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Mean square displacement from self-distribution function evaluation by elastic incoherent neutron scattering

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Abstract

The determination of the different contributions to the mean square displacement (MSD) associated with different relaxation mechanisms together with their time and thermal behaviour is performed by evaluating the self-distribution function derived by Elastic Incoherent Neutron Scattering (EINS). The analysis of the standard approach for MSD determination leads to an operational recipe that highlights the connection with the self-distribution function. The approach is tested on EINS data collected by the backscattering spectrometer IN13 (ILL, Grenoble) on a model system such as PolyEthylene Glycol with mean molecular weight $M_w = 400$ (PEG 400).
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1. Introduction

It is well known that Quasi Elastic Neutron Scattering (QENS) allows to characterize the space and time properties through the time-dependent spatial correlation functions $G(r,t)$ [1]. When the scattering cross section is mainly incoherent the relevant correlation function is for the most part the self-distribution function $G_s(r,t)$. This latter function, following van Hove, represents the probability to find the same particle at distance r after a time t.

When dealing with spectra collected in the ω-space, one of the main drawbacks is related to the high number of fit parameters. In addition from the experimental point of view, especially when studying biological systems, one has often to cope with a relatively great amount of sample [2,3]. This restriction excludes a relevant number of interesting systems. In such cases a statistical accuracy increase necessarily requires an increment of measurement time. This latter limit is partially attenuated in the case of hydrogenous systems thanks to the high hydrogen cross-section which allows to improve the statistics or to decrease the measurement time. In this case, taking advantage from the fact that the elastic contribution is often a factor 100–1000 higher than the quasi-elastic one, at low energy transfer [4–6], Doster et al. have proposed an effective way to get dynamical information by extracting the elastic component of the quasi-elastic scattering spectrum [6] or, otherwise, by performing EINS measurements at different resolution values [4].

In this work, a comparative analysis of some approaches applied for MSD evaluation is shown and a procedure based on the self-distribution function evaluation is taken into account. The approach is tested on data collected on PEG 400.

2. Experimental

The backscattering spectrometer IN13 at the Institute Laue Langevin (Grenoble, France) is characterized by a relatively high energy of the incident neutrons (16 meV) which makes it possible to span a wide range of momentum transfer Q ($\leqslant 5.5$ Å^{-1}) with a very good energy resolution (~ 8 μeV). Therefore, neutron scattering

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experiments on IN13 provide information on the motions of the sample hydrogens in a space–time window of 1 Å and 0.1 ns given by its scattering vector modulus range and energy resolution and allow to characterize both flexibility, which can be connected with the fluctuation amplitudes, and rigidity, which can be related with their temperature behaviour.

Measurements were carried out across the glass transition temperatures in a temperature range of 20–310 K. The incident wavelength was 2.23 Å; the Q-range was 0.28–4.27 $Å^{-1}$; the elastic energy resolution (FWHM) was 8 μeV. Raw data were corrected for cell scattering and detector response and normalized to unity at $Q = 0$ $Å^{-1}$. EINS data have been collected on polyethylene glycol with mean molecular weight $M_w = 400$ (PEG 400), a polymeric model system useful in the comprehension of more complex systems (i.e. proteins).

3. Theoretical background

It is well known that QENS allows to determine the scattering law $S(Q,\omega)$ or its time Fourier transform, the intermediate scattering function $I(Q,t)$ [7]. In the ω-space, due to energy resolution, the experimentally accessible quantity is the scattering function $S_R(Q,\omega,\Delta\omega)$ i.e. the convolution of the scattering law with the instrumental resolution function $R(\omega,\Delta\omega)$:

$$S_R(Q,\omega,\Delta\omega) = S(Q,\omega)\otimes R(\omega,\Delta\omega) = \int_{-\infty}^{\infty} R(\omega-\omega',\Delta\omega)S(Q,\omega')\mathrm{d}\omega' \quad (1)$$

In order to obtain the elastic contribution to the scattering one should evaluate Eq. (1) at $\omega = 0$ [8]:

$$S_R^{\mathrm{el}}(Q,\Delta\omega) := S_R(Q,0,\Delta\omega) = [S(Q,\omega)\otimes R(\omega,\Delta\omega)]_{\omega=0} = \int_{\infty}^{\infty} R(\omega-\omega',\Delta\omega)S(Q,\omega')\mathrm{d}\omega'\Big|_{\omega=0} \quad (2)$$

As elegantly shown by Doster et al. in Ref. [4], the scattering function $S_R^{\mathrm{el}}(Q,\Delta\omega)$ can be interpreted as the intermediate scattering function $I(Q,t_R)$, calculated at t_R corresponding to the instrumental resolution time:

$$t_{\mathrm{R}} = \frac{1}{\Delta\omega} \quad (3)$$

where $\Delta\omega$ is the instrumental resolution [4].

Therefore, a change in the instrumental energy resolution implies a change of the time at which the intermediate scattering function is evaluated and hence performing EINS measurements at different energy resolutions a set of intermediate scattering function values at different times can be obtained.

For the most part, EINS experiments are performed as a function of temperature, $I(Q,t_{\mathrm{R}};T)$, in order to get information on the degrees of freedom release with temperature at different Q-values [9]. Fig. 1 shows the elastic intensity as a function of temperature for PEG 400.

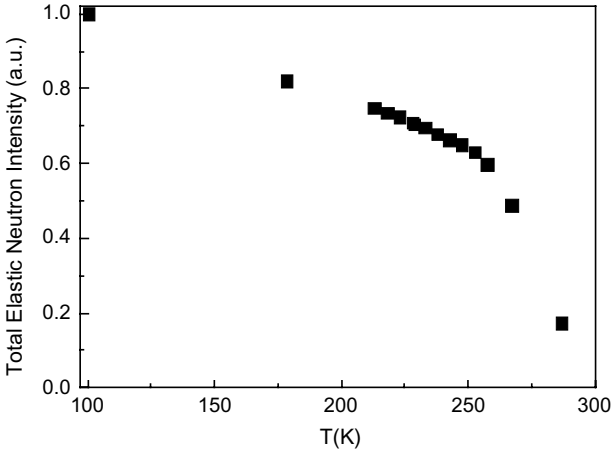

Fig. 1. Total EINS Intensity as a function of temperature for PEG 400.

As a rule a standard procedure to derive the MSD is furnished by the Gaussian approximation:

$$I^{\mathrm{Gaussian}}(Q,t_{\mathrm{R}}) = \mathrm{e}^{-\frac{1}{6}Q^2\left\langle(\Delta r(t_{\mathrm{R}})^2)\right\rangle} \cong 1 - \frac{1}{6}Q^2\left\langle(r(0)-r(t_{\mathrm{R}}))^2\right\rangle \quad (4)$$

where $\left\langle(\Delta r(t_{\mathrm{R}}))^2\right\rangle$ represents the full amplitude of motion (not the displacement from an equilibrium position) [7]. Eq. (4) is obtained from the general form of the intermediate scattering function truncating the Plazcek expansion to the second order; for its validity the following inequality has to be satisfied:

$$\left\langle(\Delta r(t_{\mathrm{R}}))^2\right\rangle Q^2 \leqslant 2 \quad (5)$$

Eq. (4) shows the relationship between the measured MSD and the instrumental resolution which fixes the time distance at which it is evaluated and points out the importance of comparing MSDs for the same sample at different instrumental resolutions and the MSDs of different samples at the same instrumental resolution.

Using the Gaussian approximation the MSD can be obtained by a linear regression in a plot tracing the logarithm of the elastic intensity as a function of Q^2 (Guinier plot) for a set of points that satisfy the inequality (5).

It should be noticed that, for the MSD evaluation, this procedure takes into account only the experimental data in a given Q-range fixed by Eq. (5).

4. Results and discussion

Now we shall consider a procedure for the MSD evaluation based on the self-distribution function evaluating.

Let us consider the EINS intermediate correlation function. $I^{\mathrm{inc}}(Q,t_{\mathrm{R}})$. If $I^{\mathrm{inc}}(Q,t_{\mathrm{R}})$ shows a single relaxation the data can be fitted with a single Gaussian function (a straight line in the Guinier plot). In more complex systems, where different relaxations are present, one can use a set of Gaussian functions:

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