

Collective Behavior of Supercooled Liquids in Porous Media

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The macroscopic behavior of a restricted liquid has been studied through ultrasonic velocity and attenuation measurements utilizing a picosecond colliding-pulse optical technique. Transparent porous sol-gel glasses allowed a study of the collective fluid dynamics as a function of confining pore radius and temperature. The acoustic response of the supercooled state was found to be strikingly different from that of any ordinary liquid, and consistent with a simple model.

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The role of a confining geometry in the modification of the fundamental properties of a fluid and its respective phase transitions is only now beginning to be understood. In particular, it is well established that liquids confined in very small pores exhibit strong supercooling and ultimately freeze well below the free liquid-solid transition temperature.¹⁻⁵ Although some progress has been made in the study of the unusual behavior of such liquids at the molecular level,⁶ very little is known about the dynamical properties of this state over length scales which are larger than the radius of confinement, but much smaller than the dimensions of the sample.⁷⁻⁹ We have used a nonintrusive optical technique to study the acoustic velocity and attenuation of liquid ethanol confined in porous glasses. The experiment relies on picosecond laser pulses both to generate phonons at ultrasonic frequencies, and to monitor their propagation through the liquid. Temperature-dependent measurements in several restricting geometries have allowed a systematic investigation of the effects of confinement on the macroscopic properties of the liquid. In marked contrast to ordinary fluid dynamics, we find that a geometrically supercooled liquid shows solidlike collective relaxation which is independent of temperature.

Porous sol-gel glasses¹⁰ with various pore sizes were used to confine the fluid. The fabrication process of the glasses yielded samples with high porosity, good optical quality, and a well-defined pore radius, R , controllable over a range from ≈ 10 to 200 \AA . Vapor-pressure isotherms, mercury porosimetry, stereo transmission electron microscopy, and optical scattering data were used to characterize the glasses, and attested to the uniformity of the pore radii and their homogeneous distribution over much longer length scales. The glasses were polished to an optical finish and placed in a gold-plated brass cuvette having a small dead volume. An assembly of glass having larger pores was also introduced into the cuvette, and sufficient anhydrous ethanol was added to fill all the porous glass. This buffer assembly acted as a reservoir to maintain saturated vapor pressure in the cell at all temperatures. A partial pressure of helium gas was added to ensure good thermal equilibrium, and the cuvette

was then cooled in an optical Dewar with a temperature stability of $\pm 0.03 \text{ K}$.

A picosecond optical technique^{11,12} was used to generate monochromatic phonons and probe their propagation through the multiply connected fluid. A Q -switched, mode-locked Nd-doped yttrium-aluminum-garnet laser frequency doubled to 532 nm provided 70-ps pulses at a 400-Hz repetition rate. A Pockels cell was used to select a single $60\text{-}\mu\text{J}$ pulse from the Q -switched packet for the experiment. The resulting pulse train was split into three beams: two pump beams each about 5 times as intense as the third beam, which served to probe the system. The pump beams were horizontally polarized, focused to a common spot of about $150 \mu\text{m}$, and directed at a fixed angle to collide temporally and spatially, producing an optical intensity grating within the fluid-filled glass. Heating of the liquid was minimal, since ethanol has an extremely small optical absorption coefficient at the wavelength used.¹²⁻¹⁴ However, electrostriction caused by the intense electric fields in the grating¹³ generates counterpropagating monochromatic phonons having a wavelength equal to the grating space Λ . The delayed probe pulses were vertically polarized and focused at the Bragg angle to a $100\text{-}\mu\text{m}$ spot centered on the transient grating. A portion of the probe beam was diffracted from the standing density wave resulting from the counterpropagating phonons, and was spatially selected, passed through a polarizer to eliminate much of the scattered pump light, and detected with a photodiode. The time resolution was obtained by the systematic delay of the arrival of the probe pulses with respect to the excitation pulses. A more detailed description of the experiment will be presented elsewhere.¹⁴

The dynamics of the transient grating were monitored by observation of the diffracted beam intensity as a function of the relative delay between the pump and probe pulses. Figure 1(a) shows an example of the diffracted beam intensity as a function of probe delay for ethanol in $R=22\text{-}\text{\AA}$ pores and a grating spacing of $\approx 2 \mu\text{m}$. The data show two clear features: a periodic signal modulated by an exponential decay. Since the amplitude of the diffracted probe beam is proportional to the square of the

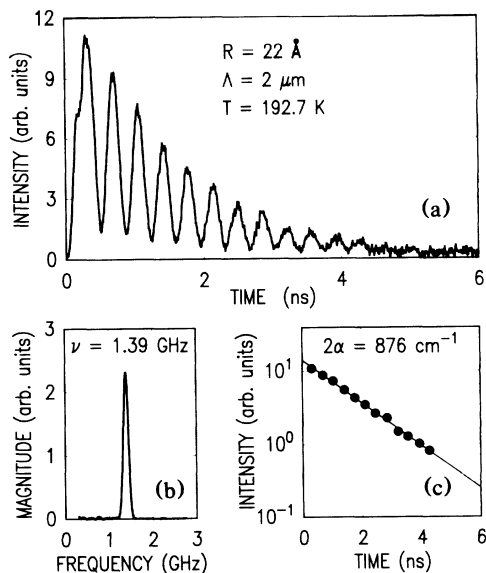


FIG. 1. (a) Magnitude of the diffracted signal as a function of time for ethanol filling $R=22\text{-\AA}$ pores at $T=193 \text{ K}$. (b) Fourier transform of (a) to obtain ν . (c) The signal maxima as a function of time.

grating's amplitude, the intensity of the diffracted beam will oscillate with a frequency of $\nu=2V_s/\Lambda$, where V_s is the sound speed and Λ is the phonon wavelength. By Fourier transformation of the periodic signal to obtain ν , V_s can be determined to better than 0.5% [Fig. 1(b)]. Because the viscous penetration depth was greater than the pore radius at all temperatures and in all samples studied, only one sound mode was observed.¹⁵ The decay of the phonon-induced grating amplitude can be written as $A(x) = A_0 e^{-\alpha x}$, where α is the sound absorption coefficient of phonon decay; then the diffracted-signal amplitude decays as¹² $A_D(x) \propto A_0^2 e^{-2\alpha x}$. Therefore, the diffracted-signal intensity can be directly related to the sound absorption coefficient by $I_D(x) \propto e^{-4\alpha x}$, where $I_D(x)$ is the diffracted signal as a function of the distance, x , traveled by the phonons. If we use the phonon velocity to relate the time measured to the distance the phonons travels, α may be calculated from the slope of a log-linear plot of the intensity peaks versus time [Fig. 1(c)].

In Figs. 2 and 3 we present the temperature-dependent sound velocity and attenuation for free (bulk) ethanol and ethanol confined in a series of glasses having pores with radii as indicated. These data are for a phonon wavelength of 2.0 \mu m which, in free ethanol at 295 K , corresponds to an ultrasonic frequency of 600 MHz . The monotonic increase in sound velocity of the free liquid is in good agreement with previous results^{16,17} using conventional acoustic techniques over a smaller temperature range. As expected for a fixed-wavelength study, the attenuation of the free liquid also increases monotonically, even for moderate undercooling of the

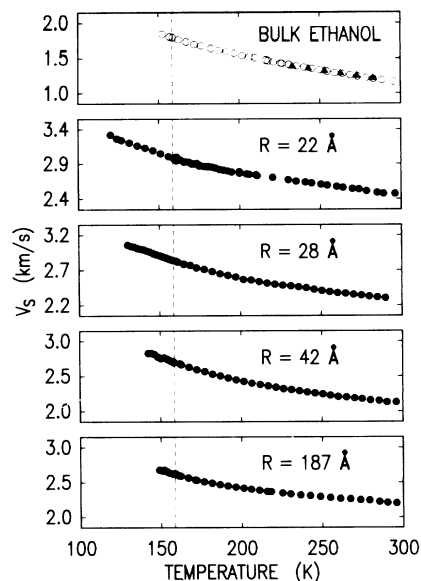


FIG. 2. The sound velocity ($\Lambda=2 \text{ \mu m}$) as a function of temperature for free and confined ethanol. The dashed line marks the equilibrium free-liquid freezing temperature $T_0=158.6 \text{ K}$. The error bars are equal to the size of the data points. The triangles are data for bulk ethanol from Ref. 16.

liquid. Note also that $\alpha/\nu^2 = 56 \times 10^{-17} \text{ s}^2 \text{ cm}^{-1}$ at 296 K , in good agreement with the tabulated value¹⁷ of $54 \times 10^{-17} \text{ s}^2 \text{ cm}^{-1}$. Taken as a whole, the above evidence for the free liquid implies that the phonon frequencies used are well below any internal relaxation fre-

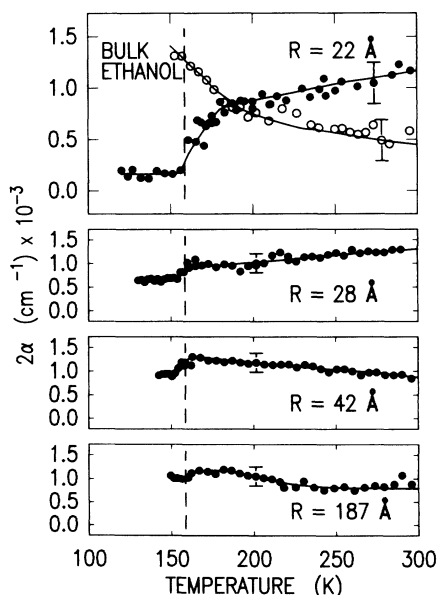


FIG. 3. The sound attenuation coefficient ($\Lambda=2 \text{ \mu m}$) for free and confined ethanol. The dashed line marks the equilibrium free-liquid freezing temperature $T_0=158.6 \text{ K}$.

quency intrinsic to the liquid. As a further test of the experimental technique, the excitation pulses were attenuated to vary the intensity of the generated phonons by 3 orders of magnitude. We find linear acoustic response over the entire range, thereby ruling out any significant nonlinear acoustic and heating effects in our measurements. To rule out systematic errors which might arise in the measurement, the phonon wavelength was varied, and the pump-probe spot-size ratio was increased to ensure that the phonons were not propagating out of the probe region.

The most striking difference between the free and constrained ethanol can be seen in the degree of supercooling and the attenuation of the fluid confined in $R=22\text{-\AA}$ pores (Fig. 3). From 296 to 150 K, the attenuation decreases by almost a factor of 2, then drops sharply just above the bulk freezing temperature T_0 and maintains a small, temperature-independent value throughout the supercooled region. In addition, there is an increase in the slope of the velocity data at the temperature associated with the sharp drop in attenuation. The variation in the room-temperature sound velocity observed in these gels is consistent with effective medium theory,¹⁸ which would predict that the least-porous sample would have the greatest sound velocity. The data show that the fluid does not freeze until ≈ 123 K, which represents a supercooling of about 20% below the bulk freezing temperature. At T^* , the new freezing temperature for the confined ethanol, the scattering abruptly increased and the quality of the beams passing through the sample deteriorated to the point that the scattered light was completely diffuse and no clear diffracted beam could be detected. This freezing-point depression was found to be inversely proportional to the confining pore radius as predicted from geometrical considerations.^{6,19} We observe approximately the same percentage undercooling for ethanol as previously seen² in liquid oxygen, where $\Delta T = T_0 - T^*$ scales as T_0/R with the same proportionality constant for the two liquids. The frozen ethanol melted at about 156 K, 2° below the bulk melting temperature. The ultrasonic velocity and attenuation at this melting point were the same as that taken while cooling.

To gain more insight into this unusual acoustic behavior, velocity and attenuation measurements were made in ethanol-filled glasses having progressively larger pore sizes. For temperatures greater than the bulk freezing temperature, da/dT systematically decreases with increasing pore size, being positive for the smallest pore sample and becoming negative and very much like the free liquid for confinement in $R=187\text{-\AA}$ pores. The attenuation in the supercooled region also increases with pore size. We note that our observations do not support the conjecture that ethanol is freezing from the walls inward or at inhomogeneous spots in the glass matrix. The magnitude of the diffracted signal remained constant until the liquid finally froze, which would not be expected if liquid were being progressively converted into a solid

with much lower compressibility or large blocks of solid were appearing within the sample. In addition, if a rapidly growing layer or large regions of solid were responsible for the sharp drop in α and the kink in V_s , one would expect the light scattering to increase, but no increase was seen until the liquid had supercooled to its new freezing point 20% below the bulk freezing temperature. Therefore, another mechanism must be responsible for the unusual nature of the liquid within the pores.

To describe these changes in the acoustic properties of the fluid, we propose a simple physical picture which takes into account the large surface area as well as the constraining geometry. At room temperature, relatively few ethanol molecules are strongly bound to the pore walls. However, as the temperature decreases towards T_0 , more molecules become coupled to the surface and are therefore unable to participate in dissipative processes. These adsorbed molecules do not form an ordered solid state because of the randomness of the substrate potential.² This effect would be most pronounced in the smallest geometry, which has the largest surface-to-volume ratio. Therefore, the behavior seen over the range of pore sizes studied represents a crossover from bulklike behavior in $R=187\text{-\AA}$ pores to attenuation which decreases with temperature as the adsorbed layer grows in the smallest-pore samples. This growth has been observed by other methods for a variety of fluids filling porous media,^{2,4,20} and is known to cease at and below the bulk transition temperature. The connection with acoustic attenuation is clarified by continuous variation of the radius of confinement.

In the vicinity of and below T_0 , earlier molecular reorientation results and $1/R$ dependence of the consequent supercooling have been shown to be consistent with the suggestion that solid plugs form through thermodynamic fluctuations in the confined fluid.⁶ In order to qualitatively describe the acoustic properties of a multiply connected fluid containing a random distribution of plugs, we take the following phenomenological approach. The free-energy change associated with the presence of a solid plug can be written as⁶

$$\Delta F = 2\pi R \Delta\sigma \left(\frac{T - T^*}{T_0 - T^*} \right) L + \gamma R^2,$$

where $\Delta\sigma$ is the difference between the solid-wall interfacial energy and the liquid-wall interfacial energy, L the plug length, and γ a constant describing the liquid-solid interface. Since the number density of plugs of length L is proportional to⁶ $e^{-\Delta F/kT}$, there will be a greater number of plugs of length $L \geq R$ which can block the pores in the smaller radius gels. To compare the relative number of blocking plugs, we scale the number of blocking plugs in a particular sample to the number of plugs in the $R=22\text{-\AA}$ glass. The ratio for four successive samples in order of increasing pore diameter is estimated¹⁴ to be 1:0.43:0.03:0.00. If one assumes that there is less

dissipation in a liquid constrained by many plugs than in a liquid free to move in response to phonon propagation, then this description accounts for the trends observed in the data. This model is consistent with the sharp drop in attenuation, since microscopic solid clusters are known to form significantly above the bulk freezing temperature.²¹ In addition, the appearance of blocking clusters would be expected to decrease the compressibility of the liquid, thereby increasing the ultrasonic velocity as observed. Altogether, this presents a physically appealing description. The liquid is confined between plugs which have a spacing much smaller than the phonon wavelength and hence it behaves more like a solid, having an attenuation which is smaller and less temperature dependent than that of the corresponding liquid by itself.

In summary, we have used a picosecond time-resolved optical technique to measure the dynamical response of fluid-filled porous media over macroscopic length scales. Both the ultimate freezing temperature and the temperature-dependent response of the liquid to long-wavelength excitations are strongly affected by the confining walls. The supercooled state was found to be remarkably different from that of a free liquid, in that the temperature-independent collective response mimics that of a solid and is consistent with the presence of metastable solid plugs within the interconnected fluid network. The nucleation dynamics controlled by the reduced dimensions are seen to play a vital role in the determination of the macroscopic properties of the undercooled fluid. Systematic studies with variable degrees of confinement reveal that this unique behavior is intrinsic to the restricting geometry.

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