Specific-heat spectroscopy of glycerol and propylene glycol near the glass transition

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We have measured the frequency-dependent specific heat of glycerol and propylene glycol near the glass transition. The measurements, covering a frequency range of five decades, probe the linear response of these supercooled liquids to small perturbations from equilibrium. The specific heat of these two liquids contains a contribution which relaxes increasingly slowly as the temperature is lowered. The relaxation time measured by specific-heat spectroscopy has the same temperature dependence as that measured by other techniques. This suggests that a single mechanism is responsible for all of the observed phenomena associated with the glass transition in these materials.

I. INTRODUCTION

When a liquid is supercooled sufficiently far below its equilibrium freezing temperature without crystallizing, it inevitably undergoes a glass transition into a state with thermodynamic and elastic properties appropriate to a solid. The most obvious thermodynamic signature of the transition is the drop in the measured specific heat which occurs over a narrow range of temperature. The transition also has a strong dynamical signature, as is seen in measurements of viscosity, ultrasonics, or dielectric relaxation. These measurements show that the characteristic relaxation times of the liquid increase rapidly as the glass transition is approached from above. The thermodynamic and dynamic signatures of the glass transition are closely related: As the relaxation times of the liquid increase, one must wait an ever longer time for any thermodynamic quantity to attain its equilibrium value. (The word equilibrium in this paper will refer to ergodicity in the liquid region of phase space, excluding the stable crystalline phase.) If one cools a liquid without waiting sufficiently long at each temperature for complete equilibration to occur, then a measurement of a thermodynamic quantity such as specific heat will not properly reflect the contribution of the unequilibrated degrees of freedom. One generally accepted view of the transition is that "... the major phenomena observed ... are no more than the consequences of the system under observation falling out of complete thermodynamic equilibrium at some point in the experiment."[1]

The traditional measurements of the specific heat c_p involve cooling or heating the sample at a constant rate. The temperature T_g at which c_p changes abruptly, signaling the crossover from equilibrium to nonequilibrium behavior (or vice versa), depends on the cooling or heating rate of the experiment.[2] When the system is cooled more slowly, T_g is lower because the system has more time to equilibrate at each temperature. One might ask if the glass transition can be avoided altogether simply by cooling the liquid slowly enough so that it always remains in equilibrium. Kauzmann showed that most liquids cannot be cooled indefinitely due to the following thermodynamic argument.[3] The specific heat of the supercooled liquid is

greater than that of the crystal. If this were to remain true as the liquid is cooled, then its entropy would eventually become less than that of the crystalline phase. In all known cases the glass transition intervenes, c_p drops to a value close to that of the crystal, and this entropy catastrophe is avoided. It is not at all clear why the existence of a stable crystalline phase far away from the liquid in phase space should have any influence on the dynamics of the liquid phase. Nevertheless, the Kauzmann paradox indicates that some sort of transition from liquid to glass must occur in order to prevent the entropy from becoming negative at $T=0$.

The problem with studying static thermodynamic quantities such as c_p is that their significance changes at the temperature T_g where the system falls out of equilibrium. How does one interpret a quantity such as c_p in a nonequilibrium situation? Clearly, the dynamics of how one performs the measurement enters into the measured value. If we want to study well-defined, equilibrium quantities in the liquid state and still learn something about the glass transition, then we must look *explicitly* at their dynamical behavior. For example, Moynihan and coworkers have measured the enthalpy response as a function of time to a single temperature step.[2] These measurements, however, were not in the linear-response regime, so that nonlinear and nonequilibrium behavior could get intertwined.

We have developed a new technique that allows us to measure the frequency dependence of the specific heat in the linear-response regime, over a wide range of frequency, on a system in thermal equilibrium. The first measurements using this "specific-heat spectroscopy" were made on glycerol near the glass transition.[4] We emphasize that we are measuring the dynamics of the liquid, not of the glass. One of the aims of this experiment is to show that the thermodynamic, as well as the relaxational, properties of the glass transition are apparent in the equilibrium liquid state. We would also like to test whether the relaxation times probed by specific-heat spectroscopy are the same as those probed by other techniques, such as dielectric spectroscopy or ultrasonics. Of course, if we want to obtain thermodynamic information then we must extrapolate our measurements to zero frequency. Although one can never be sure that the results

of such an extrapolation are accurate, we feel that it makes more sense to extrapolate an equilibrium dynamical quantity to zero frequency than it does to extrapolate a series of nonequilibrium measurements to zero cooling rate.

In this paper we give a thorough discussion of the experiment and its interpretation, and we present measurements on a second sample, propylene glycol, over a frequency range of five decades, 0.035 Hz—3.5 kHz. The organization of the paper is as follows: Section II contains a brief review of the concept of frequency-dependent specific heat $c_p(\omega)$ and its relation to linear response theory. In Sec. III we describe the experimental technique that we use to measure $c_p(\omega)$, and we derive the results concerning thermal diffusion that are needed to analyze our data. In Sec. IV we present the experimental data and discuss its interpretation in relation to the glass transition. In Sec. V we present data from a second experiment designed to test whether the thermal conductivity of the sample is also frequency dependent. In Sec. VI we present our conclusions.

II. FREQUENCY-DEPENDENT SPECIFIC HEAT

While the specific heat c_p is traditionally thought of as a static or equilibrium quantity, we can define a dynamic susceptibility $c_p(\omega)$ in the same way that we do for other linear susceptibilities such as the dielectric constant or the compressibility. The specific heat of a system tells us how much heat per unit volume the system will absorb from its surroundings q if we change its temperature by a small amount, ΔT. If the system is kept at constant pressure, then q is equal to the change in enthalpy per unit volume, h,

$$q = h = c_p \, \Delta T \quad \text{at constant pressure .} \tag{1}$$

Equation (1) is an equilibrium thermodynamic expression and says nothing about how long it takes the system to reach equilibrium after the temperature step. In this section we will assume that the system in question has negligible spatial extent so that we may ignore the time involved in thermal diffusion, which will be treated in the next section. In general, the heat absorbed by this system will be a function of time after we change the temperature. This will be particularly apparent if the system contains come degrees of freedom that relax slowly to equilibrium. If we step the temperature at $t=0$, we can write

$$q(t) = \begin{cases} 0 & \text{for } t < 0 \, , \\ \{c_{p\infty} + (c_{p0} - c_{p\infty})[1 - \Phi(t)]\}\Delta T & \text{for } t > 0 \, . \end{cases} \tag{2}$$

Here, $c_{p\infty}$ includes all the degrees of freedom that equilibrate very quickly, and c_{p0} is the equilibrium specific heat. In this notation the relaxation function $\Phi(t)$ describes the time dependence only of the slow degrees of freedom. It is normalized so that $\Phi(t=0)=1$ and $\Phi(t \to +\infty)=0$. The quantity in curly brackets is sometimes called the time-dependent specific heat.

If the temperature is an arbitrary function of time, we can determine $q(t)$ by using Eq. (2) and the principle of linear superposition. If $T(t)$ always stays close to the

same nominal value, then c_{p0} and $c_{p\infty}$ will be constants, and $\Phi(t)$ will have a fixed functional form. Then we can write

$$q(t) = \int_{-\infty}^{t} \{c_{p\infty} + (c_{p0} - c_{p\infty})[1 - \Phi(t - t')]\}\dot{T}(t')dt' \, , \tag{3}$$

where $\dot{T}(t')$ is the derivative with respect to time of $T(t')$.

As with any other linear susceptibility, the specific heat can be measured in the frequency domain as well as in the time domain. If we integrate Eq. (3) by parts, and then take its Fourier transform, we obtain

$$q(\omega) = c_p(\omega)T(\omega) \, , \tag{4}$$

where $c_p(\omega)$ is the frequency-dependent specific heat given by

$$c_p(\omega) = c_{p\infty} + (c_{p0} - c_{p\infty}) \int_0^{\infty} -\dot{\Phi}(t)e^{i\omega t}dt \, . \tag{5}$$

The static specific heat is then $c_p(\omega=0)=c_{p0}$. We see immediately that if the system has some slowly relaxing degrees of freedom, i.e., $c_{p0} - c_{p\infty} > 0$, then $c_p(\omega)$ must be a complex susceptibility. This simply reflects the fact that the heat oscillations lag in phase behind the temperature oscillations whenever the inverse of the measurement frequency is comparable to the characteristic relaxation time of the slow modes. The real and imaginary parts of $c_p(\omega)$, c_p' and c_p'', must obey the Kramers-Kronig relations, as a result of causality and linearity, which are explicit in Eqs. (2) and (3). Usually, one associates the imaginary part of a linear susceptibility with the absorption of energy by the sample from the applied field, but during a complete cycle of a frequency-domain 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, by an amount proportional to c_p''. The second law of thermodynamics therefore ensures that $c_p'' \geq 0$.

We can relate $c_p(\omega)$ to an equilibrium time-dependent correlation function in the usual way. The static specific heat is related to the equilibrium fluctuations of the entropy. If the pressure is kept constant, then these are proportional to the fluctuations of the enthalpy.[5] The relationship is

$$c_p = V/k_B T^2 \langle [h(t) - \bar{h}]^2 \rangle \quad \text{at constant pressure ,} \tag{6}$$

where the angular brackets can be thought of either as an ensemble average or as a time average, $\bar{h}$ is the average value of $h(t)$, and the factor of volume V reflects the fact that squared fluctuations of an intensive variable are proportional to the inverse of the size of the system. The fluctuation-dissipation theorem[6] also tells us how to generalize this result to the dynamical susceptibility. The theorem says that the dynamics which govern how a system responds to an external perturbation are the same as those which govern how spontaneous fluctuations decay. The complete description of the time dependence, where both slow and fast modes are explicitly included in $\Phi(t)$, is

$$\Phi(t) = \langle [h(t) - \bar{h}][h(0) - \bar{h}] \rangle / \langle [h(t) - \bar{h}]^2 \rangle \, . \tag{7}$$

The correlation function is averaged over initial times. This function has a piece which decays rapidly, and sometimes a second piece which decays slowly.[7] The frequency-dependent specific heat is then

$$c_p(\omega) = (V/k_B T^2) \int_0^\infty -\frac{d}{dt} \langle [h(t) - \bar{h}][h(0) - \bar{h}] \rangle e^{i\omega t} dt .$$

$$(8)$$

This follows from Eqs. (5)–(7), where we have set $c_{p\infty} = 0$.

Two real physical systems have a frequency-dependent (or, equivalently, a time-dependent) specific heat. At low temperatures, the specific heat of glasses has a large component due to tunneling levels, or two-level systems.[8,9] If the tunneling barrier is large, then the time it takes a tunneling system to equilibrate can be very long. The existence of a time-dependent specific heat in such systems has been predicted[8,10] and observed experimentally.[11]

The second case, the subject of this paper, is that of supercooled liquids near the glass transition.[4,12] We will show that the specific heat of a supercooled liquid can be divided into two parts, one which equilibrates quickly, and another which equilibrates more and more slowly as the glass transition is approached.

III. EXPERIMENT

A. Method

The traditional adiabatic method of measuring specific heat consists of first applying a short heat pulse to a sample that is well isolated thermally from its surroundings and then measuring the temperature increase after the heat has diffused throughout the sample. Alternatively, one can make adiabatic specific-heat measurements in the frequency domain[13] by applying a sinusoidal heat current at frequency $\omega = 2\pi f$ and measuring the amplitude of the temperature oscillations at that frequency. In either case the measurement time, or inverse frequency, must be long compared to the thermal-diffusion time τ_D of the sample. If the heat must traverse a distance d, then we have

$$\tau_D = c_p d^2 / \kappa .$$

$$(9)$$

However, the measurement time must also be short compared to the time τ_{ext} it takes the sample temperature to decay back to the temperature of the surrounding heat bath. Thus we have the two constraints:

$$\tau_D \ll 1/\omega \ll \tau_{ext} .$$

$$(10)$$

The thermal diffusivities of organic glass forming liquids are typically very low ($\kappa/c_p \approx 10^{-3}$ cm^2/sec), and so even if the sample is only 0.1 mm thick, the measurement frequency will be limited to below about 1 Hz. If c_p is independent of frequency, then one need only satisfy the constraints (10) over a narrow operating frequency range, and this method can be used successfully.[14]

However, our aim is to cover as wide a frequency range as possible, so we have developed a new *nonadiabatic* technique to measure $c_p(\omega)$.[4] Our technique is based on heat diffusion from a thin heater which is producing a

heat flux sinusoidal in time, and which is immersed in a bath of the liquid sample to be studied. If the heater has a simple geometry, such as a plane or a wire, then the temperature oscillations at the heater itself will be simply related to the thermal properties of the surrounding liquid. We exploit this geometry by using the same metal resistor element as both a heater and as a thermometer. With this technique there is no need to make an extremely thin sample cell, as the high-frequency limit is determined by the thickness of the heater-thermometer itself.

The measurement is made as follows: We pass a current of frequency $\omega/2$ through the heater,

$$I(t) = I_0 \cos(\omega t/2) .$$

$$(11)$$

The power dissipated in the heater has two components, a dc component and a component oscillating at frequency ω:

$$P(t) = (I_0^2 R/2)[1 + \cos(\omega t)] .$$

$$(12)$$

The dc component simply produces a constant temperature gradient in the cell. The ac component produces diffusive thermal waves. (We will solve the heat-diffusion equation in the appropriate geometries later.) The temperature of the heater oscillates at the frequency ω of the heat oscillations,

$$T = T_{dc} + T_\omega \cos(\omega t - \varphi) .$$

$$(13)$$

T_{dc} is the average temperature of the heater and T_ω is the amplitude of the oscillations. The phase lag φ depends both on the geometry of the heater and on the thermal properties of the medium. Since the resistance of the metal heater depends on temperature, it has a small component that oscillates at the frequency ω of the temperature oscillations,

$$R = R_{dc} + R_\omega \cos(\omega t - \varphi) ,$$

$$(14)$$

$$R_\omega = \alpha R_{dc} T_\omega ,$$

$$(15)$$

where α is the temperature coefficient of resistance of the heater. The voltage across the heater is the product of the current passing through it, which is at frequency $\omega/2$, and its resistance, which has a small component at frequency ω. The mixing of these two frequencies gives rise to a small signal at frequency $3\omega/2$, as well as at $\omega/2$,

$$V(t) = I(t)R(t) = V_{\omega/2}\cos(\omega t/2 - \varphi')$$
$$+ V_{3\omega/2}\cos(3\omega t/2 - \varphi) ,$$

$$(16)$$

$V_{\omega/2}$ is equal to $I_0 R_{dc}$ plus a small contribution from the mixing of I_0 and R_ω. $V_{3\omega/2}$, on the other hand, is exactly equal to $\frac{1}{2} I_0 R_\omega$, which is proportional to T_ω, the temperature oscillation of the heater.

In order to measure the small voltage $V_{3\omega/2}$ in the presence of the much larger voltage $V_{\omega/2}$, we put the heater into one arm of a Wheatstone bridge. If we balance the bridge and measure the differential voltage across it, then we effectively isolate $V_{3\omega/2}$. We then measure the amplitude and phase of $V_{3\omega/2}$ with a lock-in amplifier referenced to 3 times the driving frequency. Since the bridge-balance condition does not depend on frequency, any spurious $3\omega/2$ component in the driving oscillator will not

affect the signal. Only the $3\omega/2$ signal produced in one arm of the bridge from the heating of the sample will be measured. We have covered over five decades of frequency with this technique, 0.01 Hz $< f < 6$ kHz, using commercial lock-in amplifiers for the upper frequency range and a computer-controlled digital lock-in technique for the low frequencies. A detailed discussion of the electronics and software will be presented in a separate publication.[15]

B. Thermal diffusion

Before we solve the heat-diffusion equation in the geometries appropriate for our experiment, we should ask if this equation is valid when applied to a system with a frequency-dependent specific heat. To answer this, let us look at the derivation of the heat equation. Again, we will use the variable q to represent the heat density (or entropy density times temperature) following the notation of Ref. 6. The associated heat current is j_q. The heat-diffusion equation comes from two equations. The first is a version of energy conservation (combined with particle conservation). It is microscopically rigorous:

$$\dot{q} + \nabla \cdot \mathbf{j}_q = 0 .$$ (17)

The second equation is a phenomenological constitutive relation:

$$\mathbf{j}_q = -\kappa \nabla T ,$$ (18)

where κ is the thermal conductivity. These two equations combine to give

$$\dot{q} = \kappa \nabla^2 T .$$ (19)

Normally, we replace $\dot{q}$ by $c_p \dot{T}$ to obtain the heat-diffusion equation in standard form. However, if c_p is time or frequency dependent, then, in general, we must use Eq. (3) to express q as an integral over the temperature at all previous times. We can simplify the situation considerably by going into the frequency domain. If T and q both have a sinusoidal time dependence with frequency ω, then we can write

$$\dot{q} = -i\omega q(\omega) = -i\omega c_p(\omega) T(\omega) ,$$ (20)

so that (19) becomes

$$-i\omega c_p(\omega) T(\omega) = \kappa \nabla^2 T(\omega) .$$ (21)

Operating in the frequency domain gives us two simplifications: The heat-diffusion equation retains its simple form even when the specific heat is frequency dependent, and what was formerly a partial differential equation is now an ordinary differential equation, which is easy to solve.

The simplest experimental geometry is that of a plane heater. We have physically realized this geometry by evaporating a thin nickel film onto a thick substrate of window glass. Nickel is chosen because of its high temperature coefficient of resistance. In order to simplify the algebra we will assume that the heater lies in the plane $x = 0$, and that it has infinite area and zero thickness. The

liquid surrounding it fills all space for $x > 0$, while the substrate fills the region $x < 0$. The heat flux from the heater, equal to the power per unit area dissipated in the heater, is sinusoidal in time, $j_q(t) = \text{Re}\{j_0 e^{-i\omega t}\}$. The steady-state solution to Eq. (21) consistent with the boundary conditions $T \to T_{dc}$ as $x \to \pm \infty$ is

$$T(x,t) = T_{dc} + \begin{cases} \text{Re}\{T(x=0,\omega)e^{-kx}e^{-i\omega t}\} & \text{for } x > 0 , \\ \text{Re}\{T(x=0,\omega)e^{k_{sub}x}e^{-i\omega t}\} & \text{for } x < 0 . \end{cases}$$ (22)

$T(x=0,\omega)$ is the complex amplitude of the temperature oscillations at the heater. In the notation of Eq. (13), $T(x=0,\omega) = T_\omega e^{i\varphi}$. The thermal wave vector k is complex, because it describes diffusive waves. It is equal to

$$k = (\omega c_p/\kappa)^{1/2} e^{-i\pi/4} = (\omega c_p/2\kappa)^{1/2}(1-i) ,$$ (23)

where c_p and κ are the thermal parameters of the liquid, which may be complex and frequency dependent. The wave vector k_{sub} has the same form as (23), except it contains the thermal parameters of the substrate, c_{sub} and κ_{sub}, which are always real and frequency independent. To find $T(x=0,\omega)$, we use the boundary condition at $x=0$ relating the heat flux to the temperature gradient. From Eq. (18) we have

$$\kappa_{sub} \frac{\partial T}{\partial x}\bigg|_{x\to 0^-} - \kappa \frac{\partial T}{\partial x}\bigg|_{x\to 0^+} = j_q(t) ,$$ (24)

where the two derivatives are evaluated on opposite sides of the heater. If we insert (22) into (24), we obtain the solution

$$T(x=0,\omega) = j_0/(\kappa k + \kappa_{sub}k_{sub})$$

$$= j_0 e^{i\pi/4}/[(\omega c_p \kappa)^{1/2} + (\omega c_{sub}\kappa_{sub})^{1/2}] .$$ (25)

In order to extract $c_p\kappa$ from the data, we must first make a measurement with an empty sample cell to determine the substrate contribution $c_{sub}\kappa_{sub}$ over the whole temperature range of the experiment. We can then subtract this from the data with the full sample cell to find $c_p\kappa$ of the sample. We have used window glass as a substrate because it has a low value of $c_{sub}\kappa_{sub}$.

The approximations used in deriving the solution (25) are valid if the thermal wavelengths $|k|^{-1}$ and $|k_{sub}|^{-1}$ are much longer than the thickness of the heater, d, and much shorter than the shortest lateral dimension of the heater, L_1, and the distance from the heater to the walls of the sample cell, L_2. Thus we have the two constraints

$$d \ll (\kappa/\omega c_p)^{1/2} \ll L_1, L_2 .$$ (26)

The same constraints apply for $|k_{sub}|^{-1}$. The thickness of the metal film is less than 10^{-5} cm. If L_1 and L_2 are on the order of 1 cm, then we can satisfy the constraints (26) over a wide frequency range.

We see from (25) that if c_p and κ are real and frequency independent, as they are in a normal liquid far from the glass transition, then the amplitude of the temperature oscillations will be proportional to $\omega^{-1/2}$, and their phase

lag with respect to the heat oscillations will be $\pi/4$ rad or 45°. We use these two criteria to monitor the performance of the plane heaters. As the sample approaches the glass-transition region, $c_p\kappa$ becomes complex and frequency dependent. φ, the phase lag in Eqs. (13) and (16) which is measured in our experiment, deviates from $\pi/4$ in this temperature range due to the complex specific heat. Also, the amplitude of the oscillations no longer varies as $\omega^{-1/2}$.

Note that with this geometry we measure the product $c_p\kappa$, rather than just c_p, as do the adiabatic measurements. We suspect that any unusual behavior of this product near the glass transition will be dominated by the behavior of c_p, since static measurements of κ show little change from above to below T_g.[16] However, the possibility still exists that there is some interesting frequency dependence to κ as well as to c_p. We have attempted to explore this possibility by utilizing a second heater geometry. If the heater-thermometer is a thin wire rather than a plane, then we measure a different combination of c_p and κ. In principle, the two experiments together should allow us to extract c_p and κ independently even if both quantities are frequency dependent. We will discuss this experiment in detail in Sec. V.

There is an alternative way to view heat diffusion through a slowly relaxing system, due to Oxtoby.[17] Although Oxtoby prefers not to use the term "frequency-dependent specific heat," he shows how the behavior discussed above can arise out of a rigorous hydrodynamic treatment of a liquid with a set of slow modes put in by hand. (Oxtoby's theory is a phenomenological treatment of a liquid near the glass transition and as such it does not attempt to explain the origin of the slow modes.) In his formalism the frequency dependence is carried by a frequency- and wave-vector-dependent thermal conductivity. To solve the model for observable quantities in a given experimental geometry, one must integrate over wave vector. In several different geometries (including those in our experiments), one obtains the result that the wave-vector dependence integrates out in such a way so as to reproduce the standard solutions to the heat-diffusion equation (21) with a frequency-dependent specific heat and a bare, frequency-independent thermal conductivity. Oxtoby's work is thus consistent with our analysis in terms of a frequency-dependent specific heat. Presumably, one could obtain a different result by assuming a more complicated form of coupling between the slow modes and the other hydrodynamic variables. From this point of view, the aim of the wire experiment is to determine the validity of Oxtoby's original assumptions.

IV. PLANE-EXPERIMENT RESULTS

We have studied both glycerol and propylene glycol (1,2-propanediol) near the glass transition. Their glass-transition temperatures are about 193 and 172 K, respectively,[18] as determined by differential-scanning-calorimetry measurements at a cooling rate of 10 K/min. Both of these materials are good glass formers. Glycerol can crystallize if kept sufficiently long in the temperature range 230–260 K, but it can easily be supercooled past
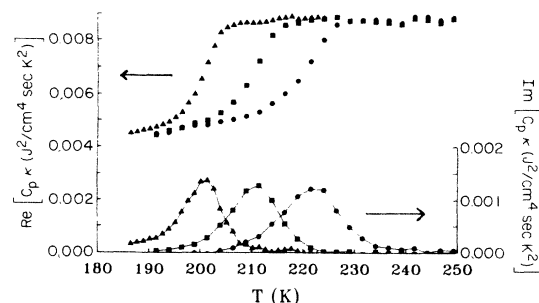

FIG. 1. The real and imaginary parts of $c_p\kappa$ (units of $J^2/cm^4 sec K^2$) for glycerol as a function of temperature. The measurement frequencies are $f=0.62$ Hz (▲), $f=34$ Hz (■), and $f=1100$ Hz (●). This figure is taken from Ref. 4, but with the vertical scale corrected.

that range. Propylene glycol does not crystallize at all because it has two incompatible stereoisomers that do not fit into each other's crystal lattices.[18]

In Fig. 1 we reproduce data from Ref. 4, showing $c_p\kappa$ versus temperature for glycerol at three different frequencies. Near T_g, the real part of $c_p\kappa$ drops by about a factor of 2, which is what we expect from measurements of c_p alone. The temperature where $c_p\kappa$ drops depends strongly on the measurement frequency, indicating that the relaxation times in the liquid increase as T is lowered. Since there is dispersion in the real part of $c_p\kappa$, there must be an imaginary part as required by the Kramers-Kronig relations. Our technique gives a direct measurement of this quantity, which we also show in Fig. 1. The imaginary part of $c_p\kappa$ has a peak at the same temperature where the real part drops. In Fig. 2 we show measurements of $c_p\kappa$ for propylene glycol, at four different frequencies. Except for the shift in temperature scale reflecting the lower glass-transition temperature, the data look very similar to those for glycerol.

At first glance, the real part of $c_p\kappa$ looks very similar to scanning-calorimetry data. However, there is an important difference: Figures 1 and 2 show an equilibrium, linear susceptibility as a function of frequency and temperature. The curves in these figures are reversible, i.e.,
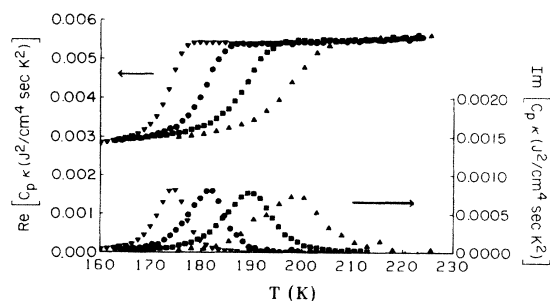

FIG. 2. The real and imaginary parts of $c_p\kappa$ (units of $J^2/cm^4 sec K^2$) for propylene glycol as a function of temperature. The measurement frequencies are $f=0.11$ Hz (▼), $f=4$ Hz (●), $f=110$ Hz (■), and $f=1900$ Hz (▲).
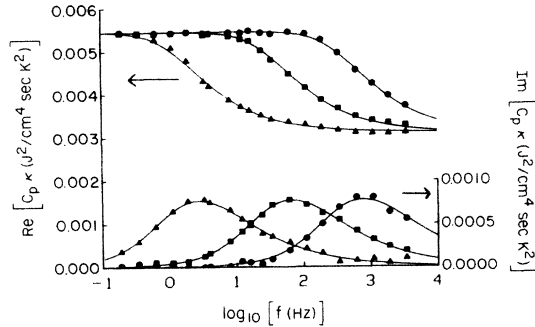
FIG. 3. The real and imaginary parts of $c_p\kappa$ (units of $J^2/cm^4 sec K^2$) for propylene glycol as a function of frequency. The temperatures are $T=180.5$ K (▲), $T=188$ K (■), and $T=195.5$ K (●). The solid lines are fits to the data with a Kohlrausch-Williams-Watts function with $\beta=0.61$.

there is no difference between the data taken while cooling and those taken while heating the sample. Scanning-calorimetry data show hysteresis between cooling and heating[2] which reflects the fact that the sample falls out of equilibrium during the experiment. In a typical run we keep the sample at a fixed temperature for ~ 1 h while we scan frequency and then step the temperature down by 1 K over 15 min. (The data are identical if instead we cool the sample steadily, at the same average rate as above.) At a cooling rate of ~ 1 K/h we expect to see the onset of nonequilibrium behavior at $T \sim 184$ K in glycerol and $T \sim 163$ K in propylene glycol, i.e., at the lower end of the temperature ranges shown in Figs. 1 and 2, respectively. The amplitude of the temperature oscillations in these runs never exceeds 0.1 K, and is considerably lower (~ 1 mK) at the high frequencies. We have checked that the measurements stay within the linear-response regime.

To obtain spectroscopic information from these measurements, we plot $c_p\kappa$ as a function of frequency at fixed temperature. In Fig. 3 we show the real and imaginary parts of $c_p\kappa$ versus $\log_{10}f$ for propylene glycol. In this form the data clearly show the characteristic form of all relaxation processes, discussed in Sec. II. The low-frequency limit of $c_p\kappa$ includes the contribution of all the degrees of freedom of the liquid sample. This is the thermodynamic, or static, value of the susceptibility. The high-frequency limit reflects only the contribution of the fast modes. The difference between the low- and high-frequency limits of $c_p\kappa$ at a single temperature, $(c_p\kappa)_0-(c_p\kappa)_\infty$, is about equal to the difference between $c_p\kappa$ of the liquid and that of the glass. Thus the fast modes in the liquid are precisely the modes that survive the glass transition. The slow modes, corresponding to liquid rearrangements, are completely frozen out in the glass. The nature of the two types of degrees of freedom near T_g has been known for a long time,[3] but this experiment clearly demonstrates that the distinction persists in the equilibrium liquid well above T_g.

We have fitted the data in Fig. 3 with several of the empirical relaxation functions used to fit dielectric data. The peaks in the imaginary part are wider than Debye peaks, and slightly asymmetric. The two functions that give good fits to both the glycerol data and the propylene

glycol data are the Davidson-Cole form, described by the frequency-domain response function $\Phi(\omega)=(1-i\omega\tau)^{-B}$, and the Kohlrausch-Williams-Watts form, described by the time-domain response $\Phi(t)=\exp[-(t/\tau)^\beta]$. Both of these functions were originally proposed as phenomenological functions to fit relaxation data, although there have been several attempts in recent years to derive the second form.[19] The fits to the real and imaginary parts of $c_p\kappa$ are not independent, but must be Kramers-Kronig transforms of each other. When we fit the imaginary part alone, we obtain the three parameters: (i) the area under the peak, $(c_p\kappa)_0-(c_p\kappa)_\infty$, (ii) the logarithm of the peak frequency, $\log_{10}f_{peak}$, and (iii) the width of the peak, given either by the exponent β or B. Using those parameters we then fit the real part, where the only free parameter left is the value of $(c_p\kappa)_\infty$. In Fig. 3 we show the Kohlrausch-Williams-Watts fits to the data with $\beta=0.61\pm0.04$. The quality of the fits shows that the data are consistent with the Kramers-Kronig relations. For the Davidson-Cole form, the best fits are obtained with the exponent $B=0.44\pm0.04$.

Glycerol and propylene glycol have both been measured[18,20] using dielectric spectroscopy. It is interesting to compare the results of the specific-heat and dielectric spectroscopies, to see if the shapes of the relaxation functions and the temperature dependence of the peak frequencies is the same in the two cases. In Table I we summarize the parameters used to fit the specific-heat data and dielectric data. In all cases the widths of the relaxation spectra are nearly temperature independent over the range of measurement frequencies; however, the specific-heat spectra have consistently wider peaks than the dielectric data for both materials. A recent study of ultrasound in glycerol[21] found that the shapes determined by a number of different experimental probes excluding dielectric response are consistent with each other. The dielectric peaks are narrower than any of the others. Unfortunately, there is no microscopic theory for the shape of non-Debye relaxation functions (other than the general theories in Ref. 19), but we speculate that the dielectric peaks are
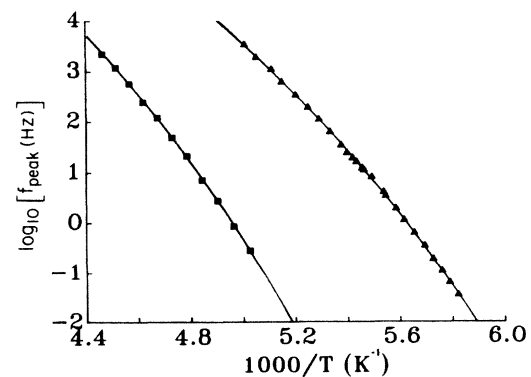

FIG. 4. The peak frequency, on a log scale, versus inverse temperature for glycerol (■) and for propylene glycol (▲). The solid lines in both cases are two indistinguishable fits to the data with a Vogei-Fulcher-Tammann law and with a scaling law. The parameters for the fits are given in Table II.

TABLE I. Width exponents β for the Kohlrausch-Williams-Watts (KWW) fits, $\Phi(t)=\exp[-(t/\tau)]^{\beta}$, and B for the Davidson-Cole (DC) fits, $\Phi(\omega)=(1-i\omega\tau)^{-B}$, both for our specific-heat data, and for the dielectric data of Refs. 16 and 33.

		KWW width β	DC width B
Specific heat	Glycerol	0.65 ± 0.03	0.51 ± 0.03
	Propylene gylcol	0.61 ± 0.04	0.44 ± 0.04
Dielectric	Glycerol[a]	0.80 ± 0.02^c	0.58 ± 0.03^d
	Propylene glycol[b]	0.75^c	0.66 ± 0.01^d

[a]The width is weakly temperature dependent. The value shown corresponds to the temperature range of our experiment.
[b]The value taken from Ref. 33 is not consistent with the observation of Ref. 16 that glycerol has a narrower dielectric width than propylene glycol.
[c]Reference 16.
[d]Reference 33.

narrower because the slow modes only contribute to the dielectric response in proportion to their dipole moment, while they contribute to the specific heat in proportion to their entropy content. One can imagine the existence of modes in liquids that carry entropy but have a very small dipole moment. One must be cautious, however, in interpreting non-Debye relaxations as a superposition of distinct modes. If one chooses this interpretation then one must explain why the superposition of modes maintains the same shape over a broad temperature range while the mean relaxation time is changing by many decades.

We plot the peak frequency versus inverse temperature for both samples in Fig. 4. In both cases we can fit the data with two very different functional forms. The first is the Vogel-Fulcher-Tamman equation, $f=f_0\exp[-A/(T-T_0)]$, which has been used to fit a wide range of glass-transition data. The parameters of the fits are given in Table II. For glycerol, the temperature T_0 where the relaxation time diverges is very close to the Kauzmann temperature T_K, where the entropy of the supercooled liquid extrapolates to that of the crystal. $T_K=135\pm3$ K for glycerol.[18] (T_K has not been determined for propylene glycol because of its inability to crystallize.) In Table II we also compare our Fulcher fits to those obtained from dielectric data. Although the fitting parameters differ

slightly, the peak frequencies found by the specific-heat and dielectric spectroscopies agree closely in the temperature range of the experiments. This suggests that one relaxation mechanism governs all of the observed phenomena in these materials. This is not the case in all glass formers.[2]

The second function we have used to fit the peak frequencies as a function of temperature is a scaling law, $f=f_0[(T-T_0)/T_0]^{\alpha}$, predicted by several recent theories of the glass transition.[22,23] Some of these theories[22] can be derived from nonlinear hydrodynamics, and therefore should be generally applicable to a wide variety of liquids. The theories first predicted the existence of a purely dynamical glass transition and a divergence of liquid relaxation times with a scaling-law power $\alpha\approx2$. However, further investigations of the hydrodynamic theories[24] have shown that higher-order corrections cut off the divergence. One should therefore only expect to see power-law behavior with $\alpha\approx2$ in the low-viscosity (or short-relaxation-time) regime, but not in the high-viscosity regime probed by our experiment.[25] The fits to the data using a scaling law give anomalously large exponents, $\alpha\sim15$. The fitting parameters are given in Table II.

The temperature T_0, where the scaling law diverges, is

TABLE II. Parameters for the Vogel-Fulcher-Tammann (VTF) fits, $f=f_0\exp[-A/(T-T_0)]$, and for the scaling-law fits, $f=f_0[(T-T_0)/T_0]^{\alpha}$, to our specific-heat data. We also show the VTF fits to the dielectric data of Ref. 16.

		Vogel-Fulcher-Tammann fit		
		$\log_{10}f_0$	T_0	A
Specific heat	Glycerol	14.6 ± 0.9	128 ± 5	2500 ± 300
	Propylene glycol	13.8 ± 0.4	114 ± 7	2020 ± 130
Dielectric	Glycerol	13.8	137 ± 10	1740
	Propylene glycol	12.4	122 ± 11	1650

		Scaling-law fit		
		$\log_{10}f_0$	T_0	α
Specific heat	Glycerol	10.6 ± 0.1	169 ± 1	15.0 ± 0.6
	Propylene glycol	10.3 ± 0.1	148 ± 1	14.6 ± 0.6

considerably higher than the T_0 obtained from the Fulcher fits. The large difference between the values of T_0 using different functional forms to fit the same data demonstrates the uncertainty inherent in extrapolating finite-frequency measurements to zero frequency. However, we suspect that the Fulcher fits are more appropriate than the scaling fits for the following reason. The parameters to the Fulcher equation have some theoretical justification, either through the free-volume theories[26] or the entropy theories[27,28] of the glass transition. In particular, the relation between excess entropy and relaxation times predicted by the Adam-Gibbs theory[28] appears to describe well the behavior of a series of polyalcohols,[18] including the materials studied here, glycerol and propylene glycol. In contrast, the theoretical models that predict a scaling law predict exponents much smaller than those we observe, and the scaling law is only expected to describe the behavior of the relaxation times at much higher temperatures.

The frequency-dependent specific heat of glycerol has also been measured recently by Christensen.[29] He used the standard adiabatic method discussed at the beginning of Sec. III and hence could only cover a very limited frequency range, 2.4–35 mHz. The difficulty with analyzing data over such a narrow range is that one must assume that the spectral shape of the relaxation is temperature independent. With that assumption one can then slide the various curves on a log-frequency plot until they superpose to estimate the time-temperature relation. The Arrhenius relation which Christensen obtains matches our Fulcher law for glycerol at $T = 195$ K, but is not as steep as the extrapolation of our Fulcher law into the temperature range of his experiment, 176–191 K. Qualitatively, his data look very similar to ours. However, we find from our analysis over a much wider range of frequency that the specific heat falls off more quickly at high frequency than he claims. When possible, it is better to have the entire peak in one's experimental frequency window than to rely on the temperature-shift procedure to obtain the shape of the relaxation. The shift procedure is particularly problematic in the tails of the structure.

V. WIRE EXPERIMENT

The purpose of carrying out a second experiment, using a thin wire instead of a plane as the heater-thermometer, is to find whether the dispersion in the real and imaginary parts of the product $c_p\kappa$ near the glass transition is due to the behavior of c_p alone, or whether κ also has a non-negligible frequency dependence. The wire experiment measures a different combination of c_p and κ than is measured by the plane experiment, so we hope to distinguish between the behavior of c_p and of κ by comparing the data from the two experiments.

The solution to the heat-diffusion equation (21) in the wire geometry proceeds in a manner analogous to the solution in the plane geometry. Again we will assume at first that the wire is infinitely long, and that its radius a is very small compared to the thermal wavelength $|k|^{-1}$, where k is given in Eq. (23). We assume that the temperature is uniform within the wire, because it is made of

metal and has a much higher thermal conductivity than the surrounding liquid. The steady-state solution to Eq. (21) in this geometry is

$$T(r,t) = T_{dc} + \text{Re}\{T(r=a, \omega)[K_0(kr)/K_0(ka)]e^{-i\omega t}\}$$

$$\text{for } r > a , \quad (27)$$

where K_0 is the modified Bessel function of zero order, and r is the radial coordinate in the cylindrical coordinate system determined by the wire. The Bessel function K_0 satisfies the boundary condition $K_0(kr) \rightarrow 0$ as $r \rightarrow \infty$. To find the amplitude of the temperature oscillations at the wire, $T(r=a, \omega)$, we use the boundary condition at $r=a$ that is analogous to Eq. (24). This time we will also include a term that accounts for the heat capacity of the wire itself. The boundary condition is

$$-\kappa\frac{\partial T}{\partial r}\bigg|_{r=a} = j_q(t)$$

$$= p(t)/2\pi a - (a/2)c_{\text{wire}}T(r=a, t) , \quad (28)$$

where $p(t) = \text{Re}\{p_0 e^{-i\omega t}\}$ is the power per unit length being dissipated in the wire, and the factor $a/2$ in the last term is the ratio of volume to surface area of the wire. When we insert (27) into (28), we find

$$T(r=a, \omega) = (p_0/2\pi\kappa)K_0(ka)$$

$$\times [-kaK_0'(ka)$$

$$-(i\omega c_{\text{wire}}a^2/2\kappa)K_0(ka)]^{-1} . \quad (29)$$

At very low frequencies we can ignore the second term in the denominator of (29). If we expand the Bessel functions to lowest order in the argument ka, we obtain

$$T(a,t) = \text{Re}\{(p_0 e^{-i\omega t}/2\pi\kappa)$$

$$\times(-\gamma - \ln|ka/2| - i\arg k)\} , \quad (30)$$

where $\gamma = 0.5772\ldots$ is Euler's constant, and $\arg k$ is the phase of k in the complex plane. The solution (30) looks rather complicated at first, but it has some rather attractive features. If c_p and κ are real and frequency independent, as they are in a normal liquid, then $\arg k = -\pi/4$ according to Eq. (23), and $|ka/2| \sim \omega^{-1/2}$. This means that the component of $T(a,t)$ that is 90° out of phase with respect to the heat oscillation is independent of frequency, and only depends on the thermal conductivity κ of the liquid surrounding the wire, but not on its specific heat. The component of $T(a,t)$ that is in phase with the heat oscillations depends on c_p and ω through the logarithm in (30). One can therefore use the wire technique to measure both κ and c_p independently if they are both real. This same principle is used in hot-wire experiments to measure κ and c_p for normal liquids.[16]

In order to test our experimental method, we have measured κ and c_p of ethanol over the temperature range 180–300 K and over the frequency range 0.1–10 Hz. We find that both c_p and κ are independent of frequency over this entire range, and the values we obtain are within a few percent of published values.[30] The upper frequency

range is limited by the radius of the platinum wire used; in our case $a = 13.0$ μm. We expanded the Bessel functions in Eq. (29) to fourth order in ka in order to analyze the data up to a frequency of 10 Hz. We can measure to frequencies as low as 0.01 Hz, but at very low frequency there are small corrections to Eq. (30) due to the finite length of the wire, which is 9 cm in our experiment.

In Fig. 5 we show the in-phase and out-of-phase components of the temperature oscillations of the wire with respect to the heat oscillations at two frequencies when the wire is surrounded by glycerol. At high temperature glycerol acts like a normal liquid, i.e., c_p and κ are real and frequency independent in the frequency range of the experiment. [The difference in the out-of-phase components between the two frequencies is due to higher-order terms in (29) not included in the asymptotic expression (30).] The most salient features of the data are the sharp rise in the in-phase component and the large dip in the out-of-phase component that occur at the same temperature, where the real part of $c_p\kappa$ drops and the imaginary part peaks, as measured by the plane experiment (see Fig. 1). These two features are qualitatively consistent with the interpretation that the frequency dependence is mostly in c_p. We can see this by examining Eq. (30). Both the in-phase and out-of-phase components of the wire signal are proportional to $1/\kappa$. If there were a change in the magnitude or in the complex phase of κ, then the corresponding change in the wire signal would be proportional to the amplitude of that signal. The data in

Fig. 5 show that the salient features in both components of the wire signal are approximately independent of frequency, and hence independent of the amplitude of the signal. Therefore these features are not due primarily to the behavior of κ. However, these features can be explained if we assume that they are due to the behavior of $c_p(\omega)$. The data in Fig. 1 show that the real part of c_p drops. This drop causes the magnitude of the thermal wave vector k, defined in Eq. (23), to decrease. The in-phase component of the wire signal therefore increases due to the term $-\ln|ka/2|$ in Eq. (30). (Remember that $|ka/2| < 1$, so that $\ln|ka/2| < 0$.) This increase, which is independent of frequency, is shown by the data of Fig. 5(a). The data in Fig. 1 also show us that the imaginary part of c_p peaks. This causes the complex phase of k to deviate positively from its nominal value of $-\pi/4$. Hence the out-of-phase component of the wire signal dips, as shown by the data of Fig. 5(b).

In Fig. 6 we show wire data for propylene glycol. The two frequencies shown are the same as the lowest two frequencies in Fig. 2. As we saw with the glycerol data, the primary features in the wire experiment are consistent with the plane experiment, given that the dispersion and imaginary part in the product $c_p\kappa$ are due to the behavior of c_p. The peak in c_p'' occurs at $T \sim 181$ K for $f = 4$ Hz and at $T \sim 174$ K for $f = 0.11$ Hz. The dips in Fig. 6(b) occur at these same temperatures.

We are now in a position to understand the anomalous behavior seen by Sandberg, Andersson, and Backstrom[16]
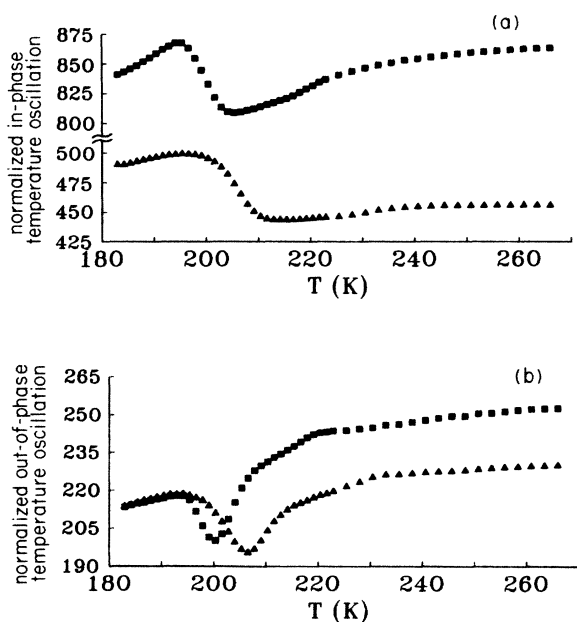

FIG. 5. Temperature oscillation of wire versus nominal temperature for glycerol. (a) The in-phase component of the oscillation and (b) the out-of-phase component. The frequencies are $f = 0.62$ Hz (■) and $f = 8$ Hz (▲). The magnitude of the oscillation is normalized to the power per unit length dissipated in the wire, so it has units of κ^{-1}, i.e., K cm sec/J. See Eq. (29).
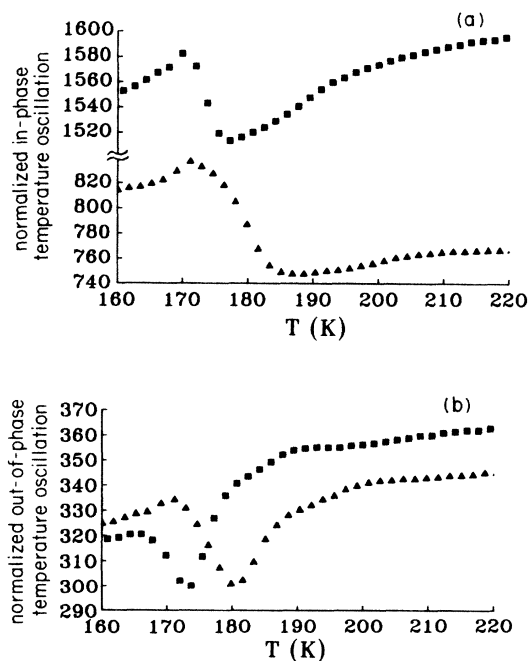
FIG. 6. Temperature oscillation of wire versus nominal temperature for propylene glycol. (a) The in-phase component of the oscillation and (b) the out-of-phase component. The frequencies are $f = 0.11$ Hz (■) and $f = 4$ Hz (▲). The units are the same as in Fig. 5.

in a hot-wire experiment on glycerol. These authors used the traditional hot-wire technique to study both the thermal conductivity and the specific heat of glycerol over a wide temperature range covering both the liquid and glass states. The measurement consists of passing a step-function current through the wire and then measuring its resistance (and hence its temperature) as a function of time after the step. One can obtain c_p and κ from a plot of temperature versus log time if both quantities are real and frequency independent. The authors found that, as the sample passed through the glass-transition region, the measured value of κ had a large peak and c_p dropped suddenly with a large overshoot. They speculated that this behavior might be an artifact of the analysis, given that the system relaxes slowly near T_g. We can understand this behavior if we analyze our data according to Eq. (29) while assuming that both c_p and κ are real quantities. This type of analysis is appropriate in the normal liquid regime, but produces spurious results near the glass transition where c_p has an imaginary part. Figure 7 shows the results of such an analysis performed on the glycerol data from Fig. 5. At high temperatures both c_p and κ are frequency independent, so the analysis is valid. However, as we pass through the dispersion region, we see a peak in κ and an overshoot in the drop in c_p. These two features are very similar to those seen in Ref. 16, and they are due entirely to the nonzero imaginary part of c_p which has been neglected in the analysis. Below the dispersion re-
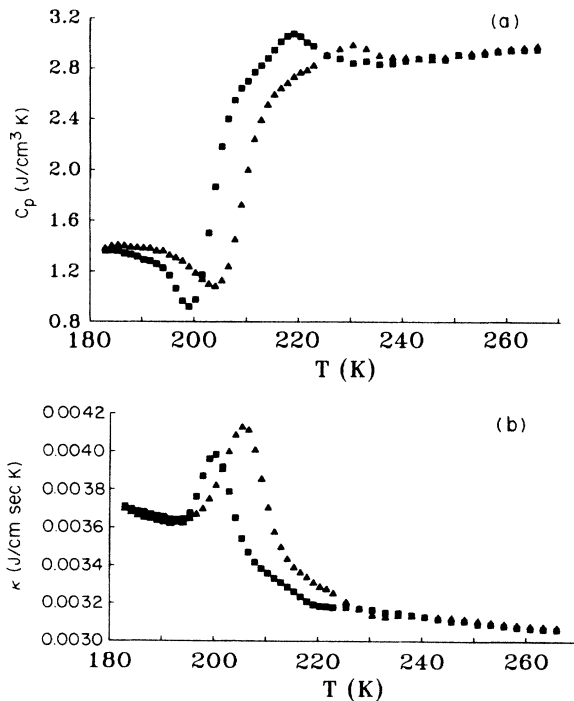

FIG. 7. Analysis of wire data for glycerol using real values of c_p and κ. (a) c_p (in J/cm^3) and (b) κ (in J/cm sec K). The frequencies are the same as in Fig. 5: $f=0.62$ Hz (■) and $f=8$ Hz (▲). This type of analysis is not valid when c_p is complex. This is the reason for the spurious peak in κ and overshoot in c_p as is discussed in the text.

gion, c_p and κ are again frequency independent. This example demonstrates the strength of our frequency-domain technique. As we have shown in Sec. III, the heat-diffusion equation cannot be analyzed in the usual manner in a time-domain experiment if the specific heat is time or frequency dependent. On the other hand, this equation does maintain the same form in the frequency domain even when c_p is frequency dependent and complex. With our technique we are able not only to measure the imaginary part of c_p, but also to see explicitly its frequency dependence over a wide range of frequency.

There are two features in Figs. 5—7 which are difficult to interpret. The first is the appearance of some frequency dependence in the response at a temperature about 20—25 K higher than the peak in c_p'' just discussed. This is most easily seen in the out-of-phase component in Figs. 5 and 6, or in either c_p or κ in Fig. 7. As we cool glycerol from room temperature, the out-of-phase component measured at $f=8$ Hz has a sudden change in its temperature coefficient at $T \sim 231$ K [see Fig. 5(b)]. The same quantity measured at $f=0.6$ Hz has a similar kink at $T \sim 219$ K. Propylene glycol shows similar behavior at $T \sim 202$ K for $f=4$ Hz and at $T \sim 191$ K for $f=0.11$ Hz [see Fig. 6(b)]. In each case the kink appears at a temperature above that where the plane experiment shows dispersion in $c_p\kappa$. Since this new feature has the same frequency dependence as a relaxational process, i.e., it moves to lower temperature with lower frequency, one is at first tempted to identify it as a second liquid relaxation that has not been seen before because it is overshadowed by the primary relaxation already discussed. However, if that were the case, then one would expect to see some signature of this relaxation in the plane experiment also. The data in Fig. 1 show no frequency dependence except that due to the primary relaxation discussed in Sec. IV and above. Although we do not have a satisfactory explanation of this behavior, we do know that it is associated with the glass transition, or with the high viscosity of the liquid sample as it approaches the transition. Measurements of the normal liquids ethanol and toluene show no anomalous behavior over the temperature range shown in Figs. 5 and 6. The behavior in propylene glycol and glycerol are very similar, except the temperature of the anomalous behavior differs in the two cases due to the difference in the glass-transition temperatures.

The second peculiar feature in Figs. 5—7 is the increase in thermal conductivity which seems to have occurred over the temperature range where c_p is complex and frequency dependent. This is most easily seen in Fig. 7(b). Remember that the particular analysis leading to the quantities shown in Fig. 7 is not valid when c_p or κ is complex. However, the analysis should be valid both above and below the dispersion region. Figure 7(b) shows that κ for glycerol has a small negative temperature coefficient between room temperature and the dispersion region. This result agrees with Ref. 16. However, the value of κ below the dispersion region is $\sim 15\%$ higher than it is just above that region, and it has a large negative temperature coefficient. Andersson et al. obtained the result that κ in the glass has a value very close to that in the liquid, except that its temperature coefficient reverses

sign. Unfortunately, we cannot easily extend our measurements to lower temperature because the sample will fall out of equilibrium and we will lose thermal contact between the wire and the sample. (The authors of Ref. 16 circumvented the latter problem by making measurements at high pressure.) If κ does increase through the dispersion region, then we might expect this increase to have the same frequency dependence as the drop in c_p. This would explain why the plane experiment only shows one feature at each frequency. While the behavior of κ in question could have a small quantitative effect on the drop in $c_p\kappa$ seen in the plane experiment, it does not affect qualitatively the interpretation of our experiments.

VI. SUMMARY AND CONCLUSIONS

We have developed a technique to measure the frequency-dependent specific heat of a supercooled liquid over a frequency range exceeding five decades. The technique enables us to measure the linear response of the sample to a small perturbation from equilibrium. Our experimental technique measures the product $c_p\kappa$ rather than just c_p. We have made measurements using a wire-heater geometry in order to see whether κ has any frequency dependence, or whether all of the observed dispersion is due to the behavior of c_p alone. The data are consistent with the hypothesis that most of the frequency dependence is in c_p; however, there are some features of the data which remain unexplained, and which may indicate some frequency dependence to κ.

We have used our technique to study the relaxations near the glass transition in glycerol and in propylene glycol. These two materials behave similarly in several ways:

(i) The specific-heat data show a non-Debye relaxation which moves to lower frequency as the temperature is lowered. This relaxation is responsible for the glass transition that occurs when one cools the sample to the point where it falls out of equilibrium.

(ii) The mean relaxation time in the specific heat is the same as that found by other probes of relaxation, such as dielectric or ultrasonics. This suggests that all of the observed phenomena associated with the glass transition in these materials are governed by a single relaxation mechanism.

(iii) The mean relaxation time as a function of temperature can be fitted either by a Fulcher law or a power law, although in the latter case the exponent is anomalously large, $\alpha \sim 15$. In the former case the temperature T_0, where the relaxation time diverges, is close to the Kauzmann temperature, T_K, where the liquid entropy ex-

trapolates to that of the crystal.

By extrapolating our data to zero frequency we can conceptualize the transition into the "ideal glass" state, i.e., the state obtained in the limit of cooling the liquid infinitely slowly so that it stays in equilibrium until it reaches T_0. This extrapolation indicates that the specific heat would have a step discontinuity at T_0. At this point the glass state formed would have a minimum of excess entropy over the crystal. A theoretical framework for this idea has been provided by Adam and Gibbs.[28] Their model directly relates the relaxation time of a liquid to its excess entropy.

However, not all glass formers behave in the same way as glycerol and propylene glycol.[31] Many liquids have viscosities which obey a Fulcher law over a wide range of temperature, but then depart from that law at low temperatures, and instead show Arrhenius behavior.[32] Since an Arrhenius law stays finite until $T=0$, one immediately asks what happens to the specific heat in such systems. Such liquids will undergo an entropy catastrophe if the equilibrium specific heat remains high and the relaxation time does not diverge above the Kauzmann temperature. Such a catastrophe could be avoided in several ways. For example, the relaxation time for specific heat could diverge even though the time associated with the viscosity does not. Also, the equilibrium specific heat of the liquid may drop to a value close to that of the crystal due to thermodynamic effects (as opposed to dynamic ones). We expect that a study of the frequency-dependent specific heat will indicate in which way these systems manage to avoid violating thermodynamics.

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[1]C. A. Angell and W. Sichina, Ann. N.Y. Acad. Sci. **279**, 53 (1976).

[2]C. T. Moynihan et al., Ann. N.Y. Acad. Sci. **279**, 15 (1976), and references therein.

[3]W. Kauzmann, Chem. Rev. **43**, 219 (1948).

[4]N. O. Birge and S. R. Nagel, Phys. Rev. Lett. **54**, 2674 (1985).

[5]L. D. Landau and E. M. Lifshitz, Statistical Physics (Pergamon, New York, 1980).

[6]D. Forster, Hydrodynamic Fluctuations, Broken Symmetry, and Correlation Functions (Benjamin, Reading, Mass., 1975), or see L. P. Kadanoff and P. C. Martin, Ann. Phys. (N.Y.) **24**, 419 (1963).

[7]Remember that in all of Sec. II we are assuming that the system being discussed has negligible spatial extent, so that we

can neglect thermal diffusion. The slow piece in the correlation function in this case is due only to whatever slow modes exist in the system. In a system with finite spatial dimensions the correlation functions of quantities such as energy or heat have a complicated dependence on both frequency and wave vector even in the absence of any slow modes. See Ref. 6 for a full discussion of this. We will not attempt to describe the full form of the correlation functions in a large system with slow modes.

[8]P. W. Anderson, B. I. Halperin, and C. M. Varma, Philos. Mag. 25, 1 (1972).

[9]W. A. Phillips, J. Low Temp. Phys. 7, 351 (1972).

[10]J. L. Black, Phys. Rev. B 17, 2740 (1978).

[11]M. T. Loponen, R. C. Dynes, V. Narayanamurti, and J. P. Garno, Phys. Rev. Lett. 45, 457 (1980); Phys. Rev. B 25, 1161 (1982); M. Meissner and K. Spitzmann, Phys. Rev. Lett. 46, 265 (1981).

[12]C. A. Angell and L. M. Torell, J. Chem. Phys. 78, 937 (1983).

[13]P. F. Sullivan and G. Seidel, Phys. Rev. 173, 679 (1968).

[14]Several groups have used the adiabatic technique successfully to measure samples near phase transitions. A representative paper is J. E. Smardyk and J. M. Mochel, Rev. Sci. Instrum. 49, 988 (1978).

[15]N. O. Birge and S. R. Nagel (unpublished).

[16]O. Sandberg, P. Andersson, and G. Backstrom, J. Phys. E 10, 474 (1977).

[17]D. Oxtoby, J. Chem. Phys. (to be published).

[18]C. A. Angell and D. L. Smith, J. Phys. Chem. 86, 3845 (1982).

[19]R. Palmer, D. L. Stein, E. Abrahams, and P. W. Anderson, Phys. Rev. Lett. 53, 958 (1984); M. F. Shlesinger and E. W. Montroll, Proc. Nat. Acad. Sci. U.S.A. 81, 1280 (1984); M. H. Cohen and G. S. Grest, Phys. Rev. B 24, 4091 (1981); K.

Ngai, Comments Solid State Phys. 9, 127 (1979); 9, 141 (1980).

[20]D. W. Davidson and R. H. Cole, J. Chem. Phys. 19, 1484 (1951).

[21]Y. H. Jeong, S. R. Nagel, and S. Bhattacharya, Phys. Rev. A (to be published).

[22]S. P. Das, G. F. Mazenko, S. Ramaswamy, and J. J. Toner, Phys. Rev. Lett. 54, 118 (1985); U. Bengtzelius, W. Gotze, and A. Sjolander, J. Phys. C 17, 5915 (1984); E. Leutheusser, Phys. Rev. A 29, 2765 (1984).

[23]G. H. Fredrickson and H. C. Andersen, Phys. Rev. Lett. 53, 1244 (1984); J. Chem. Phys. 83, 5822 (1985).

[24]S. Das and G. F. Mazenko (unpublished).

[25]G. F. Mazenko (private communication). See also P. Taborek, R. N. Kleiman, and D. J. Bishop, Phys. Rev. B (to be published).

[26]M. H. Cohen and D. Turnbull, J. Chem. Phys. 31, 1164 (1959); D. Turnbull and M. H. Cohen, ibid. 34, 120 (1961); 52, 3038 (1970); M. H. Cohen and G. S. Grest, Phys. Rev. B 20, 1077 (1979).

[27]J. H. Gibbs and E. A. DiMarzio, J. Chem. Phys. 28, 373 (1958).

[28]G. Adam and J. H. Gibbs, J. Chem. Phys. 43, 139 (1965).

[29]T. Christensen, J. Phys. (Paris) Colloq. 46, C8-635 (1985).

[30]Thermophysical Properties of Matter, The TPRC Data Series, edited by Y. S. Touloukian (IFI/Plenum, New York, 1970).

[31]C. A. Angell, in Relaxation in Complex Systems, edited by K. Ngai and G. B. Wright (National Technical Information Service, U.S. Dept. of Commerce, Springfield, VA, 1983), p. 3.

[32]W. T. Laughlin and D. R. Uhlmann, J. Phys. Chem. 76, 2317 (1972); M. Cukierman, J. W. Lane, and D. R. Uhlmann, ibid. 59, 3639 (1973).