

Supercooled liquids and solids in porous glass

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Liquid and solid supercooling of molecular oxygen has been observed and studied in well-characterized porous sol-gel glasses. The depression of the solid-solid phase transition temperature was measured as a function of pore size, showing the strong influence of confinement on the solid phases. The liquid freezing-point depression was also measured, and a picosecond optical technique was used to probe the dynamics of the supercooled liquid. The liquid's geometrical confinement is observed to have an important effect on its properties, leading to behavior unlike that of ordinary bulk fluids.

It has been well established that the behavior of a liquid confined in very small pores can be radically different from its behavior in the normal bulk form. Studies of liquid helium in porous Vycor glass and in packed powders¹ have yielded results which although controversial, suggest that the interactions of the liquid and solid with the pore walls is extremely important in determining the properties of the liquid, and how it freezes. Despite historical experimental evidence for these interactions² and more recent observations at much higher temperatures,^{3,4} the effects of these surface interactions on the freezing of liquids has only begun to be understood.^{1,5} One example concerns the observed freezing-point depression of liquids in porous media, where controversy has existed surrounding the question of whether the depression is a result of a finite-size-related shifting of the phase diagram, or in fact, a consequence of genuine supercooling below the normal freezing point. In addition, manifestations of these effects are expected to arise during solid-solid phase transitions in restricted geometries, where experimental conditions typically make this behavior more difficult to observe. Clearly there are many fundamental questions remaining to be answered.

We report here on a series of optical experiments which have allowed us to systematically study both liquid and solid supercooling as a function of confining pore size. Using an ultrafast time-resolved optical technique, we have probed the properties of confined liquid oxygen as it is cooled below the normal bulk freezing point. The use of a new transparent porous glass as a host material allowed us to investigate the behavior of the supercooled liquid as a function of confining pore radius, revealing in detail how the liquid's properties change as a result of the restricting geometry.

Porous sol-gel glasses were used as a host material. The glasses are of good optical quality, and high porosity ($\sim 70\%$) with a well-defined pore size and aspect ratio. The glasses are essentially pure silica, prepared by the sol-gel technique⁶ and then dehydrated to porous xerogels at elevated temperatures.^{3,7} The pore size is controlled in the fabrication process, allowing the production of glasses with a pore radius ranging from about 10 to 250 Å. The

pore size was determined from mercury porosimetry measurements, low-temperature gas-adsorption isotherms, and stereo transmission electron microscopy. The glasses have a mechanical strength which is adequate to allow polishing of two parallel surfaces. Samples were first dry-polished with emery paper, then given an optical polish using 1-micron diamond paste with oil. The glasses were cleaned by repeated soakings in trichlorethylene, acetone, and then water. Finally, they were heated in a 30% H_2O_2 solution in water at 70° C for about 12 h. The glasses were then rinsed with distilled water and placed in a vacuum desiccator to dry.

The glass samples were mounted in a copper and brass optical cell with intracavity copper clamps to align and support the sample. The cell was then loaded into a variable temperature cryostat, and connected to a gas handling system via a flexible capillary tube. After pumping on the cell for several hours with a turbomolecular pump, a few millimeters of helium gas was added to ensure thermal equilibrium of the glass with the surrounding cell. The temperature of the cell was stable to within ± 0.005 K, and could be held at a given temperature for several days without the need to transfer liquid helium or nitrogen to the cryostat. Thus mechanical disturbances were kept to a minimum while studying the supercooled liquid. To determine the internal surface area of a particular sample, oxygen adsorption-desorption measurements were taken using research-grade oxygen, and with the sample at a temperature of 90 K. A typical measurement is shown in Fig. 1. Although the detailed characteristics of such a curve are described elsewhere,³ some of the features will be discussed here. The initial part of the adsorption isotherm is characteristic of a layering of the gas molecules on a random substrate. The inset shows the results of a Brunauer-Emmett-Teller analysis,⁸ which yields the internal surface area of the sample. The total pore volume is obtained from the point at which the pressure reaches the vapor pressure of the bulk liquid. Assuming a cylindrical pore shape, a pore radius can then be calculated. It was found that this calculation gave results which were consistent (generally within a few percent) with the results of the mercury porosimetry measurements. This is

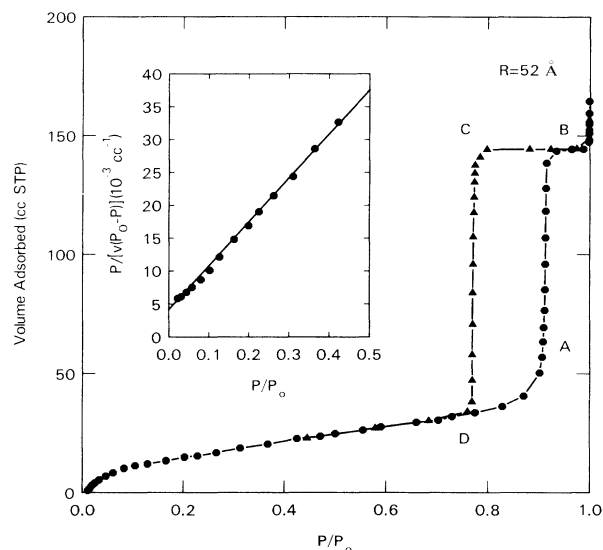


FIG. 1. Oxygen adsorption isotherm at $T = 89.50$ K. The inset shows the results of a Brunauer-Emmett-Teller analysis.

in accord with the electron microscopy results, which indicate that the pores are, to a first approximation, cylindrical with an average length to diameter ratio of about 7:1.

The time-resolved birefringence measurements were performed in a manner similar to that described by Greene and Farrow.⁹ A schematic of the optical system is shown in Fig. 2. A dual-jet dye laser is synchronously pumped by a mode-locked argon-ion laser, producing optical pulses of 500-femtosecond duration at a 76-MHz repetition rate. For the time resolved measurements, the dye-laser wavelength was set at 584 nm, far enough from the oxygen bimolecular absorption line at 577 nm to avoid significant absorption of energy by the liquid. The dye-laser pulse shape is monitored by a real-time scanning optical autocorrelator, and an acousto-optic shutter is used to reduce the average intensity without greatly reducing the peak intensity. Thus the energy per pulse is 0.4 nJ, while the average power is kept below 3 mW, thereby avoiding thermal perturbations to the sample. The train of pulses is split into pump and probe beams with an intensity ratio of 10:1. Timing of the probe pulses with respect to the pump pulses is varied via a computer controlled linear air stage, whose position determines the distance that the probe beam must travel before being recombined with the pump beam. A linear polarizer is used to rotate the polarization of the probe beam by 45° relative to the pump. The beams are then focused to a common spot in the sample, about 50 microns in diameter. After exiting from the cryostat, the pump beam is blocked and the probe beam is recollimated and passed through a Soleil-Babinet compensator, set for quarter-wave compensation, with its axes 45° from the perpendicular. A Glan Thompson prism splits the beam into horizontal and vertical polarization components. The relative sizes of the two components are compared using a differential

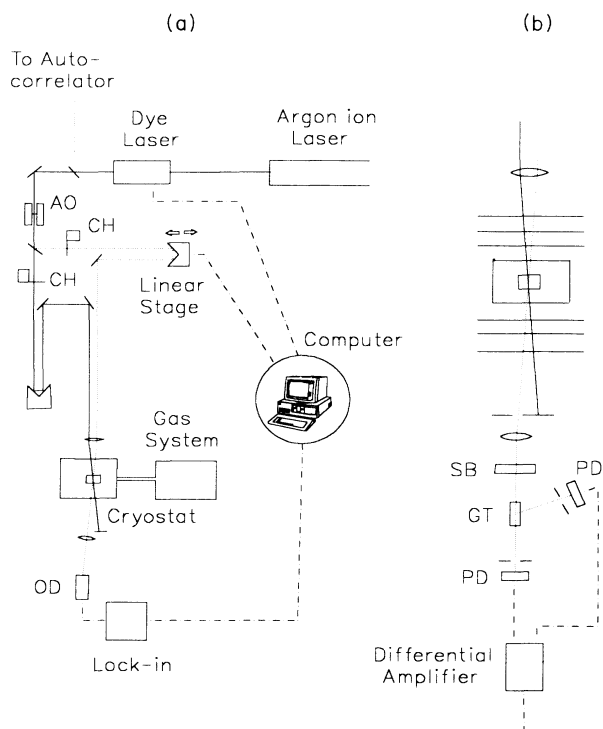


FIG. 2. (a) Schematic view of the apparatus. AO is the acousto-optic shutter, CH denotes the choppers, and OD is the optics and detectors which are shown in detail in part (b). (b) Detailed view of the optics and detectors. SB is a Soleil-Babinet compensator, GT is the Glan-Thompson prism, and PD a photovoltaic detector.

amplifier and a lock-in amplifier. In order to remove background signals, the pump and probe beams are chopped at different frequencies and the signal is measured at the sum frequency. Thus the system is sensitive only to effects of the pump beam on the probe beam. Also the optical configuration is such that scattered light from pump and probe beams goes equally into the two photodiodes and hence is nulled out. This allows the maximum sensitivity for the detection of small pump-induced ellipticities in the probe beam polarization. In this way the optically induced birefringence of the liquid is measured. By varying the time of arrival of the probe pulses with respect to the pump pulses, the initial response and the subsequent relaxation are observed. Although the optically induced birefringence is a result of several different physical processes,¹⁰ it is the molecular reorientation time τ_r which is the most sensitive to temperature,¹¹ since τ_r is directly related to η the liquid viscosity^{4,12,13} through the relation

$$\tau_r = C \left(\frac{\eta}{T} \right) + \tau_0$$

where C is a constant, and τ_0 is only important in the low-viscosity limit. Thus the viscosity of the confined fluid can be studied in a nonperturbing way through the measurement of τ_r .

For the static optical absorption measurements, the beam is attenuated to 15 mW and the intensity of the transmitted beam is monitored as a function of its wavelength. The incident power is monitored separately and used to normalize the signal as the laser wavelength is tuned by the computer, thereby allowing us to determine the strength of the absorption band centered at 577 nm. Since this band corresponds to a bimolecular transition,¹⁴ its intensity provides information on the density and the structure of the oxygen present.

The results of the static absorption studies will be discussed first. The strength of the optical absorption was measured as a function of temperature for different coverages of oxygen within different pore sizes, thus allowing an extension of previous studies of adsorbed oxygen.¹⁵ A typical absorption spectrum for liquid oxygen in the pores is shown in Fig. 3. The strength of the optical absorption is shown in Fig. 4 at two different coverages for a glass sample with 54-Å-radius pores. In Fig. 4(a) the results with 0.75 monolayers of oxygen (as determined by adsorption isotherms) show no evidence of any bulklike phase transitions, nor is there any temperature-dependent hysteresis. For coverages under about 2 monolayers, the data are qualitatively similar. For higher coverages, as seen in Fig. 4(b), a sharp break is observed as the system is cooled, associated with the γ - β solid-solid transition. The nature of this discontinuity was determined by its observance for oxygen in very large pores, where the transition occurred at close to the bulk γ - β solid-solid transition temperature of 43.8 K. Unlike the data at lower coverages, a definite temperature-dependent hysteresis is observed in the transition.

The liquid-to- γ -solid transition was observed through a sudden increase in the amount of light scattered by the sample, although the optical absorption did not change drastically. Hysteretic behavior was also observed, the liquid freezing at a temperature well below the bulk freez-

ing point, whereas the solid melting temperature was only slightly below that of the bulk. These observations, combined with the monolayer data, indicate that the first few monolayers of oxygen tend to plate the pore walls, forming an amorphous layer similar to that observed at lower temperatures in helium experiments.¹ This layer by itself does not undergo any abrupt phase transitions as it is cooled. As the oxygen coverage is increased phase transitions appear, although at temperatures shifted from the normal bulk transition temperatures.

The data for oxygen in various pore radii are shown in Figs. 5 and 6. The data were taken with the pores completely filled with liquid. In Fig. 5(a), the results are shown for 187-Å-radius pores, where supercooling and hysteresis effects are small. The effects become noticeable in 42-Å pores [Fig. 5(b)], and even more pronounced in commercial Vycor silica glass (~ 28 -Å pores) [Fig. 6(a)] and in 22-Å pores [Fig. 6(b)]. As an experimental check, comparative measurements between the commercial Vycor glass and a closely sized sol-gel glass show the liquid behavior to be quite similar. In the smallest pores, the liquid undercools by 10.1 K, or 19% before ultimately freezing. We have also succeeded in observing size effects

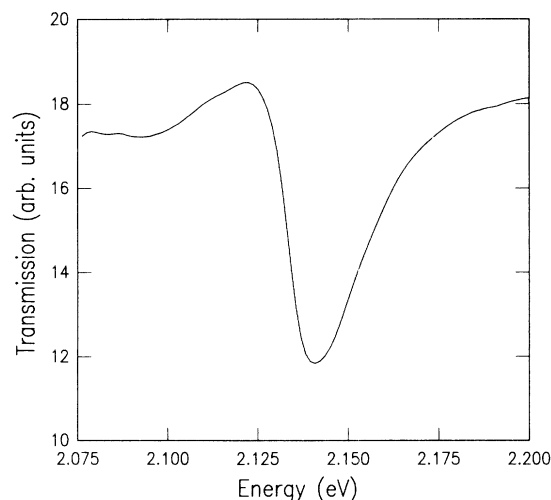


FIG. 3. Optical absorption spectrum of oxygen filling 108-Å porous sol-gel glass over the energy range of the static optical absorption measurements.

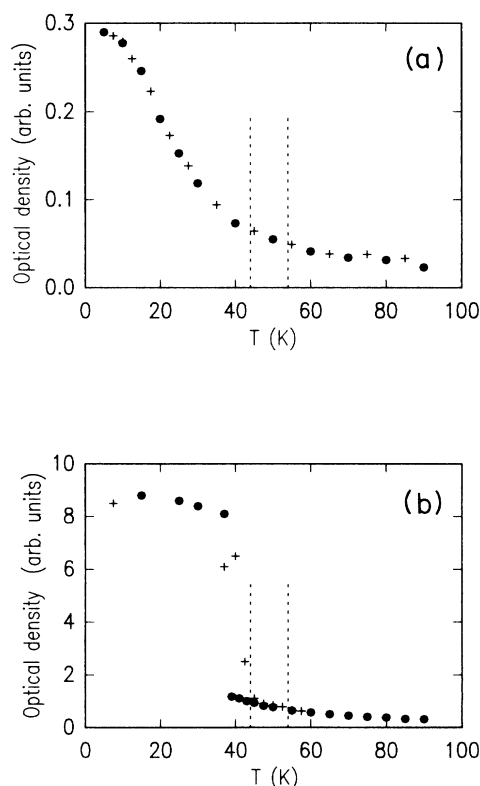


FIG. 4. (a) Optical density as a function of temperature for 0.75 monolayers of oxygen in 54-Å-radius pores. Circles represent the data taken while cooling and crosses are data taken while warming. Dashed lines indicate the positions of two phase transitions in bulk oxygen; the liquid-solid transition at 54.4 K, and the γ - β transition at 43.8 K. (b) As in (a) except with the pores completely filled.

on the oxygen γ - β solid-solid phase transition through static optical absorption measurements. The γ solid supercooling was observed to also be dependent on pore size, with transition temperature depressions as high as 25% of the bulk temperature in the smallest pores studied.

In order to understand the effect of the geometry on the transition temperatures, we start by considering the liquid-solid phase transition in an idealized cylindrical pore of radius R . The free energy of a solid nucleus forming a cylindrical plug of length L and radius R is first calculated by simply adding up the volume free energy of the nucleus, ΔF_v , the surface free energy at the pore wall ΔF_s , and the free energy of the liquid-solid interface ΔF_i . Thus

$$\Delta F = \Delta F_v + \Delta F_s + \Delta F_i$$

$$= \frac{-\pi R^2 L}{v} \Delta h_f \left[\frac{T_0 - T}{T_0} \right] + 2\pi R L \Delta \sigma + 2\pi R^2 \alpha, \quad (1)$$

where Δh_f is the heat of fusion, T the temperature, T_0 the bulk freezing point, v the molar volume, $\Delta \sigma$ the difference between the solid/wall interfacial energy and the liquid/wall interfacial energy, and α is a constant describing the liquid-solid interface. The quantity $\Delta \sigma$ is expected to be positive for this system, since the pore wall is

coated with an amorphous solid or highly viscous liquid layer,¹ and it is the interfacial energy between this layer and the solid which determines $\Delta \sigma$.

In Eq. (1), it is evident that ΔF either increases or decreases monotonically with the nucleus length L at a given temperature. The temperature T^* at which $\partial \Delta F / \partial L = 0$ then defines the new freezing point, leading to

$$T_0 - T^* \equiv \Delta T = \frac{2\Delta \sigma v T_0}{\Delta h_f R}. \quad (2)$$

This can be shown to be essentially equivalent to the result derived from the properties of the liquid-solid interface and its contact angle with a pore wall.^{16,17}

From Eq. (1), it is clear that the energetics of nucleation are strongly affected by the confining walls. In three dimensions, at a temperature below the freezing point, the free energy of a nucleus initially increases as its radius increases, then decreases after the radius reaches a critical size. Thus only solid nuclei larger than a certain temperature-dependent critical size will grow. However, in a very small pore at a temperature below T^* , nuclei of any length L will tend to grow, and the concept of a critical size does not apply. Above T^* , nuclei formed through thermodynamic fluctuations will always tend to shrink. This is consistent with the observed stability of

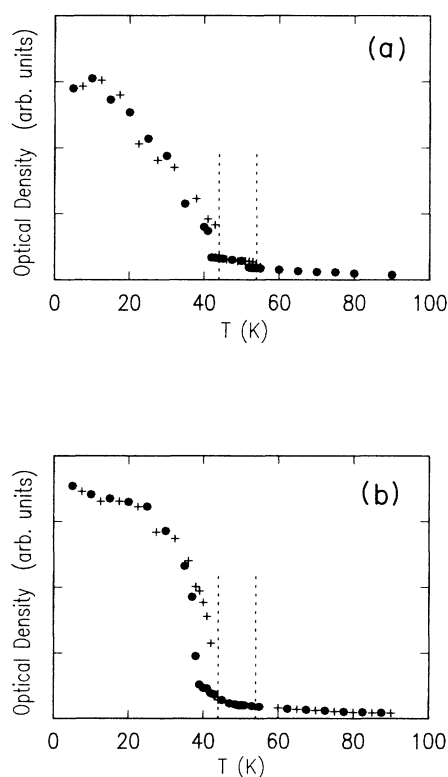


FIG. 5. (a) Optical density as a function of temperature with completely filled 188-Å-radius pores. Symbols and dashed lines are as described in Fig. 4. (b) As in (a), but with 42-Å-radius pores.

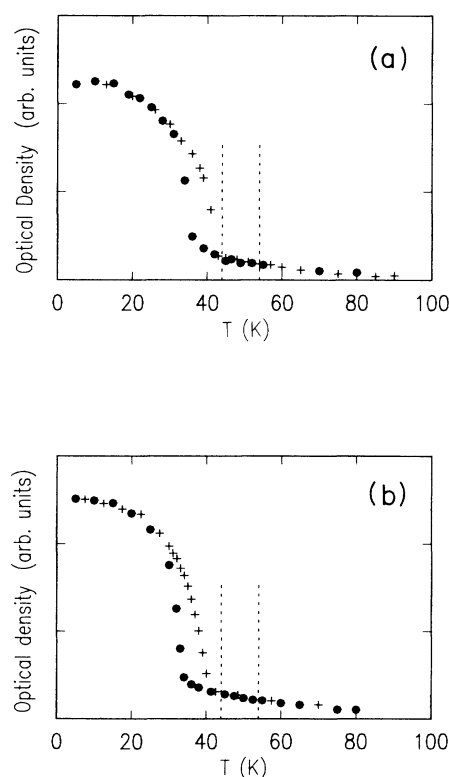


FIG. 6. (a) Optical density as a function of temperature with completely filled 28-Å-radius pores from commercial Vycor glass. Symbols and dashed lines are as described in Fig. 4. (b) As in (a), but with 22-Å-radius pores of sol-gel porous glass.

the liquid in the pores. The liquid never spontaneously froze when left for several days at a temperature which was only a fraction of a degree above the observed freezing temperature T^* . In addition, the freezing point was well defined and could be measured repeatedly with consistent results. The observed hysteresis between freezing and melting could be caused by the amorphous layer of oxygen at the wall. After the liquid in the center of the pores freezes, the freezing front may propagate partially through the wall layer, thus effectively changing $\Delta\sigma$. The latter explanation is somewhat speculative, and further studies are needed to clarify this matter.

Equation (2) displays a linear dependence of the freezing-point depression on $1/R$, where R is the pore radius. Figure 7 is a summary of the freezing-point depression data, which in fact exhibits the $1/R$ dependence. At the largest pore size, the cross-over to bulklike behavior is observed, where the supercooling is due to the metastability of the liquid and is independent of the pore size. The same type of analysis as is expressed in Eq. (2) should also be valid in the case of the solid-solid transition, with the appropriate substitution of parameters. The results, plotted in Fig. 8 show that this is indeed the case. The linear behavior extends over the entire range of pore sizes studied. Recent theoretical work emphasizing the importance of a substrate on the melting transition also predicts a geometrical dependence as a consequence of surface-induced disorder at the interface.^{18,19}

The optical birefringence technique was used to probe the *in situ* dynamical properties of the confined supercooled liquid. Time-resolved experiments were carried out at a laser energy of 2.123 eV, close enough to the absorption band to give an enhancement of the signal, yet far enough to avoid any heating effects (see Fig. 3). For reference and comparison purposes, the experimental results from ordinary bulk liquid oxygen¹¹ are shown in Fig. 9. The response of the liquid in the pores was similar

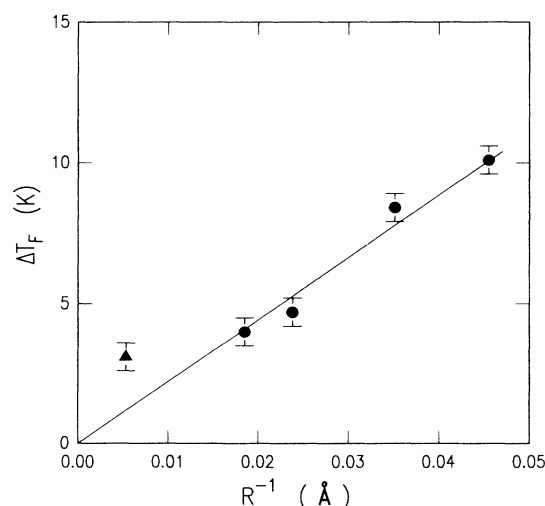


FIG. 7. Observed freezing point depression plotted as a function of $1/R$. The line was constrained to pass through the origin. The triangle is the result from oxygen in 188-Å pores.

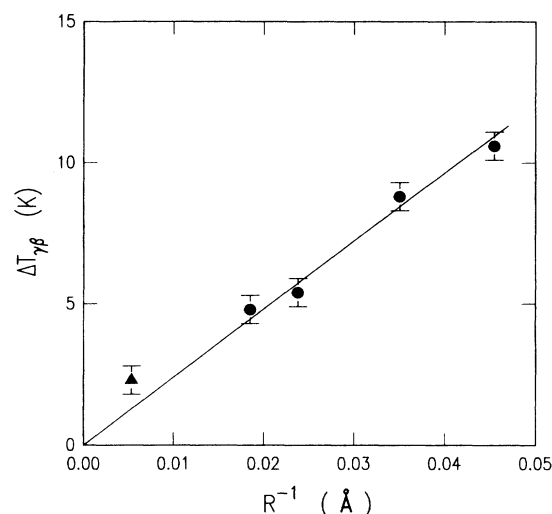


FIG. 8. Observed depression in the γ - β solid-solid transition temperature plotted as a function of $1/R$. The line was constrained to pass through the origin.

to that of the bulk at temperatures above the freezing point of the bulk liquid. The relaxation time of the confined liquid is observed to increase as the liquid viscosity increases, until the freezing point is reached at 54.4 K. No anomalies in the response were observed as this freezing point was approached. However as the confined liquid was further cooled, the relaxation time increased

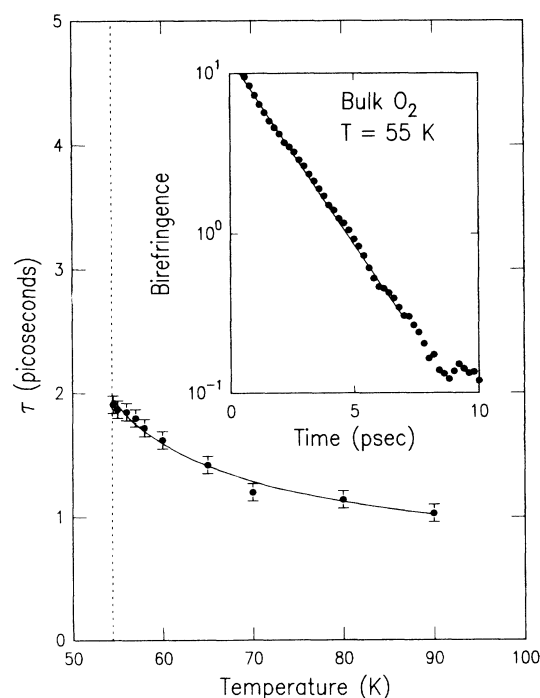


FIG. 9. Birefringence relaxation time in bulk liquid oxygen. Dashed line marks the freezing point. The inset shows a sample of the smoothed, deconvoluted data, taken at $T = 55$ K.

rapidly. A sample of the data is shown in Fig. 10, where the long response is clearly seen. After smoothing and deconvolving the data with the pulse shape, the results are shown in Fig. 11 for a given pore size at several temperatures. The slow component of the response is associated⁴ with τ_r , while the faster component (inseparable from τ_r at high temperatures) is temperature independent, and is associated with a characteristic intermolecular interaction time. This time was measured to be ~ 1.2 psec. The solid lines in Fig. 11 thus represent two-exponential fits to the data, with one time constant fixed at 1.2 psec.

A summary of the results is given in Fig. 12. The data indicate that the pore size determines not only the freezing point of the liquid but also the temperature-dependent properties of the supercooled liquid. In this respect the liquid is quite unlike a normal supercooled liquid. The results are inconsistent with a model based on a viscous layer growing out from the walls, since at any particular temperature the relaxation is the fastest in the smallest pores where wall-related effects are expected to be important.² Also the amplitude of the response does not change significantly as a function of pore size, even though the surface to volume ratio of the pore spaces increases as the pore diameter decreases. These observations indicate a rather unusual behavior of the liquid in the pores.

A qualitative description of this behavior may be obtained through a model which attributes the observed slow relaxation time to the presence of solid clusters which appear through thermodynamic fluctuations. Although the connection between solid cluster formation, fluid viscosity and molecular relaxation time are not obvious in the case of a tightly confined liquid, we will assume as in the case for bulk liquids,²⁰ that the viscosity is determined only by x , where x is the fraction of the molecules involved in cluster formation. The simplest approach is then to postulate that the viscosity (and hence the

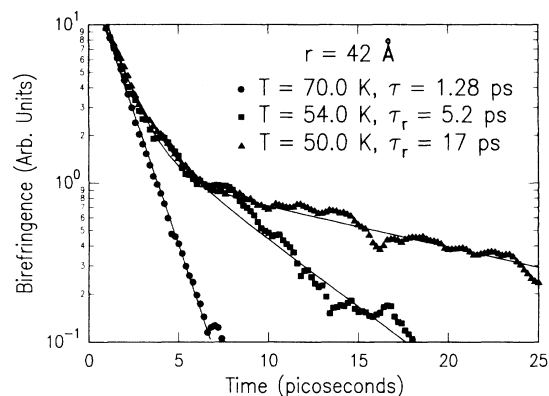


FIG. 11. Semilog plot of the smoothed and deconvoluted data at several temperatures for oxygen in 42-Å-radius pores. Solid lines are 1 or 2 exponential fits as described in the text.

birefringence relaxation time) is to first-order proportional to x . This approach will allow a qualitative calculation of the relaxation time as a function of temperature for various pore sizes. We start by rewriting the free energy Eq. (1) in terms of T^* defined through Eq. (2);

$$\Delta F = 2\pi R \Delta \sigma \left[\frac{T - T^*}{T_0 - T^*} \right] L + \alpha R^2. \quad (3)$$

To simplify the discussion, we assume that all the clusters are of the idealized shape as discussed earlier, and we neglect clusters which are smaller than the pore diameter. The number density of clusters is proportional to $\exp(-\Delta F/k_B T)$, so the overall fraction of molecules involved in cluster formation is

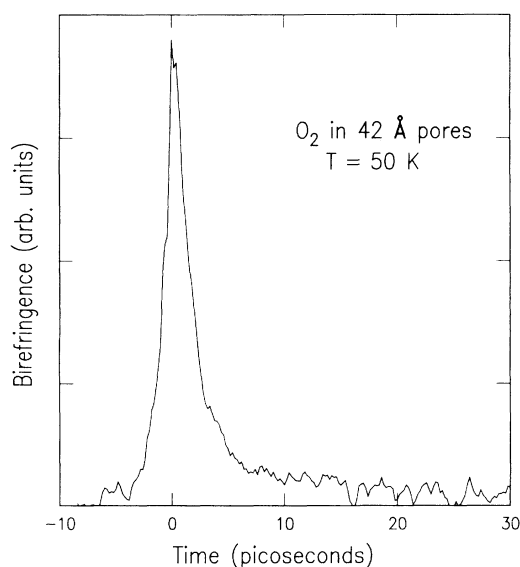


FIG. 10. Time-resolved birefringence signal from oxygen in 42-Å-radius pores at a temperature of 50 K.

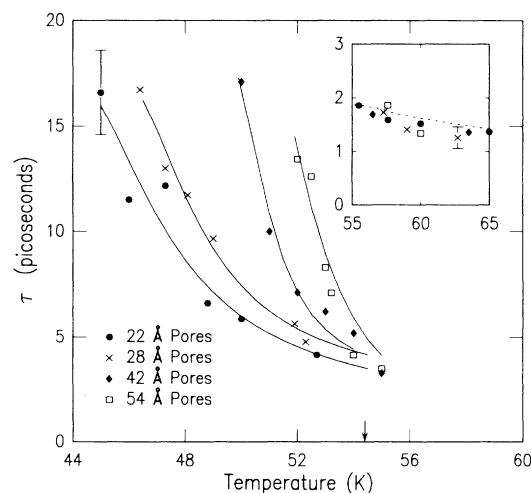


FIG. 12. Birefringence relaxation time of liquid oxygen in different pore sizes. The curves are described in the text. The inset shows the high-temperature behavior, where the dashed line represents bulk oxygen data. Representative error bars are included on several data points. The arrow marks $T_0 = 54.4$ K.

$$x = \frac{C \int L e^{-\Delta F/k_B T} dL}{1 + C \int e^{-\Delta F/k_B T} dL}, \quad (4)$$

where C is a proportionally constant. Using Eq. (3) for the free energy and integrating gives

$$x = \left[C' \left[1 - \frac{T^*}{T} \right]^2 \exp \left[\frac{\alpha R^2}{k_B T} \right] + 1 \right]^{-1}, \quad (5)$$

where C' is a constant. The curves shown in Fig. 12 are based on Eq. (5). The measured value of T^* was used for each pore size, along with $\alpha/k_B = 0.4 \text{ K } \text{\AA}^3$. The constant C' is expected to be dependent on the pore size, and was treated as a separate fitting parameter. This analysis suggests that the cluster model phenomenologically describes the observed trends in the relaxation times. It should be pointed out that Eq. (5) is not applicable for temperatures above T_0 , where in the limit of no cluster

formation, temperature-dependent free liquid terms are important. Also, no account was taken of the tortuosity or interconnectivity of the pores. These factors would tend to limit the size of the clusters.

In conclusion, we have observed the supercooling of liquids and solids in a restricted geometry. By varying the confining geometry, the supercooling phenomena were studied in a systematic way, allowing us to follow the transition from bulklike behavior to that of the tightly confined liquid or solid. Both liquid-solid and solid-solid phase-transition temperatures were seen to be strongly affected by the pore size, with the transition temperature depression increasing linearly with the inverse of the pore radius. In addition, the effective viscosity of the supercooled liquid was found to be dependent on the size of the confining pores. Thus the geometrical constraints were seen to cause significant changes in the properties of both the confined liquid and the confined solid.

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