

Appendix C Neutron scattering experiment: supplementary information

The geometry of the scattering experiment and angle definitions are shown in Fig. C1. In most of the experiments performed and/or analyzed in the frame of this work, the sample container was a plain slab. Throughout all calculations the approximation of an infinite plane slab was employed; therefore, the corrections for the self-attenuation and self-absorption by the sample and corrections for multiple scattering were greatly simplified. Such an approximation is justified when the neutron beam cross section, A_{beam} , is significantly smaller than the area of the slab, A_{slab} . Calculations show that even for the ratio $A_{\text{beam}}/A_{\text{slab}} \approx 0.7$ the approximation is still valid for all scattering angles, except for $\varphi = \alpha \pm 5^\circ$.

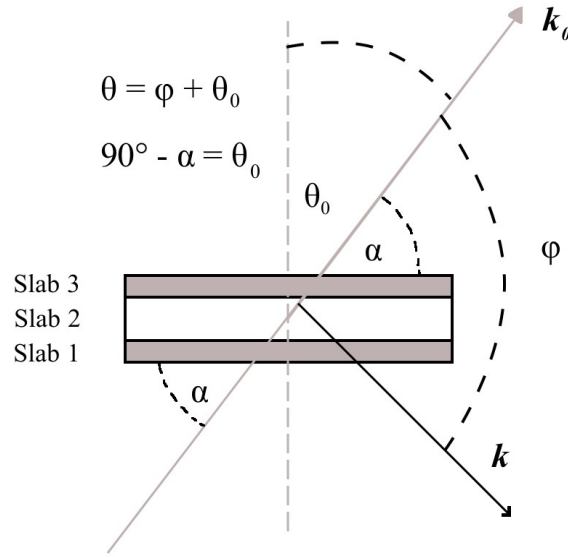


Figure C1 **Geometry of scattering and angle definitions.** The Slabs 1 and 3 are the walls of the sample container and the Slab 2 is the sample. Incident neutrons have wave vector \mathbf{k}_0 , the angle between the incident neutron beam and the sample plane is the sample angle α . Scattered neutrons have wave vector \mathbf{k} and the scattering angle φ is defined as the angle between the wave vectors \mathbf{k}_0 and \mathbf{k} . Instead of α and φ one sometimes uses θ_0 and θ , respectively (θ_0 and θ are counted from the normal to the sample slab).

Note that the volume exposed to the beam, V_s , number density, n , and all the scattering lengths and/or cross sections are included in the expression for $S(\mathbf{Q}, \omega)$ in the present work (as opposed to the presentation given e.g. in [110] and many other articles). In a conventional approach, neglecting multiple scattering and scattering by the sample container, eq. (2.46) can be rewritten as:

$$d^2\sigma/d\Omega d\hbar\omega = V_s \times (k/k_0) \times (n\sigma_s/4\pi) \times \eta(E) \times H_1(\mathbf{k}_0, \mathbf{k}) \times S(\mathbf{Q}, \omega) \quad (\text{C1})$$

where σ_s is the scattering cross section of the sample. However, for molecular liquids scattering lengths and/or cross sections necessarily come into the expression for $S(\mathbf{Q}, \omega)$; for solutions,

number densities of all components come into the expression for $S(\mathbf{Q}, \omega)$ as well. One can see that the approach used in the present work is aimed at the practical application in the QENS spectra analysis.

The macroscopic *scattering* cross section of the sample, Σ_S , [cm^{-1}] is the total number of neutrons scattered per unit volume per unit time per unit incident neutron flux; it is related to the experimental scattering function, $S_{\text{EXP}}(\mathbf{Q}, \omega)$:

$$\Sigma_S = \frac{1}{V_S} \int \frac{k}{k_0} S_{\text{EXP}}(\mathbf{Q}, \omega) d\Omega d\hbar\omega \quad (\text{C2})$$

The macroscopic *absorption* cross section of the sample, Σ_A , [cm^{-1}] is the sum of the atomic absorption cross sections, σ_{Ai} , for all atomic species $i=1, 2 \dots$ weighted by the corresponding number density (n_i [cm^{-3}]):

$$\Sigma_A = \sum_{i=1} n_i \sigma_{Ai} \quad (\text{C3})$$

The macroscopic cross section, Σ , is a sum of macroscopic absorption cross section, Σ_A , and macroscopic scattering cross section, Σ_S :

$$\Sigma = \Sigma_S + \Sigma_A \quad (\text{C4})$$

Appendix D The scattering of the sample container

D.1 Attenuation of the container scattering

Neutron scattering spectra always contain contribution from the sample container (SC), further denoted as $S_{\text{SC}}(\mathbf{k}_0, \mathbf{k})$; it is appropriate to reproduce here eq. (2.52):

$$S_{\text{TOTAL}}(\mathbf{k}_0, \mathbf{k}) = S_{(1)S}(\mathbf{k}_0, \mathbf{k}) + S_{\text{SC}}(\mathbf{k}_0, \mathbf{k}) + S_{\text{MSC}}(\mathbf{k}_0, \mathbf{k}) \quad (\text{D1})$$

$S_{\text{SC}}(\mathbf{k}_0, \mathbf{k})$ is related to the scattering by the *empty* sample container, $S_{\text{EC}}(\mathbf{k}_0, \mathbf{k})$:

$$S_{\text{SC}}(\mathbf{k}_0, \mathbf{k}) = \text{Att}(\mathbf{k}_0, \mathbf{k}) \times S_{\text{EC}}(\mathbf{k}_0, \mathbf{k}) \quad (\text{D2})$$

where $\text{Att}(\mathbf{k}_0, \mathbf{k})$ is the attenuation factor taking into account that neutrons scattered by the container walls will be partially absorbed and/or re-scattered by the sample.

In the course of the experiment a measurement of $S_{\text{EC}}(\mathbf{k}_0, \mathbf{k})$ is usually performed, and it is the factor $\text{Att}(\mathbf{k}_0, \mathbf{k})$ which must be evaluated in order to correct $S_{\text{TOTAL}}(\mathbf{k}_0, \mathbf{k})$ (or $S_{\text{TOTAL}}(\mathbf{Q}, \omega)$) for the scattering by the sample container.

The sample container is considered to be a plain slab, the geometry of the system is shown in Fig. C1. The slab 1 and slab 3 are the container walls and they are equivalent, the (hypothetical) effective scattering function of a container wall, $S_{\text{EC}/2}(\mathbf{k}_0, \mathbf{k})$ is defined as:

$$S_{\text{EC}/2}(\mathbf{k}_0, \mathbf{k}) = H_{1\text{-SLAB1}}(\mathbf{k}_0, \mathbf{k}) \times S_{\text{SLAB1}}(\mathbf{Q}, \omega) = H_{1\text{-SLAB3}}(\mathbf{k}_0, \mathbf{k}) \times S_{\text{SLAB3}}(\mathbf{Q}, \omega) \quad (\text{D3})$$

where $H_1(\mathbf{k}_0, \mathbf{k})$ is the 1st order attenuation factor. In eq. (D3) $S_{EC/2}(\mathbf{k}_0, \mathbf{k})$ is assumed to be due to single scattering only. The thickness of the container wall and the sample layer are d_{WALL} and d_S , respectively. Additional abbreviations (to shorten the expressions) include:

$$\beta = \alpha - \varphi \quad (D4)$$

$$\Sigma(k)_S \times d_S = \text{sam}(k) \quad \Sigma(k_0)_S \times d_S = \text{sam}(k_0) \quad (D5)$$

$$\Sigma(k)_{EC} \times d_{WALL} = \text{ec}(k) \quad \Sigma(k_0)_{EC} \times d_{WALL} = \text{ec}(k_0) \quad (D6)$$

where $\Sigma(k)_S$ and $\Sigma(k)_{EC}$ are macroscopic cross sections of the sample and container, respectively.

Depending on the scattering angle, there are two cases: transmission and reflection.

Transmission:

$$S_{EC}(\mathbf{k}_0, \mathbf{k}) = S_{EC/2}(\mathbf{k}_0, \mathbf{k}) \times \exp(-\text{ec}(k_0)/\sin \alpha) + S_{EC/2}(\mathbf{k}_0, \mathbf{k}) \times \exp(-\text{ec}(k)/\sin \beta) \quad (D7)$$

$$S_{EC/2}(\mathbf{k}_0, \mathbf{k}) = S_{EC}(\mathbf{k}_0, \mathbf{k}) / \{ \exp(-\text{ec}(k_0)/\sin \alpha) + \exp(-\text{ec}(k)/\sin \beta) \} \quad (D8)$$

$$S_{SC}(\mathbf{k}_0, \mathbf{k}) = S_{EC/2}(\mathbf{k}_0, \mathbf{k}) \times \{ \exp(-\{ \text{ec}(k_0) + \text{sam}(k_0) \} / \sin \alpha) + \exp(-\{ \text{ec}(k) + \text{sam}(k) \} / \sin \beta) \} \quad (D9)$$

Thus, $\text{Att}(\mathbf{k}_0, \mathbf{k})$ can be found from eqs. (D2, D8 and D9).

Reflection:

$$S_{EC}(\mathbf{k}_0, \mathbf{k}) = S_{EC/2}(\mathbf{k}_0, \mathbf{k}) + S_{EC/2}(\mathbf{k}_0, \mathbf{k}) \times \exp(-\text{ec}(k_0)/\sin \alpha) \times \exp(\text{ec}(k)/\sin \beta) \quad (D10)$$

$$S_{EC/2}(\mathbf{k}_0, \mathbf{k}) = S_{EC}(\mathbf{k}_0, \mathbf{k}) / \{ 1 + \exp(-\text{ec}(k_0)/\sin \alpha) \times \exp(\text{ec}(k)/\sin \beta) \} \quad (D11)$$

$$S_{SC}(\mathbf{k}_0, \mathbf{k}) = S_{EC/2}(\mathbf{k}_0, \mathbf{k}) \times \{ 1 + \exp(-\{ \text{ec}(k_0) + \text{sam}(k_0) \} / \sin \alpha) \times \exp(\{ \text{ec}(k) + \text{sam}(k) \} / \sin \beta) \} \quad (D12)$$

Thus, $\text{Att}(\mathbf{k}_0, \mathbf{k})$ can be found from eqs. (D2, D11 and D12).

D.2 Importance of corrections for the container scattering

In practice, both eq. (D7) and (D10) can be approximated as $S_{EC}(\mathbf{k}_0, \mathbf{k}) \approx 2 \times S_{EC/2}(\mathbf{k}_0, \mathbf{k})$, because the values of $\text{ec}(k)$ and $\text{ec}(k_0)$ are small. For the same reason, it holds:

$$S_{EC/2}(\mathbf{k}_0, \mathbf{k}) = H_{1EC/2}(\mathbf{k}_0, \mathbf{k}) \times S_{EXP EC/2}(Q, \omega) \approx S_{EXP EC/2}(Q, \omega) \quad (D13)$$

and it follows:

$$S_{EC}(\mathbf{k}_0, \mathbf{k}) = 2 \times S_{EXP EC/2}(Q, \omega) = S_{EXP EC}(Q, \omega) \quad (D14)$$

where $S_{EXP EC}(Q, \omega)$ is the experimental scattering function of the sample container. Note that similarly to the case of the sample scattering (eq. (2.55)), the expression for $S_{EXP EC}(Q, \omega)$ contains V_{SC} , the volume of the sample container exposed to the beam.

For the following discussion, eq. (D1) can be expanded as:

$$S_{TOTAL}(\mathbf{k}_0, \mathbf{k}) = S_{EXP}(Q, \omega) \times H_1(\mathbf{k}_0, \mathbf{k}) + \text{Att}(\mathbf{k}_0, \mathbf{k}) \times S_{EXP EC}(Q, \omega) + S_{S MSC}(\mathbf{k}_0, \mathbf{k}) \quad (D15)$$

Often containers made of aluminum (because of its low scattering and absorption cross section) are employed in order to minimize the contribution of $S_{EXP EC}(Q, \omega)$. The following facts must however be kept in mind:

- 1) The value of $I_{QENS EC}(Q_{EL})$ (i.e. QENS integral of $S_{EXP EC}(Q, \omega)$) increases towards low Q , i.e. there is small angle scattering from the sample container.
- 2) For the given value of $I_{QENS EC}(Q_{EL})$, the elastic intensity (i.e. $S_{EXP EC}(Q, \omega=0)$) is

increasing with increasing energy resolution (that is, with decreasing ΔE).

Consequently, results of the fitting of the model to the experimental spectra become more sensitive to errors in the determination of $S_{\text{EXP SC}}(Q, \omega)$ (and to errors in the determination of $\text{Att}(\mathbf{k}_0, \mathbf{k})$).

- 3) In the experiments on water/aqueous solutions at temperatures $> 30 - 40$ °C, the corrosion of the surface of the conventional sample containers was observed. Corrosion leads to the formation of gas, increase of the pressure inside the container, and, sometimes, to leakage of the sample containers. Specifically, in the experiment with HFBS (see Chapter 3, Tab. 3.1), signs of corrosion were seen on the surface of the cylindrical container made of aluminum (sample container did not leak). In order to avoid potential sample leakage, containers covered with gold were used in a number of experiments performed in the frame of this work. However, the nickel and gold layers led to an increase of $I_{\text{QENS EC}}(Q_{\text{EL}})$ at least by the factor of 2, which made an exact correction for the container scattering more crucial.

For reasons given above, it was chosen *not to subtract the scattering by the sample container at the stage of data reduction* (which is the conventional way, see e.g. [34,102]). Therefore, $S_{\text{FIT}}(Q, \omega)$ (i.e. the expression fitted to the total scattering function, $S_{\text{TOTAL}}(Q, \omega)$) always contained the term “ $f_{\text{EC}} \times C \times S_{\text{SC EXP}}$ ”, see eq. (5.1). Such an approach allowed to adjust the sample container scattering either by changing the parameter f_{EC} or by allowing “ $S_{\text{SC EXP}}$ ” to be free and Q_{EL} -dependent fitting parameter.

Appendix E Multiple scattering correction

E.1 Definitions

The approach given here was developed by Sears [110].

The angle θ_0 is defined as the angle between the beam and the normal to the slab; thus, θ_0 lies in $[0; \pi/2]$, see Fig. C1. The polar angle for the incident beam is denoted by ψ_i . and $\psi_i = 0$ for the case shown in Fig. C1. The scattering angle is θ and the polar angle of the scattered neutron is ψ_f . The relation with the previously used notations (sample angle α and scattering angle φ) reads:

$$\theta_0 = 90^\circ - \alpha \quad \theta = \varphi + \theta_0 \quad (\text{E1})$$

Note that the polar angle $\psi_i = 0$ for the sample angle α smaller than 90° , else $\psi_i = \pi$.

Generally, multiple scattering component includes such neutrons which were scattered both by the sample and container walls. However, for conventional sample containers

calculations show that “container-sample” or “sample-container” contributions to the double scattering are very small and can be neglected.

The expression for the effective scattering function of the sample reads:

$$S_S(\mathbf{k}_0, \mathbf{k}) = \sum_{j=1}^{\infty} s_{(j)S}(\mathbf{k}_0, \mathbf{k}) \quad (\text{E2})$$

where $s_{(j)S}$ is the contribution from the neutrons which have been scattered j times (by the sample only). Consider single scattering, $s_{(1)S}$:

$$s_{(1)S}(\mathbf{k}_0, \mathbf{k}) = S(\mathbf{Q}, \omega) \times H_1(\mathbf{k}_0, \mathbf{k}) \quad (\text{E3})$$

$H_1(\mathbf{k}_0, \mathbf{k})$ is the 1st order transmission factor; for an infinite plane slab, it is given by:

$$H_1(\mathbf{k}_0, \mathbf{k}) = \exp(-\xi_0 - \xi) \frac{\exp(\xi - \xi_0) - \exp(\xi_0 - \xi)}{2(\xi - \xi_0)} \quad (\text{E4})$$

$$\text{where } \xi = \Sigma \times d_S / 2 \cos \theta \quad (\text{E5})$$

The expression for the double scattering component, $s_{(2)S}$, reads:

$$s_{(2)S}(\mathbf{k}_0, \mathbf{k}) = S(\mathbf{Q}_1, \omega_1) \otimes S(\mathbf{Q}_2, \omega_2) \times H_2(\mathbf{k}_0, \mathbf{k}) \quad (\text{E6})$$

and an analytical expression for the case of an infinite plane slab exists for $H_2(\mathbf{k}_0, \mathbf{k})$ [110].

The momentum and energy transfers are given by:

$$\mathbf{Q} = \mathbf{Q}_1 + \mathbf{Q}_2 \quad \mathbf{Q}_1 = \mathbf{k}_1 - \mathbf{k}_0 \quad \mathbf{Q}_2 = \mathbf{k} - \mathbf{k}_1 \quad (\text{E7})$$

$$\hbar\omega = \hbar\omega_1 + \hbar\omega_2 \quad \hbar\omega_1 = E_1 - E_0 \quad \hbar\omega_2 = E - E_1 \quad (\text{E8})$$

The relationship between different wave vectors is given in Fig. E1.

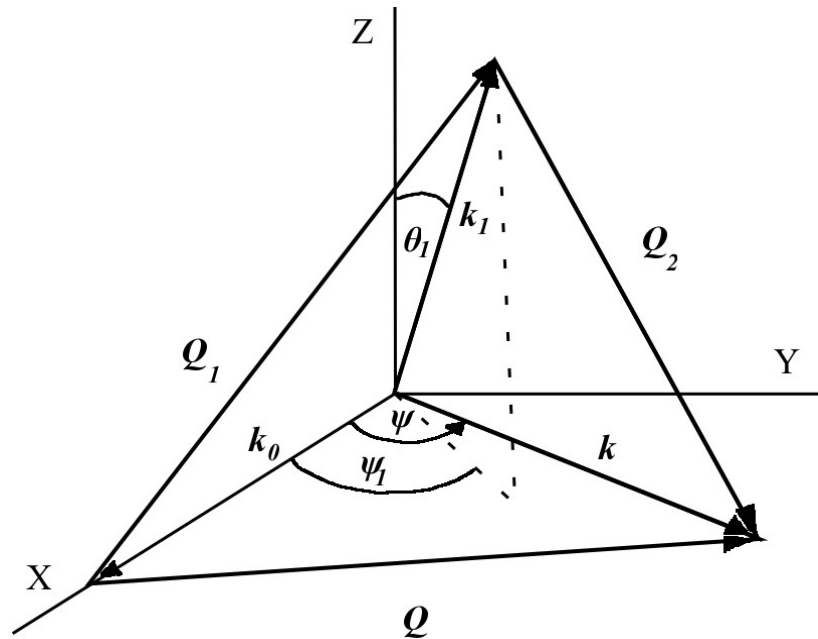


Figure E1 **Wave vectors relationship for double scattering.** Relation between \mathbf{k}_0 , \mathbf{k}_1 and \mathbf{k} and the momentum transfers \mathbf{Q} , \mathbf{Q}_1 and \mathbf{Q}_2 are shown.

From eqs. (E2, E3) it follows:

$$S_s(\mathbf{k}_0, \mathbf{k}) = H_1 \times \{S(\mathbf{Q}, \omega) + (H_2/H_1) \times S(\mathbf{Q}_1, \omega_1) \otimes S(\mathbf{Q}_2, \omega_2) + (H_3/H_1) \times (\dots) + \dots\} \quad (E9)$$

where $H_1 = H_1(\mathbf{k}_0, \mathbf{k})$, $H_2 = H_2(\mathbf{k}_0, \mathbf{k})$ etc.

E.2 Approximation

The central formula from [110] is:

$$S_s(\mathbf{k}_0, \mathbf{k}) = H_1(\mathbf{k}_0, \mathbf{k}) \times \{S(\mathbf{Q}, \omega) + \Delta \times R_2(\mathbf{k}_0, \mathbf{k})\} \quad (E10)$$

where for an infinite plane slab one has:

$$\Delta = \{(\exp(2\delta) - 1)/2\delta\} - 1 \quad (E11)$$

$$\delta = 2\pi \int B(\mathbf{k}_1) \sin \theta_1 d\theta_1 \quad (E12)$$

$R_2(\mathbf{k}_0, \mathbf{k})$ is a three dimensional integral:

$$R_2(\mathbf{k}_0, \mathbf{k}) = \frac{1}{\delta} \int d\Omega_1 d\hbar\omega_1 S(\mathbf{Q}_1, \omega_1) S(\mathbf{Q}_2, \omega_2) B(\mathbf{k}_1) \quad (E13)$$

This integral (if the axis of symmetry is taken as polar axis) can be represented as:

$$R_2(\mathbf{k}_0, \mathbf{k}) = \frac{1}{\delta} \int R(\mathbf{k}_0, \theta_1, \mathbf{k}) b(\theta_1) d\theta_1 \quad (E14)$$

where:

$$R(\mathbf{k}_0, \theta_1, \mathbf{k}) = \int_0^{2\pi} d\phi_1 \int d\hbar\omega_1 S(\mathbf{Q}_1, \omega_1) S(\mathbf{Q}_2, \omega_2) \quad (E15)$$

$$b(\theta_1) = 2\pi \times B(\mathbf{k}_1) \times \sin(\theta_1) \quad (E16)$$

$$B(\mathbf{k}_1) = \{p/\Sigma(\mathbf{k}_1)\} \times \{1 - \exp(-q \times \Sigma(\mathbf{k}_1) \times d_s / \cos(\theta_1))\} \quad (E17)$$

The macroscopic cross section $\Sigma(\mathbf{k}_1)$ is calculated according to eqs.(C2-C4). The coefficients p , q depend on the geometry of the sample; for an infinite plain slab $p = 0.75$ and $q = 0.667$.

A further approximation is valid for $\Sigma \times d_s \leq 0.2$ and further referred to as “ $\pi/2$ approximation”:

$$R_2(\mathbf{k}_0, \mathbf{k}) = R(\mathbf{k}_0, \pi/2, \mathbf{k}) \quad (E18)$$

This approximation can be illustrated as follows: for the once scattered neutron, the probability to be re-scattered depends on the length of the path, which neutron has to take before it leaves the sample; this length increases as θ_1 becomes closer to 90° .

In “ $\pi/2$ approximation”, eq. (E10) can be rewritten as:

$$S_s(\mathbf{k}_0, \mathbf{k}) = H_1(\mathbf{k}_0, \mathbf{k}) \times \{S(\mathbf{Q}, \omega) + \Delta \times R(\mathbf{k}_0, \pi/2, \mathbf{k})\} \quad (E19)$$

For small δ , $\Delta = \delta$, meaning that multiple scattering is, to a great extent, double scattering. It is important that $R(\mathbf{k}_0, \pi/2, \mathbf{k})$ is just a two dimensional integral, which can be evaluated numerically by standard methods.

In order to fit the expression $S_{FIT}(\mathbf{Q}, \omega)$ (see eq. (5.1)) to the spectra, the term

“ $C \times V_S \times S_{MSC\ THEO}$ ” has to be evaluated. It follows:

$$C \times V_S \times S_{MSC\ THEO} = Sc.F(Q_{EL}) \times \Delta \times R(\mathbf{k}_0, \pi/2, \mathbf{k}) / H_1(\mathbf{k}_0, \mathbf{k}) = Sc.F(Q_{EL}) \times S_{MSC\ THEO}(\varphi, \omega) \quad (E20)$$

Note that the factor $Sc.F(Q_{EL})$ normally comes into the expression for $S_{THEO}(Q, \omega)$, see section 5.3. However, in evaluation of $R_2(\mathbf{k}_0, \mathbf{k})$, $S_{THEO}(Q_1, \omega_1)$ and $S_{THEO}(Q_2, \omega_2)$ are taken *without* this factor.

E.3 Implementation

Expressions for Q_1^2 and Q_2^2 , required for the evaluation of the multiple scattering, are:

$$Q_1^2 = k_1^2 + k_0^2 - 2 \times k_1 \times k_0 \times (\cos \theta_0 \times \cos \theta_1 + \sin \theta_0 \times \sin \theta_1 \times \cos \psi_1) \quad \text{for } \alpha < 90^\circ \quad (E21)$$

$$Q_1^2 = k_1^2 + k_0^2 - 2 \times k_1 \times k_0 \times (\cos \theta_0 \times \cos \theta_1 - \sin \theta_0 \times \sin \theta_1 \times \cos \psi_1) \quad \text{for } \alpha > 90^\circ \quad (E22)$$

$$Q_2^2 = k^2 + k_l^2 - 2 \times k \times k_l \times (\cos \theta \times \cos \theta_1 + \sin \theta \times \sin \theta_1 \times \cos (\psi_f - \psi_1)) \quad (E23)$$

Note that the value of ψ_f depends, generally, on the instrument and the angle grouping procedure; often $\psi_f = 0$ or $\psi_f = \pi$. For “ $\pi/2$ approximation” the values of Q_1^2 and Q_2^2 are obtained by substituting $\theta_1 = \pi/2$, into eqs. (E21-E23).

In the process of fitting the theoretical model to the spectra, a subroutine evaluating the scattering function, $S_{FIT}(Q, \omega)$, is called by the program for every pair of values (φ, ω) . In principle, *every* such call can be accompanied by the evaluation of the multiple scattering component, $S_{MSC\ THEO}(\varphi, \omega)$, as well. One would need, however, a lot of CPU time to complete such a fit, even if the “ $\pi/2$ approximation” is employed.

In this work it was chosen to evaluate $S_{MSC\ THEO}(\varphi, \omega)$ only for the predefined array of points $\omega_1, \omega_2, \dots, \omega_N$ for every scattering angle. Whenever the value of a free fit parameter was changed, the array $S_{MSC\ THEO}(\varphi, \omega_i)$ was re-evaluated. Because the quasielastic peak has the shape of a Voigt function (which is the convolution of a Gaussian with a Lorentzian), it is a reasonable approximation, to find $S_{MSC\ THEO}(\varphi, \omega)$ for any point ω which lies in the interval (ω_i, ω_{i+1}) by the Lorentzian interpolation:

$$S_{MSC\ THEO}(\varphi, \omega) = a_i(\varphi) \times Lor(b_i(\varphi), \omega) \quad (E24)$$

and $a_i(\varphi)$ and $b_i(\varphi)$ can be found from $S_{MSC\ THEO}(\varphi, \omega_i)$ and $S_{MSC\ THEO}(\varphi, \omega_{i+1})$ and eq. (E24). If no solution of eq. (E24) exists for given $\omega_i, S_{MSC\ THEO}(\varphi, \omega_i), \omega_{i+1}, S_{MSC\ THEO}(\varphi, \omega_{i+1})$, a linear interpolation is used:

$$S_{MSC\ THEO}(\varphi, \omega) = a_i(\varphi) + \omega_i \times b_i(\varphi) \quad (E25)$$

and $a_i(\varphi)$ and $b_i(\varphi)$ are found from $S_{MSC\ THEO}(\varphi, \omega_i)$ and $S_{MSC\ THEO}(\varphi, \omega_{i+1})$ and eq. (E25).

The number of ω -points for the evaluation of multiple scattering was kept below 50. On a PC with 1.6 GHz processor, the time required to perform the simultaneous fit of the spectra for several angles could be kept shorter than 5 - 15 minutes.