Crossover from Debye to Non-Debye Dynamical Behavior of the α Relaxation Observed by Quasielastic Neutron Scattering in a Glass-Forming Polymer

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The dynamics of a very fragile glass-forming polymer is studied by time of flight neutron scattering in a time scale from 10^{-13} to 10^{-11} s. We observe a crossover from a Debye-like to a non-Debye behavior at a characteristic time which is effectively independent of temperature and momentum transfer Q. We also confirm the results previously obtained about the non-Debye α relaxation in a different time scale (10^{-11} to 10^{-8} s). The results here reported open a new outlook for understanding the fast dynamics of glass-forming systems.

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The dynamical behavior of glass-forming systems is today a subject of increasing interest in connection with the poorly understood glass-transition phenomenon. Two different dynamical processes are involved. The main process, known as α relaxation, has been studied usually by relaxation techniques and photon correlation spectroscopy (PCS) in a macroscopic time scale (10 to 10^{-6} s) and recently by quasielastic neutron scattering in a mesoscopic time scale (10^{-11} to 10^{-8} s) (see as representative general references [1,2]). Second, a fast dynamical process (time scale slower than a few picoseconds) has been recently found by inelastic neutron scattering (time of flight spectroscopy, TOF) in several glass-forming systems [3-6] at $T \gtrsim T_g$ (T_g is the experimental glass-transition temperature). The physical origin of such a fast process and its possible connection to the α relaxation are questions which are at present completely unclear. In general, the interpretations of the neutron data corresponding to the fast process have been guided by mode coupling theory (MCT) [7] which predicts a fast relaxation process (called β relaxation) in the time scale mentioned above (10^{-12}–10^{-11} s). Other authors try to understand the observed fast process in terms of vibrational properties of the softening glass structure [8]. However, the main problem for analyzing and interpreting the fast process is that additional low-frequency vibrational excitations also contribute to the dynamic structure factor $S(Q,\omega)$ of supercooled liquids and glasses at the same frequency range where the quasielastic contribution of the fast process appears. In the low-frequency Raman (LFR) spectra these kinds of excitations are very well known and give rise to the so-called "boson peak." Taking into account LFR data, Sokolov *et al.* have recently shown [9] that the LFR spectra of fragile systems [10] are mainly dominated by relaxational contributions and the boson peak is not observed in some very fragile systems even at temperatures below T_g. Several studies with neutrons also appear to support this empirical correlation [9].

With these ideas in mind we have studied the dynamics of a glass-forming polymer (polyvinyl chloride, PVC) by means of TOF neutron scattering trying to look at the crossover from fast dynamics to slow α relaxation. PVC is suitable for this kind of study. First of all it is a main-chain polymer without internal degrees of freedom associated with side groups. Second it shows an extremely low value of the Kohlrausch-Williams-Watts (KWW) β parameter ($\beta \cong 0.2$) characterizing the non-Debye behavior of α relaxation and a very fragile behavior ($D \cong 3$) [11]. Both aspects should favor the observation of slow α relaxation in the frequency window covered by TOF spectrometers where the fast process should also be observed. Moreover, the very fragile behavior of this system suggests that the contribution of the low-frequency inelastic excitations to $S(Q,\omega)$ should be weak. In fact, the boson peak has not been observed in the LFR spectra of PVC samples [12] and in direct correlation, the heat capacity does not show a low-temperature maximum in the variable C/T^3. These aspects should also favor an investigation of the fast dynamics and the crossover towards slow α relaxation by TOF spectroscopy without interference from the low-frequency excitations.

The PVC samples used in this work show a number-average molecular weight $M_n = 45.5 \times 10^3$ and a glass-transition temperature $T_g \cong 358$ K. The noncrystalline character of the samples was determined by standard x-ray measurements.

The quasielastic neutron scattering measurements were performed on the TOF spectrometer IN6 at the Institut Laue-Langevin (ILL) in Grenoble, France. The wavelength of the incident neutrons was set to 5.12 Å resulting in a Q range roughly between 0.2 and 2 Å^{-1} and an elastic energy resolution of 70 μeV. This resolution together with the energy window used allow us to explore the dynamics in a time scale roughly between 10^{-13} and 10^{-11} s. The samples (thickness 0.07 mm) were placed in a flat Al container yielding a transmission of about 95%. The data were corrected for detector efficiency, self-screening, sample container, and cryostat scattering using standard ILL programs. Because of the high sample transmission, multiple scattering corrections were not applied. The experimental curves for the incoherent scattering function $S(Q,\omega)$ at constant Q were calculated by interpolation from $S(\phi,\omega)$ where ϕ is a given scattering angle. We followed the same procedure for the measured instrumental resolution. After this procedure our practical Q scale was reduced to a range between 0.5 and 1.8 Å^{-1}. Neutron scattering of PVC is dominated by the incoherent cross section of the hydrogen. The ratio between the incoherent cross section σ_i and the scattering cross section σ_s is $\sigma_i/\sigma_s = 0.92$. The temperature range covered was between 2 and 450 K, although here we mainly report on the results corresponding to temperatures around and above T_g. Figure 1 shows some resulting spectra corresponding to temperatures in the range $T_g - 248 \leq T \leq T_g + 92$ K. According to the LFR results and to the fragile character of PVC, the spectra do not show any clear evidence of a low-frequency inelastic contribution even at temperatures below T_g. In this temperature range, the spectra only show an almost flat contribution merging with the elastic intensity. Around $T = T_g - 50$ K, additional scattering starts to accumulate at the low energy range below 3 meV. This contribution grows in intensity as the temperature is increased. In order to check whether or not the behavior obtained below T_g only corresponds to harmonic vibrations, all the spectra were corrected for Bose and Debye-Waller factors and scaled to an arbitrary reference temperature of 350 K. The procedure followed has been widely described in the literature [3,4]. The scaled spectra clearly fall on a master curve up to a temperature of about 290 K (see the inset in Fig. 1) indicating that the spectra are dominated by harmonic contributions in this temperature range. Above this temperature the spectra only overlap for energy transfers $E > 3$ meV, showing the existence of a quasielastic contribution which increases with temperature.

As we are interested in the nonharmonic additional scattering appearing around T_g, the most direct way of analyzing the data is to remove the harmonic part from the experimental spectra. To do this we can consider that the two processes are statistically independent. Thus, we can write a model scattering function as a convolution product,

$$S(Q,\omega) \equiv S^{\text{rela}}(Q,\omega) \otimes S^{\text{harm}}(Q,\omega) , \tag{1}$$

where we have adopted the term "rela" (relaxation) for the nonharmonic scattering. This procedure can be considered to be a first approach to the problem, justified by the apparent statistical independence of the processes (see inset in Fig. 1). To compare the model function [Eq. (1)] to the experimental curves we have to convolute the expression in Eq. (1) with the measured instrumental resolution function of IN6 $R(Q,\omega)$. In this framework, the experimental spectra should be given by

$$S^{\text{exp}}(Q,\omega) = S^{\text{rela}}(Q,\omega) \otimes S^{\text{harm}}(Q,\omega) \otimes R(Q,\omega) . \tag{2}$$

We can rewrite Eq. (2) as

$$S^{\text{exp}}(Q,\omega) = S^{\text{rela}}(Q,\omega) \otimes R^{\text{effect}}(Q,\omega) , \tag{3}$$

where $R^{\text{effect}}(Q,\omega)$ plays the role of an effective resolution for the relaxation process given by $R^{\text{effect}}(Q,\omega) = S^{\text{harm}}(Q,\omega) \otimes R(Q,\omega)$. Therefore, $R^{\text{effect}}(Q,\omega)$ is the experimental scattering curve corresponding to harmonic vibrations at the temperature considered. It can be obtained from the harmonic spectra at low temperatures ($T \leq 290$ K) properly scaled by the Bose and Debye-Waller factors. Fourier transforming Eq. (3) into the time domain we obtain $I^{\text{exp}}(Q,t) = I^{\text{rela}}(Q,t) I^{\text{effect}}(Q,t)$. Then, we can calculate $I^{\text{rela}}(Q,t)$ by dividing the Fourier transformation of the experimental spectra by the Fourier transformation of the effective resolution spectra obtained as described above. We have exhaustively checked this deconvolution procedure by using several theoretical model functions for $S^{\text{rela}}(Q,\omega)$. We convolute these functions with the experimental effective resolution and then we apply the deconvolution procedure. We always recover the time domain behavior corresponding to the model function considered.

Figure 2 shows the behavior obtained for the normalized $I^{\text{rela}}(Q,t)[I_0(Q,t)]$ at different temperatures [Fig. 2(a)] and at different Q values for 450 K [Fig. 2(b)]. It is clear that, above T_g, $I_0(Q,t)$ shows a two step decay. In principle the slower one should be associated with the α relaxation. This second decay is obviously clearer at higher temperatures. However, the most relevant feature of the results obtained is that the critical time separating the two regimes appears to be nearly independent of both Q and temperature. From the $I_0(Q,t)$ obtained we can calculate a mean squared displacement of the scattering centers $\langle r^2(t) \rangle$ as $\langle r^2(t) \rangle = (6/Q^2) \ln[1/I_0(Q,t)]$. If the Gaussian approximation is verified, the behavior obtained for $\langle r^2(t) \rangle$ at a given temperature should be Q independent. In Fig. 3 we have represented the values of $\langle r^2(t) \rangle$ obtained at different temperatures. For two tempera-

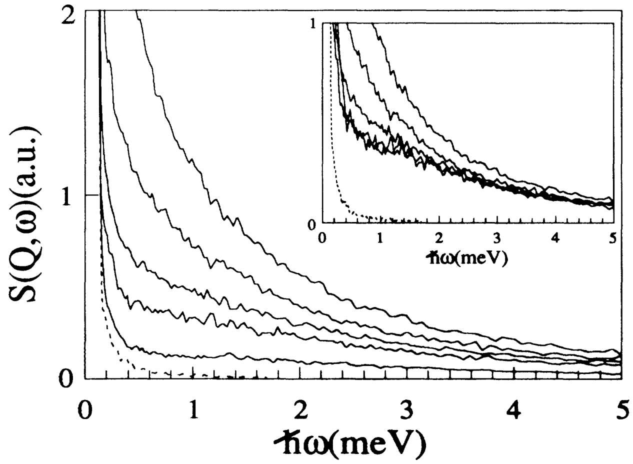

FIG. 1. Incoherent scattering function $S(Q,\omega)$ as measured by IN6 for $Q = 1.5$ Å^{-1} and at different temperatures: 450, 410, 350, 290, and 110 K (top to bottom). Dotted curve is the instrumental resolution. Inset: The same spectra but with Bose and Debye-Waller factors scaled to their values at 350 K.

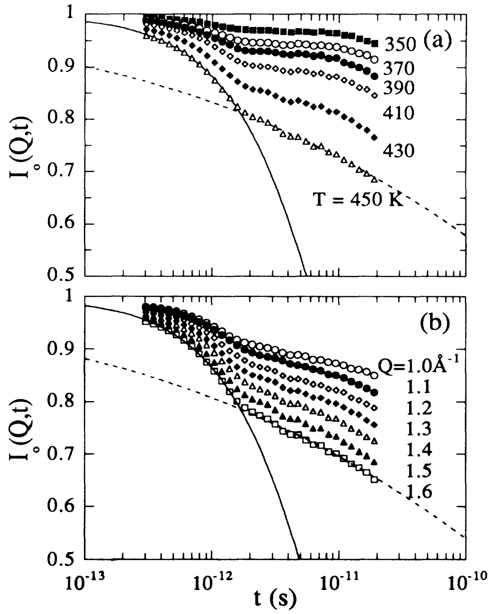

FIG. 2. Normalized intermediate scattering function $I_0(Q,t)$. (a) Temperature behavior for $Q=1.5$ Å^{-1}. (b) Q behavior for $T=450$ K. Lines through the curves corresponding to $T=450$ K (a) and $Q=1.6$ Å^{-1} (b) are representative fitting curves (see text).

tures, 450 and 410 K, we have also drawn the behavior corresponding to the different Q values investigated. It is clear that $\langle r^2(t)\rangle$ is independent of Q within the experimental uncertainties, indicating that the intermediate scattering function follows approximately a Gaussian-like behavior $I_0(Q,t)=\exp[-Q^2\langle r^2(t)\rangle/6]$. Moreover, the mean squared displacement displays two different dynamical regimes separated by a critical time t_c of the order of 1.7 ps which depends on neither Q nor T. In the fast regime ($t<t_c$), the mean squared displacement is proportional to the time, suggesting a diffusionlike behavior. Figure 3 also shows that this process exists even at temperatures just below T_g where the nonharmonic "relaxation" scattering contribution starts to appear in the low energy range of the IN6 dynamical window (see Fig. 1). Above t_c, the mean squared displacement shows, in the high-temperature range, a sublinear diffusion behavior $\langle r^2(t)\rangle \propto t^{\beta}$ with a β value in the range of $\beta \cong 0.23$. This kind of behavior was previously found by us [11] for the α relaxation of PVC in the time scale covered by neutron backscattering instruments (IN10 and IN13 at the ILL in Grenoble) roughly between 10^{-11} and 10^{-8} s. In those papers, we showed the sublinear diffusion behavior results to be compatible with a Gaussian intermediate scattering function given by a non-Debye KWW expression. We also showed that the exponent giving account for the sublinear diffusion is in fact the exponent of the KWW function accounting for the non-Debye character of the α relaxation. The sublinear behavior found is less evident in the time scale covered by IN6 as the temperature decreases towards T_g (see Fig. 3). This could be due to the temperature dependence of the characteristic time scale of the α relaxation of PVC [11] which, close to T_g, is clearly far away from the time scale window of IN6. Therefore $\langle r^2(t)\rangle$ is almost constant between 1 and 10 ps in this temperature range. The increase of the tail of $\langle r^2(t)\rangle$ at $t>10^{-11}$ s in the low-temperature range is probably an artifact related to cutoff problems in the deconvolution process because we are in the limit of the effective resolution in this time range. It is interesting to point out that the behavior found for $\langle r^2(t)\rangle$ is similar to the recently obtained one by molecular dynamics simulations of the short time dynamics of a polyethylenelike glass-forming system [13].

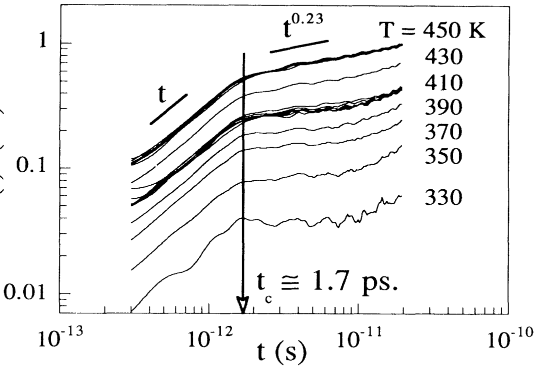

FIG. 3. Mean squared displacement obtained from $I_0(Q,t)$ data. For the case of 450 and 410 K, different lines at each temperature correspond to different Q values.

Taking into account these results we have fitted the fast regime of $I_0(Q,t)$ by a Debye-like expression $I_D(Q,t)=A_D\exp[-t/\tau_D(Q,T)]$ and the slow regime by a KWW function

$$I_{\mathrm{WW}}(Q,t)=A_{\mathrm{WW}}\exp\{-[t/\tau_{\mathrm{WW}}(Q,T)]^{\beta}\}\,.$$

In the last case we have fitted only the data corresponding to 450 and 430 K, where a time decay in the slow regime of the experimental $I_0(Q,t)$ is more evident. We have used as the β parameter the average value for these two temperatures deduced from the $\langle r^2(t)\rangle$ behavior, i.e., $\beta \cong 0.23$. Some representative fitting curves are shown in Fig. 2. These curves describe quite well the experimental $I_0(Q,t)$ behavior. The prefactors A_D and A_{WW} are found to be close to 1. By this fitting procedure we obtain the Q and T behavior of the relaxation times τ_D and τ_{WW} corresponding to the fast and slow α-relaxation regimes, respectively. We obtain that the relaxation time of the fast Debye regime behaves with Q as $\tau_D \propto Q^{-2}$. This is the Q behavior one can expect for a diffusion process. Concerning the Q dependence of the relaxation time of the non-Debye KWW regime, we obtain $\tau_{\mathrm{WW}} \propto Q^{-n}$ with an n value of 9. This value is completely compatible with the n value previously obtained ($n=9.5\pm1$) by fitting directly in the frequency domain the quasielastic broadening of the α relaxation measured by IN10 and

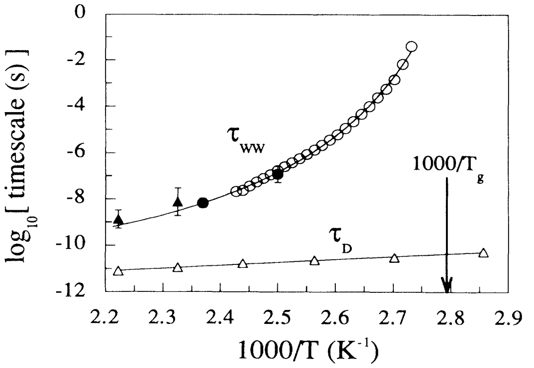

FIG. 4. Temperature dependence of the relaxation times τ_D and τ_{WW}: (△)τ_D and (▲)τ_{WW} from TOF neutron scattering at $Q = 1.5$ Å^{-1}; (●)τ_{WW} from neutron backscattering at $Q = 1.5$ Å^{-1}; and (○)τ_{WW} from dielectric spectroscopy.

IN13 [11]. It is also interesting to point out that the value of n now obtained fits even better the correlation between n and β ($n\beta \cong 2$) previously found by us in several glass-forming polymers [11].

The temperature behavior of the relaxation times τ_D and τ_{WW} at $Q = 1.5$ Å^{-1} is shown in Fig. 4 together with previous results of $\tau_{WW}(T)$ obtained by IN10 and IN13 backscattering instruments ($Q = 1.5$ Å^{-1}) and wide frequency range dielectric spectroscopy [11]. The temperature dependence of τ_D follows an Arrhenius-like behavior with an activation energy of 6 kcal/mol. This value is in the range we can expect for the energy barrier for internal rotation isomerism in polymers like PVC [14]. The values of τ_{WW} obtained at 450 and 430 K and $Q = 1.5$ Å^{-1} follow, within the experimental error, the same temperature dependence of the τ_{WW} obtained by backscattering techniques at 420 and 400 K and $Q = 1.5$ Å^{-1}, as well as the temperature dependence of the dielectric data. Therefore, the results obtained by TOF confirm the results obtained for α relaxation in a different time scale by backscattering techniques.

As we mentioned in the introduction the fast process observed by TOF in other systems [3-6] was mainly identified with the β process predicted by the MCT [7]. This process should be observed as a power-law time decay of the intermediate scattering function in a time range $t \gtrsim 10^{-12}$ s. However, the intermediate scattering function of the fast process measured by us clearly follows an exponential time decay (Debye behavior) which in fact is only observable until the crossover time $t_c \approx 2 \times 10^{-12}$ s. Then this process cannot be identified with the β process of the MCT, at least in PVC.

Our high-temperature results also give clear support to a scenario we previously proposed [15] for explaining the Q dependence found for the KWW relaxation times ($\tau_{WW} \propto Q^{-2/\beta}$). This scenario was based on the so-called "coupling model" of Ngai for describing dynamical processes in complex correlated systems. This scheme assumes that below a characteristic time t_c a given relaxing unit behaves as if uncoupled from the system (Debye-like "primitive motion"). At higher times, the effects of correlations set in and the dynamics is modified towards a KWW behavior. The order of magnitude of t_c is not given in the model but it is supposed to be shorter than 10^{-10} s. In this framework, our results can be considered as the first experimental determination of this critical time which was proposed a long time ago.

To conclude, a clear crossover from a Debye-like to a non-Debye behavior is for the first time observed in the intermediate scattering function characterizing the dynamics of a glass-forming polymer above T_g. The crossover time appears to be Q and T independent. These results furnish a new way to understand the fast dynamics of glass-forming systems, but also raise new questions which should be addressed in the future. The microscopic mechanism driving the crossover at t_c is of particular importance.

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