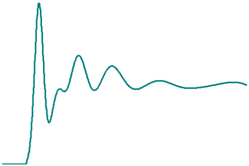
Neutron Powder Diffraction: Long- and Short-Range Order

Gabriel Cuello

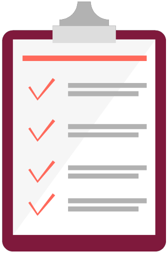
Institut Laue Langevin, Grenoble, France

SFEL, November 7$^{\text{th}}$, 2022



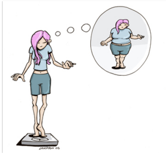
Outline

1. What do we understand by disorder?
2. Total scattering
3. Static structure factor - LRO
4. Static structure factor - SRO
5. Multiatomic systems
6. Isotopic substitution
7. Instruments
8. Polarised neutrons



Disorder on internet

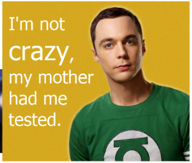
Eating disorder



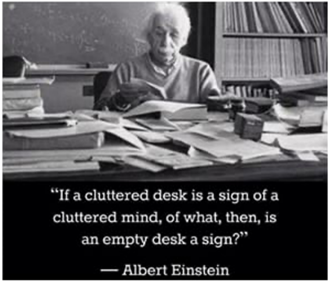
Sleep disorder

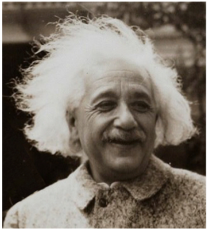
Sexual disorder

Mental disorder

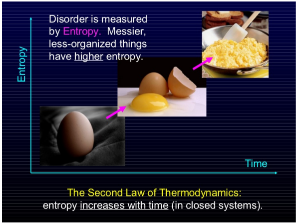


Disordered things in our everyday life

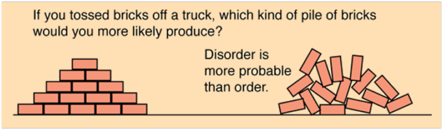




Physical meaning of disorder: $\Delta S > 0$

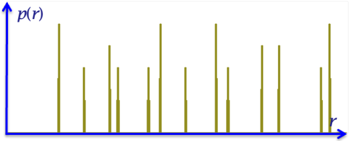


Time arrow



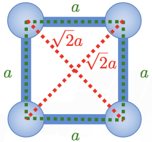
Order versus disorder

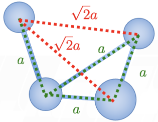
What do you prefer?

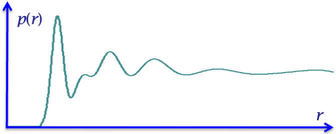


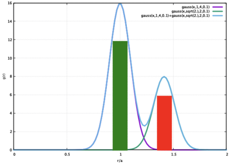
Disorder is funnier than order

Pair correlations in a disordered system

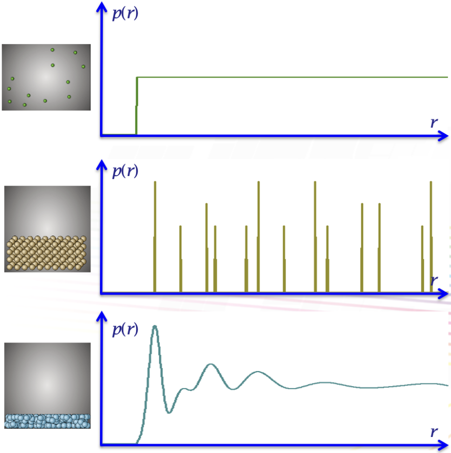




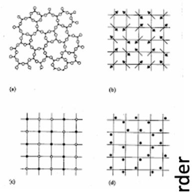




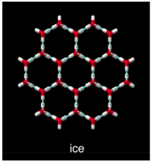
The PDF and states of matter

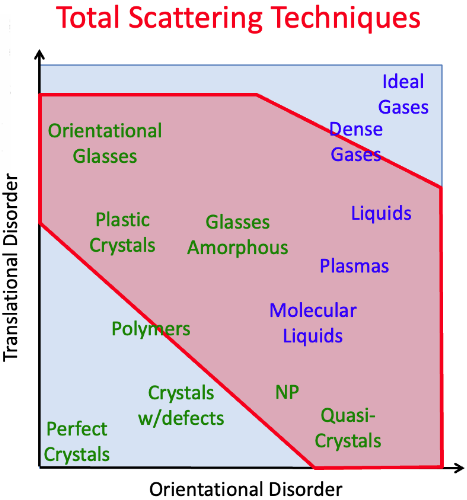


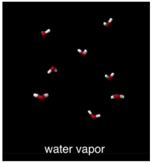
Disorder in solids and fluids



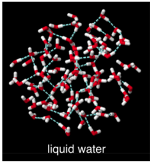
Solids





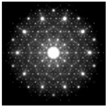


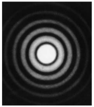
Fluids



Structure by diffraction

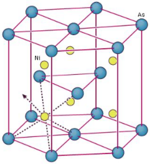
Spatial distribution of atoms or molecules in the system

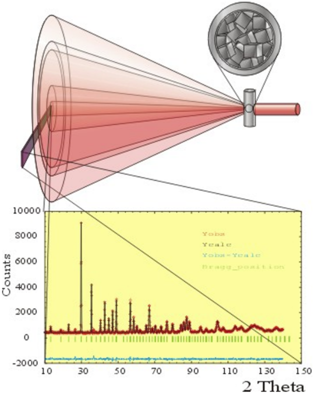




Crystalline solids

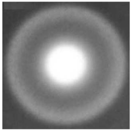
- Equilibrium positions
- Well defined Bragg peaks





Disordered systems

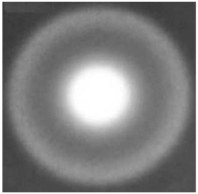
- Distribution of equilibrium positions
- No Bragg peaks

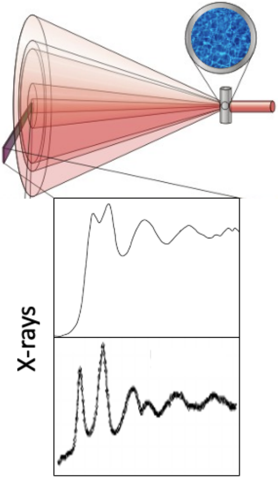


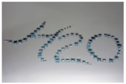
Diffuse scattering

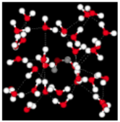
Information about local order

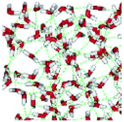
Total scattering









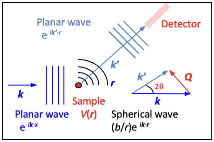


A typical scattering experiment

From the experimental intensity to the microscopic properties

Experiment

Microscopic properties



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

$$I(2\theta,\omega) = C\,\Phi_0\,\frac{\mathrm{d}^2\sigma}{\mathrm{d}\sigma\mathrm{d}\omega}(2\theta,\omega)\,\epsilon(k')$$

Beam Sample Detector

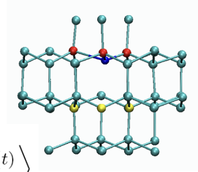
$$\frac{\mathrm{d}^2\sigma}{\mathrm{d}\sigma\mathrm{d}\omega}(2\theta,\omega) = N\,\frac{k'}{k}\,\frac{\sigma}{4\pi}\,S(\vec{Q},\omega)$$

Interaction System

Dynamical Structure Factor

It contains microscopic structural and dynamical information

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



Microscopic Configuration $\{\mathbf{r}_1(t), \mathbf{r}_2(t), \dots, \mathbf{r}_N(t)\}$

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

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

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

Microscopic particle density

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

van Hove's correlation function

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

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

Coherent and incoherent scattering

NEUTRONS FOR SOCIETY

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

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

coherent incoherent

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

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

Collective dynamics
Structural information

Diffusive Motions
Internal Dynamics

Scattering cross section

$$\sigma = \sigma_{coh} + \sigma_{inc}$$

Diffraction
(Elastic scattering)

Total Scattering
(No energy discrimination)

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

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

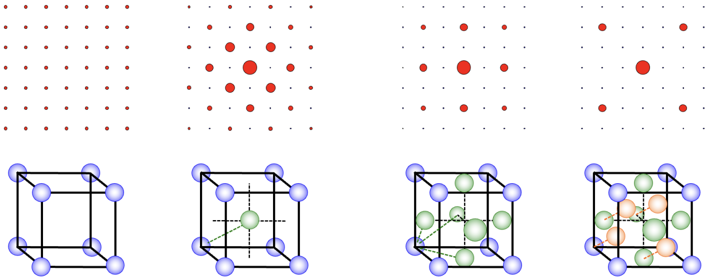
Definition

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

$$\boxed{\begin{aligned} F(\vec{Q}) &= \int_V \mathrm{d}\vec{r}\, \frac{G(\vec{r})}{4\pi r}\, \mathrm{e}^{\mathrm{i}\vec{Q}\cdot\vec{r}} \\ \frac{G(\vec{r})}{4\pi r} &= \frac{1}{(2\pi)^3} \int \mathrm{d}\vec{Q}\, F(\vec{Q})\, \mathrm{e}^{-\mathrm{i}\vec{Q}\cdot\vec{r}} \end{aligned}}$$

Reciprocal and real spaces

- The position of the reflections tells you where the atoms are (lattice of the crystal).
- The intensity of the reflections tells you the base of the crystal.



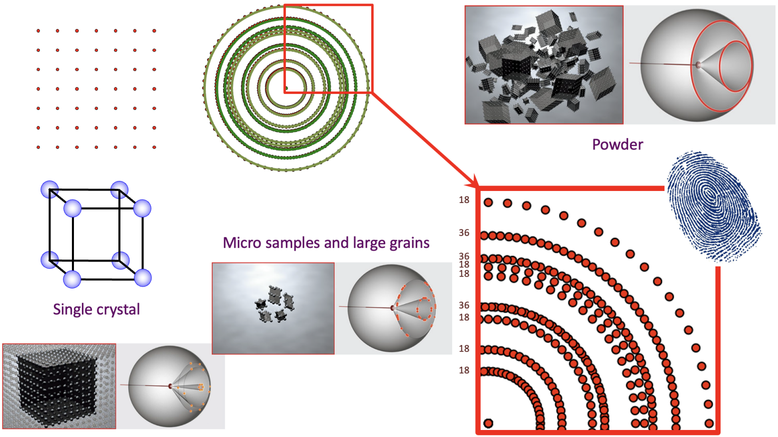
Simple cubic

Body-centred cubic (bcc)

Face-centred cubic (fcc) (cubic-close-packing)

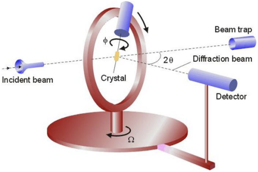
Diamond

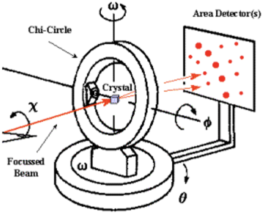
Powder diffraction



Single crystal and Powder Diffraction

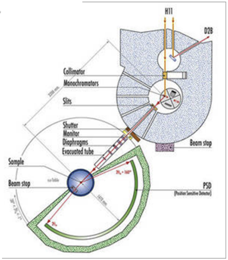
Typical instruments



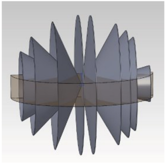


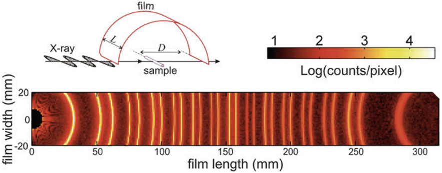
Single crystal diffraction

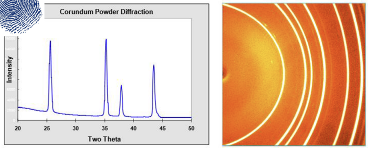
Powder diffraction



Debye-Scherrer geometry

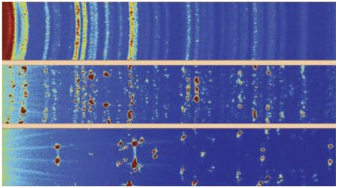






(a) (b)

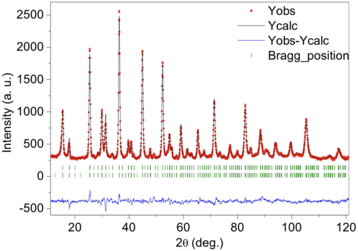
Figure 2. The diffraction pattern of corundum powder: (a) the conventional diffraction pattern; (b) the two-dimensional diffraction pattern.

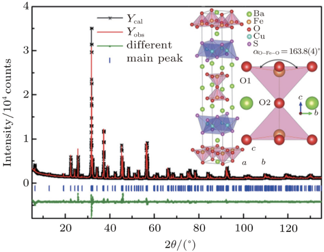


Rietveld refinement

$$\chi^2 = \frac{1}{N}\sum_{i=1}^{N}\left(y_{\mathrm{obs},i} - y_{\mathrm{calc},i}(\mathrm{str},\mathrm{instr})\right)^2$$

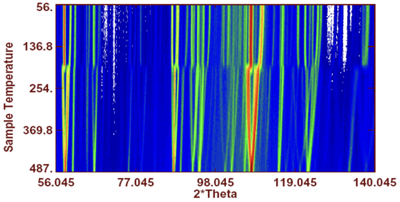
Hugo Rietveld
(1932 - 2016)
Dutch crystallographer





Thermodiffraction

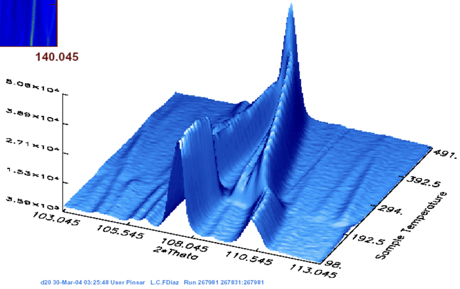
In situ experiments with changing parameters



D20: High Flux Diffractometer

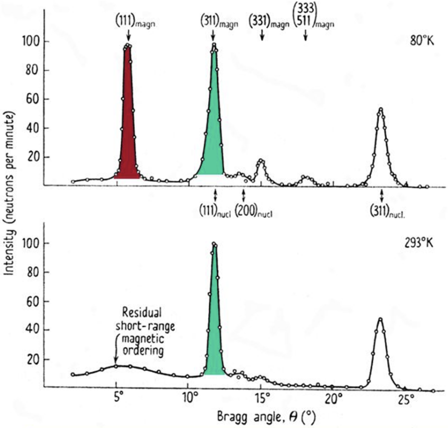
Data collection rate:
3/5 minutes per pattern

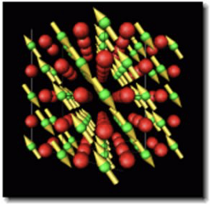
Ge-monochromator
Take-off angle: 120 deg.



Neutrons and magnetism

Neutron has a magnetic moment





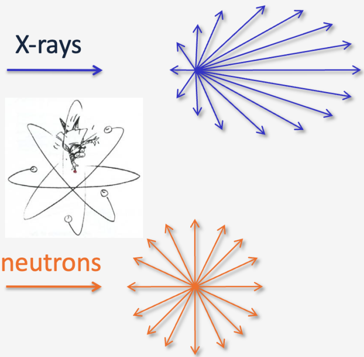
The Nobel Prize in Physics 1994

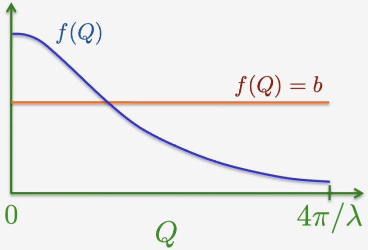
In 1949 Shull showed the magnetic structure of the MnO crystal, which led to the discovery of antiferromagnetism (where the magnetic moments of some atoms point up and some point down).

Weighting Factors

Short parenthesis on form factors

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





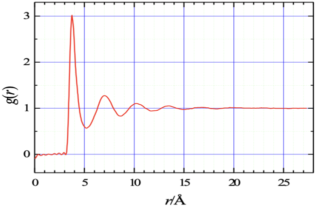
Bragg law $\quad Q = \frac{4\pi}{\lambda} \sin\left(\frac{2\theta}{2}\right)$

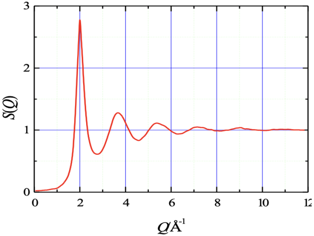
Isotropic approximation

In the case of disordered systems

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

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





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

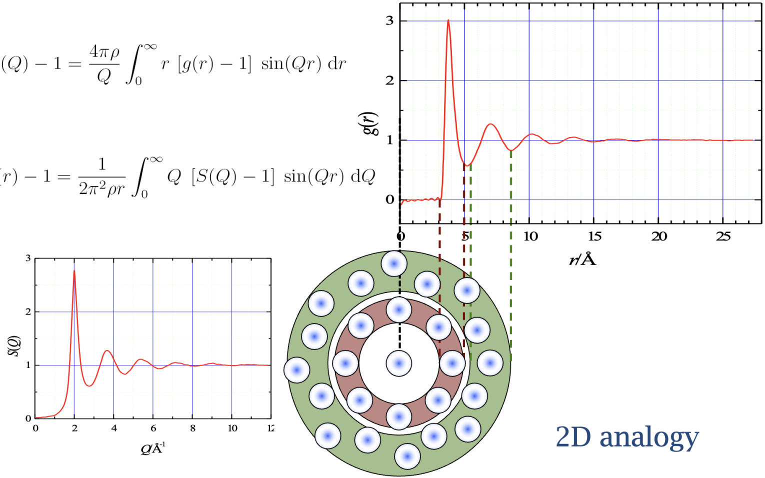
$$g(r) - 1 = \frac{1}{2\pi^2 \rho r} \int_0^\infty Q\ [S(Q) - 1]\ \sin(Qr)\ \mathrm{d}Q$$

Pair distribution function

Coordination shells

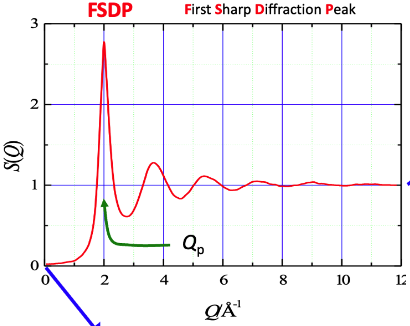
$$S(Q) - 1 = \frac{4\pi\rho}{Q} \int_0^\infty r\ [g(r) - 1]\ \sin(Qr)\ \mathrm{d}r$$

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



2D analogy

First sharp diffraction peak

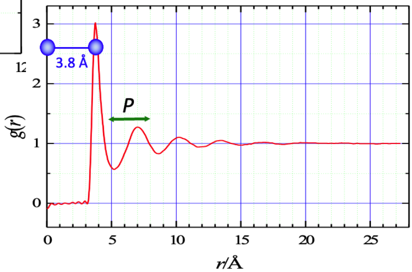


Liquid Ar @ 85K

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

$$S(\infty) = 1$$

Fourier Transformation



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

Limiting values → Normalisation

Static structure factor: Ideal case

Approximations

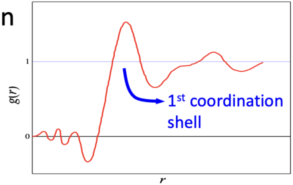
1. Monochromatic $\lambda' = \lambda$
2. Elastic scattering
3. Single scattering (CW) $Q = \frac{4\pi}{\lambda}\sin\theta$
4. No attenuation
5. No background (TOF) $Q = \frac{2mL}{ht}\sin\theta$
6. Monoatomic

$$I_{2\theta,\lambda}(Q) = C\ \Phi_0(\lambda)\ \frac{N}{4\pi}\ \epsilon(\lambda)\ \left(\sigma_{\text{coh}}\ S(Q) + \sigma_{\text{inc}}\right)$$

$$\boxed{S(Q) = \frac{I_{2\theta,\lambda}(Q)/\sigma_{\text{coh}}}{C\ \Phi_0(\lambda)\ \epsilon(\lambda)}\ \frac{4\pi}{N} - \frac{\sigma_{\text{inc}}}{\sigma_{\text{coh}}}}$$

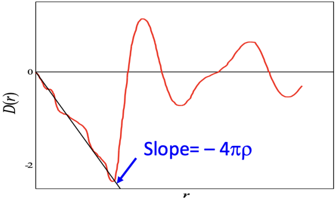
Real space correlation functions

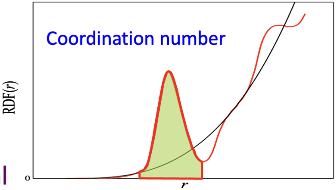
Pair distribution function $g(r)$



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

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





Radial distribution function RDF(r)

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

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

Remember!

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

Multiatomic systems: Isotopic substitution

A system of linear equations

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

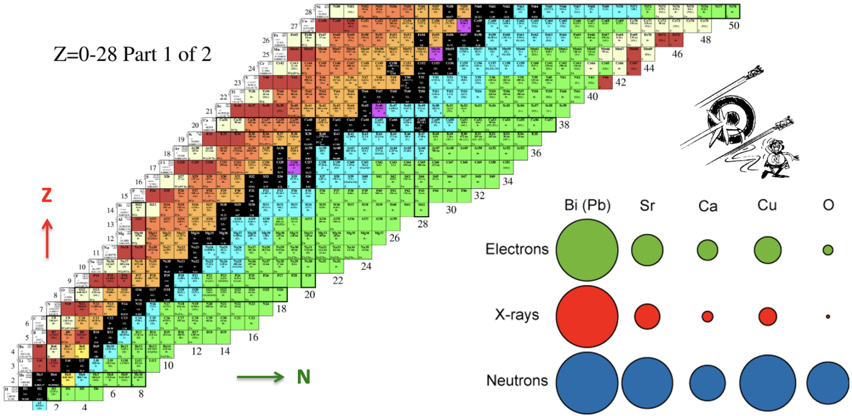
Isotopes with good contrast

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

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

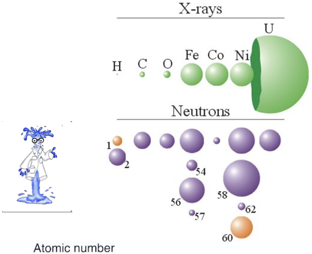
Chart of nuclides

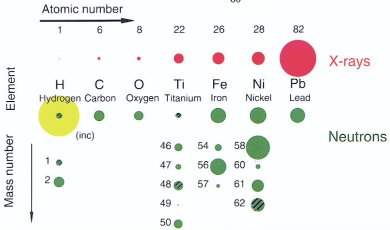
Isotopes vary the cross sections for the same Z

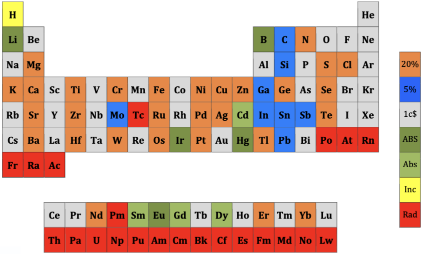


Periodic table

Good candidates for isotopic substitution







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).

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.
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Example: A binary system

Fast ion conductor glasses

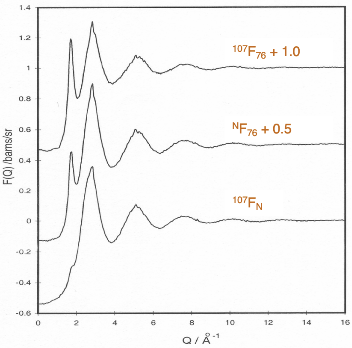
Silver chalcogenides Ag_2X + Network formers AsX or As_2X_3

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

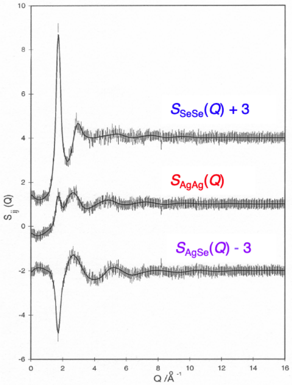
$$\begin{bmatrix} {}^{107}_{nat}F_{S1}(Q) \\ {}^{109}_{76}F_{S2}(Q) \\ {}^{nat}_{76}F_{S3}(Q) \end{bmatrix} = \begin{bmatrix} 0.2594 & 0.0706 & 0.2706 \\ 0.0780 & 0.1654 & 0.2272 \\ 0.1559 & 0.1654 & 0.3211 \end{bmatrix} \begin{bmatrix} F_{AgAg}(Q) \\ F_{SeSe}(Q) \\ F_{AgSe}(Q) \end{bmatrix}$$

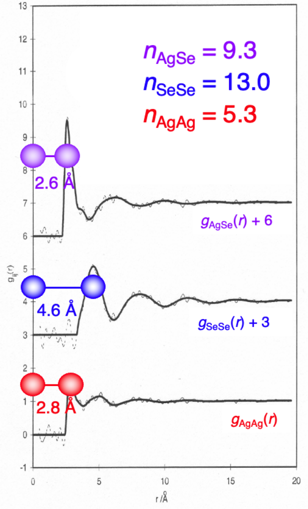


Partial structure factors

Inverse matrix

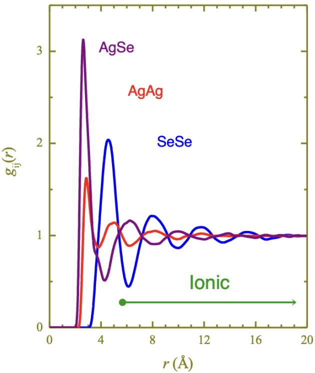
$$\begin{bmatrix} F_{\mathrm{AgAg}}(Q) \\ F_{\mathrm{SeSe}}(Q) \\ F_{\mathrm{AgSe}}(Q) \end{bmatrix} = \begin{bmatrix} 12.17 & 17.31 & -22.50 \\ 8.11 & 32.22 & -29.63 \\ -10.09 & -25.00 & 29.30 \end{bmatrix} \begin{bmatrix} {}^{107}_{\mathrm{nat}}F_{\mathrm{S1}}(Q) \\ {}^{109}_{76}F_{\mathrm{S2}}(Q)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





Two conduction regimes

The short range order reveals two conduction regimes



First difference method

A way to reduce the number of unknowns

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

Substitution -----> γ: γ_1, γ_2

Important! We change scattering lengths but not 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

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

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

small

Example: A ternary system

Lithium Ammonia mixtures

Li in ND_3

Metal-nonmetal transition at 7 MPM

Class A metals

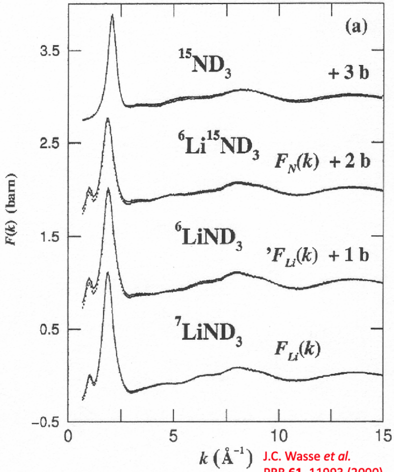
Conductivity 15000 Ω^{-1} cm^{-1} mol^{-1}

3 species $\Rightarrow$ 6 different experiments!

First difference method

Samples:

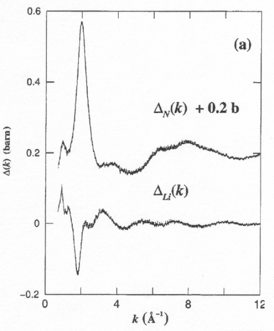
- ^6Li in $^{nat}ND_3$
- ^7Li in $^{nat}ND_3$
- ^6Li in $^{15}ND_3$
- $^{15}ND_3$

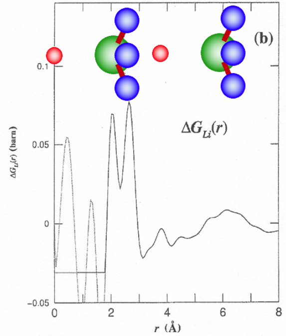


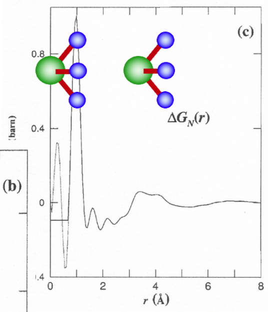
J.C. Wasse *et al.* PRB **61**, 11993 (2000)

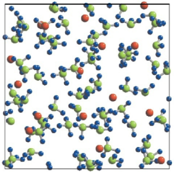
Real space correlations

Ammonia molecules are easily identified









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

Second difference method

At least one partial correlation is determined

New substitution δ: δ_1, δ_2

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

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

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

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

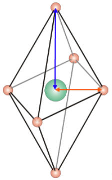
Partial structure factor
for pairs γ and δ

Example: A complex system

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

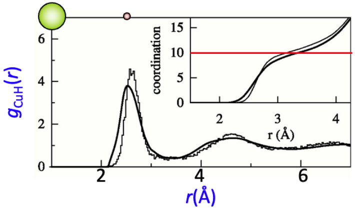
Second difference method

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

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

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

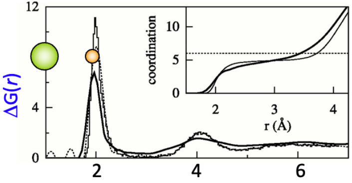
Samples:
$^{65}Cu(ClO_4)_2$+$HClO_4$ in H_2O
$^{63}Cu(ClO_4)_2$+$HClO_4$ in H_2O
$^{65}Cu(ClO_4)_2$+$DClO_4$ in D_2O
$^{63}Cu(ClO_4)_2$+$DClO_4$ in D_2O



Local environment of Cu(II)

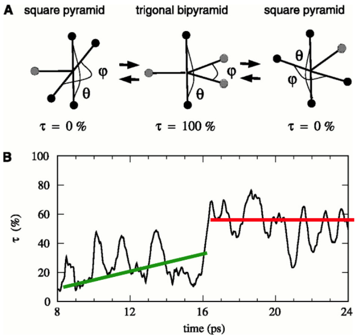
Cu-O correlation

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



First-principles Molecular Dynamics Simulation

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



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

Cu(II) aqua ion is **five-fold** coordinated

1. What do we understand by disorder?
2. Total scattering
3. Static structure factor - LRO
4. Static structure factor - SRO
5. Multiatomic systems
6. Isotopic substitution
7. Instruments
8. Polarised neutrons

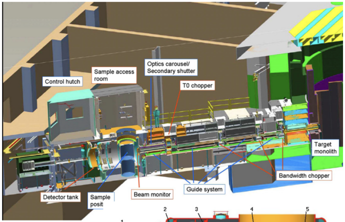
Experiments

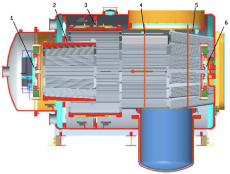
Two techniques for Neutron Total Scattering

Reactor → 2-axis → Scattering angle

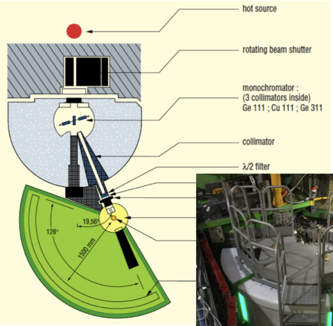
Accelerator → TOF → Time-of-flight

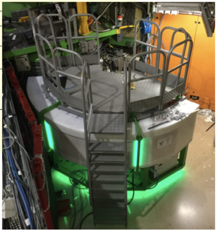
} Elastic scattering → Q





NOMAD (ORNL)



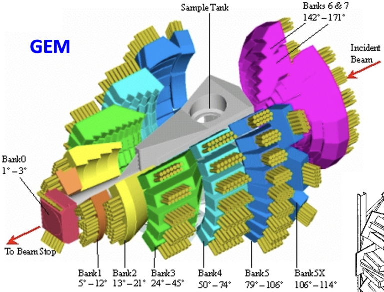


7C2 (LLB)

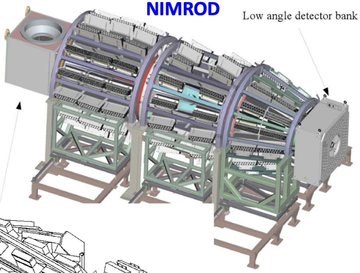
Instruments @ ISIS (UK)

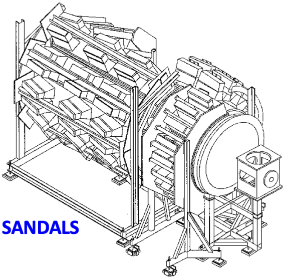
Time-of-Flight instruments

GEM



NIMROD

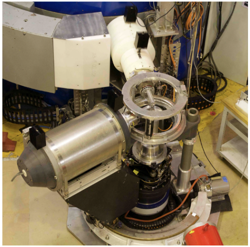




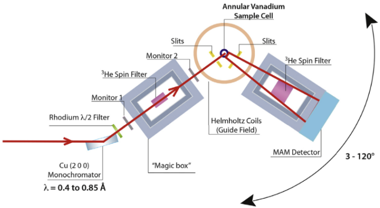
SANDALS

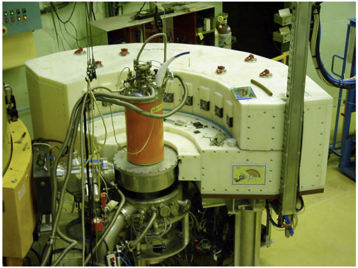
Instruments @ ILL (France)

2-axis instruments

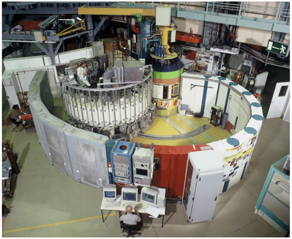


D3



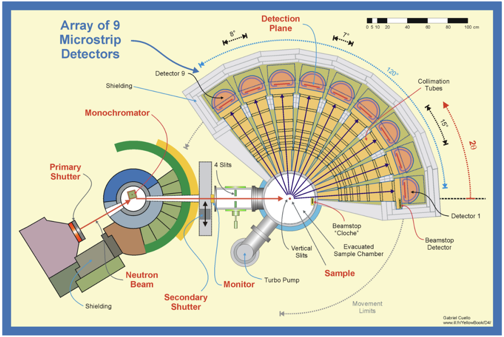


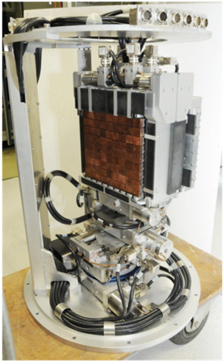
D4



D20

D4: A dedicated diffractometer at ILL



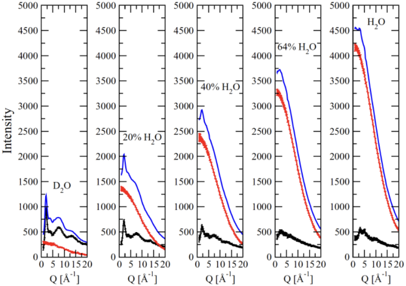


Face	d-spacing (Å)	λ (Å)	Flux (10^7 n cm^{-2} s^{-1})	Filter
Si111	1.807	0.7	5.0	Ir
Cu220	1.278	0.5	4.5	Rh
Cu331	0.829	0.35	0.3	Non

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

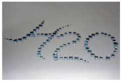
The incoherence problem

Water as example



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



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

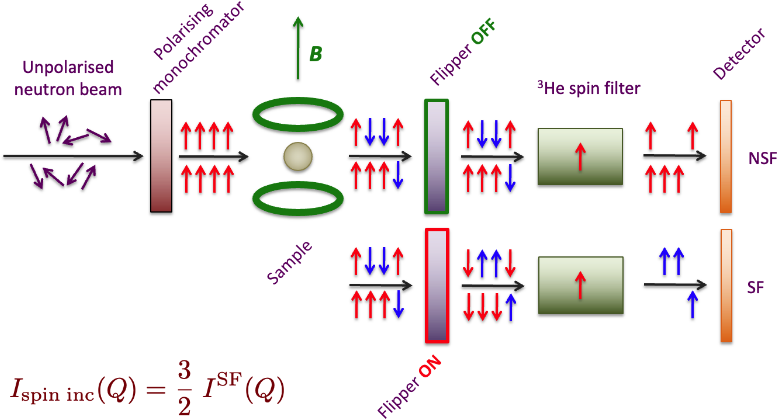
Experimental Methods in the Physical Sciences, Vol. 44.

Elements and Their Isotopes

Element	Z	A	$I(\pi)$	c_a	b	b^+	b^-	b_i	σ_c	σ_i	σ_s	σ_a
n	0	1	1/2(+)		−37.8(8)	0	−37.8 (8)	0	44.89 (4)	0	44.89 (4)	0
H	1				−3.7390 (11)				1.7568 (10)	80.26(6)	82.02 (6)	0.3326 (7)
^{1}H		1	1/2(+)	99.9885	−3.7423 (12)	10.817 (5)	−47.420 (14)	25.217(6)	1.7589 (11)	79.91(4)	81.67 (4)	0.3326 (7)
^{2}H		2	1(+)	0.0115	6.674(6)	9.53 (3)	0.975 (60)	4.03(3)	5.597 (10)	2.04(3)	7.64(3)	0.000519 (7)
^{3}H		3	1/2(+)	12.32 y	4.792(27)	4.18 (15)	6.56(37)	−1.04(17)	2.89(3)	0.14(4)	3.03(5)	<6E−06

Polarisation analysis

Principe of functioning

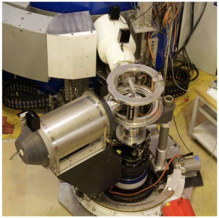


$$I_{\text{spin inc}}(Q) = \frac{3}{2}\, I^{\text{SF}}(Q)$$

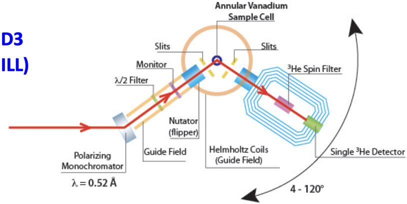
$$I_{\text{coh}}(Q) + I_{\text{isotope inc}}(Q) = I^{\text{NSF}}(Q) - \frac{1}{2}\, I^{\text{SF}}(Q)$$

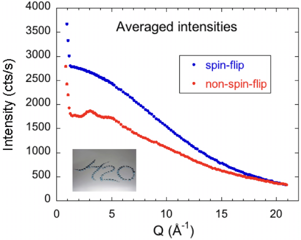
Experiment on light water

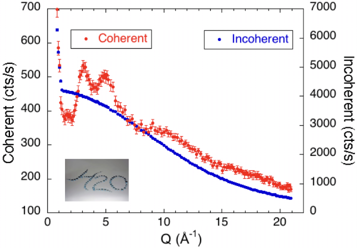
Separation of coherent and incoherent signals



D3 (ILL)



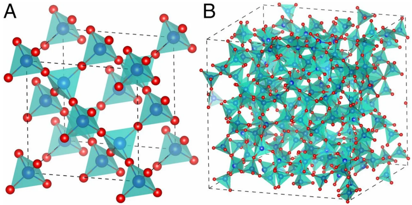


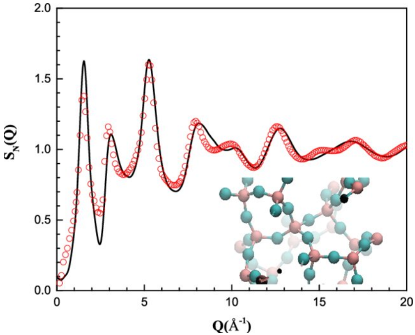


Beyond the experiments

Numerical simulations

- RMC: Reverse Monte Carlo
- EPSR: Empirical Potential Structure Refinement
- MD: Molecular Dynamics





Further reading

Placzek1952 G. Placzek, *The scattering of neutrons by systems of heavy nuclei*, Phys. Rev. **86**, 377 (1952).

Paalman1962 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).

Blech1965 I. A. Blech and B. L. Averbach, *Multiple scattering of neutrons in vanadium and copper*, Phys. Rev. **137**, A1113 (1965).

Yarnel1973 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).

Soper1980 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).

Fischer2002 H. E. Fischer, G. J. Cuello, P. Palleau, D. Feltin, A. C. Barnes, Y. S. Badyal, J. M. Simonson, *D4c: A very high precision diffractometer for disordered materials*, Appl. Phys. A **74**, S160 (2002).

Fischer2006 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 (2006).

Cuello2008 G. J. Cuello, *Structure factor determination of amorphous materials by neutron diffraction*, J. Phys.: Condensed Matter **20**, 244109 (2008).

Thanks for your attention!