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Self-motion and the α -relaxation in glass-forming polymers. Molecular dynamic simulation and quasielastic neutron scattering results in polyisoprene

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Abstract

The momentum transfer dependence of the self-motion of main chain hydrogens in the α -relaxation regime of a glass forming polymer, polyisoprene, has been thoroughly investigated by a combined effort involving fully atomistic molecular dynamic simulations and quasielastic neutron scattering measurements. In this way, we have established the existence of a crossover from a Gaussian regime of sublinear diffusion to a strongly non-Gaussian regime at short distances. We show that an anomalous jump diffusion model with a distribution of jump lengths gives rise to such a crossover. This model leads to a time-dependent non-Gaussian parameter exhibiting all features revealed so far from various simulations of different glass forming systems.

1. Introduction

Valuable information on the dynamics taking place in the supercooled liquid state—the α -relaxation—can be obtained by quasielastic neutron scattering (NS). In particular, the direct microscopic observation of the structural relaxation in glass forming systems is realized by studying the behaviour of the dynamic structure factor at its first maximum, which is due to the correlations between the structural units. Such an investigation is possible by NS measurements on fully deuterated samples. But also an additional insight on this problem can be obtained by means of NS through an *indirect* probe as it is the scattered intensity from protonated samples. This is directly related to 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 of

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finding an atom at time t at a position \vec{r} if it was at $\vec{r} = 0$ for $t = 0$. Its Fourier transform in the time domain, the intermediate scattering function $F_s(Q, t)$, can be measured by neutron spin echo (NSE) techniques; finally, the counterpart in the frequency domain, the incoherent scattering function $S_{inc}(Q, \omega)$, is accessible by e.g. time of flight (TOF) or backscattering (BS) techniques [1]. Here, $\hbar Q$ and $\hbar\omega$ are the momentum and energy transfers in the scattering experiment respectively.

For some simple cases—free nuclei in a gas, harmonic crystals, simple diffusion (SD) at long times— $G_s(\vec{r}, t)$ is a Gaussian function [2, 3]; in an isotropic system this implies

$$G_s^{gauss}(r, t) = \left[\frac{\alpha(t)}{\pi} \right]^{3/2} \exp[-\alpha(t)r^2]. \quad (1)$$

The calculation of the moments

$$\langle r^{2n} \rangle = \int_0^\infty r^{2n} G_s(r, t) 4\pi r^2 dr \quad (2)$$

is then straightforward. For instance, the mean squared displacement of the atom $\langle r^2(t) \rangle$ is given in the Gaussian approximation by $\langle r^2(t) \rangle = 3/[2\alpha(t)]$. The intermediate scattering function is in such a Gaussian case entirely determined by $\langle r^2(t) \rangle$ with the simple Q -dependence given by

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

In a general case, deviations of $G_s(r, t)$ from the Gaussian form (equation (1)) may be expected. These can be quantified in a first approximation by the so called second order non-Gaussian parameter α_2 defined as [4]

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

which is of course null in the Gaussian case.

To date, incoherent quasielastic NS experiments on the α -relaxation regime of glass-forming polymers have revealed the following main features for the self-motion of hydrogens:

- (i) the stretched time behaviour of $F_s(Q, t)$ and
- (ii) a Q -dependent characteristic time indicating some kind of diffusive-like character.

Concerning the stretching property, it is well established that $F_s(Q, t)$ assumes the form of a Kohlrausch–Williams–Watts (KWW) function

$$F_s(Q, t) = A \exp\left[-\left(\frac{t}{\tau_w}\right)^\beta\right], \quad (5)$$

where τ_w is the Q - and T -dependent KWW-relaxation time and $\beta < 1$ the stretching exponent. A is a Lamb–Mössbauer-factor (LMF)

$$A = \exp\left(-\frac{\langle u^2 \rangle}{3} Q^2\right), \quad (6)$$

which accounts for faster processes and it is characterized by an effective mean squared displacement $\langle u^2 \rangle$. It was found [5] that the Q -dependence of τ_w can approximately be described by a power law determined by the stretching exponent β ,

$$\tau_w(Q) \sim Q^{-2/\beta}. \quad (7)$$

As polymers show typical values for β around 0.4–0.6, equation (7) predicts much stronger Q -dependences than that characteristic for SD (Q^{-2}). In figure 1(a) data corresponding to

poly(vinyl methyl ether) [5] are shown. The master curve here represented has been obtained by shifting the results for the characteristic time corresponding to different temperatures towards those obtained at a reference temperature T_R . The resulting curve shows a strong Q -dependence that is very well described by equation (7) (solid line) for $Q \leq 2 \text{ \AA}^{-1}$. Such a behaviour has been found in a large number of polymer systems [5–8] in the low Q -regime ($Q \leq 1 \text{ \AA}^{-1}$ approximately). As an example, a master curve considering data corresponding to six different polymer systems is depicted in figure 1(b). Since the β -value depends on the system investigated, in order to check the universality of equation (7) the representation of figure 1(b) shows the results for τ_w exponentiated to β . Polymer-dependent shift factors have then been applied to superimpose the data in a single curve. The good agreement found between different data is noteworthy, implying universality of behaviour. In this kind of plot, the Q -dependence expressed by equation (7) translates into a Q^{-2} -law. It is clear that the power law proposed (solid line) gives account of the Q -dependence found experimentally in these systems for $Q \leq 1 \text{ \AA}^{-1}$. At higher Q -values slight deviations towards a weaker dependence can be found in figure 1(b). These become evident for poly(vinyl methyl ether) at $Q > 2 \text{ \AA}^{-1}$ approximately, as can be realized from figure 1(a).

The correlation between non-Debye behaviour (characterized by the stretching exponent β) and Q -behaviour of τ_w in the α -relaxation of glass-forming polymers expressed by equation (7) has important implications: for instance, the Gaussian approximation holds for the self-motion of the hydrogens in the supercooled liquid state. Introducing equation (7) in (5) and considering equation (6), it is found that $F_s(Q, t)$ reads

$$F_s(Q, t) = \exp \left[- \left(2(u^2) + \left[\frac{t}{a(T)} \right]^\beta \right) \frac{Q^2}{6} \right] \quad (8)$$

where $a(T)$ is a factor giving the T -dependence of the characteristic time. In equation (8) we can recognize just the functional form of equation (3). This means that, within the experimental uncertainties, the self-part of the van Hove correlation function is a Gaussian function and consequently the non-Gaussian parameter α_2 has to be very close to zero. Moreover, the increase of the mean squared displacement associated with the α -relaxation is sublinear in time, as can be immediately deduced from the comparison of equations (8) and (3).

The result about the vanishing non-Gaussian parameter is in principle in apparent contradiction to recent molecular dynamics (MD) simulation results on glass-forming systems of different nature, e.g. water [9], Lennard-Jones liquids [10], selenium [11] and orthoterphenyl [12]. In all these cases, an almost universal behaviour for this parameter is found (see e.g. [11]). On the other hand, the validity of equation (7) has been mainly checked by standard BS spectrometers, i.e., the Q -range accessed is usually restricted to $Q \leq 1 \text{ \AA}^{-1}$. It is noteworthy that in the case of poly(vinyl methyl ether), where the study was extended up to $Q \approx 5 \text{ \AA}^{-1}$ by the thermal BS instrument IN13 at the Institut Laue Langevin (ILL, Grenoble, France), indications of deviations from equation (7) appear at high Q , as has already been mentioned (see figure 1(a)). These two facts motivated us to perform a critical check of the validity of equation (7) in a wide Q -range. Two actions were taken:

- (i) we carried out fully atomistic MD simulations on an archetypal polymer, polyisoprene (PI);
- (ii) we performed careful NS measurements on the same sample combining three spectrometers, trying to experimentally cover the widest Q -range available.

In this paper we summarize the main results obtained from this combined effort. Both the simulations and the measurements reveal a crossover from a Gaussian regime of sublinear diffusion to a strongly non-Gaussian regime at short distances. Here, we propose a simple

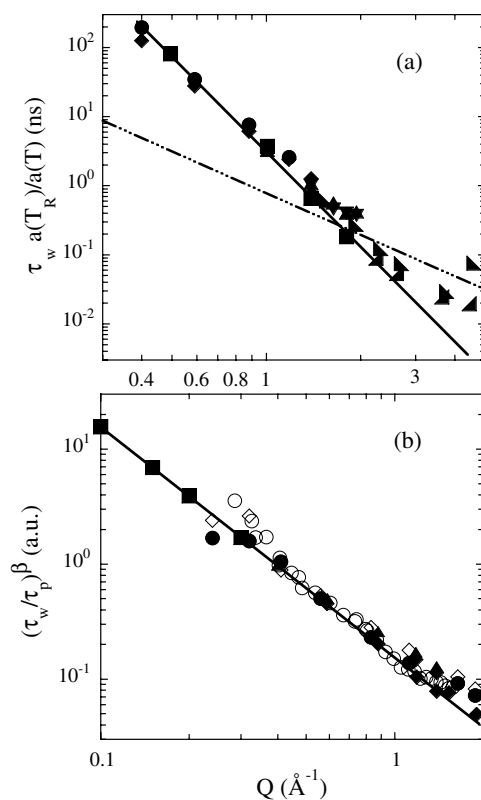


Figure 1. Momentum transfer dependence of the characteristic time associated with the self-motion of protons in the α -relaxation regime. (a) Master curve of poly(vinyl methyl ether) built removing the T -dependence by using the shift factors $a(T)$ ($T_R = 350$ K) [5] (different symbols correspond to different temperatures). The dashed-dotted line shows a Q^{-2} law, the solid line the $Q^{-2/\beta}$ ($\beta = 0.44$) dependence. (b) Master curve (time exponentiated to β) constructed with results of six polymers: polyisoprene (340 K, $\beta = 0.57$) (■); polybutadiene (280 K, $\beta = 0.41$) (●) [7]; polyisobutylene (390 K, $\beta = 0.55$) (○) [8]; poly(vinyl methyl ether) (375 K, $\beta = 0.44$) (full triangles) [5]; phenoxy (480 K, $\beta = 0.40$) (full rhombs) [5] and poly(vinyl ethylene) (340 K, $\beta = 0.43$) (◇) [7]. The data have been shifted by a polymer-dependent factor τ_p to obtain superposition. The solid line displays a Q^{-2} -dependence corresponding to the Gaussian approximation (equation (7)).

model based on an anomalous jump diffusion model with a distribution of jump lengths which accounts for the behaviour observed. This model also leads to a time-dependent non-Gaussian parameter exhibiting all features revealed so far from various simulations.

2. MD simulations and NS experiments

2.1. Simulation method

Fully atomistic MD simulations were carried out by using the Insight (Insight II 4.0.0 P version) and the Discover-3 programs from MSI with the so called Polymer Consortium Force Field (PCFF). The model system was built using the Amorphous Cell protocol. The polymer simulated was polyisoprene, PI ($-\text{[CH}_2\text{-CH=C(CH}_3\text{)-CH}_2\text{]}_n-$), with $n = 100$. A first MD simulation at 363 K was run for 1 ns using the Discover-3 program collecting data every 0.01 ps

and a subsequent one (taking the previous output sample as an input for the following dynamics) was run for 2 ns collecting data every 0.5 ps. The results of the second run agreed with those of the first run, indicating that the sample was well equilibrated at this high temperature. This procedure was also repeated for a number of temperatures (314, 338, 388, 413, 463 and 513 K). Further details on the simulation method and validation can be found in [13–15].

2.2. Neutron scattering experiments

In order to avoid effects from the methyl group motions, a monodisperse PI sample with deuterated methyl groups was investigated: $-\text{[CH}_2\text{-CH=C(CD}_3\text{)-CH}_2\text{]}_n\text{-}$ (PI*d*3). In this way the scattering is dominated by the very high incoherent cross section of the hydrogens along the main chain. The glass transition temperature T_g is 210 K. Details of the synthesis and characterization can be found elsewhere [15]. To cover a very wide Q -range and connect with it a huge dynamical range, we combined the following instruments:

- (i) the Jülich NSE instrument ($100 \text{ ps} \leq t \leq 22 \text{ ns}$; $0.1 \leq Q \leq 0.3 \text{ \AA}^{-1}$; $T = 340 \text{ K}$),
- (ii) the NSE spectrometer IN11c (ILL) ($8.4 \text{ ps} \leq t \leq 1.4 \text{ ns}$; $0.34 \leq Q \leq 1.68 \text{ \AA}^{-1}$; $T = 280, 300, 320 \text{ and } 340 \text{ K}$) and
- (iii) the thermal BS instrument IN13 for the coverage of high Q -values $1.2 \leq Q \leq 4.7 \text{ \AA}^{-1}$ (resolution 10 \mu eV , energy window $-130 \text{ \mu eV} \leq \hbar\omega \leq 100 \text{ \mu eV}$; $T = 260, 280 \text{ and } 300 \text{ K}$).

3. Results

Starting from the atomic coordinates computed in the MD simulations at 363 K, the $F_s(Q, t)$ was calculated for the main chain protons. The second slow decay above $\sim 2 \text{ ps}$ of such curves, attributed to the α -relaxation, could be well described by the usual KWW function (equation (5)). The prefactor A followed equation (6) with $\langle u^2 \rangle \sim 0.41 \text{ \AA}^2$. The values found for the shape parameter β varied around $\beta = 0.40$, which is a value well compatible with previous measurements (e.g. dielectric spectroscopy and NSE [16]). Fixing the value of β to 0.40, the characteristic time τ_w was determined as a function of Q . Figure 2(a) displays the obtained values of τ_w exponentiated to β (white squares). We use this representation, which was already presented in figure 1(b), because it allows us to check the validity of equation (7) building master curves even when the different data brought together correspond to different β -values. We can appreciate that, though below about 1.3 \AA^{-1} the Gaussian approximation (equation (7) corresponding to a Q^{-2} -law in figure 2(a) (dotted line)) is perfectly fulfilled, severe deviations are present at higher Q -values. There, a much weaker Q -dependence than that expected from the Gaussian approximation is clearly observed. We thus find a clear crossover from Gaussian to non-Gaussian behaviour in the Q -dependence of the τ_w associated with the self-motion of the main chain protons in the α -relaxation regime. This crossover takes place at about 1.3 \AA^{-1} , which in this case corresponds to the Q -region where the static structure factor of PI shows its first maximum [15].

The deviations from Gaussianity reflected in the Q -dependence of the characteristic time at high Q -values should be associated with non-vanishing values of the $\alpha_2(t)$ parameter. This is demonstrated in figure 2(b), where the values for $\alpha_2(t)$ computed from the MD simulations according to equations (4) and (2) are displayed. This parameter shows two maxima, the first of which can be attributed to the particular microscopic dynamics, which is mainly determined by the relative motion of the protons with respect to the main chain carbons [13]. The second peak, centred at $t^* \sim 4 \text{ ps}$, is responsible for the deviations found from Gaussian behaviour

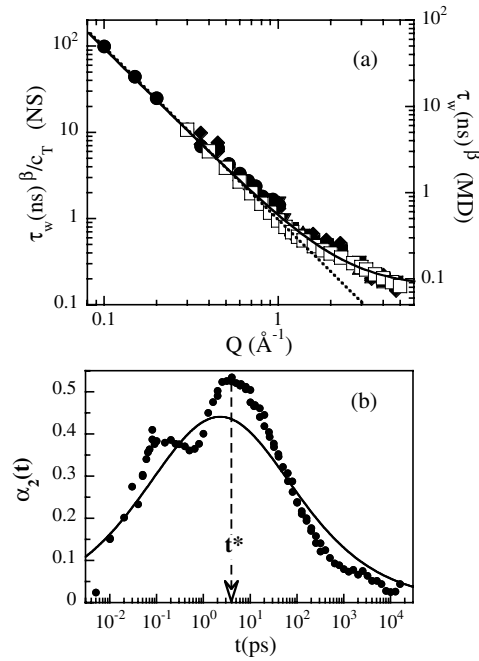


Figure 2. (a) Momentum transfer dependence of the master curve obtained for the characteristic time associated with the self-motion of the main chain protons in polyisoprene (exponentiated to the shape parameter β). Quasielastic NS results [17] (full symbols) have been shifted taking 300 K as the reference temperature (left-hand scale). MD simulation results at 363 K [13] (empty squares) are also shown (right-hand scale). (b) Non-Gaussian parameter α_2 as obtained from MD simulations at 363 K for polyisoprene. The dashed vertical arrow indicates the position of the maximum of α_2 , t^* . The dashed line in (a) shows a $\tau_w \sim Q^{-2/\beta}$ law, the solid lines the prediction of the anomalous jump diffusion model (equations (13) and (18)).

at high Q -values. This can easily be realized with the following argument. At low Q , below 1.3 \AA^{-1} , the characteristic time τ_w is slow, $\tau_w(Q \leq 1 \text{ \AA}^{-1}) \geq 100 \text{ ps}$. As can be deduced from figure 2(b), the value of the non-Gaussian parameter corresponding to $t \geq 100 \text{ ps}$ is quite small, i.e., $\alpha_2[\tau_w(Q \leq 1 \text{ \AA}^{-1})] \leq 0.2$. However, above the crossover Q -value, the characteristic time becomes fast, showing values below 10 ps for $Q \geq 2 \text{ \AA}^{-1}$. These times correspond just to the region where $\alpha_2(t)$ presents its second maximum, i.e., they are close to t^* . Thus we can see that the deviations towards non-Gaussian behaviour of τ_w are intimately linked to the main peak of $\alpha_2(t)$ and therefore their origin should be common.

What about the experimental results? Does the real sample also show such a crossover from Gaussian to non-Gaussian behaviour? Following the same procedure as for the MD-simulation results, the NSE experimental curves were fitted to KWW functions (equation (5)). As BS techniques measure in the frequency domain, for the IN13 spectra the Fourier transform of the KWW function was used. In the temperature range investigated, we observed a slight increase of the experimental value for the β -parameter with increasing temperature ($\beta : 0.4\text{--}0.57$ in the interval $T : 260\text{--}340 \text{ K}$) [17]. The Q -dependent characteristic times obtained from these fittings are plotted in figure 2(a) together with the MD-simulation results. Temperature-dependent shift factors c_T in this representation have been applied to the values of τ_w^β corresponding to the different temperatures in order to superimpose them over those at the reference temperature $T_R = 300 \text{ K}$. As can be seen, this figure shows the clear answer

to the question asked above. A nearly perfect agreement is found between experiments and simulation results on PI, revealing just the same crossover. Though it is not the aim of this paper to present a quantitative and exhaustive comparison of NS and MD simulation results, we note that the MD simulation data at 363 K coincide with the experimental ones at 320 K. On the other hand, it is noteworthy that the Q -range experimentally covered is even larger than that accessed by MD simulations. This was only possible by the combination of results corresponding to different temperatures obtained by the three spectrometers used. Concerning the amplitude of the α -relaxation, from the IN13 data the following values are obtained for $\langle u^2 \rangle$: $0.43 \pm 0.02 \text{ \AA}^2$ at 260 K, $0.55 \pm 0.02 \text{ \AA}^2$ at 280 K and $0.58 \pm 0.01 \text{ \AA}^2$ at 300 K, in good agreement with previous BS results on a similar sample [18].

We have thus shown by both MD simulations and incoherent quasielastic NS the existence of a crossover from a Gaussian regime of sublinear diffusion to a strongly non-Gaussian regime at short distances for the α -relaxation in polyisoprene.

4. Discussion

Any theoretical approach or model considered for interpreting the crossover found in the Q -dependence of $\tau_w(Q)$ should also reproduce the behaviour of $\alpha_2(t)$. Several frameworks, such as those discussed in [13], can be invoked. For instance, the mode coupling theory (MCT) for the glass transition [19–22] predicts a Q -dependence for the characteristic time of the self correlation function that at high Q -values strongly deviates from that expected in the Gaussian case. Qualitative agreement between MCT predictions and the behaviour observed by us for $\tau_w(Q)$ is found [13]. Moreover, $\alpha_2(t)$ calculated in the framework of the MCT for a hard-sphere system also shows a qualitatively similar behaviour to that reported here as pointed out in [13].

Most of the interpretations given in the literature for the behaviour of α_2 have been based on the existence of the so called ‘mobile particles’ or on considerations related to the ill defined concept of dynamical heterogeneity [23]. A possible scenario based on the widely assumed idea of identifying Gaussian behaviour with dynamically homogeneous behaviour has already been discussed in [13]. In such a framework, the crossover found could be understood as a homogeneous to heterogeneous crossover of the incoherent dynamics involved in the α -relaxation. As mentioned in [13], this interpretation would imply that the results obtained by different techniques could be affected by the underlying dynamic heterogeneity at t^* in a different way. The closer the timescale of the α -process probed by a particular technique is to the t^* -range, the more sensitive this technique is to the heterogeneous dynamics. On the other hand, it is noteworthy that in most of the works invoking the concept of dynamical heterogeneity the origin of the non-vanishing values of α_2 is usually sought in connection with the origin of the non-exponential behaviour of the α -relaxation, i.e., the stretching of the relaxation function. In none of these works is the Q -dependence of the characteristic relaxation time considered.

Here we will focus on another possible explanation for the crossover found, which was recently pointed out [17], based on the existence of a distribution of discrete jumps underlying the self atomic motions in the α -process. As we will see, this simple interpretation, which, in principle, is compatible with the framework of the MCT, accounts for the observed behaviour in PI and allows us to deduce all the universal features reported to date for the non-Gaussian parameter α_2 in different glass-forming systems.

We have shown a clear correlation between the non-Gaussian parameter α_2 and the deviations from Gaussian behaviour found for $\tau_w(Q)$. On the other hand, these deviations recall in some way the behaviour described in the text books for the simple jump diffusion

(see, e.g. [2, 24]). In the framework of this model, proposed a long time ago (see [2, 24, 25]), finite jump lengths tend to cause a bending of the dispersion for the diffusive relaxation time away from the Q^{-2} law which takes place for SD at low Q and which in such a simple case corresponds to the Gaussian behaviour of $G_s(r, t)$ or $F_s(Q, t)$.

The jump diffusion model [2, 24, 25] assumes that an atom remains in a given site for a time τ_0 , where it vibrates around a centre of equilibrium. After τ_0 , it moves rapidly to a new position separated by the vector $\vec{\ell}$ from its original site. For SD the incoherent intermediate scattering function is

$$F_s^{jump,SD}(Q, t) = A \exp\left[-b(Q)\frac{t}{\tau_0}\right], \quad (9)$$

where $b(Q)$ depends on the particular geometry of the jumps involved, i.e., on the vectors $\vec{\ell}$. A reasonable assumption for liquids and disordered systems is that these vectors are randomly oriented and their moduli are distributed according to a function

$$f_0(\ell) = \frac{\ell}{\ell_0^2} \exp\left(-\frac{\ell}{\ell_0}\right), \quad (10)$$

which involves a preferred jump distance ℓ_0 . The average value of the jump length is then $\langle \ell \rangle = \sqrt{6}\ell_0$. For such a kind of mechanism it is obtained [24] that

$$b(Q) = \frac{Q^2 \ell_0^2}{1 + Q^2 \ell_0^2}. \quad (11)$$

Note that for $Q\ell_0 \rightarrow 0$, $b(Q) \rightarrow Q^2 \ell_0^2$. In that limit, $F_s^{jump,SD}(Q, t)$ has a Gaussian form with an associated mean squared displacement that increases in a way proportional to the time. Glass-forming systems exhibit stretched exponential forms for the self-correlation function (equation (5)). An incoherent scattering function analogous to that for the simple jump diffusion (equation (9)) may be constructed by introducing the stretching in the time-dependent part:

$$F_s^{jump}(Q, t) = A \exp\left[-b(Q)\left(\frac{t}{\tau_0}\right)^\beta\right]. \quad (12)$$

In this way, in the limit $Q\ell_0 \rightarrow 0$ the Gaussian approximation is recovered; but now a sublinearly increasing mean square displacement would be obtained for small Q -values, as observed from experiments and simulation. The resulting characteristic time is then given by

$$\tau_w = \tau_0 \left[1 + \frac{1}{Q^2 \ell_0^2}\right]^{\frac{1}{\beta}}, \quad (13)$$

for which the asymptotic low- Q limit is just $\tau_w \propto Q^{-2/\beta}$ (equation (7)). Our results can be perfectly described by this model with a value of $\ell_0 \sim 0.42$ Å. This is shown in figure 2(a), where the solid line is a fit with equation (13) (exponentiated to β) and the value of ℓ_0 fixed to 0.42 Å. At the reference temperature of 300 K, for the only adjustable parameter the result τ_0 [ns] = 0.167^{1/β} is obtained. We can thus conclude that both the experimental and the MD-simulation results on this polymer are compatible with a scenario of sublinear diffusion for the self-motions of the hydrogen atoms which involves a distribution of elemental jump lengths with a most probable value of $\ell_0 \approx 0.42$ Å.

We can now ask whether this model also accounts for other observables accessed by the simulations, such as α_2 . To obtain α_2 for this model, the total expression used for describing

the self-correlation function has to be considered. It consists of the jump anomalous diffusion incoherent scattering function (equations (12) and (11)) with equation (6) for the prefactor A :

$$F_s(Q, t) = \exp\left(-\frac{\langle u^2 \rangle}{3} Q^2\right) \exp\left[-\left(\frac{Q^2 \ell_0^2}{1 + Q^2 \ell_0^2}\right) \left(\frac{t}{\tau_0}\right)^\beta\right]. \quad (14)$$

For small values of the variable $Q^2 \ell_0^2$, equation (14) can be approximated as

$$F_s(Q, t) = \exp\left[-\frac{\langle u^2 \rangle}{3} Q^2 - Q^2 \ell_0^2 \left(\frac{t}{\tau_0}\right)^\beta \left(1 - Q^2 \ell_0^2 + \dots\right)\right]. \quad (15)$$

Comparing this with the general expression for the expansion of $F_s(Q, t)$ in Q (see, e.g., [26])

$$F_s(Q, t) = \exp\left[-\frac{\langle r^2(t) \rangle}{6} Q^2 + \frac{\alpha_2(t) \langle r^2(t) \rangle^2}{72} Q^4 + \dots\right], \quad (16)$$

the following results are obtained for $\langle r^2(t) \rangle$ and $\alpha_2(t)$:

$$\langle r^2(t) \rangle = 2\langle u^2 \rangle + 6\ell_0^2 \left(\frac{t}{\tau_0}\right)^\beta, \quad (17)$$

$$\alpha_2(t) = \frac{72\ell_0^4 \left(\frac{t}{\tau_0}\right)^\beta}{[2\langle u^2 \rangle + 6\ell_0^2 \left(\frac{t}{\tau_0}\right)^\beta]^2}. \quad (18)$$

In order to compare the results of equations (17) and (18) with those of the simulations, the values of the different parameters involved have to be known for 320 K, the equivalent temperature to the 363 K of the simulations. From the results obtained by IN13 for $\langle u^2 \rangle$, a linear temperature dependence extrapolates to $\langle u^2 \rangle \approx 0.66 \text{ \AA}^2$ at 320 K. ℓ_0 is assumed to be temperature independent in a first approximation. With the shape parameter found in the simulations $\beta = 0.4$ and using the appropriate c_T -value ($c_{320\text{K}} = 0.42$), $\tau_0 = 1.3$ ps is obtained. The values so calculated for $\alpha_2(t)$ are plotted in figure 2(b) as a solid line. As can be appreciated, a semiquantitative agreement is found between the values obtained from the model of anomalous diffusion with distribution of jump lengths and those resulting from the simulations. Naturally, the comparison applies only to timescales longer than that characteristic for the fast dynamics, since the fast process has been simply parametrized by the LMF (equation (6)), i.e., through the effective contribution to the displacement characterized by $\langle u^2 \rangle$. In the range of applicability ($t > 1$ ps) the shape and the position of the peak of $\alpha_2(t)$ are quite similar for both sets of data.

With this result at hand we now exploit the model further in order to see whether it is able to reproduce the main features of $\alpha_2(t)$ that are reported in the literature from simulations of glass-forming systems in general. Figure 3(a) shows the T -behaviour of $\alpha_2(t)$ calculated taking into account the values experimentally determined for PI for the different parameters involved in the model. At first sight, the qualitative similarity shown by the non-Gaussian parameter so calculated with the data usually reported in the literature becomes evident. Moreover, we can check whether this model also accounts for other seemingly universal features of α_2 : (i) in the asymptotic short time limit, $t\alpha_2(t) \propto t^{3/2}$; (ii) the time t^* where the maximum of α_2 occurs shifts with τ_w ; (iii) the magnitude of α_2 increases with decreasing temperature.

- (i) First of all, figure 3(b) explores the prediction of Caprion *et al* [27]: the collapse of $t\alpha_2(t)$ in the short time regime to a universal function proportional to $t^{3/2}$. It is evident that the simple anomalous jump diffusion model also accounts for this very general feature.

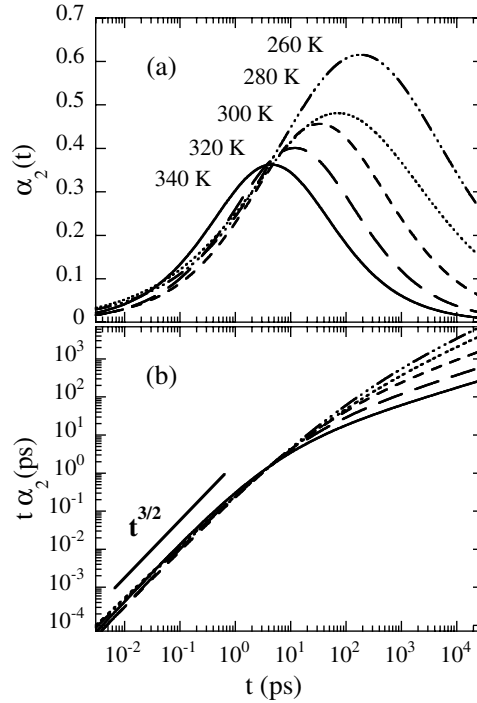


Figure 3. Time evolution of the non-Gaussian parameter α_2 as predicted by the anomalous jump diffusion model with the parameters obtained from the quasielastic NS results on polyisoprene for the temperatures indicated. Figure (b) shows the data in (a) multiplied by the time.

- (ii) From equation (18) it is straightforward to calculate t^* as the time where $\alpha_2(t)$ exhibits its maximum. We arrive at $t^* = \tau_0(\langle u^2 \rangle / 3\ell_0^2)^{1/\beta}$. Given the weak temperature dependences of $\langle u^2 \rangle$ and β , to a good approximation the temperature dependence of t^* follows that of τ_0 . Using the experimental parameters, figure 4 displays t^* and τ_0 as a function of $1/T$. Both times are basically identical. t^* agrees nearly quantitatively with the jump time τ_0 —a very plausible result. Moreover, figure 4 also shows that $t^*(T)$ approximately follows $\tau_w(T)$. This is naturally understood because, according to equation (13), the temperature dependence of τ_w and τ_0 are the same apart from the slight changes of β with temperature.
- (iii) Inserting t^* into equation (18), $\alpha_2^{max} = \alpha_2(t^*) = 3\ell_0^2/2\langle u^2 \rangle$ is obtained. With ℓ_0 approximately constant and $\langle u^2 \rangle$ decreasing linearly with T , α_2^{max} increases significantly with decreasing temperature. The values of α_2^{max} calculated by using the experimentally determined values for the parameters involved in the model are shown in figure 5 in comparison with the MD simulation results at different temperatures. The temperature scale has been shifted in order to compatibilize NS and MD simulation results (as already mentioned, MD simulations at 363 K are equivalent to experimental results at 320 K).

We can thus conclude that the main ‘universal’ features reported in the literature for $\alpha_2(t)$ are well reproduced by a simple anomalous jump diffusion model with a distribution of jump lengths.

Now we can discuss the implications of the anomalous jump diffusion concerning the so called heterogeneity of the α -relaxation. First of all, we can say that the above mentioned model in fact involves a heterogeneous picture for the self atomic motions in the α -relaxation

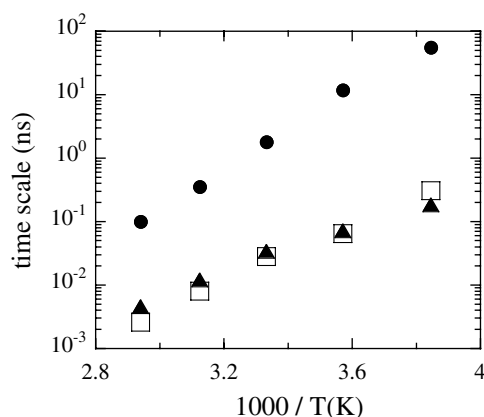


Figure 4. Temperature dependence of t^* (full triangles), τ_0 (□) and τ_w ($Q = 0.9 \text{ \AA}^{-1}$) (●).

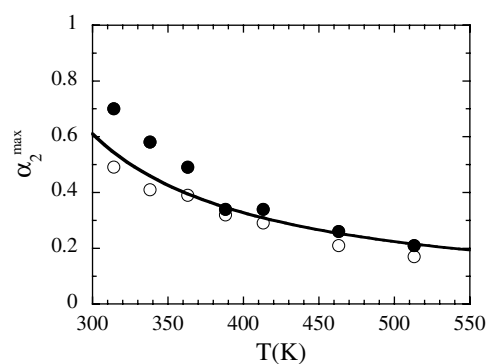


Figure 5. Temperature dependence of the maximum value of α_2 , $\alpha_2^{\max} = \alpha_2(t^*)$, as obtained from the anomalous diffusion jump model with the experimental parameters determined for polyisoprene (solid line) and from the simulations for the main chain protons (●) and for the main chain carbons (○). The temperature scale for the model data has been shifted 43 K to match that of the simulations.

regime which is manifest at short length scales. There, each atom can jump over different distances at each moment; therefore, at large Q , where the neutron wavepacket interacts only along a single step of the diffusion process, the system looks heterogeneous-like and non-Gaussianity is evident. However, for small Q , the contributions to $F_s(Q, t)$ originate from a large space volume of size $\sim 1/Q$; the scattering process observes the motion over long paths, i.e., over many diffusive elemental steps. Then, the result does not depend on the nature of the single step: at large scales the sublinear regime is reached and the system becomes Gaussian. In this framework, we could take t^* , i.e., the time at which $\alpha_2(t)$ displays its maximum, as a measure of the ‘lifetime’ of the heterogeneous behaviour. From the simulation results at 363 K (corresponding to experimental results at about 320 K) we can see that $\tau_w \sim t^*$ only for Q -values of the order of 3 \AA^{-1} . However, at Q -values of the order of 0.8 \AA^{-1} , $\tau_w \sim 25t^*$. It is noteworthy that in this framework the non-Gaussian behaviour, characterized by the $\alpha_2(t)$ peak, is not related to the existence of any distribution of single-exponential relaxations giving rise to the observed α -relaxation stretching. This kind of distribution is usually invoked when the so-called heterogeneity of the α -relaxation is discussed in connection with the non-Gaussian

behaviour. As the simple anomalous jump diffusion model here proposed can explain most of the ‘universal’ features of the $\alpha_2(t)$ behaviour reported so far (see, e.g., [10–12, 27–29]), we may ask whether the origin of $\alpha_2(t)$ in glass-forming systems in general is just the existence of a jump length distribution.

Finally, we would like to remark that the scenario of anomalous jump diffusion is, in principle, compatible with the framework of the MCT. The jumps leading to the sublinear diffusion would correspond in this framework to the dynamics allowing the decaging mechanism.

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