Correlation between Non-Debye Behavior and Q Behavior of the α Relaxation in Glass-Forming Polymeric Systems

J. Colmenero, A. Alegría, and A. Arbe
Departamento de Física de Materiales, Universidad del País Vasco, Apartado 1072, 20080 San Sebastián, Spain

B. Frick
Institute Max von Laue-Paul Langevin (ILL), Grenoble, France

(Received 11 November 1991)

By means of quasielastic neutron scattering we have shown that the dynamics of the α relaxation on three different polymeric glasses shows a clear non-Debye behavior on a mesoscopic time scale. The spectral shape is found to be independent of temperature and momentum transfer (Q). The characteristic relaxation time follows a power-law Q dependence, $\tau(Q)\propto Q^{-n}$ ($n>2$), n being dependent on the system. We found that the Q behavior and the non-Debye behavior are directly correlated. These results have important implications concerning the physical mechanisms behind the dynamics of the α relaxation.

PACS numbers: 64.70.Pf, 61.12.Ex

The dynamics of the α relaxation in glass-forming systems above and near their glass-transition temperature range has been a subject of increasing interest over the past several years. It is now experimentally well established that the shape of the relaxation function characterizing the dynamics of the α relaxation shows a clear non-Debye behavior. In the time domain this behavior can be well described by means of the Kohlrausch-Williams-Watts "stretched exponential" function $\phi(t)=\exp[-(t/\tau_{\rm WW})^{\beta}]$ [1], which can be derived from different theoretical models. Here $\tau_{\rm WW}$ is a characteristic relaxation time and β is a shape parameter ranging between 0 and 1. In the frequency domain, several empirical forms have been proposed to describe the non-Debye behavior, the most general being the Havriliak-Negami relaxation function $\Phi^*(\omega)=[1+(i\omega\tau_{\rm HN})^{\alpha}]^{-\gamma}$ [2]. Here α and γ are two shape parameters $0<\alpha,\gamma<1$ and $\tau_{\rm HN}$ is a relaxation time. However, almost nothing is known about the Q dependence of the shape parameters and the relaxation times which characterize the dynamics of the α relaxation (Q being the modulus of the change of the wave vector in a scattering experiment). Results from photon correlation spectroscopy (a light scattering time-domain technique) suggest that the characteristic magnitudes of the α relaxation do not depend noticeably on Q at the small-Q values covered in such experiments ($Q\sim10^{-3}$ Å^{-1}) [3]. Information about the Q behavior of the α relaxation in a mesoscopic time scale (10^{-10}–10^{-7} s) can be obtained by means of quasielastic neutron scattering in a high-Q range roughly between 0.1 and 5 Å^{-1}. Several papers have been published recently in the field of the dynamics of glass-forming systems studied by neutron scattering techniques [4–7]. However, most of these studies aim to check the mode-coupling theories of the glass transition. In a previous paper [8] we reported preliminary results corresponding to a glass-forming polymeric system poly(vinyl methyl ether), PVME. In this Letter we report on incoherent quasielastic neutron scattering measurements performed on three structurally different glass-forming polymeric systems including PVME. We have focused our attention on the Q dependence of the magnitudes characterizing the dynamics of the α relaxation.

The samples investigated were poly(vinyl methyl ether), poly(vinyl chloride) (PVC) and poly(bisphenol A, 2-hydroxypropylether) (PH). These glass-forming polymeric systems have the advantage that they do not crystallize, allowing us to explore a wide temperature range above the glass-transition temperature T_g. However, for PVC, we are limited both in temperature and measuring time due to the known tendency of PVC to degrade chemically above T_g. On the other hand, for this polymer extreme non-Debye behavior ($\beta\cong0.2$) is reported by dielectrical and mechanical spectroscopies [9,10] (see Table I), a feature which we show to be very crucial for our studies. We have checked by dielectric spectroscopy that the thermal treatment followed during the neutron scattering measurements does not noticeably affect the shape and temperature behavior of the relaxation function. The glass-transition temperatures were determined by differential scanning calorimetry and were found to be $T_g=250$ K (PVME), $T_g=350$ K (PVC), and $T_g=358$ K (PH).

Incoherent quasielastic neutron scattering measurements were carried out using the neutron backscattering spectrometers IN10 and IN13 at the Institute Laue Langevin (ILL) in Grenoble. The incident wavelengths used by us were $\lambda=6.28$ Å (IN10) and $\lambda=2.23$ Å (IN13), giving energy resolutions of $\delta E\sim1$ μeV and $\delta E\sim8$ μeV, respectively. The Q range covered was roughly between 0.2 and 2 Å^{-1} on IN10 and 0.2 and 5.4 Å^{-1} on IN13. The samples (thickness 0.15 mm) were placed in a cylindrical Al container yielding a transmission of about 85%. Typical measuring times at each temperature were 24 h for IN10 and 36 h for IN13. The initial data treatment was carried out in the normal way, correcting for effects of detector efficiencies, scattering from the sample container, and instrumental background. The experimental curve for the incoherent scattering function $S(Q,\omega)$ was finally obtained at each temperature as a function of the frequency change on scattering, ω, and the modulus of the change of wave vector, Q.

As a result of the fact that we used protonated samples we mainly observed the incoherent scattering arising from the self-correlation function which involves the motion of protons. In the α-relaxation range, the dynamics of the polymers investigated was detected by neutron scattering as a quasielastic broadening at temperatures higher than T_g+50 K. Figure 1 shows typical spectra corresponding to the polymers investigated. The spectral shape of all experimental data is clearly not well described by a single Lorentzian function, i.e., by the Fourier transformation of a simple exponential relaxation function in time. Thus, as for other neutron scattering experiments on different glass-forming systems [4–7], we observe non-Debye relaxation on a microscopical scale. A stretched exponential or Kohlrausch-Williams-Watts (KWW) function is an appropriate representation of the relaxation in time. It is well known that the analytical Fourier transformation of the KWW function does not exist. However, we have shown in a previous paper [11] that the numerical Fourier transformation of the KWW functions can be well described by a family of Havriliak-Negami (HN) functions. In that paper we obtained, by numerical calculation, empirical relationships between the HN parameters (α, γ, and $\tau_{\rm HN}$) and the corresponding KWW ones (β and $\tau_{\rm WW}$). These can be expressed as

$$\log_{10}\left[\frac{\tau_{\rm HN}}{\tau_{\rm WW}}\right]=2.6(1-\beta)^{0.5}\exp(-3\beta)\,, \tag{1a}$$

$$\alpha\gamma=\beta^{1.23}\,,\quad \gamma=0.3[1-\log_{10}(1-\alpha)]\,. \tag{1b}$$

Therefore, in order to analyze the scattering data, we have followed the same procedure we described for PVME in Ref. [8]. We express the scattering function $S(Q,\omega)$ in terms of the imaginary part of the HN relaxation function $\Phi^*(\omega)$,

$$S_{\rm HN}(Q,\omega)\propto -(1/\omega)\,{\rm Im}(\{1+[i\omega\tau_{\rm HN}(Q,T)]^{\alpha}\}^{-\gamma})\,, \tag{2}$$

and fit the experimental data directly in frequency. However, we have restricted our analysis to the HN family of functions which can be considered to be good analytical approximations of the Fourier transforms of the KWW functions. Therefore, although we use an HN scattering function, our procedure implies that we are actually assuming a KWW functional form for the intermediate scattering function, i.e., only one independent shape parameter.

The values of α and γ (or equivalently β) and the values of $\tau_{\rm HN}(Q,T)$ were determined from the fitting of the experimental data by means of Eq. (1), allowing in addition for a flat background. Possible explanations for the latter are widely discussed in Ref. [8]. In order to check the Q dependence of the shape of the relaxation function, we have carried out a systematic test of the standard deviations between experimental data and the fitting model function at different Q values (as in Ref. [8]). We have found that the value of β at which the minimal deviations occur appears to be not only independent of Q but also weakly dependent on temperature within the experimental uncertainties. Thus, the only Q- and T-dependent parameter becomes the relaxation time. This finding agrees with results from relaxation techniques, which also gave a temperature-independent spectral shape [8]. Moreover, it is also important to point out that data corresponding to different instruments, i.e., different energy windows, are reasonably well described by the same shape parameters. We have summarized the fit results for the shape parameters in Table I. The error bars on β have been estimated by taking into account different fitting curves coresponding to different Q values and temperatures. The spectral shape parameters found are similar to the values found by relaxation techniques

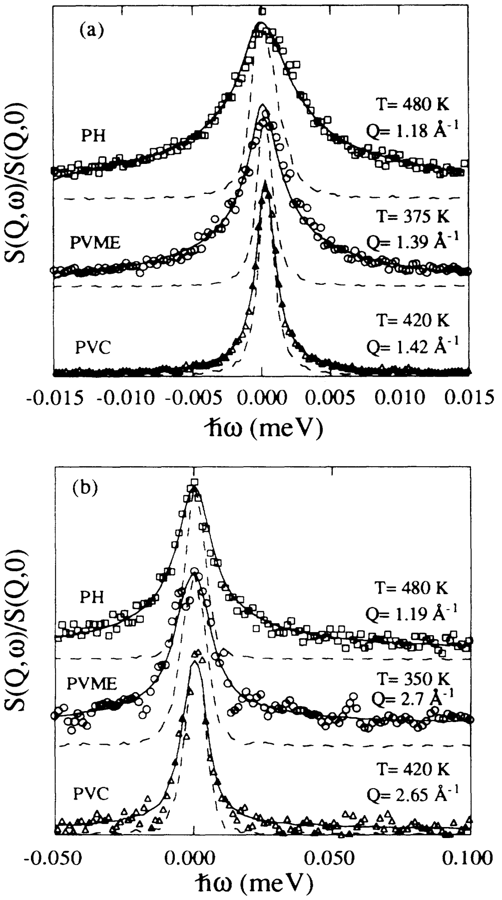

FIG. 1. Normalized $S(Q,\omega)$ measured by (a) IN10 and (b) IN13. Solid lines are the fitted curves obtained through the $S_{\rm HN}(Q,\omega)$ with the parameters shown in Table I. The measured resolutions are also shown for comparison (dashed lines).

TABLE I. Parameters characterizing the non-Debye behavior (α and γ or β) and the Q behavior (n) of the α relaxation obtained from neutron scattering. $^*\beta$ refers to β values obtained from relaxation techniques.

Polymer	α	γ	β	$^*\beta$	n	$n\beta$
PVME	0.68	0.65	0.44 ± 0.02	0.44 [a]	3.8 ± 0.4	1.7 ± 0.3
PH	0.76	0.42	0.40 ± 0.02	0.44 [b]	4.6 ± 0.4	1.8 ± 0.3
PVC	0.47	0.38	0.23 ± 0.03	0.21–0.27 [c]	9.5 ± 1.0	2.2 ± 0.5

[a] Reference [8].

[b] Reference [12].

[c] References [9,10].

for these polymers [8–10,12]. They are also shown in Table I for comparison.

The values of $\tau_{\rm HN}(Q,T)$ obtained from fitting of experimental spectra as described above have been plotted in Fig. 2 on a double-log plot. The Q behavior found is almost independent of the temperature for the three polymers investigated, at least in the temperature range measured and within the experimental errors involved (errors estimated by us are shown as error bars in Fig. 2). This implies that the Q and temperature dependence of $\tau_{\rm HN}$ may be factorized as $\tau_{\rm HN}(Q,T)=a(T)\bar{\tau}(Q)$, allowing construction of a master curve $\bar{\tau}(Q)$ formed by shifting the curves for different temperatures by a factor $a(T)$ on a logarithmic τ scale. This is done in Fig. 3, using arbitrary reference temperatures T_R. Within the experimental errors, we may describe the Q dependence of the relaxation times, $\bar{\tau}(Q)$, by a power law $\bar{\tau}(Q) \propto Q^{-n}$ indicated by the straight lines in Fig. 3. The results for n are summarized in Table I. Errors in n shown in the table are the maximum errors estimated taking into account all the error sources involved.

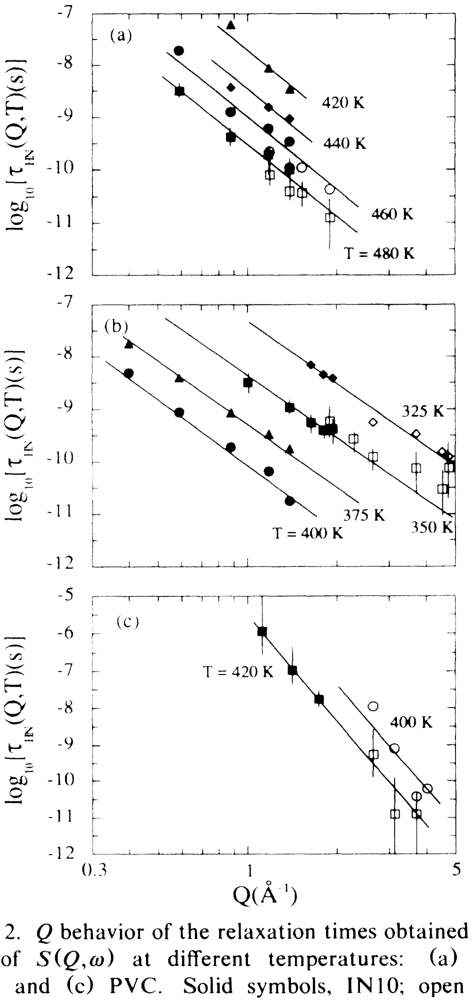

FIG. 2. Q behavior of the relaxation times obtained from the fitting of $S(Q,\omega)$ at different temperatures: (a) PH, (b) PVME, and (c) PVC. Solid symbols, IN10; open symbols, IN13. Solid lines for each sample are obtained from a linear-regression fit from the highest-temperature data.

Our results imply a stretched exponential intermediate scattering law

$$I(Q,t)=\exp\{-[t/\tau(Q,T)]^{\beta}\} \qquad (3)$$

for incoherent scattering, where the Q dependence of $\tau(Q,T)$ is given by $\bar{\tau}(Q)\propto Q^{-n}$. Therefore, Eq. (3) can be rewritten as

$$I(Q,t)=\exp(-Ct^{\beta}Q^{n\beta}), \qquad (4)$$

where C is a constant which depends only on temperature. The Q dependence of $I(Q,t)$ is given by the exponent $n\beta$, a product which we find to be close to 2 for all three polymers (even for the extreme case of PVC) as

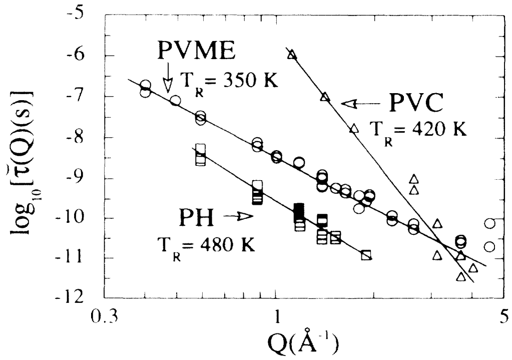

FIG. 3. $\bar{\tau}(Q)$ master plot for the three systems investigated at the reference temperatures shown. Solid lines are linear-regression fits showing the Q dependence of the relaxation times.

may be seen in Table I. Thus our experimental finding suggests that the time and Q (spatial) behaviors, i.e., the β and n values, are directly correlated. This correspondence between β and n would also explain earlier neutron scattering data [13], without evoking the Rouse model, which is unrealistic at such high Q values. The results obtained, summarized by Eq. (4), have important implications which cannot be derived only from the time dependence of the relaxation function.

First of all, since $n\beta \cong 2$, we can consider that $I(Q,t)$ approximately follows a Gaussian-like behavior [14] $I(Q,t) = \exp[-Q^2\langle r^2(t)\rangle]$, where $\langle r^2(t)\rangle$ is the mean-squared displacement. This is not a trivial result. The Gaussian form can be shown to hold exactly only in certain special cases: a harmonic crystal, an ideal gas, and a system for which the motion of the atoms is governed by Langevin's equation [14]. Furthermore it holds rigorously in any case only for $t \rightarrow 0$, because the atoms behave as if they were free. Our experimental results are the first experimental evidence showing that the Gaussian approximation approximately holds for the dynamics of the α relaxation in glass-forming polymer melts. In the framework of the Gaussian approximation, our results indicate that $\langle r^2(t)\rangle \propto t^\beta$, implying anomalous diffusion of the scattering centers, similar to observations made for different diffusion processes in disordered systems [15].

On the other hand, the KWW normalized relaxation function can be alternatively written as a Laplace transform. This suggests the explanation of the stretching of the relaxation function as a superposition of elementary processes each one following a Debye time behavior. When we take into account not only the time dependence but also the Q behavior, the KWW normalized relaxation function is replaced by the intermediate scattering function $I(Q,t)$, which from our results is given by Eq. (4). Moreover, for small Q values, the intermediate scattering function corresponding to any elementary process we could consider (continuous diffusion, jump diffusion, diffusion and trapping, etc.) can be approximated by a single exponential function $\exp(-DQ^2t)$, where D is a diffusion coefficient [14]. Therefore, the intermediate scattering function resulting from the superposition of such processes should be written as

$$I(Q,t) = \int_{-\infty}^{\infty} \rho(Q,\ln D)\exp(-DQ^2t)\,d(\ln D)\,, \qquad (5)$$

where $\rho(Q,\ln D)$ gives the probability of each Debye process. If one considers this possibility for explaining the stretching of the α relaxation, our results should imply strong restrictions on the Q dependence of $\rho(Q,\ln D)$. For example, we have found a Q-independent spectral shape (β value) for the three polymers investigated. If Eq. (5) is considered, this should imply that the shape of the probability distribution $\rho(Q,\ln D)$ should not change with the Q value. This in fact implies that $\rho(Q,\ln D) = \rho(\ln[Df(Q)])$. Here $f(Q)$ is a function that accounts for the shifting of $\rho(Q,\ln D)$ on the $\ln D$ axis. If one considers as the simplest case that $f(Q)$ is a constant, the Q dependence of $\ln[I(Q,t)]$ [Eq. (5)] will always be less than Q^2 in the same way that the time dependence is less than t. Therefore, in this case we could reproduce the stretching in the time behavior of the experimental $I(Q,t)$, but never the Q behavior ($Q^{n\beta}$, $n\beta \cong 2$) that is found. This Q behavior would only be reproduced by taking into account a $f(Q)$ whose functional form should depend on the n or β value. However, this point would need a deeper analysis which falls outside the goal of this paper.

In summary, we have obtained that the dynamics of the α relaxation of glass-forming systems, investigated on a mesoscopic time scale, shows a clear non-Debye behavior. The spectral shape is found to be independent of temperature and momentum transfer within the observed range. Moreover, the characteristic relaxation time follows a power-law Q dependence. Both signatures appear to be directly correlated, implying sublinear diffusion characterized by a power-law time decay of the mobility.

[1] G. Williams and D. C. Watts, Trans. Faraday Soc. **66**, 80 (1970).

[2] S. Havriliak and S. Negami, Polymer **8**, 161 (1967).

[3] G. Fytas, G. Fluodas, and K. L. Ngai, Macromolecules **23**, 1104 (1990).

[4] F. Mezei, W. Knaak, and B. Farago, Phys. Rev. Lett. **58**, 571 (1987); W. Knaak, F. Mezei, and B. Farago, Europhys. Lett. **7**, 529 (1988); F. Mezei, J. Non-Cryst. Solids **131–133**, 317 (1991).

[5] B. Frick *et al.*, Z. Phys. B **70**, 73 (1987); D. Richter, B. Frick, and B. Farago, Phys. Rev. Lett. **61**, 2465 (1988); B Frick, B. Farago, and D. Richter, Phys. Rev. Lett. **64**, 2316 (1990).

[6] W. Doster, S. Cusak, and W. Petry, Phys. Rev. Lett. **65**, 1080 (1990).

[7] F. Fujara and W. Petry, Europhys. Lett. **4**, 921 (1987); E. Bartsch *et al.*, Ber. Bunsenges. Phys. Chem. **93**, 1252 (1989); W. Petry *et al.*, Z. Phys. B **83**, 175 (1991).

[8] J. Colmenero *et al.*, Phys. Rev. B **44**, 7321 (1991).

[9] J. J. del Val *et al.*, Makromol. Chem. **190**, 3252 (1989).

[10] D. J. Plazek and K. L. Ngai, Macromolecules **24**, 1222 (1991).

[11] F. Alvarez, A. Alegría, and J. Colmenero, Phys. Rev. B **44**, 7306 (1991).

[12] A. Alegría, E. Macho, and J. Colmenero, Macromolecules **24**, 5196 (1991).

[13] G. Allen *et al.*, Chem. Soc. Faraday Trans. II **78**, 2117 (1982).

[14] T. Springer, *Quasielastic Neutron Scattering for the Investigation of Diffusive Motions in Solids and Liquids* (Springer-Verlag, Berlin, 1972).

[15] K. L. Ngai, Comments Solid State Phys. **9**, 127 (1979); **9**, 141 (1980).