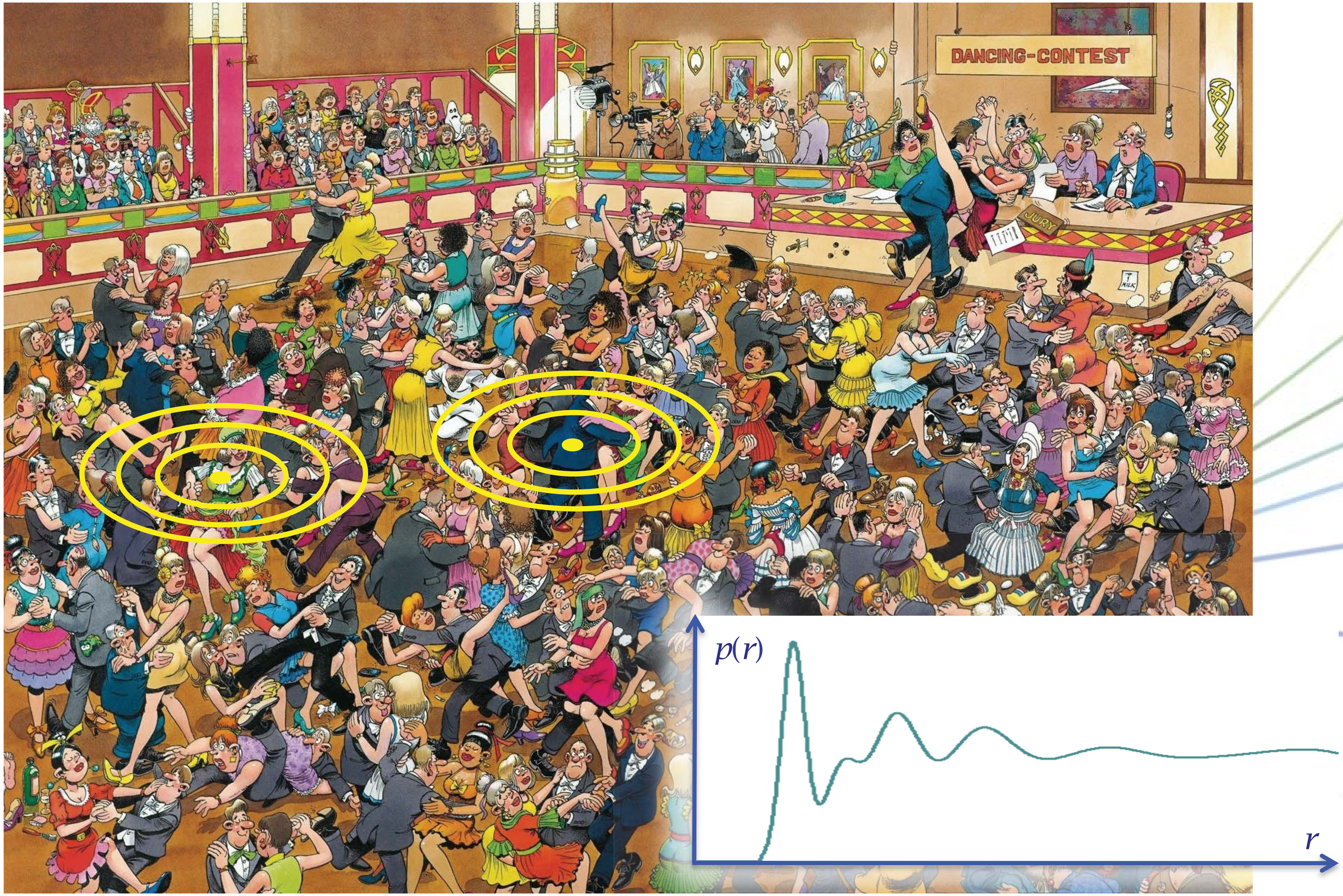
-Anonymous

Order is boring 😉



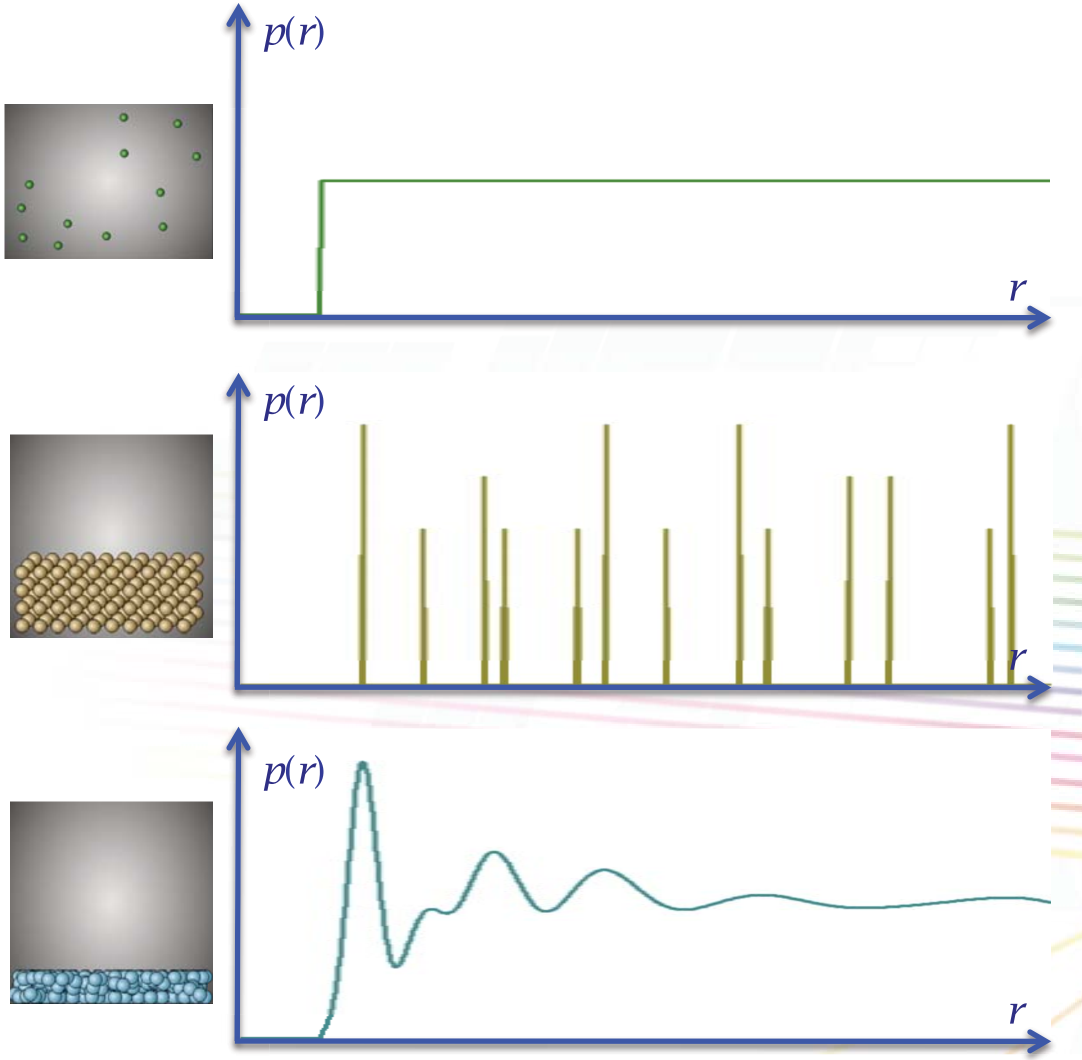
© Kim Jong-un

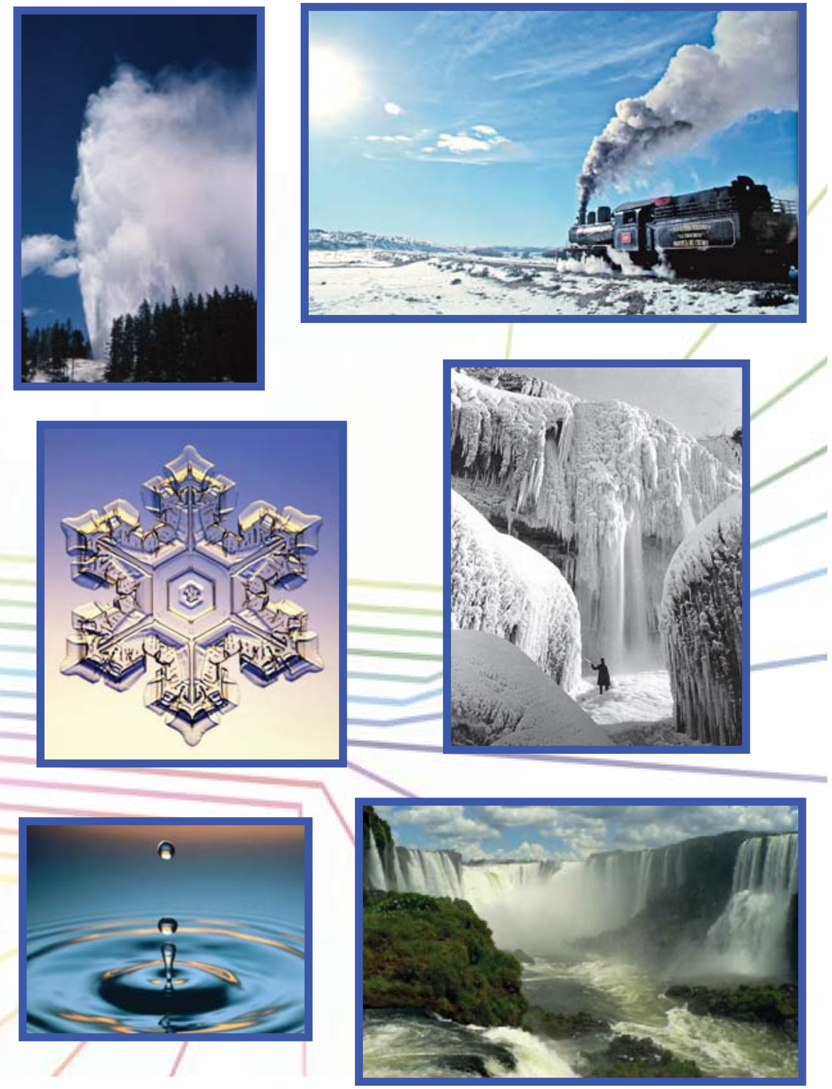
Pair distribution function



©Jan van Haasteren

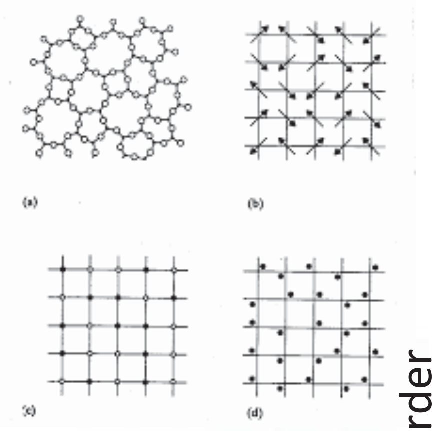
Structure in real space



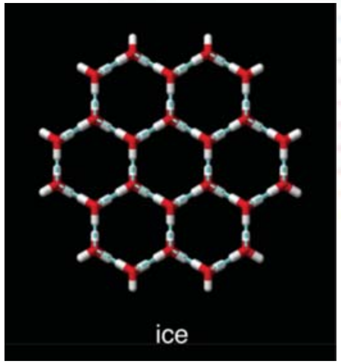


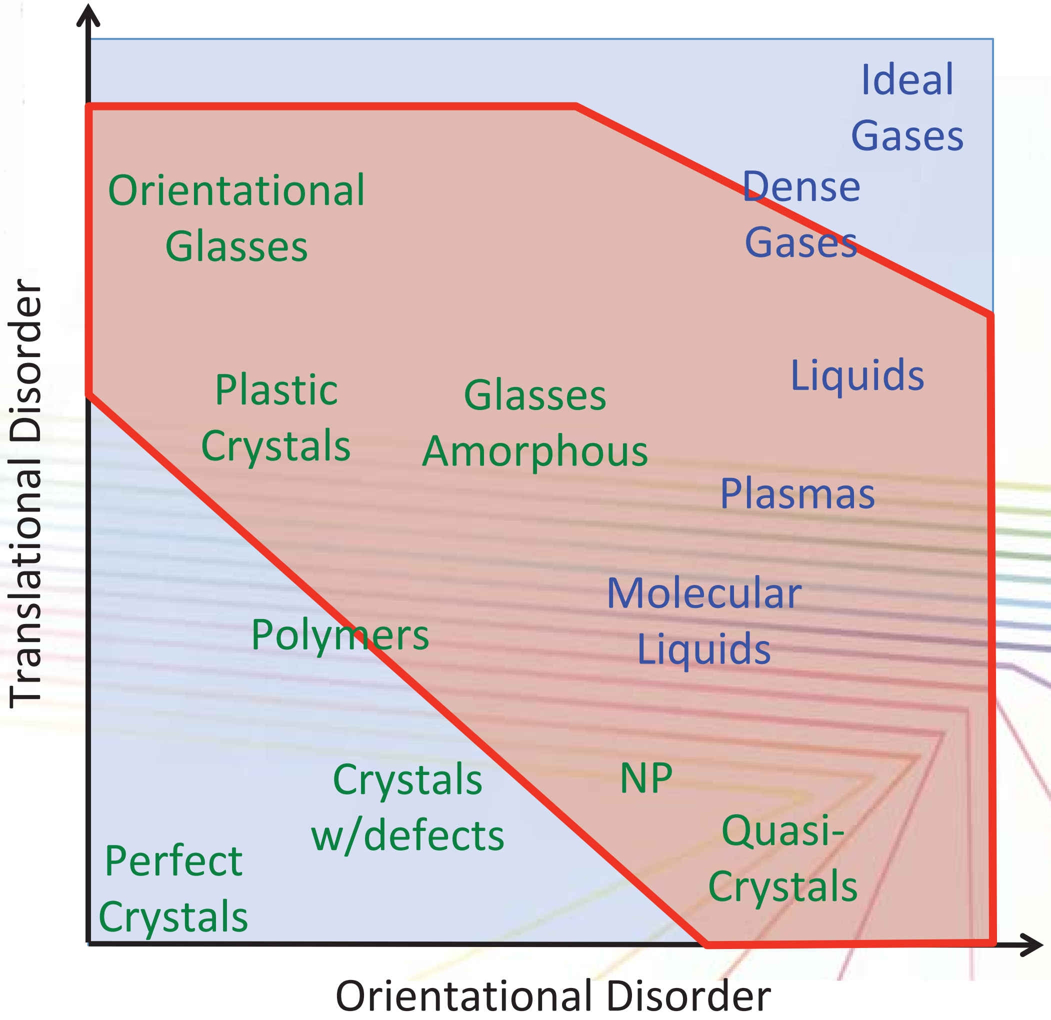
Disorder in solids and fluids

Total Scattering Techniques



Solids





Ideal Gases

Dense Gases

Orientational Glasses

Liquids

Plastic Crystals

Glasses Amorphous

Plasmas

Molecular Liquids

Polymers

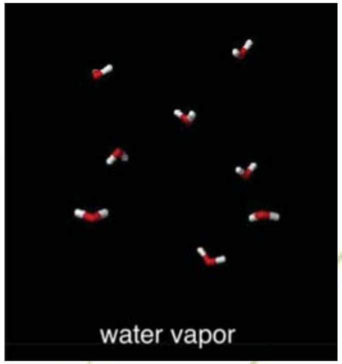
Crystals w/defects

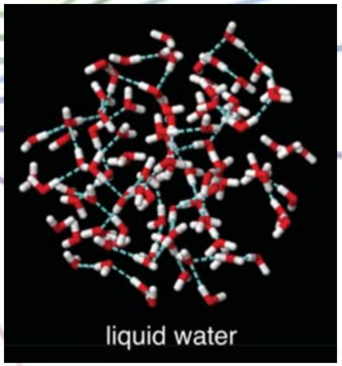
NP

Quasi-Crystals

Perfect Crystals

Fluids





Amorphous solids and glasses

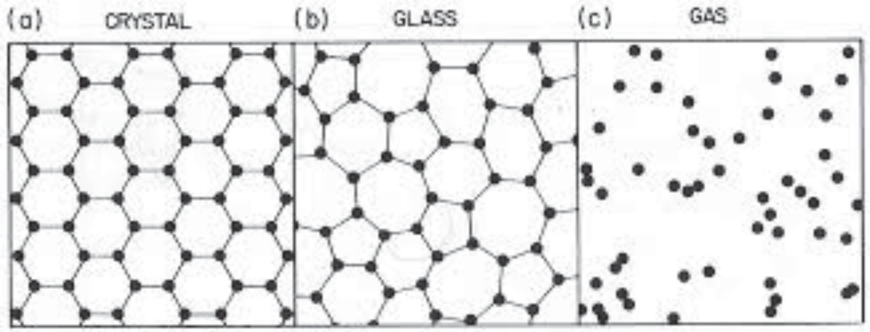
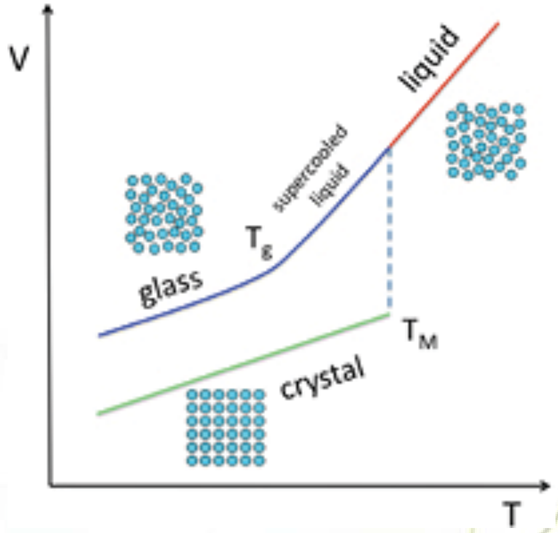
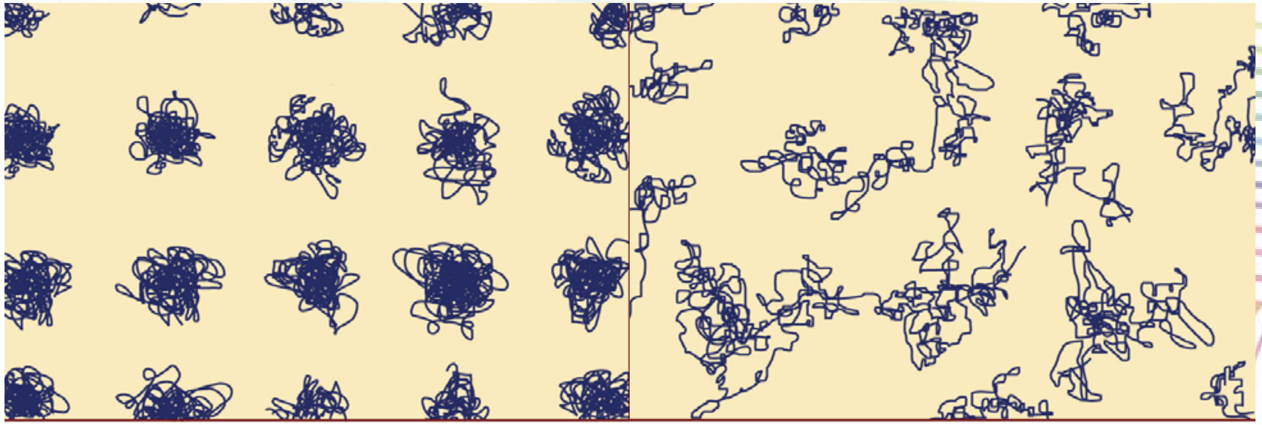


Figure 1.6 Schematic sketches of the atomic arrangements in (*a*) a crystalline solid, (*b*) an amorphous solid, and (*c*) a gas.

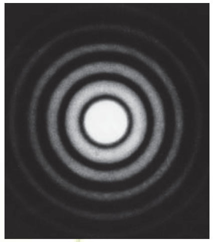




solid liquid

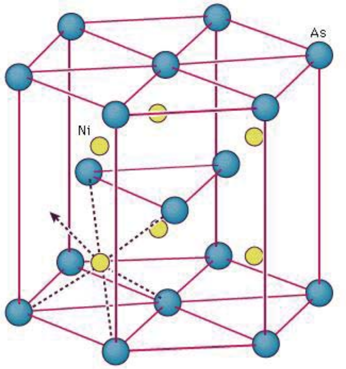
Structure by diffraction

Spatial distribution of atoms or molecules in the system



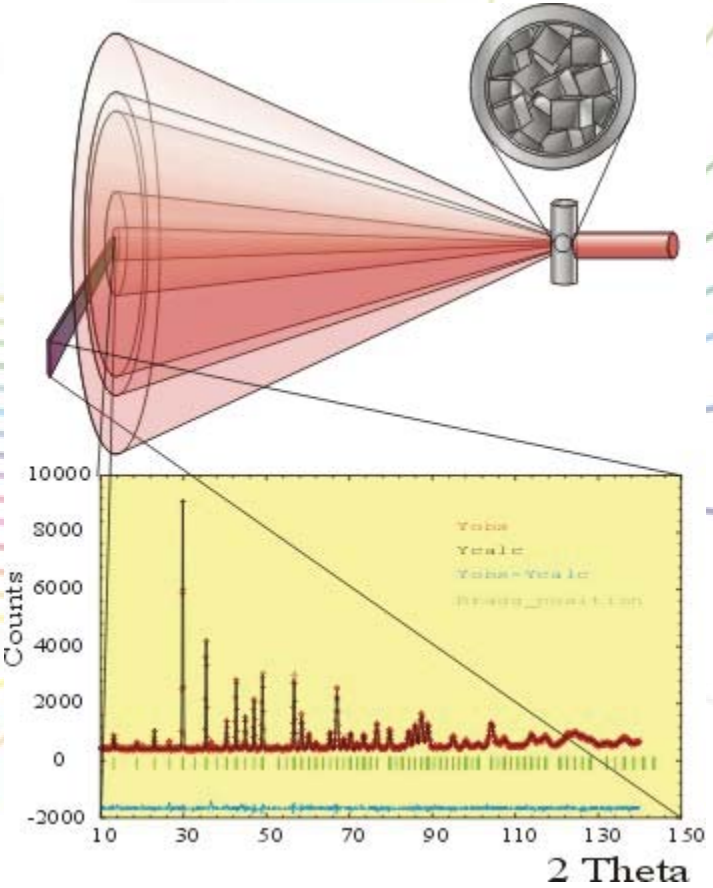
Crystalline solids

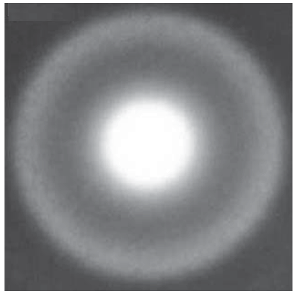
- Equilibrium positions
- Well defined Bragg peaks



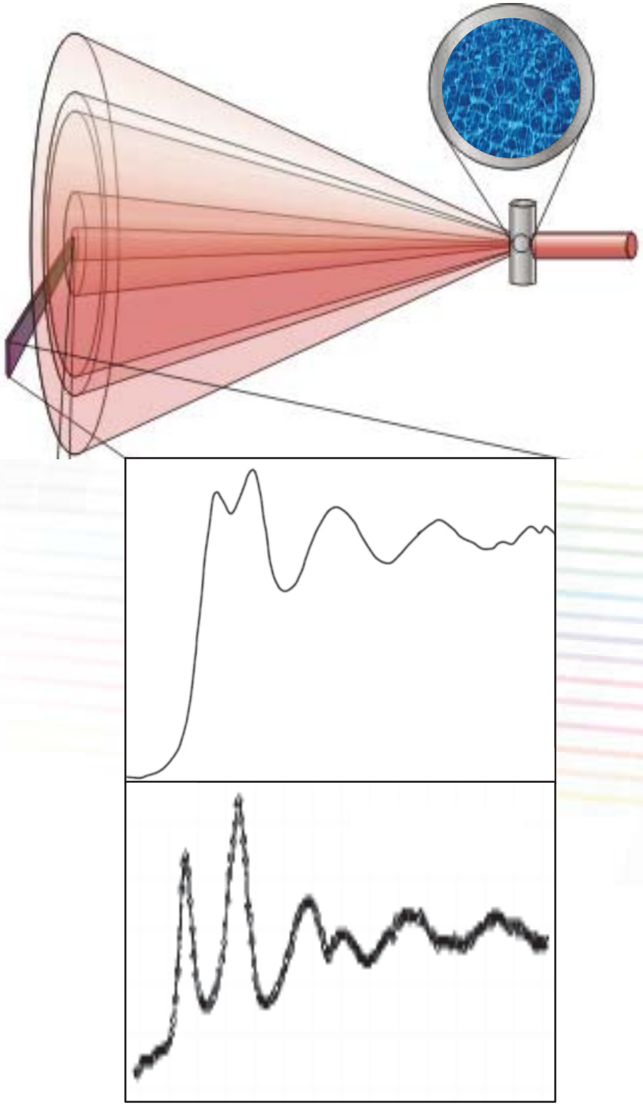
Disordered systems

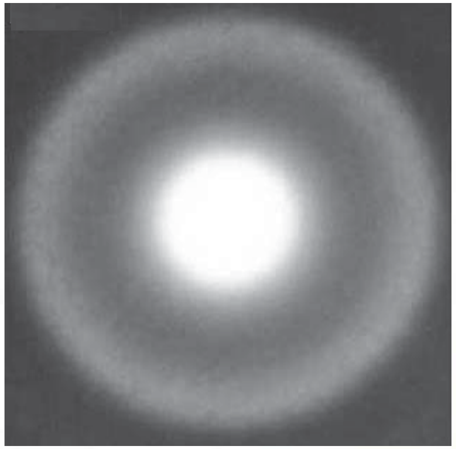
- Distribution of equilibrium positions
- No Bragg peaks

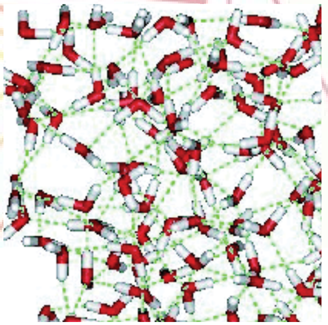




Disordered systems







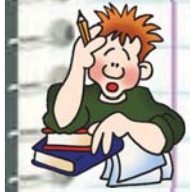
Structure factor for a gas

Exercise

A- Determine the static structure factor for a monoatomic gas of punctual non-interacting particles.

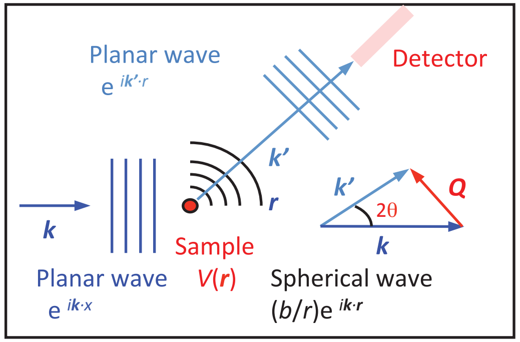
B- Determine the static structure factor for a gas where the particles have finite size and consequently an effective repulsion distance. Determine the maximum possible density of such a gas.

C- Study the low-Q limit of the structure factor. Should the structure factor be null at the origin?



Neutron scattering

Experiment → Microscopic properties



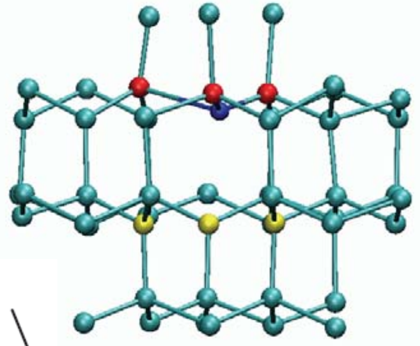
Intensity $I(2\theta,\omega)$ ● Scattering Cross Section $d^2\sigma/d\Omega d\omega$ ● Dynamical SF $S(\boldsymbol{Q},\omega)$

$$\overbrace{I(2\theta,\omega) = \underbrace{C\,\Phi_0}_{\text{Beam}}\,\underbrace{\frac{\mathrm{d}^2\sigma}{\mathrm{d}\sigma\mathrm{d}\omega}(2\theta,\omega)}_{\text{Sample}}\,\underbrace{\epsilon(k')}_{\text{Detector}}}$$

$$\overbrace{\frac{\mathrm{d}^2\sigma}{\mathrm{d}\sigma\mathrm{d}\omega}(2\theta,\omega) = N\,\underbrace{\frac{k'}{k}\,\frac{\sigma}{4\pi}}_{\text{Interaction}}\,\underbrace{S(\vec{Q},\omega)}_{\text{System}}}$$

Microscopic properties

Dynamical Structure Factor $S(\boldsymbol{Q},\omega)$



Microscopic Configuration

$\{\boldsymbol{r}_1(t), \boldsymbol{r}_2(t), \ldots , \boldsymbol{r}_N(t)\}$

$$S(\vec{Q},\omega) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} \mathrm{d}t\ \mathrm{e}^{-\mathrm{i}\omega t}\ \frac{1}{N}\sum_{i,j}^{N} \left\langle \mathrm{e}^{-\mathrm{i}\vec{Q}\cdot\vec{r}_i(0)}\mathrm{e}^{-\mathrm{i}\vec{Q}\cdot\vec{r}_j(t)} \right\rangle$$

$$\delta(\vec{r}) = \frac{1}{(2\pi)^3}\int\limits_{\text{all }\vec{Q}} \mathrm{e}^{\mathrm{i}\vec{Q}\cdot\vec{r}}\mathrm{d}\vec{Q}$$

$$\rho(\vec{r},t) = \sum_{i=1}^{N} \delta\left(\vec{r}-\vec{r}_i(t)\right)$$

Microscopic particle density

$$S(\vec{Q},\omega) = \frac{1}{2\pi}\iint \mathrm{d}\vec{r}\mathrm{d}t\ \mathrm{e}^{\mathrm{i}(\vec{Q}\cdot\vec{r}-\omega t)}G(\vec{r},t)$$

Probability density of having a given atom somewhere,
e.g. at (**0**, 0), and *any* atom at (***r***, *t*)

van Hove’s correlation function

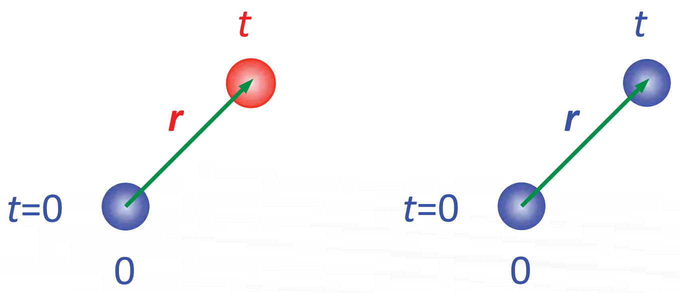
$$G(\vec{r},t) = \frac{1}{N}\int \mathrm{d}\vec{r'}\left\langle \rho(\vec{r'},0)\rho(\vec{r}+\vec{r'},t)\right\rangle$$

Correlation functions

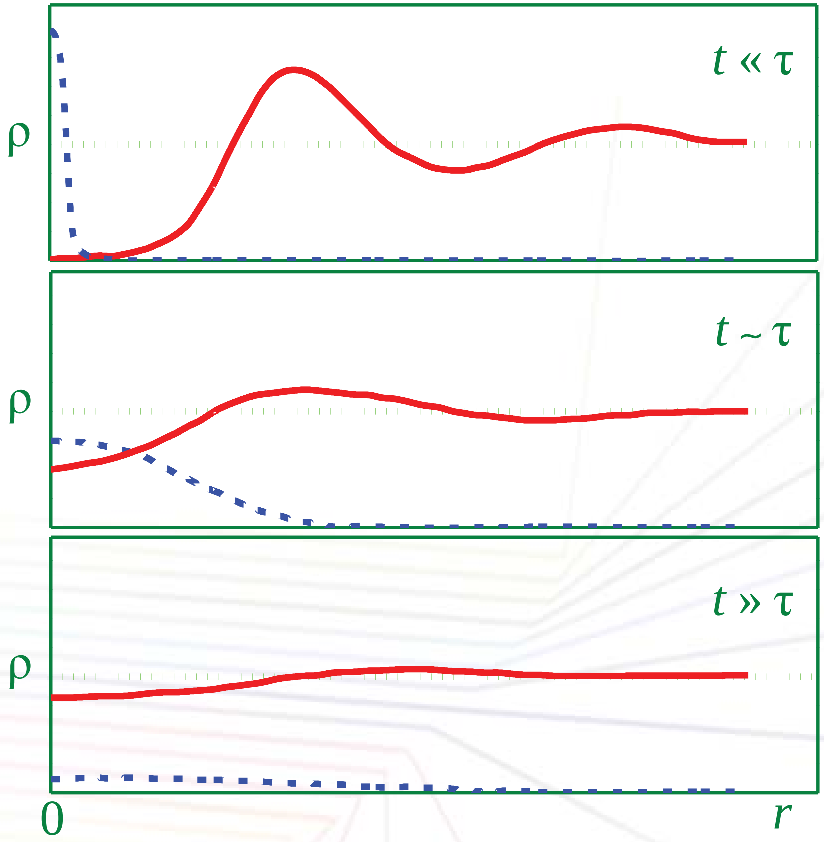
distinct self

$$G(\mathbf{r}, t) = G_\mathrm{d}(\mathbf{r}, t) + G_\mathrm{s}(\mathbf{r}, t)$$

$\alpha \neq \beta$ $\alpha = \beta$



Normalisation	N	$N-1$	1
Large r	ρ	ρ	0
Large t	ρ	ρ	0

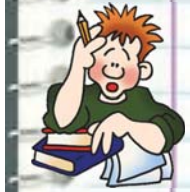


$$\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega\mathrm{d}\omega}(2\theta,\omega) = N\frac{k'}{k}\left\{|\langle b\rangle|^2\,\underset{\text{distinct}}{S_\mathrm{d}(\vec{Q},\omega)} + \langle|b|^2\rangle \underset{\text{self}}{S_\mathrm{s}(\vec{Q},\omega)}\right\}$$

Coherent and incoherent xs

Exercise

Starting with the total scattering cross section and considering the self and distinct contributions, derive the expression showing explicitly the coherent and incoherent contributions.



Coherent and incoherent scattering

$$\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega\mathrm{d}\omega}(2\theta,\omega) = N\frac{k'}{k}\left\{\frac{\sigma_{\mathrm{coh}}}{4\pi}S(\vec{Q},\omega) + \left(\frac{\sigma_{\mathrm{inc}}}{4\pi}\right)S_{\mathrm{s}}(\vec{Q},\omega)\right\}$$

coherent

incoherent

Diffusive
Motions
Internal
Dynamics

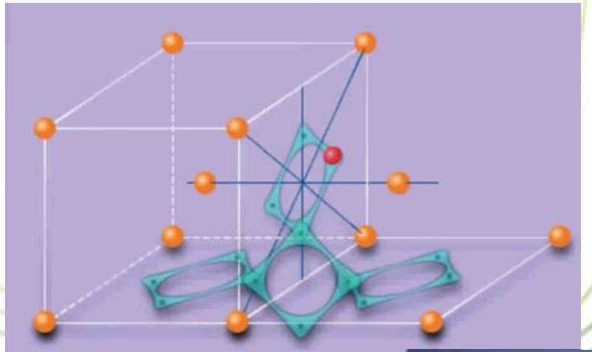
$$\sigma_{\mathrm{coh}} = 4\pi\,|\langle b\rangle|^2$$ squared mean

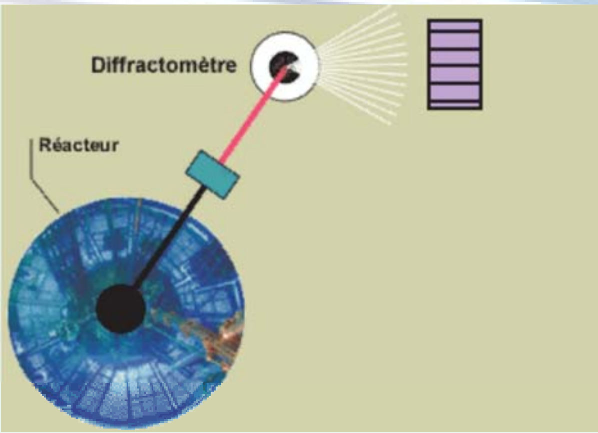
$$\sigma_{\mathrm{inc}} = 4\pi\left(\langle|b|^2\rangle - |\langle b\rangle|^2\right)$$ variance

Scattering cross section $\sigma = \sigma_{\mathrm{coh}} + \sigma_{\mathrm{inc}}$

Structural information
Collective dynamics

Diffraction
(no energy discrimination)





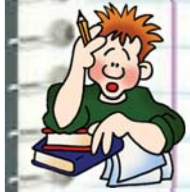
Static structure factor

Exercises

Find the relationship between the van Hove time-dependent correlation function $G(\boldsymbol{r},t)$ and the static structure factor $S(\boldsymbol{Q})$.

Propose an expression for the static correlation function using the macroscopic density of the material and the real space pair distribution function $g(\boldsymbol{r})$.

Using this expression, find the relationship between the static structure factor $S(\boldsymbol{Q})$ and and $g(\boldsymbol{r})$.



Static structure factor

$$S(\vec{Q}) = \int_{-\infty}^{+\infty} \mathrm{d}\omega\; S(\vec{Q},\omega) = \int \mathrm{d}\vec{r}\; \mathrm{e}^{\mathrm{i}\vec{Q}\cdot\vec{r}} G(\vec{r},0)$$

Static approximation

S(Q)-1 & g(r)-1 become a FT pair

$$S(\vec{Q}) - 1 = \rho \int_V \mathrm{d}\vec{r}\; [g(\vec{r}) - 1]\; \mathrm{e}^{\mathrm{i}\vec{Q}\cdot\vec{r}}$$

$$\rho\,[g(\vec{r}) - 1] = \frac{1}{(2\pi)^3} \int \mathrm{d}\vec{Q}\; \left[S(\vec{Q}) - 1\right]\; \mathrm{e}^{-\mathrm{i}\vec{Q}\cdot\vec{r}}$$

Definition

$$F(\vec{Q}) = S(\vec{Q}) - 1$$

$$G(\vec{r}) = 4\pi\rho r\,[g(\vec{r}) - 1]$$

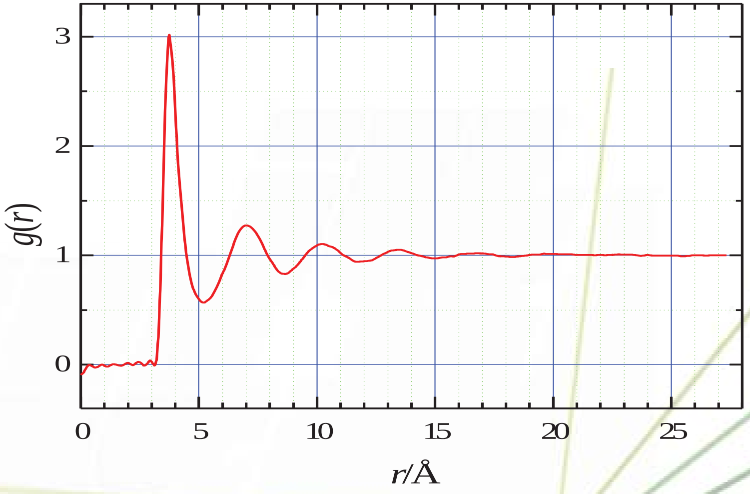
$$F(\vec{Q}) = \int_V \mathrm{d}\vec{r}\; \frac{G(\vec{r})}{4\pi r}\; \mathrm{e}^{\mathrm{i}\vec{Q}\cdot\vec{r}}$$

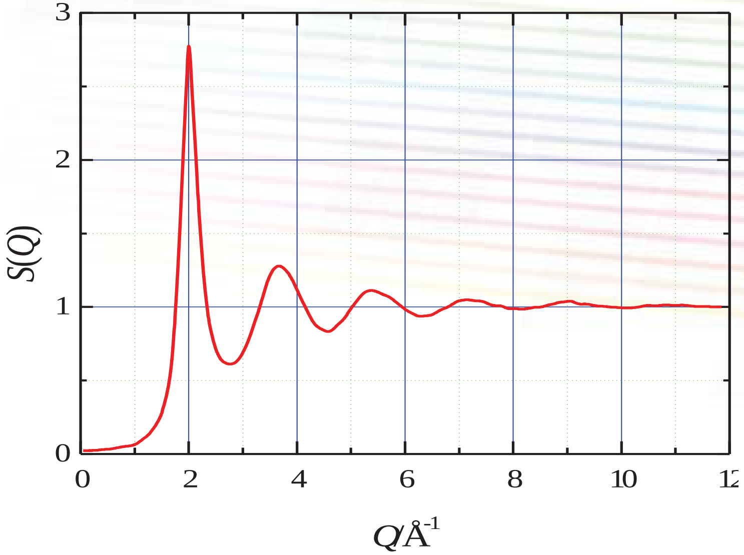
$$\frac{G(\vec{r})}{4\pi r} = \frac{1}{(2\pi)^3} \int \mathrm{d}\vec{Q}\; F(\vec{Q})\; \mathrm{e}^{-\mathrm{i}\vec{Q}\cdot\vec{r}}$$

Isotropic case

$$Q\ F(Q) = \int_0^\infty G(r)\ \sin(Qr)\ \mathrm{d}r$$

$$G(r) = \frac{2}{\pi}\int_0^\infty Q\ F(Q)\ \sin(Qr)\ \mathrm{d}Q$$





$$S(Q) - 1 = \frac{4\pi\rho}{Q}\int_0^\infty r\ [g(r) - 1]\ \sin(Qr)\ \mathrm{d}r$$

$$g(r) - 1 = \frac{1}{2\pi^2\rho r}\int_0^\infty Q\ [S(Q) - 1]\ \sin(Qr)\ \mathrm{d}Q$$

Isotropic structure factor

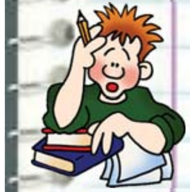
Exercises

Consider now the isotropic case and find the relationship between the isotropic structure factor $S(Q)$ and the isotropic pair distribution function $g(r)$.

A- Consider a well-ordered system with a single (sharp) peak in the real space correlation function and calculate the corresponding structure factor.

B- Discuss the changes you could expect in the structure factor if you had a distribution of distances around a single mean-value.

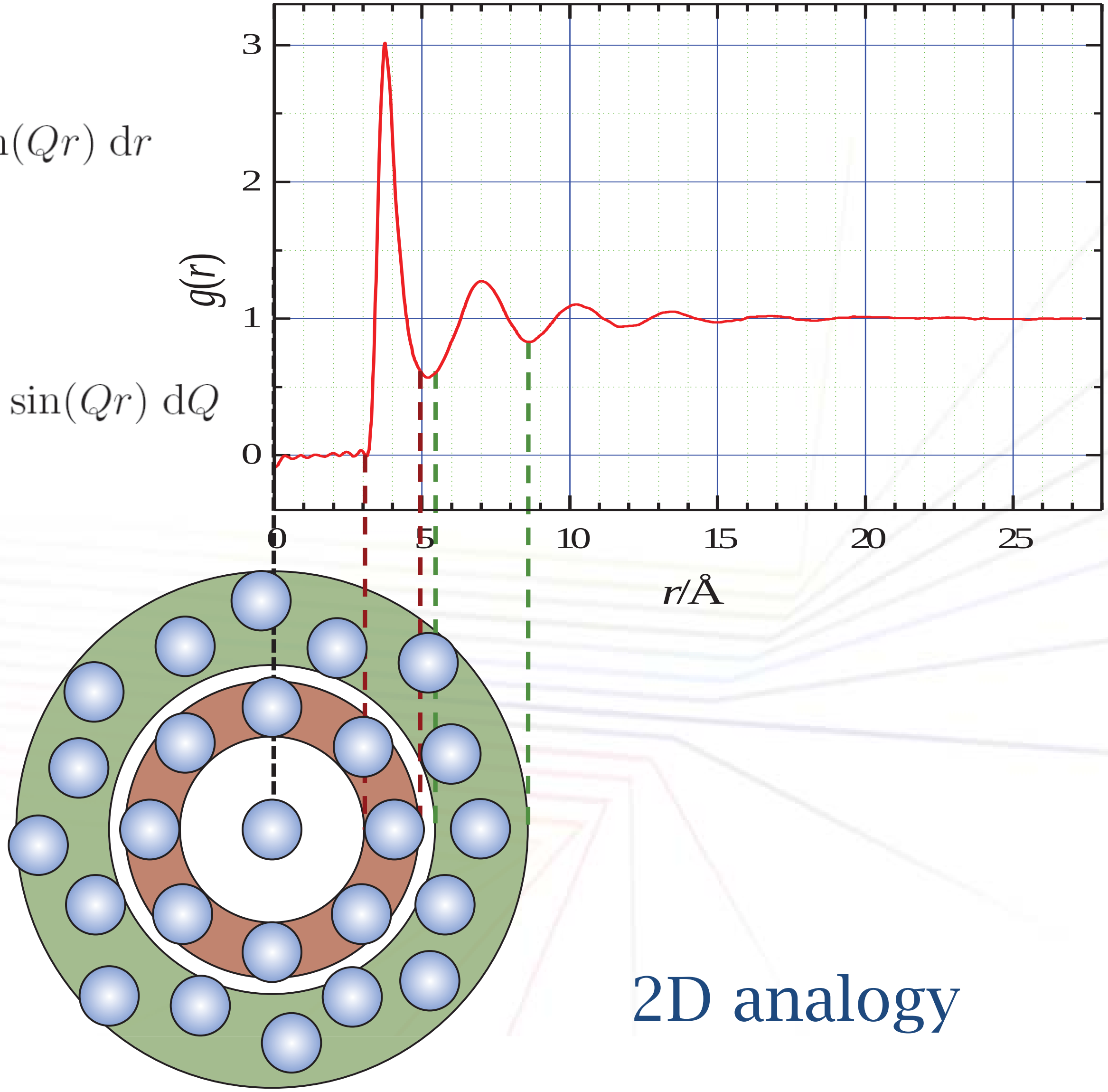
C- Discuss now what you should observe if you had multiple distances, each one with a distribution around the mean value.

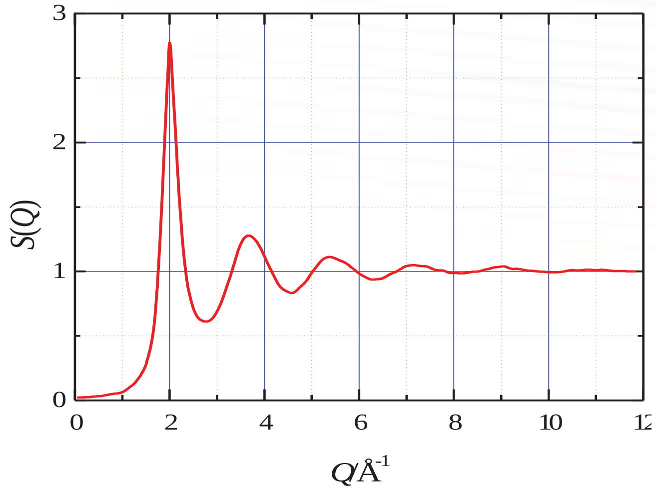


Pair distribution function

$$S(Q) - 1 = \frac{4\pi\rho}{Q} \int_0^\infty r\ [g(r) - 1]\ \sin(Qr)\ \mathrm{d}r$$

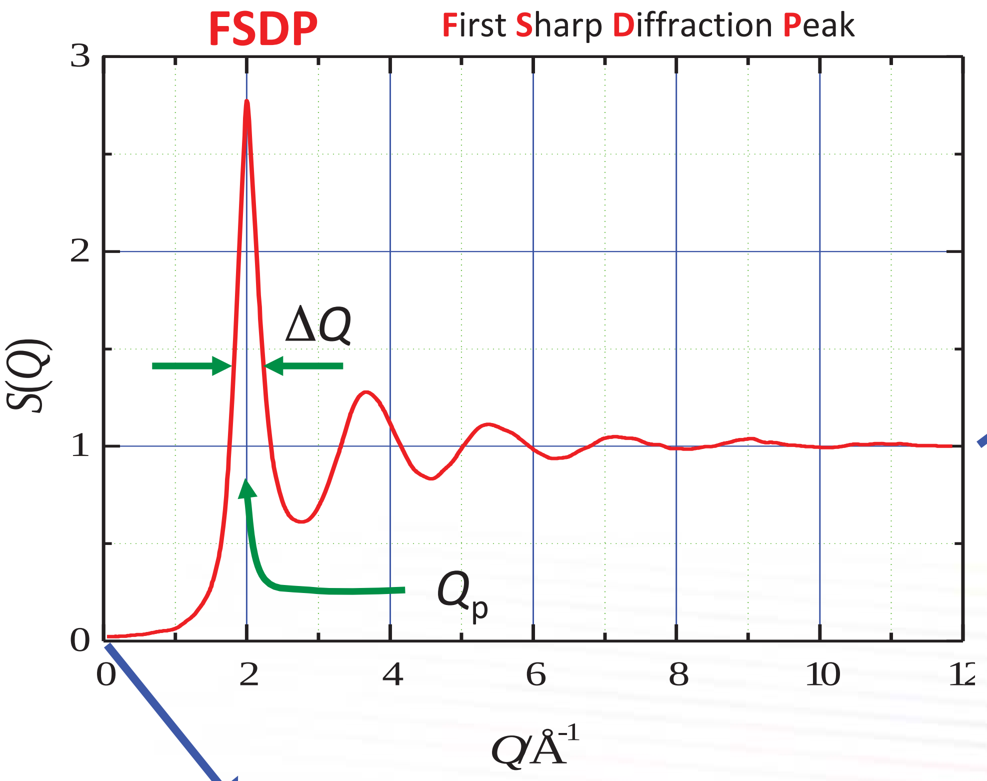
$$g(r) - 1 = \frac{1}{2\pi^2 \rho r} \int_0^\infty Q\ [S(Q) - 1]\ \sin(Qr)\ \mathrm{d}Q$$





2D analogy

First Sharp Diffraction Peak

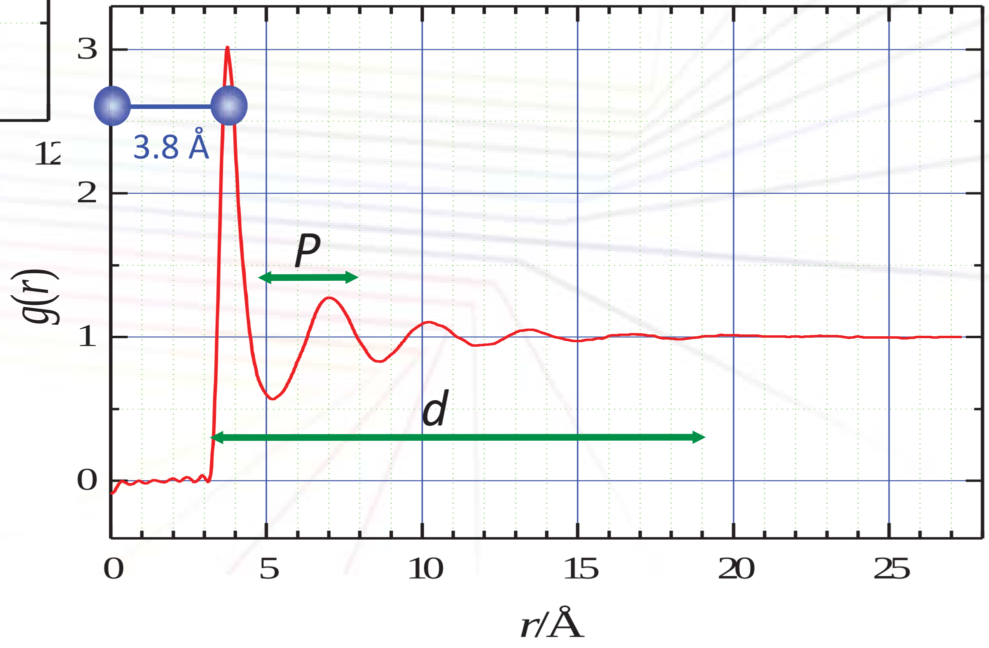


Liquid Ar @ 85K

J.L. Yarnell *et al.* (1973) PRA **7**, 2130

$$S(\infty) = 1$$

Fourier Transformation

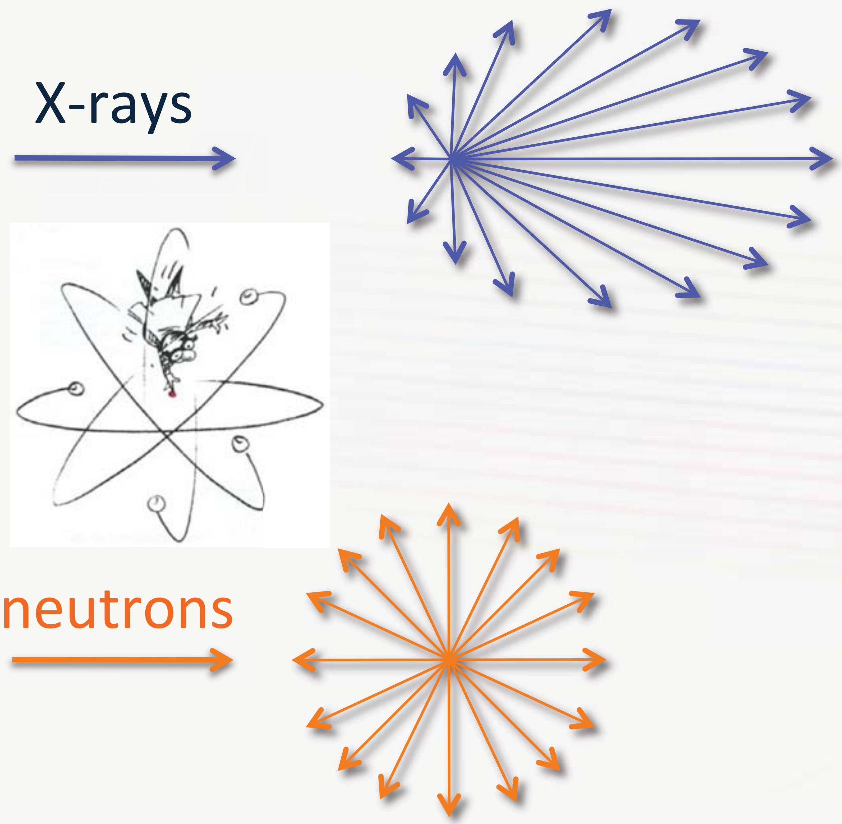


$$S(0) = \rho\,\chi_T\,k_{\mathrm{B}}T$$

Limiting values → Normalisation

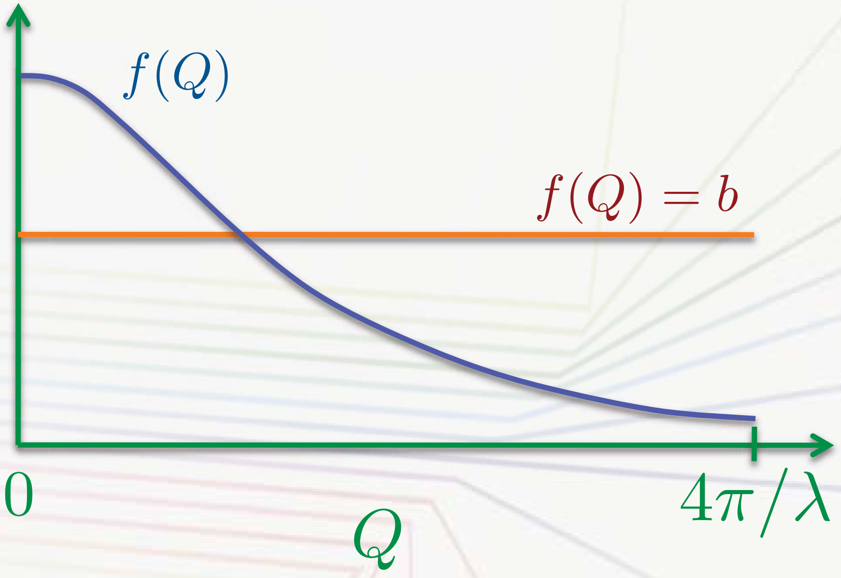
Neutrons *vs* X-rays

$$\left(\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega \mathrm{d}E'}\right) = \frac{k'}{k}\frac{1}{2\pi\hbar}\sum_{jj'} f_j(\vec{Q}) f_{j'}(\vec{Q}) \int_{-\infty}^{\infty} \langle \mathrm{e}^{-i\vec{Q}\cdot\vec{r}_{j'}(0)} \mathrm{e}^{i\vec{Q}\cdot\vec{r}_j(t)}\rangle \mathrm{e}^{-i\omega t}\mathrm{d}t$$



X-rays

neutrons



Bragg law $$Q = \frac{4\pi}{\lambda}\sin\left(\frac{2\theta}{2}\right)$$

Form factor

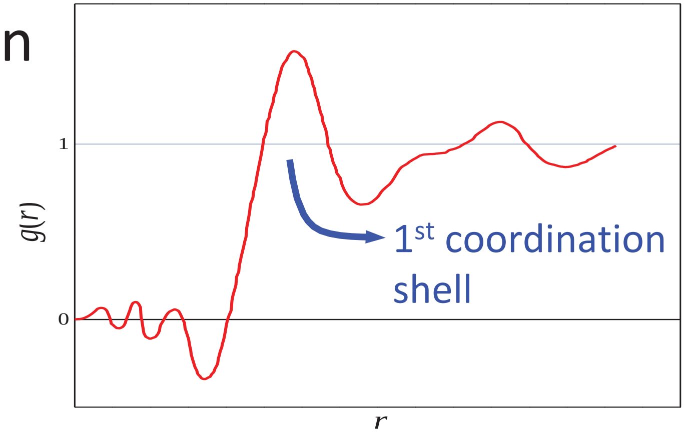
Exercise

The Fermi's pseudo-potential works well for the neutron-nucleus interaction yielding to a constant scattering length.

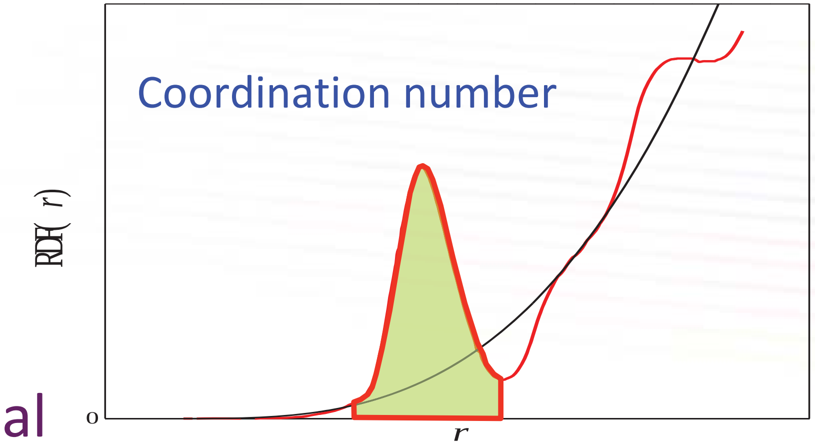
Explain qualitatively the effect that a non-punctual potential has on the structure factor.

Related functions

Pair distribution function $g(r)$



1^{st} coordination shell



Coordination number

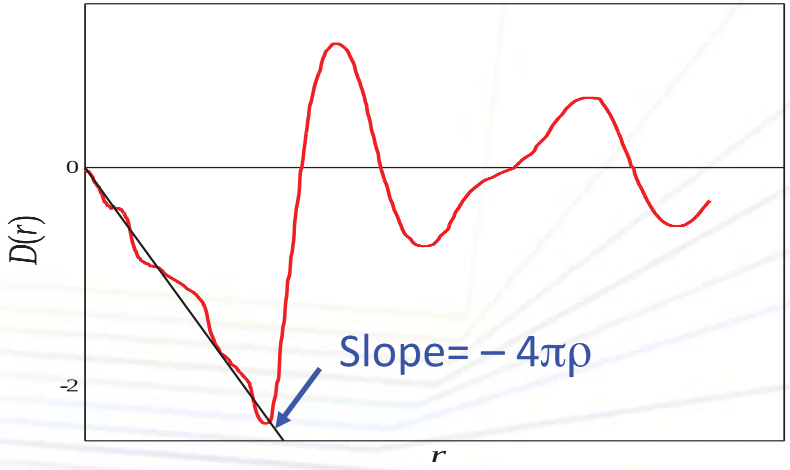
Radial distribution function RDF(r)

$$\mathrm{RDF}(r) = 4\pi\, r^2\, \rho\, g(r)$$

$$T(r) = \mathrm{RDF}(r)/r = 4\pi\, r\, \rho\, g(r) = 4\pi\, r\, \rho + G(r)$$

Pair correlation function $G(r)$ or density function $D(r)$

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



Slope= – 4πρ

Remember!

$$g(r) - 1 \propto \text{FT}\{S(Q) - 1\} / \rho$$

Correlation functions

Exercises

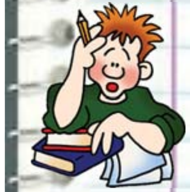
Consider a system with a FSDP at 2.1Å^{-1} with a FWHM of 0.62 Å^{-1}.

What could you say about the characteristics of the corresponding pair distribution function?

How many coordination shells could you observe in such a system?

- - - - - - - - - - - -

Taking into account the repulsion region in the interaction potential, show that the low-*r* region of density function is proportional to the density.



Multiatomic systems

System of *n* chemical species ⇒

$$\bar{b}^2 \underbrace{\left[S(Q)-1\right]}_{F(Q)} = \sum_{\alpha=1}^{n}\sum_{\beta=1}^{n} c_\alpha c_\beta b_\alpha b_\beta \left[S_{\alpha\beta}(Q)-1\right]$$

n (*n*+1)/2 independent partial $S_{\alpha\beta}(Q)$

$$\bar{b}^2 = \sum_{\alpha=1}^{n}\sum_{\beta=1}^{n} c_\alpha c_\beta b_\alpha b_\beta$$

Change b_α by

- Isotopic substitution
- X-ray experiments
- Anomalous diffraction

$$\mathbf{F}_{\mathrm{exp}}(Q) = \mathbf{A}\ \mathbf{F}_{\mathrm{p}}(Q)$$

NDIS: $|\mathbf{A}| < 0.1$

Binary system:

Two different species: x, y

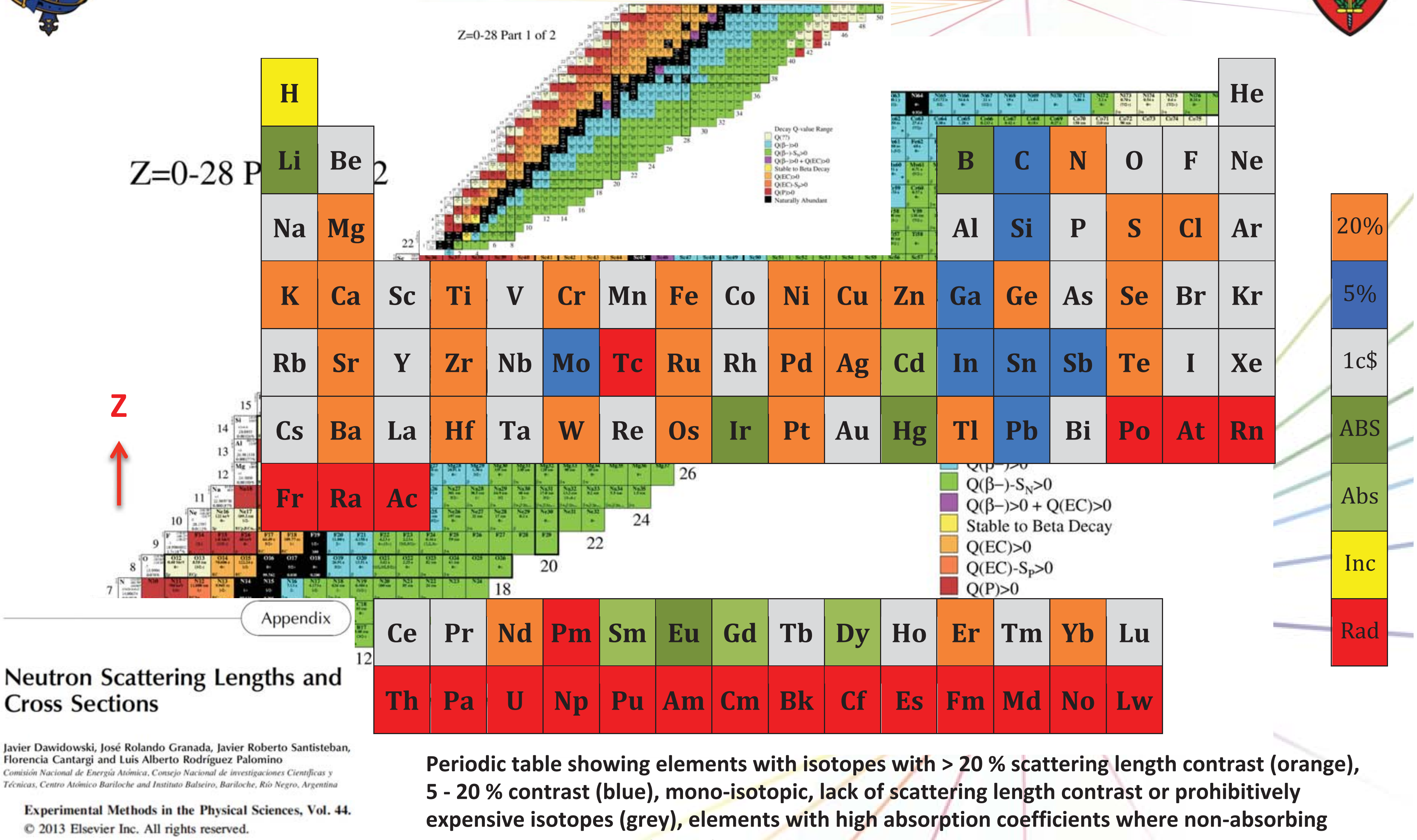
Fixed composition: constant c_x , c_y

Isotopes with good contrast

$b_{\alpha i}$: scattering length of isotope *i* of species α

$$\bar{b}^2 \begin{pmatrix} F_{\mathrm{S1}}(Q) \\ F_{\mathrm{S2}}(Q) \\ F_{\mathrm{S3}}(Q) \end{pmatrix} = \begin{pmatrix} c_{\mathrm{X}}^2 b_{\mathrm{X1}}^2 & c_{\mathrm{Y}}^2 b_{\mathrm{Y1}}^2 & 2c_{\mathrm{X}}c_{\mathrm{Y}}b_{\mathrm{X1}}b_{\mathrm{Y1}} \\ c_{\mathrm{X}}^2 b_{\mathrm{X2}}^2 & c_{\mathrm{Y}}^2 b_{\mathrm{Y2}}^2 & 2c_{\mathrm{X}}c_{\mathrm{Y}}b_{\mathrm{X2}}b_{\mathrm{Y2}} \\ c_{\mathrm{X}}^2 b_{\mathrm{X3}}^2 & c_{\mathrm{Y}}^2 b_{\mathrm{Y3}}^2 & 2c_{\mathrm{X}}c_{\mathrm{Y}}b_{\mathrm{X3}}b_{\mathrm{Y3}} \end{pmatrix} \begin{pmatrix} F_{\mathrm{XX}}(Q) \\ F_{\mathrm{YY}}(Q) \\ F_{\mathrm{XY}}(Q) \end{pmatrix}$$

Isotopic substitution



H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac															
		Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu		
		Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lw		

20%
5%
1c$
ABS
Abs
Inc
Rad

Neutron Scattering Lengths and Cross Sections

Javier Dawidowski, José Rolando Granada, Javier Roberto Santisteban, Florencia Cantargi and Luis Alberto Rodríguez Palomino
Comisión Nacional de Energía Atómica, Consejo Nacional de investigaciones Científicas y Técnicas, Centro Atómico Bariloche and Instituto Balseiro, Bariloche, Río Negro, Argentina

Experimental Methods in the Physical Sciences, Vol. 44.
© 2013 Elsevier Inc. All rights reserved.

Periodic table showing elements with isotopes with > 20 % scattering length contrast (orange), 5 - 20 % contrast (blue), mono-isotopic, lack of scattering length contrast or prohibitively expensive isotopes (grey), elements with high absorption coefficients where non-absorbing isotopes are available (green), elements with isotopes to overcome incoherent scattering effects (yellow) and radioactive elements (red).

Weighting factors

Exercise

Consider a binary system for which you have performed three different total scattering experiments with three different isotopic compositions.

A- Write down the expression of the weighting factors matrix

B- Evaluate this matrix for the case of the Ag_2Se, if you used the following isotopic compositions:

^{107}Ag-^{nat}Se, ^{109}Ag-^{76}Se and ^{nat}Ag-^{76}Se.

Assume that for each substitution, you have replaced 100% of the atoms by its corresponding isotopes.

C- Invert the matrix to obtain the partial structure factors from the three experimental structure factors.

A binary system

Fast-ion conductor or semiconductor glasses

Silver chalcogenides
Ag_2X

+

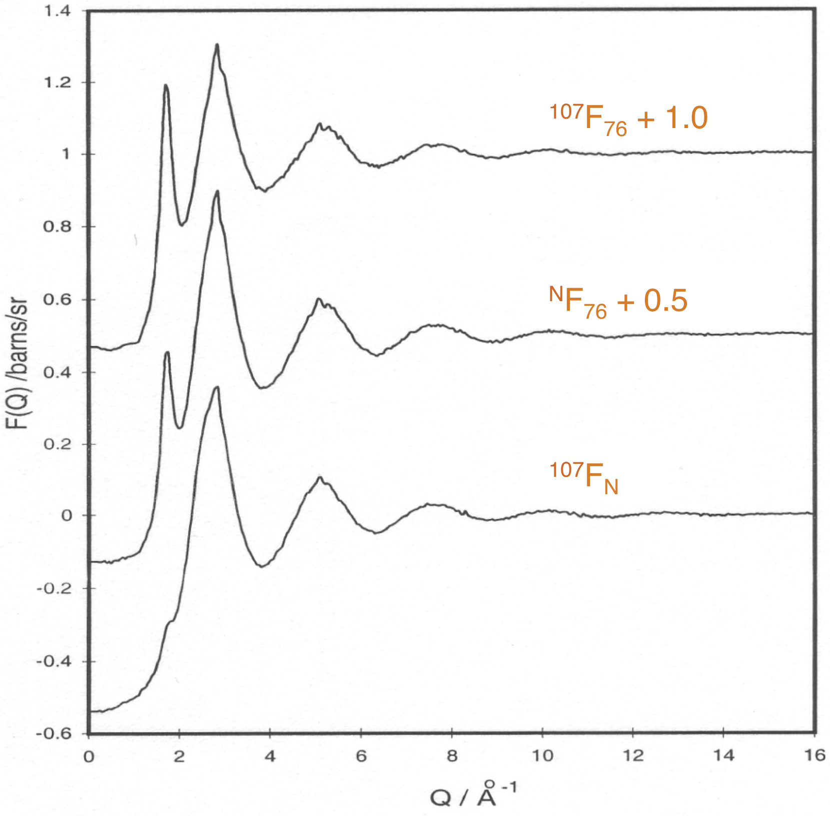
Network formers
AsX or As_2X_3

X= S, Te or Se

Samples: $^{107}Ag_2{}^{nat}Se$, $^{109}Ag_2{}^{76}Se$, $^{nat}Ag_2{}^{76}Se$

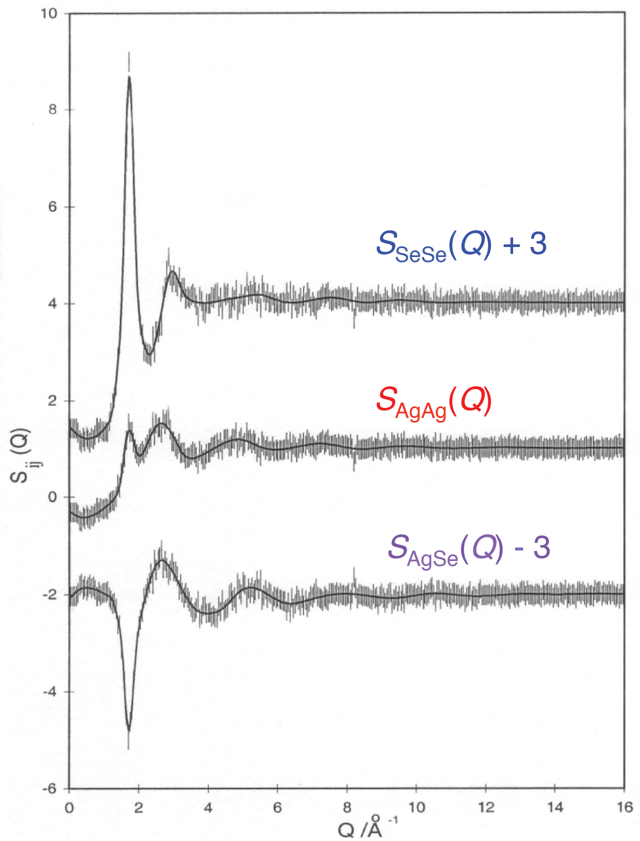
Isotope	*b* (fm)	σ_a (b)	σ_s (b)
^{n}Ag	**5.922**	**24.6**	**4.99**
^{107}Ag	7.64	14.6	7.44
^{109}Ag	4.19	35.4	2.55
^{n}Se	**7.97**	**4.55**	**8.31**
^{76}Se	12.2	33.1	18.7

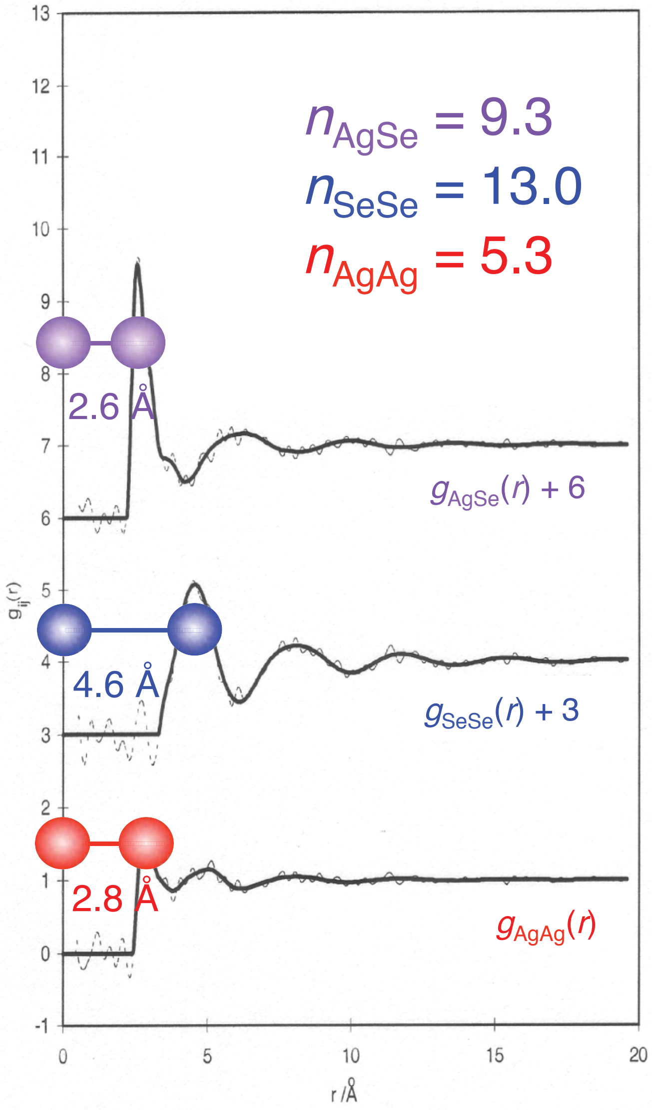
$$\begin{bmatrix} {}^{107}_{\text{nat}}F_{S1}(Q) \\ {}^{109}_{76}F_{S2}(Q) \\ {}^{\text{nat}}_{76}F_{S3}(Q) \end{bmatrix} = \begin{bmatrix} 0.2594 & 0.0706 & 0.2706 \\ 0.0780 & 0.1654 & 0.2272 \\ 0.1559 & 0.1654 & 0.3211 \end{bmatrix} \begin{bmatrix} F_{AgAg}(Q) \\ F_{SeSe}(Q) \\ F_{AgSe}(Q) \end{bmatrix}$$



Partial structure factors

$$\begin{bmatrix} F_{\mathrm{AgAg}}(Q) \\ F_{\mathrm{SeSe}}(Q) \\ F_{\mathrm{AgSe}}(Q) \end{bmatrix} = \begin{bmatrix} 12.17 & 17.31 & -22.50 \\ 8.11 & 32.22 & -29.63 \\ -10.09 & -25.00 & 29.30 \end{bmatrix} \begin{bmatrix} {}^{107}_{\mathrm{nat}}F_{\mathrm{S1}}(Q) \\ {}^{109}_{76}F_{\mathrm{S2}}(Q) \\ {}^{\mathrm{nat}}_{76}F_{\mathrm{S3}}(Q) \end{bmatrix}$$



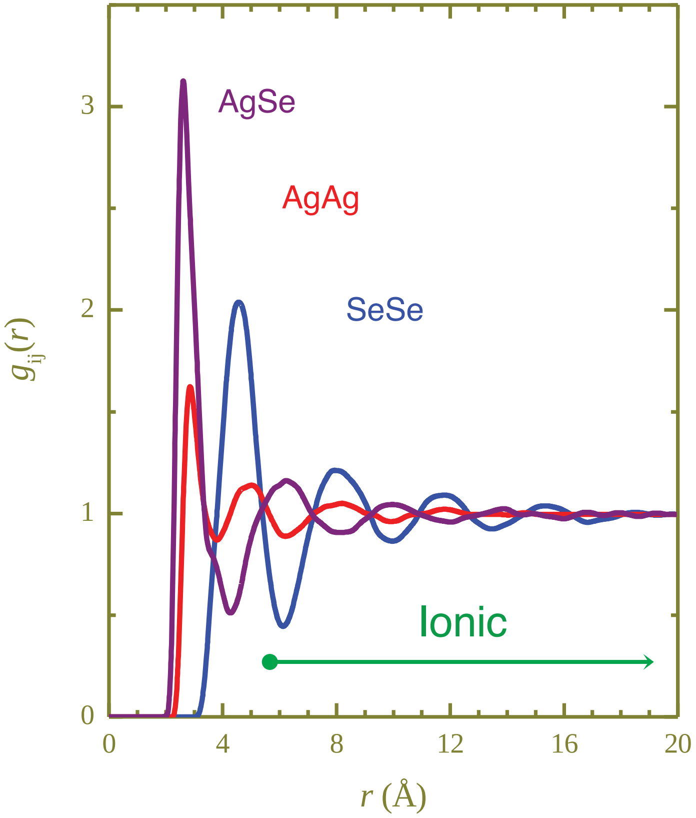


$n_{AgSe} = 9.3$

$n_{SeSe} = 13.0$

$n_{AgAg} = 5.3$

Ionic behaviour



First difference method

$$\bar{b}^2\ F(Q) = \sum_{\alpha=1}^{n}\sum_{\beta=1}^{n} c_\alpha c_\beta b_\alpha b_\beta\ F_{\alpha\beta}(Q)$$

Substitution ------→ γ: γ_1, γ_2

Important! We change scattering lengths but <u>not</u> composition

$$\bar{b}^2\ F_{\gamma 1}(Q) = c_\gamma^2 b_{\gamma 1}^2\ F_{\gamma\gamma}(Q) + c_\gamma b_{\gamma 1} \sum_{\alpha\neq\gamma}^{n} c_\alpha b_\alpha\ F_{\alpha\gamma}(Q) + \sum_{\alpha,\beta\neq\gamma}^{n} c_\alpha c_\beta b_\alpha b_\beta\ F_{\alpha\beta}(Q)$$

$$\bar{b}^2\ F_{\gamma 2}(Q) = c_\gamma^2 b_{\gamma 2}^2\ F_{\gamma\gamma}(Q) + c_\gamma b_{\gamma 2} \sum_{\alpha\neq\gamma}^{n} c_\alpha b_\alpha\ F_{\alpha\gamma}(Q) + \sum_{\alpha,\beta\neq\gamma}^{n} c_\alpha c_\beta b_\alpha b_\beta\ F_{\alpha\beta}(Q)$$

Correlation function of atom γ with all other components

$$\bar{b}^2\ \Delta F_\gamma(Q) = c_\gamma^2 (b_{\gamma 1}^2 - b_{\gamma 2}^2) \boxed{F_{\gamma\gamma}(Q)} + c_\gamma (b_{\gamma 1} - b_{\gamma 2}) \sum_{\alpha\neq\gamma}^{n} c_\alpha b_\alpha \boxed{F_{\alpha\gamma}(Q)}$$

$$\frac{\bar{b}^2\ \Delta F_\gamma(Q)}{c_\gamma^2 (b_{\gamma 1}^2 - b_{\gamma 2}^2)} = F_{\gamma\gamma}(Q) + \cancelto{\text{small}}{\frac{\sum_{\alpha\neq\gamma}^{n} c_\alpha b_\alpha\ F_{\alpha\gamma}(Q)}{c_\gamma\ (b_{\gamma 1} + b_{\gamma 2})}}$$

A ternary system

Li in ND_3

Metal-nonmetal transition at 7 MPM

Class A metals

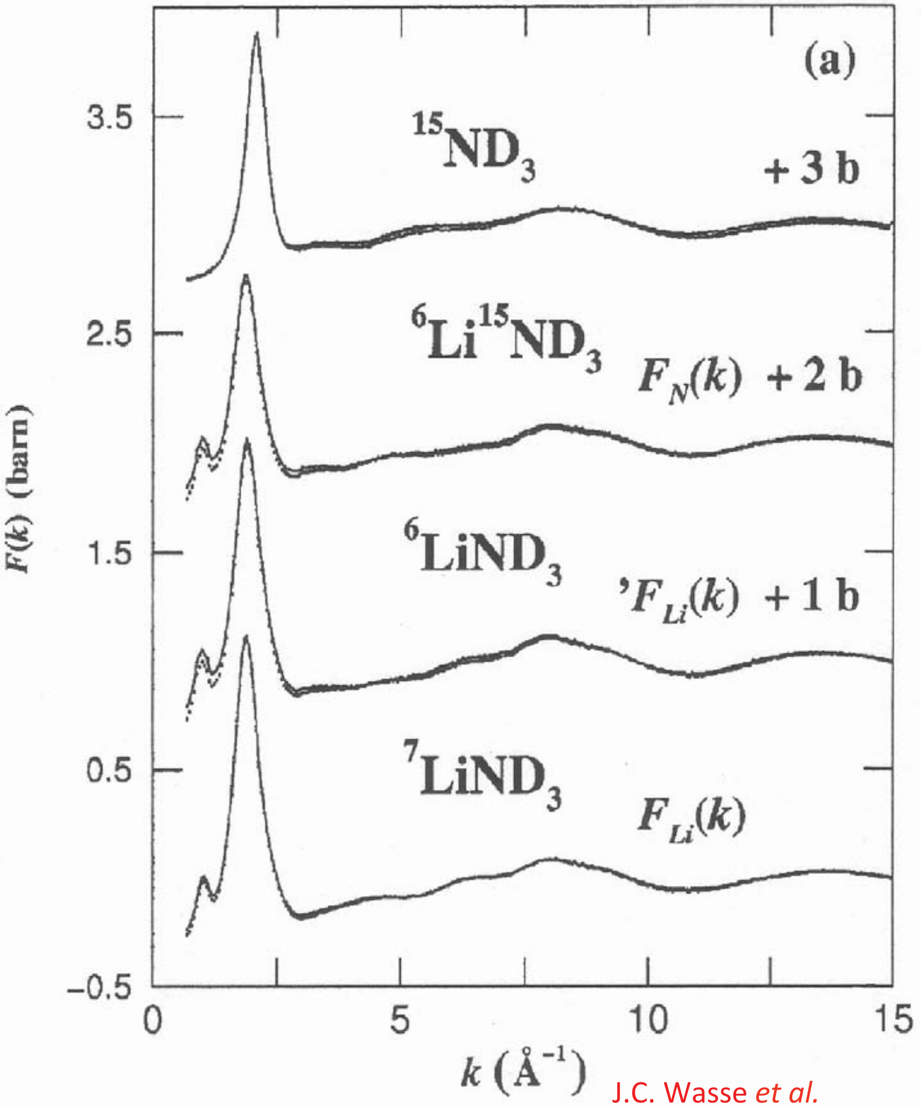
Conductivity 15000 Ω^{-1} cm^{-1} mol^{-1}

3 species ⇒ 6 different experiments!

First difference method

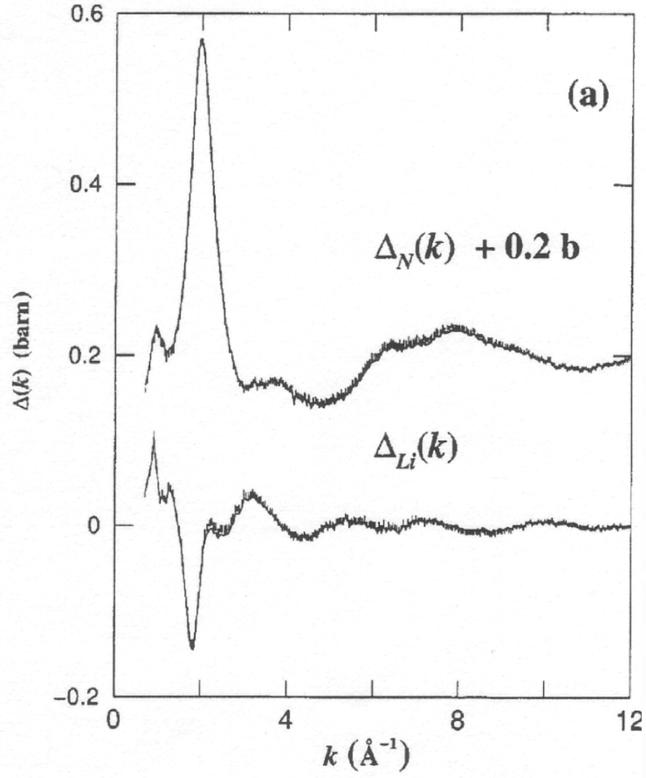
Samples:

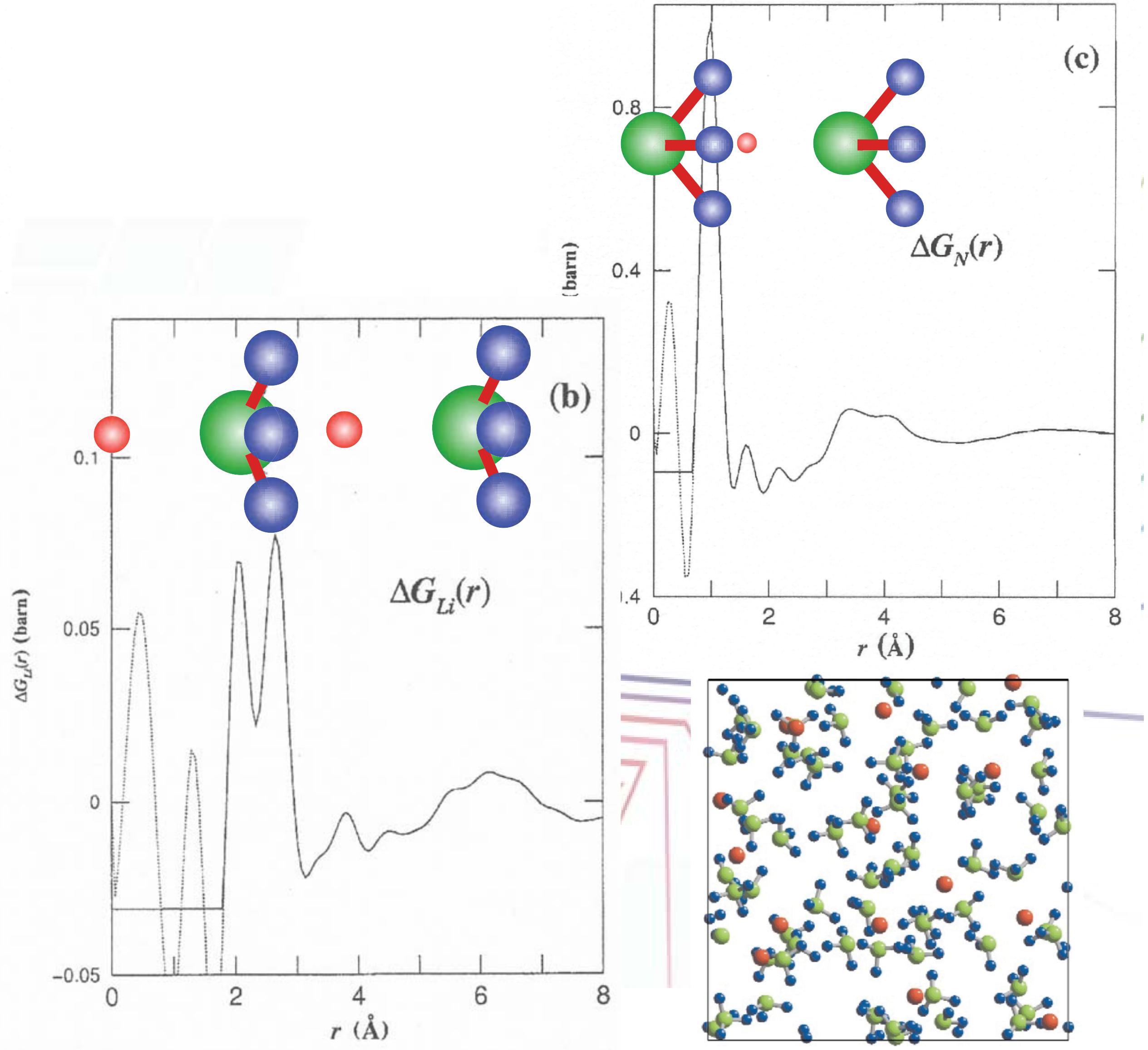
- ^{6}Li in $^{nat}ND_3$
- ^{7}Li in $^{nat}ND_3$
- ^{6}Li in $^{15}ND_3$
- $^{15}ND_3$



J.C. Wasse *et al.*
PRB **61**, 11993 (2000)

Partials… not really





J.C. Wasse *et al.*
PRB **61**, 11993 (2000)

Second difference method

New substitution δ: δ$_1$, δ$_2$

$$\bar{b}^2\;\Delta F_{\gamma\delta 1}(Q) = c_\gamma^2(b_{\gamma 1}^2 - b_{\gamma 2}^2)\;F_{\gamma\gamma}(Q) + c_\gamma c_\delta(b_{\gamma 1} - b_{\gamma 2})\,b_{\delta 1}\boxed{F_{\gamma\delta}(Q)} + c_\gamma(b_{\gamma 1} - b_{\gamma 2})\sum_{\alpha\neq\gamma,\delta}^{n} c_\alpha b_\alpha\;F_{\alpha\gamma}(Q)$$

$$\bar{b}^2\;\Delta F_{\gamma\delta 2}(Q) = c_\gamma^2(b_{\gamma 1}^2 - b_{\gamma 2}^2)\;F_{\gamma\gamma}(Q) + c_\gamma c_\delta(b_{\gamma 1} - b_{\gamma 2})\,b_{\delta 2}\boxed{F_{\gamma\delta}(Q)} + c_\gamma(b_{\gamma 1} - b_{\gamma 2})\sum_{\alpha\neq\gamma,\delta}^{n} c_\alpha b_\alpha\;F_{\alpha\gamma}(Q)$$

$$\bar{b}^2\;\Delta^2 F_{\gamma\delta}(Q) = c_\gamma c_\delta(b_{\gamma 1} - b_{\gamma 2})\,(b_{\delta 1} - b_{\delta 2})\boxed{F_{\gamma\delta}(Q)}$$

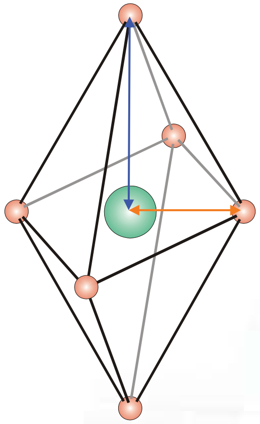
$$F_{\gamma\delta}(Q) = \frac{\bar{b}^2\;\Delta^2 F_{\gamma\delta}(Q)}{c_\gamma c_\delta(b_{\gamma 1} - b_{\gamma 2})\,(b_{\delta 1} - b_{\delta 2})}$$

Partial structure factor
for pairs γ and δ

Cu(II) aqua ion

A. Pasquarello *et al.*
Science **291**, 856 (2001)

Model Octahedral complex $[Cu(H_2O)]^{2+}$
Sixfold coordination



X-ray diffraction
EXAFS
XANES
A priori assumptions about structure

NDIS
Overlap axial Cu-O and Cu-H

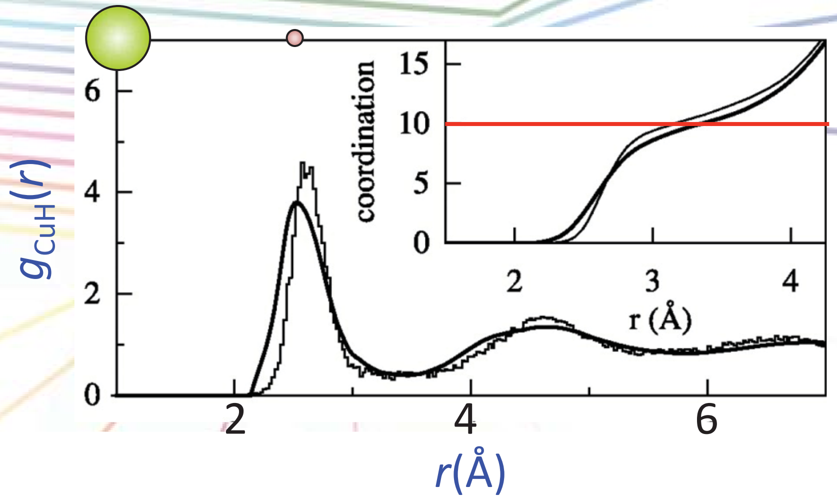
System:
$Cu(ClO_4)_2 + HClO_4$ in H_2O
→ 10 expts!

Samples:
$^{65}Cu(ClO_4)_2 + HClO_4$ in H_2O
$^{63}Cu(ClO_4)_2 + HClO_4$ in H_2O
$^{65}Cu(ClO_4)_2 + DClO_4$ in D_2O
$^{63}Cu(ClO_4)_2 + DClO_4$ in D_2O

Second difference method

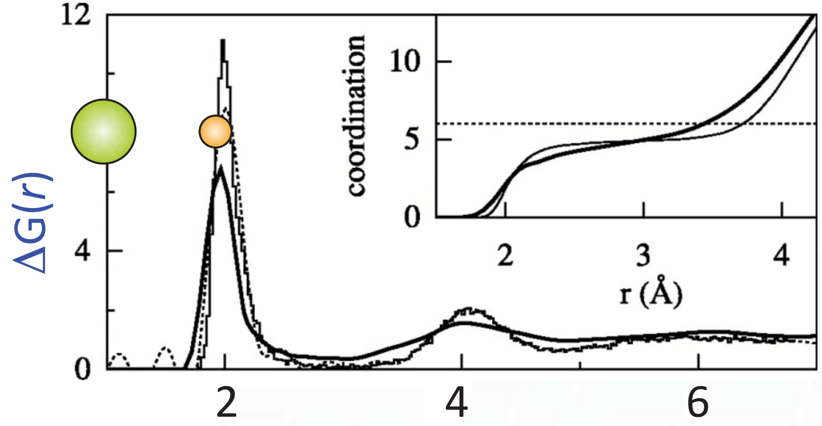
$$\Delta F_{\underset{D}{H}} = c_{Cu}^2 (b_{65}^2 - b_{63}^2) F_{CuCu} + 2 c_{Cu} (b_{65} - b_{63}) \times (c_{Cl} b_{Cl} F_{CuCl} + c_O b_O F_{CuO} + c_H b_{\underset{D}{H}} F_{CuH})$$

$$\boxed{\Delta^2 F = 2 c_{Cu} c_H (b_{65} - b_{63}) (b_D - b_H) F_{CuH}}$$



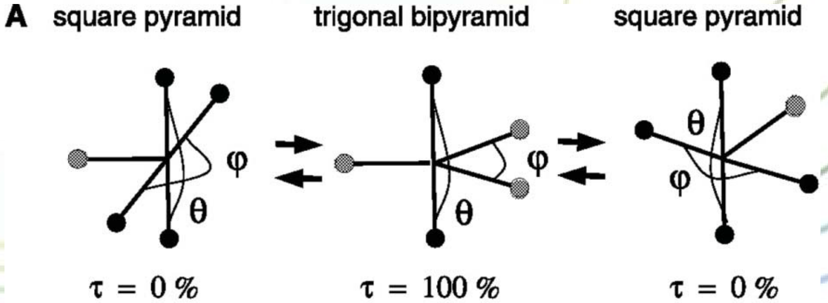
Five-fold coordinated ion

A. Pasquarello *et al.*
Science **291**, 856 (2001)

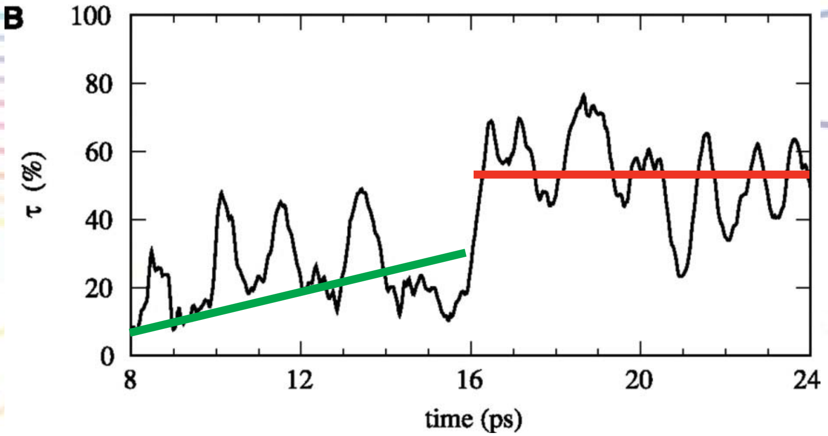


First-principles Molecular Dynamics Simulation

$$\Delta F = F_{\mathrm{CuO}} + 0.044\, F_{\mathrm{CuCu}} + 0.102\, F_{\mathrm{CuCl}}$$

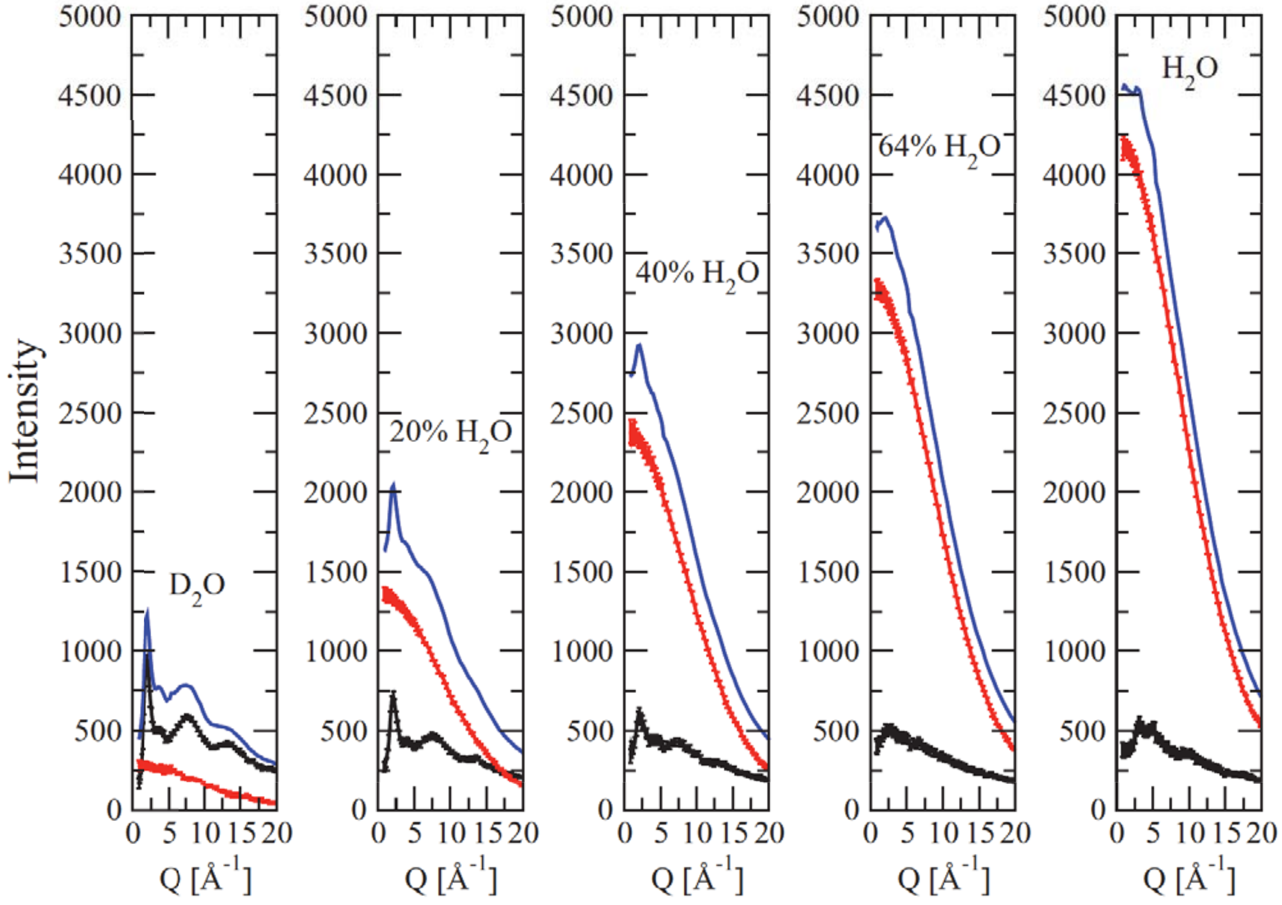


$$\tau = (\theta - \varphi)/60 \times 100\%$$



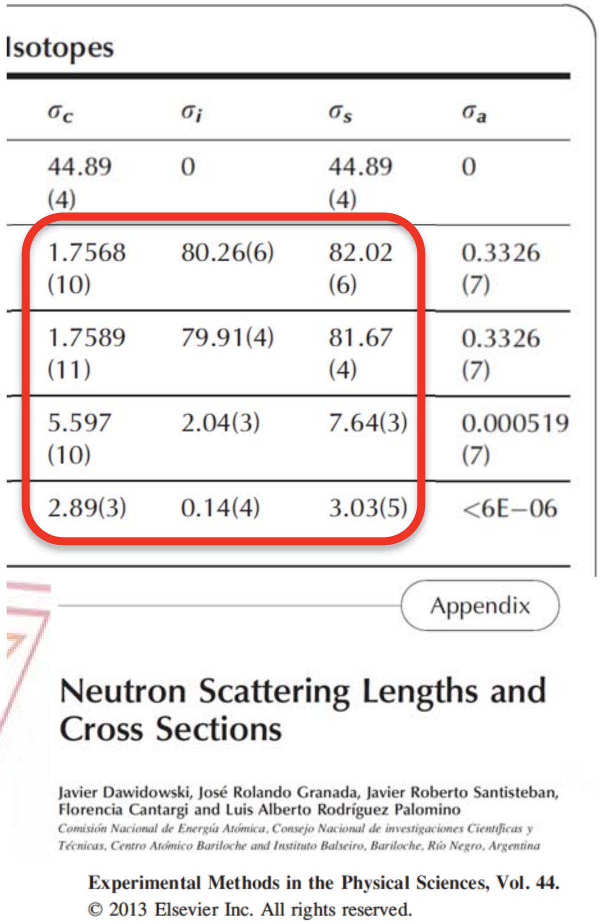
Cu(II) aqua ion is
five-fold coordinated

H incoherence problem



Neutron diffraction of hydrogenous materials: Measuring incoherent and coherent intensities separately

László Temleitner, Anne Stunault, Gabriel J. Cuello, and László Pusztai
Phys. Rev. B **92**, 014201 – Published 1 July 2015



Isotopes

σ_c	σ_i	σ_s	σ_a
44.89 (4)	0	44.89 (4)	0
1.7568 (10)	80.26(6)	82.02 (6)	0.3326 (7)
1.7589 (11)	79.91(4)	81.67 (4)	0.3326 (7)
5.597 (10)	2.04(3)	7.64(3)	0.000519 (7)
2.89(3)	0.14(4)	3.03(5)	<6E−06

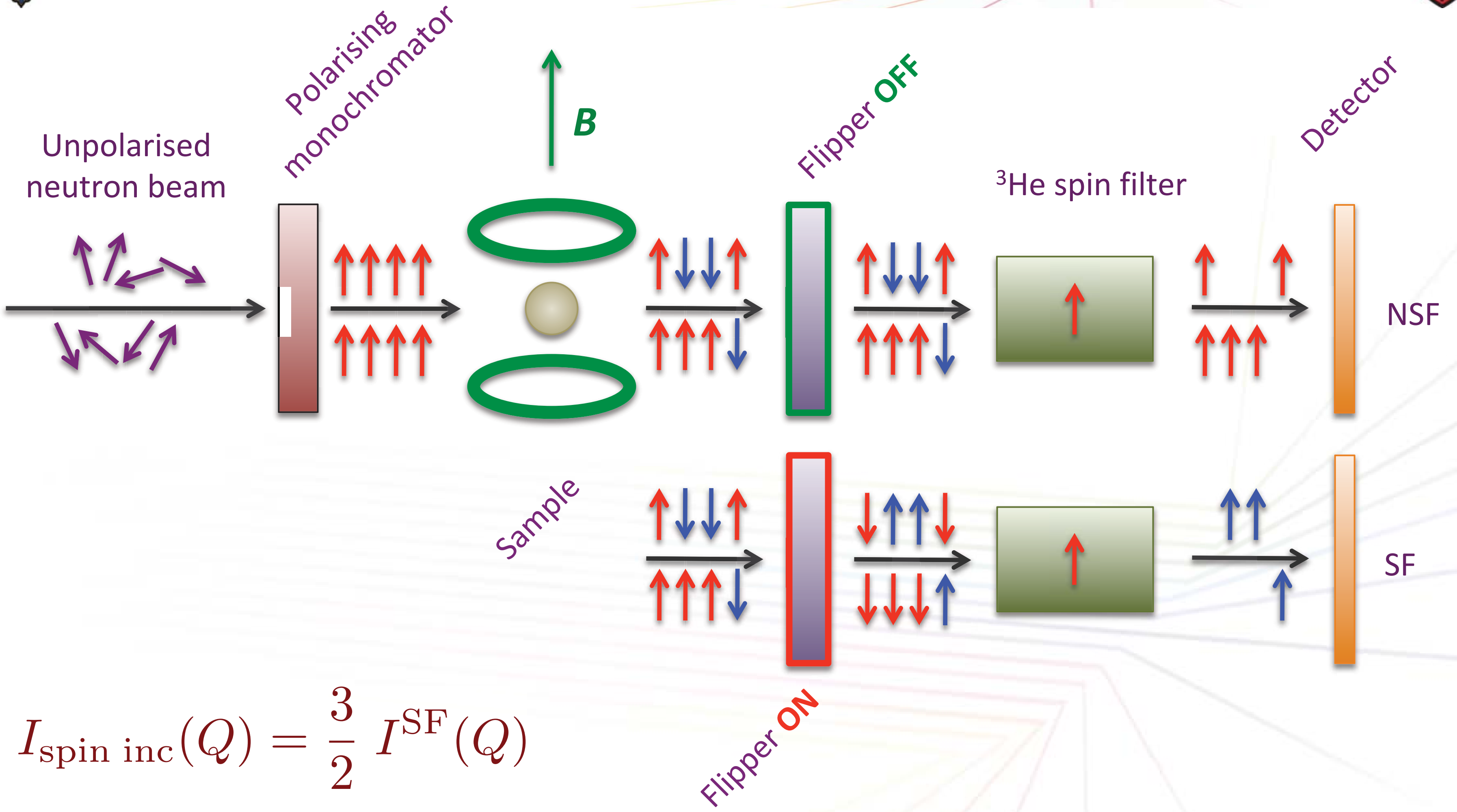
Appendix

Neutron Scattering Lengths and Cross Sections

Javier Dawidowski, José Rolando Granada, Javier Roberto Santisteban, Florencia Cantargi and Luis Alberto Rodríguez Palomino
Comisión Nacional de Energía Atómica, Consejo Nacional de investigaciones Científicas y Técnicas, Centro Atómico Bariloche and Instituto Balseiro, Bariloche, Río Negro, Argentina

Experimental Methods in the Physical Sciences, Vol. 44.
© 2013 Elsevier Inc. All rights reserved.

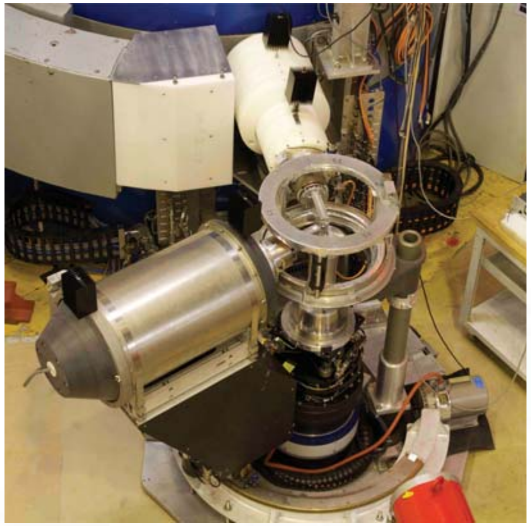
Polarised neutrons



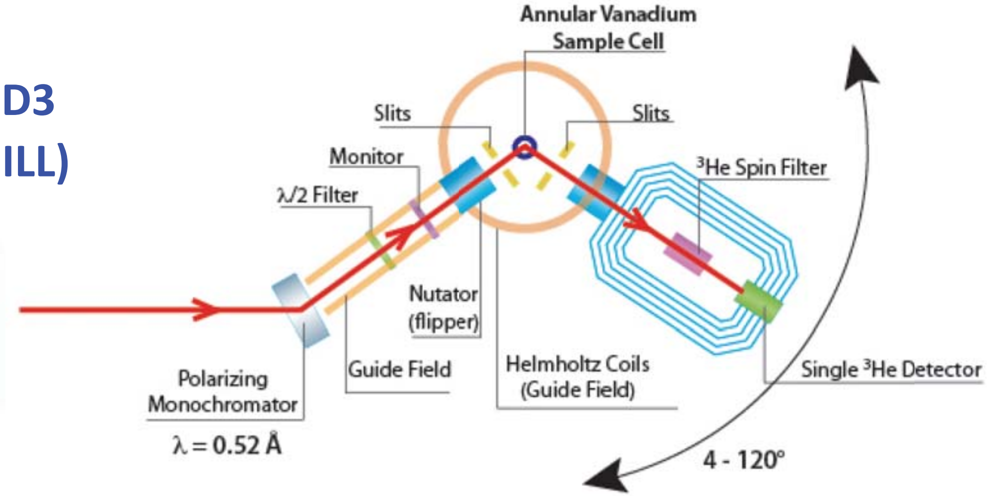
$$I_{\text{spin inc}}(Q) = \frac{3}{2}\, I^{\text{SF}}(Q)$$

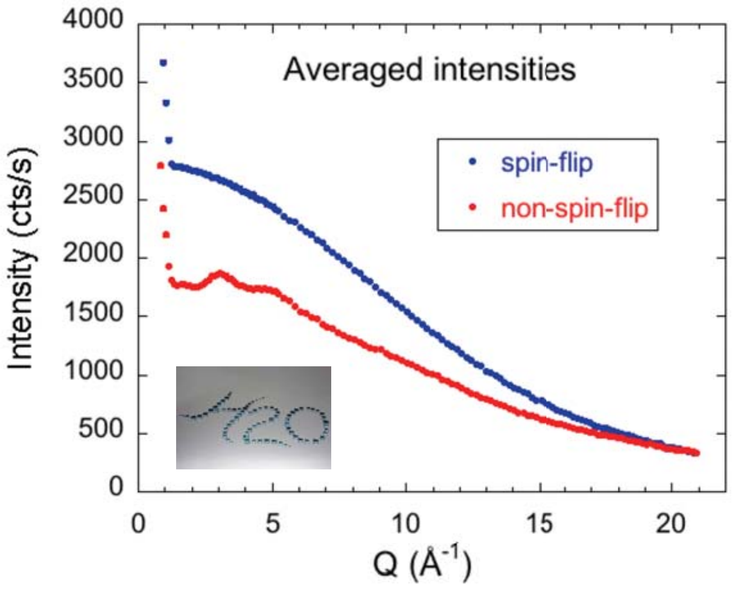
$$I_{\text{coh}}(Q) + I_{\text{isotope inc}}(Q) = I^{\text{NSF}}(Q) - \frac{1}{2}\, I^{\text{SF}}(Q)$$

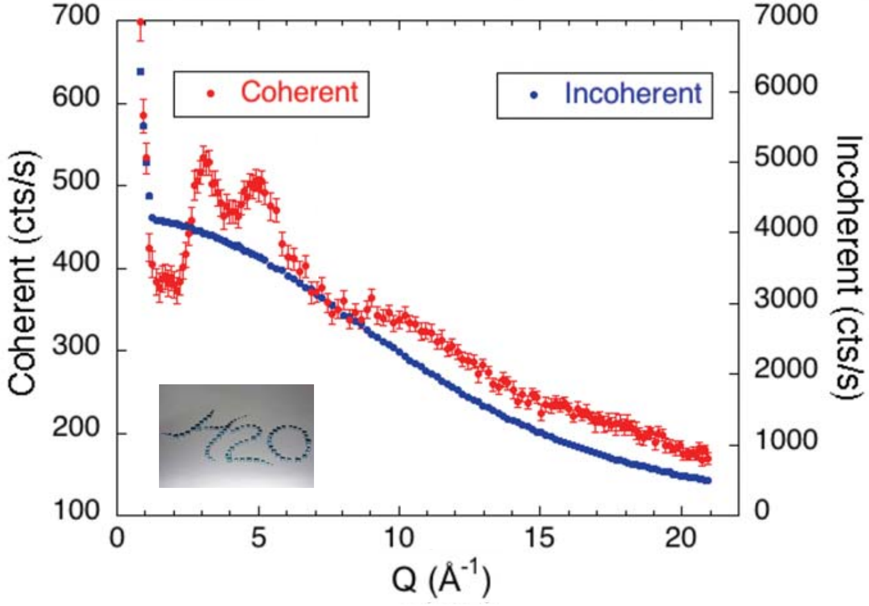
The case of water



D3
(ILL)


Annular Vanadium Sample Cell
Slits
Slits
Monitor
$\lambda/2$ Filter
^{3}He Spin Filter
Nutator (flipper)
Polarizing Monochromator
Guide Field
Helmholtz Coils (Guide Field)
Single ^{3}He Detector
$\lambda = 0.52$ Å
4 - 120°



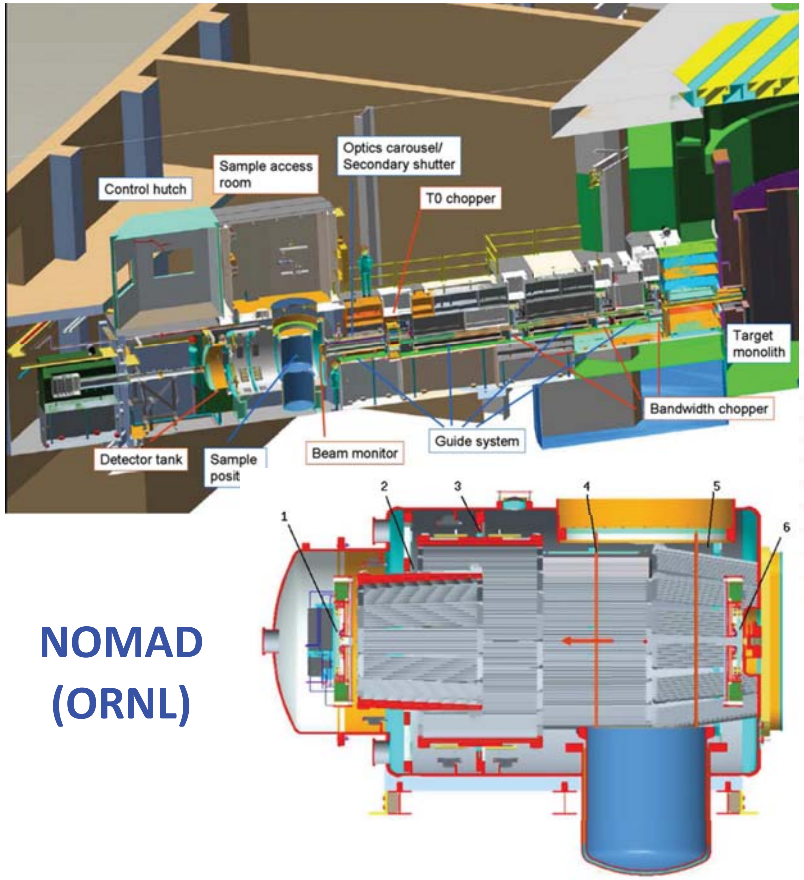


Instruments

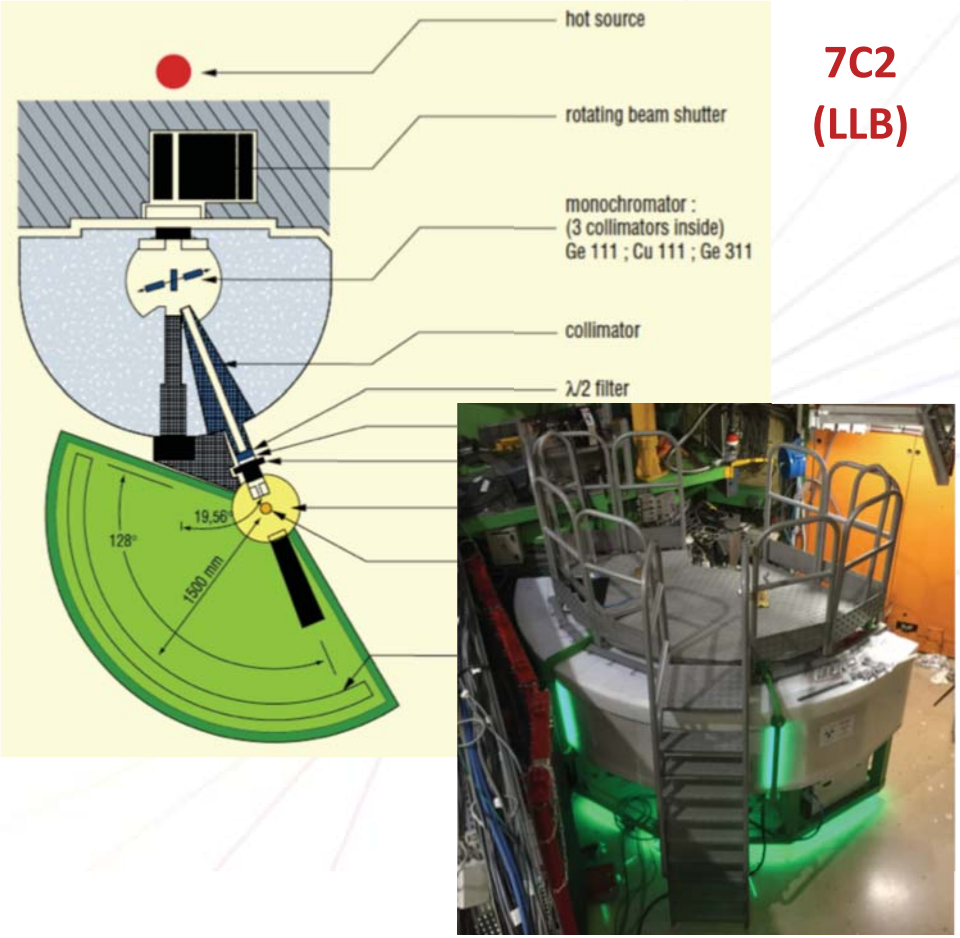
Reactor → 2-axis → Scattering angle

Accelerator → TOF → Time-of-flight

} Elastic scattering → *Q*

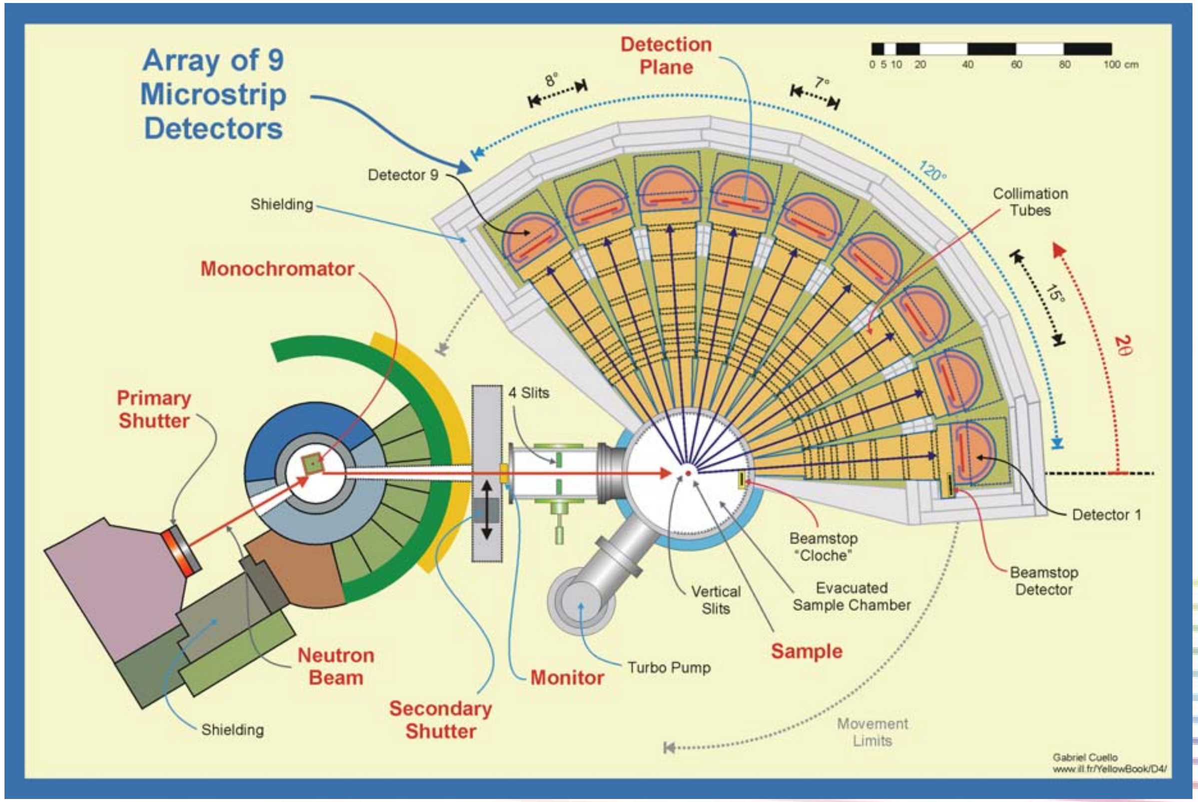


NOMAD (ORNL)



7C2 (LLB)

D4C @ ILL

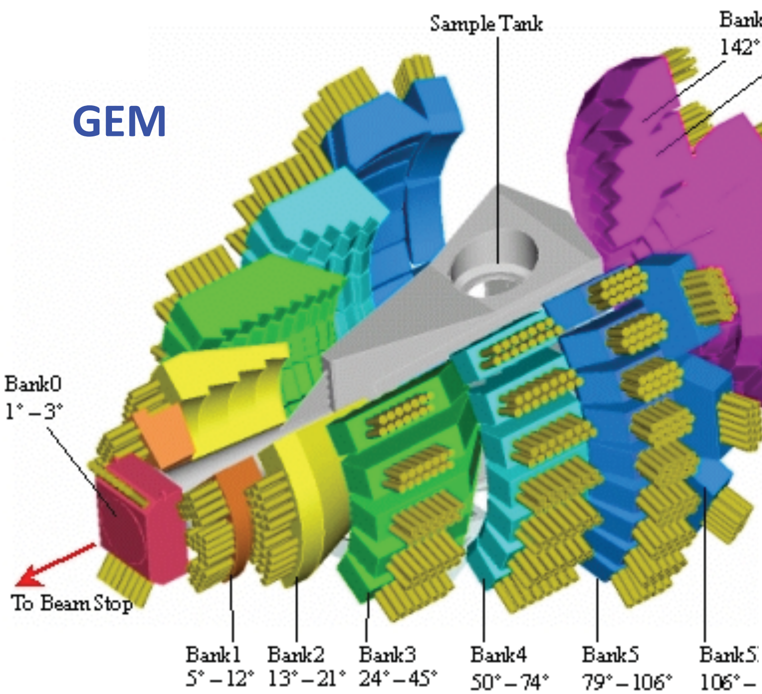


Face	d-spacing (Å)	λ (Å)	Flux (10^7 n cm^{-2} s^{-1})	Filter
Si111	1.807	0.7	5.0	Ir
Cu220	1.278	0.5	4.5	Rh
Cu331	0.829	0.35	0.3	Non

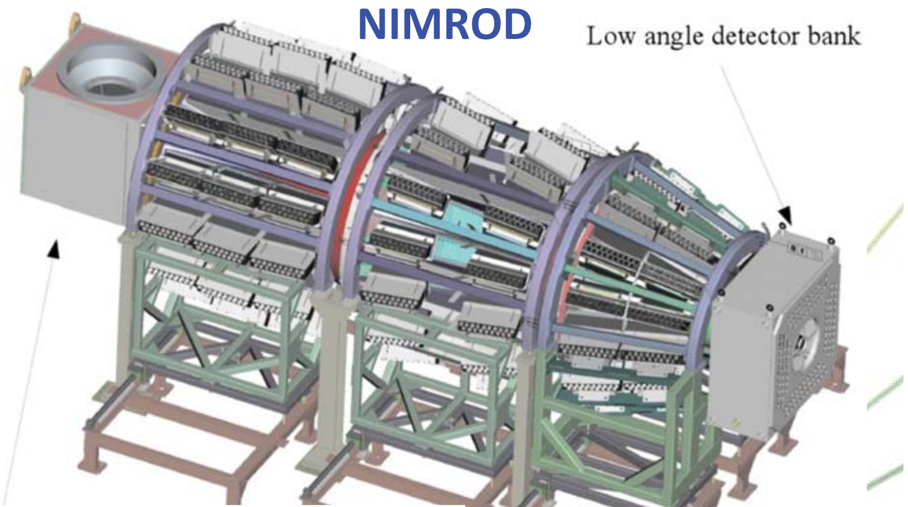
$$Q = \frac{4\pi}{\lambda}\sin\left(\frac{2\theta}{2}\right)$$

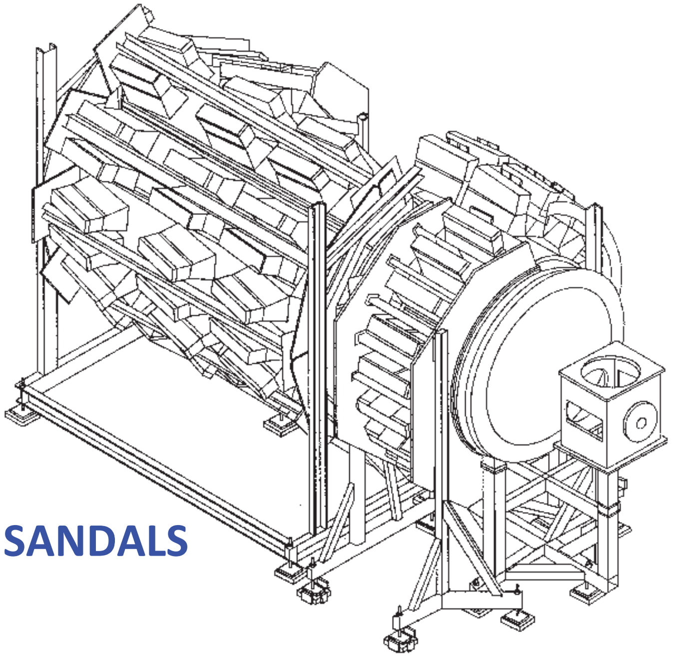
Instruments @ ISIS

GEM



NIMROD





SANDALS

Data reduction

$$I(2\theta,\omega) = C\,\Phi_0\;N\,\frac{k'}{k}\,\frac{\sigma}{4\pi}\,S(\vec{Q},\omega)\,\epsilon(k')$$

$$I(2\theta) = C\,\Phi_0\;N\,\frac{\sigma}{4\pi}\int\limits_{\substack{-\infty \\ \text{constant } 2\theta}}^{E_{\mathrm{max}}} \mathrm{d}\omega\,\frac{k'}{k}\,S(\vec{Q},\omega)\,\epsilon(k')$$

Formal aspects

- Elastic scattering (diffraction) { Bragg's law (for *Q*) / Integration limits (±∞)
- Stationary beam
- Constant efficiency detector
- One interaction processes (single scattering)

$$I(2\theta) = C\,\Phi_0\;\;N\,/4\pi\;\;(\sigma_{coh}\,S(Q) + \sigma_{inc})\;\varepsilon(k)$$

Practical aspects

- Monochromatic beam
- No background
- No attenuation
- Single scattering

⇒

No beam
No container
No sample
No environment
No detector

⇒

No problem!

Experimental corrections

Instrumental effects

- Background
- Detector efficiency
- Detector dead-time
- Instrumental resolution

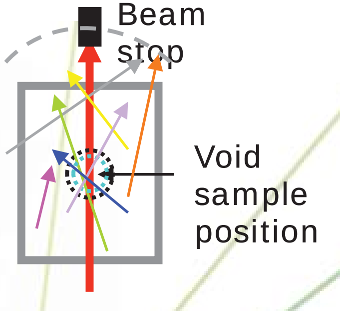
Sample effects

- Inelasticity
- Attenuation (container)
- Multiple scattering
- Normalisation

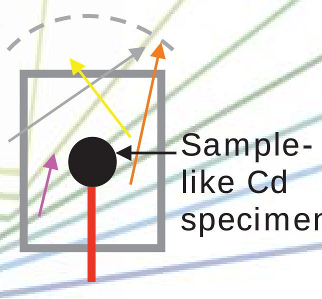
Background noise

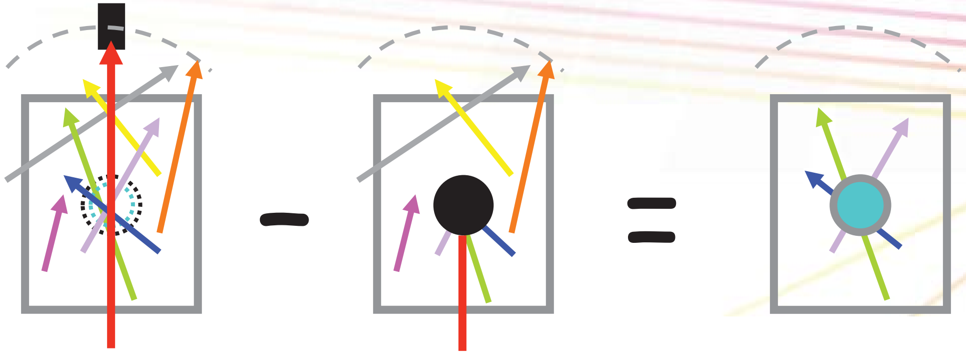
Requires two measurements:

- Empty beam
  (no sample, no container)



- Sample-like Cd specimen





$$I_b(2\theta) \approx I_{Cd}(2\theta) + T_{SC}\,[I_E(2\theta) - I_{Cd}(2\theta)]$$

$$T = \exp\{-\,n\,\sigma_T(E)\,d\}$$

Inelasticity effects

∞

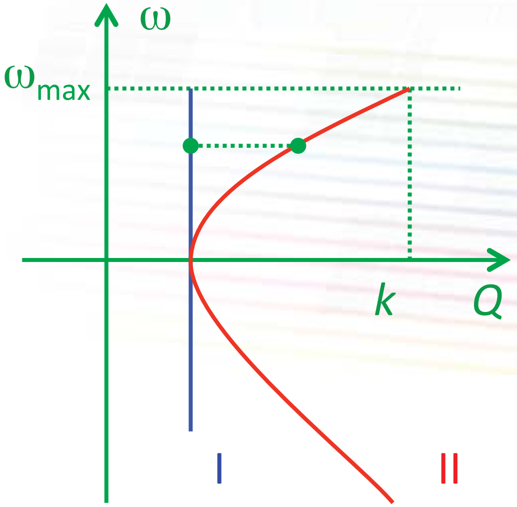
1

ε(*k*)

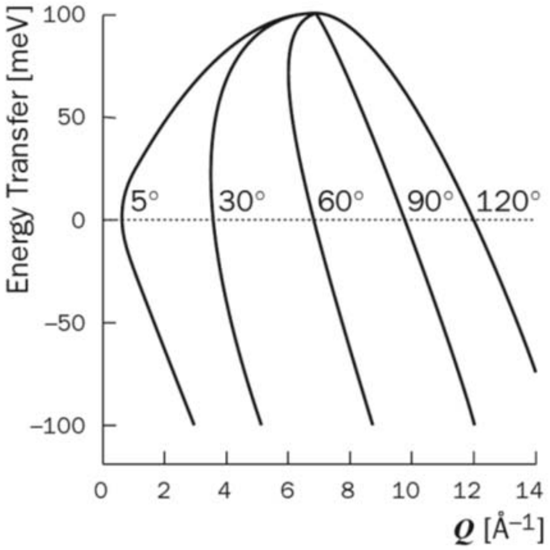
$$I(2\theta) = C\;\Phi_0\;N\;\frac{\sigma}{4\pi}\int_{-\infty}^{\boxed{E_{\max}}}\boxed{\frac{k'}{k}}\,S(\boxed{\vec{Q}},\omega)\,\boxed{\epsilon(k')}\,\mathrm{d}\omega$$

Constant 2θ

Constant 2Θ



$$\frac{\hbar^2 Q^2}{2m} = 2E + \hbar\omega - 2\sqrt{E^2 + \hbar\omega E}\;\cos 2\theta$$



Placzek’s correction

These effects are closely associated to the detector efficiency

Placzek's expansion

Efficiency

- Black detector, $\varepsilon(E) = 1$
- 1/*v* detector, $\varepsilon(E) \propto E^{-1/2}$
- Exponential detector, $\varepsilon(E) = 1 - \exp\{-\alpha\ (E/E')^{1/2}\}$

- Taylor expansion of $S(Q_{\mathrm{I}},\omega)$ around $(Q_{\mathrm{I}},\omega) \longrightarrow S(Q_{\mathrm{II}},\omega)$
- Expansion of $Q_{\mathrm{II}}^2 - Q_{\mathrm{I}}^2$, $\varepsilon(k)$ and k'/k in powers of $\omega/\omega_{\max}$
- Energy integration

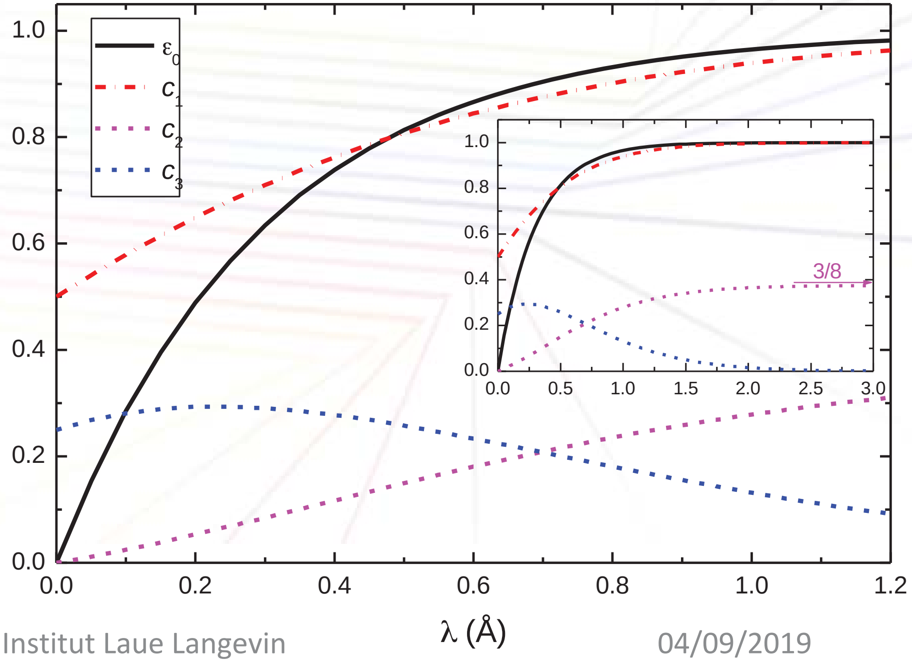
$$S(Q) = \frac{1}{\epsilon_0}\,\frac{1}{b_{\mathrm{coh}}^2}\left(\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}\right)_{\mathrm{corr}} + \left(1 + \frac{b_{\mathrm{inc}}^2}{b_{\mathrm{coh}}^2}\right)\left(C_1\delta - C_2\delta^2 + C_3\delta\gamma - \frac{m}{2M}\,(\delta+\gamma)\right) - \frac{b_{\mathrm{inc}}^2}{b_{\mathrm{coh}}^2}$$

For an exponential detector

$$C_1 = 1 - \frac{\alpha/2}{\mathrm{e}^{\alpha} - 1}$$

$$C_2 = \frac{3}{8} - \frac{\alpha\,(\alpha+3)}{8\,(\mathrm{e}^{\alpha} - 1)}$$

$$C_3 = \frac{\alpha(\alpha+1)}{4\,(\mathrm{e}^{\alpha} - 1)}$$



Sample related corrections

Attenuation

Multiple Scattering

Sample
+
Container

Minimisation by choosing an adequate sample geometry

$$I_{\mathrm{S}}^{\mathrm{corr}}(2\theta) = \frac{1}{\boxed{\alpha_{\mathrm{S,SC}}(2\theta)}}\left(I_{\mathrm{S}}(2\theta) - I_{\mathrm{S}}^{\mathrm{B}}(2\theta) - \frac{\alpha_{\mathrm{C,SC}}(2\theta)}{\alpha_{\mathrm{C,C}}(2\theta)}\left(I_{\mathrm{C}}(2\theta) - I_{\mathrm{C}}^{\mathrm{B}}(2\theta)\right)\right) - \boxed{\Delta}$$

Paalman & Pings’ coefficients

Cylindrical geometry

Blech & Averbach’s correction

Complete knowledge of $S(\boldsymbol{Q},\omega)$
Numerical simulation

Normalisation

Absolute scale
Vanadium diffractogram

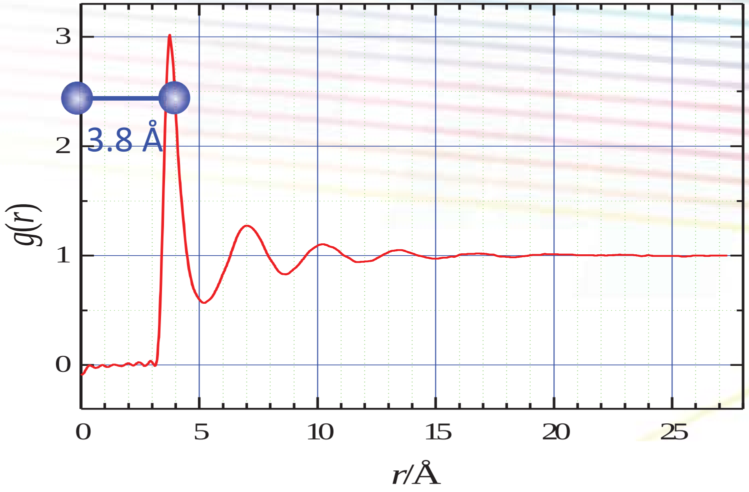
Final analysis

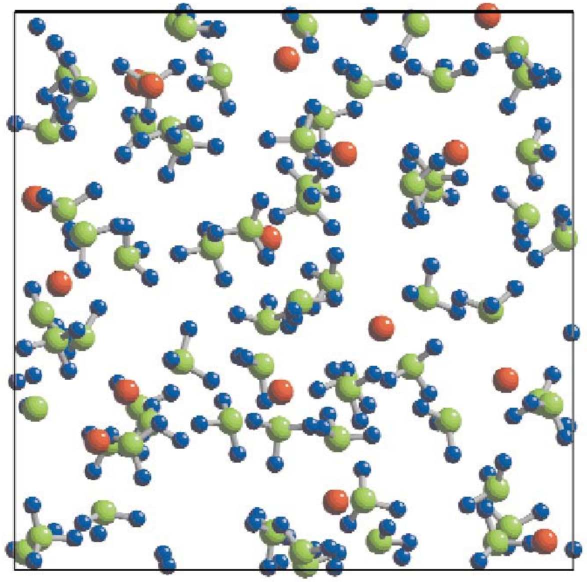
$$I_{exp}(2\theta) \xrightarrow{\text{Corrections}} S(Q) \xrightarrow{\text{FT}} g(r)$$

Truncation effects
Window functions

Interpretation

- Model
- Simulation, *e.g.* RMC, EPSR, MD, etc.





Further reading

General

D.I. Page, *The structure of liquids by neutron diffraction*, p. 173, Chap. 8 in *Chemical applications of thermal neutron scattering*, B.T.M. Willis (Ed.), Oxford University Press (1973).

J.G. Powles, *The structure of molecular liquids by neutron scattering*, Advances in Physics **22**, 1 (1973).

A.C. Wright, *The structure of amorphous solids by x-ray and neutron diffraction*, Advances in Structure Research by Diffraction Methods **5**, 1 (1974).

P.A. Egelstaff, *Classical fluids*, p. 405, Chap.14 in *Methods of experimental physics*, vol. 23, part B, Academic Press (1987).

P. Chieux, *Introduction to accurate structure factor measurements of disordered materials by neutron scattering*, J. Molec. Struct. **296**, 177 (1993).

G. J. Cuello, *Structure factor determination of amorphous materials by neutron diffraction*, J. Phys.: Condensed Matter **20**, 244109 (2008)

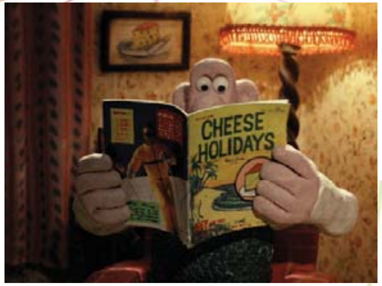
H. E. Fischer, A. C. Barnes, P. S. Salmon, *Neutron and x-ray diffraction studies of liquids and glasses*, Reports on Progress in Physics **69**, 233-299 (2006)

Examples

See the D4 web site (www.ill.fr/YellowBook/D4/pub/) for a list of publications arisen from D4 expts.

Visit the Disordered Materials Group at ISIS (www.isis.stfc.ac.uk/groups/disordered-materials/)

Further reading



Examples with useful information about data treatment

D.M. North, J.E. Enderby and P.A. Egelstaff,
The structure factor for liquid metals:
I. The application of neutron diffraction techniques,
J. Phys. C **1**, 784 (1968).

H. Bertagnolli, P. Chieux and M.D. Zeidler, *A neutron-diffraction study of liquid acetonitrile: I.* $CD_3C^{14}N$, Molec. Phys. **32**, 759 (1976).

J.L. Yarnell, M.J. Katz R.G. Wenzel and S.H. Koenig, *Structure factor and radial distribution function for liquid Ar at 85 K*, Phys. Rev. A **7**, 2130 (1973).

Corrections

G. Placzek, Phys. Rev **86**, 377 (1952).

A.K. Soper and P.A. Egelstaff, *Multiple scattering and attenuation of neutrons in concentric cylinders: I. Isotropic first scattering*, Nucl. Instr. Meth. **178**, 415 (1980).

I.A. Blech and B.L. Averbach, *Multiple scattering of neutrons in vanadium and copper*, Phys. Rev. **137**, A1113 (1965).

H.H. Paalman and C.J. Pings, *Numerical evaluation of x-ray absorption factors for cylindrical samples and annular sample cells*, J. Appl. Phys. **33**, 2635 (1962).