

Hydrogen motions and the α -relaxation in glass-forming polymers: Molecular dynamics simulation and quasi-elastic neutron scattering results

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Abstract. The combination of molecular dynamics simulations and neutron scattering measurements on three different glass-forming polymers (polyisoprene, poly(vinyl ethylene) and polybutadiene) has allowed to establish the existence of a crossover from Gaussian to non-Gaussian behavior for the incoherent scattering function in the α -relaxation regime. The deviation from Gaussian behavior observed can be reproduced assuming the existence of a distribution of discrete jump lengths underlying the sublinear diffusion of the atomic motions during the structural relaxation.

Keywords. Dynamics in glass-forming polymers; α -relaxation; fully atomistic molecular dynamics simulations; quasi-elastic neutron scattering.

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The freezing of the structural (α) relaxation in a glass-forming system leads to the glass transition phenomenon – still one of the most intriguing problems in condensed matter physics. Therefore, the understanding of the molecular motions during this relaxation is of utmost importance to shed some light on the glass formation process. Neutron scattering (NS) is essential for this goal. For instance, NS on protonated samples is directly related with the self-part of the van Hove correlation function $G_s(\vec{r}, t)$ corresponding to the hydrogens in the system. $G_s(\vec{r}, t)$ is the probability to find an atom at time t at \vec{r} if it was at $\vec{r} = 0$ for $t = 0$. Neutron spin echo (NSE) accesses its Fourier transform $F_s(Q, t)$, and e.g. time of flight or backscattering techniques its counterpart $S_{\text{inc}}(Q, \omega)$ ($\hbar Q$, $\hbar\omega$: momentum- and energy-transfer). During the last few years, extensive NS investigations have allowed to establish a universal behaviour for the self-atomic motions in the

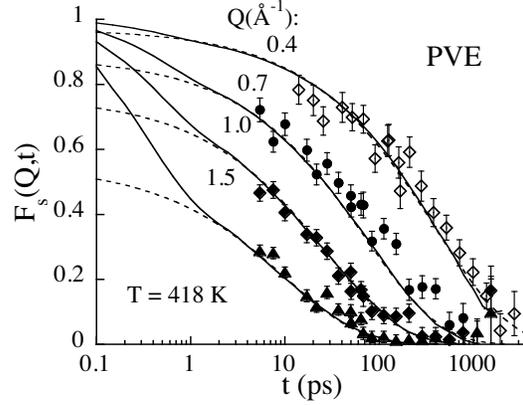


Figure 1. Incoherent intermediate scattering function corresponding to all protons in PVE at 418 K: Simulation results (lines) and IN11C results (empty symbols stand for measurements with incident wavelength $\lambda = 8 \text{ \AA}$, and solid symbols for $\lambda = 5.6 \text{ \AA}$) at the Q -values indicated. The amplitudes of the experimental have been corrected for the bandpass of the spectrometer using the MD-simulation results at $t = 0.3 \text{ ps}$. The dotted lines correspond to KWW descriptions of the second decay with $\beta = 0.55$.

α -relaxation regime of glass forming systems including polymers. As shown in figure 1, the long time decay of $F_s(Q, t)$, due to the α -process, shows a stretched exponential or Kohlrausch–Williams–Watts (KWW) functional form characterized by the stretching exponent β :

$$F_s(Q, t) = A \exp \left[- \left(\frac{t}{\tau_w} \right)^\beta \right], \quad (1)$$

A is the Lamb–Mössbauer factor giving account for the fast first step of $F_s(Q, t)$. A depends on Q as

$$A = \exp \left[-Q^2 \frac{\langle u^2 \rangle}{3} \right], \quad (2)$$

where $\langle u^2 \rangle$ is the associated mean squared displacement. From the example shown in figure 1, it is evident that the characteristic time τ_w in eq. (1) depends on Q , $\tau_w(Q)$. This observation implies a kind of diffusive nature for the atomic motions in this regime. Furthermore, polymer results accumulated for more than ten years [1–5] show that in the Q -range usually accessed for this kind of experiments (approx. $0.2 \leq Q \leq 1.5 \text{ \AA}^{-1}$), the Q -dependence of τ_w can be described as $\tau_w(Q) \propto Q^{-2/\beta}$. Introducing this expression for τ_w in eq. (1), one immediately realizes that $F_s(Q, t)$ fulfills the Gaussian approximation:

$$F_s^{\text{Gauss}}(Q, t) = \exp \left[-Q^2 \frac{\langle r^2(t) \rangle}{6} \right]. \quad (3)$$

Thus, for this process the non-Gaussian parameter $\alpha_2(t)$, which quantifies the deviations from Gaussian behavior, has to be very close to 0. $\alpha_2(t)$ is defined as

$$\alpha_2(t) = \frac{3}{5} \frac{\langle r^4(t) \rangle}{\langle r^2(t) \rangle^2} - 1, \quad (4)$$

where the mean squared displacement $\langle r^2(t) \rangle$ and $\langle r^4(t) \rangle$ are moments of $G_s(\vec{r}, t)$.

As NS delivers the spatial information only in the reciprocal space, the interpretation of experimental results is sometimes not straightforward. Magnitudes such as $G_s(\vec{r}, t)$ and its moments are not directly accessed. In this direction, MD-simulations have proven to be a very useful complementary tool for unraveling NS data, providing one has realistic enough models [6–9]. Simulations have also been important to scrutinize the dynamics of glass-forming systems other than polymers. In those works, clearly non negligible values for $\alpha_2(t)$ have been deduced for Lennard–Jones liquids [10], water [11], ortho-terphenyl [12] and selenium [13]. Even some kind of general behaviour has been found for $\alpha_2(t)$: the existence of a maximum that reaches increasing values with decreasing temperature and shifts according to the structural relaxation time. Since deviations from Gaussian behaviour are usually understood as a signature of dynamical heterogeneities, implications in this direction have been drawn from such MD-simulation results. Thus the question arises: Do polymers behave in a different way?

In order to unravel this question we have combined fully atomistic MD-simulations and NS measurements on three different polymers. The first system considered was polyisoprene (PI) [8,9]. NSE and MD simulation results on poly(vinyl ethylene) (PVE) are now being published [14,15], and in this work we present for the first time MD-simulation results on 1,4-polybutadiene (PB), that will be compared with existing NS measurements [3]. Details about the simulation method can be found in the above referred papers for PI and PVE. Firstly, we will focus on PI where the experiments included NSE (Jülich and IN11C (ILL, Grenoble)) and IN13 (ILL) measurements. In this way the investigated Q -range was extended as much as possible, specially towards high Q . Using a sample with deuterated methyl groups the experimental result reflect the self-motions of the main chain protons, that can also be followed from the atomic trajectories delivered by the MD-simulations.

Figure 2a displays the calculated $F_s(Q, t)$ for PI main chain protons at several Q -values. The curves show the above-mentioned stretching reflecting Q -dependent time-scales. Taking advantage of the MD-simulations we can also compute magnitudes that are not experimentally accesible, for instance $\alpha_2(t)$ and $\langle r^2(t) \rangle$ of the main chain protons. They are shown in figure 2b. As reported for the other glass-forming systems, a main maximum is indeed found for $\alpha_2(t)$ at $t^* \approx 4$ ps, just in the early stages of the decaging process identified with the α -relaxation. Thus polymers also seem to show clear deviations from Gaussian behavior. These deviations have to be noticeable in $F_s(Q, t)$ as well. With the knowledge of $\langle r^2(t) \rangle$ at hand, the prediction of the Gaussian approximation is easily calculated from eq. (3). The resulting curves $F_s^{\text{Gauss}}(Q, t)$ are displayed for comparison in figure 2a. It is clear that for Q -values above $\approx 1 \text{ \AA}^{-1}$ $F_s(Q, t)$ does not coincide with $F_s^{\text{Gauss}}(Q, t)$. The discrepancies between the two sets of curves increase with increasing Q -value. The hatched area in figure 2 shows the region where $\alpha_2(t)$ takes significant values. We

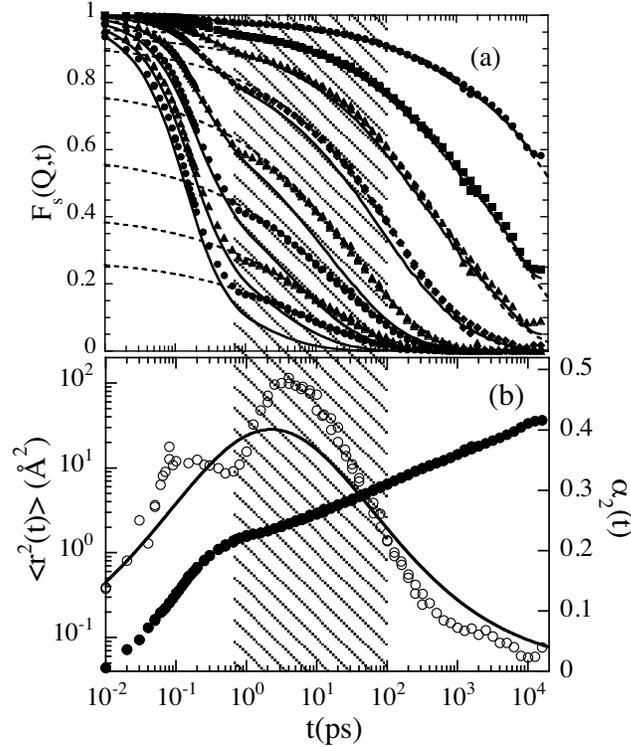


Figure 2. Results from MD-simulations at 363 K for the main chain protons in PI. (a) Intermediate incoherent scattering function $F_s(Q, t)$ (symbols) and result of applying the Gaussian approximation $F_s^{\text{Gauss}}(Q, t)$ (eq. (3)) (solid lines) for $Q = 0.3, 0.5, 0.7, 1.0, 1.5, 2.0, 2.5$ and 3.0 \AA^{-1} (top to bottom). The dotted lines are descriptions of the slow decay of $F_s(Q, t)$ ($t > 5 \text{ ps}$) by KWW functions (eq. (1)) with $\beta = 0.4$. (b) Mean squared displacement $\langle r^2(t) \rangle$ (full symbols) and non-Gaussian parameter $\alpha_2(t)$ (empty symbols). The solid line shows the prediction of the anomalous jump diffusion model for $\alpha_2(t)$ (eq. (6)). The hatched area shows the region where $\alpha_2(t)$ takes appreciable values.

can immediately see that for low Q -values such area only covers the initial part of the slow decay (α -regime) of $F_s(Q, t)$. However, as Q increases, this time range starts to cover the slow decay almost completely. This naturally explains the finding of the deviations from Gaussian behavior of $F_s(Q, t)$ at high Q -values, usually not accessed experimentally.

The description of the slow decay of $F_s(Q, t)$ in terms of KWW functions (eq. (1)), see dotted lines in figure 2a) allows to obtain the Q -dependent relaxation times $\tau_w(Q)$. Figure 3a shows $\tau_w(Q)$ for PI from both NS measurements and MD-simulations. A master curve has been built starting from the experimental data removing the influence of the T -dependent shape parameter β [9] by plotting τ_w^β . To match this curve, the MD-simulation results have been affected by a factor that gives account for a slight shift in temperature with respect to the real sample [9].

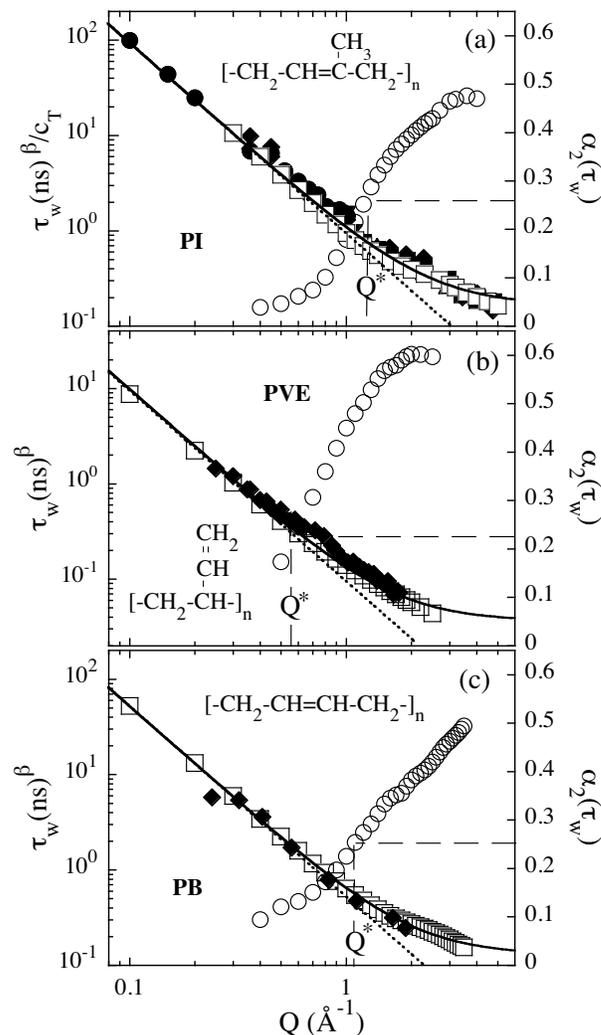


Figure 3. Q -dependence of the characteristic times exponentiated to β , $\tau_w(Q)^\beta$, and the non-Gaussian parameter evaluated at $\tau_w(Q)$, $\alpha_2[\tau_w(Q)]$ (empty circles), for (a) main chain PI protons, (b) all PVE protons and (c) all PB protons. Empty squares correspond to MD-simulation results for $\tau_w(Q)^\beta$, while full symbols are obtained from NS experiments. Dotted lines show the Gaussian prediction $\tau_w(Q)^\beta \propto Q^{-2}$; solid lines the description in terms of the anomalous jump diffusion model. The dashed lines indicate the positions of Q^* . For PI and PB the simulation data have been shifted to match the experimental ones.

Apart from this, we note an impressive agreement between both kinds of results, validating the MD-simulations. In this representation, the suggested dispersion relationship corresponding to Gaussian behavior [$\tau_w \propto Q^{-2/\beta}$] translates into a Q^{-2}

law (dotted line). The data univocally confirm the Gaussian-like behavior in the Q -range $Q \leq 1 \text{ \AA}^{-1}$, while clear signatures of deviations become evident at higher Q -values. A crossover Q , Q^* can be defined as the Q -value where deviations from Gaussian behavior start. For PI, $Q^* \approx 1 \dots 1.3 \text{ \AA}^{-1}$. It is interesting to display together with the relaxation times the value of the non-Gaussian parameter evaluated at the characteristic time corresponding to the Q -value considered, $\alpha_2[\tau_w(Q)]$. We realize that Q^* is located in the region where this function takes significant values, of the order of $\alpha_2[\tau_w(Q^*)] \approx 0.25$.

The new results on PVE and PB confirm the existence of such deviations. In the case of PVE, figure 1 shows the $F_s(Q, t)$ measured at 418 K by IN11C on a fully protonated sample at different Q -values in comparison with those calculated from MD-simulations for identical conditions. As can be seen, the agreement is almost perfect, indicating that our simulations of PVE provide a very convincing mimic of reality. This agreement is also evident in comparison with the characteristic times obtained (see figure 3b). We realize that for this polymer the deviation from the Q -dependence which characterizes the Gaussian behavior of $F_s(Q, t)$ takes place at rather low Q -values ($Q^* \approx 0.6 \text{ \AA}^{-1}$). However, as for PI, this deviation also corresponds to values of about 0.25 for $\alpha_2[\tau_w(Q)]$. The fact that the crossover occurs in PVE at lower Q -values can be understood taking into account that PVE is a polymer with a large side group in the monomer (see chemical composition in figure 3b). This introduces an additional heterogeneity in the dynamics [14,15].

Finally, for PB at 280 K figure 3c shows the Q -dependence of the relaxation times obtained from both, the new MD-simulations and previously reported backscattering (BSS, Jülich) results [3]. For both kinds of data the β parameter used is 0.41. In this case, the NS-data have been shifted by a factor 1.4 to match the MD-simulation results. It is noteworthy that the Q -dependence is very much the same for both sets of data. Again this polymer shows similar deviations from the Gaussian expectation. In conclusion, we can say that the crossover from Gaussian to non-Gaussian behavior found for PI definitively is not a particularity of this system but seems to be a general feature of the α -relaxation dynamics in glass-forming polymers.

What could be the origin of such deviations? As it was discussed in ref. [9], different theoretical approaches can be invoked to understand the observed crossover. The way the characteristic time departs from the Gaussian expectation (figure 3) strongly reminds the well-known manifestation of the discrete nature of diffusion in jump diffusion models. Based on this similarity, in ref. [9] we have developed a simple picture which, in principle, seems to be compatible with the framework of the mode coupling theory [16]. This simple interpretation is based on the existence of a distribution of discrete jumps underlying the atomic motions in the α -process. In this framework, at low Q corresponding to large distances, we deal with a Gaussian sublinear diffusion process. At higher Q (shorter distances) the Gaussianity breaks down due to the discrete character of the sublinear diffusion. The distribution of jump lengths ℓ , is assumed to have the simple functional form $f(\ell) = (\ell/\ell_0^2) \exp(-\ell/\ell_0)$. It would result from the disorder characterizing glass-forming polymers. ℓ_0 is the preferred jump distance. In the framework of such a model (see ref. [9])

$$\tau_w = \tau_0 \left[1 + \frac{1}{Q^2 \ell_0^2} \right]^{1/\beta}, \quad (5)$$

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where τ_0 is the microscopic residence time. On the other hand, the non-Gaussian parameter approximately reads:

$$\alpha_2(t) = \frac{72\ell_0^4 \left(\frac{t}{\tau_0}\right)^\beta}{\left[2\langle u^2 \rangle + 6\ell_0^2 \left(\frac{t}{\tau_0}\right)^\beta\right]^2}. \quad (6)$$

As can be seen in figure 3, for the three polymers investigated so far, such an approach allows to very accurately describe the Q -dependence of the relaxation time in the whole Q -range investigated. The maxima of the associated distributions of jump lengths occur at about 0.4 Å (PI), 0.6 Å (PVE) and 0.5 Å (PB). Recent results on the T and density dependence of the crossover in PI indicate that the distribution of jumps hardly depends on temperature and density [17]. It is worth emphasizing that, as can be seen in figure 2b, in this framework also the behavior of $\alpha_2(t)$ can be well-reproduced, within the range of validity of the model (above ≈ 1 ps) [8,9]. Finally, we have also shown that with this approach the main universal features reported for $\alpha_2(t)$ in the literature are also naturally deduced [8,9,18]. This fact supports that the essence of the universal deviations from Gaussian behavior in the self-motions of atoms during the structural relaxation regime lies in the discrete origin of their anomalous diffusion.

In conclusion, by combining NS- and MD-simulations on three different glass-forming polymers we have established the existence of a crossover from Gaussian to non-Gaussian behavior of the self-atomic motions in the α -regime. These results can be understood in the framework of the anomalous jump diffusion model previously introduced by us.

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