

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

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(Received 7 February 2008; revised manuscript received 3 April 2008; published 6 June 2008)

In the present work an operational recipe for the mean square displacement (MSD) determination, highlighting the connection between elastic incoherent neutron scattering (EINS) intensity profiles and the associated self-distribution function, is presented. The determination of the thermal behavior of the total MSD and of its partial contributions is tested on EINS data collected by the backscattering spectrometer IN13 (ILL, Grenoble) on a model system such as PolyEthylene Glycol with a mean molecular weight of 400 Dalton (PEG 400).

DOI: [10.1103/PhysRevE.77.061802](https://doi.org/10.1103/PhysRevE.77.061802)

PACS number(s): 36.20.-r, 87.64.-t, 05.40.-a

I. INTRODUCTION

It is well known that quasielastic neutron scattering (QENS) allows one to characterize the space and time properties of a particle system through the time-dependent spatial correlation functions $G(r, t)$ [1]. When the scattering cross section is mainly incoherent the relevant correlation function is the self-distribution function $G_s(r, t)$ which, following Van Hove, represents the probability to find the same particle at distance r after a time t .

When dealing with QENS spectra in ω space, one of the main drawbacks can be connected with the high number of fit parameters. Furthermore, in some cases, one has to cope with a relatively great amount of material and when this latter is not available in reasonable times or is too much expensive a relevant number of interesting systems have to be excluded [2–4]. In addition in such cases a statistical accuracy increase necessarily requires an increment of measurement time. Taking advantage of the fact that the elastic contribution is often a factor 100–1000 higher than the quasielastic one, at low-energy transfer, [5–7] Doster has proposed an effective way to get dynamical information by extracting the elastic component of the quasielastic scattering spectrum or, otherwise, by performing elastic incoherent neutron scattering (EINS) measurements at different resolution values.

In the present work the attention is focused on the dynamical properties of polyethylene glycol (PEG) by EINS measurements at different temperature values. PEGs have been extensively investigated both theoretically and experimentally since 1960s, exploring also the opportunities at the interface of polymer chemistry and biology [8–11]. The polymers of this class represent a good model system for the study of proteins mainly because they are soluble in water in all proportions for temperatures lower than 100 °C, and because in water they assume a helical conformation, such as DNA, allowing them to mimic the primary, secondary, and tertiary structure of proteins [12]. In this work a procedure which allows one to determine the mean square displacement (MSD) together with its MSD partial contributions is presented.

II. EXPERIMENTAL SECTION

Experimental data were collected at the Institute Laue Langevin (Grenoble, France) by the IN13 spectrometer which 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 ($\leq 5.5 \text{ \AA}^{-1}$) with a very good energy resolution ($\sim 8 \text{ \mu eV}$). Measurements on PEG 400, purchased by Sigma-Aldrich, were carried out in the temperature range of 20–310 K. From a structural point of view PEGs are polymers formed by chains of Ethylene Glycol (EG), or 1,2-ethanediol, 1,2-dihydroxyethane ($\text{HOCH}_2\text{CH}_2\text{OH}$). Their structure is described by the formula $\text{HO}[-\text{CH}_2-\text{CH}_2-\text{O}]_n\text{H}$, where n is the degree of polymerization (for PEG 400 it is $n=9$). The incident wavelength was 2.23 Å, the Q range was 0.28–4.27 \AA^{-1} and the elastic energy resolution (FWHM) was 8 \mu eV . Raw data were corrected for cell scattering and detector response and normalized to unity at $Q=0.28 \text{ \AA}^{-1}$ (i.e., dividing all the intensity values to the intensity value at $Q=0.28 \text{ \AA}^{-1}$). In Fig. 1 the EINS intensity for PEG 400 in the 100 K $< T < 287$ K temperature range is shown, while Fig. 2 shows the elastic intensity as a function of the squared exchanged wave vector Q , in the 0.038–20.720 \AA^{-2} range, at temperature values of $T=100, 178, 213, 237, 257,$ and 267 K.

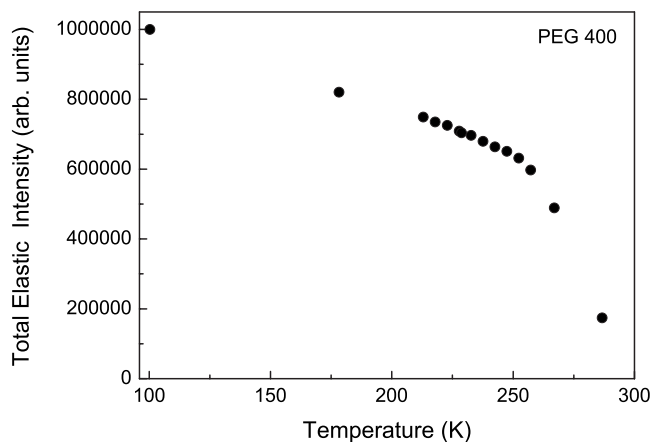


FIG. 1. EINS intensity as function of temperature for PEG 400.

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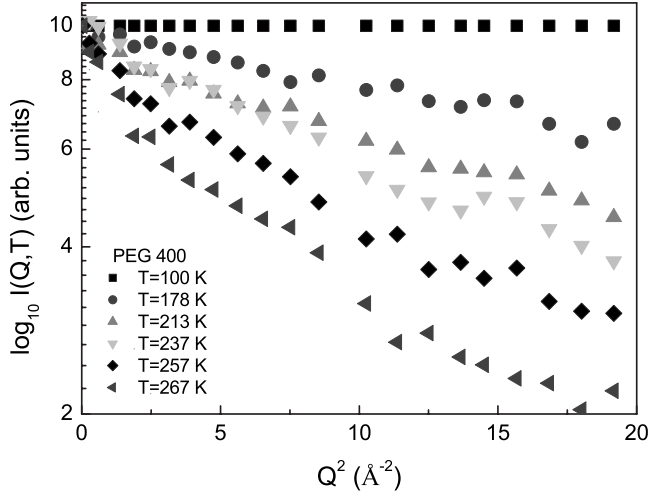


FIG. 2. $\log_{10} I(Q)$ as a function of Q^2 , at different temperatures, for PEG 400.

III. 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 $I(Q, t)$ [13]. In the ω space, due to energy instrumental resolution $\Delta\omega$, 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 $R(\omega, \Delta\omega)$

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

In order to obtain the elastic contribution to the scattering one should evaluate Eq. (1) at $\omega=0$ [14]:

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

As shown by Doster [5], the scattering function $S_R^{\text{el}}(Q, \Delta\omega)$ can be interpreted as the intermediate scattering function $I(Q, t_R)$, calculated at the instrumental resolution time t_R :

$$t_R = \frac{1}{\Delta\omega}. \quad (3)$$

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 functions at different times can be obtained. The application of different spectrometers covering different time and space windows, can furnish useful information for identifying the different molecular motions. EINS experiments are usually performed as a function of temperature $I(Q, t_R, T)$ in order to get information on the degrees of

freedom release with temperature [15]. The molecular motions which are fast enough to be resolved by the instrument contribute to the loss in the elastic scattering intensity; in some cases, the temperature analysis facilitates the spectral separation of different molecular processes according to their time scale.

As a rule, a standard procedure to derive the MSD is furnished by the Gaussian approximation that, taking into account the Doster's interpretation of EINS, results

$$I^{\text{Gaussian}}(Q, t_R) = e^{-(1/2)Q^2 \langle [\Delta r(t_R)]^2 \rangle} \sim 1 - \frac{1}{2} Q^2 \langle [r(0) - r(t_R)]^2 \rangle, \quad (4)$$

where $\langle [\Delta r(t_R)]^2 \rangle$ represents the full motion amplitude with

$$\langle [\Delta r(t_R)]^2 \rangle Q^2 \leq 1. \quad (5)$$

Equation (4) shows the relationship between the measured MSD and the instrumental resolution which fixes the time 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.

Therefore 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 (in the following referred to as Guinier plot) for a set of points that satisfy the inequality of Eq. (5). Let us focus the attention now on the Gaussian approximation. It is well known that the single particle contribution is

$$I^{\text{inc}}(\vec{Q}, t) = \langle e^{i\vec{Q} \cdot [\vec{r}(t) - \vec{r}(0)]} \rangle. \quad (6)$$

Let us express the vector \vec{r} in the form

$$\vec{r} = \vec{d} + \vec{u} \quad (7)$$

in which \vec{d} defines the motions with nonzero average value and \vec{u} defines the motions with zero average value (i.e., vibration and isotropic rotation). Under the hypothesis of \vec{d} and \vec{u} motions decoupling,

$$\langle e^{i\vec{Q} \cdot [\vec{r}(t) - \vec{r}(0)]} \rangle = \langle e^{i\vec{Q} \cdot [\vec{d}(t) - \vec{d}(0)]} \rangle \langle e^{i\vec{Q} \cdot [\vec{u}(t) - \vec{u}(0)]} \rangle. \quad (8)$$

Now, as far as the motion with zero average value contribution is concerned, it can be expressed by its Taylor expansion and if we consider that the average of a sum is the sum of the averages and that the averages of the odd terms are zero, one obtains

$$\begin{aligned} \langle e^{i\vec{Q} \cdot \vec{\Delta}u(t)} \rangle &= \left\langle 1 + i\vec{Q} \cdot \vec{\Delta}u(t) - \frac{1}{2} [\vec{Q} \cdot \vec{\Delta}u(t)]^2 + \dots \right\rangle \\ &= 1 - \frac{1}{2} \langle [\vec{\Delta}u(t)]^2 \rangle Q^2 + \dots \end{aligned} \quad (9)$$

Now under the assumption that correlations higher than those of the second order are not present, one obtains:

$$\begin{aligned}
 \langle e^{i\vec{Q}\cdot[\vec{u}(t)-\vec{u}(0)]} \rangle &= \langle e^{i\vec{Q}\cdot\vec{\Delta u}(t)} \rangle \\
 &= \left\langle 1 + i\vec{Q}\cdot\vec{\Delta u}(t) - \frac{1}{2}[\vec{Q}\cdot\vec{\Delta u}(t)]^2 + \dots \right\rangle \\
 &= 1 - \frac{1}{2}\langle [\vec{Q}\cdot\vec{\Delta u}(t)]^2 \rangle + \frac{1}{24}\langle [\vec{Q}\cdot\vec{\Delta u}(t)]^4 \rangle + \dots \\
 &\sim 1 - \frac{1}{2}\langle [\vec{Q}\cdot\vec{\Delta u}(t)]^2 \rangle \\
 &\quad + \frac{1}{24}\langle [\vec{Q}\cdot\vec{\Delta u}(t)]^2 \rangle^2 + \dots \\
 &\sim e^{-(1/2)Q^2\langle \Delta u(t)^2 \rangle}. \tag{10}
 \end{aligned}$$

The Gaussian approximation holds for all the motions for which the odd moments are zero (e.g., vibration and rotation). Let us consider now the difference between the theoretical intensity and the Gaussian approximation, which is expressed by

$$\begin{aligned}
 \langle e^{i\vec{Q}\cdot\vec{\Delta u}(t)} \rangle - e^{-(1/2)Q^2\langle [\Delta u(t)]^2 \rangle} \\
 \sim \sum_{i=2}^{\infty} \frac{1}{(2i)!} \{ \langle [\vec{Q}\cdot\vec{\Delta u}(t)]^{2i} \rangle - \langle [\vec{Q}\cdot\vec{\Delta u}(t)]^2 \rangle^i \}. \tag{11}
 \end{aligned}$$

For an ideal system in which the scatterers have the same identical motion, i.e., $\langle u^2 \rangle = u_i^2$ for all i :

$$\left. \begin{aligned}
 \langle u^{2j} \rangle &= \frac{u_1^{2j} + u_2^{2j} + \dots + u_N^{2j}}{N} = u_i^{2j} \\
 \langle u^2 \rangle^j &= \left(\frac{u_1^2 + u_2^2 + \dots + u_N^2}{N} \right)^j = (u_i^2)^j = u_i^{2j}
 \end{aligned} \right\} \Rightarrow \langle u^{2j} \rangle - \langle u^2 \rangle^j = 0. \tag{12}$$

Equation (11) is equal to zero; in such a case the spatial observation windows, determined by the Q range, is not influent.

When the motions are distributed Eq. (11) is different from zero and it is related to their distribution. In this case the difference between the theoretical intensity and the Gaussian approximation decreases with Q and it is zero at $Q=0$: it is a polynomial even function in Q (which starts from Q^4). This implies that the choice of spatial observational window becomes important since it determines the Gaussian approximation deviation.

In addition it should be noticed that, in general, since the atoms can be linked in different ways and since the neighbors atoms can influence the atom vibration behavior, different vibration contributions can simultaneously exist in a given system. Therefore Eq. (11), which is deduced for a system in which only one motion with zero average value is active, shows that since the evaluated MSD change depends on the chosen Q range, the Gaussian approximation is not a good recipe to MSD evaluation.

Let us now consider the case in which the system is characterized by different vibration and rotation motions; the expression for incoherent elastic neutron intensity is

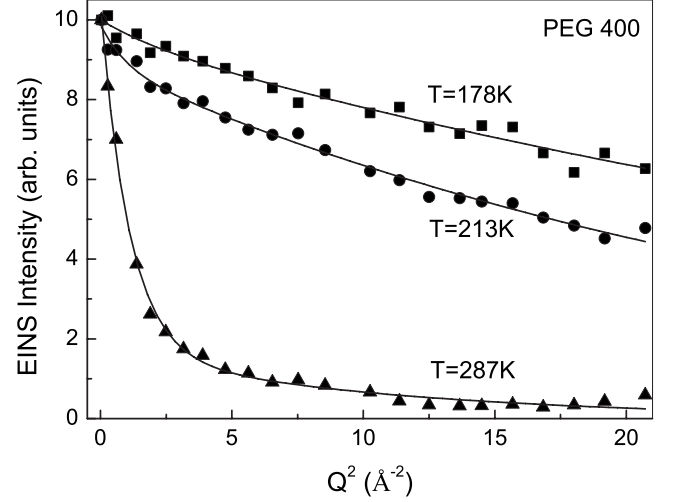


FIG. 3. $I(Q)$ vs Q^2 for PEG 400 at $T=178, 213,$ and 287 K. The points represent the experimental data; the continuous lines are the fit curves performed by using Eq. (14).

$$I^{\text{inc}}(\vec{Q}, t) = \frac{1}{N} \sum_i b_i^{\text{inc} 2} \langle e^{i\vec{Q}\cdot[\vec{r}_i(t)-\vec{r}_i(0)]} \rangle \tag{13}$$

in which the index i refers to the generic scatterer contribution to the scattered intensity. In the specific case in which in a given system hydrogen vibrations and rotations are present, the elastic incoherent intensity can be expressed by the relation

$$\begin{aligned}
 I^{\text{inc}}(\underline{Q}, t) &= \frac{1}{N} \sum_i b_i^{\text{inc} 2} \langle e^{i\vec{Q}\cdot[\vec{r}_i(t)-\vec{r}_i(0)]} \rangle \\
 &= \frac{1}{N} \sum_i b_i^{\text{inc} 2} e^{-(1/2)Q^2\langle [\Delta r_i(t)]^2 \rangle} \\
 &= \frac{1}{N} [b_{\text{vibration}}^{\text{inc} 2} e^{-(1/2)Q^2\langle [\Delta \rho(t)]^2 \rangle} \\
 &\quad + b_{\text{rotation}}^{\text{inc} 2} e^{-(1/2)Q^2\langle [\Delta \rho(t)]^2 \rangle}]. \tag{14}
 \end{aligned}$$

In such a case only one Gaussian contribution cannot fit all the experimental data, i.e., the Guiner plot of intensity is not a straight line. In fact Eq. (14) does not represent a Gaussian function: a sum of Gaussian function isn't a Gaussian function.

However, when different kinds of motions with zero odd moments (as in the case of isotropic vibrations and rotations) are present, a sum of Gaussian functions can properly describe the behavior of the incoherent intensity. This justifies the employment of a sum of Gaussian function for fitting the experimental data. Figure 3 shows $I_{\text{el}}^{\text{inc}}(Q, t_R=50 \text{ ps})$ of PEG 400 together with the fit curves, performed according to Eq. (14), at three different temperatures (178, 213, and 287 K).

The use of a sum of Gaussian contributions to analyze the behavior of EINS intensity is diffused in literature, and often represents the first step that leads to the MSD evaluation. Smith and co-workers [16] have furnished the motivations to use a combination of Gaussian and Lorentzian functions to

fit the data and in order to evaluate the MSD they perform a convolution with a model resolution function. The procedure proposed in the present paper does not require an *a priori* justified choice for the fit function: it can be directly applied to the experimental data without defining a specific physical model, but it should only provide a good numerical fit of the data.

IV. SELF-DISTRIBUTION FUNCTION PROCEDURE: DISCUSSIONS AND RESULTS

It is well known that the space Fourier transform of the intermediate scattering function $I(Q, t)$ is the time-dependent pair distribution function $G(r, t)$. In the case of incoherent scattering experiments it becomes the so-called self-distribution function $G^{\text{self}}(r, t)$. The space Fourier transform of EINS intensity corresponds to the self distribution function evaluated at the time corresponding to the resolution energy of the instruments $G^{\text{self}}(r, t_R)$.

In the following a new procedure for the MSD evaluation from EINS experiment, that we call the self-distribution function (SDF) procedure, is proposed. The SDF procedure is essentially based on the determination of the self-distribution function and on its use in the evaluation of the average statistical values of the physical quantities of interest $\langle A(t_R) \rangle$, in agreement with the statistical mechanics procedures

$$\langle A(t_R) \rangle = \int_{-\infty}^{\infty} A(r, t_R) G^{\text{self}}(r, t_R) dr. \quad (15)$$

In the specific case of the MSD evaluation, the dynamic observable A corresponds to the second power of the displacement r^2 :

$$\langle r^2(t_R) \rangle = \int_{-\infty}^{\infty} r^2 G^{\text{self}}(r, t_R) dr. \quad (16)$$

Let us consider the EINS experimental data in the general case when different relaxations are simultaneously present; in such a case, as previously discussed, one can use a set of Gaussian functions to fit the experimental data:

$$I^{\text{inc}}(Q, t_R) = \sum_n A_n e^{-Q^2 a_n} \quad (17)$$

in which n is the minimum number of Gaussian functions necessary to fit the data; the fit will furnish the set of a_n and A_n values.

By calculating the spatial Fourier transform of Eq. (17), we obtain

$$\text{FT}\{I^{\text{inc}}(Q, t_R)\} = \text{FT}\left\{\sum_n A_n e^{-Q^2 a_n}\right\} = \sum_n A_n \text{FT}\{e^{-Q^2 a_n}\}, \quad (18)$$

$$G^{\text{self}}(r, t_R) = \sum_n A_n G_n^{\text{self}}(r, t_R), \quad (19)$$

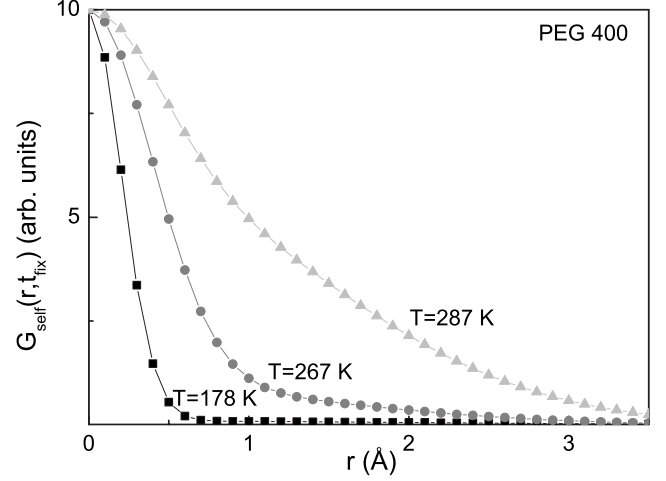


FIG. 4. Self-distribution functions $G_n^{\text{self}}(r, 50 \text{ ps})$ at different temperature values (178, 267, and 287 K), for PEG 400.

$$\text{FT}\{A_n e^{-Q^2 a_n}\} = \frac{A_n}{(2a_n)^{1/2}} e^{-(r^2/4a_n)}, \quad (20)$$

in which $G_n^{\text{self}}(r, t_R)$ are the partial self-distribution functions. Before performing the calculation of the averaged values of the physical quantities of interest, it is necessary to normalize the total self-distribution function and it is convenient to normalize the single partial self-distribution functions

$$\int_{-\infty}^{\infty} G_n^{\text{self}}(r, t_R) dr = 1 \rightarrow G_n^{\text{self}}(r, t_R) = \frac{1}{2(\pi a_n)^{1/2}} e^{-(r^2/4a_n)}, \quad (21)$$

$$\int_{-\infty}^{\infty} G^{\text{self}}(r, t_R) dr = 1 \rightarrow \sum_n A_n \int_{-\infty}^{\infty} G_n^{\text{self}}(r, t_R) dr = \sum_n A_n = 1, \quad (22)$$

$$B_n = \frac{A_n}{\sum_n A_n} \rightarrow \sum_n B_n \int_{-\infty}^{\infty} G_n^{\text{self}}(r, t_R) dr = 1. \quad (23)$$

In other words, at first we normalize to unity the partial self-distribution functions; starting from them we find the normalization condition for the total self-distribution function by operating on their weights A_n .

Figure 4 shows the obtained self distribution function as a function of r , at the temperature values of $T=178, 267$, and 287 K ; as expected, by increasing temperature, the self-distribution function broadens. The expressions for the mean displacement and for the mean square displacement value are

$$\langle r \rangle = \int_{-\infty}^{\infty} r G^{\text{self}}(r, t_R) dr = \sum_n B_n \int_{-\infty}^{\infty} r G_n^{\text{self}}(r, t_R) dr = 0, \quad (24)$$

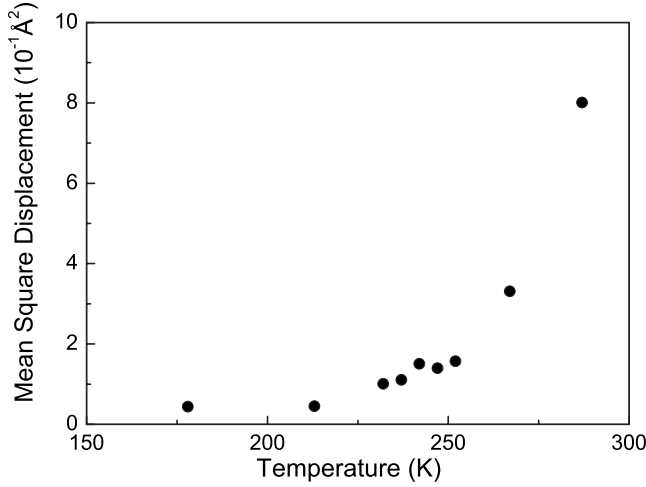


FIG. 5. MSD temperature behavior for PEG 400 obtained with the self-distribution function procedure.

$$\begin{aligned}
 \langle r^2 \rangle &= \int_{-\infty}^{\infty} r^2 G^{\text{self}}(r, t_R) dr \\
 &= \sum_n B_n \int_{-\infty}^{\infty} r^2 G_n^{\text{self}}(r, t_R) dr \\
 &= \sum_n B_n 2a_n = 2 \frac{\sum_n A_n a_n}{\sum_n A_n}, \quad (25)
 \end{aligned}$$

$$\langle r^2 \rangle = 2 \frac{\sum_n A_n a_n}{\sum_n A_n}. \quad (26)$$

In Fig. 5 the average MSD, evaluated by the SDF procedure, in the range 178–287 K is shown. Following our discussion it is equal to a weighted sum of the coefficients a_n , in which the weights are the A_n .

It is possible to associate a specific spatial observation window to each Gaussian function; therefore the corresponding $G_n^{\text{self}}(r, t_R)$ function can be interpreted as the partial self-distribution function associated with the n th relaxation. It is possible now to obtain a MSD value of the different relaxation processes resolved in a given system:

$$\langle r \rangle_n = \int_{-\infty}^{\infty} r G_n^{\text{self}}(r, t_R) dr = 0, \quad (27)$$

$$\langle r^2 \rangle_n = \int_{-\infty}^{\infty} r^2 G_n^{\text{self}}(r, t_R) dr = 2a_n \quad (28)$$

the exponent of each Gaussian being the MSD relative to a particular type of relaxation, as determined in Eq. (14). On the other hand, the weight A_n is interpretable as the percentage weight of the relative relaxation process; we can connect it to the relative number of groups involved in the relaxation process times their incoherent cross section. If one plots the

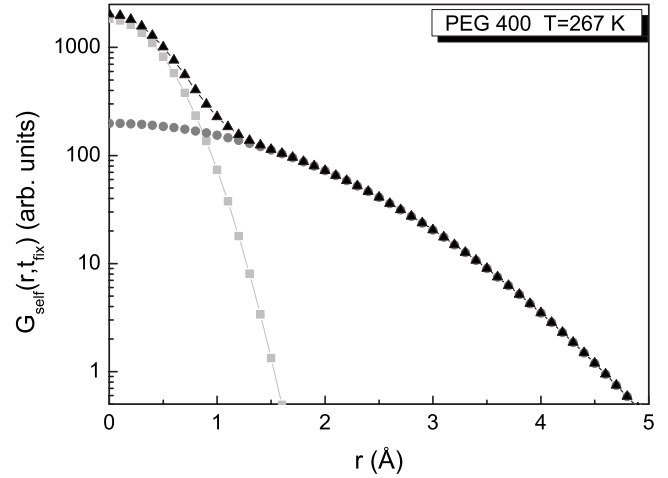


FIG. 6. Self-distribution function (black) together with their different contributions (gray) for PEG400 at $T=267$ K.

autocorrelation function $G^{\text{self}}(r, t)$ versus r together with its different Gaussian terms, it is possible to show the behavior of the different contributions.

Figure 6 shows the self distribution function and its different contributions at $T=267$ K. As it can be seen the different kinds of motion are spatially well separated; furthermore the self-distribution function very closely follows the first partial self distribution function in the range 0–1 Å and the second one in the range 1–5 Å. This behavior clarifies the role played by the partial self-distribution functions connected with the different relaxation processes.

Therefore this procedure allows one to obtain the autocorrelation function $G^{\text{self}}(r, t)$ versus r , together with its different partial contributions, as well to determine the partial MSDs, their weights and the total MSD. Equation (26) can be also expressed by

$$\langle r^2 \rangle = 2 \frac{\sum_n A_n a_n}{\sum_n A_n} = \frac{\sum_n A_n \langle r^2 \rangle_n}{\sum_n A_n}. \quad (29)$$

As it can be seen, the MSD is not the simple sum of the different displacements contributions but the MSD corresponds to a weighed sum of the MSD contributions associated with the different relaxations in which the weights are obtained by the fitting procedure of EINS data.

A clear example of this result is furnished by the experimental findings of Frick and Fetters [17]. The authors performed an EINS experiment on a polymeric system, i.e., polyisoprene (PI-8H), and on its partially deuterated homologous derivatives: the first isotopic substitution (PI-D3) concerns with the methyl hydrogen atoms, while the second one (PI-D5) concerns with all the other hydrogen atoms. Here, the fully hydrogenated system (PI-8H) presents two transitions: the first one has been related to the activation of the methyl group rotation, while the second one has been attributed to the onset of fast dynamics near the glass transition, which affects the main chain. In the case in which the system has deuterated methyl groups (PI-D3) the first kind of tran-

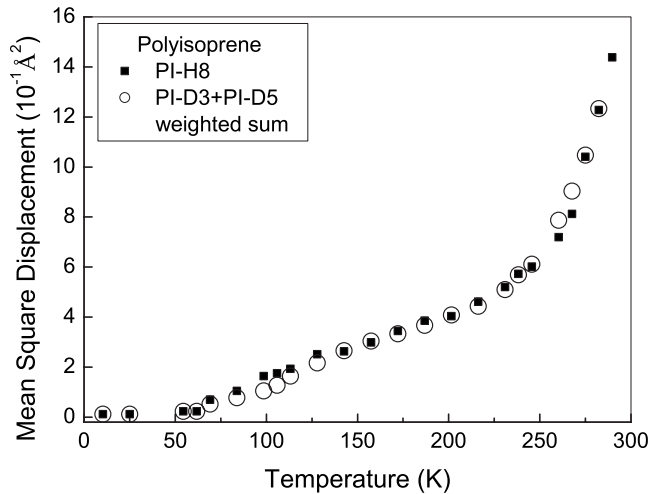


FIG. 7. Experimental and calculated MSD temperature behavior for polyisoprene.

sition is absent. However, it should be noticed that, see Fig. 5 in Ref. [17], the MSD values of the totally hydrogenated system, at all the investigated temperature values, are intermediate between the values of the two differently deuterated systems. This circumstance confirms the fact that the resulting MSD is a weighted sum of the different displacement contributions. The quantitative accordance is also excellent, as shown in Fig. 7; in fact by evaluating the MSDs average between PI-D5, in which the hydrogen relative weight in respect to the PI-H8 is 0.625, and PI-D3, in which the rela-

tive hydrogen number weight in respect to the PI-H8 is 0.375, we find the experimental MSD of PI-H8.

V. CONCLUSIONS

The Gaussian approximation usually employed to evaluate the MSD from EINS experimental data, furnishes MSD values which depend on the choice of the Q range, around $Q=0$, where to fit the intensity data. In addition, as shown in the present paper, the Gaussian approximation does not hold when the odd moments of the displacements are different from zero and when different relaxation processes with zero odd moments are present.

This paper shows a new theoretical and operational recipe for the determination of MSD from EINS data. The procedure, called self-distribution function (SDF) procedure, gives the opportunity to evaluate the $G^{\text{self}}(r, t)$ by using both fit functions [FT of $I^{\text{inc}}(\vec{Q}, t)$] and raw data (FFT) and corresponds to an integral definition since it takes into account the whole experimental Q range. This procedure allows one to obtain the MSD, through the autocorrelation function evaluation, and to get information related with the different molecular motions associated to different spatial windows. Furthermore it is shown that the MSD corresponds to a weighed sum of the MSD contributions associated with the different relaxations in which the weights are obtained by the fitting procedure of EINS data. Therefore the proposed SDF procedure allows one to obtain the total and the partial autocorrelation functions, the different MSD's contributions with their weights and the average MSD.

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