Frequency-dependent shear modulus of glycerol near the glass transition

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(Received 12 February 1987)

We have measured the frequency-dependent shear modulus of glycerol near the glass transition. The measurements, which covered three decades of frequency, probed the stress response of super-cooled glycerol to small shear deformations. The shear response function has the same shape as the one obtained from ultrasonic experiments. Combined with previous measurements of ultrasound and specific heat, this result suggests that a single relaxation mechanism is responsible for such diverse phenomena as volume, shear, and enthalpy relaxations of the supercooled liquid of glycerol.

I. INTRODUCTION

When a liquid is cooled below the freezing temperature, it usually undergoes a first-order phase transition into a crystal. However, there are many materials which can be easily supercooled mainly due to the fact that they have a large viscosity at the melting temperature. The dynamics of this supercooled state and the glass transition, which occurs when a liquid is sufficiently supercooled, have been a subject of intensive research since the turn of the century. Despite these efforts, a proper understanding of this phenomenon is still lacking.

There are some outstanding questions which still remain to be answered. (i) Is there or is there not a true glass transition[1-3] (in the thermodynamic sense)? It has been suggested that there is a true underlying phase transition which is masked by kinetic effects due to the liquid falling out of equilibrium. If there is such a phase transition, one would expect the growth of a length scale associated with this transition. So far no evidence for such a diverging length scale has been found. (ii) The second question concerns the dynamics of the liquid in the super-cooled state. This has been the focus of much research[4] and plays an important role in answering the previous question. Is there a single relaxation mechanism which governs different relaxations in the supercooled state and if yes, what is the mechanism for this relaxation?

In a recent publication,[5] we have measured the speed and attenuation of ultrasound in glycerol and compared the data with those of a specific-heat experiment[6] on the same sample. We concluded from that experiment that there seems to be a single relaxation mechanism responsible for different relaxations due to different perturbations. In this paper we report the measurements of the frequency-dependent shear modulus in glycerol. Since longitudinal sound involves the bulk modulus as well as the shear modulus,[7] it is of interest to compare pure quantities such as the shear modulus with other response functions. In addition to this, the shear modulus is a key quantity which distinguishes solids from liquids. Therefore, it is of great importance to study the shear modulus as a liquid becomes an amorphous solid.

There is a vast amount of literature on the subject of rheology,[8] the measurement of the shear modulus, and various methods have been developed to measure shear moduli over the years. These include transient methods, sinusoidal techniques, and wave-propagation methods at high frequencies. In transient methods one measures the stress (or strain) as a function of time after the sudden imposition of strain (or stress). In sinusoidal techniques one works in the frequency domain. Here one imposes a sinusoidal strain (or stress) and measures the stress (or strain) as a function of frequency. Either a single- or a double-transducer technique can be used. These two complimentary methods can be used when the dimension of the sample is small compared with the wavelength of the shear wave. At higher frequencies one measures reflection coefficients of a shear wave between a material whose properties are known and the sample.

In our experiment we adopt a sinusoidal technique and measure the shear modulus of glycerol as a function of frequency. Since at lower frequencies, where the dimensions are small compared to a wavelength an X-cut quartz transducer can be used as a generator of a shear strain and a detector of a shear stress, we have applied the two-transducer technique which is frequently used in ultrasonic experiments to low-frequency shear-modulus measurements. In this way we were able to cover three decades of frequency.

This paper is organized as follows. In Sec. II we present a brief discussion of the frequency-dependent shear modulus in liquids. In Sec. III we explain the experimental methods we have used. In Sec. IV we present and discuss the data.

II. FREQUENCY-DEPENDENT SHEAR MODULUS

One of the most conspicuous features of a liquid compared to a solid is that it cannot support shear strains. While one does not face any difficulty with this notion in ordinary liquids, one has trouble understanding the behavior of supercooled liquids in this context. This is due to the fact that in a supercooled liquid the relaxation time of the system becomes so large that it is comparable to the duration of an external perturbation. In this situation the response of a liquid depends on the relative duration of the applied stress and the relaxation time associated with the change of equilibrium due to the stress. If the time

scale over which the shear stress is applied is long compared with the relaxation time, the liquid responds to the stress by flowing. The behavior is then characterized by viscous flow. If, on the other hand, the time scale of the external stress is less than the relaxation time, then the response is elastic which is characteristic of a solid. In the region where these two time constants are comparable to each other, the liquid is said to be viscoelastic and the properties of the liquid are frequency dependent.

In a viscoelastic system, as in an elastic medium, the state of deformation at a given point is described by a strain tensor.[9] The strain tensor represents the relative change in position of a small element at that point. For an infinitesimal deformation, the strain tensor γ_{ij} is defined by

$$\gamma_{ij} = \alpha \left[\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right], \quad \alpha = \begin{cases} \frac{1}{2} & \text{if } i = j \\ 1 & \text{if } i \neq j \end{cases}, \quad (1)$$

where x_i and u_j are, respectively, the Cartesian coordinates of the point where the strain is specified and its displacement. The corresponding stress tensor σ_{ij} is defined as follows:

$$t_{ij} = -p\delta_{ij} + \sigma_{ij}, \quad (2)$$

where t_{ij} is a second-rank stress tensor that represents the force applied in the j direction per unit area of a plane whose normal lies in the i direction. For an isotropic medium, the stress tensor can be resolved arbitrarily as the sum of a hydrostatic pressure p and a residual stress tensor σ_{ij}.

In our case we are interested in a shear deformation which is described by the off-diagonal elements of γ_{ij} and σ_{ij}. When the system is under a shear deformation, γ_{ij} and σ_{ij} are related by the constitutive equation

$$\sigma_{ij}(t) = \int_{-\infty}^{t} \Gamma(t - t') \left[\frac{d\gamma_{ij}(t')}{dt'} \right] dt', \quad i \neq j \quad (3)$$

where $\Gamma(t)$ is called the decay function. The decay function $\Gamma(t)$ describes the response of the stress to a steplike strain and goes to zero as t approaches infinity. Notice that for isotropic systems there is only one decay function for shear deformations. The basic principle on which Eq. (3) is based is that the effects of sequential changes in strain are additive when they are infinitesimal (i.e., Boltzmann's linear superposition principle).

As with any other linear response function, the shear response can be measured in the frequency domain as well as in the time domain. In this case we integrate Eq. (3) by parts and then take its Fourier transform

$$\sigma_{ij}(\omega) = G(\omega)\gamma_{ij}(\omega), \quad i \neq j \quad (4)$$

where $G(\omega)$ is the frequency-dependent shear modulus given by

$$G(\omega) = 1 - \int_{0}^{\infty} \left[-\frac{d\Gamma}{dt} \right] e^{-i\omega t} dt. \quad (5)$$

In the ideal case, where there is only one relaxation time, one can write the shear modulus in the frequency domain as follows:

$$G = G_\infty \frac{i\omega\tau}{1 + i\omega\tau}, \quad (6)$$

where G_∞ is a high-frequency limit of the shear modulus and τ is a characteristic shear relaxation time. The imaginary part has a familiar Debye form whose full width at half maximum is 1.14 decades. If one measures the response in the time domain, rather than in the frequency domain, a single relaxation time would imply that the shear stress decays exponentially in response to a step function in the strain applied to the system. In general, however, the response is never characterized by an exponential decay but by a more complex functional form.[10] It has been the usual procedure to describe such a behavior by a distribution of relaxation times. That is,

$$G(\omega) = G_\infty \int g(\tau) \frac{i\omega\tau}{1 + i\omega\tau} d\tau, \quad (7)$$

where $g(\tau)$ is the distribution function of such times. Although one can always fit the data by assuming a distribution of relaxation times, it is not clear that such an interpretation of the data is justified since there is no universally accepted theoretical model that accounts for the similarity in the distributions that are found in many different experiments on the same sample as well as in different samples.[11]

It is one of the purposes of the present experiment to see if this similarity, already found in glycerol by the ultrasound,[5,12] dielectric,[13] light scattering,[14] and specific-heat experiments,[6] persists to the shear modulus. Shear and bulk deformations are essentially different in character, one involving a shape change and the other a volume change, and it might therefore be expected that they are accompanied by quite different molecular processes.

Before going into Sec. III, we mention, in passing, the relationship between the shear modulus and the dynamic viscosity. The dynamic viscosity $\eta(\omega)$ is the quantity which is used when one describes viscoelastic systems from the liquid point of view. The dynamic viscosity, which is the ratio of the stress to the rate of the shear strain, is simply related to the shear modulus by

$$G(\omega) = i\omega\eta(\omega). \quad (8)$$

We will use the shear modulus $G(\omega)$ in describing the experimental results throughout this paper.

III. EXPERIMENTAL METHOD

In a typical experiment measuring a mechanical property,[8] such as the shear modulus, one measures the extrinsic quantities (i.e., the displacement and force). The ratio of these is related to the shear modulus by a form factor which depends on apparatus geometry. To measure a shear modulus as an absolute quantity, one must take pains to keep the geometry simple and thereby be able to calculate the form factor. This limits the experimental geometry to simple configurations such as two parallel planes or two concentric cylinders.

On the other hand, there are many occasions where one is more interested in the relative change of a shear modulus as a function of external parameters such as tem-

perature and frequency, rather than the absolute value itself. In these cases, one is not interested in the form factor of the apparatus at all as long as it remains constant throughout the measurements. Indeed, the study of the glass transition is one of those occasions where one is more interested in how the shear modulus changes as a function of temperature and frequency rather than its absolute magnitude. In this experiment we take advantage of this and the fact that one can use quartz crystal as stable and reliable transducers of shear deformations at lower frequencies to measure the shear modulus of glycerol.

Central to the whole experiment is the idea that quartz be used as a shear transducer. Due to the crystal structure of quartz,[15] there are five piezoelectric constants with only two independent values. In the case of X-cut plates which were used in this experiment, only three of these five constants are relevant. The relationships between the electric field and the strains in the free crystal without external stresses are

$$X_x = d_{11} E_x , \tag{9a}$$

$$Y_y = d_{12} E_x , \tag{9b}$$

$$Y_z = d_{14} E_x , \tag{9c}$$

where E_x is the electric field across the x axis and

$$X_x = \frac{\partial u_x}{\partial x}, \quad Y_y = \frac{\partial u_y}{\partial y}, \quad Y_z = \frac{\partial u_y}{\partial z} + \frac{\partial u_z}{\partial y} .$$

The values of d_{ij} at room temperature are the following:[16]

$$d_{11} = -d_{12} = 6.9 \times 10^{-8} \text{ esu}, \quad d_{14} = -2 \times 10^{-8} \text{ esu} .$$

Notice that $Z_z = 0$. Among Eqs. (9), Eq. (9c) describes a shear deformation which does not change the volume. On the other hand, Eqs. (9a) and (9b) describe extension and compression. It is this property that is used to generate ultrasonic longitudinal waves in the megahertz range. When the wavelength of the wave is much larger than the dimensions, it is necessary to consider the deformation as a whole. Since $d_{11} = -d_{12}$ due to the symmetry, it is easy to see this deformation does not change the total volume. Let the dimensions of the plate be l_x and l_y parallel to the x axis and y axis. When a potential difference V is applied to the x direction, the following expressions hold:

$$\Delta l_x = d_{11} V ,$$
$$\Delta l_y = d_{12}(l_y/l_x)V = -d_{11}(l_y/l_x)V . \tag{10}$$

The area change is then,

$$\Delta S = l_y \Delta l_x + l_x \Delta l_y = d_{11} l_y V - d_{11} l_y V = 0 . \tag{11}$$

Since $Z_z = 0$, there is no volume change. Figure 1 shows how a combined extension and compression represent a pure shear.

The above considerations show that if one applies a sinusoidal voltage to an X-cut quartz crystal, one gets an oscillatory shear deformation. The basic idea of the experiment is the following. Let us fill a closed vessel with the liquid sample (glycerol) and immerse two quartz transducers in it. Here the dimensions of the cell have to

be much smaller than the wavelength of the sound in the liquid. This sets the limit for the highest frequency of the experiment. At the highest frequency (10 kHz) the experiment was done, the ratio of the size of the cell to the wavelength was approximately $\frac{1}{15}$. If we apply the sinusoidal voltage on a transducer, then it will generate the shear strain field in the liquid. This is due to the fact that (i) since the wavelength of the sound is much larger than the dimensions of the cell, there is no density variation in the liquid, (ii) the total volume of the liquid in the cell is constant, and (iii) there is a shear deformation of the transducer.[17]

Since piezoelectricity is a reversible effect, the external shear stress induced by the shear strain will generate a charge on the electrodes of the second transducer. Another property of quartz is that it does not respond to (no charge is induced by) hydrostatic pressure (see Ref. 15, Chap. VIII). Indeed one can divide the piezoelectric crystals into two classes according to the response to hydrostatic pressure. Quartz belongs to the class which does not respond to hydrostatic pressure. We can detect only the shear stress in the liquid by monitoring the induced charge. If we keep the input voltage to the first transducer constant with variation of frequency and temperature, the output voltage from the second one will directly reflect any change in the shear modulus in the sample. (Here we are assuming that a constant input voltage generates a constant shear strain regardless of frequency and temperature and it will be a major source of error.[18])

One fundamental difference of our setup from the ones with simple geometry is that, in our case, the strain field is not uniform. As a matter of fact, the strain field induced in the liquid would be quite complicated depending on the shape of the vessel which provides the rigid boundary conditions. Fortunately, however, we are dealing with an isotropic medium. And, as a result, there is only one shear modulus, i.e., the ratio of the stress to the strain is the same regardless of the magnitude and direction of the strain. Consequently, nonuniformity of the strain field does not present any problem in our case as long as we keep the relative configurations of the two transducers
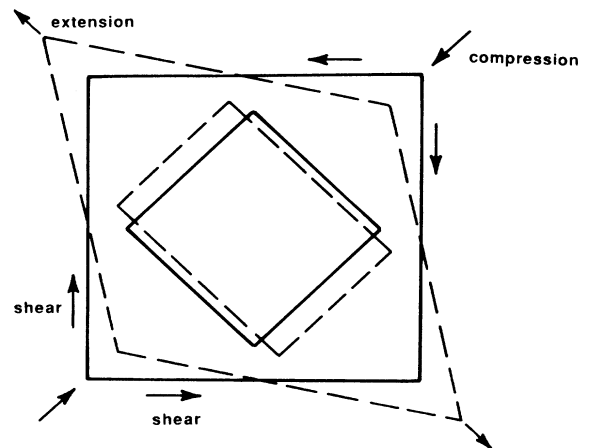

FIG. 1. Equivalence of pure shear to combined extension and compression.

intact throughout the experiment. In other words, the first transducer generates the same strain field (as a result of constant input voltage) at the position of the second transducer. Likewise, the second transducer detects the stress which is the shear modulus times the strain which is constant throughout the experiment.

The sample cell we used in this experiment is shown in Fig. 2(a). It was made of copper to ensure the lack of thermal gradient, and has a cylindrical shape with inside diameter $\frac{5}{8}$ in., outside diameter $1\frac{5}{8}$ in. and length $\frac{3}{4}$ in. The cell was closed by two thick copper caps. The cell which contains two transducers (X-cut quartz plates with diameter $\frac{1}{2}$ in. and fundamental frequency 1 MHz) is connected to the reservoir through a hole of diameter $\frac{1}{16}$ in. and length $\frac{3}{4}$ in. The reservoir was necessary to keep the cell full of liquid in the presence of the large thermal contraction of glycerol. The distance between the transducers was approximately $\frac{1}{4}$ in.

Temperature was measured with the copper-Constantan thermocouple and controlled within 0.1 K by the software developed in this laboratory for a Hewlett-Packard 86 computer in conjunction with a programmable power source. As we show in Fig. 2(b), the output voltage (~ 20 $V_{p.p}$) of the Hewlett-Packard 3325A frequency synthesizer was directly fed into the transducer. The signal from the second transducer was measured with the Princeton applied Research 124A lock-in amplifier and/or the Hewlett-Packard 3561A signal analyzer. The data were taken every 2 K. We cooled (or heated) the system, waited for an hour (or even two hours at lower temperatures) to ensure that equilibrium had been reached and then took the data as a function of frequency. Since we want to measure the linear response of the system in equilibrium, we have checked the linearity of the output signal to
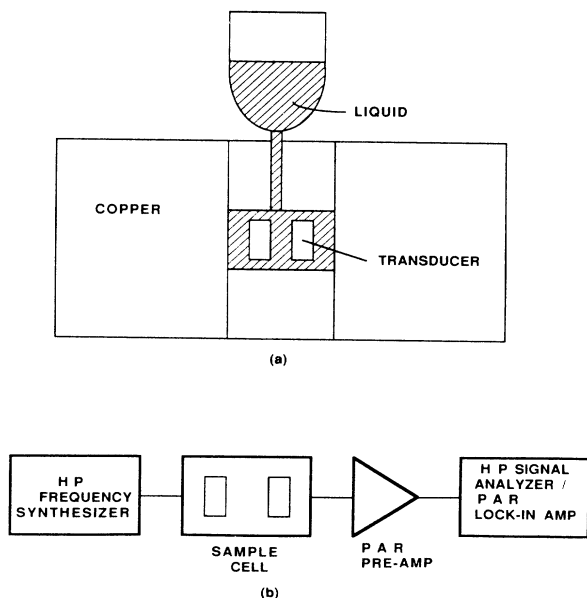

FIG. 2. (a) Schematic diagram of the sample cell and (b) a block diagram of the experimental measurement apparatus.
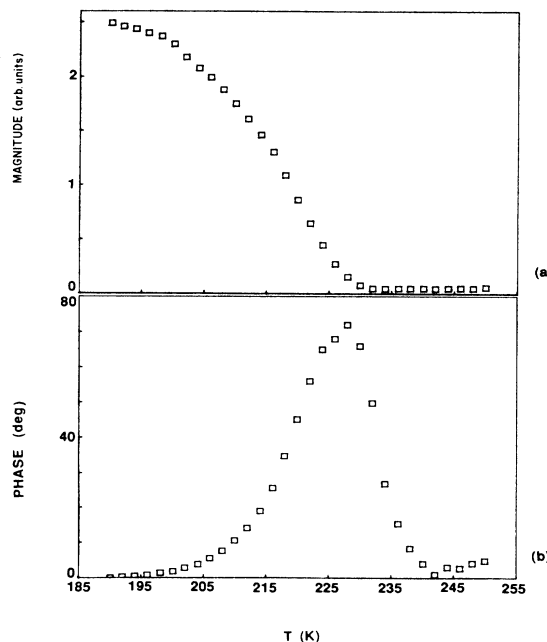

FIG. 3. Typical raw data (lock-in output) as a function of temperature at $f = 1$ kHz. (a) Magnitude and (b) phase change of the output signal.

the input voltage. Within the voltage level we used, no nonlinearity was discovered for the entire temperature region.

In Fig. 3 we show typical raw data (magnitude and phase change of the signal with respect to the reference) at $f = 1$ kHz. The data show what we expect from relaxation phenomena. The magnitude increases from a very small value (characteristic of a liquid)[19] to a large value (characteristic of a solid) in a narrow temperature region. In association with this increase in magnitude is the phase change which goes through a peak. From the magnitude and phase change of the signal, one can calculate the real part G' and the imaginary part G'' of the shear modulus. The result, especially the phase change, was very sensitive to the existence of bubbles in the sample cell. We have paid careful attention to the procedure used to fill up the sample cell in order to avoid trapping bubbles in the cell.

IV. EXPERIMENTAL RESULTS AND DISCUSSION

In Fig. 4 we show the real and imaginary part of the shear modulus of glycerol, $G(\omega, T) = G' + iG''$, as a function of temperature at different frequencies. In plotting the results, we have normalized the data with respect to the shear modulus at $T = 186$ K where the shear modulus does not show any frequency dependence. The data are those of typical relaxation phenomena with the peak in the imaginary part moving to lower temperature as the frequency is lowered. Associated with a peak in the imaginary part is a frequency dispersion in the real part.

In order to compare the shear response function with

other response functions, we plot the shear modulus as a function of frequency at fixed temperatures. In Fig. 5 we show the real and imaginary parts versus $\log_{10} f$ at three different temperatures. As the temperature changes, the peak in the imaginary part moves through our frequency window. Note that $G''(\omega)$ has a wider full width at half maximum than the Debye form (1.14 decades) and is asymmetric with a tail to the high-frequency side. Due to a limited width of the frequency window of our experiment, we cannot see the whole shape of the response function. This is a typical problem one always faces in any relaxational spectroscopy. However, in many complex systems it is known that time-temperature superposition works.[20] Indeed we have used this technique in the previous experiment[5] in glycerol.

To test the validity of this method in the shear-modulus case, we attempt to construct the master curve by rigidly shifting the curves in $G(\omega)$ versus $\log_{10}\omega$. The shift factor we use for this purpose is $\omega_p = 15.7 \times 10^{14} \exp[-2310/(T-129)]$ which was the mean relaxation time obtained from the combined results of the previous ultrasonic and specific-heat measurements (see Ref. 5). If we can construct a master plot with this mean relaxation time, it would suggest that there exists a single average relaxation time in the system. As we show in Fig. 6, this is indeed the case. The shape of the master curve shows a familiar form, that is, skewed with a tail to the high-frequency (or low-temperature) side.[21] Notice that although we have used the Vogel-Fulcher fit as a shift factor, it would have

been equally good to use the scaling fit $\omega_p = 15.7 \times 10^{10}[(T/175.5)-1]^{12.5}$. While the former form has been used widely in this field, this latter form was introduced recently by various hydrodynamic theories of the glass transition.[3] These hydrodynamic theories are quite different from the theories that existed previously (e.g., the entropy theory[1] or the free-volume theory[2]). Although the details of the theories differ, the basic ingredient seems to be a dynamic feedback mechanism. The glass transition is brought about dynamically and no thermodynamic transition is predicted even in the limit of infinitely slow cooling rate.

As we saw above, the fact that we can construct the master curve with a mean relaxation time which was obtained from the ultrasonic and the specific-heat experiments, implies that a single relaxation mechanism is operating in this supercooled liquid. To further test this notion, we compare two master curves from the ultrasonic and shear-modulus measurements. One can certainly imagine a situation where one has the same average relaxation time but different spectral shapes of response functions. (For instance, the dielectric response of glycerol has the same average relaxation time, but does not have the same spectral shape as other responses such as specific heat and ultrasound.[5]) Indeed if one adopts the point of view that there is a distribution of relaxation times, one would guess a priori that the shapes of these response functions would be different. This is due to the fact that the spectral shape of the response functions, one involving a pure shear and the other involving a volume change as well, reflects the molecular processes accompanying the changes. We show, in Fig. 7, two master curves. Except
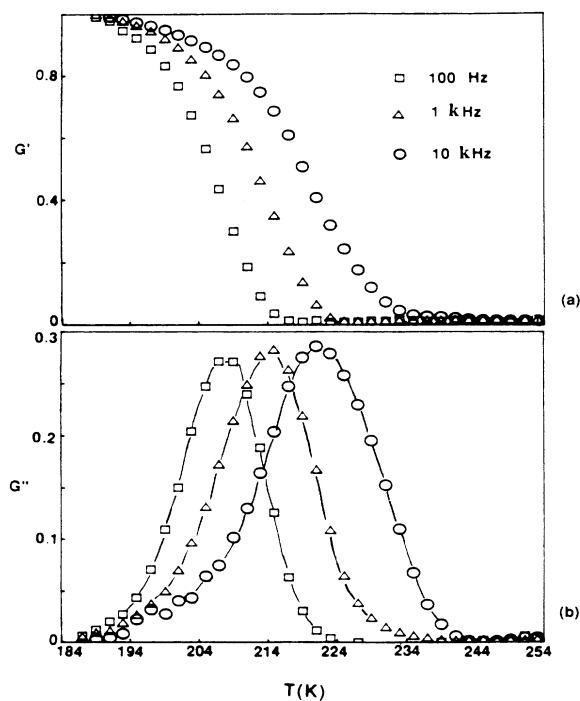

FIG. 4. Plots of (a) the real part G' and (b) the imaginary part G'' of the shear modulus vs temperature. The lines are guides for the eye.
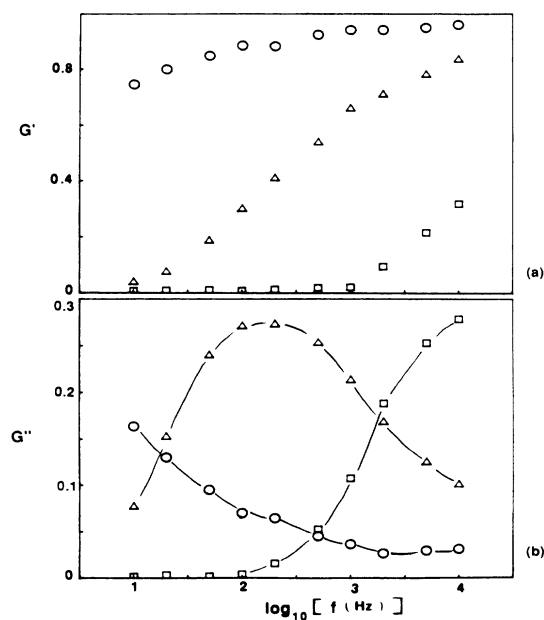

FIG. 5. Plots of (a) the real part G' and (b) the imaginary part G'' of the shear modulus vs $\log_{10} f$ at 197 K ($\bigcirc$), 209 K ($\triangle$), and 223 K ($\square$). The lines are guides for the eye.
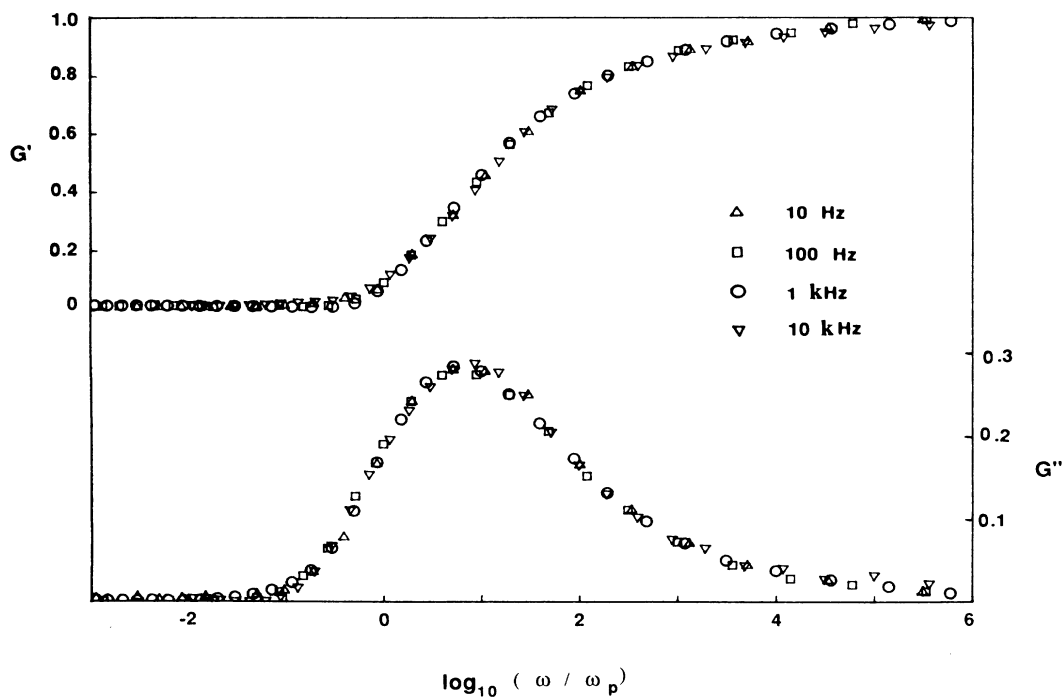
FIG. 6. Master plot of G' and G'' vs $\log_{10}(\omega/\omega_p)$. A Vogel-Fulcher fit $\omega_p = 15.7 \times 10^{14} \exp[-2310/(T-129)]$ (from Ref. 5) was used as a shift factor.
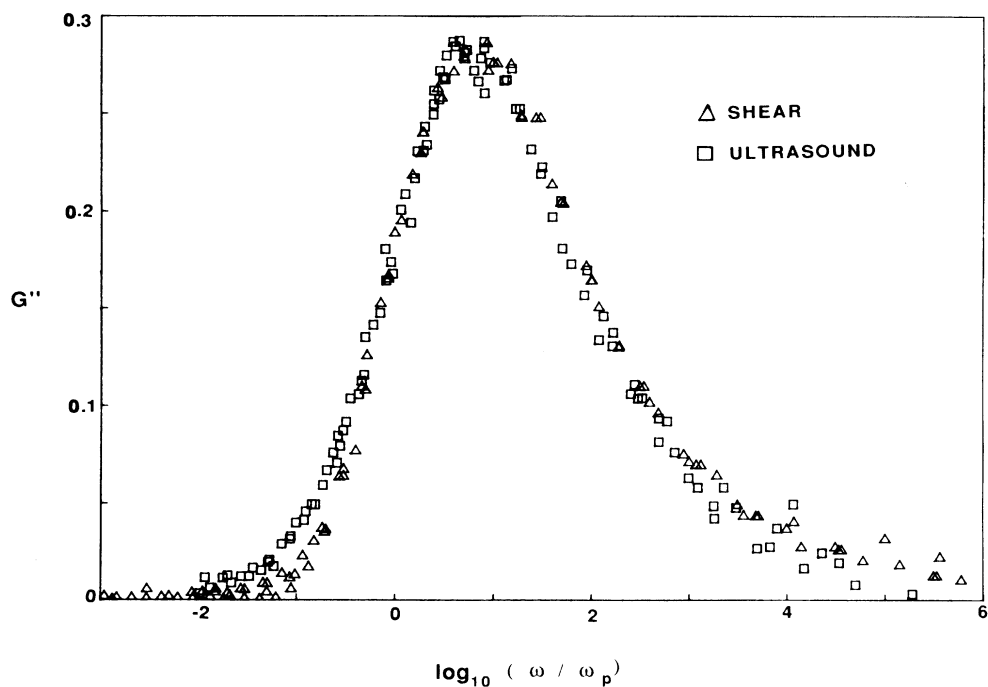
FIG. 7. Master plots of shear modulus (this work) and longitudinal modulus (from Ref. 5).

at the wings where the data are less reliable, it shows excellent coincidence. In view of the fact that the shapes of the specific-heat and ultrasonic response functions were the same within the experimental error, we therefore conclude that a single relaxation mechanism is operating and is responsible for different relaxations such as volume, shear, and enthalpy.

V. CONCLUSION

We now summarize the experimental findings and discuss their implications in the following.

(i) The shear modulus data, the ultrasonic data, and the specific-heat data obtained from experiments performed on the same sample all show the same non-Debye relaxation which slows down as the temperature is lowered. In this regard, it is suggestive that the recent computer-simulation experiment done by Grest and Nagel[22] finds that most of what happens in the glass transition occurs in $C_p - C_v$. That is, they see a very large change in C_p, but only a minimal change in C_v as a Lennard-Jones fluid is cooled through the glass transition. Since $C_p - C_v = TV\alpha^2/\kappa_T$ (where α and κ_T are the thermal expansion coefficient and the isothermal compressibility, respectively), and the ultrasound involves the compressibility, their results seem to suggest some connection between the specific heat and the mechanical properties in the glass transition.

(ii) The *average* relaxation time probed by different perturbations show the same behavior. They are well described either by a scaling law $\tau = \tau_0[(T/T_h) - 1]^{-\alpha}$ or a Vogel-Fulcher law $\tau = \tau_0 \exp[-\Delta/(T - T_0)]$, although the former requires the anomalously large exponent $\alpha = 12.5$. In the latter case T_0 (129 K) is very close T_K (134 K), the Kauzmann temperature[23] where the entropy of the supercooled liquid would extrapolate to less than that of the corresponding equilibrium crystal.

We can now go back and address the questions which were raised in Sec. I. If we push our data and extrapolate to zero frequency, we would have a setup discontinuity in the specific heat, the compressibility, and the shear modulus at $T = T_0$. This is due to the fact that the difference between the high-temperature and the low-temperature values in these quantities (often called relaxation strength) does not change as one changes the measuring frequency. This discontinuity is reminiscent of Ehrenfest's second-order phase transition.[24] According to his definition, the transition has a discontinuity in the second-order derivatives of the free energy such as the

specific heat, the compressibility, and the thermal expansion coefficient, while the first-order derivatives such as volume and entropy are continuous.

It is dangerous practice, however, to extrapolate to zero frequency, not only because the extrapolation cannot be confirmed experimentally, but also because there are other glass-forming liquids which behave differently. Many liquids have been found to have viscosities which obey Vogel-Fulcher law over one range of temperatures and then cross over to an Arrhenius form as the temperature is lowered further.[25]

As far as the dynamics of supercooled glycerol is concerned, it now seems clear that there is a single relaxation mechanism.[26] At the moment we are not able to answer what it is. In this context it is interesting to compare the glass transition with the critical slowing down in critical phenomena.[27] As a critical point is approached by changing the external parameter, the characteristic time arises in association with the characteristic length scale. Although it is not intuitively clear what kind of order exists in the glassy state, one can imagine an (undoubtedly subtle) order parameter[28] on a macroscopic level which distinguishes the glassy state from the fully disordered liquid state. If we suppose the slow relaxation is associated with this ordering, it would provide some justification for having the same relaxation for different phenomena which seem to be accompanied by different molecular processes. We have tried to identify the order parameter by measuring the nonlinear dielectric susceptibility, the magnetic analog of which showed a divergence in spin glasses.[29] This attempt to find the diverging length scale was so far unsuccessful. Other experiments in this direction are underway in this laboratory.

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[10] One of the more common forms is the fractional exponential decay $\exp[-(t/\tau)^\beta]$.

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[16] There seem to be some discrepancies about the numerical values of d_{ij} in the literature. (These values were quoted from Ref. 15.) Nevertheless, the relationship $d_{11} = -d_{12}$ still holds.

[17] Remember that our argument for a shear deformation of the transducer was done on the free crystal. Since the experiment is performed under the presence of hydrostatic pressure, one cannot rule out a volume change. It does not, however, affect the experiment since the stress detecting quartz transducer shows no polarization under hydrostatic pressure (Ref. 15, Chap. VIII).

[18] Since the measuring frequency is far enough off the resonance frequency (1 MHz), the frequency dependence seems to be negligible. The main source of error lies in the temperature dependence of d_{ij}. Here once again discrepancies are found in the literature. Between the room temperature and the liquid air temperatures (-192 C), the relative change of d_{11} ranges from less than 1% to 2% or 3%, but certainly not more than 5%. Over the temperature range of 50° or 60° of our interest, this seems to have a negligible effect. We have neglected this effect.

[19] This is an experimental proof that we measure the shear modulus.

[20] This is a scaling relation. As the temperature changes, only the time scale changes without changing the form of the response functions. That is, $G(\omega) = bG(\omega a_T)$ where $b \sim 1$ and a_T is a scaling factor which includes the temperature dependence.

[21] No explicit temperature dependence in the factor b (Ref. 20) was found within our experimental uncertainty. It was assumed that the only effect of temperature on the data is contained in the shift factor. The shape of the curve seems to be different from the symmetric one found in the real-part data by a reflection method at higher frequencies (Ref. 12). We note, however, that it is not easy to determine the shape of the curve from the real-part data only. It is more reliable to use the imaginary part to determine the shape of the response function. It is interesting to note that the similar shape was found in the shear modulus measurements of soda-silica glasses [J. J. Mills, J. Non-Cryst. Solids **14**, 255 (1974)].

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[26] C. T. Moynihan et al., Ann. N.Y. Acad. Sci. **279**, 15 (1976). One must be cautious to generalize this result. The above authors find different relaxation times for different perturbations in other glass-forming liquids. We note, however, that their measurements were done on nonequilibrium samples and they relied on the complex data analysis method which is not unambiguous as to how to extract the relaxation time from the raw data.

[27] See, for example, S. K. Ma, *Modern Theory of Critical Phenomena* (Benjamin-Cummings, Mass., 1976).

[28] Several authors developed the order parameter model for the thermodynamics of the structural relaxations (Ref. 24 and references therein). The order parameter in the model seems to refer to microscopic specifics such as the number of flexed bonds and the number of "holes" in polymers, the number of broken bonds, and the number of "holes" in network glasses, and so on. We, however, use the term *order parameter* in the same sense as it is used in critical phenomena. That is, it involves some sort of symmetry breaking although it is not clear at all at the present time what kind of symmetry is involved in the glass transition. See, E. A. DiMarzio in Ref. 11 for more discussion on order parameters used in this field.

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