Non-Gaussian Nature of the α Relaxation of Glass-Forming Polyisoprene

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We report quasielastic neutron scattering experiments exploring the α relaxation in polyisoprene over an unprecedented range in momentum transfer. Corroborating and validating earlier molecular dynamics simulations, the measurements reveal a crossover from a Gaussian regime of sublinear diffusion to a strongly non-Gaussian regime at short distances. We show that a consistent interpretation in terms of a distribution of finite jumps underlying the α process is possible. This model leads to a time-dependent non-Gaussian parameter exhibiting all features revealed so far from various simulations.

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The heterogeneity in the dynamics of undercooled liquids and, connected with it, the deviations from Gaussianity of the dynamic correlation functions is an issue of long-standing interest and one of the challenges along the way to understand glass formation. Recently, the main dynamical process, the α relaxation, came into focus. Computer simulations as well as various experimental techniques have provided different and partially conflicting evidence for heterogeneous behavior or the absence of it (see, e.g., [1] and references therein). Dynamical heterogeneities are often discussed in terms of the Gaussian character of the van Hove self-correlation function $G_s(r, t)$ of the moving atoms. $G_s(r, t)$ is the probability to find an atom at time t at a position "r" if it was at $r = 0$ for $t = 0$. For simple diffusive motion $G_s(r, t)$ is a Gaussian function, but complex, e.g., heterogeneous, dynamics may cause deviations from Gaussian behavior.

Incoherent neutron scattering (NS) experiments directly reveal the Fourier transform of $G_s(r, t)$: the intermediate scattering function $F_s(Q, t)$ or the dynamic structure factor $S_s(Q, \omega)$, where $Q = 4\pi \sin(\theta/2)/\lambda$ (λ: neutron wavelength; θ: scattering angle) is the momentum transfer and $\hbar\omega$ the energy transfer during scattering. For the α relaxation $F_s(Q, t)$ assumes the form of a Kohlrausch-Williams-Watts (KWW) function

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

where A is a Lamb-Mössbauer factor (LMF), τ_w the Q dependent KWW-relaxation time, and $\beta < 1$ the stretching exponent. A Gaussian correlation function implies a relation between the Q dependence of τ_w and β as $\tau_w \sim Q^{-2/\beta}$ [2]. Extensive NS experiments on many different polymers have verified this Gaussian relationship in the low Q regime ($Q \lesssim 1$ Å^{-1}) [3]. However, very recent molecular dynamics simulations on a polyisoprene melt (PI) revealed a clear crossover from $\tau_w \sim Q^{-2/\beta}$ to $\tau_w \sim Q^{-2}$ [4] at $Q \approx 1.3$ Å^{-1}. Furthermore, it was found to be connected with a strong increase of the non-Gaussian parameter

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

where $\langle r^{2n}\rangle$ are moments of $G_s(r, t)$.

This Letter reports a quasielastic NS approach to study the characteristic time $\tau_w(Q)$ in PI in a very extended Q range ($0.1 \leq Q \leq 4.7$ Å^{-1}). The measurements reveal a crossover in $\tau_w(Q)$ in perfect agreement with the simulation results. The Q dependence of $\tau_w(Q)$ is described in terms of a jump length distribution underlying the sublinear diffusion present in the α process. We find that this simple approach accounts for all universal features of $\alpha_2(t)$ reported so far in the literature for glass-forming systems in general.

A monodisperse PI sample with deuterated methyl groups was investigated: $-[\mathrm{CH_2} - \mathrm{CH} = \mathrm{C(CD_3)} - \mathrm{CH_2}]-_n$ (PId3). The scattering is thus dominated by the very high incoherent cross section of the hydrogens along the main chain and effects from the methyl group motions are avoided. To cover very wide Q range and connected with it a huge dynamical range, we combined (i) the Jülich neutron spin echo (NSE) instrument (100 ps $\leq t \leq$ 22 ns; $0.1 \leq Q \leq 0.3$ Å^{-1}; $T = 340$ K), (ii) the NSE spectrometer IN11c (8.4 ps $\leq t \leq$ 1.4 ns; $0.34 \leq Q \leq$ 1.68 Å^{-1}; $T = 280$, 300, 320, and 340 K), and (iii) the thermal backscattering (BS) instrument IN13 for the coverage of high Q values $1.2 \leq Q \leq 4.7$ Å^{-1} (resolution: 10 μeV, energy window: -130 μeV $\leq \hbar\omega \leq$ 100 μeV; $T = 260$, 280, and 300 K). IN11c and IN13 are located at the Institute Laue Langevin in Grenoble. NSE instruments reveal $F_s(Q, t)$ and IN13 measures $S_s(Q, \omega)$. Figure 1 displays some representative NSE and

BS spectra. While the NSE results are already corrected for the instrumental resolution function (simple division), the spectra at IN13 contain it [dotted line in Fig. 1(b)] in the form of a convolution with $S_s(Q, \omega)$. The results were analyzed in terms of KWW functions [Eq. (1)]. For the IN13 spectra the Fourier transform of the KWW function was used.

As first ingredient, a KWW analysis requires the determination of the stretching parameter β—in NS a notoriously difficult task which, due to the convolution problems, is hardly feasible on the basis of the BS data. At low T, dielectric measurements reveal $0.39 \leq \beta \leq 0.40$ in good agreement with previous NSE data on the collective relaxations of fully deuterated PI close to the first maximum of the static structure factor $Q_{\max}$ ($Q_{\max} \approx 1.3$ Å^{-1}) ($T = 280$ K: $\beta = 0.43 \pm 0.03$) [5]. The same data reveal $\beta = 0.55 \pm 0.025$ at 320 K. At 340 K the high quality of the Jülich NSE data [Fig. 1(a)] allows for an independent fit revealing $\beta = 0.57 \pm 0.08$. Thus, β changes with temperature. On the basis of the data at hand for the further evaluation, we interpolated β to $\beta = 0.40$ for 260 and 280 K, $\beta = 0.50$ for 300 K, $\beta = 0.55$ for 320 K, and $\beta = 0.57$ for 340 K and kept it fixed. With this choice of β a good description of all data is obtained (e.g., solid lines in Fig. 1). The spectral amplitudes deduced from IN13 follow a LMF form: $A \sim \exp(-\langle u^2 \rangle Q^2/3)$, where $\langle u^2 \rangle$ is the mean squared displacement (MSD) associated with the fast process. The fit results are $\langle u^2 \rangle = 0.43 \pm 0.02$ Å^2 at 260 K, 0.55 ± 0.02 Å^2 at 280 K, and 0.58 ± 0.01 Å^2 at 300 K. The resulting characteristic times are displayed in Fig. 2(a). A strong decrease of τ_w with increasing Q takes place. It is noteworthy that at 300 K a very wide Q range ($0.34 \leq Q \leq 4.7$ Å^{-1}) has been covered by the combination of IN13 and IN11c measurements; in this Q range, $\tau_w(Q)$ spread over almost four decades and both sets of data join perfectly. At 280 K the dynamics becomes too slow to be well characterized in the low Q range. The Q dependence of τ_w in this range has nevertheless been perfectly determined for 340 K: combining the results of both NSE machines, the full decade $0.1 \leq Q \leq 1$ Å^{-1} has been covered.

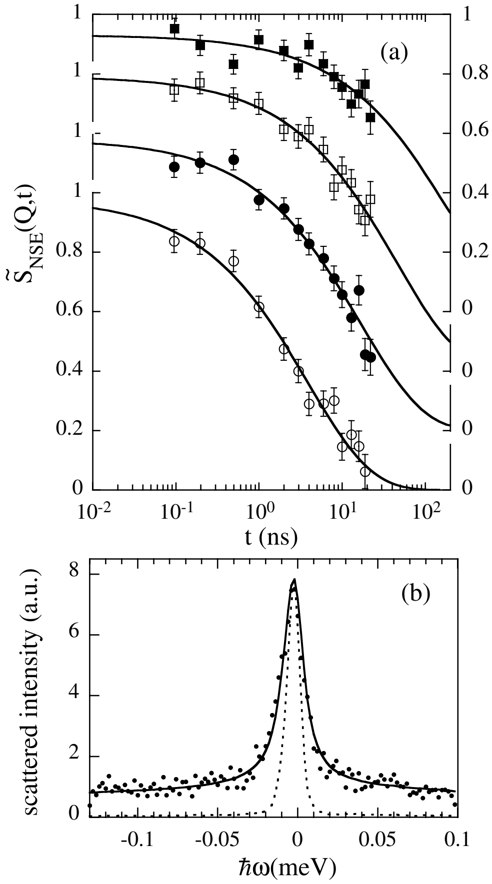

FIG. 1. Spectra obtained for PId3 (a) by the Jülich NSE at 340 K and $Q = 0.10$, 0.15, 0.20, and 0.30 Å^{-1} (top to bottom), and (b) by IN13 at 2.9 Å^{-1} and 300 K. Solid lines correspond to KWW descriptions with $\beta = 0.57$ (a) and $\beta = 0.50$ (b). The dotted line shows the IN13 instrumental resolution function obtained at 1.5 K.

To scrutinize the Gaussian character of $G_s(r, t)$, in Fig. 2(a) we have compared the Q-dependent characteristic times with the Gaussian prediction $\tau_w \sim Q^{-2/\beta}$ (solid lines). As the value of β slightly increases with T, the slopes of the predicted power laws decrease in absolute value towards higher temperatures. Figure 2(a) shows that in each case the Gaussian prediction describes

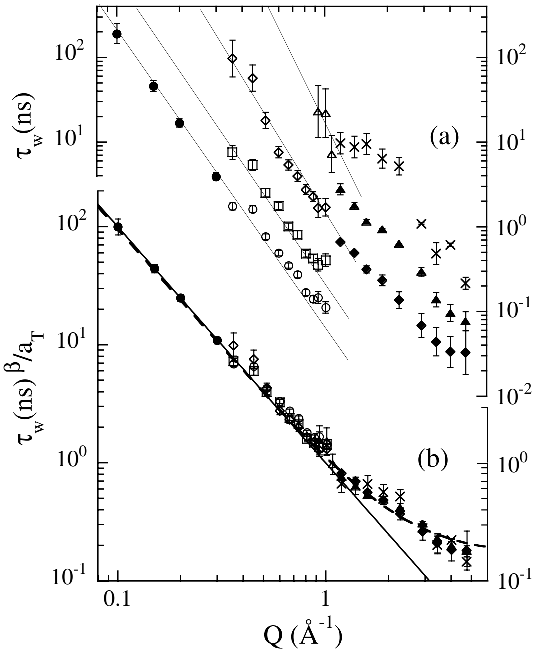

FIG. 2. (a) Q dependence of τ_w obtained for PId3 by IN13 (×: 260 K; ▲: 280 K; ◆: 300 K), IN11c (△: 280 K; ◇: 300 K; □: 320 K; ○: 340 K) and Jülich NSE spectrometer (● : 340 K). (b) Master curve built with the data in (a) (see the text). The straight solid lines display the Q dependence expected from the Gaussian approximation. The dashed line shows the description of the master in terms of the anomalous jump diffusion model [Eq. (4)] with $\ell_0 = 0.42$ Å.

very well the Q dependence of the experimentally determined τ_w in the range $Q \lesssim 1$ Å^{-1} for $T \geq 300$ K and is compatible with the results at 280 K. However, above 1 Å^{-1} the times deviate and follow a weaker Q dependence. In Fig. 2(b) all data from Fig. 2(a) are condensed to a single master curve. This is done, first of all, by exponentiating $\tau_w(Q)$ to the power of β. According to the Gaussian prediction $\tau_w^\beta \sim Q^{-2}$, and the effect of the change of β is eliminated. Secondly, the T dependence is removed applying shift factors a_T relative to a reference temperature T_R [300 K in Fig. 2(b)] to the results corresponding to the different temperatures. Within the experimental uncertainties, the coincidence of the different data is nearly perfect by applying similar shift factors to those obtained from earlier coherent NSE data close to $Q_{\max}$ and dielectric results [5]. A Q^{-2} dependence of τ_w^β is obtained at low Q, crossing over to a weaker power law at $Q \approx 1.3$ Å^{-1}. Thus, covering the largest $Q-t$ range ever in a single NS experiment, we have experimentally established a crossover from Gaussian to non-Gaussian character of the α relaxation similar to that reported for the simulated sample [4]. Indications of deviations from Gaussian behavior at $Q \sim 1$ Å^{-1} can also be found in experimental works on polyisobutylene [6] and poly(vinyl methyl ether) [7].

The likely origin of the deviation from Gaussianity at short length scales will be discussed using recent simulation results of the PI dynamics [4]. Therefore, an experimental validation of these simulations is essential. The detailed comparison will be published elsewhere. Here, we note that the experimentally determined $\tau_w(Q)$ agree quantitatively with those obtained from the simulation if the latter are shifted by about 40 K to lower T. Moreover, the value of β obtained from the simulations also changes with T, although at 363 K—corresponding to the experimental results at 320 K—$\beta \approx 0.4$, and the reduction of stretching occurs only at higher T.

In jump diffusion models, finite jump lengths tend to cause a bending of the dispersion for the diffusive relaxation times away from the Q^{-2} law which is valid for simple diffusion at low Q. Can such an explanation also be invoked for the interpretation of our data? The jump diffusion model (see, e.g., [8]) assumes that an atom remains in a given site for a time τ_0, where it moves around a center of equilibrium. After τ_0, it moves rapidly to a new position located at a distance $\vec{\ell}$ with respect to the original site. For such a process, the incoherent intermediate scattering function has the form

$$F_s^{\mathrm{JD}}(Q,t) = \exp\left[-\frac{\langle u^2\rangle}{3}Q^2 - b(Q)\left(\frac{t}{\tau_0}\right)^{\beta}\right], \tag{3}$$

where $b(Q)$ depends on the particular geometry of the jumps involved, i.e., on the vectors $\vec{\ell}$, and $\beta = 1$. Assuming randomly oriented jump directions with an exponential distribution of jump lengths $f_0(\ell) = \ell\ell_0^{-2} \times \exp(-\ell/\ell_0)$, where ℓ_0 is the most likely jump distance, $b(Q) = Q^2\ell_0^2(1 + Q^2\ell_0^2)^{-1}$. Note that for $Q\ell_0 \to 0$, $b(Q) \to Q^2\ell_0^2$. In that limit, $F_s^{\mathrm{JD}}(Q,t)$ has a Gaussian form with an associated MSD that increases linearly with time. Glass-forming systems exhibit KWW forms for $F_s(Q,t)$ [Eq. (1)]. An incoherent scattering function analogous to that for the simple jump diffusion [Eq. (3)] may be built by introducing the stretching in the time-dependent part ($\beta < 1$). In this way, in the limit $Q\ell_0 \to 0$ the Gaussian approximation is recuperated; but now a sublinearly increasing MSD would be obtained for small Q values, as observed from experiments and simulation. By comparing Eqs. (1) and (3), τ_w reads

$$\tau_w = \tau_0\left[1 + \frac{1}{Q^2\ell_0^2}\right]^{1/\beta}. \tag{4}$$

Equation (4) provides a good description of the experimental results displayed in Fig. 2(b) (dashed line). At $T_R = 300$ K we find $\tau_0 = 27.9$ ps and $\ell_0 = 0.42$ Å, the latter being T independent within the uncertainties. Obviously, the experimental results are compatible with a scenario of sublinear diffusion for the segmental relaxation with an underlying distribution of elemental jump lengths with a most probable value of $\ell_0 \approx 0.42$ Å.

The simulations have shown that deviations of $\tau_w(Q)$ from the Gaussian $Q^{-2/\beta}$ law set in, if $\tau_w(Q)$ reaches a time regime where $\alpha_2(t)$ becomes significantly different from zero. While it is very difficult to extract α_2 directly from the experimental data, it is easily calculated in the simulation. Figure 3 displays the simulation results for α_2 together with the time-dependent MSD $\langle r^2(t)\rangle$ [4].

Within the jump diffusion approach, α_2 may be calculated straightforwardly. Starting from Eq. (3) and inserting $b(Q)$, we may expand with respect to $Q^2\ell_0^2$. The result may be directly compared with the general expression for the expansion of $F_s(Q,t)$ with respect to Q [9], $F_s(Q,t) = \exp[-\langle r^2(t)\rangle Q^2/6 + \alpha_2(t)\langle r^2(t)\rangle^2 Q^4/72 + \ldots]$ revealing

$$\langle r^2(t)\rangle = 2\langle u^2\rangle + 6\ell_0^2\left(\frac{t}{\tau_0}\right)^{\beta}, \tag{5}$$

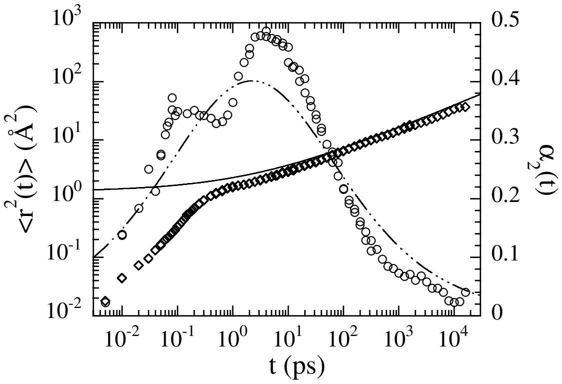

FIG. 3. Time evolution of $\langle r^2\rangle$ (◇) and α_2 (∘) obtained from the simulations at 363 K for the main chain protons [4]. The anomalous jump diffusion model with the parameters deduced from the experimental data at 320 K yields the functions displayed as lines: solid for $\langle r^2\rangle$ and dash-dotted for α_2.

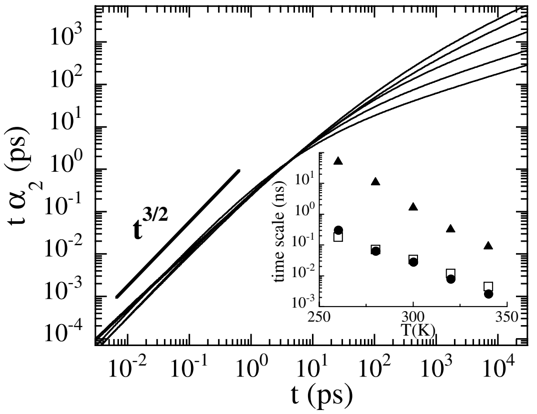

FIG. 4. Time evolution of α_2 multiplied by the time as obtained from the model of anomalous jump diffusion with the parameters experimentally deduced for PI at the different temperatures investigated (top to bottom: 260, 280, 300, 320, 340 K). The inset displays the T dependence of t^* (□), τ_0 (●), and $\tau_w(Q = 0.9\ \text{Å}^{-1})$ (▲).

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

For a comparison with the simulation which corresponds to an experimental temperature of 320 K, we extrapolate the $\langle u^2\rangle$ from IN13 linearly resulting in $\langle u^2\rangle \approx 0.66\ \text{Å}^2$. Shifting τ_0 to 320 K yields $\tau_0 = 1.3$ ps when imposing $\beta = 0.4$ (the value obtained from the simulations). With these parameters, $\langle r^2\rangle$ and $\alpha_2(t)$ are calculated using Eqs. (5) and (6). The results are displayed in Fig. 3 and show a behavior similar to that of the simulations for times longer than the microscopic times. At shorter times, $\langle u^2\rangle$ becomes time dependent and the jump diffusion approach breaks down. The good agreement suggests that at least to a reasonable approximation the non-Gaussianity observed for the α process at short enough times finds a simple explanation in terms of a sublinear diffusion process ($Q^{-2/\beta}$ regime) with a distribution of finite jump lengths. This process, being heterogeneous at short length scales (high Q), becomes homogeneous at larger scales (low Q). This interpretation is qualitatively compatible with the mode coupling theory. The jumps leading to the sublinear diffusion would correspond to the dynamics allowing the decaging mechanism. It is worth remarking that the value found for $\ell_0 \approx 0.42$ Å is in the range of that estimated from the simulations for the mean characteristic localization length $r_{sc} \sim 0.45$ Å [4].

We now exploit the model further, in order to see whether it is able to reproduce the main conjectures on $\alpha_2(t)$ that are reported in the literature from simulations of glass-forming systems in general (see, e.g., [10–14]). These are (i) the time t^* where the maximum of α_2 occurs approximately shifts with τ_w; (ii) the magnitude of α_2 increases with decreasing T; and (iii) in the asymptotic short time limit $t\alpha_2(t) \sim t^{3/2}$. From Eq. (6) it is straightforward to calculate t^* as the time where $\alpha_2(t)$ exhibits its maximum. We arrive at $t^* = \tau_0\langle u^2\rangle^{1/\beta}(3\ell_0^2)^{-1/\beta}$. Given the weak T dependencies of $\langle u^2\rangle$ and β, to a good approximation the thermal behavior of t^* follows that of τ_0 [which is similar to that of τ_w; see Eq. (4)]. Inserting the experimental parameters for PI which are determined in this work, we find the T dependencies of t^*, τ_0, and τ_w which are shown in the inset of Fig. 4. We note that t^* agrees nearly quantitatively with the jump time τ_0 — a very remarkable result. Furthermore, $\alpha_2^{\max} \equiv \alpha_2(t^*) = 3\ell_0^2(2\langle u^2\rangle)^{-1}$ is obtained from Eq. (6). With $\ell_0 \approx$ const and $\langle u^2\rangle$ decreasing linearly with T, $\alpha_2^{\max}$ increases significantly with decreasing temperature. In the experimental range, our data predict $\alpha_2^{\max}(340\text{ K}) \approx 0.34$ and $\alpha_2^{\max}(260\text{ K}) \approx 0.62$. Finally, Fig. 4 explores the prediction of Ref. [10]: 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 this simple jump model also accounts for this very general feature. Seemingly, this approach captures universal properties shown by so different glass-forming systems as orthoterphenyl, water, polymers, selenium, and Lennard-Jones liquids.

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