INTRODUCTION TO THE NEUTRON SCATTERING DIFFERENTIAL CROSS-SECTION

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I. NEUTRON SCATTERING: BASIC FORMALISM

In a scattering experiment, an incident beam of neutrons with momemtum $\hbar\vec{k}$ and energy E, after the interaction with the sample, is scattered within the solid angle Ω, with final momentum and energy equal to $\hbar\vec{k}'$ and E' respectively (see Fig. 1). The incident neutron flux, Φ, is defined as:

$$\Phi = \frac{\#neutrons}{area \cdot time} = \frac{\#particles}{volume} \cdot velocity \tag{1}$$

Scattered particles are collected by a detector placed at a distance $\vec{r} = \vec{r}(\theta, \phi)$ from the sample: this counts all the neutrons arriving within a solid angle $d\Omega$ around $\Omega(\theta, \phi)$. If it can perform an energy analysis, then we have access to the double differential cross section, that is the counting rate in Ω per unit solid angle and energy interval, normalized to the incident flux:

$$\frac{d^2\sigma}{d\Omega dE'} = \frac{\#neutrons\ within\ d\Omega\ around\ \Omega}{time\ \Phi\ dE'} \tag{2}$$

If instead all neutrons are collected without energy analysis, the measured quantity is called differential cross section and represents the counting rate

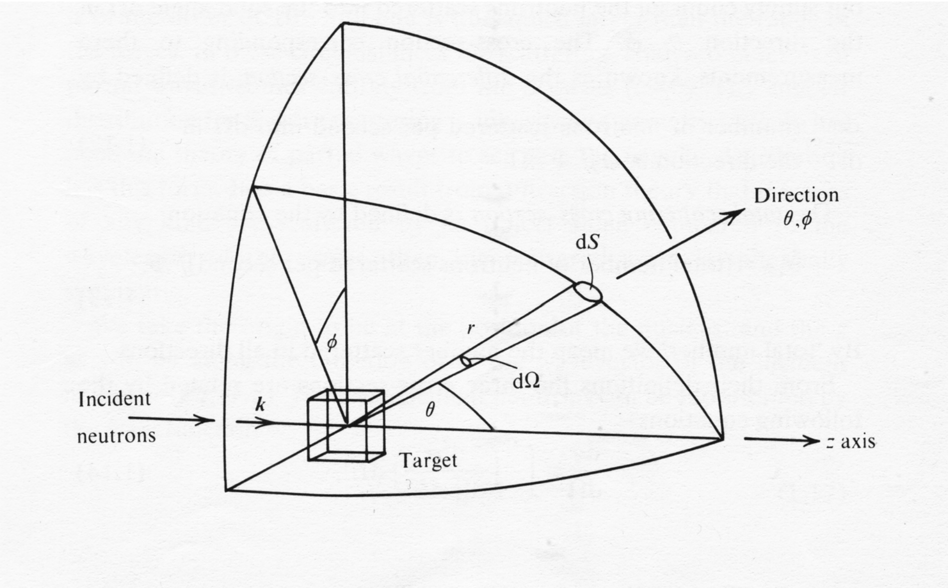

FIG. 1: Typical geometry of a scattering event.

in Ω:

$$\frac{d\sigma}{d\Omega} = \int \frac{d^2\sigma}{d\Omega dE'} dE' \tag{3}$$

The total neutron scattering from the sample is instead:

$$\sigma = \int \frac{d^2\sigma}{d\Omega dE'} dE' d\Omega \tag{4}$$

In this school we will focus our attention on the differential cross section and in particular on techniques which allow to extract information on the microscopic structure of liquids and soft matter.

A formally correct derivation of $\frac{d\sigma}{d\Omega}$ requires application of the scattering theory. Nevertheless in the case of neutrons it can be calculated within the Born approximation, as the perturbation brought by the scattering event to the incident beam is so small that the wavefunction of the neutron-nucleus system can be factorized as the product of the wave functions of the unperturbed components of the system. This means in practice that the amplitude of the neutron wave scattered by a nucleus is already very small at a distance from the scattering center of the order of the first neighbor distance. When this conditions are realized, the cross section can be evaluated within the linear response theory: under the hypothesis that the probe does not sensibly perturbs the target, the total scattering from an ensemble of N molecules is the sum of the scattering from the individual nuclei. We can therefore evaluate the cross section starting from the Fermi's gold rule for the transition probability between the initial and final state of the neutron-nucleus system.

Let $|\lambda>$ be the target initial state, of energy E_λ, and $|k,s>=|k>|s>$ the plane wavefunction of the incident neutron, with momentum $\hbar\vec{k}$ and spin $\vec{s}$. In the absence of magnetic fields, the neutron energy is $E=\frac{\hbar^2k^2}{2m_n}$, independent on $\vec{s}$, where m_n is the mass of a neutron, and the transition probability from the initial state $|\lambda>|k,s>$ to the final state $|\lambda'>|K',s'>$ is:

$$W_{ks\lambda\rightarrow k's'\lambda'}=\frac{2\pi}{\hbar}|<\vec{k}s\lambda|\hat{U}|\vec{k'}s'\lambda'>|^2\delta(E+E_\lambda-E'-E_{\lambda'}) \qquad (5)$$

where $\hat{U}$ is the neutron-nucleus interaction potential. The measured quantity however depends on $W_{ks\rightarrow k's'}$, i.e. the probability associated with the transition between the initial and final state of the probe, which can be obtained from Eq.5, after summing over all the initial and final states of the nucleus (the latter weighted according to their statistical population, p_λ):

$$W_{ks\rightarrow k's'}=\frac{2\pi}{\hbar}\Sigma_{\lambda\lambda'}p_\lambda W_{ks\lambda\rightarrow k's'\lambda'} \qquad (6)$$

If the incident beam contains N neutrons in the state $|k,s>$, the number of scattered neutrons in the state $|k', s>$ per second is $NW_{ks\rightarrow k's'}$. After integration over all possible $|k'>$, this equals the product of the incident flux times the total neutron scattering cross section:

$$\Phi\sigma_{tot}|_{s\rightarrow s'} = N\Sigma_{k'}W_{ks\rightarrow k's'} = NV\int\frac{d^3k'}{(2\pi^3)}W_{ks\rightarrow k's'} \tag{7}$$

If we now remind that: $E' = \frac{\hbar^2 k'^2}{2m_n}$; $dk' = \frac{m_n}{\hbar^2 k'}dE'$, and that: $\frac{\Phi V}{N} = \frac{\hbar k}{m_n}$, the latter equation gives:

$$\sigma_{tot}|_{s\rightarrow s'} = \frac{V^2}{(3\pi)^3}\frac{k'}{k}\frac{m_n^2}{\hbar^3}\int W_{ks\rightarrow k's'}\ dE'\ d\Omega \tag{8}$$

and the double differential cross section can be expressed as:

$$\frac{d^2\sigma}{d\Omega dE'} = \frac{k'}{k}\frac{m_n^2}{(2\pi\hbar^2)^2}\Sigma_{\lambda\lambda' ss'}p_\lambda p_s| < ks\lambda|\hat{U}|k's'\lambda' > |^2\delta(E_\lambda - E_{\lambda'} + \hbar\omega) \tag{9}$$

with $\hbar\omega = E - E'$.

Since the neutron wavelength is of the order of $\sim$10^{-8} cm and the range of the nuclear forces is of the order of $\sim$10^{-13} cm, neutrons see the atoms as if they were points. As a consequence the scattering from a single atom can only be isotropic: in practice this means that it is characterized by a single scalar parameter, b, named scattering length.[1] This means that the differential cross section can be calculated by substituting $\hat{U}$ with the Fermi's effective potential:

$$\hat{U} = \Sigma_\alpha\frac{2\pi\hbar^2}{m_n}b_\alpha\delta(r - r_\alpha) \tag{10}$$

where $\vec{r}_\alpha$ is the time dependent position of the α-th nucleus and b may be a complex number, which imaginary part represents the absorption of neutrons during the interaction. The absorption probability is small for most atomic species: for this reason neutrons are a good probe for studies of condensed matter, as they can pass through thick samples, and in particular for liquids, which require a sample container and sometimes massive sample environment. In general b depends on the atomic species and on its isotopic state.

The Fermi potential gives the correct value of the scattering from a single bound nucleus, within the Born approximation. A thermal neutron ($\lambda \sim 1$ Å) cannot indeed excite nuclear transitions (requiring energy of the order of 1 Mev), moreover all other quantum numbers cannot change for a bound atom, hence the element of matrix in eq. 9 is becomes: $< \lambda\lambda' >< k|\delta(x)|k' >= \delta_{\lambda\lambda'} \int d^3r \ e^{-i\vec{k}\cdot\vec{r}}\delta(r)e^{i\vec{k'}\cdot\vec{r}} = \delta_{\lambda\lambda'}$; and the differential and total scattering cross section are: $\frac{d\sigma}{d\Omega} = |b^2|$ and $\sigma = 4\pi|b^2|$, respectively. If instead the nucleus can freely recoil after the interaction, the scattering has to be studied within the reference frame of the center of mass and the reduced mass $\mu = \frac{m_n M}{m_n + M}$ substitutes the neutron mass into the expression of the Fermi's potential. This is equivalent to saying that the scattering length of the neutron has changed from the "bound nucleus" value, b, to the "free nucleus" one, $b_F = \frac{M}{m_n+M}b$. This effect is sensible when high energy neutrons ($E \sim 1$eV) interact with light atoms, such as for instance hydrogens.

Let us consider an array of nuclei and let b_α be the scattering length of α-th nucleus. The interaction of the neutron beam with the array is described by: $\hat{U}(\vec{r}) = \frac{2\pi\hbar^2}{m_n}\Sigma_\alpha b_\alpha \delta(\vec{r}-\vec{R}_\alpha)$ and its element of matrix between the initial and final states of the neutron is:

$$< k|\hat{U}|k' >= \Sigma_\alpha b_\alpha \int d^3r e^{-i\vec{k}\cdot\vec{r}}\delta(\vec{r} - \vec{R}_{alpha})e^{i\vec{k'}\cdot\vec{r}} = \Sigma_\alpha b_\alpha e^{i(\vec{k}-\vec{k'})\cdot\vec{R}_\alpha} \qquad (11)$$

If we now define the exchanged wavevector $\vec{q} = (\vec{k} - \vec{k}')$ the double differential cross-section is:

$$\frac{d^2\sigma}{d\Omega dE'} = \frac{k'}{k}\Sigma_{\lambda\lambda'}p_\lambda\Sigma_{\sigma\sigma'}p_\sigma| < \lambda, \sigma|\Sigma_\alpha b_\alpha e^{i(\vec{q})\cdot\vec{R}_\alpha}|\lambda', \sigma' > |^2\delta(E_\lambda - E_{\lambda'} + \hbar\omega) \tag{12}$$

If the nuclei are bound, $\hat{U}$ is not an operator and consequently the product $< \lambda|\lambda' >$ gives a delta function in $\lambda\lambda'$; E_λ equals $E_{\lambda'}$ and $\delta(E_\lambda - E_{\lambda'} + \hbar\omega)$ becomes $\delta(\hbar\omega)$, implying that there is no energy exchange and $k = k'$. In this case the differential cross-section is immediately found to be:

$$\frac{d\sigma}{d\Omega} = \Sigma_{\sigma\sigma'}p_\sigma\Sigma_{\alpha\alpha'}e^{i\vec{q}\cdot(\vec{R}_\alpha - \vec{R}_{\alpha'})} < \sigma|b^*_\alpha b_{\alpha'}|\sigma > \tag{13}$$

that is:

$$\frac{d\sigma}{d\Omega} = \Sigma_{\alpha\alpha'}e^{i\vec{q}\cdot(\vec{R}_\alpha - \vec{R}_{\alpha'})} < b^*_\alpha b_{\alpha'} > \tag{14}$$

where $< b^*_\alpha b_{\alpha'} >$ represents the average over the nuclear spin states and allows to drop hereafter the sum over these states. On the other hand the sum over $\alpha\alpha'$ can be separated into the sum over $\alpha = \alpha'$ and the sum over $\alpha \neq \alpha'$, and being $< b^*_\alpha b_{\alpha'} >$ equal to: $| < b > |^2$ if $\alpha \neq \alpha'$ and to $< |b|^2 >$ if $\alpha = \alpha'$, we can write:

$$< b^*_\alpha b_{\alpha'} >= | < b > |^2 + \delta_{\alpha\alpha'}(< |b|^2 > -| < b > |^2) \tag{15}$$

As a consequence:

$$\frac{d\sigma}{d\Omega} = | < b > |^2|\Sigma_\alpha e^{i\vec{q}\cdot\vec{R}_\alpha}|^2 + N[< |b|^2 > -| < b > |^2] = (\frac{d\sigma}{d\Omega})_{coh} + (\frac{d\sigma}{d\Omega})_{inc} \tag{16}$$

From the physical point of view this means that neutrons don't see the array of nuclei as a crystal with uniform scattering potential, since the scattering length depends on the isotopic state and on the orientation of the nuclear spin with respect to the neutron spin. The scattering potential changes from site to site, nevertheless we can define an average potential, represented by the average scattering length $< b >$ and imagine the array of nuclei as an "average array", giving coherent interference between the scattered neutrons, plus a random distribution of deviations from the average. These random disordered contributions to the scattering potential cannot give coherent interference, but contribute to the incoherent scattering from the sample.

II. NEUTRON SCATTERING LENGTHS

The neutron spin is equal to $\frac{1}{2}$, as a consequence the total spin of neutron-nucleus system during the interaction may be $t^+ = i + \frac{1}{2}$ and $t^- = i - \frac{1}{2}$, the two spin being parallel or anti-parallel, respectively (i represents here the nuclear spin). Since the interaction potential depends on the relative orientation of the two spin, let us call b^+ and b^- the scattering length associated with t^+ and t^-. For a given nucleus, $< b >$ is then calculated as the average of b^+ and b^-, weighted according to the multiplicity of the states of angular momentum t^+ and t^-:

$$< b >= \frac{2t^+ + 1}{2(t^+ + t^-) + 2} b^+ + \frac{2t^- + 1}{2(t^+ + t^-) + 2} b^- = \frac{i+1}{2i+1} b^+ + \frac{i}{2i+1} b^- \quad (17)$$

similarly:

$$< |b|^2 >= \frac{i+1}{2i+1} |b^+|^2 + \frac{i}{2i+1} |b^-|^2 \quad (18)$$

In the case of hydrogen, for instance $i = \frac{1}{2}$, b^+ =1.085 10^{-12} cm and b^- = -4.75 10^{-12} cm, giving $< b >$=-0.374 10^{-12} cm and $< b^2 >$=6.52

10^{-24} cm^2 and finally a coherent atomic cross section $\sigma_{coh} = 4\pi| < b > |^2$ =1.76 barn and a total scattering one $\sigma_{tot} = 4\pi < |b|^2 >$=82 barn. As a consequence the incoherent scattering cross section of a hydrogen atom is $\sigma_{inc} = 4\pi(< |b|^2 > -| < b > |^2)$ =80 barn. In the case of deuterium, being i =1 and b^+ =0.95 10^{-12} cm and b^- =0.10 10^{-12} cm, $\sigma_{coh} = 5.6$ barn and σ_{tot} =7.6 barn. Neutrons can consequently distinguish hydrogen from deuterium, as well as other isotopes, contrarily to X rays, which interact with the electrons.

The nuclear interaction between neutrons and atoms determines an irregular dependence of b on the atomic number, as shown in Fig. 2. As a consequence, while X-rays interact more strongly with the heavier atoms, the interaction of neutrons with atoms changes without any regularity along the periodic table. In this respect the two probes can be considered sometimes as complementary. Notice also that there are atoms with a negative scattering length: this means that it is possible to prepare mixtures with $< b >$=0, i.e. with no coherent scattering.

What shown so far is the basis for the so-called **isotopic substitution method**, widely applied in all the experimental techniques described in this school.

III. DOUBLE DIFFERENTIAL CROSS SECTION

If our sample is made of N atoms, the element of matrix in eq. 9 can be written as:

$$< ks\lambda|\hat{U}|k's'\lambda' >=< ks\lambda|\Sigma_\alpha \frac{2\pi\hbar^2}{m_n} b_\alpha \delta(r - r_\alpha)|k's'\lambda' >= \tag{19}$$

$$\int d^3r \delta_{ss'} < k|r >< r|k' >< \lambda|\Sigma_\alpha \frac{2\pi\hbar^2}{m_n} b_\alpha \delta(r - r_\alpha)|\lambda' >=$$

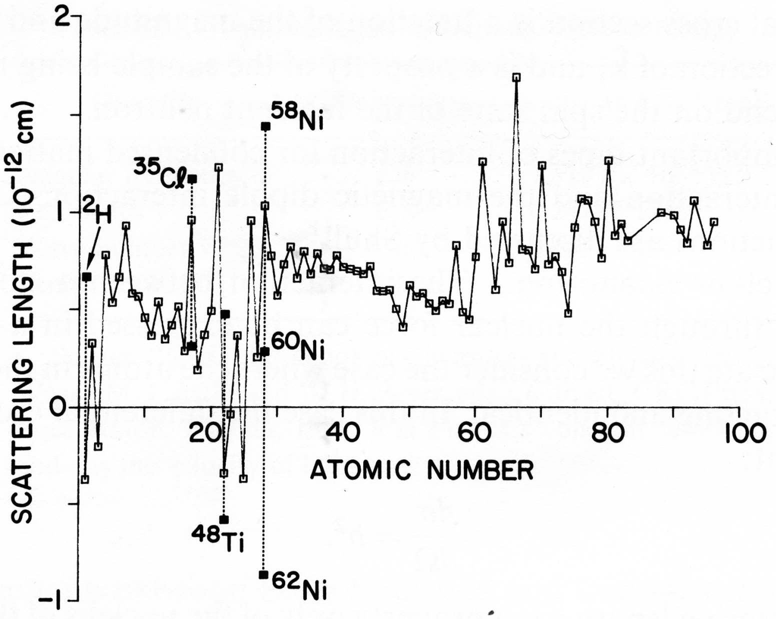

FIG. 2: Scattering length as a function of the atomic mass.

$$\delta_{ss'} \int d^3r \; e^{i\vec{q}\cdot\vec{r}_\alpha} < \lambda | \Sigma_\alpha \frac{2\pi\hbar^2}{m_n} b_\alpha \delta(r - r_\alpha) | \lambda' > =$$

$$\delta_{ss'} \Sigma_\alpha < \lambda | \frac{2\pi\hbar^2}{m_n} b_\alpha e^{(i\vec{q}\cdot\vec{r}_\alpha)} | \lambda' >$$

If we now remember the integral definition of the δ function:

$$\delta(E_\lambda - E_{\lambda'} + \hbar\omega) = \int_{-\infty}^{+\infty} \frac{d(t-t')}{2\pi\hbar} exp[\frac{i}{\hbar}(E_\lambda - E_{\lambda'} + \hbar\omega)(t-t')] \quad (20)$$

being:

$$< \lambda | f(x) | \lambda' > exp[\frac{i}{\hbar}(E_\lambda - E_{\lambda'})t] =< \lambda | f(x(t)) | \lambda' > \quad (21)$$

and:

$$\Sigma_{\alpha\alpha'} | \lambda >< \lambda' | = 1 \quad (22)$$

the **Double Differential Cross Section** is:

$$\frac{d^2\sigma}{d\Omega dE'} = \frac{k'}{2\pi\hbar k}\int dt\ e^{i\omega(t-t')} < \Sigma_{\alpha\alpha'} b_\alpha b_{\alpha'}\ e^{-i\vec{q}\cdot\vec{r}_\alpha(t)} e^{i\vec{q}\cdot\vec{r}_{\alpha'}(t')} > \tag{23}$$

Also in this case we can separate the sum over α, α' into the coherent and incoherent contributions and set t' =0:

$$\frac{d^2\sigma}{d\Omega dE'} = [\frac{d^2\sigma}{d\Omega dE'}]_{coh} + [\frac{d^2\sigma}{d\Omega dE'}]_{inc} \tag{24}$$

$$[\frac{d^2\sigma}{d\Omega dE'}]_{coh} = \frac{\sigma_{coh}}{4\pi}\frac{k'}{k}\frac{1}{2\pi\hbar}\Sigma_{\alpha\alpha'}\int dt\ e^{i\omega t} < e^{-i\vec{q}\cdot\vec{r}_\alpha(t)} \cdot e^{i\vec{q}\cdot\vec{r}_{\alpha'}(0)} > \tag{25}$$

$$[\frac{d^2\sigma}{d\Omega dE'}]_{inc} = \frac{\sigma_{inc}}{4\pi}\frac{k'}{k}\frac{1}{2\pi\hbar}\Sigma_{\alpha}\int dt\ e^{i\omega t} < e^{-i\vec{q}\cdot\vec{r}_\alpha(t)} e^{i\vec{q}\cdot\vec{r}_{\alpha}(0)} > \tag{26}$$

Equations 25 and 26 contain information about the collective and single particle dynamics, respectively. The time dependence of $\vec{r}_\alpha(t)$ brings information on the peculiarities of the system: it can for instance be expressed in terms of phonons in the case of solid samples.

IV. DIFFERENTIAL CROSS-SECTION AND STATIC STRUCTURE FACTOR

In the **Static Approximation** incident and scattered neutrons have the same energy and hence $k = k'$ and $\hbar\omega << E$. In this approximation the **Differential Cross Section** is:

$$\frac{\partial\sigma}{\partial\Omega} = \int dE' \frac{\partial^2\sigma}{\partial\Omega\partial E'} = \hbar\int d\omega \frac{\partial^2\sigma}{\partial\Omega\partial E'} = \frac{1}{2\pi} \int d\omega \int dt e^{i\omega t} \langle \sum_{\alpha,\alpha'} b_\alpha b_{\alpha'} e^{i\vec{q}\times\vec{r}_\alpha(0)} e^{-i\vec{q}\times\vec{r}_{\alpha'}(t)} \rangle \tag{27}$$

$$= \int dt\delta(t)\langle\sum_{\alpha,\alpha'} b_\alpha b_{\alpha'} e^{i\vec{q}\times\vec{r}_\alpha(0)} e^{-i\vec{q}\times\vec{r}_{\alpha'}(t)}\rangle =$$

$$\langle\sum_{\alpha,\alpha'} b_\alpha b_{\alpha'} e^{i\vec{q}\times\vec{r}_\alpha(0)} e^{-i\vec{q}\times\vec{r}_{\alpha'}(0)}\rangle$$

where the $\int d\omega$ is performed at constant q and $\frac{\partial\sigma}{\partial\Omega}$ is a well defined function of the exchanged wavevector.

Moreover the spin state of the nucleus does not depend on the atomic coordinate $\vec{r}_\alpha$, and $\sum_{\alpha,\alpha'}$ can be separated into $\sum_\alpha$ and $\sum_{\alpha,\alpha'\neq\alpha}$, to give:

$$\frac{\partial\sigma}{\partial\Omega} = \sum_\alpha \langle b_\alpha^2\rangle + \sum_{\alpha,\alpha'}(1-\delta_{\alpha\alpha'})\langle b_\alpha\rangle\langle b_{\alpha'}\rangle\langle e^{i\vec{q}\times\vec{r}_\alpha(0)} e^{-i\vec{q}\times\vec{r}_{\alpha'}(0)}\rangle \qquad (28)$$

that for a monoatomic system gives:

$$\frac{\partial\sigma}{\partial\Omega} = N\langle b^2\rangle + \sum_{\alpha,\alpha'}(1-\delta_{\alpha\alpha'})\langle b\rangle^2\langle e^{i\vec{q}\times[\vec{r}_\alpha(0)-\vec{r}_{\alpha'}(0)]}\rangle \quad (29)$$

$$= N(\langle b^2\rangle - \langle b\rangle^2) + \langle b\rangle^2 \sum_{\alpha,\alpha'}\langle e^{i\vec{q}\times[\vec{r}_\alpha(0)-\vec{r}_{\alpha'}(0)]}\rangle = N[\frac{\sigma_{inc}}{4\pi} + \frac{\sigma_{coh}}{4\pi}S(q)]$$

where σ_{inc} and σ_{coh} are the incoherent and coherent cross section of the scatterer[1] and $S(q)$ is the **Static Structure Factor**, SSF, of the sample:

$$S(q) = \frac{1}{N}\sum_{\alpha,\alpha'}\langle e^{i\vec{q}\times[\vec{r}_\alpha(0)-\vec{r}_{\alpha'}(0)]}\rangle \qquad (30)$$

Given that for $\alpha = \alpha'$ $S(q) = 1$ and $S(0) = N$, the SSF can be written as:

$$S(q) = 1 + \frac{1}{N}\sum_{\alpha,\alpha'\neq\alpha}\langle e^{i\vec{q}\times[\vec{r}_\alpha(0)-\vec{r}_{\alpha'}(0)]}\rangle - N\delta(q) \qquad (31)$$

where $N\delta(q)$ represents the forward scattering.

We remind here that eq. 30 has been derived for a single scattering event, in the static approximation. As a matter of fact for most condensed systems the characteristic relaxation time is of the order of $t_0 \sim 10^{-12}$ s and the atomic spacing is $\sim 10^{-10}$ m, thus thermal neutrons traveling with velocity $v \sim 10^3$ m/s take a time $t_1 \sim 10^{-13}$ s to pass from one particle in the system to the next and the static approximation does not strictly apply, since r_α and r'_α cannot be sampled at the same time. Moreover the cross section measured in a real experiment is biased by multiple scattering and absorption events, and last but not least fluid samples need a container, which will interact with neutrons as well.

V. STATIC STRUCTURE FACTOR AND RADIAL DISTRIBUTION FUNCTION

We define the **Intermediate Scattering Function**, $I(q,t)$, as:

$$I(q,t) = \frac{1}{N} \sum_{\alpha,\alpha'} \langle e^{i\vec{q}\times\vec{r}_\alpha(t)} e^{-i\vec{q}\times\vec{r}_{\alpha'}(0)} \rangle \tag{32}$$

and its Fourier transform $G(r,t)$, i.e. the **Van Hove Correlation Function**,

$$G(r,t) = \frac{1}{(2\pi)^3 N} \sum_{\alpha,\alpha'} \int d^3q e^{-i\vec{q}\times\vec{r}} \langle e^{i\vec{q}\times\vec{r}_\alpha(t)} e^{-i\vec{q}\times\vec{r}_{\alpha'}(0)} \rangle \tag{33}$$

Both these functions have a *self* counterpart, $I_S(q,t)$ and $G_S(r,t)$, with obvious definitions. $G(r,t)$ and $G_S(r,t)$ can both be written in terms of delta functions as:

$$G(r,t) = \frac{1}{N} \sum_{\alpha,\alpha'} \int d^3r \langle \delta(r' - r_{\alpha'}(0)) \delta(r' + r - r_\alpha(t)) \rangle \tag{34}$$

$$G_S(r,t) = \frac{1}{N}\sum_{\alpha}\int d^3r\langle\delta(r' - r_\alpha(0)) \\ \delta(r' + r - r_\alpha(t))\rangle \tag{35}$$

If we now consider the classical limit, that is appropriate in most cases when dealing with liquid and amorphous samples, $\vec{r}_\alpha(t)$ and $\vec{r}_{\alpha'}(0)$ commute. Moreover assuming that all nuclei are equivalent, we can write the classical limits of the $G(r,t)$ and $G_S(r,t)$ as:

$$G^{Cl}(r,t) = \sum_{\alpha}\langle\delta(r - r_\alpha(t) + r_0(0))\rangle \tag{36}$$

$$G_S^{Cl}(r,t) = \langle\delta(r - r_0(t) + r_0(0))\rangle \tag{37}$$

where $G^{Cl}(r,t)$ is the probability that given a nucleus at the origin at $t = 0$, any nucleus (including the particle in the origin) is found at a distance r at time t. Consequently $G_S^{Cl}(r,t)$ is the probability that given a nucleus at the origin at $t = 0$, the same nucleus is found at a distance r at time t. These functions obey the following sum rules:

$$\begin{aligned} \int d^3r\ G^{Cl}(r,t) &= N \\ \int d^3r\ G_S^{Cl}(r,t) &= 1 \end{aligned} \tag{38}$$

Obviously when $t \to \infty$ in a liquid both G^{Cl} and G_S^{Cl} approach a constant (ρ and $1/V$ respectively), and we have: $I(q,\infty) = C\delta(\vec{q})$. Since $I(q,\infty)$ is proportional to the elastic scattering, the above finding implies that in a liquid sample the elastic scattering can take place only in the forward direction: this means that there is no elastic scattering at all from a liquid, as this coincides with the transmitted beam.

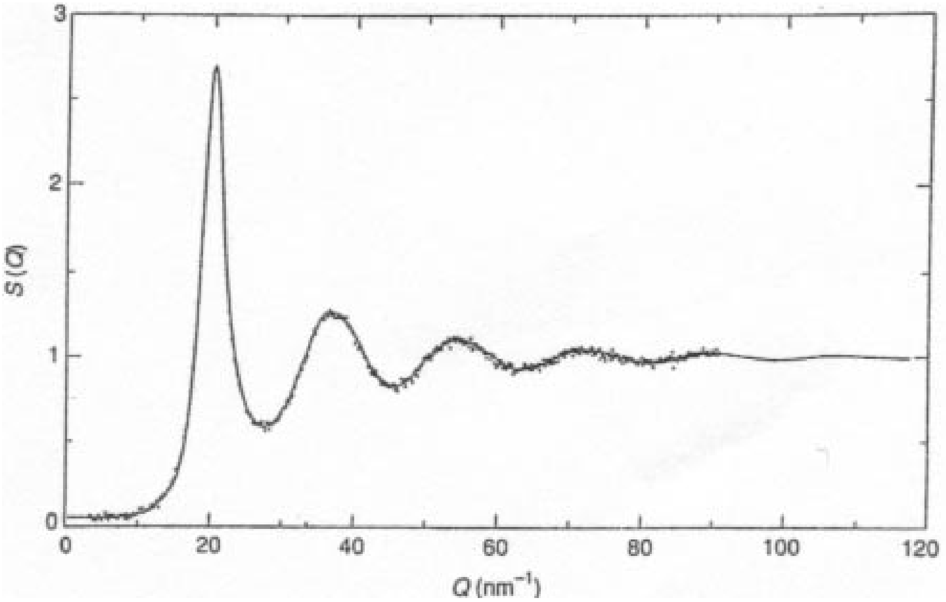

FIG. 3: Example of $S(q)$ for an atomic liquid. Notice that the first peak is centered at about 20nm^{-1}.

When the limit $t \rightarrow 0$ is considered, we have:

$$G^{Cl}(r,0) = \sum_{\alpha} \langle \delta(r - r_\alpha + r_0) \rangle = \delta(r) + \sum_{\alpha \neq 0} \langle \delta(r - r_\alpha + r_0) \rangle = \delta(r) + \rho g(r) \tag{39}$$

$$G_S^{Cl}(r,0) = \delta(r) \tag{40}$$

The $g(r)$ function defined in eq. 39 is the **Pair Distribution Function** or **Site-Site Radial Distribution Function** of the sample, that is the average particle density with respect to any particle at the origin. This function is the quantity that we want to extract from a neutron diffraction experiment.

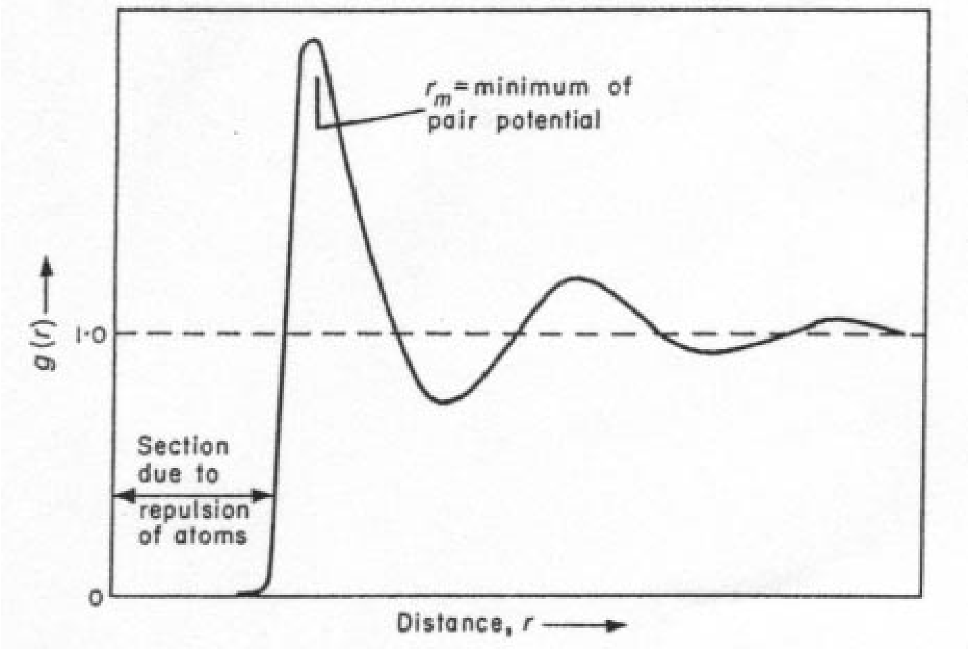

FIG. 4: Fig.2 - Sketch of the typical form of the pair distribution function for a dense atomic liquid. The principal peak of $g(r)$ occurs at a position close to the principal minimum r_m of the interaction potential between pair of atoms. For very low densities these two positions are coincident, and as the density is increased the maximum in $g(r)$ moves to slightly shorter distances compared to r_m. The second peak of the $g(r)$ is centered at about twice the first peak position.

Indeed, by combining eqs. 30, 33 and 39 and after subtraction of the forward scattering one obtains:

$$S(q) = 1 + \rho \int d^3 r e^{i\vec{q}\times\vec{r}}[g(r) - 1] \tag{41}$$

where the Static Structure Factor is also defined as the zeroth energy momentum of $S(q, \omega)$:

$$S(q) = \int_{-\infty}^{+\infty} S(q,\omega) d\omega \tag{42}$$

provided that the integral is performed along a constant-q path. Thus the differential cross-section is finally obtained as:

$$\frac{\partial\sigma}{\partial\Omega} = N\frac{\sigma_{sc}}{4\pi} + N\frac{\sigma_{coh}}{4\pi}\rho \int d^3 r e^{i\vec{q}\times\vec{r}}[g(r) - 1] \tag{43}$$

where $\frac{\sigma_{sc}}{4\pi} = [\frac{\sigma_{inc}}{4\pi} + \frac{\sigma_{coh}}{4\pi}]$ and ρ is the sample density. Hence the differential cross section is given by modulations over a constant background and the degree of structural information delivered by the experiment depends on the ratio $\sigma_{coh}/\sigma_{inc}$. Fig.1 shows the $S(q)$ function of a typical Lennard Jones liquid; the corresponding $g(r)$ function is shown in Fig.2

VI. LIMITING VALUES OF THE STRUCTURE FACTOR

At high q values, i.e. at $qa >> 1$ (being a the average atomic distance), $S(q)$ approaches its limiting value $S(\infty) = 1$, while it can be shown that as $q \to 0$ the SSF is related to the density fluctuations in the liquid. Indeed as the number n of nuclei in a volume V fluctuates about its mean value $\langle n\rangle = \rho\langle V\rangle$, and $\rho\vec{dr}$ is the a priori probability of finding a nucleus in the volume element $\vec{dr}$ at r, while $G(r-r',0)\vec{dr}'$ is the probability that at the same time another nucleus is found in the volume $\vec{dr}'$ at r', we have:

$$\langle n^2\rangle = \rho \int_V \vec{dr} \int_V \vec{dr}' G(r-r',0) \tag{44}$$

Being $S(0) = 1 + \rho\int d^3 r[g(r) - 1]$, it is easy to show^2 that:

$$S(0) = \frac{\langle n^2\rangle}{\langle n\rangle} - \langle n\rangle = \frac{\langle(\Delta n)^2\rangle}{\langle n\rangle} \tag{45}$$

The fluctuation of the number of nuclei is obviously related to the volume fluctuations $\frac{\langle(\Delta n)^2\rangle}{\langle n\rangle} = \rho\frac{\langle(\Delta V)^2\rangle}{\langle V\rangle}$ and from thermodynamic considerations we find $\langle(\Delta V)^2\rangle = V\chi_T K_B T$. Hence:

$$S(0) = \rho\chi_T K_B T \tag{46}$$

where K_B is the Boltzmann constant and χ_T the isothermal compressibility. The latter equation gives $S(0) = 1$ for a perfect gas and $S(0) << 1$ for a liquid. In the vicinity of the liquid-vapor critical point, where large density fluctuations are present an enhancement of the low-q scattering is predicted.

Generally we can say that shape of the $S(q)$ function in the q range from 0 to the first maximum is influenced by the attractive part of interaction potential and by many body interactions. The magnitude of the scattering at $q \to 0$ depends upon the compressibility and is therefore small and difficult to be determined in dense liquids. The $S(q)$ at q-values beyond the first peak depends mainly upon the short range repulsive interactions: the amplitude of the oscillations depends on its steepness and their period on the distance σ where the potential vanishes. However it can be shown for instance by computer simulation that strong changes in the potential produce small changes in the $S(q)$.

VII. EXTENSION TO A MULTICOMPONENT FLUID

For a multicomponent or molecular fluid it is convenient to define the **Partial Structure Factors**, PSF, as :

$$S_{\alpha\beta}(q) = \sum_{\alpha,\beta}\langle e^{i\vec{q}\times[\vec{r}_\alpha(0)-\vec{r}_\beta(0)]}\rangle \tag{47}$$

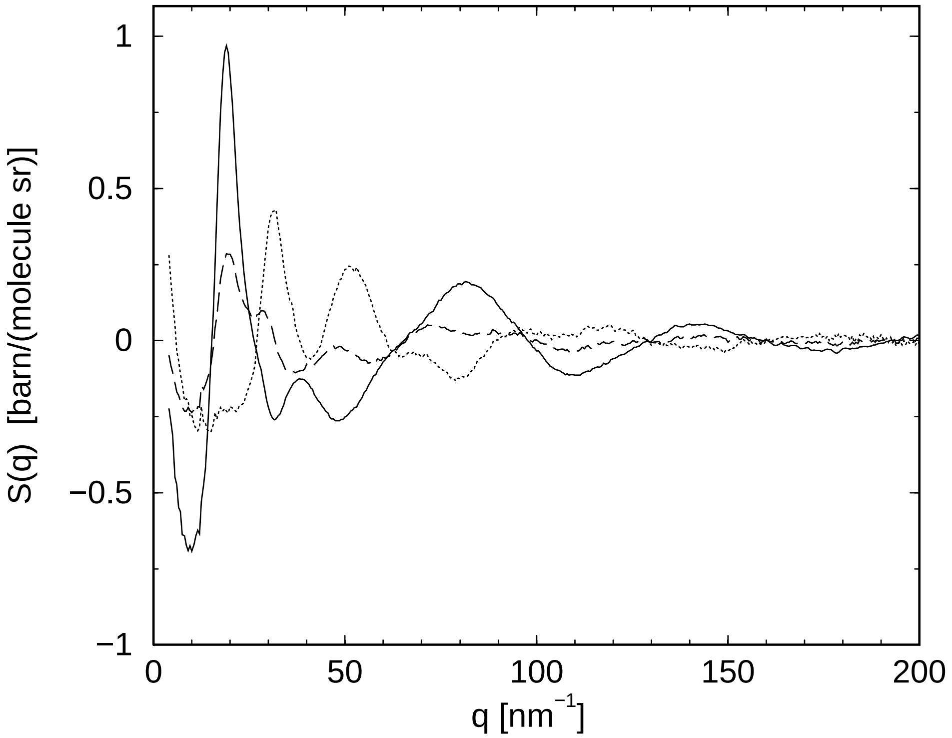

FIG. 5: The neutron weighted $S(q)$ of supercooled heavy water (full line), light water (dotted line), and a 50% mixture of the two liquids (dashed line)

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where α and β label two different atomic species. At each PSF corresponds a **Site-Site Radial Distribution Function**, $g_{\alpha\beta}(r)$, which is the probability that given a nucleus of species α at the origin, a nucleus of species β is found at distance r. The differential cross section per atom of the sample is in this case a linear combination of PSF, weighted by the concentration and scattering length of the nuclei:

$$\frac{\partial\sigma}{\partial\Omega} = \sum_{\alpha} c_{\alpha} \frac{\sigma_{sc}^{\alpha}}{4\pi} + \sum_{\alpha\beta} c_{\alpha} c_{\beta} b_{\alpha} b_{\beta} S_{\alpha\beta}(q) \tag{48}$$

When dealing with a molecular fluid, the $\sum_{\alpha\beta}$ may be further separated into an intramolecular contribution plus an intermolecular one.

The first term of eq.48 is the atomic self scattering contribution. The second term is the total interference scattering: its Fourier transform gives the so-called neutron weighted radial distribution function. Although this function contains all the structural information, nevertheless its interpretation may not be straightforward.

It is possible, for a molecular fluid to express the atomic positions in eq.22 in terms of the molecular center of mass position plus the distance of the individual atoms from this point. If the molecular orientations and the distances between neighboring centers of mass are uncorrelated, then it can be shown[3] that the intermolecular contribution to the SSF equals the static structure factor of the centers of mass times a molecular form factor. The comparison of the experimental data with the results of an appropriate simulation for a Lennard-Jones fluid, can then evidence the presence of orientational correlations and their dependence on the thermodynamic state.

However in order to get the deepest information available about the orientational order in the system the separation of the individual PSF's is needed.

This can be in some cases achieved thanks to the existence of isotopes with different scattering lengths.[1] In such cases it is indeed possible to perform a series of experiments on samples with different isotopic concentration of a given species (**Isotopic Contrast Method**[4]) in order to eventually extract the individual PSF's or simple combinations of few of them. Hydrogen containing molecules represent the most favorable case for the application of this method, since the scattering length of H and D have opposite signs: $b_H = -3.74$ fm and $b_D = +6.67$ fm. In Fig. 5 we report as an example the total interference scattering, or neutron weighted

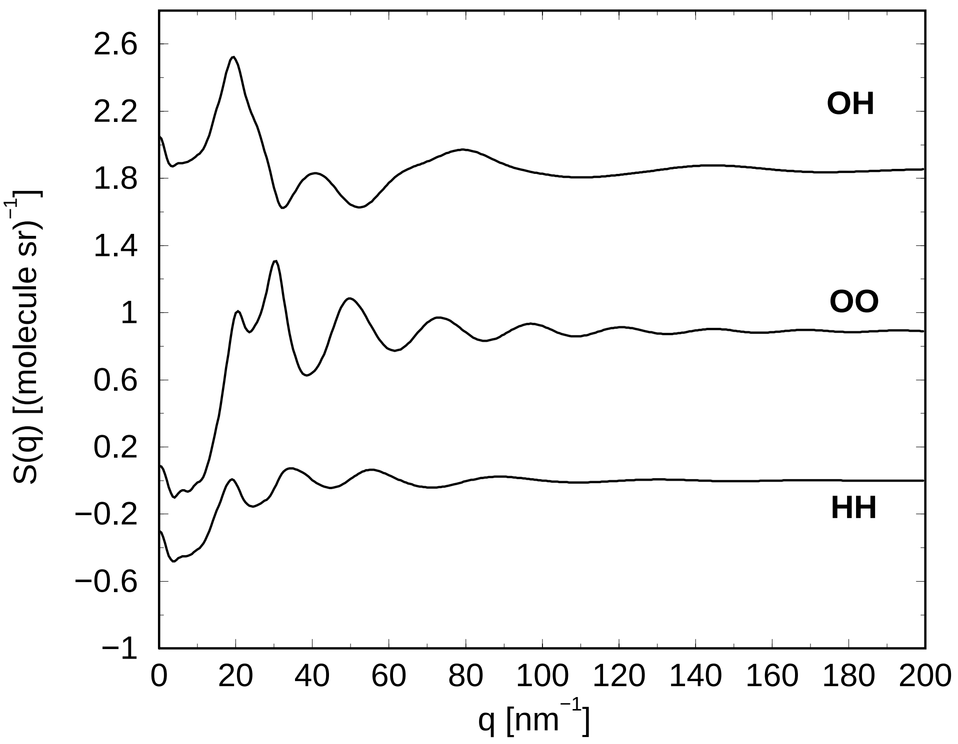

FIG. 6: The partial structure factors extracted from the total neutron weighted shown in Fig.5. Data have been vertically shifted by an arbitrary quantity.

$S(q)$, for D_2O, H_2O and an equimolar mixture of the two at $T = 267$ K, in order to evidence the contrast among the three measurements. The three PSF extracted from this experiment[5], namely S_{OH}, S_{OO} and S_{HH} are plotted in Fig. 6. A Fourier transform of these functions gives the three relevant site-site radial distribution functions of water. However since we have so far considered an ideal experiment, where neutrons interact only once with the sample, the scattering is elastic and no absorption occurs, the data shown here have been subject to corrections for systematic errors due to multiple scattering, absorption, inelasticity. These corrections, along with techniques for extracting information in r-space will be the subject of forthcoming lessons.

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