

Dynamics of Glass-Forming Polymers: “Homogeneous” versus “Heterogeneous” Scenario

A. Arbe and J. Colmenero

Departamento de Física de Materiales, Universidad del País Vasco, Apartado 1072, 20080 San Sebastián, Spain

M. Monkenbusch and D. Richter

Institut für Festkörperforschung, Forschungszentrum Jülich, 52425 Jülich, Germany

(Received 20 January 1998)

The question of whether the primary α relaxation in glass-forming systems is homogeneous or heterogeneous in nature is investigated by incoherent neutron scattering techniques in glass-forming polymers. It is shown that the momentum transfer dependence of the Kohlrausch-Williams-Watts relaxation time allows one to discriminate between these two limiting scenarios. From the results obtained we can conclude that the apparent stretching of the α -relaxation function relates dominantly to sublinear diffusion and is not a result of heterogeneities in the material. [S0031-9007(98)06525-9]

PACS numbers: 61.41.+e, 61.12.Ex, 64.70.Pf

For the main dynamical process in supercooled glass-forming liquids—the so-called α relaxation—the time dependence of the different correlation functions can be well approximated by the stretched exponential or Kohlrausch-Williams-Watts (KWW) function

$$\phi(t) = \exp[-(t/\tau_w)^\beta], \quad (1)$$

where β is a phenomenological shape parameter measuring the deviation from a single exponential decay ($\beta = 1$), and τ_w is the KWW relaxation time. Two limiting scenarios are invoked to explain the KWW functional form. Since a monotonous function can always be written as Laplace transform of a non-negative function, the KWW function can easily be interpreted as arising from the superposition of different simple exponential relaxations weighted by a broad distribution of relaxation times $g(\ln \tau)$,

$$\begin{aligned} \phi(t) &= \exp[-(t/\tau_w)^\beta] \\ &= \int_{-\infty}^{+\infty} g(\ln \tau) \exp(-t/\tau) d(\ln \tau). \end{aligned} \quad (2)$$

This picture is usually known as the “heterogeneous” scenario. The other extreme picture, the “homogeneous” scenario, considers that all of the particles in the system relax identically but by an intrinsically nonexponential process.

The heterogeneous picture was involved in some of the first theoretical approaches to the dynamics of supercooled liquids [1,2]. This scenario has also recently been invoked in connection to the question of the cooperative rearranging regions in glass-forming systems [3]. On the other hand, most of the experimental work accumulated over the past years was analyzed in the framework of the mode coupling theory [4] which does not address this question. Recent experimental results (see, e.g., [5–7]) have stimulated a new revival of the heterogeneous picture which is usually related to spatial heterogeneities. It has been suggested [6] that the size of the

spatial heterogeneities close to the glass transition temperature T_g should range in the nanometer scale (2–5 nm for low molecular weight glass-forming systems and up to about 10 nm for polymers), and that these heterogeneities mainly develop in the temperature range below about $1.2T_g$. For glass-forming polymers, however, it has also been suggested [8] that a heterogeneous structure should be present even at $T > 1.2T_g$.

All of the above mentioned experimental results correspond to spectroscopic techniques, which give only indirect information about the spatial scale of the molecular motions. Surprisingly, neutron scattering results, giving direct information about the spatial scales through the momentum transfer (Q) dependence of the dynamical magnitudes, still have not been exploited in order to address this question. In this Letter we show that incoherent neutron scattering results agree rather well with a homogeneous scenario for the α relaxation in glass-forming polymers, at least in the time scale covered by neutron scattering techniques.

Neutron scattering experiments measure the scattering function $S(Q, \omega)$, where Q and $\hbar\omega$ are the momentum and energy transfer, respectively. $S(Q, \omega)$ is the Fourier transform of the intermediate scattering function $S(Q, t)$ which in turn is the spatial Fourier transform of the pair and self-correlation functions of the moving nuclei. In some way $S(Q, t)$ can be considered as a spatially sensitive version of the correlation function $\phi(t)$. Both incoherent and coherent neutron scattering results from different glass-forming systems agree with an approximate KWW functional form for $S(Q, t)$ associated with the α relaxation [9], where now the KWW relaxation time τ_w is Q dependent. In the case of incoherent scattering, $S(Q, t)$ represents the self-part of the particle dynamics, which for the α relaxation is diffusive in nature. Here we examine the possibility of discriminating between homogeneous and spatially heterogeneous dynamics on the basis of the Q dependence of τ_w . In the heterogeneous

scenario, and in parallel with the procedure followed for developing Eq. (2), we may consider a distribution of local diffusivities associated with the different regions of the sample. The resulting $S(Q, t)$ can be expressed as

$$S(Q, t) = \exp[-(t/\tau_w)^\beta] \\ = \int_{-\infty}^{+\infty} g(\ln D^{-1}) \exp(-Q^2 t/D^{-1}) \\ \times d(\ln D^{-1}), \quad (3)$$

where $\exp(-Q^2 D t)$ is the intermediate scattering function corresponding to simple diffusion in the Gaussian approximation, and D is the corresponding diffusion coefficient. As in the case of Eq. (2), by properly choosing the distribution $g(\ln D^{-1})$, a KWW time dependence of the resulting $S(Q, t)$ can be easily reproduced. However, now the "stretched variable" is $X = Q^2 t$, i.e., the "conjugated" variable (showing the same dimension) of the distributed magnitude D^{-1} . As a consequence, the resulting $S(Q, t)$ reads as

$$S(Q, t) = \exp[-(Q^2 t/D_w^{-1})^\beta], \quad (4)$$

which can also be written in the phenomenological KWW form of Eq. (1) with $\tau_w = Q^{-2} D_w^{-1}$. Therefore, in the heterogeneous scenario the Q dependence of the phenomenological KWW relaxation time is the same as the Q dependence of each of the elementary diffusion times associated with each spatial region: $\tau = Q^{-2} D^{-1}$.

If we now invoke the homogeneous scenario, an $S(Q, t)$ can be obtained by considering an anomalous diffusion process in which the mean-squared displacement is sublinear in time, i.e., $\langle r^2(t) \rangle \propto t^\beta$ with $\beta < 1$. The corresponding $S(Q, t)$ in the Gaussian approximation can be written as

$$S(Q, t) = \exp[-Q^2 \langle r^2(t) \rangle / 6] = \exp(-Q^2 \mathcal{D} t^\beta), \quad (5)$$

where \mathcal{D} is a factor giving the temperature dependence of $S(Q, t)$. Equation (5) is equivalent to Eq. (1) with a KWW relaxation time given by $\tau_w = Q^{-2/\beta} \mathcal{D}^{-1/\beta}$. For a typical value of $\beta = 0.5$ this expression gives a Q dependence of $\tau_w \propto Q^{-4}$, which should be discriminable from the Q^{-2} law found in the heterogeneous scenario. Previous incoherent neutron scattering results on several polymers [10,11] indicated such strong power law behavior.

In order to investigate the different scenarios, we performed quasielastic incoherent neutron scattering experiments on four simple polymers in the low- Q regime ($0.19 \leq Q \leq 1 \text{ \AA}^{-1}$). Choosing this Q range, the experiments average spatial regions ($r \approx 2\pi/Q$) extending from about 6 to 33 Å. In this spatial regime local jump processes, which have been found recently in a number of polymers [12,13], do not or only weakly influence the scattering function, and the measured spectra can be considered as relating to diffusive processes alone. Taking into account the resolution of the neutron backscattering

spectrometers, as well as the problems of chemical degradation of polymers at high temperature, the temperature range where the diffusive α process can be observed in the low- Q range is rather narrow. We have chosen a representative temperature in the corresponding range for each of the polymers considered.

Experiments were performed on polyisoprene (PI) at 340 K, polybutadiene (PB) at 280 K, polyisobutylene (PIB) at 365 K, and polyvinylether (PVE) at 340 K. The measurements were carried out on the high resolution backscattering spectrometers IN16 at the Institut Laue-Langevin (ILL) in Grenoble, France, and BSS1 at the Forschungszentrum Jülich, Germany. Figure 1 presents spectra taken on PIB at 0.32 and 0.76 Å⁻¹. For comparison, the instrumental resolution function determined from the elastic scattering of the sample at 4 K is displayed and clear quasielastic broadenings are visible.

For an accurate data treatment, knowledge about the spectral shape is of great importance. For each of the investigated polymers, such information is available both from dielectric as well as from neutron spin echo

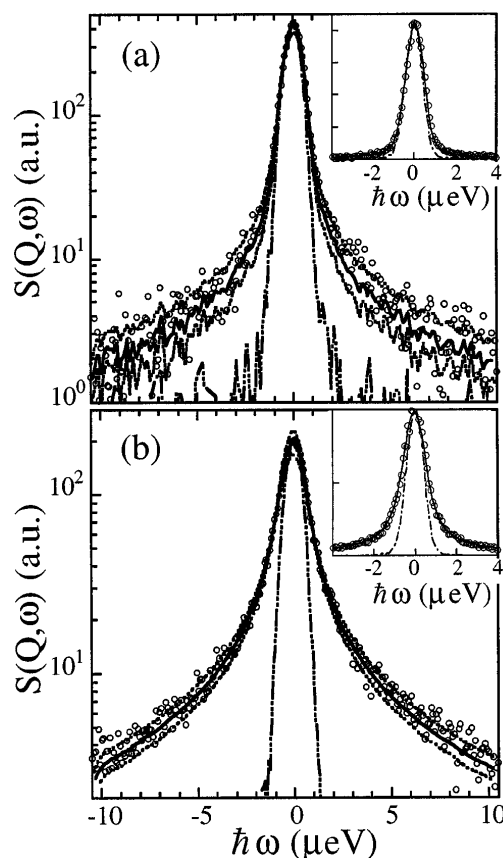


FIG. 1. Incoherent $S(Q, \omega)$ of PIB as measured by IN16 at 365 K for (a) $Q = 0.32 \text{ \AA}^{-1}$ and (b) $Q = 0.76 \text{ \AA}^{-1}$ in a logarithmic representation. Solid lines are the fit results corresponding to the KWW law. Dotted lines show the theoretical curves encompassing the error band. Dash-dotted lines are the instrumental resolution. Insets: Linear plot of experimental data, resolution, and fit results.

spectroscopy leading for all of these polymers to the same shape parameters in each case (PI: $\beta = 0.40$ [14], PB: $\beta = 0.41$ [15], PIB: $\beta = 0.55$ [16], and PVE: $\beta = 0.43$ [17]). These β values were kept constant in the evaluation of the present data.

The incoherent quasielastic neutron spectra were fitted with a numerical convolution of the Fourier transform of a stretched exponential and the experimental resolution function varying the KWW relaxation time τ_w and an amplitude factor for each spectrum.

Even though the transmissions T_{\perp} of the samples were high ($T_{\perp} = 0.9$), for the evaluation of neutron spectra resulting from diffusion in the low- Q regime multiple scattering corrections are essential (see, e.g., [18]). For this purpose the Monte Carlo (MC) program DISCUS [19] was employed. DISCUS calculates the multiple scattering contributions arising from the considered scattering function and yields a correction factor for the single scattering cross section. The approximate complete cross section obtained by application of this factor is then fitted again to the experimental data. After an iteration of four to five steps convergence was achieved. Figure 2 displays the multiple scattering correction process at the example of PIB. We like to emphasize the great importance of these corrections in particular for the low Q results. The corrections amount to about 1 order of magnitude changes in the KWW time and change the apparent power law of the Q dependent relaxation times from 2.2 to 3.2 in the case of PIB. By this iterative fitting and correction process, Q dependent relaxation times were established for the four polymers under investigation.

The data evaluation scheme involving MC procedures as intermediate steps precludes a direct calculation of errors by simple error propagation. We therefore estimate the errors considering theoretical curves which encompass the experimental error band (dotted lines in Fig. 1). The

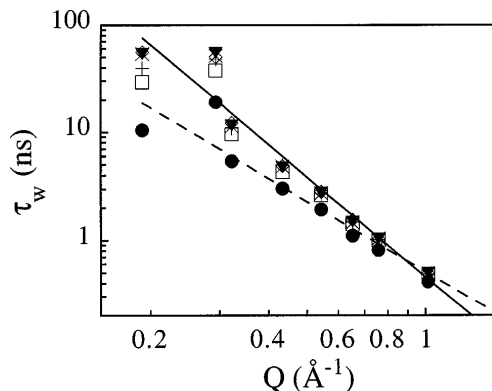


FIG. 2. Momentum transfer dependence of the characteristic time of the α relaxation of PIB at 365 K. Without multiple scattering corrections (\bullet) and after the 1st (\square), 2nd ($+$), 3rd (\times), 4th (\blacktriangledown), and 5th (\diamond) iteration of DISCUS. Dashed and solid lines are the fits of the noncorrected data and the asymptotic result of the corrections to a power law in Q , respectively.

resulting parameter range gives the confidence interval for the deduced characteristic times. They are included as error bars in Fig. 3.

We can now investigate the two limiting scenarios. In the case of homogeneous dynamics, following Eq. (5) we expect $(\tau_w)^\beta \propto Q^{-2}$. Figure 3(a) displays the obtained values of $(\tau_w)^\beta$ for the different polymers as a function of momentum transfer Q . As may be seen, in all cases the data agree well with the limiting Q^{-2} law. In the heterogeneous scenario, on the other hand, $\tau_w \propto Q^{-2}$ [Eq. (4)] is expected. Therefore, in Fig. 3(b) we display τ_w itself as a function of Q . As may be seen, none of the polymers is even close to what is expected from a heterogeneous scenario, and the homogeneous scenario seems to prevail. Thus, the origin of the stretched exponential relaxation functions for the α process relates to anomalous diffusion rather than to a heterogeneous sample.

One may argue that the neutron scattering results have been obtained at relatively high temperatures far above the glass transition temperature, and that the observations in this temperature regime may be irrelevant for the glass transition itself. We note, however, that for polymers the stretching exponent for the α relaxation, which in the heterogeneous scenario describes the breadth of the rate

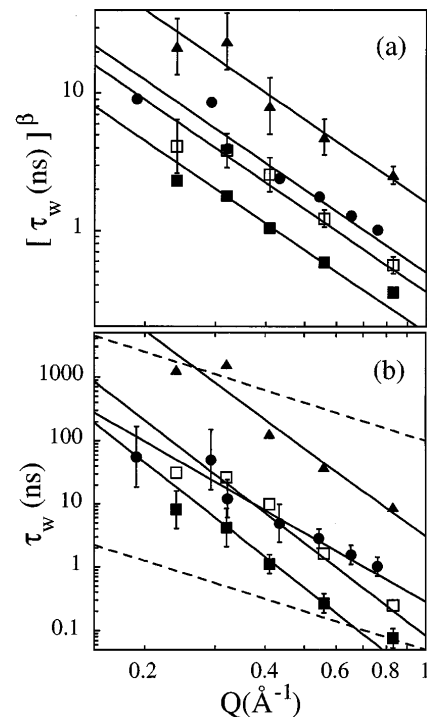


FIG. 3. Momentum transfer dependence of the characteristic time of the α relaxation for the polymers investigated: PVE at 340 K (\blacktriangle), PIB at 365 K (\bullet), PB at 280 K (\square), and PI at 340 K (\blacksquare). (a) $(\tau_w)^\beta$ as a function of Q in a double logarithmic plot; (b) the same plot for τ_w versus Q . Solid lines represent, in both cases, the Q dependence expected in the homogeneous scenario. Dashed lines in (b) display the behavior expected in the heterogeneous case.

distribution function, in general, is hardly changing with temperature and for our polymers stays constant down to the glass transition (with the possible exception of the β value of PIB from dielectric measurements). The finding that at high temperatures the stretching exponent, to a large extent, is related to homogeneous anomalous diffusion makes it hard to believe that basically the same stretching exponent at lower temperatures should relate to something else, namely, heterogeneous relaxation.

Figure 3(a) shows that, while PVE behaves close to the asymptotic limit $(\tau_w)^\beta \propto Q^{-2}$, the other polymers exhibit some deviations from this law. Such deviations may be either due to an intrinsic jump length distribution for the diffusive jumps or due to a remaining small heterogeneity, causing a distribution of anomalous diffusion coefficients.

Finally, we comment on the relation to the Rouse relaxation. It is well known that for polymers the regime of segmental diffusion is limited and crosses over at larger length scales to the regime of Rouse relaxation which displays the well known $\tau \propto Q^{-4}$ power law. For polydimethylsiloxane, a very flexible polymer, by quasielastic neutron scattering this crossover has been identified to occur at about $Q \cong 0.2-0.3 \text{ \AA}^{-1}$ [20]. For stiffer polymers, such as those we have been investigating, this crossover is expected to shift to even lower momentum transfers. Although details about the crossover are not yet known, the regime of Rouse relaxation should have only minor influence on our results.

In summary, exploiting the space-time sensitivity of quasielastic neutron scattering we investigated the long standing question, whether the primary relaxation in glass-forming materials, here polymers, is heterogeneous or homogeneous in nature. From the Q dependent KWW relaxation times τ_w , it could be demonstrated that the apparent stretching of the α -relaxation function relates dominantly to sublinear diffusion and is not a result of heterogeneities in the material. Although this result was obtained at temperatures well above the glass transition, the almost temperature independent stretching exponents suggest that this behavior also prevails close to T_g .

J.C. acknowledges financial support from the projects: MEC No. PB94-0468, G.V. No. PI95/005, and UPV No. 206.215-EC245/96. The BBV-Foundation (programa Cátedra) is acknowledged by D.R. and J.C. We are thankful to Dr. L. Willner for the sample characterization,

to Dr. B. Frick and Dr. M. Pionke for experimental help, and to ILL for neutron facilities.

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