

Neutron Diffraction: from theory to the actual experiments

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IX School of Neutron Scattering

“Francesco Paolo Ricci”

Application of Neutrons to Structural Determination in Soft Matter:

From Short and Medium Range Order

to Wetting Processes

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The scattering of a neutron by a system of N identical atoms can be described through the ***double differential scattering cross section*** $d^2\sigma/d\Omega dE$

$$\frac{d^2\sigma}{d\Omega dE_f} = \frac{k_s}{k_0} \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dt \exp(-i\omega t) \sum_{j,j'=1}^N \left\langle b_j^* b_{j'} e^{-i\mathbf{q}\cdot\mathbf{R}_j(0)} e^{i\mathbf{q}\cdot\mathbf{R}_{j'}(t)} \right\rangle \quad (1)$$

$$= N \frac{k_s}{k_0} \left[b_c^2 S_c(\underline{q}, \omega) + b_i^2 S_i(\underline{q}, \omega) \right] \quad (2)$$

where:

- j, j' run over all the N nuclei of the target;
- $\mathbf{R}_j(t)$ is the interaction Heisemberg operator for the position operator \mathbf{R}_j of nucleus j at the time t ;
- b_j is the scattering length of the nucleus j ;
- $\langle \dots \rangle$ is both a quantum and a thermal average;
- $\underline{k}_0, \underline{k}_s$ are the wavevectors of the incident and scattered at θ neutron;
- $\hbar\omega = \hbar^2/2m_n (k_0^2 - k_s^2) = E_0 - E_s$ is the energy exchange; (*)
- $\underline{q} = \underline{k}_0 - \underline{k}_s$ is the momentum transfer to the target; (**)
- m_n is the neutron mass;
- $S_c(q, \omega)$ and $S_i(q, \omega)$ are the Van Hove coherent and incoherent scattering functions which characterize the structure and dynamics of the system;

Expression (2) is obtained in the ***first Born approx.*** with the usual ***assumptions*** that the ***neutrons*** are ***unpolarized***, and the ***nuclear spins*** are statistically ***independent*** on the atomic positions; moreover terms of ***second order*** in the ***electromagnetic scattering lengths*** have been ***neglected*** (see later).

In the **Static Approximation** ($\hbar\omega \ll \hbar\omega_0$) the expression for the **differential scattering cross-section** $d\sigma / d\Omega$ is:

$$\frac{d\sigma}{d\Omega}(\underline{q}) = \int_{-\infty}^{\infty} \frac{d^2\sigma}{d\Omega dE_f} dE = \left\langle \left| \sum_{i=1}^N b_i e^{i\underline{q} \cdot \underline{R}_i} \right|^2 \right\rangle = \left\langle \sum_{i,j} \overline{b_i b_j^*} e^{i\underline{q} \cdot \underline{R}_{ij}} \right\rangle \quad (3)$$

where the vector $\underline{R}_{ij} = \underline{R}_i - \underline{R}_j$ represents the relative position of scattering centres i and j .

Why the name **Static Approximation (SA)**?

The SA holds when $E_0 = \hbar\omega_0 \gg \hbar\omega_{max}$, where $\hbar\omega_{max}$ represents the largest energy exchange compatible with the excitations spectrum featuring the sample at the given temperature.

The corresponding characteristic time of the related atomic motions is $\tau_{min} \sim 1 / \omega_{max}$ (*relaxation time in a liquid*).

The velocity $v_0 = \hbar k_0 / m_n$ of the incoming neutron allows the particle to cover one interatomic distance a in a time $\tau_0 \sim (1 / \omega_0) (a / \lambda_0)$. In neutron diffraction experiments generally a is of the same order of λ_0 , so that $\tau_0 \sim (1 / \omega_0)$.

The SA is valid when $\hbar\omega_0 \gg \hbar\omega_{max}$, that is when

$$\tau_0 \ll \tau_{min}$$


during the characteristic time for diffraction the sample structure changes very little, **it is almost static**, so that the scattering event provides a ‘snapshot’ of the local structure.

The lower incident energies commonly used in NS correspond to $10^{-15} < \tau_0 < 10^{-13}$ s, values which are only about **1** or **2** orders of magnitude smaller than τ_{min} : this incomplete validity of the SA requires the need for inelastic corrections (see later)

Monatomic systems


Assuming *no correlation* between the scattering lengths and positions of different scattering centres:

$$\frac{d\sigma}{d\Omega}(\underline{q}) = \overline{b}^2 \left\langle \sum_{i, j \neq i}^N e^{i\underline{q} \cdot \underline{R}_{ij}} \right\rangle + N \overline{b^2} \quad (4)$$


$$= \overline{b}^2 \left\langle \sum_{i, j}^N e^{i\underline{q} \cdot \underline{R}_{ij}} \right\rangle + N \left(\overline{b^2} - \overline{b}^2 \right) \quad (5)$$

distinct *self*

By introducing the *coherent* and *incoherent* scattering lengths of the sample:


$$b_c = \overline{b} \qquad b_i = \left(\overline{b^2} - \overline{b}^2 \right) = \overline{|b - \overline{b}|^2} \quad (6)$$

which are the *average* and the *standard deviation* of the sample's scattering length distribution, respectively

and the *static structure factor* $S(\underline{q})$ defined as:

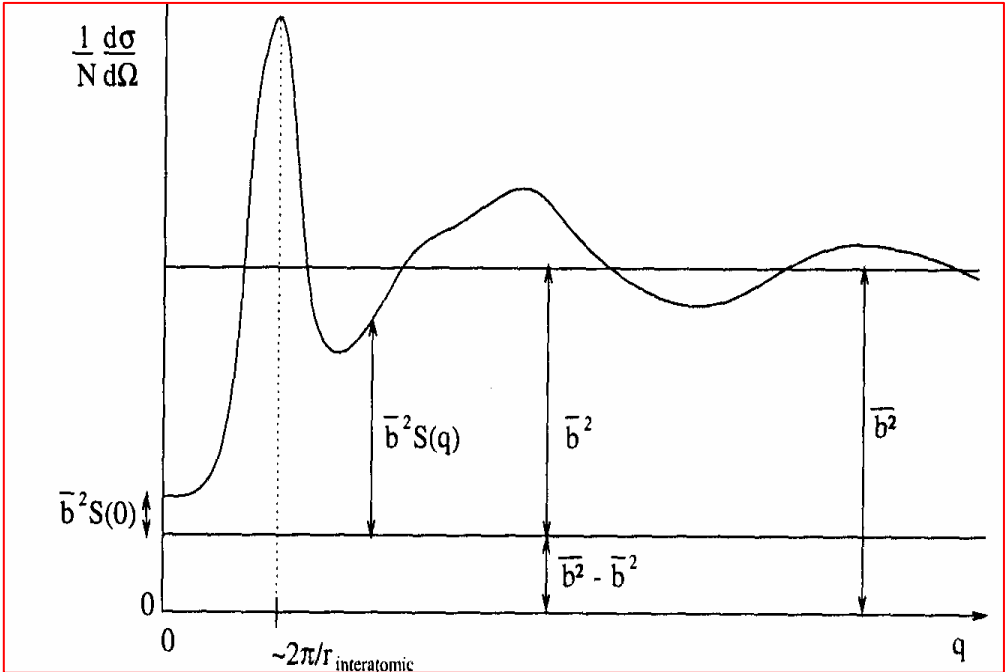
$$S(\underline{q}) = \frac{1}{N} \left\langle \sum_{i,j}^N e^{i\underline{q} \cdot \underline{R}_{ij}} \right\rangle \quad (6)$$

we obtain for the *differential scattering cross section per atom of a monatomic sample*:

$$\frac{1}{N} \left[\frac{d\sigma}{d\Omega}(\underline{q}) \right] = \frac{1}{N} \left[\frac{d\sigma}{d\Omega}(\underline{q}) \right]_{\text{coh}} + \frac{1}{N} \left[\frac{d\sigma}{d\Omega}(\underline{q}) \right]_{\text{incoh}} \quad (8)$$

$$= \bar{b}^2 S(\underline{q}) + (\bar{b}^2 - \bar{b}^2) \quad (9)$$

$$= b_c^2 S(\underline{q}) + b_i^2 \quad (10)$$



In fluid systems for which the *average structure* is *isotropic*, only the vector norms $r = |\underline{r}|$ and $q = |\underline{q}|$ are relevant. By averaging over the relative orientations of \underline{q} the structure factor can be written using the zeroth-order spherical-Bessel functions:

$$S(q) = 1 + \frac{1}{N} \left\langle \sum_{i, j \neq i}^N \frac{\sin(qR_{ij})}{(qR_{ij})} \right\rangle \quad (11)$$

with the expressions for the Fourier transforms linking $S(q)$ to the *pair distribution function* $g(r)$:

$$\left\{ \begin{array}{l} S(q) - 1 = \frac{4\pi\rho}{q} \int_0^\infty r [g(r) - 1] \sin(qr) dr \end{array} \right. \quad (12)$$

$$\left\{ \begin{array}{l} g(r) - 1 = \frac{1}{2\pi^2 r \rho} \int_0^\infty q [S(q) - 1] \sin(qr) dq \end{array} \right. \quad (13)$$

$$S(0) = \rho \chi_T k_B T \quad (14)$$

Compressibility equation

The neutron-electron interaction and b_c (Sears 1986 and references therein quoted)

Let's write again the expression for the differential scattering cross-section of a monatomic system:

$$\frac{1}{N} \left[\frac{d\sigma}{d\Omega}(\underline{q}) \right] = b_c^2 S(\underline{q}) + b_i^2 \quad (25)$$

If we consider also the neutron-electron interaction (neglected in Eq (25)) the expression for b_c can be generalized as (Sears 1986):

$$b_c(\underline{q}) = b_c - b_e Z [1 - f(\underline{q})] \quad (26)$$

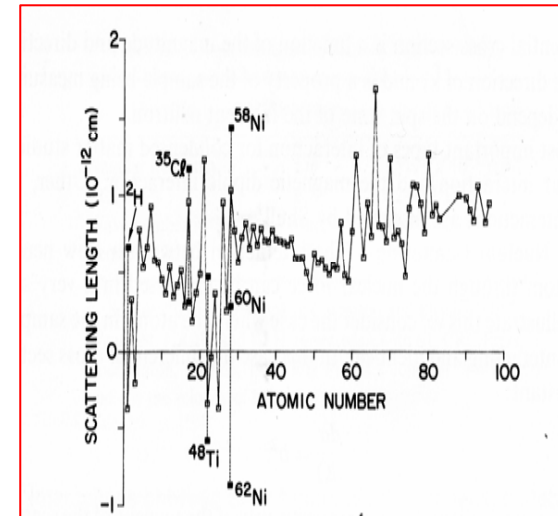
where b_c is the neutron-electron scattering length, Z the atomic number, and $f(q)$ the atomic form factor;

Comments:

a) $b_e = -1.31 \cdot 10^{-3} \text{ fm} = -1.31 \cdot 10^{-18} \text{ m}$

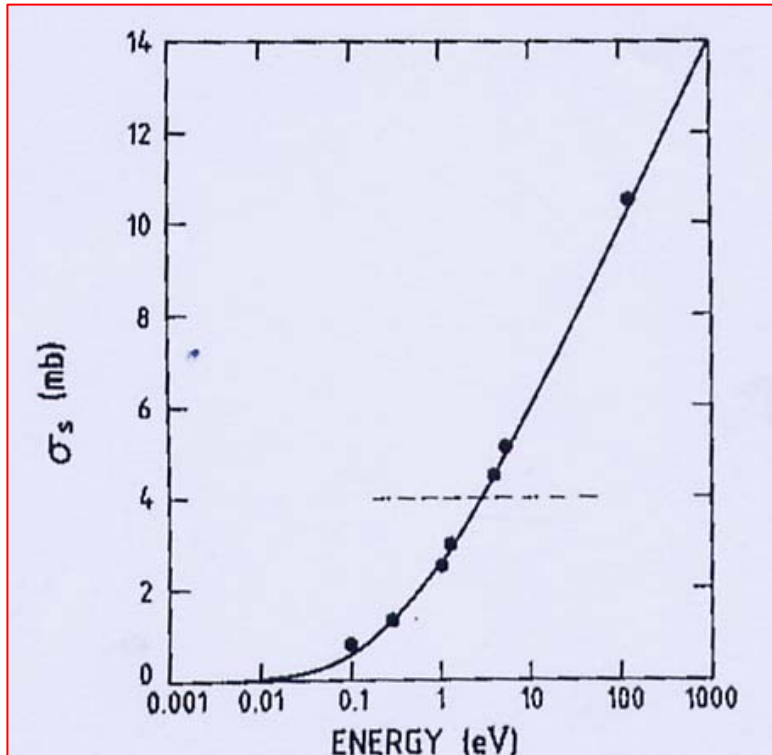
Except for the lightest atoms $b_e Z$ is typically 1.0 to 1.5 % of b_c , and is a factor of 25 to 50 larger than the current experimental uncertainty in b_c .

As a consequence, the usual choice of putting $b_c(q) = b_c$ will produce significant errors of up to 2 to 3% in neutron scattering experiments.



**Scattering length as a function
of the atomic mass**

b) Among the second-order electromagnetic corrections neglected in (25) the one which may be important for the accuracies at which the measured scattering lengths are presently known is the **Schwinger (or spin-orbit) interaction**: this is negligible for thermal neutrons but might be **important** for **epithermal neutrons** with energies **larger** than **1 eV** (spallation sources).



Energy variation of the Schwinger scattering cross section σ_s for bismuth as analytically calculated (smooth line) and by numerical integration (circles). The horizontal dashed line shows the current experimental uncertainty in the measured coherent σ_c which is ± 4 mbarn [from Sears 1986].

c) Finally, in **magnetic** materials the magnetic dipole interaction between the neutron and the electrons gives an **additional contribution** to the cross section which allows the magnetic structure and dynamics of the system to be studied by neutron diffraction and inelastic scattering experiments.

Polyatomic systems

The expression for $d\sigma/d\Omega$ can be generalized to a system of n chemical species:

$$\frac{1}{N} \left[\frac{d\sigma}{d\Omega} (q) \right] = F(q) + \sum_{\alpha}^N c_{\alpha} \overline{b_{\alpha}^2} \quad (15)$$

where $F(q)$ is the *total interference function* and c_{α} is the *concentration* of chemical species α . The second term of Eq (15) is:

$$\sum_{\alpha}^N c_{\alpha} \overline{b_{\alpha}^2} = \overline{b^2} \quad \text{where} \quad \overline{b_{\alpha}^2} = b_{coh, \alpha}^2 + b_{inc, \alpha}^2 \quad (16)$$

It is often chosen the **Faber** and **Ziman** (1965) convention for defining *partial structure factors* $S_{\alpha\beta}(q)$:

$$F(q) = \sum_{\alpha, \beta}^n c_{\alpha} c_{\beta} \overline{b_{\alpha}} \overline{b_{\beta}} [S_{\alpha\beta}(q) - 1] \quad (17) \quad \text{Faber and Ziman partial structure factors}$$

where each $S_{\alpha\beta}(q)$ depends only on the distribution of α atoms around β atoms (or vice-versa). Note that also the definition proposed by Ashcroft and Langreth (1967) is often adopted. The relationship between the two definitions is:

$$S_{\alpha\beta}^{AL}(q) = \delta_{\alpha\beta} + (c_{\alpha} c_{\beta})^{1/2} [S_{\alpha\beta}^{FZ}(q) - 1] \quad (18)$$

In an analogous way to what done for monatomic systems, the **FZ** partial structure factors for an isotropic system are defined as:

$$S_{\alpha\beta}(q) = S_{\beta\alpha}(q) = 1 + \frac{1}{c_{\alpha}c_{\beta}N} \left\langle \sum_{i,j \neq i}^{N_{\alpha}, N_{\beta}} \frac{\sin(qR_{ij})}{(qR_{ij})} \right\rangle \quad (19)$$

where $N_{\alpha} = c_{\alpha}N$ is the number of α atoms, while i and j refer to sites among the α and β atoms, respectively. Applying Fourier transformation:

$$\left\{ \begin{array}{l} S_{\alpha\beta}(q) - 1 = \frac{4\pi\rho}{q} \int_0^{\infty} r [g_{\alpha\beta}(r) - 1] \sin(qr) dr \end{array} \right. \quad (20)$$

$$\left\{ \begin{array}{l} g_{\alpha\beta}(r) - 1 = \frac{1}{2\pi^2 r \rho} \int_0^{\infty} q [S_{\alpha\beta}(q) - 1] \sin(qr) dq \end{array} \right. \quad (21)$$

with $S_{\alpha\beta}(q \rightarrow \infty) = 1$ for all α, β .

The partial pair-distribution functions $g_{\alpha\beta}(r)$ are a measure of the probability of finding a β atom at a distance r from an α atom.

An useful sum-rule for checking the normalization of partial structure factors is obtained by taking the $r \rightarrow 0$ limit of Eq (21):

$$\int_0^{\infty} q [S_{\alpha\beta}(q) - 1] dq = -2\pi^2 \rho \quad (22)$$

For a binary system **Bathia and Thornton** (1970) suggested an alternative set of partial structure factors, $S_{NN}(q)$, $S_{CC}(q)$ and $S_{NC}(q)$, describing, respectively, the *distributions of atomic number density*, of *concentration* and the *correlation between the two*. The function $F(q)$ is then:

$$F(q) = \langle b \rangle^2 S_{NN}(q) + |\bar{b}_1 - \bar{b}_2|^2 S_{CC}(q) + \left[\langle b \rangle (\bar{b}_1^* - \bar{b}_2^*) + \langle b \rangle^* (\bar{b}_1 - \bar{b}_2) \right] S_{NC}(q) - \left(c_1 \bar{b}_1^2 + c_2 \bar{b}_2^2 \right) \quad (23)$$

where c_1 and c_2 are the atomic concentrations and $\langle b \rangle = c_1 \bar{b}_1 + c_2 \bar{b}_2$ is the overall average scattering length.

Fourier transformation then gives the **BT** partial pair-distribution functions $g_{NN}(r)$, $g_{CC}(r)$ and $g_{NC}(r)$.

$S_{NN}(q)$ is measured directly in a diffraction experiment if both chemical species have the same average (i.e. coherent) scattering length; the corresponding $g_{NN}(r)$ gives the sites of the scattering nuclei but does not distinguish between the chemical species that occupy those sites.

The chemical ordering is described by $g_{CC}(r)$, which has positive or negative peaks when there is a preference for like or unlike neighbours, respectively.

The correlation between sites and their occupancy by a given chemical species is described by $g_{NC}(r)$.

The connection between Bathia-Thornton and Faber-Zimann coefficients is given by:

$$\left\{ \begin{array}{l} S_{NN}(q) = c_1^2 S_{11}(q) + c_2^2 S_{22}(q) + 2c_1 c_2 S_{12}(q) \\ S_{CC}(q) = c_1 c_2 [1 + c_1 c_2 (S_{11}(q) + S_{22}(q) - 2S_{12}(q))] \\ S_{NC}(q) = c_1 c_2 [c_1 (S_{11}(q) - S_{12}(q)) - c_2 (S_{22}(q) - S_{12}(q))] \end{array} \right. \quad (24)$$

Ideal solution:

- a) the two chemical species mix randomly \rightarrow all three **FZ** partial structure factors are equal $\rightarrow S_{CC}(q) = c_1 c_2 \rightarrow S_{CC}(q) \neq \text{const}$ indicates non-ideal substitution between the two species;
- b) There is no correlation between site and chemical species $\rightarrow S_{NC}(q) = \mathbf{0} \rightarrow$ all structural information in **F(q)** is contained in **S_{NN}(q)**.

Neutron diffraction with isotopic substitution (NDIS)

$F(q)$ is measured for several samples of identical structure and chemical composition but with different isotopic compositions for one or more of the species α :

$$F_i(q) = \sum_{\alpha, \beta}^n c_\alpha c_\beta \overline{b_{\alpha i} b_{\beta i}} [S_{\alpha\beta}(q) - 1] \quad (25)$$

where $\overline{b_{\alpha i}}$ is the average scattering length of the α atoms in sample i .

A sample with n chemical species: $m = n(n+1)/2$ independent partial structure factors $\rightarrow m$ samples of different isotopic composition for a complete determination of the $S_{\alpha\beta}(q)$. It is therefore useful to express Eq (25) in matrix form; for a binary system with two species x and y the equation reads:

$$\begin{bmatrix} F_1(q) \\ F_2(q) \\ F_3(q) \end{bmatrix} = \begin{bmatrix} c_x^2 \overline{b_{x1}^2} & c_y^2 \overline{b_{y1}^2} & 2c_x c_y \overline{b_{x1} b_{y1}} \\ c_x^2 \overline{b_{x2}^2} & c_y^2 \overline{b_{y2}^2} & 2c_x c_y \overline{b_{x2} b_{y2}} \\ c_x^2 \overline{b_{x3}^2} & c_y^2 \overline{b_{y3}^2} & 2c_x c_y \overline{b_{x3} b_{y3}} \end{bmatrix} \begin{bmatrix} S_{xx}(q) - 1 \\ S_{yy}(q) - 1 \\ S_{xy}(q) - 1 \end{bmatrix} \quad (26)$$

$$\equiv \begin{bmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{bmatrix} \begin{bmatrix} S_{xx}(q) - 1 \\ S_{yy}(q) - 1 \\ S_{xy}(q) - 1 \end{bmatrix}$$

which can be written in a more compact way as:

$$[F(q)] = [A][S(q) - 1] \quad (27)$$

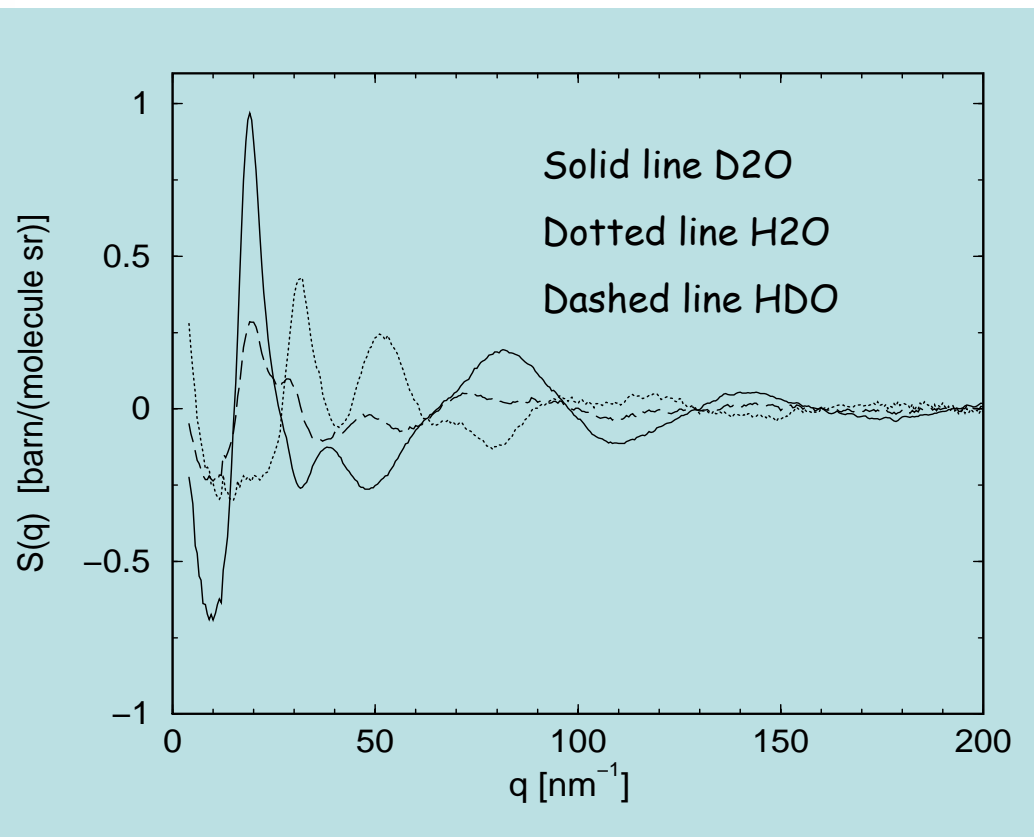
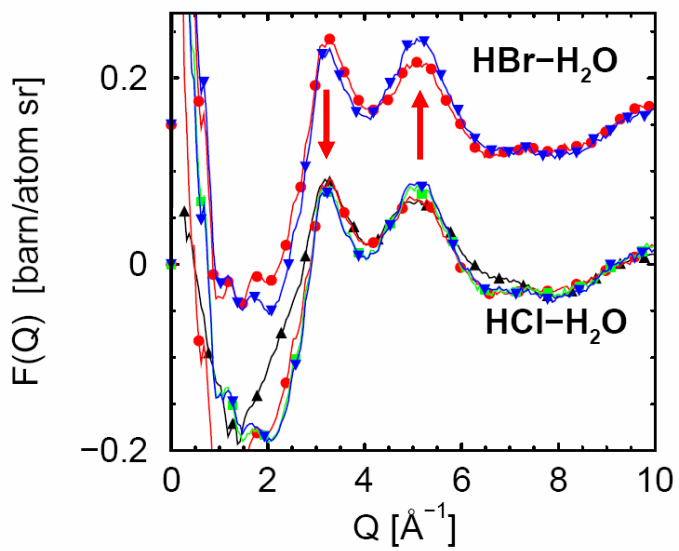
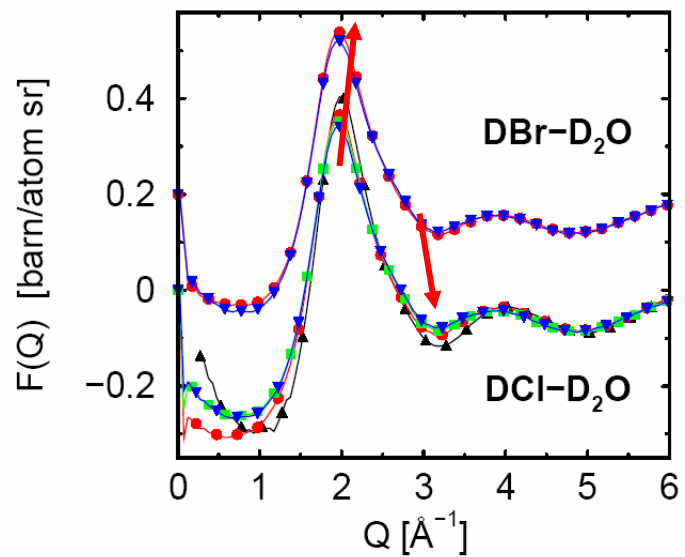
By inverting (27) we can solve for the partial structure factors $S_{\alpha\beta}(q)$:

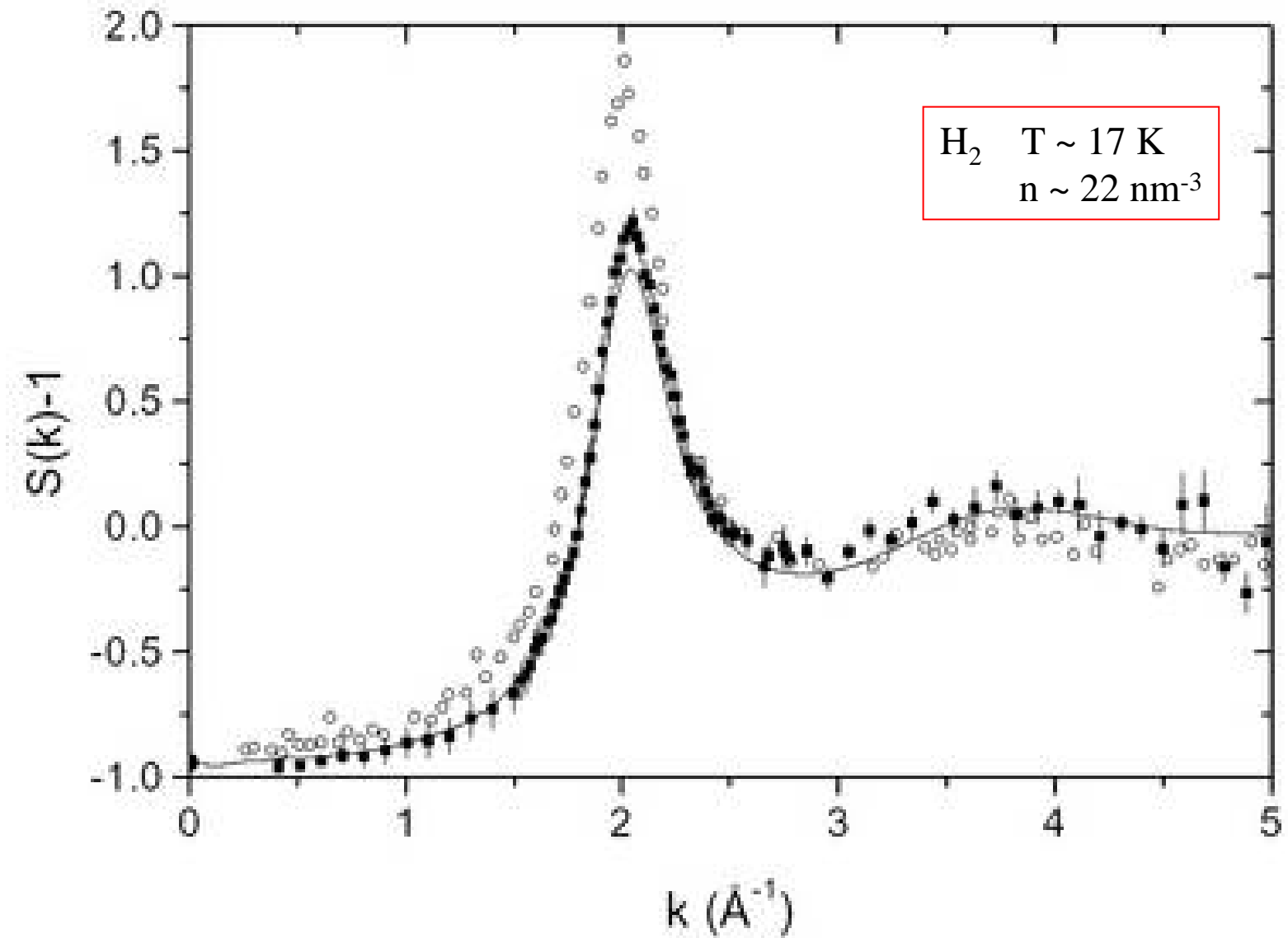
$$[S(q) - 1] = [A]^{-1}[F(q)] \quad (28)$$

The determinant $|A|$ depends on the scattering length contrast between the $F_i(q)$; its value is a measure of the robustness in the determination of the $S_{\alpha\beta}(q)$.

The ideal case is $|A| = 1$; however, in NDIS are very often present values less than 0.1.

When the NDIS matrix is poorly conditioned it is preferable to make use of the singular value decomposition (SVD): with this numerical technique one obtains also the relative errors and its sign (+/-) for each of the $n(n+1)/2$ partial structure factors.





- **First and second difference measurements**

When not all the requested NDIS experiment can be performed, some information can still be gained from a limited number of experiments. For example, in the case of only two exps. wherein the isotopic composition of only one chemical species x is varied, a simple subtraction of the measured $F_i(q)$ for samples **1** and **2** gives information on the partial factors involving atoms of chemical species x .

- **'Zero' scattering element**

'Null water': approx. 2 parts H₂O and 1 part D₂O, so that the average coherent scattering length of the Z=1 sites is zero. The neutrons then see only the oxygen atoms of the water molecules.

Ti-Zr 'zero alloy'

- **Quantum isotope effects**

Isomorphic substitution: similar chemical species are substituted, rather than the different isotopes of a given species. The two species must be as chemically identical as possible, with nearly equivalent atomic radii, such that they can substitute freely for each other without chemical correlation (see, for example, Martin et al. 2003a *Phys. Rev. Lett* **90** 185501, Martin et al. 2003b *J. Phys.: Condens. Matter* **15** 8235–52).

Data analysis

Several effects influence the measured intensities, so that to extract the structural information contained in a set of neutron diffraction data a sequence of corrections has to be applied.

Here is a list (not exhaustive) of experimental corrections usually needed:

- 1) Dead time
- 2) Spatial Resolution
- 3) Background scattering
- 4) Attenuation
- 5) Multiple scattering
- 6) Inelastic scattering
- 7) Absolute units normalization

Dead Time

Detectors are always ‘*dead*’ for a short period of time after a neutron event has occurred.

For a ${}^3\text{He}$ tube this ‘deadtime’ might be $3\ \mu\text{s}$, whilst for a *glass scintillator* it is something like $250\ \text{ns}$.

Usually the effect for ‘deadtime’ amounts to a few percent of the recorded intensity, so it can be corrected for by a simple formula.

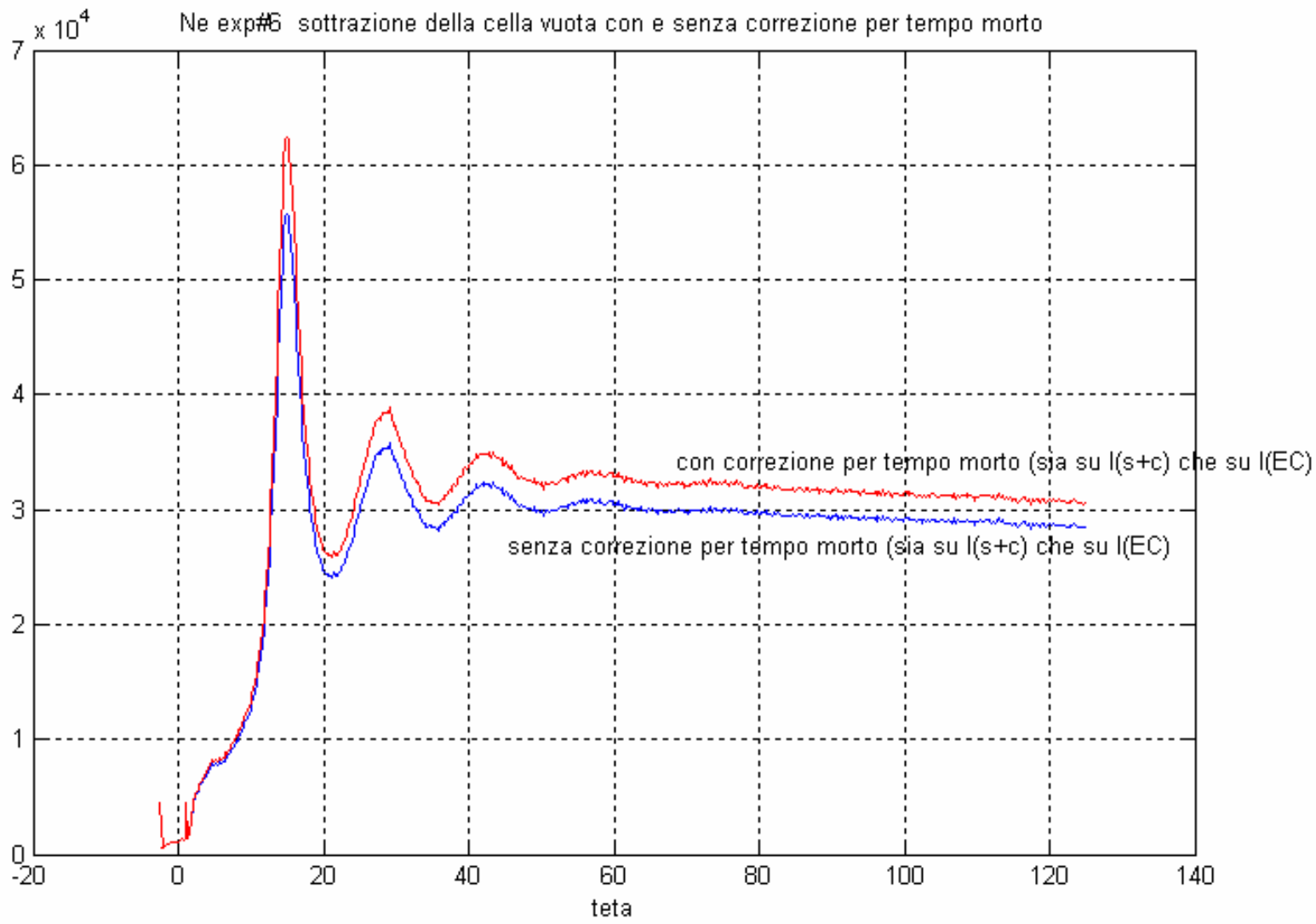
When the width Δ of the time channel is broad compared to the deadtime τ , if R_m is the measured counting rate in the time channel, then the detector is dead for a time t_D :

$$t_D = \Delta R_m \tau \quad (27)$$

Hence the count rate, R , which would have been measured if the detector had zero deadtime, is greater than R_m in proportion to the time that the detector is dead:

$$R = [\Delta / (\Delta - t_D)] R_m = R_m / (1 - R_m \tau) \quad (28)$$

When more detectors are encoded in a single encoder, it is the encoder’s deadtime which has to be considered. Even though the deadtime for an individual detector may be small, the counting rate can be significantly affected because of the number (for example: 30) of detectors grouped in the same encoder.



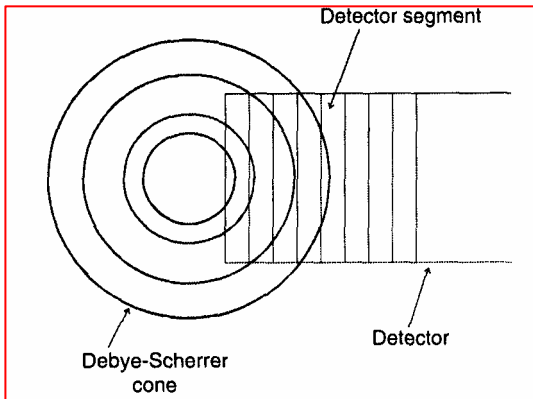
Resolution effects

The resolution function of a two-axis diffractometer has several components:

- incident wavelength;
- focussing setup;
- sample sizes;
- detector height and distance from the sample.

Depending on the instrument set-up, the so-called '*umbrella effect*' can show up and be of particular relevance especially at small diffraction angles.

The origin of this effect can be attributed to the intersection between the rings of the Debye-Scherrer cone with a detector of finite size.



At small θ -angles the radius of the ring is small and each detector segment (the cathodic wire) can detect some intensity coming from θ -values larger than the nominal value where the detector is located.

If the diffraction intensity is increasing with θ , the measured intensity at the nominal angle will increase as well (and vice versa): *peaks are therefore asymmetrically broadened and shifted to lower angles.*

The effect is larger if large size of the container are used.

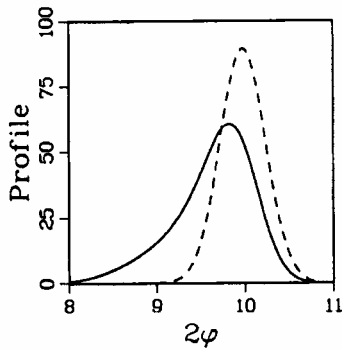


Fig. 7. The total profiles of a reflection at $2\theta = 10^\circ$ obtained by folding the diffraction profiles from Fig. 4 with a Gaussian with FWHM $\Gamma = 0.6^\circ$.

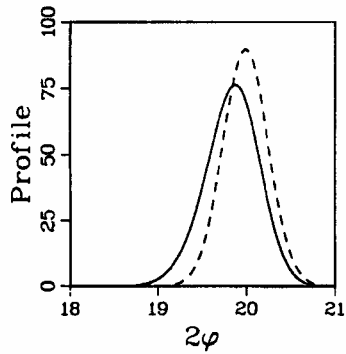


Fig. 8. The total profiles of a reflection at $2\theta = 20^\circ$ obtained by folding the diffraction profiles from Fig. 5 with a Gaussian with $\Gamma = 0.6^\circ$.

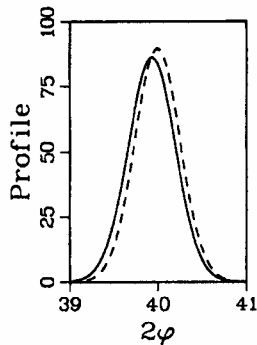


Fig. 9. The total profiles of a reflection at $2\theta = 40^\circ$ obtained by folding the diffraction profiles from Fig. 6 with a Gaussian with $\Gamma = 0.6^\circ$.

$$2\theta = 10^\circ$$
$$2H_D = 10 \text{ cm}$$
$$2H_S = 4 \text{ cm}$$

$$2\theta = 20^\circ$$
$$2H_D = 10 \text{ cm}$$
$$2H_S = 4 \text{ cm}$$

$$2\theta = 40^\circ$$
$$2H_D = 10 \text{ cm}$$
$$2H_S = 4 \text{ cm}$$

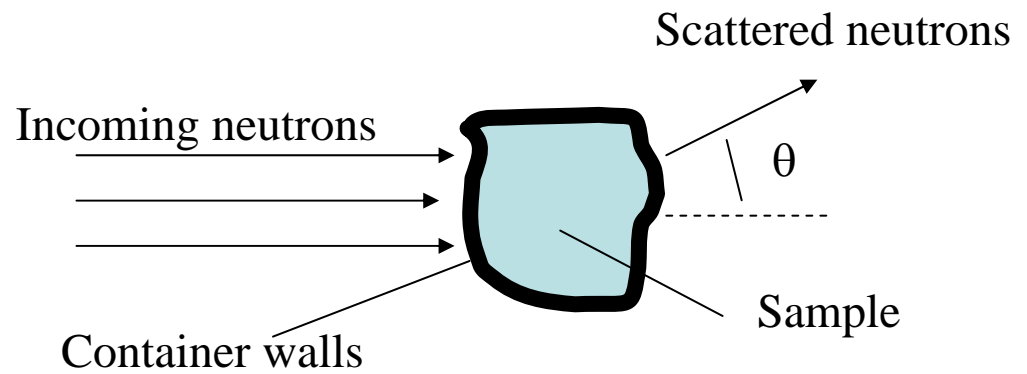
Background, attenuation and multiple scattering

The diffraction intensities coming from the background, the sample container (if present) and the sample environment (e.g. cryostat, furnace) have to be subtracted.

The correction must account for the processes of *attenuation* of *incoming* and *scattered* beams (through absorption and scattering) and *multiple scattering*, which originate not only from the sample environment but also from the sample itself.

a) Background scattering

Let's consider a sample in a container:



The total intensity I_{S+C} diffracted by the fluid sample S in the container C can be written as

$$I_{S+C}^{meas}(\theta) = I_S(\theta) + I_C^S(\theta) + I_B^S(\theta) \quad (29)$$

A measurement of the background intensity $I_B^S(\theta)$ can be performed removing both sample and container (*empty diffractometer*).

However, we must note that $I_B^S(\theta)$ is composed by two contributions:

- a) a part that is modified if container and/or sample are present (*through scattering and absorption*);
- b) an unattenuated part (bkg neutrons which do not pass through the sample/container position).

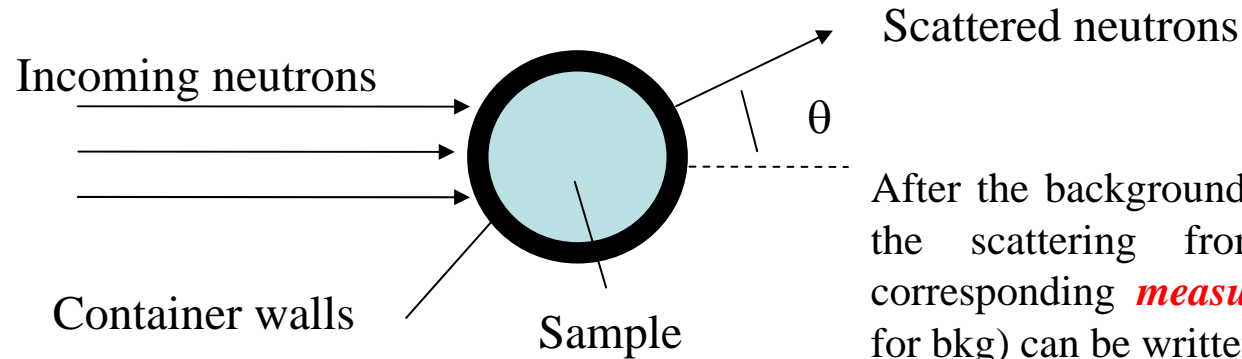
The unattenuated contribution (whose intensity level is usually very low) can be measured separately using for example a Cd bar (*Cadmium is an almost perfect neutron adsorber*) of exactly the same outer dimensions as the container: let's be $I_{Cd}(\theta)$ the corresponding intensity.

The contribution attenuated by the presence of the sample and/or container can be evaluated by numerically computing the transmission $T_{S+C}(\theta)$ due to sample and/or container, so that the intensity $I_{S+C}(\theta)$ scattered by sample and/or container and corrected for background reads:

$$I_{S+C}(\theta) = I_{S+C}^{meas}(\theta) - I_{Cd}(\theta) - T_{S+C}(\theta) \left[I_B^S(\theta) - I_{Cd}(\theta) \right] \quad (30)$$

b) Attenuation and Multiple Scattering

For simplicity let's consider a fluid sample contained in a cylindrical container. The longitudinal cylindrical axis be perpendicular to the incoming beam and let's have a look at the scattering process from the top of the cylinder.



After the background, we need to remove also the scattering from the container. The corresponding *measured* intensities (corrected for bkg) can be written as:

$$I_{S+C}(\theta) = A_{S,SC}(\theta) I_S^{(1)}(\theta) + A_{C,SC}(\theta) I_C^{(1)}(\theta) + I_{S+C}^{(m)}(\theta) \quad (31)$$

$$I_C(\theta) = A_{C,C}(\theta) I_C^{(1)}(\theta) + I_C^{(m)}(\theta) \quad (32)$$

where:

- I_{S+C} and I_C are the measured intensities, corrected for *bkg*, in presence of *Sample + Container* and *Container*, respectively;
- the apexes (1) and (m) refer to single and multiple scattering, respectively, for *sample (S)*, *sample + container (S+C)* and *container (C)*;
- the A coefficients, introduced by Paalman and Pings, account for the *attenuation* of incoming and single scattered beam.

In the Paalman and Pings coefficients $A_{i,j}$ the first suffix i refers to where the scattering process takes place, while the second one j indicates where the attenuation, through absorption and/or scattering, occurs.

The single scattering sample intensity $I_S^{(1)}$ can now be written as:

$$I_S^{(1)}(\theta) = \frac{1}{A_{S,SC}(\theta)} \left\{ I_{S+C}(\theta) - I_{S+C}^m(\theta) - \frac{A_{C,SC}(\theta)}{A_{C,C}(\theta)} [I_C(\theta) - I_C^{(m)}(\theta)] \right\} \quad (33)$$

Comments:

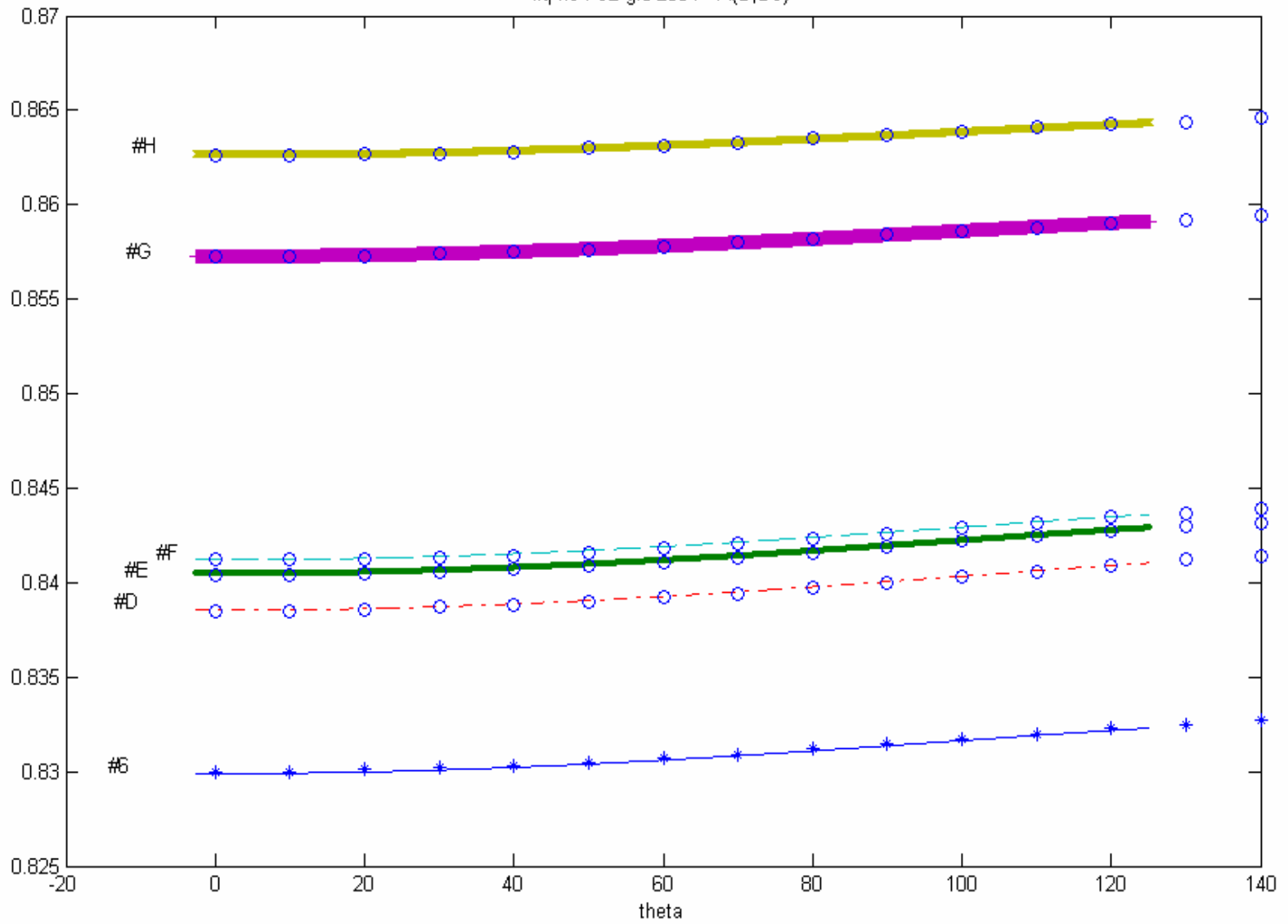
- 1) The general form for the attenuation factors is:

$$A_{i,j}(\theta) = \frac{1}{V} \int_V dV e^{-\sum_k \rho_k \sigma_k l_k} \quad (34)$$

where ρ_k , σ_k and l_k are the *number density*, the *neutron cross section* and the *length* of the k -th element of sample and/or container crossed by the neutron, and the integral extends over the relevant volume V of sample and/or container.

- 2) The **attenuation factors** $A_{i,j}(\theta)$ depend only on the sample geometry and the total neutron cross section and so can be evaluated exactly in the static approximation, within the limits of numerical precision.

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On *reactor-based* diffractometer a (partially) alternative way to subtract the intensities from sample environment and empty diffractometer can be adopted: the sample is then replaced by a nearly perfectly absorbing specimen as ${}^3\text{He}$.

This technique, based on the extremely high absorption cross section of ${}^3\text{He}$ (5333 barn at 2200 m/s, i.e. 1.8 Å) that makes it a practically perfect thermal neutron absorber, can allow a more accurate subtraction of the container and background scattering.

We have seen that the total intensity I_{S+C} diffracted by the fluid sample S in the container C can be written as

$$I_{S+C}(\theta) = I_S(\theta) + I_C^S(\theta) + I_B^S(\theta) \quad (39)$$

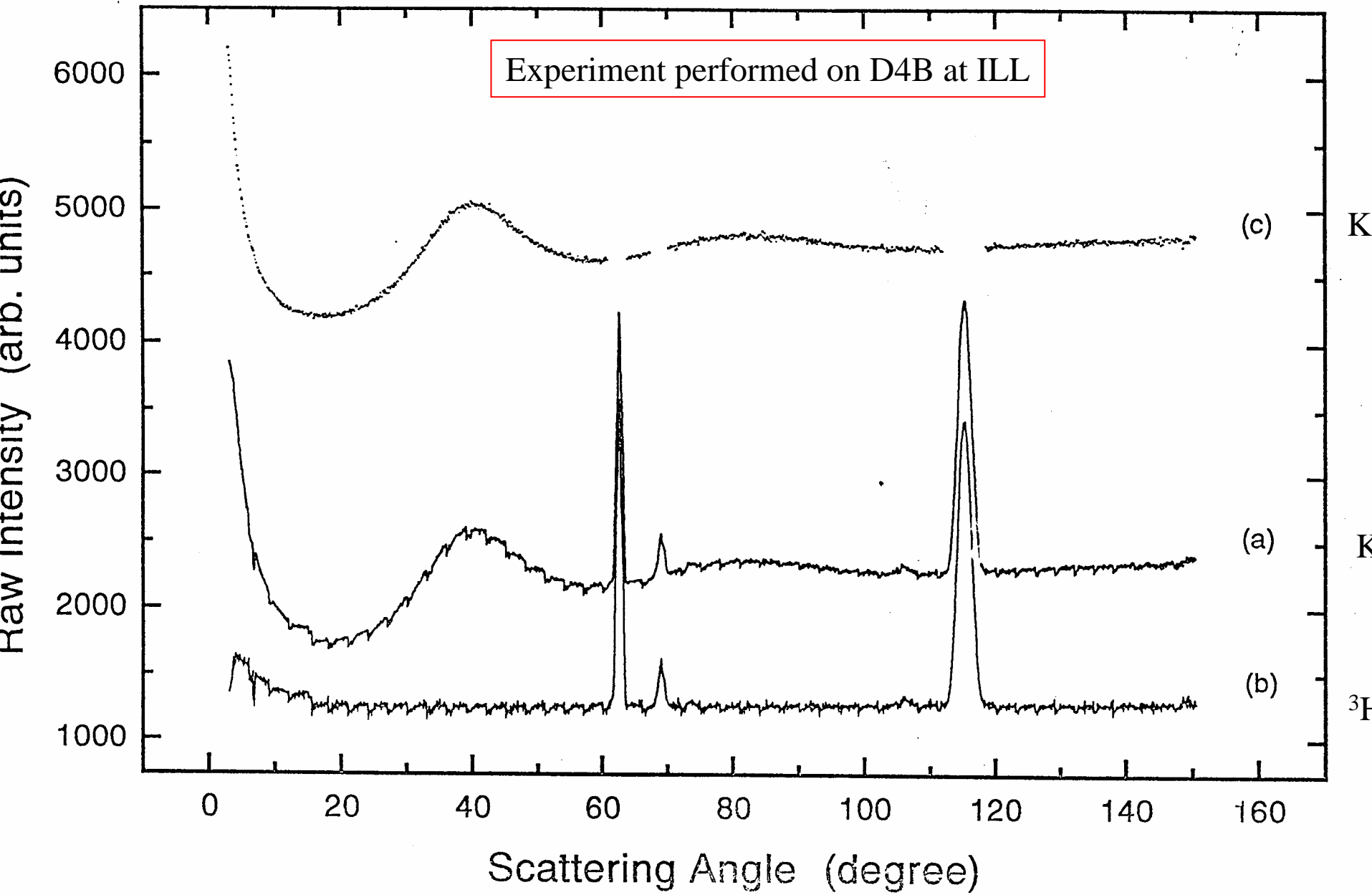
where I_B^S is the intensity coming from the background in the presence of the sample.

The scattering from the container and the environment can be *directly measured*. In fact, if the container is filled with ${}^3\text{He}$, the corresponding intensity can be analogously written as

$$I_C(\theta) = I_C^{(\text{He})}(\theta) + I_B^{(\text{He})}(\theta) \quad (40)$$

The term corresponding to the intensity scattered by ${}^3\text{He}$ has been omitted because of the extremely low neutron scattering cross section of ${}^3\text{He}$ compared to its absorption cross section.

When the ${}^3\text{He}$ density is chosen in order to match the sample transmission, $I_C(\theta)$ can be considered a *direct measurement* of the last two terms on the right-hand of Eq (39).



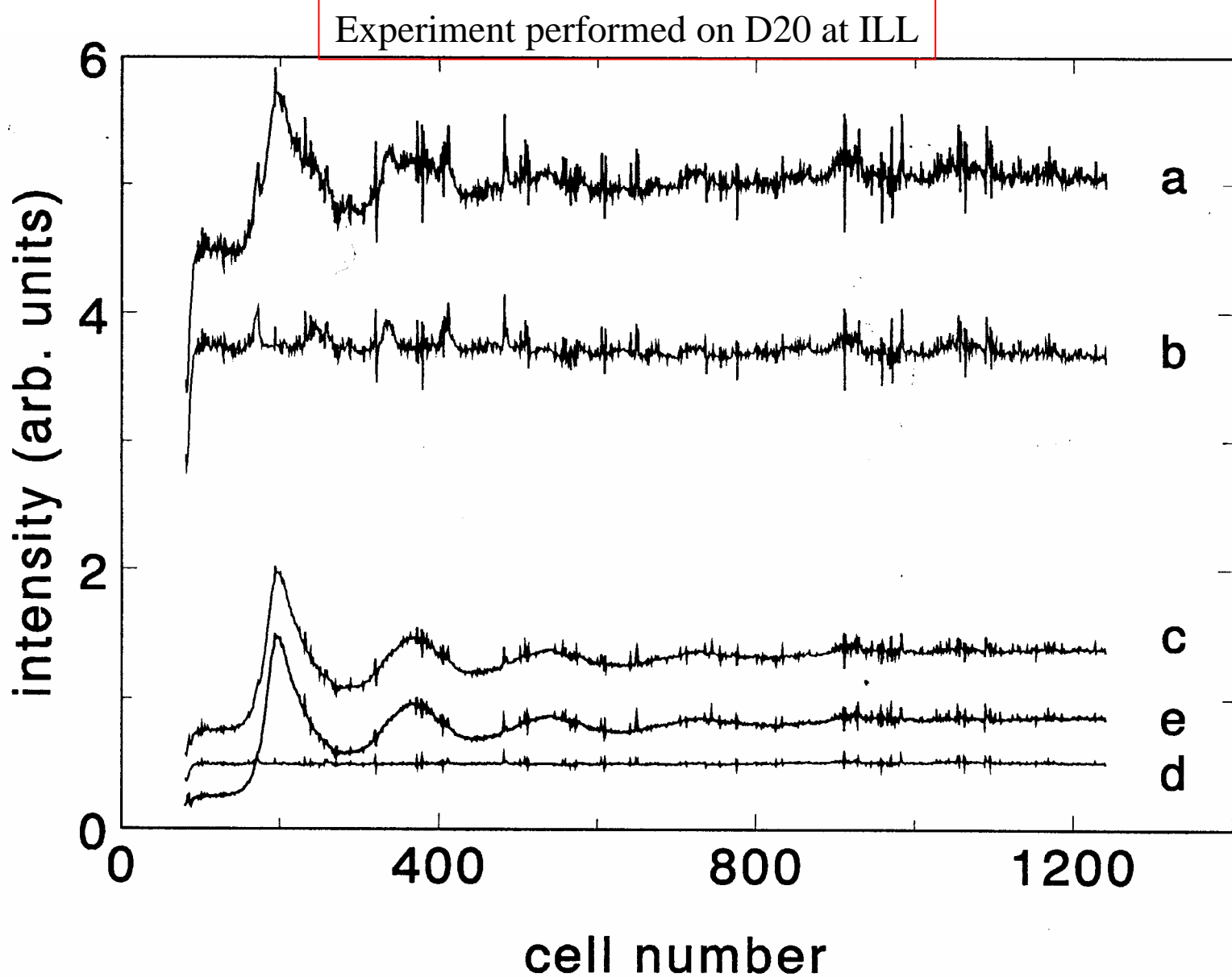


Fig. 3 - (a) total scattering of Hg+V; (b) single scattering in V, corrected for attenuation in Hg and V; (c) difference (a)–(b); (d) total multiple scattering in the presence of Hg; (e) single scattering of Hg, still to be corrected for self-attenuation

3) The methods reported in literature for the evaluation of the **Multiple Scattering** intensity can be classified as:

a) analytical procedure from a transport theory; for cylindrical samples of finite sizes numerical evaluations of the involved integrals are required (*see for example Blech and Averbach 1965, Sears 1975, Soper and Egelstaff 1980*);

b) computer simulation of the system: see for example the *MSCAT* and similar codes.

In both the procedures a largely adopted approximation is the so called **ISOTROPIC APPROXIMATION** which amounts to consider the *primary* scattering as *isotropic*.

The scattering is usually considered as **ELASTIC**.

If the scattering response of the sample and/or container is markedly dependent on the scattering angle, the isotropic approximation can be released and some information on the (*dynamic*) *structure factor* inserted (for instance, some preliminary structure factor can be introduced in the computation which can then be refined in an iterative way).

4) Information concerning the beam profile can be inserted, when known, in order to have more reliable results for both the attenuation factors and the multiple scattering intensities.

For a more detailed treatment see the lesson by R. Mancinelli

We have seen that the numerical evaluations of the *attenuation coefficients* ($P\&P$'s) and the *multiple scattering* (MS) contribution are usually performed assuming the validity of the *static approximation*; moreover, unless explicit use of a model structure factor $S(q)$ is made, the MS is evaluated in the *isotropic approximation*. Up to now, no systematic investigation has been reported in literature from which one can infer a quantitative upper limit for the sample dimensions.

However, sizes and features of the sample are usually chosen, when possible, in such a way that its *Scattering Power* be *no more than 20%* (i.e. the sample scatters no more than 20% of the incoming beam).

Experiments with larger scattering power require special care and a dedicated data analysis.

For a *cylindrical sample completely immersed* in the incoming beam the fraction F_R of neutrons removed from the beam can be expressed as:

$$F_R = \frac{\pi}{4} \sum_{k=0}^{\infty} \frac{(2\tau)^{2k+1}}{(k+1)(2k!!)^2} - \sum_{k=0}^{\infty} \frac{(2\tau)^{2k+2}}{(2k+3)((2k+1)!!)^2} \quad (35)$$

where
$$\tau = (\sigma_s + \sigma_a) \rho r \quad (36)$$

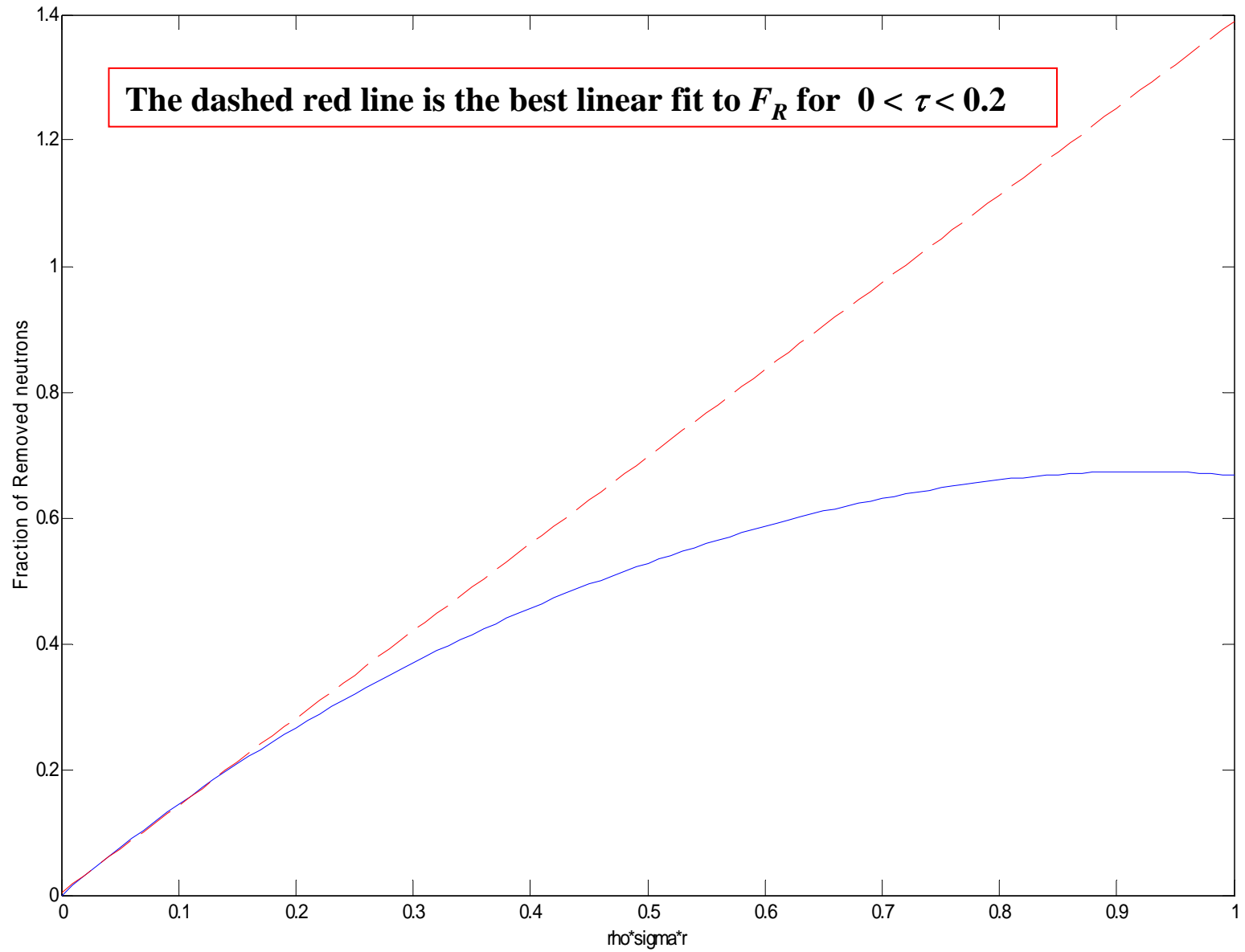
with: σ_s and σ_a scattering and absorption cross section, ρ number density, r radius } of the cylindrical sample

The *leading terms* of F_R are
$$F_R = \frac{\pi}{2} \tau - \frac{4}{3} \tau^2 + \frac{\pi}{4} \tau^3 - \frac{16}{45} \tau^4 + \dots \quad (37)$$

and for most of the samples they are enough for a reliable estimate of the sample scattering power.

The fraction F_S of neutrons scattered by the sample (its *Scattering Power*) is then

$$F_S = \frac{\sigma_s}{\sigma_s + \sigma_a} F_R \quad (38)$$



The inelasticity correction (see the lessons by M. Celli for a detailed treatment)

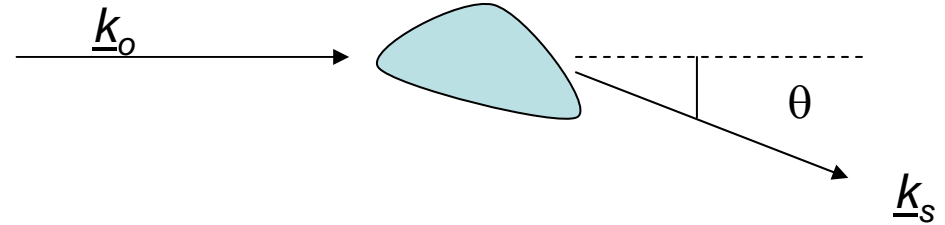
Let's consider for simplicity a *reactor-based* diffraction experiment. The double differential neutron cross section for single scattering (1° Born approximation) by a sample of N atoms with no absorption is given by:

$$\frac{d^2\sigma}{d\Omega dE_f} = \frac{k_s}{k_0} \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dt \exp(-i\omega t) \underbrace{\sum_{j,j'=1}^N \langle b_j^* b_{j'} e^{-i\mathbf{q}\cdot\mathbf{R}_j(0)} e^{i\mathbf{q}\cdot\mathbf{R}_j(t)} \rangle}_{S^*(\mathbf{q},\omega)} \quad (41)$$

with:

$S^*(\mathbf{q},\omega)$ **Dynamic scattering function**

- j, j' run over all the N nuclei of the target
- $\mathbf{R}_j(t)$ is the interaction Heisenberg operator for the position operator \mathbf{R}_j of nucleus j at the time t
- b_j is the scattering length of the nucleus j
- $\langle \dots \rangle$ is both a quantum and a thermal average
- $\mathbf{k}_s, \mathbf{k}_0$ are the scattered and the incident wavevectors of the neutron scattered at θ
- $\hbar\omega = \hbar^2/2m_n(k_0^2 - k_s^2) = E_0 - E_s$ is the exchanged energy (*)
- $\mathbf{q} = \mathbf{k}_0 - \mathbf{k}_s$ is the momentum transferred to the target (**)
- m_n is the neutron mass



From Eqs (*) and (**):

$$k_s = k_0 \left[1 - \left(2m_n\omega / \hbar k_0^2 \right) \right]^{1/2} \quad (42)$$

$$\left(q / k_0 \right)^2 = \left\{ 2 - \left(\hbar\omega / E_0 \right) - 2 \left[1 - \left(\hbar\omega / E_0 \right) \right]^{1/2} \cos \theta \right\} \quad (43)$$

When the exchanged energy $\hbar\omega = 0$ then $k_s = k_0$ and $q = q_{el}$ (44)

where

$$q_{el} \equiv 2k_0 \sin(\theta/2) = \frac{4\pi}{\lambda_0} \sin(\theta/2) \quad (45)$$

From the definition of the differential scattering cross section $d\sigma/d\Omega$

$$dN = \Phi_0 N_{sample} \varepsilon \frac{d\sigma}{d\Omega} d\Omega dt \quad (46)$$

where: $\left\{ \begin{array}{l} dN \text{ is the number of neutrons scattered in the solid} \\ \text{angle } d\Omega \text{ in the time interval } dt; \\ \Phi_0 \text{ is the incoming neutron flux (i.e. number of} \\ \text{neutrons per unit of time and area);} \\ N_{sample} \text{ is the number of sample atoms;} \\ \varepsilon \text{ is the efficiency of the detector} \end{array} \right.$

and its link with $d^2\sigma/d\Omega dE$:

$$\frac{d\sigma}{d\Omega} = \int_{-\infty}^{\infty} \frac{d^2\sigma}{d\Omega dE} dE \quad (47)$$

we see that what is really measured by a detector located at θ and of solid angle $d\Omega$ is the **counting rate** $C(E_0, \theta)$ (i.e. the **number of neutrons per unit time scattered at θ in $d\Omega$**):

$$C(E_0, \theta) = \int_{-\infty}^{E_0/\hbar} \varepsilon(k_s) \left(\frac{k_s}{k_0} \right) S^*(\underline{q}, \omega) d\omega \Big|_{\text{with } \theta = \text{const}} \quad (48)$$

Note that the detector efficiency ε depends on the neutron energy. Since $k_s = m v_s / \hbar$ we can write $\varepsilon = \varepsilon(k_s)$.

The **lower limit** of the integral is usually given by a cut-off of the detector (there is a minimum threshold): the efficiency $\varepsilon(k_s)$ takes into account this effect.

The **upper limit** is related to the fact that E_0/\hbar represents the maximum energy which the neutron can provide to the target.

Summarizing: what is measured is

$$C(E_0, \theta) = \int_{-\infty}^{E_0/\hbar} \varepsilon(k_s) \left(\frac{k_s}{k_0} \right) S^*(\underline{q}, \omega) d\omega \Big|_{\text{with } \theta = \text{const}} \quad (49) \quad \text{‘Measured’}$$

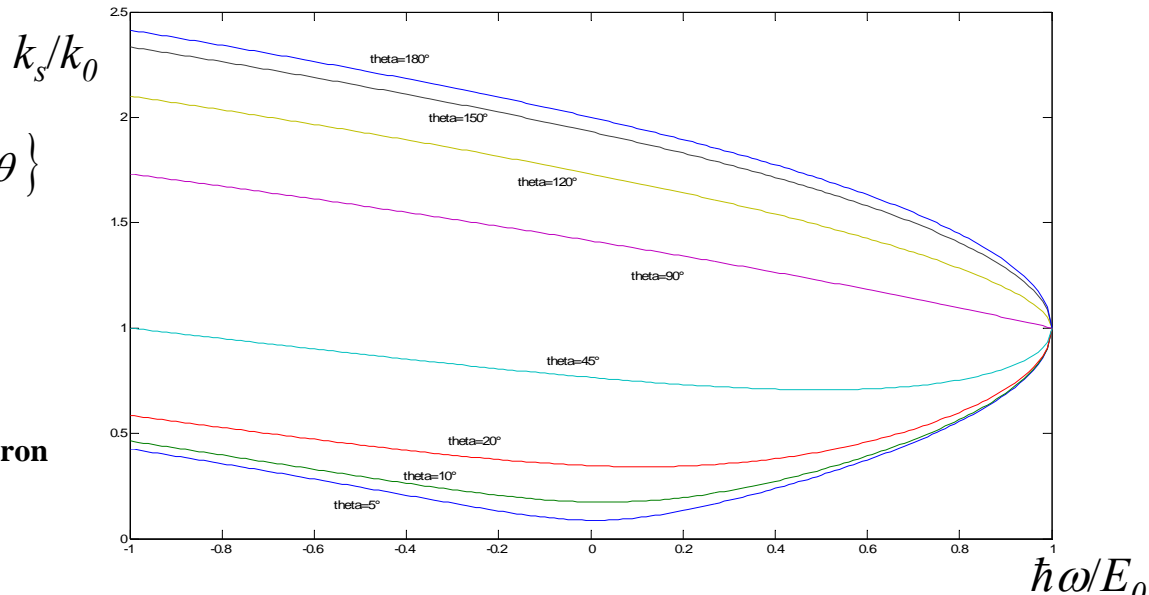
while the quantity that contains the structural properties is:

$$S^*(q) = \int_{-\infty}^{\infty} S^*(\underline{q}, \omega) d\omega \Big|_{\text{with } q = \text{const}} = \sum_{j, j'} \langle b_j^* b_{j'} e^{i\underline{q} \cdot \underline{R}_{jj'}} \rangle \quad (50) \quad \text{‘Theoretical’}$$

The *experimental* integration present in Eq (49) is with $\theta = \text{const}$, while Eq (50) requires $q = \text{const}$: in view of the kinematic relationship expressed by Eq (43) *the two requirements*, if the scattering is inelastic, *are not the same.*

$$\left(\frac{q}{k_0} \right)^2 = \left\{ 2 - \left(\frac{\hbar\omega}{E_0} \right) - 2 \left[1 - \left(\frac{\hbar\omega}{E_0} \right) \right]^{1/2} \cos\theta \right\}$$

The allowed kinematic region for a neutron scattering experiment (cfr. Eq (43))



It is almost impossible (certainly not economic) to perform the required integration with $q = \text{const.}$ We therefore need some procedure to extract the most reliable value of $S^*(q)$ from $C(E_0, \theta)$ measured through the experimental path with $\theta = \text{const.}$

Inelastic effects are more important in samples containing atoms of small mass: in that situation a neutron transfers to the target atom more energy, so that the static approximation is less valid.

They depend on the detection efficiency.

Inelasticity effects on the *distinct part* of $d\sigma / d\Omega$ are generally by far *less important* than for the self part. In that situation the momentum transfer of the neutron, $\hbar q$, cannot be seen as localized to a single atom, but must be thought as exchanged with all the atoms that lay within the *coherence volume* pertaining to the incoming neutron (*coherence volume* = size of the wavepacket of the incoming neutron which diffracts in the sample; its volume increases with the collimation and monochromaticity of the beam).

a) Reactor-based diffractometer

Inelasticity effects show up with the so-called '*Placzek falloff*' with increasing q ; except for the lightest atoms, the additive correction term $P(q)$ to the scattering cross section can be modelled using a *polynomial expansion in powers of q^2* and the ratio m_n / M .

b) Pulsed neutron sources

Inelasticity effects are generally weaker due to higher incident energies, provided the measurement is performed at small scattering angles. They show up mainly at low- q values and are more difficult to model in a simple way.

Normalization of cross section in absolute units

After corrections for dead time, bkg, attenuation, multiple scattering and inelasticity have been applied, the normalization to an absolute cross-section can be carried out by comparing the sample's diffraction intensity with the measured intensity of a sample of known scattering cross-section.

Generally *vanadium* is used as a normalization standard: its cross-section is known rather accurately (a few percent) and it is almost completely incoherent, so that its scattering is almost isotropic.

Other possibilities:

- Using gaseous reference samples such as dilute *CH₄* and *H₂* (Guarini 2003).

Compared to the use of Vanadium the main advantages are:

- same container for the calibration gas and for the sample: no removal of the cell is required, so avoiding systematic errors due to geometrical effects;
- availability of accurate quantum models for the double differential cross section.

The final absolute normalization of $S(q)$ can be obtained with an estimated accuracy of better than 3%.

- Using an 'auto-normalization' of $d\sigma/d\Omega$ by aligning the self-scattering with the theoretical value for the sample's composition (high q values requested).

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