Direct Observation of Different Mechanisms for the Inhibition of Molecular Reorientation at a Solid/Liquid Interface

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Optical Kerr effect spectroscopy has been used to study the collective orientational dynamics of 2-butyne confined in nanoporous glasses at 293 K. The high polarizability anisotropy of this weakly wetting liquid has allowed us to monitor its reorientational dynamics in nanoconfinement with a high signal-to-noise ratio for many tens of picoseconds. In all pore sizes, the decays can be fit to the sum of three exponentials—one with a time constant equal to that of the decay in the bulk liquid, one with twice this time constant, and one with a considerably larger time constant. The fastest decay arises from the liquid molecules in the centers of the pores. The intermediate decay is attributed to surface molecules that rotate off of the pore walls, and the factor of 2 change in the decay time is exactly that expected on the basis of the difference in the hydrodynamic volume required for this reorientation as compared to that of the bulk. The slowest decay is attributed to the inhibition of reorientation along the pore surfaces due to the reduced dimensionality available to the molecules. These data represent the first direct observation of the separate influences of the hydrodynamic-volume and reduced-dimensionality effects.

Developing a molecular-level understanding of the behavior of liquids at liquid/solid interfaces is a problem of great relevance to many areas of science and technology, including heterogeneous catalysis, separations, and lubrication.[1−4] The nature of the bulk liquid, the nature of the interface, and the interactions between the two all can play important roles in the structure and dynamics of the interfacial liquid. However, one major challenge in probing these issues experimentally is that the amount of liquid affected by its proximity to an interface is generally vanishingly small compared to the amount of liquid in the bulk.

Experimental techniques that are sensitive specifically to the interfacial liquid[5−8] or that limit the amount of bulk liquid[9] have improved our understanding of solid/liquid interfaces greatly in recent years. One such technique that we have employed[10] is the confinement of liquids in monolithic, nanoporous sol−gel glasses.[11] These materials feature a narrow distribution of pore sizes with an average pore diameter that can be controlled synthetically, and their high optical quality makes them ideal media for time-resolved optical studies.

Our primary technique for studying the dynamics of nano-confined liquids is ultrafast optical Kerr effect (OKE) spectroscopy.[12−14] In this technique, a linearly-polarized pump pulse of a few tens of femtoseconds' duration is used to create a transient orientational anisotropy in a liquid composed of molecules with anisotropic polarizabilities. This anisotropy is probed via the depolarization of a second ultrafast laser pulse that arrives at the sample at a variable delay time after the first pulse. The birefringence of the liquid is proportional to the amount of alignment, so the OKE decay is a direct probe of the collective orientational diffusion that returns the liquid to its equilibrium state.

In previous studies of the orientational dynamics of weakly wetting liquids in nanopores,[10,15−18] we have shown that despite the weak interaction between the liquid and the pore walls the time scale for reorientation at the pore surfaces is considerably slower than that in the bulk liquid. However, the liquid in the pore centers is unaffected by confinement. On the basis of a detailed study of the orientational dynamics of confined CS_2,[17] we proposed that two effects are responsible for the inhibition of surface reorientation. The first effect results from geometric confinement (i.e., the reduced dimensionality available for the reorientation of molecules at the pore surfaces). The second effect arises from the additional hydrodynamic volume required for a molecule to rotate off of a pore surface (as compared to the volume required for reorientation in the bulk). Although we were not able to observe the two effects independently in our study of CS_2, by extrapolating the average surface reorientational rate to that at a flat surface, we were able to determine that the hydrodynamic volume for reorienation changes by a factor of approximately 2 at the pore surfaces, as would be expected for a cylindrical molecule.[17]

Here we report the results of an OKE study of the reorientational dynamics of another weakly wetting liquid, 2-butyne, confined in nanoporous glasses. The high polarizability anisotropy[19] of the rodlike molecules of this liquid (4.72 Å^3, which is somewhat smaller than the 8.31-Å^3 anisotropy for CS_2[20]) and the use of a more stable pump laser than in previous studies have allowed us to obtain OKE data with an even better signal-to-noise ratio than that obtained for CS_2. As a result, we have been able for the first time to resolve directly the effects of the two different mechanisms for the inhibition of surface reorientation of a weakly wetting liquid.

The apparatus used for the experiments reported here has been described in detail previously,[10] and the only substantial difference in the setup is that we now use a solid-state laser rather than an argon ion laser to pump our Ti:sapphire laser. Monolithic sol−gel glass samples with average pore diameters of 42, 62, and 91 Å were polished to optical quality and placed in a 1-mm-path-length cuvette. The cuvette was then filled with

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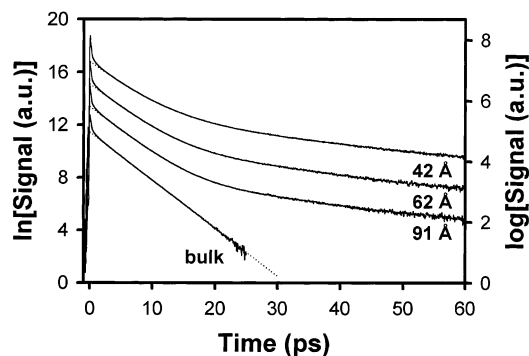
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Figure 1. Full OKE decays for bulk and confined 2-butyne plotted on a logarithmic scale. The solid lines are the data, and the dotted lines are fits. The data sets have been displaced from one another for clarity.

Figure 2. Early-time OKE decays for bulk and confined 2-butyne plotted on a logarithmic scale. The solid lines are the data, and the dotted lines are fits. The data sets have been displaced from one another for clarity.
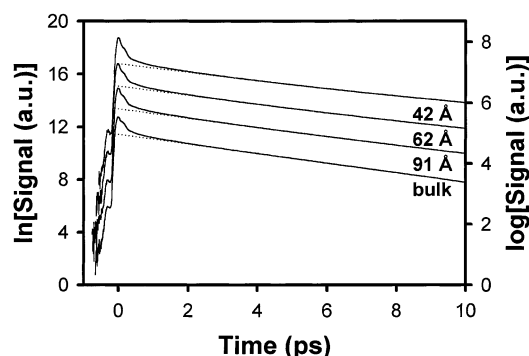
2-butyne, immersed in liquid nitrogen, and sealed with a torch under vacuum. All experiments were performed at a temperature of 293 K.

Full OKE decays for 2-butyne in the bulk and in confinement are shown in Figure 1. The earliest portions of each decay have contributions from coherently excited intermolecular vibrations, but after a few picoseconds the signal is dominated completely by collective orientational diffusion. As would be expected for a liquid composed of cylindrical molecules,[21] the bulk reorientational decay is exponential, and at this temperature it has a time constant of 2.74 ps. The OKE data for the confined liquid, however, are clearly not exponential and have a significant component that decays much more slowly than do the bulk liquid data.

A number of different functional forms were explored in attempting to fit the OKE decays for the confined liquid. As in some of our previous work on non-networked liquids,[17,22,23] a triple-exponential function of the form

$$S(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) + A_3 \exp(-t/\tau_3) \quad (1)$$

was found to reproduce the data highly accurately, whereas other functional forms, such as a stretched exponential or a power law, did not. A Levenberg−Marquart nonlinear least-squares fitting routine[24] was used to fit the confined OKE decays to this function for times ≥ 5 ps; fits begun at later times yielded nearly identical results, which indicates that the OKE signal arises almost completely from diffusive reorientation (as opposed to intermolecular oscillatory modes) at this time and after. As can be seen from Figure 2, the early-time decays in the bulk liquid and in confinement are nearly identical. Indeed, in completely unconstrained fits, the fastest time constant (τ_1) was

TABLE 1: Parameters Derived from 2-Butyne OKE Decays at 293 K with τ_1 Fixed at 2.74 ps and τ_2 Fixed at 5.48 ps[a]

	91 Å	62 Å	42 Å
A_1/A_2	24.2(5)	12.3(3)	6.0(2)
A_1/A_3	220(5)	116(3)	68(2)
τ_3 (ps)	19.1(1)	19.2(1)	21.4(2)
P_1	0.897(5)	0.818(5)	0.690(5)
P_2	0.074(5)	0.133(5)	0.231(5)
P_3	0.028(5)	0.049(5)	0.079(5)
ϵ (Å)	2.4(3)	3.0(3)	3.6(3)
P_2^s	0.72(2)	0.73(2)	0.75(2)
P_3^s	0.28(2)	0.27(2)	0.25(2)

[a] Numbers in parentheses are estimated uncertainties in the last digit.

found to be very close to the decay time for the bulk liquid in all of the different pore sizes. The data were therefore refit with the constraint that $\tau_1 = 2.74$ ps, and the R^2 values were found to be comparable to those of the unconstrained fits. As in our previous work, we find that the larger the pores, the larger the value of A_1 compared to the amplitudes of other exponentials (see Table 1). We therefore believe that the liquid that is in the centers of the pores is essentially unaffected by confinement and over the time scales studied here behaves like the bulk liquid.

According to the Debye−Stokes−Einstein equation,[25] the reorientational time of a molecule in solution is given by

$$\tau = \frac{\eta V_H f}{k_B T} \quad (2)$$

where η is the viscosity, T is the temperature, k_B is Boltzmann's constant, f is dependent on the boundary conditions for reorientation (i.e., stick or slip), and V_H is the hydrodynamic volume required for reorientation. We have argued previously that whereas a cylindrical molecule can rotate about its center of mass in the bulk liquid if the same molecule is lying flat on a surface then it must pivot about one of its ends to rotate off of the surface.[17] If the center of mass of the molecule coincides with its geometric center, then we would expect the hydrodynamic volume, and therefore the time constant, for rotation off of the surface to be twice that for reorientation in the bulk. Indeed, the value of the time constant of the intermediate exponential decay in the confined 2-butyne OKE data, τ_2, was found to be very close to twice the value of τ_1 for all of the pore sizes. We therefore added the constraint that $\tau_2 = 5.48$ ps and refit our data once more, again finding the R^2 values of the fits to be comparable. We therefore believe that this intermediate exponential represents the first direct observation of the increase in hydrodynamic volume required for a cylindrical molecule to rotate off of a surface as compared to the requirement in the bulk.

We now turn to the time constant of the slowest decay component, τ_3. As can be seen from Table 1, this relaxation is approximately 7 times slower than that of the bulk liquid for the pore sizes studied here. This factor of 7 is considerably larger than would be expected from a change in reorientational boundary conditions from slip in the bulk to stick at the pore surfaces.[26] Thus, as was the case in other weakly wetting liquids that we have studied,[16−18] we believe that this slow relaxation reflects the influence of geometric confinement on reorientation along (rather than perpendicular to) the pore surfaces. Although we have suggested previously that the degree of reorientational inhibition should depend significantly on the pore curvature,[17] it is clear that for the range of pore sizes investigated here the pore curvature has only a minor effect on the value of τ_3. The

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effect of pore curvature on the degree of reorientational inhibition due to geometric confinement will undoubtedly be larger in smaller pores, but the weak pore-size dependence observed here suggests that this inhibition has almost reached its asymptotic limit for a flat surface in the 91-Å pores. We cannot rule out the possibility that there is a weak component to the relaxation with a time constant greater than the values of τ_3 reported here, however.

As we have discussed elsewhere,[10] the population of molecules that relaxes with time constant τ_j is proportional to $A_j\tau_j$. The normalized populations P_j corresponding to the three different relaxation times observed are listed in Table 1. Since we know that the pores are roughly cylindrical,[10,11] on the basis of the value of $P_2 + P_3$ for each pore size we can estimate ϵ, the thickness of the surface layer that experiences reorientational inhibition. Since any roughness of the pore surfaces will increase the surface areas of the pores, the estimated values of ϵ should be viewed as upper bounds of the thickness. It is therefore clear that in all of the different pore sizes ϵ is less than the width of a monolayer of molecules. We have observed the same behavior previously for other weakly wetting liquids in nanoconfinement,[16-18] and we believe that it arises from the fact that molecules that lie at the pore surfaces with their cylindrical axes mostly perpendicular to the nearest pore wall do not exhibit any inhibition of reorientational dynamics. Because of packing constraints, in smaller pores, fewer surface molecules would be expected to be perpendicular to the pore walls, and indeed there is a clear trend for ϵ to increase as the pore size decreases. It is unlikely that the differences in pore roughnesses for the different average pore sizes are great enough to account for this increase, so we believe that this observation supports the idea that the orientational relaxation rate at the pore surfaces is dependent on the orientation itself.

We can also compute the fractions of the surface population P_2^s and P_3^s that relax with time constants τ_2 and τ_3, respectively. The values of these populations are listed for the different pore sizes in Table 1. For each pore size, the faster-relaxing population is about three times as large as the slower-relaxing population, although there is a slight increase in P_3^s with increasing pore size. It might be expected that the ratio of P_2^s to P_3^s should be proportional to the ratios of the respective relaxation rates. In fact, P_3^s is close to but somewhat larger than would be expected on the basis of this picture. Temperature-dependent studies of this system may shed more light on this issue.

In conclusion, we have used OKE spectroscopy to study the orientational dynamics of 2-butyne confined in nanoporous glasses at room temperature. The high quality of the OKE data has allowed us for the first time to observe directly the effects of the two different mechanisms that dominate the inhibition of surface reorientation in a weakly wetting liquid. Hydrodynamic-volume effects double the reorientational time for molecules to rotate off of the pore surfaces as compared to the time required for reorientation in the bulk, and geometric-confinement effects cause significantly greater inhibition of reorientation along the pore surfaces.

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