# Frequency-Dependent Specific Heat and Thermal Conductivity at the Glass Transition in *o*-Terphenyl Mixtures

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We report frequency-dependent measurements of the specific heat $c_p$ thermal conductivity $\kappa$ of ($o$-terphenyl)$_{1-x}$($o$-phenylphenol)$_x$ mixtures near the glass transition. $\kappa$ is flat and frequency independent and all of the dynamics is contained in $c_p$. The mean relaxation time $\tau$ shows non-Arrhenius behavior and the distribution of times broadens with decreasing temperature. The divergence of both $\tau$ and the width of the distribution is consistent with the Kauzmann temperature.

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As a liquid is cooled through the glass transition and its mean relaxation time grows, the response time of the liquid crosses practical experimental time scales; this invalidates conventional measurements of the thermal properties. When the time scale of the experiment is comparable with the microscopic relaxation time, it becomes difficult to disentangle the specific heat and thermal conductivity from each other.[1,2] Also, conventional cooling-rate experiments are plagued by uncertainties of how to treat a system which is in the process of falling out of equilibrium.[3] Our experimental technique, specific-heat spectroscopy, has been designed precisely to avoid these difficulties and is suitable for measurement of the dynamics of the specific heat and thermal conductivity through the glass transition.[4,5]

The dynamic quantity in which we are interested is the frequency-dependent specific heat $c_p(\nu)$. It is the linear response of the enthalpy of a system in equilibrium to a small temperature oscillation at a frequency $\nu$. $c_p(\nu)$ is a susceptibility analogous to other more familiar susceptibilities (e.g., dielectric susceptibility), and in the limit $\nu=0$, it is the conventional specific heat. Since the slow relaxation observed in a supercooled liquid contributes to its total enthalpy, we can use this technique to study the way in which the distribution of time scales shifts to longer times and broadens as the liquid is cooled toward the glass transition temperature, $T_g$.

The quantity measured with specific-heat spectroscopy is not simply $c_p(\nu)$; it is the frequency-dependent product of the specific heat and thermal conductivity, $c_p\kappa(\nu)$. In the present experiment, we have expanded the technique to decouple the dynamics in $c_p$ and $\kappa$ and have measured $c_p(\nu)$ and $\kappa(\nu)$ separately. We believe that this is the first successful measurement of the thermal conductivity through the glass transition.

In this experiment, we have performed measurements on a range of ($o$-terphenyl)$_{1-x}$($o$-phenylphenol)$_x$ mixtures in an attempt to study the glass transition in pure $o$-terphenyl. We have investigated whether the mean relaxation time $\tau$ is diverging at a nonzero temperature, consistent with the existence of an equilibrium glass phase, or at $T=0$. An observation in favor of the former possibility was made by Kauzmann[6]; he noted that for most glass formers, an extrapolation of the supercooled liquid entropy below $T_g$ crosses the associated crystalline value at a nonzero Kauzmann temperature $T_K$. This implies that the equilibrium liquid must change in some way at, or above, $T_K$ to avoid this catastrophe. For many glass-forming liquids it appears that $\tau$ is diverging with a Vogel-Fulcher form, $\tau=\tau_0\exp[A/(T-T_0)]$, with $T_0\sim T_K$. This suggests that $T_K$ plays a role in both the dynamics and the statics of the glass transition. For $o$-terphenyl, it is possible that $\tau$ crosses over to Arrhenius behavior, $\tau=\tau_0\exp(A/T)$, near $T_g$ as has been observed in viscosity data on other fragile glass formers.[7,8] We have taken data at low frequency near $T_g$ to resolve this issue.

Specific-heat spectroscopy is a technique that exploits a simple geometry where a thin-film ribbon heater immersed in the sample liquid also acts as the thermometer.[4] By measuring the temperature oscillation in the heater due to an ac power generated in it at a frequency $\nu$, we obtain both the real (in-phase) and imaginary (out-of-phase) components of $c_p\kappa(\nu)$ for the liquid. The asymptotic analysis that we use to obtain $c_p\kappa(\nu)$ assumes a plane heater of infinite extent; this is valid as long as the thermal wavelength of the liquid, $\lambda=(\kappa/4\pi\nu c_p)^{1/2}$, is much smaller than the heater width, $w$. We exploit the deviations from the asymptotic behavior due to this finite-size effect in order to decouple $c_p$ and $\kappa$.

This technique requires very slow cooling ($\simeq$1-3 K/h) through temperatures above the dispersion region where the viscosity is low. This has forced us to add an impurity material, $o$-phenylphenol, to suppress crystallization. $o$-phenylphenol does this better, and shifts the glass transition less, than any of the impurities for $o$-terphenyl mentioned in the literature.[9] We have made measurements over a range of concentrations, $x$, and extrapolated our results to the case of pure $o$-terphenyl.

We have performed specific-heat spectroscopy measurements on four concentrations: $x=0.09$, 0.16, 0.22,

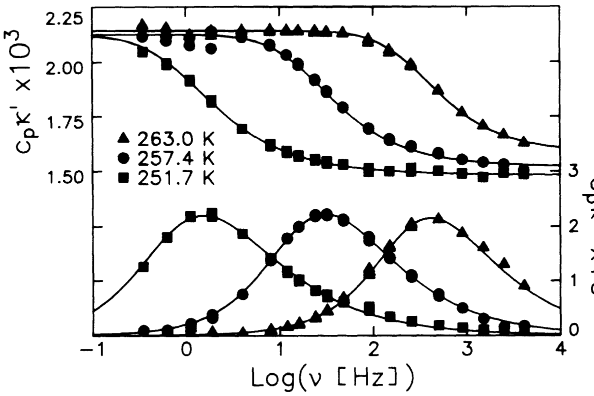

FIG. 1. The real ($c_p\kappa'$) and imaginary ($c_p\kappa''$) parts of $c_p\kappa$ ($J^2/K^2cm^4$ s) vs log($\nu$) at three temperatures for the $x=0.09$ sample. The curves are best fits to the data with the Williams-Watts form.

and 0.33 by weight. The measurements on the three higher concentrations were made with a single heater and cover the range 2.5 Hz $< \nu <$ 5 kHz; the measurements on the $x=0.09$ sample were made with three heaters of differing width and cover the range 0.02 Hz $< \nu <$ 5 kHz. In Fig. 1, we show the real ($c_p\kappa'$) and imaginary ($c_p\kappa''$) parts of $c_p\kappa(\nu)$ vs log($\nu$) for the $x=0.09$ sample at three temperatures. As can be seen from the data, the relaxing component of $c_p\kappa$ is asymmetrical and slows down with decreasing $T$. These features are typical of susceptibility measurements at the glass transition. Except for a shift in the position of the dispersion region, the data for the other concentrations are qualitatively the same.

The curves drawn through the $c_p\kappa''(\nu)$ data are best fits by use of a Williams-Watts form: The Fourier transform of $d\{\Delta(c_p\kappa)\exp[-(2\pi\nu_0 t)^\beta]\}/dt$ where $\Delta(c_p\kappa) = [c_p\kappa(\nu=0) - c_p\kappa(\nu=\infty)]$. We also tried fitting the data with the Davidson-Cole[10] form but found that the Williams-Watts form is better for all $T$ and $x$. The curves drawn through the $c_p\kappa'(\nu)$ data are obtained by use of the parameter values obtained from the $c_p\kappa''(\nu)$ data and by allowing $c_p\kappa(\nu=\infty)$ to be the only additional fitting parameter. The quality of the $c_p\kappa'(\nu)$ fits confirms that our data obey the Kramers-Kronig relations.

In Fig. 2(a), we show the logarithm of the mean relaxational frequency obtained from the Williams-Watts fits, log($\nu_0$) versus $1/T$, for all four $x$ (the lowest-frequency data for the $x=0.09$ sample, open triangles, were obtained from the peak positions after suitable correction for the finite-size heater effect and the asymmetry of the peaks). We can see from the data that the relaxation is behaving in a non-Arrhenius fashion and that the impurity has the effect of smoothly decreasing $T_g$ while not appearing to effect the form of the divergence; even at $x=0.33$, $T_g$ has decreased less than 12 K.

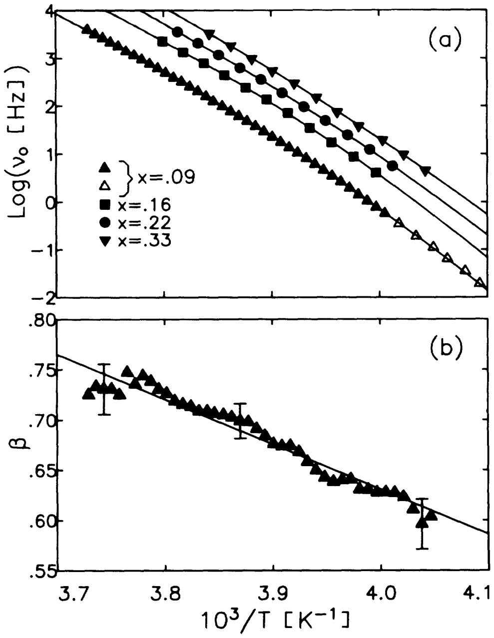

FIG. 2. (a) The logarithm of the mean relaxational frequency obtained from the Williams-Watts fits, log($\nu_0$), vs $1/T$ for all four $x$. The curves are best fits to the data with the Vogel-Fulcher form. The fitting parameters are listed in Table I. (b) The Williams-Watts fitting parameter, $\beta$, vs $1/T$ for the $x=0.09$ sample. The curve is the best fit with a form linear in $1/T$.

The curves in Fig. 2(a) are best fits to the data using a Vogel-Fulcher form, $\nu_0 = \nu_f \exp[-A_f/(T-T_0)]$; the fitting parameters are listed in Table I. To check whether or not the relaxation is crossing over to Arrhenius behavior near $T_g$, we have done a sliding three-decade Vogel-Fulcher fit to the $x=0.09$ data and have found that the fitting parameters are constant over the range of the measurement. This implies that the relaxation is not crossing over to an Arrhenius form. The divergence temperature for pure $o$-terphenyl obtained by linear extrapolation from our data is $T_0 = 184 \pm 13$ K; this value is consistent with the predicted Kauzmann temperature for $o$-terphenyl obtained from calorimetry data: $T_K = 200 \pm 10$ K.[11]

The data in Fig. (2a) can be fitted equally well by a scaling law $[\nu_0 = \nu_s(T/T_s - 1)^\alpha]$; however, the exponent $\alpha$ is very large ($\alpha \simeq 20$). Recent work indicates that the

TABLE I. Fitting parameters for the data in Fig. 2(a) with the form $\nu_0 - \nu_f \exp[-A_f/(T-T_0)]$.

| $x$ | $T_0$ (K) | $A_f$ (K) | log($\nu_f$) |
|---|---|---|---|
| 0.09 | 177 ± 6 | 3175 ± 320 | 18.7 ± 1.3 |
| 0.16 | 186 ± 12 | 2397 ± 590 | 16.9 ± 2.1 |
| 0.22 | 172 ± 13 | 3436 ± 820 | 20.2 ± 2.3 |
| 0.33 | 164 ± 15 | 4154 ± 900 | 22.2 ± 2.8 |

hydrodynamic theories that suggest this form are not applicable in this high-viscosity regime.[12] These data are also fitted well with an Adams-Gibbs form,[13], $\nu_0 = \nu_g \times \exp(-A_g/T\Delta S)$, where we obtain the configurational entropy $\Delta S$ from our $\Delta c_p\kappa(T)$ data assuming a constant $\kappa$. (This is still a three-parameter fit since $\Delta S$ includes an unknown constant of integration.)

For some glass formers (e.g., glycerol[4,14] and propylene glycol[4]), relaxation widths appear to be independent of temperature near $T_g$; for our measurements on *o*-terphenyl this is not the case. For all four $x$, the width of the relaxation in $\log(\nu)$ increases with decreasing $T$. In Fig. 2(b), we plot the Williams-Watts fitting parameter $\beta$ {which is proportional to 1/[width in $\log(\nu)$]} vs $1/T$ for the $x=0.09$ sample. The other concentrations show the same general behavior. This strong temperature dependence of $\beta$ shows that, for this material, it is incorrect to use a "time-temperature superposition principle" to map all the data onto a single curve. This is a common practice when one is dealing with relaxation phenomena[14] and has even been used (we believe inappropriately) in an analysis of the dielectric response of *o*-terphenyl itself.[9]

We have fitted the data in Fig. 2(b) with some simple forms to see how the width of the relaxation will behave at lower temperature if the observed trend continues. Fitting the data by a form linear in $1/T$ [shown in Fig. 2(b)] gives an extrapolation to $\beta=0$ at $T=185\pm11$ K (fitting by a form linear in $T$ gives an extrapolation to $\beta=0$ at $T=155\pm11$ K). This suggests that $\beta$ for the $x=0.09$ sample is approaching zero at a temperature consistent with the sample divergence temperature, $T_0=177\pm6$ K. Predictions of the free-volume theory[15] set a lower limit of $\beta=\frac{2}{3}$ for relaxations in $c_p$; our data have already surpassed this limit and the trend does not appear to be saturating. In addition, there is a recent theory[16] of the glass transition that predicts that $\beta=\frac{1}{3}$ at $T=T_0$. The trend in our data suggests a lower value, perhaps even zero, at $T_0$.

In addition to measuring $c_p\kappa(\nu)$, we have obtained $c_p(\nu)$ and $\kappa(\nu)$ vs $T$ separately over the range 0.35 Hz $< \nu <$ 1.9 Hz for the $x=0.09$ sample. We have done this by exploiting the deviations from the asymptotic behavior due to finite heater width. The solution to the ac heat diffusion equation for the case of a finite-width heater in the regime $\lambda/w \ll 1$ contains an additional phase shift, $\Phi=\lambda/2w$, in the measured signal. Thus, by taking the difference in phase shift for runs with different heater widths, we obtain a term that is proportional to $\lambda=(\kappa/4\pi\nu c_p)^{1/2}$. Since we have accurate $c_p\kappa$ data in this frequency range from the widest heater, we can solve for $\kappa$ and $c_p$ independently. Because of the difficulties in measuring *absolute* phase shifts with the necessary precision, we have based our analysis on the measurement of relative phase; this requires a knowledge of the value of $\kappa$ at a reference temperature ($T=265$ K) outside the dispersion region in order to solve for $\kappa$ through the dispersion region uniquely.

We have obtained $\kappa(T=265\text{ K})$ by two independent methods. There is high-temperature (300 K $< T <$ 400 K) $\kappa$ data for *o*-terphenyl[17] which extrapolates to $\kappa(T=265\text{ K}) = 0.00138$ J/s K cm. In addition, we have divided our $c_p\kappa$ data for the $x=0.09$ sample by $c_p$ data from calorimetry measurements on pure *o*-terphenyl[11] and have obtained $\kappa(T=265\text{ K})=0.00135$ J/s K cm. The excellent agreement of these two values gives us confidence in using an intermediate value of $\kappa(T=265\text{ K})=0.00136$ J/s K cm in our analysis.

In Fig. 3 we show the results for $\kappa$ vs $T$ and the magnitude of the specific heat $|c_p|$ versus $T$ for $\nu=0.35$ Hz and $\nu=1.12$ Hz. $\kappa$ is flat and frequency independent through the glass transition and the dynamics observed in $c_p\kappa$ is entirely due to the dynamics in $c_p$. This agrees with computer simulations of model glasses.[18] Previous measurements of $\kappa$ that have not properly accounted for the dynamic nature of $c_p$ typically have a peak structure in $\kappa$ through the dispersion region[1,2]; our results show that this structure is spurious.

Since we have shown that $\kappa$ is flat across the glass transition, we conclude that the same mechanism is responsible for $\kappa$ both in the liquid and in the glass. Alexander, Entin-Wohlman, and Orbach[19] have postulated that at high temperature in the glass, $\kappa$ is determined by phonon-assisted fracton hopping. If this is indeed true, our results imply that fractons must exist in the liquid. We find this implausible.

Our specific-heat spectroscopy measurements on the glass transition in $(o\text{-terphenyl})_{1-x}(o\text{-phenylphenol})_x$ mixtures indicate that the relaxation appears to be diverging at a temperature consistent with $T_K$. We also have found that the relaxation broadens rapidly with decreasing temperature consistent with $\beta=0$ at $T=T_0$. There have been few detailed studies of relaxation widths at such low frequencies near $T_g$. Indeed, the most care-

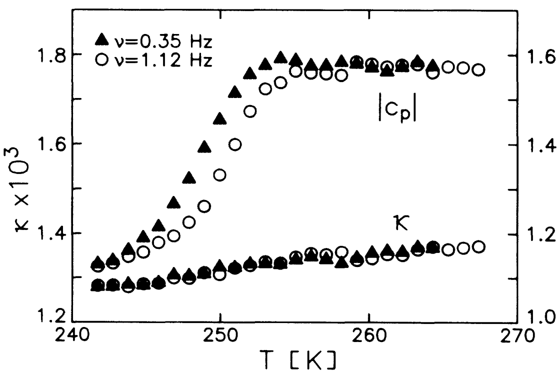

FIG. 3. The thermal conductivity, $\kappa$ (J/s K cm), and the magnitude of the specific heat, $|c_p|$ (J/K cm$^3$), vs $T$ for the $x=0.09$ sample at $\nu=0.35$ and 1.12 Hz.

ful analysis of differential-scanning-calorimetry experiments[3,20] has assumed a temperature-*independent* value of $\beta$ to interpret the strongly nonlinear response measured by that technique. Clearly, our results cast doubt on the general validity of this assumption and indicate that a much more complicated analysis of that data must be made when no independent information exists about $\beta(T)$. It is not clear how such an analysis would proceed. We intend to see if this strong temperature dependence of $\beta$ is peculiar to *o*-terphenyl or if it is typical of fragile[8] glass formers in general. We will also investigate whether this broadening is seen with susceptibility probes other than $c_p(\nu)$.

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