

Geometrical Supercooling of Liquids in Porous Glass

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The supercooling and freezing of a restricted liquid has been studied by the probing of its molecular dynamics with picosecond optical techniques. A newly developed transparent porous host material makes it possible to study the liquid viscosity as a function of the confining pore radius and temperature. The observed behavior is remarkably different from that of an ordinary liquid, and can be interpreted in terms of a simple model.

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It is well known that the properties of liquids can be modified by their confinement in very small pores. Experiments on helium in Vycor glass¹ and on other confined liquids² have revealed a variety of phenomena whose interpretation has often been difficult and frequently controversial. One example concerns the observed freezing-point depression of liquids in porous media, where it is still not clear 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. More generally, although a certain amount of progress has been made in recent years,^{1,3-5} there is not universal agreement on many fundamental issues concerning the phase transitions of a restricted liquid. We report here on a series of time-resolved optical experiments to study the dynamics of liquid oxygen in small pores. The use of a novel porous host material allowed a systematic investigation of liquid confinement effects as a function of pore size, thereby shedding new light on the properties of supercooled restricted liquid and the way it freezes. A simple model is presented which offers a qualitative interpretation of the experimental results.

Well-characterized porous sol-gel glasses⁶ of good optical quality and moderate mechanical strength were used to confine the liquid. The most important features of the glasses include their high porosity ($\sim 70\%$) and a well-defined pore size and aspect ratio as characterized by mercury porosimetry, vapor-pressure isotherms, and stereo transmission-electron-microscope images. The pore size can be controlled in the fabrication process to provide a pore radius ranging from ~ 10 to 250 \AA . The glasses were mounted in a copper and brass optical cell, which was then placed inside a variable-temperature optical cryostat. A small amount of helium gas was added to ensure thermal equilibrium of the porous glass with the surrounding cell, yielding a temperature stability of $\pm 0.005 \text{ K}$. Research-grade oxygen gas was added carefully in measured doses until the pores were completely filled with the physisorbed liquid.

A subpicosecond optical technique was used to study

the dynamical properties of the restricted liquid as it was cooled below the ordinary bulk freezing point. Optical pulses of 500-fs duration at a 76-MHz repetition rate were obtained from a dual-jet dye laser, synchronously pumped by a mode-locked argon-ion laser. The dye-laser wavelength was set at 584 nm, far enough from the oxygen bimolecular absorption line at 577 nm to avoid any significant absorption of energy by the liquid oxygen. An acousto-optic shutter was used in order to keep the average power below 3 mW while maintaining a high peak intensity. In this fashion the liquid could be studied without being thermally perturbed. The train of linearly polarized pulses from the dye laser was split into pump and probe beams with an intensity ratio of 10:1. After the polarization of the probe beam was rotated by 45° relative to that of the pump, the two beams were focused to a common spot of about $50 \mu\text{m}$ in diameter. The pump pulses create a birefringence via an orientation of the molecules in the liquid, and the subsequent relaxation is then monitored by measuring the induced component of circular polarization in the probe pulses as a function of their time delay relative to the pump pulses.⁷ A complete description of the technique and optical system will be presented elsewhere.⁸

In general, the observed optically induced birefringence is a superposition of different physical processes, each with a characteristic relaxation time.⁹ Of greatest importance here are τ_i , the characteristic intermolecular interaction time which is relatively insensitive to temperature, and τ_r , the molecular reorientation time. The molecular reorientation time provides a direct link to the viscosity of the liquid through the relation

$$\tau_r = C(\eta/T) + \tau_0, \quad (1)$$

where C and τ_0 are constants, τ_0 being important only in the low-viscosity limit. This equation has been experimentally established for a variety of liquids over a large range of viscosities.^{10,11}

The molecular reorientational relaxation time τ_r was measured as function of temperature for liquid oxygen as the confining pore radius was varied by almost an

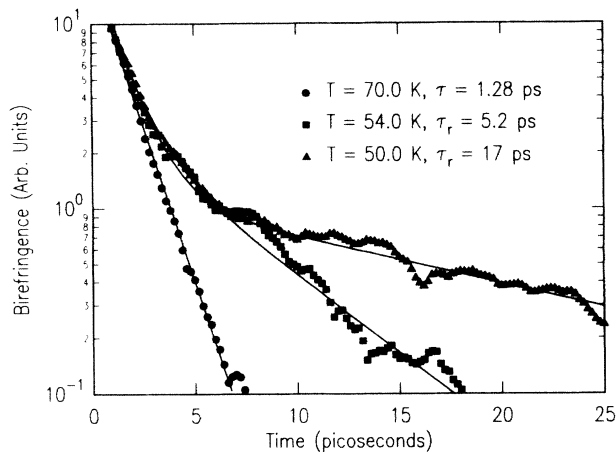


FIG. 1. Time-resolved birefringence measurements of liquid oxygen in sol-gel glass pores of $R = 42 \text{ \AA}$ at three different temperatures. Solid curves represent two exponential fits to the data.

order of magnitude from 22 to 187 \AA . Figure 1 shows an example of the results for oxygen in 42- \AA pores. At a temperature well above the freezing point of bulk oxygen ($T = 54.4 \text{ K}$), the response was found to be indistinguishable from that of the ordinary liquid,¹² where τ_r and τ_i are comparable¹³ and cannot be separately resolved. However, as the liquid was undercooled, the response evolved in a continuous manner, as shown in Fig. 1. A slow component of the signal appeared which is associated with τ_r , and increased with decreasing temperature as a consequence of the increasing fluid viscosity. The data are summarized in Fig. 2, where the orientation time τ_r is plotted as a function of temperature. The restricted liquid behaves similarly to bulk liquid at high temperatures, as shown in the inset of Fig. 2. However, as the confined liquid was cooled towards its depressed freezing point, τ_r increased rapidly in a manner dramatically different from ordinary liquid oxygen near its conventional freezing point. Moreover, both the temperature dependence of

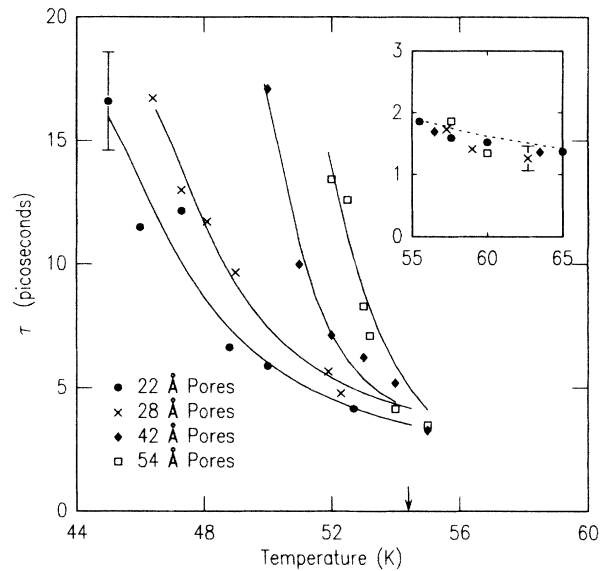


FIG. 2. The molecular reorientation time as a function of temperature for different pore radii. The inset shows higher temperature relaxation where the dashed line represents bulk-oxygen data. Representative error bars are included on several data points. The arrow marks $T_0 = 54.4 \text{ K}$.

τ_r and the degree of supercooling were strongly affected by the size of the restricted pore. A supercooling of almost 20% below the bulk liquid freezing point could be obtained in the smallest pores.

In order to understand how the confining geometry influences the properties of the liquid and how it supercools, we have developed a simple model of supercooling and freezing which implicitly includes the effects of confinement. We start by considering the free energy of a solid nucleus forming a plug of length L in a pore of radius R . The change in free energy associated with the nucleus can be divided into the volume free energy ΔF_v , the surface free energy at the pore wall ΔF_s , and the free energy of the liquid-solid interface ΔF_i . The total change in free energy due to the presence of the solid nucleus is simply the sum of these terms:

$$\Delta F = \Delta F_v + \Delta F_s + \Delta F_i = \frac{-\pi R^2 L}{v} \Delta h_f \left(\frac{T_0 - T}{T_0} \right) + 2\pi R L \Delta \sigma + 2\pi R^2 \alpha, \quad (2)$$

where Δh_f is the heat of fusion, 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 a constant which describes the interface. It has been shown that liquid helium in porous glass will coat the pore walls with a highly viscous liquid or amorphous solid layer,¹ and such observations have been confirmed by static optical absorption measurements which indicate that oxygen also forms such a layer.⁸ Therefore $\Delta \sigma$ is determined

by the interfacial energies of the liquid and solid with this amorphous layer.

Typically in three dimensions, only solid nuclei larger than a certain temperature-dependent critical size can grow in the supercooled region. However, depending on temperature, the free energy of a solid nucleus in a confining geometry either increases or decreases monotonically with its length L as described by Eq. (2). Thus the familiar concept of a critical size as

pertains to the freezing of bulk liquids does not apply here. Below the new freezing point T^* , nuclei of any length will tend to grow. This temperature T^* is determined simply by the confining radius R and defined by the condition on Eq. (2) that $\partial\Delta F/\partial L = 0$, leading to

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

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.^{4,14} The freezing point T^* was determined by observation of the sudden change in optical transmission associated with crystallization of the confined liquid. Figure 3 displays a plot of the observed freezing-point depression as a function of the restricting radius, supporting this geometric interpretation. In three dimensions, the critical-size nucleus for oxygen supercooled by a few degrees is large compared to all but one of the pore sizes studied. For the largest pore size ($R = 187 \text{ \AA}$), the crossover to bulk behavior is observed where the supercooling of the liquid is not dependent on confinement effects. The above interpretation of T^* is consistent with the observation that the liquid was never seen to freeze spontaneously, even when kept at a temperature of less than 0.5 K above T^* for several days. In addition the determination of T^* was repeatable, and T^* was quite well defined for any given pore size.

The melting of the solid oxygen in the pores was observed through static optical-absorption measurements to occur slightly below but within a few degrees of the

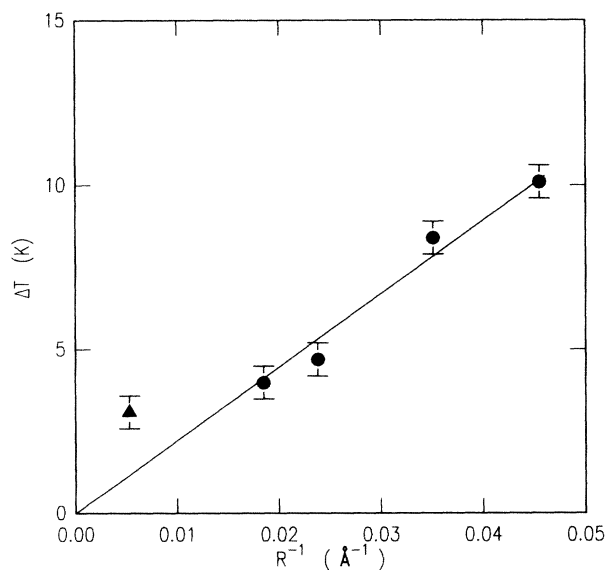


FIG. 3. Observed freezing-point depression plotted as a function of the inverse pore radius. The triangle represents an $R = 187 \text{ \AA}$ sample.

bulk melting temperature. This hysteresis between freezing and melting could possibly be explained by considering the effects of the boundary layer of highly viscous liquid or amorphous solid oxygen at the pore walls. A partial ordering of this layer induced by the freezing of the liquid in the center of the pores would decrease $\Delta\sigma$ and thus account for the observed hysteresis. Specific-heat measurements would help to clarify the situation.

The reorientational data of Fig. 2 indicate a rather remarkable behavior of the confined liquid as it is cooled below the bulk freezing temperature. The pore size not only determines the eventual freezing point, but it also controls the temperature dependence of the relaxation time. The fact that the increase in τ_r appears to be referenced from the freezing point shows that the liquid is unlike an ordinary supercooled liquid. In particular, at a fixed temperature the birefringence relaxation is fastest in the smallest pore. Furthermore, as the freezing point was approached, the amplitude of the response remained approximately constant for any given pore size. The latter two observations imply that the relaxation cannot be simply associated with a growing viscous layer at the pore walls⁷ and reflect an unusual state of the liquid within the pores.

In an attempt to understand the anomalous characteristics of the confined liquid, we describe its modified dynamical behavior in terms of the presence of solid clusters which appear through thermodynamic fluctuations. Although the effects of solid molecular clusters on a bulk fluid's viscosity is relatively clear,¹⁵ the connections between cluster formation, viscosity, and birefringence relaxation are not as obvious in the case of a confined liquid. The simplest phenomenological approach is to assume that to first order the relaxation time τ is proportional to the fraction of molecules associated with clusters. As is true for normal bulk liquids, this approach assumes that τ is a measurement of the liquid's effective viscosity and that the anomalously slow response is a result of cluster formation. In addition, in common with ordinary liquids, it is the fraction of molecules in the clusters x which then determines the viscosity. In order to determine x , we first rewrite the free energy of Eq. (2) as

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

This is the free energy associated with a dense cluster of molecules forming a solid plug of length L . Since the number density of clusters of length L is proportional to¹⁶ $\exp(-\Delta F/kT)$, the fraction of the molecules involved in the formation of all the clusters is

$$x = \frac{C \int L e^{-\Delta F/kT} dL}{1 + C \int L e^{-\Delta F/kT} dL},$$

where the denominator is obtained by summing over all clusters and unattached molecules, and C is a proportionality constant. This yields

$$x = \left[C' \left(1 - \frac{T^*}{T} \right)^2 \exp \left(\frac{\alpha R^2}{kT} \right) + 1 \right]^{-1}. \quad (3)$$

Figure 2 shows a series of curves based on Eq. (3) using the measured values of T^* for each size and $\alpha/k = 0.4 \text{ K} \cdot \text{\AA}^3$. Note that this relation is not expected to fit the data for $T > T_0$ as temperature-dependent free-liquid terms must be added to the relaxation relation in the limit of zero clusters. In addition, no attempt has been made to account for either the tortuosity or interconnectivity of the pores. Nevertheless, this model provides a qualitative description of our results.

In summary, we have taken advantage of a new transparent porous host material to study systematically the observed supercooling and freezing of a confined liquid. Not only the freezing temperature, but also the temperature-dependent viscosity of the liquid was strongly affected by the confining geometry. This was seen to be a consequence of the way a liquid freezes in a narrow cylindrical pore, and was found to be quite different from the freezing process in an ordinary free liquid. The confining walls play an important role in modifying the thermodynamic fluctuations in the liquid, leading to observable changes in the fluid's behavior.

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