

2 Method of quasielastic neutron scattering (QENS)

2.1 Introduction

Nowadays, the quasielastic neutron scattering (QENS) method is gaining increasingly more attention among the scientific community. In the past, QENS was an intensity limited technique, the time to record spectra with sufficient statistics was long, and consequently the total number of the experiments was small. The neutron scattering instrumentation at long existing world's leading neutron sources (in the first place: the Institut Laue-Langevin (ILL) in Grenoble, but also ISIS, UK; HMI, Germany; NIST CNR, USA and others) has been continuously improved. Furthermore, new powerful facilities, the nuclear reactor in München and the Spallation Neutron Source in USA came into operation, and other facilities will follow. For an experimentalist, the access to a QENS spectrometer is becoming easier. Consequently, a great interest towards this technique has appeared in biology and life science communities.

The neutron scattering provides information on the microscopic structure and dynamics in the target sample (however, limited by the experimental resolution effects). In the following no details on the interaction of the neutron with matter will be given (these can be found e.g. in [65,76,124]). Such details may be skipped due to the fact that neutron-matter interaction is weak. The nature of the neutron manifest itself in the spectra only through the strength of the neutron interaction with a nucleus, i.e. through the neutron scattering length, which is just a number. Neutron scatterings lengths for the most nuclei are known, as a consequence, it is only properties of the sample alone which are reflected in the neutron scattering spectra.

2.2 Correlation functions

The central entity in the quasielastic neutron scattering experiment is the *scattering function* $S(\mathbf{Q}, \omega)$, and it was shown to be related to the pair correlation function, $G(\mathbf{r}, t)$ [47,65,76]. In the classical limit (always tacitly assumed in the following), $G(\mathbf{r}, t)$ is the probability that if at time $t = 0$ there is a particle at the origin, $\mathbf{r} = 0$, one will find any particle (including the original one) at the position \mathbf{r} at time t . Self correlation function, $G_{\text{SELF}}(\mathbf{r}, t)$, is the probability, that if at time $t = 0$ there is a particle at the origin, $\mathbf{r} = 0$, one will find *the same* particle at the position \mathbf{r} at time t .

$G(\mathbf{r}, t)$ is the space-Fourier transform of $I(\mathbf{Q}, t)$ and $G_{\text{SELF}}(\mathbf{r}, t)$ is the space-Fourier transform of $I_{\text{SELF}}(\mathbf{Q}, t)$, so that:

$$I(\mathbf{Q}, t) = \int_{-\infty}^{\infty} \exp(i\mathbf{Q}\cdot\mathbf{r}) G(\mathbf{r}, t) d\mathbf{r} \quad (2.1)$$

$$I_{\text{SELF}}(\mathbf{Q}, t) = \int_{-\infty}^{\infty} \exp(i\mathbf{Q}\cdot\mathbf{r}) G_{\text{SELF}}(\mathbf{r}, t) d\mathbf{r} \quad (2.2)$$

and $I(\mathbf{Q}, t)$ and $I_{\text{SELF}}(\mathbf{Q}, t)$ are the intermediate and the self intermediate scattering functions, respectively.

The coherent and incoherent scattering functions are the time-Fourier transforms of the intermediate and self intermediate scattering function, respectively:

$$S_{\text{COH}}(\mathbf{Q}, \omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \exp(-i\omega t) I(\mathbf{Q}, t) dt \quad (2.3)$$

$$S_{\text{INC}}(\mathbf{Q}, \omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \exp(-i\omega t) I_{\text{SELF}}(\mathbf{Q}, t) dt \quad (2.4)$$

In the following the case of a monoatomic liquid will be considered and vibrational motions of atoms will be neglected. Thus, only the translational diffusion of atoms in the liquid has to be taken into account. A number of analytical expressions for translational incoherent scattering function, $S_{\text{TR INC}}(\mathbf{Q}, \omega)$, exist, see for instance [8]. For instance, in the case of the continuous translational diffusion, $S_{\text{TR INC}}(\mathbf{Q}, \omega)$ is given by the Lorentzian [26,143]:

$$S_{\text{TR INC}}(\mathbf{Q}, \omega) = \frac{1}{\pi} \frac{D_{\text{TR}} Q^2}{(D_{\text{TR}} Q^2)^2 + \omega^2} \quad (2.5)$$

where D_{TR} is the translational diffusion coefficient. (Throughout the present work, the Lorentzian of argument x with the half width at half maximum being HWHM is denoted as $\text{Lor}(\text{HWHM}, x)$.)

There is no analytical expression for the coherent scattering function for translational diffusion, $S_{\text{TR COH}}(\mathbf{Q}, \omega)$. Such an expression can only be obtained by making some kind of approximation. The famous convolution approximation [143] states:

$$S_{\text{TR COH}}(\mathbf{Q}, \omega) = S_{\text{TR INC}}(\mathbf{Q}, \omega) \times [1 + \gamma(\mathbf{Q})] \quad (2.6)$$

where for a monoatomic liquid $\gamma(\mathbf{Q})$ is given by:

$$\gamma(\mathbf{Q}) = \int_V \exp(i\mathbf{Q}\cdot\mathbf{r}) [g(\mathbf{r}) - g_0] d\mathbf{r} \quad (2.7)$$

The *static* pair correlation function, $g(\mathbf{r})$, is the probability to find an atom at the position \mathbf{r} , if there is an atom at the position $\mathbf{r} = 0$. The quantity g_0 is the bulk number density. It follows from the definition of $G(\mathbf{r}, t)$:

$$G(\mathbf{r}, 0) = g(\mathbf{r}) + \delta(\mathbf{r}) \quad (2.8)$$

One often splits the intermediate scattering function (eq. (2.1)) into the distinct (describing time-dependent correlations between the positions of two different atoms) and self (describing

time-dependent correlation between the positions of one atom) parts:

$$I(\mathbf{Q}, t) = I_{\text{DIST}}(\mathbf{Q}, t) + I_{\text{SELF}}(\mathbf{Q}, t) \quad (2.9)$$

where $I_{\text{DIST}}(\mathbf{Q}, t)$ is the distinct intermediate scattering function. By substituting $G(\mathbf{r}, 0)$ from eq. (2.8) into eq. (2.1), taking $t = 0$ and comparing to eq. (2.7), one gets:

$$I_{\text{DIST}}(\mathbf{Q}, 0) = \gamma(\mathbf{Q}) + \int_V \exp(i\mathbf{Q}\cdot\mathbf{r}) g_0 d\mathbf{r} \quad (2.10)$$

$$I_{\text{SELF}}(\mathbf{Q}, 0) = 1 \quad (2.11)$$

and for $\mathbf{Q} \neq 0$, from eq. (2.10) it follows: $I_{\text{DIST}}(\mathbf{Q}, 0) = \gamma(\mathbf{Q})$.

Obtaining of the expression for the scattering function, $S(Q, \omega)$, for a molecular liquid, e.g. water, requires consideration of the rotational motion of a molecule. Because the main part of the present work consists in the analysis of the neutron scattering spectra of aqueous solutions, it is appropriate to reproduce here a (shortened) approach of Sears [109].

2.3 Neutron scattering by a molecular liquid

Suppose one has a volume V filled with M molecules, and m is the number of atoms in a molecule. The general equation for the intermediate scattering function reads:

$$I(\mathbf{Q}, t) = \sum_{i=1}^M \sum_{\mu=1}^m \sum_{j=1}^M \sum_{\nu=1}^m \langle b_{i\mu} b_{j\nu} \rangle \langle \exp[-i\mathbf{Q}\cdot(\mathbf{R}_{i\mu}(0) - \mathbf{R}_{j\nu}(t))] \rangle \quad (2.12)$$

where $\mathbf{R}_{i\mu}$ is the vector giving the position of the μ th atom in the i th molecule, $b_{i\mu}$ is the neutron scattering length of the nucleus of atomic species μ . The angle brackets denote the statistical average. One splits $I(\mathbf{Q}, t)$ into the “distinct” part (containing correlations between the positions of atoms of *distinct* molecules) and the “self” part (correlations between the positions of atoms belonging to *the same* molecule):

$$I(\mathbf{Q}, t) = \sum_{i=1}^M \sum_{\mu=1}^m \sum_{j \neq i=1}^M \sum_{\nu=1}^m \langle b_{i\mu} \rangle \langle b_{j\nu} \rangle \langle \exp[-i\mathbf{Q}\cdot(\mathbf{R}_i(0) - \mathbf{R}_j(t))] \rangle \langle \exp[-i\mathbf{Q}\cdot(\mathbf{r}_{i\mu}(0) - \mathbf{r}_{j\nu}(t))] \rangle \\ + \sum_{i=1}^M \sum_{\mu=1}^m \sum_{\nu=1}^m \langle b_{i\mu} b_{i\nu} \rangle \langle \exp[-i\mathbf{Q}\cdot(\mathbf{R}_i(0) - \mathbf{R}_i(t))] \rangle \langle \exp[-i\mathbf{Q}\cdot(\mathbf{r}_{i\mu}(0) - \mathbf{r}_{i\nu}(t))] \rangle \quad (2.13)$$

where \mathbf{R}_i is the vector giving the position of the center of mass of the i th molecule, and $\mathbf{r}_{i\mu}$ is the vector giving the position of the μ th atom in the i th molecule (in the coordinate system of the center-of-mass of the i th molecule).

The neutron scattering length of an atomic nucleus depends on its composition and the orientation of the neutron spin relative to the spin of the nucleus. In most cases, different isotopes and spin orientations are randomly distributed across the sample. In eq. (2.13) $b_{i\mu}$ and $b_{j\nu}$ refer to the scattering lengths of nuclei belonging to the *distinct* molecules i and j , $b_{i\mu}$ and $b_{j\nu}$ are thus uncorrelated: $\langle b_{i\mu} b_{j\nu} \rangle = \langle b_{i\mu} \rangle \langle b_{j\nu} \rangle = \langle b_{\mu} \rangle \langle b_{\nu} \rangle$, where brackets mean averaging over all nuclei of the atomic species μ . Thus, the “distinct” part contains only *coherent scattering*

lengths, $\langle b_\mu \rangle$, $\mu=1, 2 \dots m$.

In the ‘‘self part’’ (here the index i will be temporarily dropped because all molecules are equivalent) two cases should be considered: $\mu \neq \nu$ and $\mu = \nu$. For $\mu \neq \nu$: $\langle b_\mu b_\nu \rangle = \langle b_\mu \rangle \langle b_\nu \rangle$ (i.e. for two different atoms in one molecule, b_μ and b_ν are uncorrelated). For $\mu = \nu$: $\langle b_\mu b_\nu \rangle = \langle b_\mu^2 \rangle$ and:

$$\langle b_\mu^2 \rangle = \langle b_\mu \rangle^2 + \sigma_{\mu \text{ INC}}/4\pi \quad (2.14)$$

where $\sigma_{\mu \text{ INC}}/4\pi$ is the mean square deviation of the average (over the whole sample) scattering length of the atomic species μ . The quantity $\sigma_{\mu \text{ INC}}$ is the *incoherent scattering cross section* of the μ th atom. The *coherent scattering cross section* of the μ th atom is $\sigma_{\mu \text{ COH}}$, $\sigma_{\mu \text{ COH}} = 4\pi \times \langle b_\mu \rangle^2$. The scattering cross section, σ_s , is the sum of the coherent and incoherent cross sections: $\sigma_s = \sigma_{\text{COH}} + \sigma_{\text{INC}}$. The values of neutron scattering lengths and cross sections for selected atoms and isotopes are listed in Tab. 2.1.

Table 2.1 **Neutron scattering lengths and cross sections for selected elements/isotopes.** Notations: coherent scattering length $\langle b \rangle$ [10^{-12} cm]; coherent, incoherent and total scattering cross sections σ_{COH} , σ_{INC} , and σ_s , respectively [barn]^a; absorption cross section σ_A [barn]. Taken from [8].

Atom	$\langle b \rangle$	σ_{COH}	σ_{INC}	$\sigma_s = \sigma_{\text{COH}} + \sigma_{\text{INC}}$	σ_A (for $\lambda_0 = 1.8 \text{ \AA}$) ^b
H	-0.3741	1.7586	79.90	81.66	0.3326
D	0.6674	5.597	2.04	7.640	0.00051
C	0.6648	5.554	0.001	5.555	0.00350
N	0.936	11.01	0.49	11.50	1.90
O	0.5805	4.235	0.000	4.235	0.00019
V	-0.03824	0.0184	5.187	5.205	5.08

^a 1 barn = 10^{-24} cm².

^b For the arbitrary value of λ_0 , the absorption cross section is found from: $\sigma_A(\lambda_0) = \sigma_A(1.8 \text{ \AA}) \times \sqrt{(\lambda_0/1.8)}$

In the following, both cases, $\mu \neq \nu$ and $\mu = \nu$, are considered by writing $\langle b_\mu b_\nu \rangle$ as: $\langle b_\mu b_\nu \rangle = \langle b_\mu \rangle \langle b_\nu \rangle + \sigma_{\mu \text{ INC}} \times \delta_{\mu\nu}/4\pi$. Further, one makes two separate assumptions: a) rotational and translational motion of a molecule are not correlated; b) the rotational motions of different molecules are not correlated. Eq. (2.13) can be then rewritten as:

$$I(\mathbf{Q}, t) = \sum_{i=1, j \neq i}^{M, M} \langle \exp[-i \mathbf{Q} \cdot (\mathbf{R}_i(0) - \mathbf{R}_j(t))] \rangle \sum_{\mu=1}^m \langle b_\mu \rangle \langle \exp[-i \mathbf{Q} \cdot \mathbf{r}_\mu(0)] \rangle \sum_{\nu=1}^m \langle b_\nu \rangle \langle \exp[i \mathbf{Q} \cdot \mathbf{r}_\nu(t)] \rangle \\ + \sum_{i=1}^M \langle \exp[-i \mathbf{Q} \cdot (\mathbf{R}_i(0) - \mathbf{R}_i(t))] \rangle \sum_{\mu, \nu=1}^{m, m} (\langle b_\mu \rangle \langle b_\nu \rangle + \frac{\sigma_{\mu \text{ INC}} \delta_{\mu\nu}}{4\pi}) \langle \exp[-i \mathbf{Q} \cdot (\mathbf{r}_\mu(0) - \mathbf{r}_\nu(t))] \rangle \quad (2.15)$$

Because all M molecules are equivalent, the summation over i from 1 to M can be substituted by multiplication by M . With $\mathbf{R}(0)$ and $\mathbf{R}(t)$ being the positions of a given molecule at times 0 and t , respectively, one may rewrite eq. (2.15) as:

$$I(\mathbf{Q}, t) = M \sum_{j=1}^{M-1} \langle \exp[-i\mathbf{Q} \cdot (\mathbf{R}(0) - \mathbf{R}_j(t))] \rangle \sum_{\mu=1}^m \langle b_{\mu} \rangle \langle \exp[-i\mathbf{Q} \cdot \mathbf{r}_{\mu}(0)] \rangle \sum_{\nu=1}^m \langle b_{\nu} \rangle \langle \exp[i\mathbf{Q} \cdot \mathbf{r}_{\nu}(t)] \rangle \\ + M \langle \exp[-i\mathbf{Q} \cdot (\mathbf{R}(0) - \mathbf{R}(t))] \rangle \sum_{\mu, \nu=1}^{m, m} (\langle b_{\mu} \rangle \langle b_{\nu} \rangle + \frac{\sigma_{\mu \text{INC}} \delta_{\mu \nu}}{4\pi}) \langle \exp[-i\mathbf{Q} \cdot (\mathbf{r}_{\mu}(0) - \mathbf{r}_{\nu}(t))] \rangle \quad (2.16)$$

where in the ‘‘distinct’’ part, the correlation of the position of a given molecule with positions of M-1 other molecules is expressed through the summation over j from 1 to M-1.

From eq. (2.16), the intermediate function $I(\mathbf{Q}, t)$ can be represented as:

$$I(\mathbf{Q}, t) = M \times \{ I_{\text{TR DIST}}(\mathbf{Q}, t) \times u(\mathbf{Q}) + I_{\text{TR SELF}}(\mathbf{Q}, t) \times v(\mathbf{Q}, t) \} \quad (2.17)$$

where $I_{\text{TR DIST}}(\mathbf{Q}, t)$ and $I_{\text{TR SELF}}(\mathbf{Q}, t)$ are given by:

$$I_{\text{TR DIST}}(\mathbf{Q}, t) = (M-1) \langle \exp[-i\mathbf{Q} \cdot (\mathbf{R}(0) - \mathbf{R}_j(t))] \rangle \quad (2.18)$$

$$I_{\text{TR SELF}}(\mathbf{Q}, t) = \langle \exp[-i\mathbf{Q} \cdot (\mathbf{R}(0) - \mathbf{R}(t))] \rangle \quad (2.19)$$

The functions $u(\mathbf{Q})$ and $v(\mathbf{Q}, t)$ are given by:

$$u(\mathbf{Q}) = \left| \sum_{\mu=1}^m \langle b_{\mu} \rangle f_{\mu}(\mathbf{Q}) \right|^2 \quad (2.20)$$

$$v(\mathbf{Q}, t) = \sum_{\mu, \nu=1}^{m, m} \left[\langle b_{\mu} \rangle \langle b_{\nu} \rangle + \frac{\sigma_{\mu \text{INC}} \delta_{\mu \nu}}{4\pi} \right] \chi_{\mu \nu}(\mathbf{Q}, t) \quad (2.21)$$

$$f_{\mu}(\mathbf{Q}) = \langle \exp[-i(\mathbf{Q} \cdot \mathbf{r}_{\mu})] \rangle \quad (2.22)$$

$$\chi_{\mu \nu}(\mathbf{Q}, t) = \langle \exp[-i\mathbf{Q} \cdot (\mathbf{r}_{\mu}(0) - \mathbf{r}_{\nu}(t))] \rangle \quad (2.23)$$

Averaging of eq. (2.22) over the orientation of \mathbf{Q} relative to \mathbf{r} (because the sample is a liquid) allows, by introducing the scattering amplitude of the molecule, $b_{\text{EFF}}(\mathbf{Q})$:

$$b_{\text{EFF}}(\mathbf{Q}) = \sum_{\mu=1}^m \langle b_{\mu} \rangle \frac{\sin Q r_{\mu}}{Q r_{\mu}} \quad (2.24)$$

to rewrite eq. (2.20) as follows:

$$\langle u(\mathbf{Q}) \rangle_{\Omega} = b_{\text{EFF}}^2(\mathbf{Q}) \quad (2.25)$$

For the model of the isotropic rotational diffusion, one has:

$$v(\mathbf{Q}, t) = \sum_{l=0}^{\infty} (2l+1) A_l(Q) F_l(t) \quad (2.26)$$

$$F_l(t) = \exp(-l(l+1) \times D_r \times t) \quad (2.27)$$

$$A_l(Q) = \sum_{\mu, \nu=1}^{m, m} \left[\langle b_{\mu} \rangle \langle b_{\nu} \rangle + \frac{\sigma_{\mu \text{INC}} \delta_{\mu \nu}}{4\pi} \right] j_l(Q r_{\mu}) j_l(Q r_{\nu}) P_l(\cos \theta_{\mu \nu}) \quad (2.28)$$

where $\theta_{\mu \nu}$ is an angle between \mathbf{r}_{μ} and \mathbf{r}_{ν} , P_l is the Legendre polynomial of degree l , j_l is the spherical Bessel function of order l . Note that if $\nu = \mu$, then $\theta_{\mu \nu} = 0$ and thus $P_l(\cos \theta_{\mu \nu}) = 1$.

The application of the convolution approximation [143] to the translational motion of the center of mass allows to rewrite eq. (2.17) as:

$$I(\mathbf{Q}, t) = M \times I_{\text{TR SELF}}(\mathbf{Q}, t) \times I_{\text{ROT}}(\mathbf{Q}, t) \quad (2.29)$$

where $I_{\text{ROT}}(\mathbf{Q}, t)$ is given by:

$$I_{\text{ROT}}(\mathbf{Q}, t) = \gamma(\mathbf{Q})_{\text{CM}} \times \mathbf{u}(\mathbf{Q}) + \mathbf{v}(\mathbf{Q}, t) \quad (2.30)$$

where $\gamma_{\text{CM}}(\mathbf{Q})$ has the same meaning as $\gamma(\mathbf{Q})$ in eq. (2.7), except that it applies to the center of mass of the molecule in a molecular liquid and not to an atom in a monoatomic liquid.

The final scattering function is the time-Fourier transform of $I(\mathbf{Q}, t)$ from eq. (2.29):

$$S(\mathbf{Q}, \omega) = M \times \frac{1}{2\pi} \int_{-\infty}^{\infty} \exp(-i\omega t) I_{\text{TR SELF}}(\mathbf{Q}, t) \times I_{\text{ROT}}(\mathbf{Q}, t) dt \quad (2.31)$$

From eq. (2.31), applying the convolution theorem of Fourier transform one obtains:

$$S(\mathbf{Q}, \omega) = M \times \{S_{\text{TR INC}}(\mathbf{Q}, \omega) \otimes S_{\text{ROT}}(\mathbf{Q}, \omega)\} \quad (2.32)$$

where \otimes is the convolution operator. Note that the incoherent translational scattering function, $S_{\text{TR INC}}(\mathbf{Q}, \omega)$, is the time-Fourier transform of the self part of the intermediate scattering function, $I_{\text{TR SELF}}(\mathbf{Q}, t)$ which is related to the nature of the motion of the center of mass of the molecule, i.e. to $G_{\text{TR SELF}}(\mathbf{r}, t)$, see eqs. (2.2, 2.4). A number of models is available for $S_{\text{TR INC}}(\mathbf{Q}, \omega)$, and any of them can be used since translational and rotational motions are taken to be independent.

The rotational scattering function, $S_{\text{ROT}}(\mathbf{Q}, \omega)$, is the time-Fourier transform of $I_{\text{ROT}}(\mathbf{Q}, t)$ given by eq. (2.30). For the case of isotropic rotation, $S_{\text{ROT}}(\mathbf{Q}, \omega)$ can be represented as:

$$S_{\text{ROT}}(\mathbf{Q}, \omega) = \sum_{l=0}^{\infty} S_{\text{ROT}}^l(\mathbf{Q}, \omega) \quad (2.33)$$

$$S_{\text{ROT}}^0(\mathbf{Q}, \omega) = \delta(\omega) \times \{b_{\text{EFF}}^2(\mathbf{Q}) \times \gamma_{\text{CM}}(\mathbf{Q}) + A_0(\mathbf{Q})\} \quad (2.34)$$

$$S_{\text{ROT}}^l(\mathbf{Q}, \omega) = (2l + 1) \times A_l(\mathbf{Q}) \times \text{Lor}(l(l+1)D_r, \omega) \quad (2.35)$$

Here D_r is the rotational diffusion coefficient [meV], related to the rotational correlation time τ_{ROT} [ps], with 0.6583 being reduced Planck constant, \hbar , [meV·ps]:

$$D_r = 0.6583 / 6\tau_{\text{ROT}} \quad (2.36)$$

One has to note that rotational structure factors $A_l(\mathbf{Q})$ account for *both coherent and incoherent* quasielastic neutron scattering intensity. Specifically, $A_0(\mathbf{Q})$ is the elastic structure factor (ESF), the sum of the elastic incoherent and coherent structure factors, EISF and ECSF, respectively.

The differential neutron scattering cross section for the molecular liquid is given by:

$$\frac{d\sigma}{d\Omega} = I(\mathbf{Q}, t=0) = M \left(b_{\text{EFF}}^2(\mathbf{Q}) \gamma_{\text{CM}}(\mathbf{Q}) + \sum_{\mu, \nu=1}^{m, m} [\langle b_{\mu} \rangle \langle b_{\nu} \rangle + \frac{\sigma_{\mu \text{INC}} \delta_{\mu \nu}}{4\pi}] j_0(Qr_{\mu \nu}) \right) \quad (2.37)$$

so that experimentally one can determine the quantity $\gamma_{\text{CM}}(\mathbf{Q})$. More frequently, one finds in the literature another quantity, the intermolecular structure factor of the center of mass, $S(\mathbf{Q})$ (in the following called simply “intermolecular structure factor”):

$$S(\mathbf{Q}) = 1 + \gamma_{\text{CM}}(\mathbf{Q}) \quad (2.38)$$

The second term in eq. (2.37) is $\mathbf{v}(\mathbf{Q}, t)$ from eq. (2.21) at $t=0$ and after the averaging over the

orientation of \mathbf{Q} relative to \mathbf{r} was performed. In the following this term will be denoted as $b_{\text{SELF}}(\mathbf{Q})$:

$$b_{\text{SELF}}(\mathbf{Q}) = \sum_{\mu, \nu=1}^{m, m} \left[\langle b_{\mu} \rangle \langle b_{\nu} \rangle + \frac{\sigma_{\mu \text{INC}} \delta_{\mu \nu}}{4 \pi} \right] j_0(\mathbf{Q} r_{\mu \nu}) \quad (2.39)$$

where $r_{\mu \nu} = r_{\mu} - r_{\nu}$.

2.4 Neutron scattering by a liquid solution

In case of a binary mixture (in this work: cyclodextrin solutions), similarly, one starts with a volume V , where N and M are the number of solute and solvent molecules, respectively; and the number of atoms in a solute and a solvent molecule are n and m , respectively. The general equation for the intermediate scattering function now reads (compare to eq. (2.12)):

$$I_{\text{SOLUTION}}(\mathbf{Q}, t) = \sum_{i=1}^{N+M} \sum_{\mu=1}^{N+M} \sum_{j=1}^{N+M} \sum_{\nu=1}^{N+M} \langle b_{i\mu} b_{j\nu} \rangle \langle \exp[-i\mathbf{Q} \cdot (\mathbf{R}_{i\mu}(0) - \mathbf{R}_{j\nu}(t))] \rangle \quad (2.40)$$

where $\mu = 1, 2 \dots m$ for the solvent molecule and $\mu = 1, 2 \dots n$ for the solute molecule; the same holds for ν . One may further decompose eq. (2.40) into the ‘‘solute’’, ‘‘solvent’’ and ‘‘mixed’’ terms:

$$I_{\text{SOLUTION}}(\mathbf{Q}, t) = I_{\text{SOLUTE}}(\mathbf{Q}, t) + I_{\text{SOLVENT}}(\mathbf{Q}, t) + I_{\text{MIXED}}(\mathbf{Q}, t) \quad (2.41)$$

One can define the *static* pair correlation function a) of the centers of mass of solute molecules, $g_{\text{SOL}}(\mathbf{r})$; b) of the centers of mass of solvent molecules, $g_{\text{SOLVENT}}(\mathbf{r})$; c) of the centers of mass of a solute and a solvent molecules, $g_{\text{SOL-SOLVENT}}(\mathbf{r})$ in the similar way as it is done right after eq. (2.7). Similarly to eq. (2.7), one will have $\gamma_{\text{CM SOL}}(\mathbf{Q})$, $\gamma_{\text{CM SOLVENT}}(\mathbf{Q})$, $\gamma_{\text{CM SOL SOLVENT}}(\mathbf{Q})$. The three intermolecular structure factors (all of them refer to the center of mass) are defined as:

$$S_{\text{SOLVENT}}(\mathbf{Q}) = 1 + \gamma_{\text{CM SOLVENT}}(\mathbf{Q}); S_{\text{SOL}}(\mathbf{Q}) = 1 + \gamma_{\text{CM SOL}}(\mathbf{Q}); S_{\text{SOL SOLVENT}}(\mathbf{Q}) = \gamma_{\text{CM SOL SOLVENT}}(\mathbf{Q}) \quad (2.42)$$

Both solute and solvent terms are described by the same formalism given above. The term $I_{\text{SOLVENT}}(\mathbf{Q}, t)$ and the scattering function for the solvent component will contain $S_{\text{SOLVENT}}(\mathbf{Q})$; analogously, the scattering function for the solute component will contain $S_{\text{SOL}}(\mathbf{Q})$. The ‘‘mixed’’ term $I_{\text{MIXED}}(\mathbf{Q}, t)$ (not treated here) will contain $S_{\text{SOL SOLVENT}}(\mathbf{Q})$.

In conclusion, it must be noted that

- a) in solutions, the intermolecular structure factor of the center of mass of solvent molecules, $S_{\text{SOLVENT}}(\mathbf{Q})$ will be different from $S(\mathbf{Q})$ in the pure solvent, although for the dilute solutions this difference may be expected to be small and was therefore neglected in the present work;
- b) in dilute solutions, $S_{\text{SOL}}(\mathbf{Q})$ is close to unity;
- c) in aqueous solutions hydrogen bonds may form between the solute and water molecules.

This will probably result in some contribution from the coherent scattering due to time-dependent correlations between the positions of the solute and solvent molecules. With the exception of the “hydrated solute model” (section 5.8, Appendix F), no account for this effect is attempted in the present work (meaning that the “mixed” term $I_{\text{MIXED}}(\mathbf{Q}, t)$ was neglected).

2.5 Neutron scattering experiment

The scheme of the neutron scattering experiment is represented by Fig. 2.1. The monochromatic neutron beam (wavelength λ_0 , with the corresponding wave vector \mathbf{k}_0 and energy E_0) passes through the sample, and the scattered neutrons are registered by the neutron detectors located around the sample at a number of constant angles, φ . Neutrons of energy E (wavelength λ and wave vector \mathbf{k}) detected at the angle φ suffered momentum transfer \mathbf{Q} and energy transfer $\hbar\omega$:

$$\mathbf{Q} = \mathbf{k} - \mathbf{k}_0 \quad (2.43)$$

$$\hbar\omega = E - E_0 = \hbar^2(k^2 - k_0^2)/2m_n \quad (2.44)$$

where m_n is the neutron mass. The modulus of the momentum transfer Q is given by:

$$Q^2 = k^2 + k_0^2 - 2 \times k \times k_0 \times \cos \varphi \quad (2.45)$$

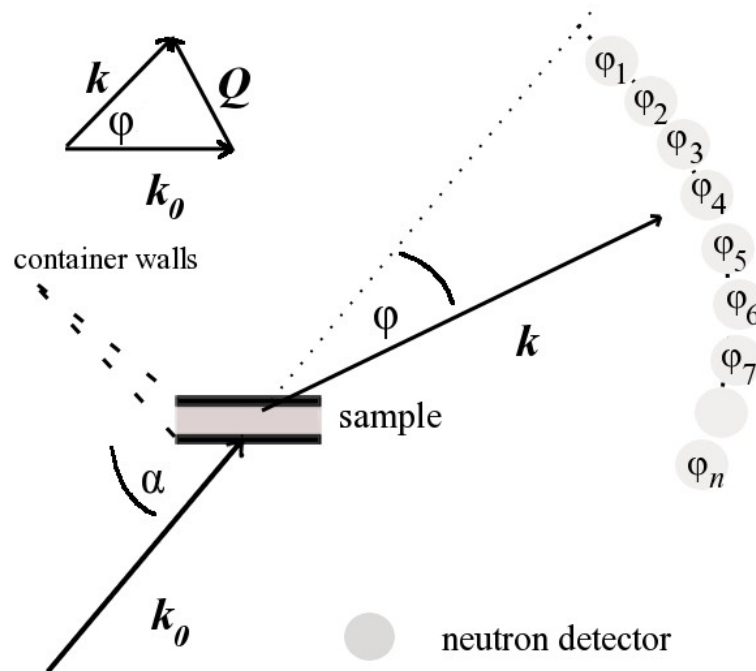


Figure 2.1 **The scheme of the neutron scattering experiment for the direct geometry time-of-flight spectrometer.** The incident neutron beam (wave-vector \mathbf{k}_0) hits the target at the sample angle α . Neutrons scattered at the scattering angle φ have wave-vector \mathbf{k} and are registered by the array of the detectors positioned at constant angles $\varphi_1, \varphi_2, \dots, \varphi_n$.

In the QENS experiment one measures the double differential scattering cross section $d^2\sigma$ that is defined as the number of neutrons per unit time per unit incident flux which are scattered into the solid angle $d\Omega$ with energy exchange between $\hbar\omega$ and $\hbar(\omega+d\omega)$. After transformation of the raw neutron scattering spectra to the energyscale, one gets:

$$d^2\sigma/d\Omega d\hbar\omega = (k/k_0) \times \eta(E) \times S_{\text{TOTAL}}(\mathbf{k}_0, \mathbf{k}) \quad (2.46)$$

where $\eta(E)$ is the neutron detector counting efficiency. The total effective scattering function, $S_{\text{TOTAL}}(\mathbf{k}_0, \mathbf{k})$ is:

$$S_{\text{TOTAL}}(\mathbf{k}_0, \mathbf{k}) = \sum_{j=1}^{\infty} s_{(j)\text{TOTAL}}(\mathbf{k}_0, \mathbf{k}) \quad (2.47)$$

where $s_{(j)\text{TOTAL}}(\mathbf{k}_0, \mathbf{k})$ is the contribution from neutrons which have been scattered j times [110]. The superscript ‘‘TOTAL’’ indicates that

- a) $S_{\text{TOTAL}}(\mathbf{k}_0, \mathbf{k})$ contains scattering contribution from the sample *and* the sample container;
- b) for $j > 1$, $s_{(j)\text{TOTAL}}(\mathbf{k}_0, \mathbf{k})$ contains neutrons which were scattered *several times*, possibly, both by the sample and the sample container.

See also Appendix C for the comparison of eq. (2.46) with its more conventional version.

In the present work the contribution of the neutrons scattered one time by the sample and one time by the sample container was found to be negligible, therefore one can rewrite eq. (2.46) as:

$$d^2\sigma/d\Omega d\hbar\omega = (k/k_0) \times \eta(E) \times \{S_S(\mathbf{k}_0, \mathbf{k}) + S_{\text{SC}}(\mathbf{k}_0, \mathbf{k})\} \quad (2.48)$$

and analogously to eq. (2.47):

$$S_S(\mathbf{k}_0, \mathbf{k}) = \sum_{j=1}^{\infty} s_{(j)S}(\mathbf{k}_0, \mathbf{k}) \quad S_{\text{SC}}(\mathbf{k}_0, \mathbf{k}) = \sum_{j=1}^{\infty} s_{(j)\text{SC}}(\mathbf{k}_0, \mathbf{k}) \quad (2.49)$$

where $S_S(\mathbf{k}_0, \mathbf{k})$ (or $S_{\text{SC}}(\mathbf{k}_0, \mathbf{k})$) contain 1, 2 .. times scattered neutrons by the sample (or the sample container) *only*. In the following, another form for $S_S(\mathbf{k}_0, \mathbf{k})$ will be used:

$$S_S(\mathbf{k}_0, \mathbf{k}) = S_{(1)S}(\mathbf{k}_0, \mathbf{k}) + S_{\text{SMSC}}(\mathbf{k}_0, \mathbf{k}) \quad (2.50)$$

where the term $S_{\text{SMSC}}(\mathbf{k}_0, \mathbf{k})$ contains all neutrons multiply scattered by the sample. The single sample scattering, $S_{(1)S}(\mathbf{k}_0, \mathbf{k})$ is:

$$S_{(1)S}(\mathbf{k}_0, \mathbf{k}) = S_{\text{EXP}}(Q, \omega) \times H_1(\mathbf{k}_0, \mathbf{k}) \quad (2.51)$$

where $H_1(\mathbf{k}_0, \mathbf{k})$ is the 1st order transmission factor, accounting for the self-attenuation and absorption of the incident neutron beam by the sample (the attenuation of the incident and scattered intensity due to the sample container is neglected). One can rewrite eq. (2.47) for $S_{\text{TOTAL}}(\mathbf{k}_0, \mathbf{k})$ as:

$$S_{\text{TOTAL}}(\mathbf{k}_0, \mathbf{k}) = S_{\text{EXP}}(Q, \omega) \times H_1(\mathbf{k}_0, \mathbf{k}) + S_{\text{SC}}(\mathbf{k}_0, \mathbf{k}) + S_{\text{SMSC}}(\mathbf{k}_0, \mathbf{k}) \quad (2.52)$$

The conventional reduction procedure includes corrections for the factor $H_1(\mathbf{k}_0, \mathbf{k})$ and the normalization of the sample spectra to the spectrum of vanadium in order to correct for the

neutron detector counting efficiency [102]. After reduction, the spectra represent the total scattering function $S_{\text{TOTAL}}(Q, \omega)$:

$$S_{\text{TOTAL}}(Q, \omega) = C \times \{S_{\text{EXP}}(Q, \omega) + S_{\text{MSC EXP}} + S_{\text{SC EXP}}\} \quad (2.53)$$

where the term $S_{\text{MSC EXP}}$ is equal to $S_{\text{MSC}}(\mathbf{k}_0, \mathbf{k})/H_1(\mathbf{k}_0, \mathbf{k})$ and the term $S_{\text{SC EXP}}$ is equal to $S_{\text{SC}}(\mathbf{k}_0, \mathbf{k})/H_1(\mathbf{k}_0, \mathbf{k})$. The factor C is given by [102]:

$$C = 1/\{n_{\text{van}} \times V_{\text{van}} \times \sigma_{\text{van}}/4\pi\} \quad (2.54)$$

where n_{van} = vanadium number density, [cm^{-3}], σ_{van} = vanadium scattering cross section [barn], V_{van} is the vanadium volume exposed to the beam [cm^3].

The experimental scattering function $S_{\text{EXP}}(Q, \omega)$ is related to the theoretical classical scattering function, $S_{\text{THEO}}(Q, \omega)$, folded with the energy resolution function $R(\varphi, \omega)$:

$$S_{\text{EXP}}(Q, \omega) = V_S \times \exp(-\hbar\omega/2k_B T) \times S_{\text{THEO}}(Q, \omega) \otimes R(\varphi, \omega) \quad (2.55)$$

where \otimes is the convolution operator, k_B - Boltzmann constant, T – absolute temperature and V_S is the sample volume exposed to the beam [cm^3]. The factor $\exp(-\hbar\omega/2k_B T)$ is the detailed balance factor, its relevance is explained elsewhere, e.g. [65,76,124]. In the present work $R(\varphi, \omega)$ is the Gaussian function and the standard deviation of this Gaussian, $\sigma_R(\varphi)$, is determined by fitting the function:

$$R_{\text{EXP}}(\omega) = \text{const} \times \exp(-(\omega - \omega_0)^2/2\sigma_R^2) / \{\sigma_R \times \sqrt{2\pi}\} \quad (2.56)$$

to the elastic component of the vanadium spectrum at each scattering angle φ . Often when referring to the energy resolution of the experiment one uses full width at half maximum (FWHM) of the resolution function, ΔE , given by:

$$\Delta E = 2\sigma_R \sqrt{2 \ln 2} \quad (2.57)$$

Strictly speaking, it is the set of spectra $S_{\text{TOTAL}}(\varphi_i, \omega)$, φ_i being the scattering angle, which is recorded in the QENS experiment; after the container and multiple scattering are corrected, the so obtained set of the experimental scattering function $S_{\text{EXP}}(\varphi_i, \omega)$ is a function of φ_i , λ_0 and λ . Since the momentum transfer Q and the scattering angle φ are related, see eq. (2.45), $S_{\text{EXP}}(\varphi_i, \omega)$ is the function of Q and ω . Thus, measurements with different instruments and/or different incident wavelengths all provide the function $S_{\text{EXP}}(Q, \omega)$, where the “experimental setup”-specific information is contained only in $R(\varphi_i, \omega)$ and V_S .

The integral of $S_{\text{EXP}}(\varphi_i, \omega)$ is denoted here as QENS integral, $I_{\text{QENS}}(Q_{\text{EL}})$:

$$I_{\text{QENS}}(Q_{\text{EL}}) = I_{\text{QENS}}(\varphi_i) = \int_{-\omega_{\text{MIN}}}^{\omega_{\text{MAX}}} S_{\text{EXP}}(\varphi_i, \omega) d\omega \quad (2.58)$$

where Q_{EL} is the elastic momentum transfer that can be found from eq. (2.45) by setting $k = k_0$, so that:

$$Q_{\text{EL}} = 2 \times k_0 \times \sin(\varphi/2) \quad (2.59)$$

2.6 Multiple scattering and container scattering

Eq. (2.53) contains the contribution from multiple scattering, which in practice is usually neglected. Indeed, one often states that with sample transmission of about 0.90, multiple scattering is negligible. This is not generally true, and a semi analytical approach allowing to account for MSC with a good degree of approximation was presented already in 1975 [10]. In the past, the absence of multiple scattering corrections was partially justified by the fact that this semi analytical approach required numerical integration of at least a double integral. Yet, the rise in computational power of the common personal computers makes it now possible to perform a fit of the theoretical models to the spectra with *simultaneous evaluation of the multiple scattering term* on a PC. Details of the approach used in this work are given in Appendix E.

$S_{\text{TOTAL}}(Q, \omega)$ in eq. (2.53) includes scattering by the sample container walls (see Fig. 2.1), $S_{\text{SC EXP}}$, which can be represented as:

$$S_{\text{SC EXP}} = S_{\text{SC}}(\mathbf{k}_0, \mathbf{k})/H_1(\mathbf{k}_0, \mathbf{k}) = \text{Att}(\mathbf{k}_0, \mathbf{k}) \times S_{\text{EXP EC}}(Q, \omega)/H_1(\mathbf{k}_0, \mathbf{k}) \quad (2.60)$$

where $S_{\text{EXP EC}}(Q, \omega)$ is the scattering function for the empty sample container and $\text{Att}(\mathbf{k}_0, \mathbf{k})$ is the angle-dependent attenuation factor, which accounts for the presence of the sample.

$S_{\text{EXP EC}}(Q, \omega)$ is related to the function $S_{\text{EC}}(\mathbf{k}_0, \mathbf{k})$ conventionally determined from a separate measurement. $\text{Att}(\mathbf{k}_0, \mathbf{k})$ can be evaluated given that the total cross section of the sample is known (see Appendices C, D for details). Because $S_{\text{EXP EC}}(Q, \omega)$ consists to large extent in the *elastic scattering*, one may write:

$$S_{\text{EXP EC}}(Q, \omega) = \text{Intensity}(\varphi) \times R(\varphi, \omega) \quad (2.61)$$

and the angle dependent quantity ‘‘Intensity(φ)’’ can be determined by fitting eq. (2.61) to the experimental scattering function $S_{\text{EXP EC}}(Q, \omega)$.

2.7 The role of the energy resolution of the experiment

The term $S_{\text{THEO}}(Q, \omega)$ in eq. (2.55) is the sum of a number of terms with different widths and different Q -dependent weighting factors (for models given in Chapter 5 all these terms are Lorentzians, except for the DHO component). Generally, there can be more than one combination of parameters, both structural and dynamical, which in the frame of a chosen theoretical model provide adequate description of the experimental spectra in the Q range accessed in the experiment.

In eq. (2.55), $S_{\text{THEO}}(Q, \omega)$ is convoluted with the resolution function, $R(\varphi, \omega)$, and the experimental scattering function $S_{\text{EXP}}(Q, \omega)$ depends therefore on the energy resolution, ΔE . An illustration of the significance of the energy resolution is given by Fig. 2.2.

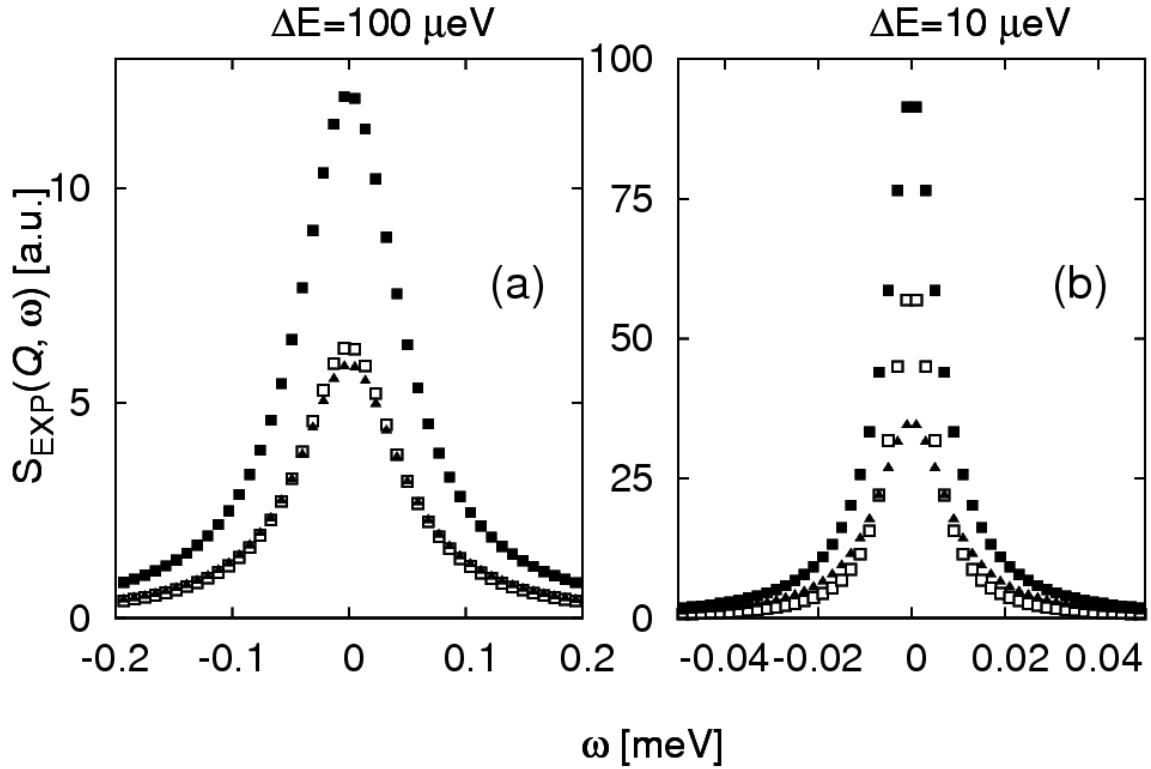


Figure 2.2 A hypothetical example showing the significance of the experimental energy resolution, ΔE . Symbols are: (\blacktriangle) the 1st scattering component, $D_{\text{TR1}}=1 \times 10^{-5} \text{ cm}^2/\text{s}$; (\square) the 2nd scattering component, $D_{\text{TR2}}=0.1 \times 10^{-5} \text{ cm}^2/\text{s}$; (\blacksquare) the total scattering intensity. (a): $\Delta E = 100 \mu\text{eV}$, slower motion (with $D_{\text{TR2}}=0.1 \times 10^{-5} \text{ cm}^2/\text{s}$) is unresolved. (b): $\Delta E = 10 \mu\text{eV}$, slower motion is partially resolved. $Q=0.25 \text{ \AA}^{-1}$.

Suppose that $S_{\text{THEO}}(Q, \omega)$ consists of only two terms, both corresponding to translational diffusion (values of D_{TR} are in $10^{-5} \text{ cm}^2/\text{s}$ units):

$$S_{\text{THEO}}(Q, \omega) = \text{Lor}(D_{\text{TR1}}Q^2, \omega) + \text{Lor}(D_{\text{TR2}}Q^2, \omega) \quad (2.62)$$

For simplicity, the resolution function of the experiment will be assumed to be Lorentzian, i.e. $R(\omega) = \text{Lor}(\Delta E/2, \omega)$. Thus, one has:

$$S_{\text{EXP}}(Q, \omega) = S_{\text{THEO}}(Q, \omega) \otimes R(\omega) = \text{Lor}(\{D_{\text{TR1}}Q^2 + \Delta E/2\}, \omega) + \text{Lor}(\{D_{\text{TR2}}Q^2 + \Delta E/2\}, \omega) \quad (2.63)$$

The spectrum recorded with the energy resolution $\Delta E = 100 \mu\text{eV}$ will be, in practice, satisfactorily fitted with just one Lorentzian, assuming $S_{\text{THEO}}(Q, \omega) = \text{Lor}(D_{\text{TR EFF}}Q^2, \omega)$, and the value of the ‘‘effective diffusion coefficient’’, $D_{\text{TR EFF}}$, of about $1.0 \times 10^{-5} \text{ cm}^2/\text{s}$ will be found (Fig. 2.2a). One says that the second component (with the intrinsic width $D_{\text{TR2}}Q^2$) is unresolved. In the experiment with $\Delta E=10 \mu\text{eV}$, (Fig. 2.2b), the spectrum $S_{\text{EXP}}(Q, \omega)$ will not be adequately described just by one Lorentzian, $\text{Lor}(D_{\text{TR EFF}}Q^2, \omega)$, and it will become clear for the experimentalist, that the spectrum contains contributions from *at least* two types of motions. The experimentalist can further attempt to determine the values of both, D_{TR1} and D_{TR2} , by

fitting eq. (2.63) to the spectrum in Fig. 2.2b.

From eq. (2.63) and the convolution theorem of Fourier transformation, it follows [64, 68]:

$$I_{\text{EXP}}(Q, t) = I_{\text{THEO}}(Q, t) \times R(t) = I_{\text{THEO}}(Q, t) \times \exp(-t/\Delta t) \quad (2.64)$$

$$\Delta t \times (\Delta E/2) = 0.6583 \quad (2.65)$$

where ΔE and Δt have dimension of [meV] and [ps], respectively. Further transformation of eq. (2.64) gives:

$$G_{\text{EXP}}(r, t) = G_{\text{THEO}}(r, t) \times \exp(-t/\Delta t) \quad (2.66)$$

where $G_{\text{THEO}}(r, t)$ reflects the motion of the atoms/molecules. It is clear from eq. (2.66) that in the experiment one “observes” motion only in the time range $t < \approx 3 \Delta t$; Δt is called the “observation time of the experiment”. In the example given above, for $\Delta E = 100 \mu\text{eV}$, $\Delta t = 13.2$ ps (as follows from eq. (2.65)). Substituting of the FWHM = $2D_{\text{TR}}Q^2$ instead of ΔE into the same equation gives the time constants of 160 ps and 1600 ps for the 1st (D_{TR1}) and 2nd component (D_{TR2}), respectively. Therefore, it is only the faster motion ($D_{\text{TR1}} = 1.0 \cdot 10^{-5} \text{ cm}^2/\text{s}$) which can be observed in the experiment with the energy resolution $\Delta E = 100 \mu\text{eV}$. With $\Delta E = 10 \mu\text{eV}$ ($\Delta t = 132$ ps), the slower motion will be partially resolved.

Generally, for the motion with the time constant τ [ps] (and the intrinsic width $0.6583/\tau$ [meV]) to be observed, the rule must be satisfied:

$$\Delta t > \tau \quad \text{or} \quad (\Delta E/2) < 0.6583/\tau \quad (2.67)$$

The energy resolution of the QENS experiment is therefore an important variable, making it possible to distinguish between different kinds of motion and to extract parameters of these motions.