Secondary relaxation in o-terphenyl glass

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We have measured the dielectric response, $\bar{\varepsilon}(\omega)$, in o-terphenyl due to the secondary relaxations that occur below the glass-transition temperature. We have found that the imaginary part of $\bar{\varepsilon}(\omega)$ has a log-normal shape that can be ascribed to a Gaussian distribution of barrier heights. The width of this distribution increases slightly as the temperature is lowered. The peak position shifts in an Arrhenius manner with temperature as was reported previously by Johari and Goldstein. The data appear to be of different origin from what has also been called β relaxation in mode-coupling theories and light-scattering experiments.

Although many susceptibility studies have investigated the properties of the primary relaxation that occurs as a liquid is supercooled into the glassy state, fewer data are available concerning the secondary relaxations that occur at higher frequencies and below the glass-transition temperature. Studies of the secondary (or β) relaxation in simple glass formers were made by Johari and Goldstein.[1,2] They showed that the frequency of the peak in the imaginary part of the susceptibility followed an Arrhenius (or activated) temperature dependence, $f_p = f_0 e^{-E_0/k_B T}$, as distinct from the primary (or α) relaxation, which can often be fit with a Vogel-Fulcher form, $f_p = f_0 e^{-A/(T-T_0)}$, indicating complete structural arrest at a finite temperature. At temperatures slightly above the glass transition, the α- and β-relaxation processes often have comparable frequencies so that the spectra of the two processes overlap and it is difficult to distinguish the shapes of the two separate contributions. It remains unclear whether these two relaxations merge smoothly with one another as the temperature is increased or whether they intersect abruptly at some finite temperature.[3]

With the advent of mode-coupling theory[4] attempts have been made to calculate the form of the relaxation processes that occur as a liquid is supercooled. This theory predicts that there would be a second slow process in addition to the primary relaxation but at slightly higher frequencies.[5] This process was assumed to be the same as that giving rise to the susceptibility peaks of the type seen by Goldstein and Johari and was called by the same name, β relaxation. Light-scattering experiments on colloidal systems[6] and several molecular glass formers[7] have shown substantial agreement with this theory in the high-frequency regime well above the glass transition. Nevertheless, we are not aware of any conclusive data that confirm that the mode-coupling theories and the scattering experiments are all probing the same phenomenon as had been traditionally designated as β relaxation in the susceptibility data.

Very few studies have addressed the shape of the secondary relaxation at low temperature in the glass phase. Such data might help address the relationship of the different experimental and theoretical investigations. Dielectric studies of the *crystalline* system $(KBr)_x(KCN)_{1-x}$ showed a relaxation process in that system which looked like secondary relaxation in glasses: it occurred in the glassy phase (where the CN molecules were frozen in disordered orientations) and had an Arrhenius temperature dependence.[8] In addition the shape of the peak in the imaginary part of the dielectric response was log normal. This could not be compared with the secondary relaxation in structural glasses since no comparable data existed at that time. Subsequently the secondary relaxation in one glass, a mixture of benzyl chloride and toluene, was also measured to have a log-normal distribution.[9] In the present paper we report data for the shape of the β relaxation in a single-component glass, o-terphenyl.

Using techniques reported elsewhere,[10] we have measured for o-terphenyl the real and imaginary part of the dielectric response, $\bar{\varepsilon}(f) = \varepsilon'(f) + i\varepsilon''(f)$, in the range 10^{-1} Hz $< f < 4 \times 10^4$ Hz. The relaxation peak in the imaginary part can be fit with a log-normal form:

$$\varepsilon''(f) = \frac{\Delta\varepsilon}{\sqrt{\pi}W} \exp[-(\log f - \log f_p)^2/W^2], \qquad (1)$$

where f_p is the frequency of the peak, W is the width [where $\varepsilon''(f_p 10^{\pm W})$ is $1/e$ of $\varepsilon''(f_p)$], $\Delta\varepsilon = (\varepsilon_0 - \varepsilon_\infty)$, and ε_0 and ε_∞ are, respectively, the low- and high-frequency asymptotic values of $\varepsilon'(f)$. In Fig. 1 we show the data for several different temperatures between 150 and 210 K collapsed onto a single master curve showing $\varepsilon''W/\Delta\varepsilon$ versus $(1/W)\log_{10}[f/f_p]$. The solid line is a parabola which indicates a log-normal frequency dependence of the form of Eq. (1). The data fall consistently on the parabola except on the low-frequency side where the primary relaxation processes overlap with the secondary peak and begin to dominate the spectrum. At higher temperatures the two relaxation processes get closer together and this problem becomes more pronounced.

From the high-frequency portion of the data we can determine the parameters f_p and W as a function of temperature. These are shown in Figs. 2(a) and 2(b), respectively. As was observed by Johari and Goldstein,[1] the
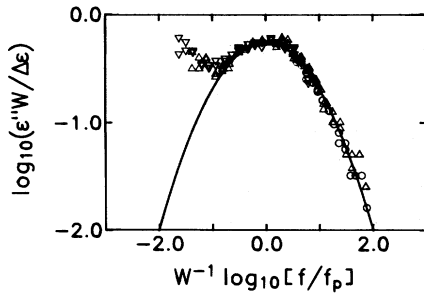
FIG. 1. A master plot of the dielectric data for o-terphenyl showing $\varepsilon''W/\Delta\varepsilon$ vs $W^{-1}\log_{10}[f/f_p]$. The solid curve is a parabola representing a log-normal fit of the form given by Eq. (1) in the text. Each different symbol represents the data taken at a different temperature. The temperature range is from $T=150$ K to $T=210$ K.

peak frequency f_p varies Arrheniusly with temperature: $f_p=f_0 e^{-E_0/k_B T}$ with $E_0/k_B=6217$ K and $f_0=4.2\times10^{15}$ Hz. The large $observed$ value of f_0 is much larger than a typical phonon frequency ($\approx10^{13}$ Hz) and therefore cannot be the $true$ attempt frequency, f_t. However we can interpret the discrepancy between f_0 and f_t, as was done[8] for (KBr)$_x$(KCN)$_{1-x}$, as due to activation over an average energy barrier that decreases linearly with temperature: $\bar{E}=E_0-AT$. This implies a peak frequency that still has an Arrhenius form:

$$f_p=f_t e^{-\bar{E}/k_B T}=(f_t e^{A/k_B})e^{-E_0/k_B T}$$
$$=f_0 e^{-E_0/k_B T} . \tag{2}$$

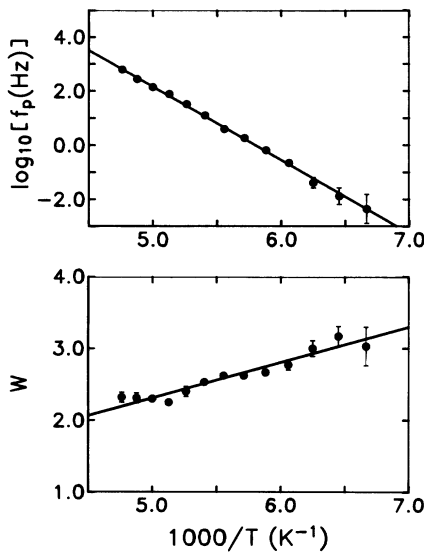In order to produce a physically reasonable value of or-

FIG. 2. Upper curve: The temperature dependence of f_p, the peak position of the imaginary part of $\varepsilon''(f,T)$. The straight line on the $\log_{10}f_p$ vs $1000/T$ plot indicates Arrhenius behavior. Lower curve: The width of the dielectric response peak W as a function of inverse temperature.

der 10^{13} Hz for the $true$ attempt frequency, $f_t\equiv f_0 e^{-A/k_B}$, we must assume that $A/k_B\approx6$.

As is shown in the bottom curve, the width W also depends strongly on temperature. Over the temperature range of our experiment a fit to our data gives $W=-0.15+493/T$. Similar dependence was also seen in the work on (KBr)$_x$(KCN)$_{1-x}$ and benzyl chloride.

We can better understand this behavior if we express the dielectric response as due to activation over energy barriers with a distribution of barrier heights. Thus we take a convolution of a Debye relaxation over a single energy barrier with a distribution of activation energies $P(E)$:

$$\bar{\varepsilon}(f,T)=\varepsilon_\infty+\Delta\varepsilon\int_0^\infty dE\, P(E)\frac{1}{1-i(f/f_t)e^{E/k_B T}} . \tag{3}$$

If we assume that the distribution of activation energies is itself Gaussian:

$$P(E)=(1/\sqrt{\pi}\sigma)e^{-(E-\bar{E})^2/\sigma^2} , \tag{4}$$

we then get

$$\bar{\varepsilon}(f,T)=\varepsilon_\infty+\Delta\varepsilon\int_0^\infty dE\frac{1}{\sqrt{\pi}\sigma}e^{-(E-\bar{E})^2/\sigma^2}$$
$$\times\frac{1}{1-i(f/f_t)e^{E/k_B T}} . \tag{5}$$

If the width of the distribution, σ, is sufficiently broad, this gives a wide approximately log-normal distribution for $\varepsilon''(f)$ with the width in energy, σ, related to the width in frequency, W, by:

$$\sigma/k_B\approx WT\ln(10) . \tag{6}$$

For o-terphenyl, our data for W therefore indicate that $\sigma/k_B=(\sigma_0-BT)/k_B=1135$ K-0.35 T.

The width of the energy distribution decreases linearly with increasing temperature. This is similar to the decrease in the average energy barrier that we proposed above to explain the discrepancy between the large observed value of f_0 and a physically reasonable value for the true attempt frequency f_t. It is plausible to assume that the two phenomena, the postulated decrease in the average energy barrier and the decrease of the width of the distribution, are related. To support this conjecture, we note that the proportional changes in these two quantities are of comparable magnitude: $A/E_0=0.9\times10^{-3}/$ K while $B/\sigma_0=3\times10^{-3}$/K. This is also what was found in a similar analysis of the secondary-relaxation data on the crystalline elastic glasses (KBr)$_x$(KCN)$_{1-x}$. The present sample is a single-component structural glass. As in that system it is tempting to associate the temperature-dependent energy barrier appearing in the secondary relaxation data as a measure of the order parameter at low temperatures of the glass phase.

We must conclude that this β relaxation is different from that probed in the light-scattering experiments[7] and predicted by the mode-coupling theories[5] which display power-law scaling and critical slowing down. We cannot fit our data for the imaginary part of the dielectric

response curve with a simple power law since it has a log-normal shape. (That this holds for the low-frequency side of the spectrum as well as the high-frequency side is shown best for the benzyl chloride sample.[9]) The peak frequency shows no evidence for critical slowing down as T_c is approached but instead increases Arrheniusly with increasing temperature. Although our data are taken at relatively low frequency and correspond to temperatures lower than the mode-coupling transition temperature T_c, we would have had to assume that the shape and temperature dependence of the susceptibility peak changed completely at higher temperature in order for this relaxation to be thought of as being the same phenomenon as that seen by light scattering. Our data are similar to those observed in the neutron spin-echo measurements[11] for the decoupled structural time scale of polybutadiene.

There are now three systems for which the shape of the secondary relaxation has been determined: one (crystalline) orientational glass, $(KBr)_x(KCN)_{1-x}$ and two structural glasses, (i) a mixture of benzyl chloride and toluene and (ii) o-terphenyl. All three cases show an Arrhenius temperature dependence of the peak frequency and a wide log-normal susceptibility curve which can be interpreted naturally in terms of a Gaussian distribution of activation barriers with a slight temperature dependence to its width.

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