

Orientalional behavior of molecular liquids in restricted geometries

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Subpicosecond optical birefringence techniques have been employed to probe directly the rotational dynamics of topologically different molecular liquids confined within porous sol-gel glasses. The glasses have extremely high surface areas with uniform and controllable pore diameters, allowing a systematic evaluation of the liquid behavior as a function of its geometrical confinement. Results with wetting and nonwetting liquids reveal differences between the dynamics of the surface layer and that of the bulk, thereby providing a method of calculating equilibrium properties of the adsorbed film.

The properties of a molecular liquid are expected to be modified in the vicinity of a surface, especially if wetting occurs. The study of this behavior has received a considerable amount of attention from both the theoretical and experimental communities. Such effects have been clearly identified in binary liquid mixtures near the critical region,¹ but in general the role of a surface in modifying the behavior of bulk liquid is difficult to study experimentally since the region of interest consists of a layer whose thickness is usually quite small. In order to increase the available surface-related effect relative to that from the bulk liquid, porous silica glass was chosen as an optically transparent substrate material. In particular, the high internal surface area and the chemical and mechanical stability of porous sol-gel glasses make them an ideal host in which to study modified liquid behavior near a surface and the effect of confinement on the liquid in the small pores.² Furthermore, the surface-area-to-volume ratio of the confined liquid can be tuned over a wide range, allowing a detailed study of surface effects as the restricting pore diameter can be varied by over an order of magnitude in the glass-making process.

The glasses used in this study are essentially pure silica prepared by the sol-gel³ technique. A careful dehydration process at temperatures between 300 and 900°C then yields porous xerogels with a typical porosity of approximately 70%, and a surface area of several hundred square meters per gram. The pore size distribution, as well as the internal surface area, was determined by mercury porosimetry, transmission electron microscopy, and low-temperature oxygen adsorption isotherms.² These characterization measurements reveal an interconnected network of extremely uniform diameter pores, with over 96% of the pores having radii within 5% from the average radius in the best samples.

It was found that two types of "gels" were necessary to obtain the desired range of pore diameters. One type, formed by the hydrolysis of the methoxide or ethoxide of silica, allowed a maximum pore size in the 100–120-Å range. The second type involved gelling LUDOX⁴ with K₂SiO₃ and later removing of the alkali by acid leaching.⁵ In both cases the pore size was found to be highly dependent on the SiO₂/H₂O or SiO₂/K₂O ratio, and was also seen to increase with dehydration temperature up to the

point of densification via viscous sintering (850–900°C). After firing, the samples were polished to an optical finish on two sides, then cleaned in several stages, including boiling in hydrogen-peroxide solution and in distilled water. Finally, the glasses were desiccated and vacuum pumped to remove any remaining contaminants. A more complete description of the porous glass preparation and characterization will be presented elsewhere.⁶

The two liquids used in these experiments were nitrobenzene and carbon disulphide (CS₂). Nitrobenzene is a platelike molecule with a permanent dipole moment, whereas CS₂ is a linear molecule with no dipole moment. Therefore, nitrobenzene, being polar, wets the glass whereas CS₂ does not.⁷ In addition, the bulk viscosity of nitrobenzene is almost 4 times larger than CS₂. The glass samples were placed in a sealed quartz cuvette at room temperature with enough liquid present to completely fill the pores.

We have employed a subpicosecond optical technique to directly probe the dynamics of these liquids confined within the glass pores, and to observe how the liquid is affected by its confinement. The ultrashort optical pulses are obtained from a synchronously pumped dye laser. Pumped by the 90-psec pulses from an acousto-optically mode-locked argon ion laser, a dual jet dye laser produces polarized pulses of approximately 600-fsec duration at a 76-Mhz repetition rate. The wavelength may easily be tuned throughout the red region of the visible spectrum, and was set at 590 nm for the present work. The train of dye laser pulses was split into both pump and probe beams with an intensity ratio of 10:1. The polarization of the probe beam was rotated 45° relative to the direction of the pump polarization by transmission through an oriented linear polarizer. Pump and probe beams were then focused to a common spot of approximately 25 μm in diameter. The pump beam was subsequently blocked, and the emerging probe light refocused and passed through a quarter wave plate into a differential polarization analyzer. Heating effects were avoided by means of an acousto-optic shutter which kept the average power below 2 mW, but allowed peak pulse intensities as high as 10⁸ W/cm². The pump beam creates a birefringence via an orientation of the molecules in the liquid, and the subsequent orientational decay is monitored by measuring the induced com-

ponent of circular polarization in the probe pulses.⁸ Thus, the molecular reorientational time of the molecules may be directly observed. A complete description of the technique and optical system will be presented elsewhere.⁹

The orientational relaxation in bulk nitrobenzene as a function of time after the initial polarizing pump pulse is shown in Fig. 1. The inset shows a semilogarithmic plot of the same data revealing a decay which is clearly exponential with a time constant of 38.6 ± 0.3 psec. This time is associated with the reorientation of the nitrobenzene molecules and is consistent with that determined by Rayleigh scattering¹⁰ and other direct picosecond measurements.¹¹ Figure 2 shows the response from nitrobenzene confined within the 44-Å-diam pores of one of the sol-gel glasses. The response is distinctly different from the bulk liquid relaxation, persisting for a longer time and deviating clearly from a single exponential behavior. The data are well described by a two exponential fit, with the shorter time constant set equal to the measured reorientational time of bulk nitrobenzene. The bulk component is indicated by a dashed line, while the overall fit is shown by a solid curve in the inset of Fig. 2. The results obtained for the different confining geometries studied are summarized in Table I, where it can be seen that the surface response becomes more pronounced with decreasing pore diameter.

In order to investigate further the nature of this slow response, a glass with 44-Å diameter pores was treated to alter the surface polarity.¹² The glass was boiled in eth-

TABLE I. Molecular reorientation times of liquids in porous glasses. Data for nitrobenzene was fit to the form $S(t) = A \exp(-t/\tau_1) + B \exp(-t/\tau_2)$, where τ_1 is fixed by the measured bulk time, and $R = B/A$.

Pore diameter (Å)	Nitrobenzene ($\tau_1 = 38.6$ psec)		CS ₂ ($\tau_1 = 1.57$ psec)
	R	τ_2 (psec)	τ (psec)
44	0.164	126	1.58
108	0.028	142	1.57
375	0	...	1.55
44 (treated)	0
Vycor glass	0.225	109	1.54

anol for 9 hours, after which the excess was removed by vacuum pumping. This simple chemical treatment replaces polar OH groups on the glass surface by less polar ethyl groups. As the polarity of the surface is reduced, the interaction of the nitrobenzene with the substrate is weakened. The fact that the slow part of the response was not observed in the treated sample (Table I), in conjunction

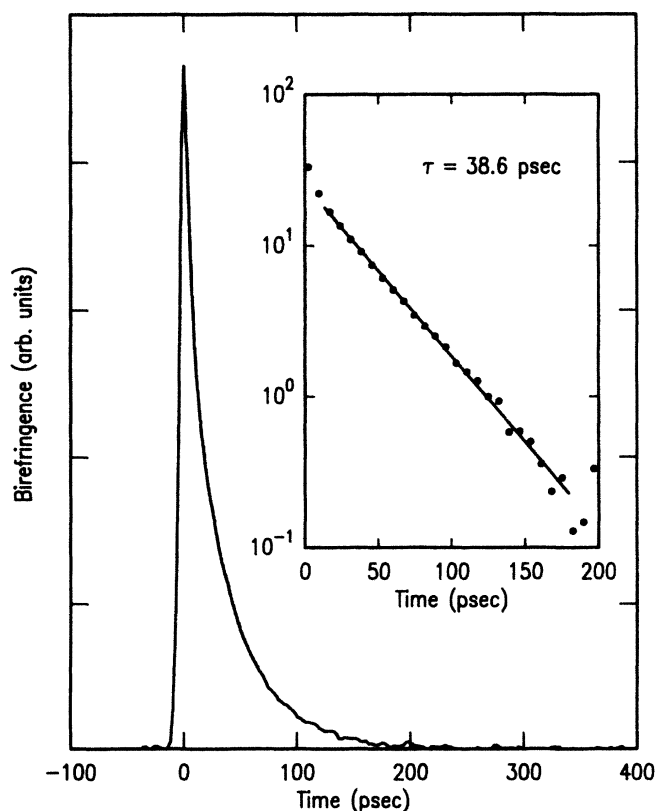


FIG. 1. Time-resolved birefringence signal from bulk liquid nitrobenzene. Inset shows a semilogarithmic plot of the bin-averaged data yielding a reorientation time of 38.6 psec.

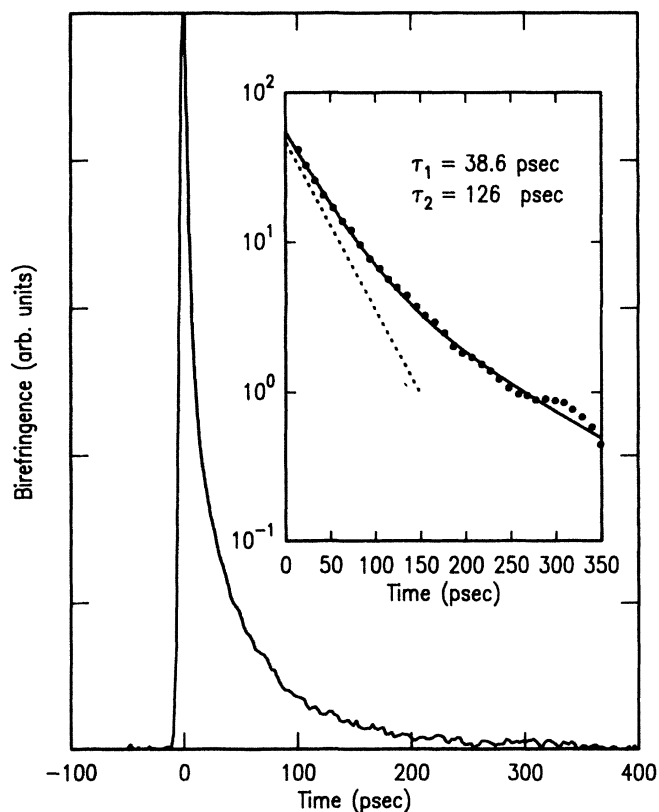


FIG. 2. Time-resolved birefringence signal from nitrobenzene confined within 44-Å-diam pores. Inset shows a smoothed semilogarithmic plot of the data. The solid line is a two exponential fit with times τ_1 and τ_2 , τ_1 being set to the measured relaxation of the bulk liquid. The dashed line shows the component with the bulk relaxation time.

with the fact that the data from the virgin glass are well described by a two exponential fit, strongly indicates that there is a distinct layer of nitrobenzene molecules near the glass wall with a high effective viscosity. This is in agreement with recent diffusion studies of molecules in porous media,¹² where forced Rayleigh scattering data reveal the importance of chemical heterogeneity in significantly reducing a molecule's self-diffusion coefficient.

The reorientational time of the molecules is known to be proportional to the viscosity of the liquid in the form⁸

$$\tau \approx \eta V / k_B T ,$$

where η is the shear viscosity, V is the molar volume, k_B is the Boltzmann constant, and T is the temperature. Therefore, the average measured relaxation time τ_2 of about 125 ± 15 psec indicates that the viscosity of the surface layer is more than 3 times larger than the bulk liquid viscosity. In addition, the thickness of the surface layer can be estimated using the time-resolved data from any two confining geometries. Assuming that the response per molecule in the surface layer is smaller than that in the bulk by a factor of γ , and that the layer has a thickness l independent of pore size, then

$$R = \gamma[r^2 - (r-l)^2]/(r-l)^2 ,$$

where R is the observed ratio of the amplitude of the surface layer response to that of the bulklike liquid in the pores, and r is the pore radius. For example, using data from the 44- and 104-Å glasses yields an estimated thickness of approximately 12 Å. The predicted ratio for the 375-Å sample is then $R = 0.006$, small enough to make its detection difficult.

It is clear that R will depend on both the diameter and topography of the pores. In order to witness these dependences, Vycor glass¹³ was chosen as a commercially available alternative to the sol-gel glasses with a nominal pore diameter of 57 Å. Vycor is known to contain a somewhat wider distribution of pore diameters, extending down to smaller radii.¹² Furthermore, the interconnectivity of the pore network is far less than the gels as a consequence of its overall lower (28%) porosity. Although these features should not affect the temporal response, as compared to the 44-Å sol-gel sample, one might expect a larger surface contribution relative to the amplitude of the bulk response. This is, in fact, observed as displayed in Table I.

The identical experiment was performed using a nonpolar liquid CS₂ which is not expected to wet the glass surface.⁷ Figure 3 shows the orientational response for this liquid contained in the 44-Å sol-gel glass sample. After deconvolving the signal using the measured pulse shape, the relaxation is shown in the inset. The liquid response is consistent with a single exponential decay with a time constant of 1.58 ± 05 picoseconds. The response did not change noticeably as a function of pore diameter, even as the pore diameter was varied over an order of magnitude, ranging from 44 to 375 Å. The molecular reorientation times from CS₂ in all the porous glass samples were con-

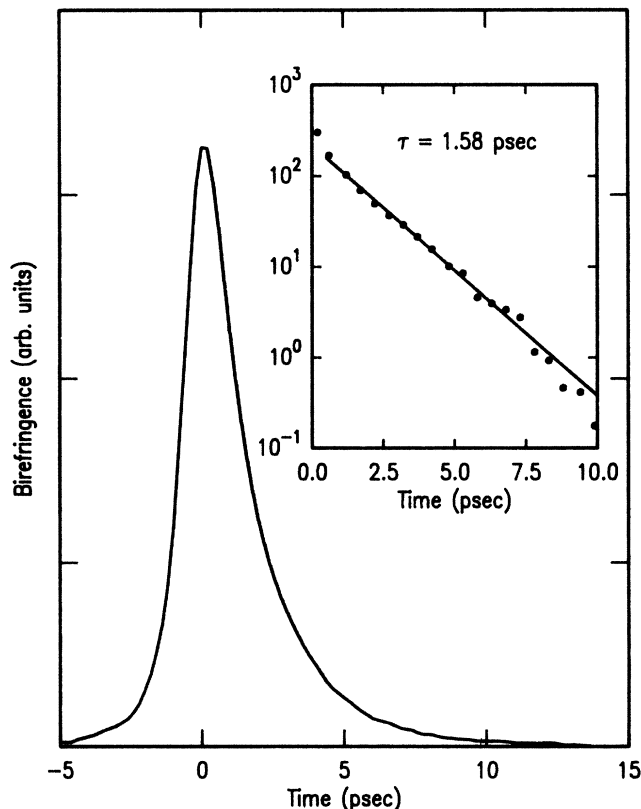


FIG. 3. Time-resolved birefringence signal from CS₂ confined within 44-Å-diam pores. Inset shows a deconvoluted semilogarithmic plot of the data yielding a time constant of 1.58 psec.

sistent with the measured time for the bulk liquid and are shown in Table I. These results also agree with the reorientation time previously measured in CS₂.¹⁴ Thus, in the case of a liquid with a weak surface interaction, no evidence of a viscous boundary layer is seen.

In summary, we have demonstrated that a polar liquid interacting strongly with a substrate forms a surface layer with a high effective viscosity. Picosecond optical techniques represent a useful method of characterizing this layer, allowing both its thickness and viscosity to be determined. Thus, the equilibrium properties of the liquid in the pore, as well as the picosecond dynamics of the liquid on the molecular scale, can be studied in the time domain. Sol-gel porous glasses prove to be ideal media for such experiments. Along with their high porosity, large surface area, and good optical quality, they combine the asset of a variable pore size, enabling one to observe the transition from bulklike liquid behavior at the largest pore sizes to that of a tightly confined liquid at the smallest pore diameter.

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