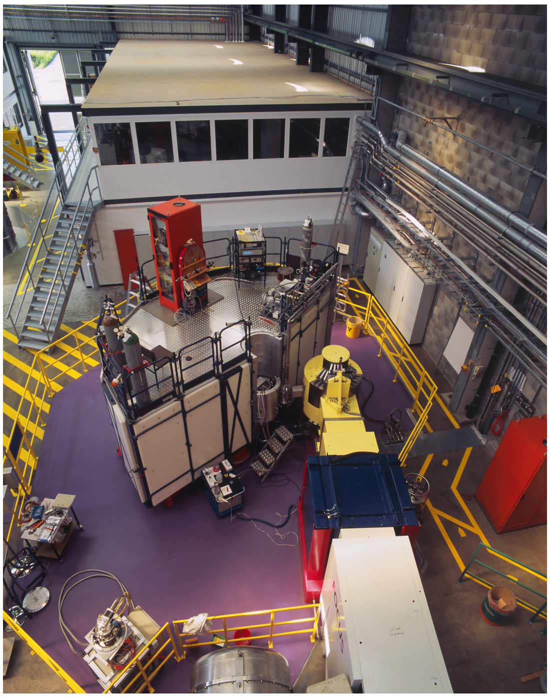

Dynamics of water by means of quasielastic neutron scattering (QENS)

J.P. Embs
version 2.1

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1 Theoretical Background

The aim of the present notes is to provide a short (but sufficiently complete) introduction into the field of quasielastic neutron scattering (QENS).
In order to prepare yourself for the experiment to be done on the cold neutron time–of–flight spectrometer FOCUS at the Swiss Spallation Source SINQ, you find within the following text several questions in red letters. We assume these questions to be answered in written form a prior to the experiment. **Without an appropriate preparation of the experiment and without having the necessary background we will not allow you to perform the experiment!**[1]

The basic equations we need to relate several quantities in this practical are the following ones :

$$E = \frac{\hbar^2 k^2}{2m_N} \tag{1.1}$$

$$k = \frac{2\pi}{\lambda} \tag{1.2}$$

The following table gives an overview about the different types of neutrons :

	energy [meV]
cold	0.1–10
thermal	10–100
hot	100–500
epithermal	≥ 500

Table 1. Neutron energy scales.

Q1: Given the values in Tab.1, calculate the corresponding wavelengths. The energy in meV of a neutron with wavelength λ, given in Å can be expressed in the following way: $E = 81.81/\lambda^2$. Show that this relation is true.

Quasielastic neutron scattering is due to stochastic (= non–periodic) motions of particles (= atoms, molecules, etc.). This type of neutron scattering results in a broadening of the elastic line, centered around zero energy transfer. Inelastic neutron scattering can be observed in the case of periodic dynamical processes.

Q2: Which processes lead to inelastic scattering? What is the advantage (or disadvantage) of using neutrons to investigate condensed matter?

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2 Scattering lengths & cross sections

The interaction of the neutron with the nucleus of an atom can be described by the so–called Fermi pseudo–potential :

$$V(\vec{r}) = \frac{2\pi\hbar^2}{m_N} \sum_l b_l \delta(\vec{r} - \vec{R}_l) \tag{2.1}$$

where b_l is the scattering length.

The scattering lengths of isotopes are distributed in a random manner across the periodic table. We define the mean scattering length by the following expression :

$$\langle b \rangle = \sum_k c_k b_k \tag{2.2}$$

c_k and b_k denote the abundance and the scattering length of the kth element, forming the sample under investigation. With the quantity defined by Eq. 2.2, we define further the coherent scattering cross section: $\sigma_{\text{coh}} = 4\pi\langle b \rangle^2$. Since the scattering lengths of isotopes are different, there appears the so–called isotope incoherence :

$$\sigma_{\text{inc}} = 4\pi \left(\langle b^2 \rangle - \langle b \rangle^2 \right) \tag{2.3}$$

with $\langle b^2 \rangle = \sum_k c_k b_k^2$. σ_{inc} describes thus the fluctuations of the scattering length due to isotope disorder. The sum of σ_{inc} and σ_{coh} gives the total scattering cross–section σ_{scatt}[1].

Q3: Assume a square lattice with N×N sites. $M < N^2$ sites are occupied by atoms which have coherent scattering length only. Show that in this case we get also an incoherent contribution, due to the fact that some sites on the lattice are not occupied. How does this contribution depend on the number of filled/empty lattice sites? Sketch σ_{inc} as a function of the number of empty sites!

For nuclei with nuclear spin $I \neq 0$ there appears an additional scattering contribution, if the scattering length depends on the relative orientation of neutron (spin 1/2) and nuclear spin.

Q4: What is the number p^+/p^- of "up"/"down"-spins for a nuclear spin I?

In the literature we find the terms *incoherent* and *coherent* scattering lengths. These quantities, often denoted as $\overline{b}$ and b_i, respectively, are related to the scattering lengths b^+ and b^- via :

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[1] cross-section ⇒ effective area presented by each scatterer

$$\bar{b} = \frac{I+1}{2I+1} b^+ + \frac{I}{2I+1} b^- \tag{2.4}$$

$$b_i = \frac{\sqrt{I(I+1)}}{2I+1} (b^+ - b^-) \tag{2.5}$$

Q5: Give an expression for $b^\pm$ as function of $\bar{b}$,b_i and I. Using the values given in the following table, calculate the coherent and incoherent scattering cross-section of ^{1}H and ^{2}H, respectively, and explain how one can benefit from these results!

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atom	b^+ [fm]	b^- [fm]	I
^{1}H	10.82	-47.42	1/2
^{2}H = D	9.53	0.975	1

Table 2. Scattering length of hydrogen and deuterium.

Q6: In the case of Ar, all three isotopes have I=0, and therefore $\sigma_{\text{inc}}(\text{spin}) = 0$, however $\sigma_{\text{inc}}(\text{isotope}) \neq 0$. Calculate the incoherent scattering cross-section, using the following values for the coherent scattering length (abundance) $\sigma(^{36}\text{Ar}) = 24.9$ fm (0.3336%), $\sigma(^{38}\text{Ar}) = 3.5$ fm (0.0629%) and $\sigma(^{40}\text{Ar}) = 1.84$ fm (99.6035%).

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3 Neutron Scattering

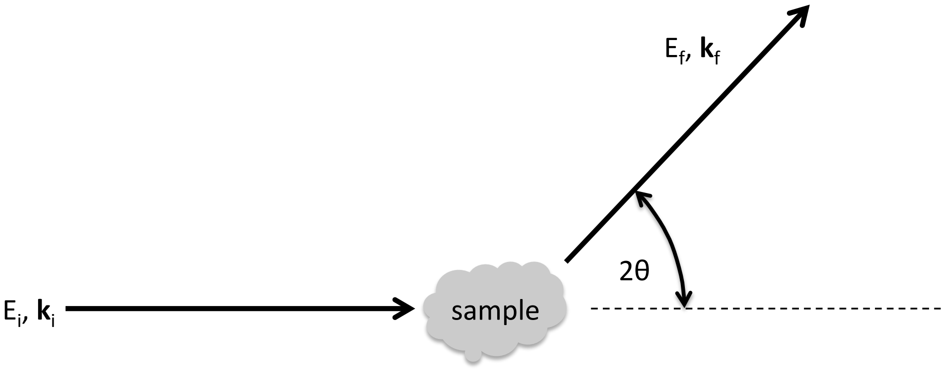

Figure 1. Schematic scattering experiment. Neutrons with initial energy E$_i$ and momentum $\hbar\vec{k}_i$ interact with a sample. Due to the interaction a detector, located in the direction given by $2\theta = \sphericalangle(\vec{k}_i, \vec{k}_f)$, detects neutrons with final energy E$_f$ and momentum $\hbar\vec{k}_f$

.

The basic scattering experiment setup is shown in Fig.1. In the experiment we can measure the energy-transfer $E = \hbar\omega \equiv E_i - E_f$ and the scattering angle $\vec{Q} \equiv \vec{k}_i - \vec{k}_f$. A detector located on the surface of a sphere (with a given fixed radius) around the sample, measures a count rate I that is proportional to so-called *double-differential cross-section*:

$$\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega \mathrm{d}E_f} \propto \frac{k_i}{k_f}\left[\sigma_{\mathrm{coh}} S_{\mathrm{coh}}(Q,\omega) + \sigma_{\mathrm{inc}} S_{\mathrm{inc}}(Q,\omega)\right] \tag{3.1}$$

The *double-differential cross-section* is proportional to the number of neutrons scattered into the solid angle $\mathrm{d}\Omega$ per second with final energies between E_f and $E_f + \mathrm{d}E_f$.

Q7: Show that

$$Q(E, E_i, \phi) = \sqrt{\frac{2m_n}{\hbar^2}\left[2E_i\left(1 - cos(\phi)\sqrt{1 - E/E_i}\right) - E\right]}$$

with $\phi \equiv 2\theta$. Make a figure showing $Q(E, E_i, \phi)$ for some selected values of ϕ!

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4 Van Hove correlation function

The so–called van Hove correlation function $G(\vec{r}, t)$ is defined as :

$$G(\vec{r}, t) = \frac{\hbar}{(2\pi)^3}\int d^3Q d\omega e^{-i(\vec{Q}\cdot\vec{r} - \omega t)} S(\vec{Q}, \omega) \tag{4.1}$$

or the dynamic structure factor can be expressed in terms of this correlation function :

$$S(\vec{Q}, t) = \frac{1}{2\pi\hbar}\int d^3r dt e^{i(\vec{Q}\cdot\vec{r}r - \omega t)} G(\vec{r}, t) \tag{4.2}$$

The quantity $G(\vec{r}, t)\mathrm{d}^3r$ is the conditional probability that, given a particle was at time $t = 0$ at the origin $\vec{r} = 0$, **any** particle is found at time t at the position $\vec{r}$ in a volume element d^3r. Furthermore one defines (in the same manner like Eq.4.1) the correlation function $G_s(\vec{r}, t)$. The meaning of this function is the following : $G_s(\vec{r}, t)\mathrm{d}^3r$ is the conditional probability that, given a particle was at time $t = 0$ at the origin $\vec{r} = 0$, the **same** particle is found at time t at the position $\vec{r}$ in a volume element d^3r.

Another important function is the so-called *intermediate scattering function*. These functions are dimensionless quantities; intermediate scattering functions are related to the dynamic structure factors via Fourier transforms:

$$S(\vec{Q}, \omega) = \frac{1}{2\pi\hbar}\int\limits_{-\infty}^{\infty} \mathrm{d}t I(\vec{Q}, t) e^{-i\omega t} \tag{4.3}$$

$$S_i(\vec{Q},\omega) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} \mathrm{d}t I_s(\vec{Q},t) e^{-i\omega t} \tag{4.4}$$

These quantities are what we measure in our experiments (cf. Eq.3.1 !). In the case the sample under investigation contains mainly incoherent scatterer, we measure $S_i(\vec{Q},\omega)$.

Q8: What are the dimensions of $S(\vec{Q},\omega)$ and $G(\vec{r},t)$?

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5 Quasielastic Neutron Scattering (QENS)

The method of quasielastic neutron scattering investigates scattering processes involving small amounts of energy transfers around zero energy transfer. The physical processes behind these scattering events are stochastic in nature: diffusion processes, jump diffusion etc.

5.1 Long–range diffusion, self–diffusion

In this section we deal with the long–range self–diffusion of tagged particles (atoms or molecules). The self–part of the van Hove correlation function, $G_s(\vec{r},t)$, obeys the following equation :

$$\partial_t G_s(\vec{r},t) = D_s \nabla^2 G_s(\vec{r},t) \tag{5.1}$$

If we treat the diffusion process as if all diffusing particles start at the origin at time zero, the solution reads :

$$G_s(\vec{r},t) = \frac{1}{(4\pi D_s|t|)^{3/2}} \exp\{-\frac{r^2}{4D_s|t|}\} \tag{5.2}$$

Q9: What boundary condition does this assumption imply? Why is this treatment correct? Using the result in Eq.5.2, you can calculate the self–part of the intermediate correlation function, $I_s(Q,t)$, and the self–part of the dynamic structure factor, $S_s(Q,\omega)$. Sketch the width of $S_s(Q,\omega)$ as function of Q and Q^2, respectively.
The case of a simple restricted diffusion can be described by $I_s(Q,t) = e^{-t/\tau} + I_c$, with $I_c = \text{const}$. Calculate and sketch the corresponding dynamic structure factor $S_s(Q,\omega)$!

5.2 Jump diffusion

On a microscopic scale, we expect deviations from the formulas calculated in Sec. 5.1.

Q10: Give an explanation why we expect deviations!

The diffusion process can be successfully described by so–called jump diffusion models (for more details see [2] and references therein).

Singwi and Sjölander proposed an exponential distribution of jump lengths, resulting in the following half width at half maximum (hwhm) :

$$\Gamma(Q) = \frac{\hbar D Q^2}{1 + D Q^2 \tau_0} \tag{5.3}$$

Q11: Sketch the relation 5.3 in an appropriate graph. Investigate the behaviour of Eq.5.3 for $Q \longrightarrow \infty$ and $Q \longrightarrow 0^+$. Show that $\Gamma(Q) \propto Q^2$ for *small* values of Q.

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6 Rotational dynamics

Here we consider the isotropic rotational diffusion. The idea is to describe the reorientation of a particle to be realized due to small–angle random rotations. The orientation of the particle is then given by an orientation vector $\vec{\Omega} = (\phi, \theta)$. The probability $P(\vec{\Omega}, t)$ to find the particle at time t with an orientation $\vec{\Omega}$ obeys the same partial differential equation as in the long–range diffusion :

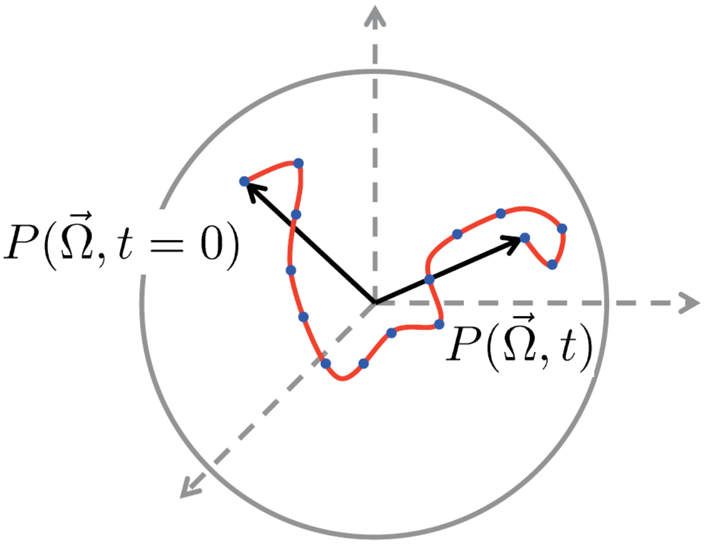

Figure 2. Diffusion on the surface of a sphere with radius one. The red line is the path of the vector of orientation in the time interval $[0, t]$.

$$\partial_t P(\vec{\Omega}, t) = D_R \nabla^2 P(\vec{\Omega}, t). \tag{6.1}$$

This equation (with appropriate boundary conditions) leads to the following intermediate scattering function :

$$I_s^R(Q,t) = \sum_{l=0}^{\infty}(2l+1)j_l^2(QR)e^{-D_R l(l+1)t} \tag{6.2}$$

The dynamic structure function reads :

$$S_s^R(Q,\omega) = j_0^2(QR)\delta(\hbar\omega) + \sum_{l=1}^{\infty}(2l+1)j_l^2(QR)\frac{1}{\pi}\frac{\hbar D_R l(l+1)}{(D_R l(l+1))^2 + (\hbar\omega)^2} \tag{6.3}$$

where $j_l(x)$ denotes the spherical Bessel function of order l.

7 The elastic incoherent structure factor

The first term in Eq.6.3 contributes only at $E = 0$, i.e. this is a purely elastic contribution. In order to explain the EISF, we start with the statement, that in general the van Hove correlation function can be written as :

$$G(\vec{r},t) = G_s(\vec{r},\infty) + \widetilde{G}_s(\vec{r},t) \tag{7.1}$$

The first term in Eq.7.1 is the long–time limit of the van Hove correlation function. If the particles under investigation explore a volume that is large in comparison to the interatomic distances, then this term vanishes identically. If however the particle's motion is restricted to some finite volume, $G_s(\vec{r},\infty)$ has a finite value. In analogy, we can split the dynamic structure factor into two terms :

$$S_{\text{inc}}(\vec{r},t) = S_{\text{inc}}^{\text{el}}(\vec{Q}) + S_{\text{inc}}^{\text{inel}}(\vec{Q},\omega) \tag{7.2}$$

The first term is a purely elastic contribution, while the second one is inelastic in nature. The elastic line can be considered as resulting from the diffraction of the neutron on the *infinite time* distribution in space of the nuclei belonging to the scattering species over a finite volume by its motion. In this sense on gets information on the structure from incoherent scattering and this is the physical reason to introduce the so–called *elastic incoherent structure factor*.

8 Separation of motions

We now want to take into account two types of dynamical processes: translation (T) and rotation (R). In order to do so we write

$$\vec{r}(t) = \vec{r}_{\text{T}}(t) + \vec{r}_{\text{R}}(t) \tag{8.1}$$

Inserting this expression into the general equation that defines the intermediate scattering function ($\langle \cdots \rangle$ denotes a thermal average)

$$I(Q,t) = \left\langle e^{-i\vec{Q}\cdot\vec{r}(0)} e^{i\vec{Q}\cdot\vec{r}(t)} \right\rangle \tag{8.2}$$

leads to the relation

$$I(Q,t) = I_{\mathrm{T}}(Q,t) \cdot I_{\mathrm{R}}(Q,t). \tag{8.3}$$

Q12: Perform every single step to get this final result. What is the assumption that has to be made ? How does the corresponding relation read for the scattering function $S(Q,\omega)$ (in energy space) ?

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9 Experimental aspects

9.1 Time-of-flight (*tof*) experiment

Fig.3 shows the distance–tof diagram of a typical tof neutron scattering experiment. Neutrons with a dedicated wavelength λ start at the monochromator M and arrive after a certain flightpath the sample located at position S. Due to interactions with the sample under investigation, some neutron gain energy ($\hbar\omega > 0$), while other neutrons lose energy ($\hbar\omega < 0$).

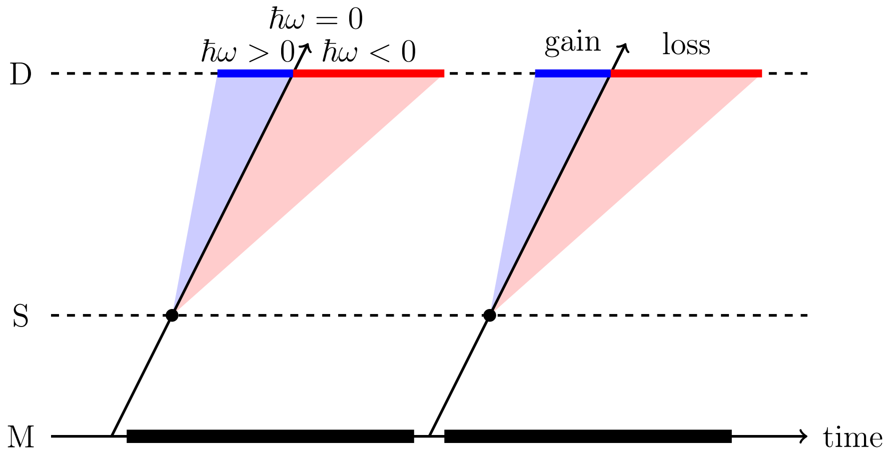

Figure 3. Time-of-flight vs distance, two frames are shown. M denotes the monochromator, S is the sample and D represents the position of the detectors. Neutrons coming from the monochromator interact with the sample and eventually loos or gain energy. The thick black lines represent time intervals for which no neutrons arrive at the monochromator. Each triangle shown is also called *frame*.

Q13: Explain Fig.3! What does the term *frame-overlap* mean?

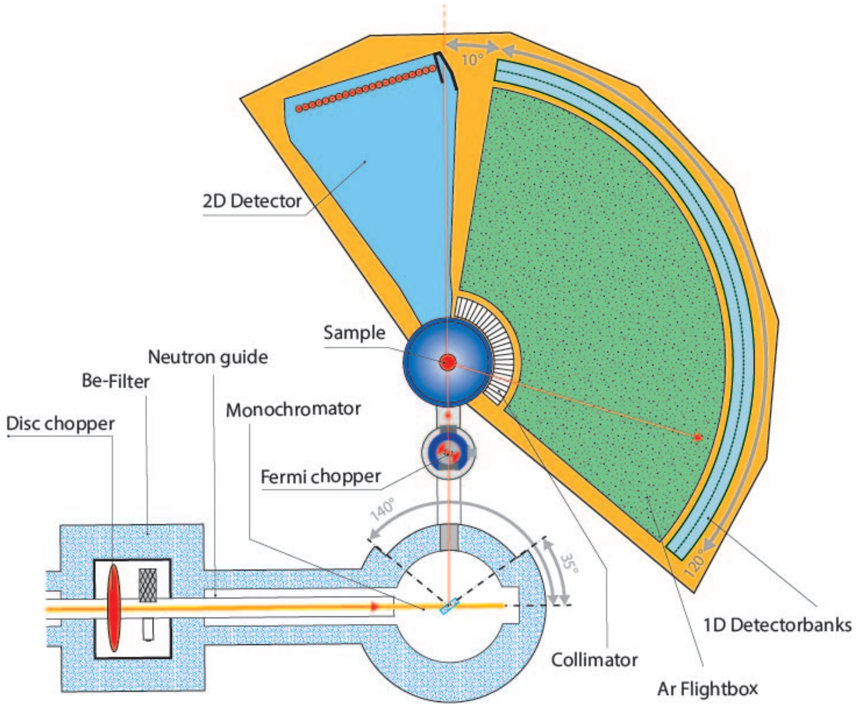

Figure 4. The FOCUS setup.

Q14: Explain the role of the different components displayed in Fig.4.

9.2 Data reduction

The term *Data reduction* refers to the transformation of the tof-data, i.e. intensities as function of 2θ and tof, into intensities as function of Q and E, i.e. Int(Q,E). The data reduction will be done using the program package DAVE[3]. Further details on how to use the data reduction tool can be found on the FOCUS homepage[2]; in the links *manuals* and *20 minutes manual* you find some (hopefully) useful pdf documents concerning data reduction and the operation of FOCUS in general.

9.3 Data analysis

Please download the DAVE–package from **http://www.ncnr.nist.gov/dave/**! Make sure that you download the *Latest Development Version* for your system (Windows, Unix or Apple). The package is free and we will need it to perform the data reduction and data analysis.

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[2] http://spectroscopy.web.psi.ch/focus/

10 Report

We assume that the results that have been obtained during your experiment will be summarized in a (written) report, together with your answers to the questions in the present manual. This report should be written in a style that is very similar to a scientific paper. Please describe the experiment in a way that non–experts in the field can read and understand the paper! The report should be divided into *Title*, *Authors*, *Abstract* and so on. It is very helpful to have a look into a current scientific paper.

Please let me know if you have ideas and comments that help to refine the manual!!

A Data reduction

The data reduction and analysis will be performed using the software package DAVE[3]. *Data reduction* means we have to transform our data from time–of–flight and 2Θ into energy and Q domain.

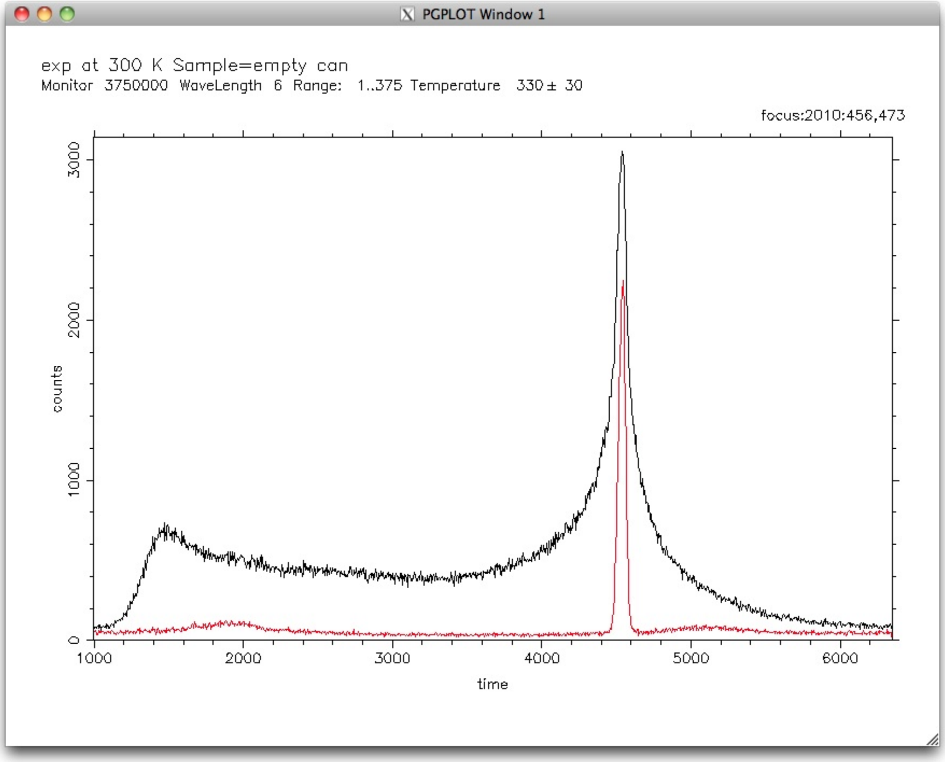

Figure 5. Comparison of time–of–flight data from the empty sample container (red) and the container filled with water (black). The time on the horizontal axis is given in μs and the counts plotted on the vertical axis represent the summed (all detectors and angles) intensity.

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[3] The software is available for **FREE** for Mac OS, Windows and Unix; you find all information you need on the webpage see http://www.ncnr.nist.gov/dave/

What do you observe in Fig.1? Note down and discuss your observations!

Steps to reduce the measured raw data (some further instructions will be provided in additional files!):

- normalize to monitor
- energy dependent detector efficiency
- ± 1 meV, ΔE = 5.1 μeV (≈ 1/10 of resolution)
- Q^{in} : (0.45 – 1.25) Å^{-1} → Q^{out} : (0.5 – 1.2) Å^{-1}; ΔQ = 0.1 Å^{-1}, 8 Q–groups
- for sample and vanadium data (energy and Q–binning)

B Data analysis

Use the following expression to fit the reduced data:

$$I_\mathrm{o}(Q) \cdot (S_\mathrm{T}(Q,E) \otimes S_\mathrm{R}(Q,E)) + a + bE \tag{B.1}$$

with

$$S_\mathrm{T}(Q,E) = \mathcal{L}(\Gamma, E) = \frac{1}{\pi} \cdot \frac{\Gamma}{\Gamma^2 + (E - E_0)^2} \quad , \tag{B.2}$$

$$S_\mathrm{R}(Q,E) = j_o^2(QR) \cdot \delta(E) + \sum_{k=1}^{\infty} (2k+1) j_k^2(QR) \frac{1}{\pi} \frac{k(k+1)\hbar/6\tau_R}{(k(k+1)\hbar/6\tau_R)^2 + (E - E_0)^2} \tag{B.3}$$

and the experimentally determined resolution function R(Q,E).

The final scattering function reads (without an explicit background):

$$S(Q,E) = j_0^2(QR)\mathcal{L}(\Gamma_T, E) + 3j_1^2(QR)\mathcal{L}(\Gamma_T + \frac{\hbar}{3\tau_R}, E) + 5j_2^2(QR)\mathcal{L}(\Gamma_T + \frac{\hbar}{\tau_R}, E) + \cdots \tag{B.4}$$

with R = 0.98 Å, the rotational radius of the water molecule; with $j_k(x)$ we denote the spherical Bessel-function of the first kind.

Start your fits using simply one Lorentzian function and a linear background. Are these two functions enough to describe the data? If so, how can you explain this finding? If not, how many Lorentzian functions do you need to describe the data?

The linewidth (hwhm) Γ_T depends on Q via

$$\Gamma_T(Q) = \frac{\hbar D_s Q^2}{1 + D_s Q^2 \tau_0} \tag{B.5}$$

with $\hbar = 6.582 \times 10^{-10}\ \mu eV \cdot s$ (Planck's constant divided by 2π), the self–diffusion coefficient D_s ($\times\ 10^{-10}$ m^2/s) and the residence time τ_0 (ps).

Use this equation to determine the temperature dependence of the self–diffusion coefficient $\mathbf{D_s}$. Plot $\mathbf{D_s(T)}$ as function of 1000/K in a log(y)-lin(x) plot! How can this dependency described? What happens for $\mathbf{Q \to 0}$ and for large Q?

To fit $D_s(T)$ we will use the following two expressions:

$$D_s(T) = D_0 \cdot \exp\left[-\frac{E_A}{k_B T}\right] \tag{B.6}$$

the so called Arrhenius law, with $k_B^{-1} = 11.6045$ K/meV. The second expression reads

$$D_s(T) = D_0 \cdot \exp\left[-\frac{A}{T - T_0}\right]; \tag{B.7}$$

this is the so called Vogel–Fulcher–Tammann law (VFT).

Use both expressions and determine $\mathbf{E_A}$, A and $\mathbf{T_0}$, respectively. Plot your results ($\mathbf{D_s(T)}$ vs T and $\mathbf{D_s(T)}$ vs 1000/T) What's the better description for your data? What's the role of the parameters $\mathbf{E_A}$ and $\mathbf{T_0}$?

References

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