High-Pressure Viscoelastic Properties and Equation of State of Liquids Derived from Brillouin Data

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Brillouin scattering in an organic glass-forming liquid up to a pressure of 12 GPa is reported. The onset of the unrelaxed regime is indicated by a distinct maximum in the acoustic attenuation at a pressure P_a, above which weak shear modes are resolved. Sound velocity data are fitted in a self-consistent way which accounts for relaxation by combining the "universal" Vinet equation of state with an expression for the dynamical modulus. This analysis yields the pressure dependences of the relaxed and unrelaxed moduli, relaxation time, and density over the pressure range studied.

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The structural and relaxation properties of viscoelastic liquids and the liquid-glass transition are currently a subject of intense interest. A number of theoretical models have been proposed to account for the rich phenomenology displayed by viscous liquids, and, in particular, for their dynamical properties as the glass transition is approached upon cooling. Experimentally, a variety of techniques have been required in order to cover the huge frequency range necessary to explore the dynamics of viscoelastic systems between the low viscosity liquid and the glass [1]. With few exceptions these studies have probed liquid-glass systems as a function of temperature, leaving the pressure domain largely unexplored.

Dynamical properties of several liquids have been studied to moderate pressures using techniques such as ultrasonics [2,3], Brillouin scattering [4,5], NMR [6], and dielectric measurements [7–9]. In general, these studies have involved pressure ranges small enough that viscosity changes have been limited to only a few orders of magnitude. This precludes a detailed understanding of the dynamical properties of these systems since relaxation times and viscosities often vary by 10–15 orders of magnitude between 0.1 MPa (1 bar) and the glass transition pressure P_g. Therefore little is known of the high-pressure static and dynamic properties of the superpressed liquid state. There have been a few reports of hypersonic velocity measurements of viscoelastic liquids [10] and molecular crystals [11] to higher pressures, but these have neglected acoustic attenuation.

Packing forces dominate the structural and dynamical properties of liquids at high pressure. It is therefore of fundamental importance to know the pressure dependence of the liquid density. There have been a number of direct measurements of the equations of state (EOS) of a variety of liquids to high pressures [12,13]. Indirect measurements of the equations of state are often made from ultrasonic and hypersonic acoustic velocity measurements employing a thermodynamic relation between the adiabatic and isothermal moduli [14]. The Birch-Murnaghan and Tait equations of state, typically applied to crystals, are reasonably successful in representing the P-V relationship of a number of liquids over a moderate strain regime $(1 \geq V/V_0 \geq 0.8)$ [13,14]. More recently, a so-called "universal" EOS proposed by Vinet *et al.* [15] has been very successful in describing a wide variety of crystalline systems with very different kinds of intermolecular interactions (covalent, metallic, ionic, and van der Waals) over very large strain ranges.

To obtain accurately the EOS of liquids from acoustic velocity data it is also essential to account for dispersion since relaxation phenomena are a dominant feature of the superpressed (or supercooled) viscoelastic liquid. At some pressure P_a, the structural relaxation time of the system becomes longer than the period of the acoustic mode probed and the system will begin to appear "glass-like." In general, the longitudinal-acoustic (LA) mode will exhibit an attenuation maximum at P_a and hypersonic shear modes can begin to be supported above P_a. Furthermore, the measured sound velocities above P_a are no longer the static or "relaxed" values and cannot therefore be used directly in an EOS. Only with attenuation data can the onset of the high-frequency "unrelaxed" state be determined.

In this Letter Brillouin scattering data obtained at 300 K in a diamond-anvil cell for a 1:1 pentane/isopentane liquid mixture between the pressures of 0.1 MPa and 12 GPa are presented. This particular system was chosen since it is a fairly simple molecular system with relatively simple intermolecular interactions, i.e., there is no hydrogen bonding, the high-pressure properties of hydrocarbons are interesting in general, and because it is a commonly used pressure transmitting medium due to its relatively high glass transition pressure. LA sound velocities and attenuations have been measured over the entire pressure range. Weak transverse-acoustic (TA) modes are resolved above ~4.5 GPa, significantly below the quasistatic glass transition pressure P_g of ~7.4 GPa. The velocity and linewidth data are fitted in a self-consistent scheme using the universal Vinet equation of state incorporating dynamical moduli. This analysis yields the pressure dependences of the relaxed and unrelaxed longitudinal and shear moduli, relaxation time, and density over the pressure range studied.

Experiments were performed in a Merrill-Bassett–type diamond-anvil cell (DAC) at scattering angles of 32° and 60° in an equal-angle forward-scattering geometry [16], in which the sound velocity v is related to the Brillouin frequency shift ν by $v = \lambda_i \nu / 2\sin(\theta/2)$, where λ_i is the incident wavelength (5145 Å) in a vacuum and θ is the external scattering angle. All spectra were recorded with a 5-pass, 4-pass tandem Fabry-Pérot interferometer [17]. Standard ruby fluorescence techniques were used to measure the pressure at more than one position in the sample. The glass transition pressure is estimated by the onset of nonhydrostatic conditions to be $P \sim 7$ GPa, consistent with previous results [18]. Further experimental details will be published elsewhere [19].

In Fig. 1 several spectra recorded at different pressures and at $\theta = 60°$ are shown along with fits to the LA modes. These fits are of Lorentzian functions appropriate for viscous liquids [20], which have been corrected for finite aperture effects and convolved with the instrumental functions [21]. The pressure dependences of the sound velocities and the acoustic-mode linewidths (HWHM) obtained from these fits are shown in Figs. 2(a) and 2(b), respectively. A distinct maximum is observed in the HWHM at $P_a = 2.25$ GPa for the $\theta = 60°$ data, and a similar peak is observed at a slightly higher pressure in the $\theta = 32°$ data.

The relaxation time associated with the dominant relaxation process of the liquid at P_a can be obtained from the inverse of the Brillouin frequency ($\omega_l \tau_l = 1$) [22]. This yields a value of $\tau_l(P_a) = 20 \times 10^{-12}$ s at 2.25 GPa, and can be compared with a value of 2.0×10^{-12} s at 0.1 MPa [23] and a typical value of 10^2–10^3 s at P_g.

To our knowledge there is no model for the relaxation time that is predictive over the extreme strain range probed in these high-pressure experiments. Simple Arrhenius behavior for the pressure dependence of τ_l is clearly inadequate. Instead, we find that an expression of the form $\tau_l(P) = A\exp[C/(P_0 - P)]$, which can be derived from the Vogel-Tammann-Fulcher expression by assuming a linear pressure dependence for the zero-mobility temperature T_0 [24], gives a reasonable representation of the average longitudinal relaxation time [19], with the values of 2.1×10^{-15}, 61.1 GPa, and 8.90 GPa for the parameters A, C, and P_0, respectively [see the inset in Fig. 2(b)].

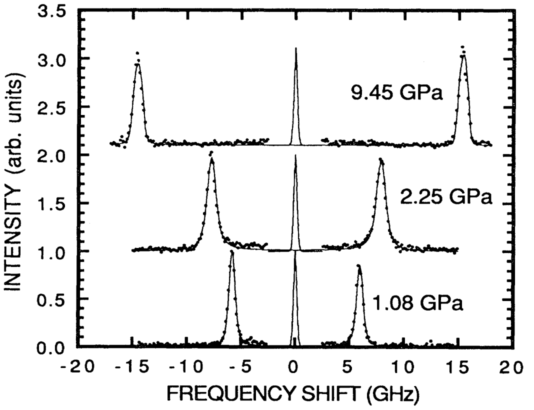

FIG. 1. A series of Brillouin spectra taken in the 1:1 pentane/isopentane system recorded at $P = 1.08$ GPa ($\omega_l \tau_l < 1$), 2.25 GPa ($\omega_l \tau_l = 1$), and 9.45 GPa ($\omega_l \tau_l > 1$). The solid lines represent fits to the LA modes. The Rayleigh lines have been scaled to fit on the plots.

The frequency-dependent adiabatic longitudinal modulus for an isotropic medium is given by $M(\omega) = K(\omega) + 4/3G(\omega)$, where K and G are the adiabatic bulk compressional and shear moduli, respectively. $M(\omega)$ can be

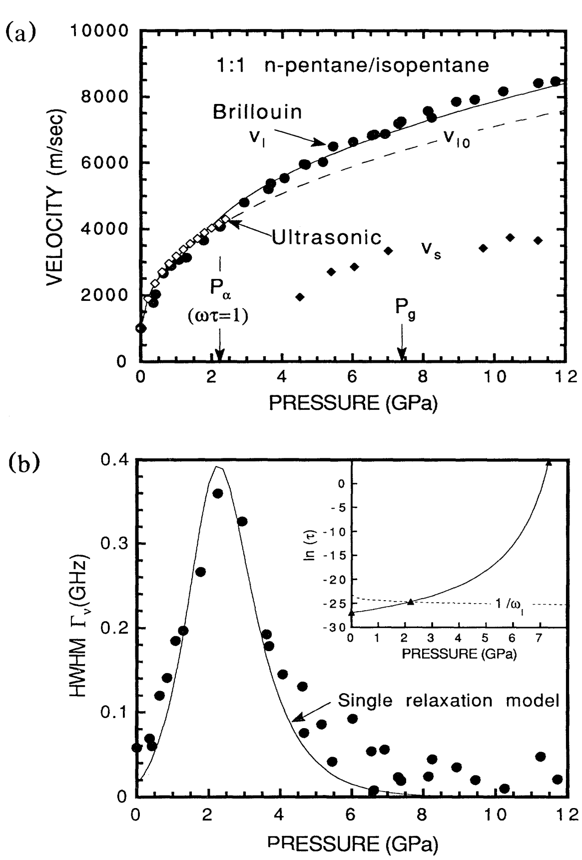

FIG. 2. Pressure dependences of the LA and TA velocities and LA linewidths (HWHM) obtained from the Brillouin data. (a) The measured LA velocities (●) and TA velocities (◆), as well as the 10-MHz ultrasonic data of Houck (Ref. [25]) (◇). The solid line represents the fit to the LA frequencies and the dashed line represents the relaxed values of the velocities obtained from these fits. (b) The measured LA mode linewidths as a function of pressure (●) and the values calculated based on a single relaxation time (——). Inset in (b): The three known values of the longitudinal relaxation time and the modified Vogel-Tammann-Fulcher fit to these values.

written as [22]

$$M(\omega)=\gamma K_T+M_r\int_0^\infty g(\tau_l)\frac{i\omega_l\tau_l}{1+i\omega_l\tau_l}d\tau_l\,, \qquad (1)$$

where γ is the ratio of the isobaric to isochoric specific heats, K_T is the static isothermal bulk modulus, $M_r=(K_\infty-K_0)+4/3G_\infty$ is the "relaxing" part of the modulus (K_∞ and G_∞ being the infinite-frequency moduli and K_0 the static modulus), τ_l is the longitudinal relaxation time, and $g(\tau_l)$ is its distribution. The LA velocity v_l is related to the real part of $M(\omega)$ as $\mathrm{Re}\{M(\omega)\}=\rho v_l^2$, where ρ is the mass density. In the static limit Eq. (1) expresses the relationship between the isothermal and adiabatic moduli, which involves the ratio γ.

For simplicity, we assume a single relaxation time resulting in an expression for the pressure-dependent LA frequency ω_l of the form

$$\omega_l^2(P)=\frac{\gamma(P)K_T(P)q^2}{\rho(P)}+\frac{M_r(P)q^2}{\rho(P)}\,\frac{\omega_l^2(P)\tau_l^2(P)}{1+\omega_l^2(P)\tau_l^2(P)}\,, \qquad (2)$$

where $q=(4\pi/\lambda_i)\sin(\theta/2)$ is the momentum transfer and the explicit pressure dependences are indicated. The Brillouin linewidth $\Gamma_l(P)$ is proportional to $\mathrm{Im}\{M(\omega)\}$:

$$\Gamma_l(P)=\frac{M_r(P)q^2}{4\pi\rho(P)\omega_l(P)}\,\frac{\omega_l(P)\tau_l(P)}{1+\omega_l^2(P)\tau_l^2(P)}\,. \qquad (3)$$

These dynamical Brillouin scattering expressions are now related to the EOS via the pressure-dependent density $\rho(P)$ and isothermal bulk modulus $K_T(P)$.

Although a variety of models for the equation of state are employed to represent high-pressure data, we find that the Vinet EOS, which is based on the premise that a universal scaling relation exists between the crystal potential energy and the interatomic separation [15], gives a superior fit over the large strain regime probed in these experiments. The Vinet EOS relates the pressure P to a strainlike variable $X=(\rho_0/\rho)^{1/3}$ by

$$P(X)=3K_T|_{P=0}\left(\frac{1-X}{X^2}\right)e^{\eta(1-X)}\,, \qquad (4)$$

where

$$\eta\equiv\frac{3}{2}\left(\frac{\partial K_T}{\partial P}\bigg|_{P=0}-1\right). \qquad (5)$$

Note that $P(X)$ depends only on two zero-pressure parameters, the equilibrium isothermal bulk modulus and its derivative. With this equation of state, the expression for the relaxed isothermal bulk modulus as a function of strain is given by

$$K_T(X)=\frac{K_T|_{P=0}}{X^2}[2+(\eta-1)X-\eta X^2]e^{\eta(1-X)}\,. \qquad (6)$$

The zero-pressure value of K_T is 0.489 GPa [25] and the only unknown parameter is $K_T'|_{P=0}$.

Zero-pressure values of M_r typically range from 0.2 to 0.4 GPa for simple organic liquids [26]. We model the pressure dependence of M_r with a linear expansion in P: $M_r(P)=M_{r0}+M_{r0}'P$. Using the measured value of the linewidth at P_a we calculate an initial value for M_{r0}' using Eq. (3) by assuming a value of the density at P_a.

The Brillouin frequency data $\omega_l(P)$ are then fitted using Eq. (2) where $K_T'|_{P=0}$ is the only adjustable parameter. From the derived value of $K_T'|_{P=0}$, a new density at P_a is obtained yielding a new M_{r0}'. The whole process is then iterated until self-consistency is obtained. Final values of $K_T'|_{P=0}=10.5$ and $M_{r0}'=1.5$ are obtained. In Fig. 2(a) the solid line is calculated directly from the fit to the frequency shift data. The dashed line represents the relaxed LA velocities, v_{l0}, derived from the fit. Note that above P_a there is a clear difference between the measured LA velocities and the relaxed velocities as expected. Also shown in Fig. 2(a) are the 10-MHz ultrasonic data of Houck [25] up to 2.5 GPa, which agree well with our data below P_a and the calculated v_{l0}. The classic dispersion behavior typically observed in temperature-dependent studies of v_l is largely masked in the pressure domain, due probably to the fact that very substantial strains are involved. This is in strong contrast to the relatively isochoric process of varying temperature.

The pressure dependence of the linewidth can be calculated from Eq. (3) using the model parameters and is shown as the solid line in Fig. 2(b). Since the pressure dependence of Γ_l is sensitive to M_r and τ_l, this indicates that our models for these parameters are reasonable. In addition, the single relaxation time approximation appears valid for $P<P_a$, but is inadequate at higher pressures as the quasistatic glass transition is approached, in good agreement with ultrasonic and hypersonic temperature-dependent studies of other glass-forming systems [27,28].

The EOS of the pentane mixed isomeric system derived from our Brillouin data is shown in Fig. 3. Our calculated EOS is in excellent agreement with an earlier direct P-V determination obtained at lower pressures and extends the strain regime probed to a compression of 50% of normal volume.

In summary, we have performed Brillouin scattering on an organic glass-forming system up to 12 GPa. The longitudinal-acoustic velocity and attenuation were measured over the entire pressure range. An absorption maximum was observed at a pressure of 2.25 GPa, above which shear modes were resolved. For the first time both acoustic velocity and attenuation data have been combined to yield information on the static and dynamic properties of a system at high pressure and strain. A modified Vogel-Tammann-Fulcher expression was used to model the pressure dependence of the longitudinal relaxation time. More importantly, a self-consistent analysis of the Brillouin data has enabled a determination of the

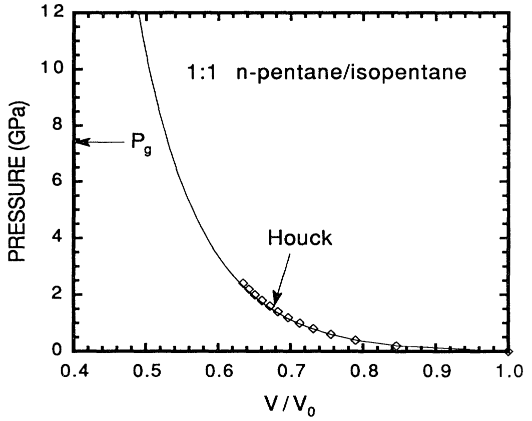

FIG. 3. The equation of state calculated from the Brillouin data (——). This calculation gives the EOS over a pressure range of 12 GPa corresponding to a strain regime of 0.5. Also shown (◇) are the direct P-V measurements of Houck (Ref. [25]) up to a pressure of 2.5 GPa. Note the excellent agreement between the calculated and directly measured values.

moduli and equation of state to 12 GPa, which furthermore agree quite well with independent experimental data at lower pressures. These techniques and results not only strengthen Brillouin scattering as a high-pressure experimental tool, but also open pressure as a new and important domain for the study of viscoelastic systems.

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