Specific-Heat Spectroscopy of the Glass Transition

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The glass transition has historically been viewed as an anomaly involving the specific heat of supercooled liquids. It is also associated with a divergence of the relaxation times for liquid rearrangements. We have developed a new spectroscopy to study the frequency dependence of the specific heat of liquids which connects these two approaches. We report measurements as a function of temperature of the distribution of relaxation times which are directly responsible for the glass transition in glycerol.

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When a liquid is supercooled below its equilibrium freezing temperature it can either nucleate into a crystal or, if cooled sufficiently far, it can form an amorphous solid called a glass. The transition between the supercooled liquid and the glass, the glass transition, has been treated by various theoretical approaches and different authors have suggested that this is a first-order,[1] second-order,[2] or even a third-order[3] phase transition. Still others have claimed that there is no true phase transition at all.[4] In real experiments the underlying thermodynamics are masked by kinetic effects, so that static equilibrium measurements cannot be obtained as a result of diverging relaxation times.

The specific heat, c_p, is of particular importance since it is the basis for the Kauzmann paradox,[5] one of the clear indications that some sort of transition must occur between the liquid and the glass. The specific heat of the supercooled liquid is greater than that of the crystal. If this situation were to continue to a low enough temperature the entropy of the supercooled liquid would become less than that of the crystal. In all known cases the glass transition intervenes and c_p drops at a slightly higher temperature than where this catastrophe would occur.

We have studied the frequency dependence of the specific heat through the glass transition. We apply a small-amplitude sinusoidal heat flux to the sample and measure the temperature response at the same frequency ν. In the limit $\nu \rightarrow 0$, this is the conventional specific heat. By varying ν we can measure how the heat relaxes into the different modes of the sample. In most cases one would not expect c_p to depend on frequency. The one exception observed so far is the low-temperature specific heat of glasses[6] where tunneling levels dominate the response. One might expect that supercooled liquids would also show a frequency-dependent c_p in the glass transition region.[7]

We emphasize that our measurements are not the same as those that look at the cooling-rate dependence[8] of c_p. In those measurements one is measuring the temperature at which the sample falls out of equilibrium[9] at any given cooling rate.[10] The departure from equilibrium always happens just before one reaches the "interesting" region of temperature. In our case the cooling rate is always very slow and our measurements are only performed while the sample is in an equilibrium liquid state. The frequency-dependent specific heat, $c_p(\nu)$, is a linear susceptibility describing the response of the system to arbitrarily small perturbations away from equilibrium. By scanning a wide range of frequency we are measuring the "specific-heat spectrum" of the system.

The traditional adiabatic technique[11] for measuring specific heat requires that the sample be extremely thin, so that the time of heat diffusion across the sample is short compared to the measurement time. The low thermal diffusivity ($\sim 10^{-3}$ cm^2/sec) of liquids places a severe constraint on the highest useful frequency for this technique. (For a thickness $d = 0.1$ mm, $\nu < 1$ Hz).

To circumvent this problem we have developed a new, nonadiabatic technique to measure c_p. By using the same electrical resistor as thermometer as well as heater and by using a simple heater geometry, we eliminate the need for a very thin sample and extend our frequency range to much higher frequencies. The heater, of resistance R, is a thin metal film evaporated onto a glass substrate. The heater is immersed in a bath of the liquid sample to be measured. We pass a sinusoidal current, i, at frequency $\nu/2$ through the heater. (We use this convention for the frequency of the current oscillations since, as we will show below, the specific heat will be measured at frequency ν.) The power dissipated, i^2R, has both a dc component and an ac component at frequency ν. The former simply produces a constant temperature gradient in the sample cell, while the latter sends diffusive thermal waves into the surrounding medium at frequency ν. The solution to the one-dimensional diffusion equation shows that the temperature oscillations at the heater have a magnitude proportional to $(\nu c_p \kappa)^{-1/2}$ and a phase lag of 45° with respect to the heat oscillations, where c_p and κ are the specific heat and thermal conductivity of the medium surrounding the heater.

In order to measure these temperature oscillations we exploit the temperature dependence of the resistance of our thin metal heater. The resistance has a small component oscillating at ν proportional to the temperature oscillations. If we now measure the voltage across the heater, we obtain a large component oscillating at $\nu/2$ and a small $3\nu/2$ component due to the mixing of current at $\nu/2$ with resistance oscillations at ν. We subtract out the large $\nu/2$ component by putting the heater into one arm of a Wheatstone bridge. We measure both the magnitude and phase of the $3\nu/2$ component with a lock-in amplifier. We have covered 4.5 decades of frequency with this technique, $0.2\ \mathrm{Hz} < \nu < 6\ \mathrm{kHz}$, and we plan to extend the measurements to lower frequencies in the near future.

Note that this method measures the product $c_p\kappa$ rather than just c_p. However, κ changes very slowly[12] near the glass transition temperature, T_g, while c_p drops sharply over a range of several degrees. Thus, changes in the product $c_p\kappa$ are dominated by the behavior of c_p.

We have studied the glass transition in glycerol. It is good glass former and it has been widely studied by other techniques. T_g of glycerol (determined by differential scanning calorimetry measurements) is about 180 K, and the Kauzmann temperature, T_K, where the extrapolated liquid entropy crosses that of the crystal, is about 134 K.[13]

Figure 1 shows $c_p\kappa$ vs temperature for three different frequencies. Near T_g, $c_p\kappa$ drops by a factor of 2, which is what we expect from measurements of c_p alone. The temperature at which $c_p\kappa$ drops depends strongly on the measurement frequency, indicating that the characteristic relaxation times in the liquid increase as T is lowered.

Because there is dispersion in the real part of c_p there must also be an imaginary part, c_p'', as required by Kramers-Kronig relations. Figure 1 shows the first direct measurements of this quantity which peaks at the glass transition. Normally the imaginary part of a linear susceptibility signifies a net absorption of energy by the sample from the applied field. But during a complete cycle of the specific-heat experiment there is no net exchange of energy between the sample and the surrounding heat bath. However the *entropy* of the bath does change during a complete cycle. If the experiment is carried out at a nominal temperature T with small oscillations of magnitude δT, then the net increase of entropy of the heat bath during one cycle is $\pi c_p''(\delta T/T)^2$. The second law of thermodynamics insures that $c_p'' > 0$. The heat oscillations thus lag behind the temperature oscillations. This is consistent with hysteresis seen in cooling-rate studies.[8]

To show the specific-heat spectra of the sample, we plot the real and imaginary parts of $c_p\kappa$ vs $\log_{10}\nu$ for three different temperatures in Fig. 2. The data show the characteristic form of all relaxation processes. The low-frequency limit of $c_p\kappa$ reflects the contribution of all the degrees of freedom in an equilibrium liquid. The high-frequency limit reflects only the contribution of the fast modes. We have fitted the peaks in the imaginary part with several of the common phenomenological functions used to fit dielectric relaxation data. Our peaks are about 1.6 decades wide, so that a Debye peak (1.14 decades wide) will not fit the data. A Cole-Cole fit is fair, but the experimental peaks are asymmetric, whereas the Cole-Cole peaks are symmetric. The best fits were obtained with the Williams-Watts function, i.e., the Fourier transform of the response $d[\exp(-t/\tau)^\beta]/dt$. The value of β is 0.65 ± 0.03 for all temperatures. This function gives a better fit than the Davidson-Cole function which has

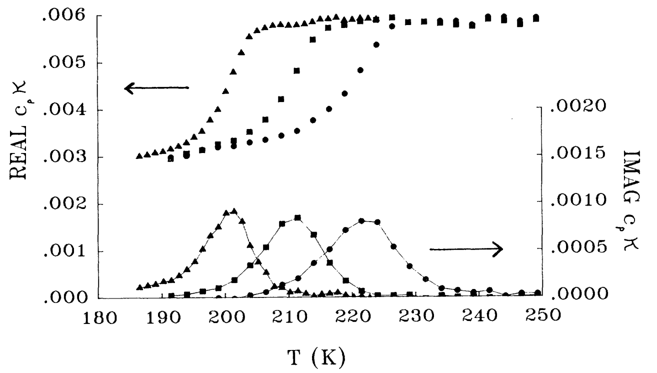

FIG. 1. The real and imaginary parts of $c_p\kappa$ (in $\mathrm{J^2/cm^4 \cdot sec \cdot K^2}$) in glycerol as a function of temperature. The measurement frequencies are (triangles) $\nu = 0.62$ Hz, (squares) $\nu = 34$ Hz, (circles) $\nu = 1100$ Hz. The lines are guides for the eye.

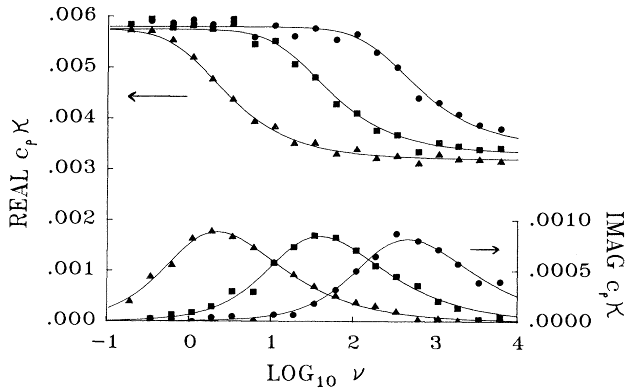

FIG. 2. The real and imaginary parts of $c_p\kappa$ (in $\mathrm{J^2/cm^4 \cdot sec \cdot K^2}$) in glycerol as a function of frequency. The temperatures are (triangles) $T = 203.9$ K, (squares) $T = 211.4$ K, and (circles) $T = 219.0$ K. The solid lines are fits to the data with a Williams-Watts function with $\beta = 0.65$.

been used to fit the dielectric susceptibility data on glycerol.[14] Using the parameters taken from these Williams-Watts fits, we also fitted the real part of $c_p\kappa$ [the additive constant $c_p\kappa(\nu=\infty)$ is the only undetermined parameter]. The high quality of these fits shows that our data are consistent with the Kramers-Kronig relations.

Figure 3 shows the peak frequency obtained from Fig. 2 vs T^{-1}. We have fitted the data with two different functional forms. The first is a Vogel-Fulcher law, $\nu=\nu_0\exp[-A/(T-T_0)]$, used historically to fit a wide range of glass-transition data. We obtained the values $\nu_0=4\times10^{14}$ Hz, $A=2500$ K, and $T_0=128\pm5$ K. These values of ν_0 and A are physically reasonable given a free-volume picture of liquid relaxation.[15] The value of T_0 is very close to T_{K}, the temperature beyond which the liquid cannot be supercooled according to the Kauzmann paradox (134 K). These numbers are close to those obtained from dielectric data. The widths of our peaks however are somewhat broader than those reported in those experiments.[14]

The second fit is a scaling law $\nu=\nu_0[(T-T_0)/T_0]^\alpha$, predicted by several recent hydrodynamical theories[4] of the glass transition. We obtain $\nu_0=4\times10^{10}$ Hz, $\alpha=15.0\pm0.6$, and $T_0=169\pm1$ K. The theories predict $\alpha=1.8$ to lowest order; however, they claim that higher-order corrections could change this value considerably. Because of the large discrepancy in T_0 between the two fits, we hope to distinguish between them by extending our measurements to lower frequency.

In summary, we have developed a "specific-heat spectroscopy" that can be used to measure both the real and the imaginary parts of the dynamical specific heat over a wide frequency range. These are linear-response measurements of a sample that is arbitrarily close to equilibrium. We have used this technique to measure the relaxation spectra of glycerol near T_g. The glass transition is observed to be simply the slowing down of a narrow distribution of modes as the temperature is lowered. The data are fitted well with a Williams-Watts distribution with $\beta=0.65$. Over our 4.5 decades of frequency, the data can be fitted with either a Fulcher law or a scaling law; however, the exponent in the latter fit is anomalously large.

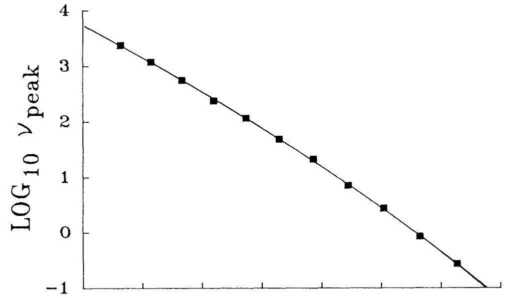

FIG. 3. The peak frequency, on a log scale, vs T^{-1} from the fits to the imaginary part of $c_p\kappa$. The solid line is actually two indistinguishable fits to these data with a Vogel-Fulcher law and with a scaling law. The parameters for the fits are given in the text.

The specific-heat-spectroscopy data look similar to dielectric data, suggesting that one relaxation mechanism is responsible for all of the observed phenomena. However, specific-heat spectroscopy has certain unique and attractive features. First $c_p(\nu)$ is closely tied with the thermodynamics of the system. The Kauzmann paradox shows that c_p must drop at a temperature above T_{K}. Thus our Fulcher law cannot change into Arrhenius behavior as has been observed in some viscosity data.[9] Second, the specific heat couples to all the modes in the system. This is not true of dielectric or mechanical susceptibilities. We are thus guaranteed that we are measuring all the relevant relaxations in the liquid. It is therefore not surprising that the peaks in c_p'' are wider than those observed in dielectric studies. Indeed, in some cases where the important modes do not couple to electric or strain fields, the specific heat might be the only low-frequency spectroscopic tool available. One can apply this technique to study relaxation behavior in a variety of solid and liquid systems.

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