effects modulate the thermal forces rather than the other way round.[24] For amphiphiles in the "gel" phase, one would still expect there to be a protrusion force, including contributions from the mobile head-groups.

In the light of the above, we can rationalize many hitherto unexplained phenomena, including those listed earlier. Thus, we can understand why exponentially repulsive forces between lecithin also occur in nonaqueous solvents[16,17] and why—as we go from water to formamide to propanediol—the decay lengths progressively increase (from 0.17 to 0.26 nm) as the interfacial tensions decrease.[17] Experimentally, one also finds that low decay lengths are generally associated with high preexponential factors;[17] this too is predicted by eq 9, which shows the opposite dependencies of λ and C on α (at the same T).

Another issue that is immediately resolved concerns the large thickness fluctuations and apparent overlap of opposing head-groups even in fully hydrated systems.[20,4] It had previously been recognized[29,4-7] that at sufficiently small separations the hydration interaction should become replaced by the steric repulsion of overlapping head-groups; yet the measured forces never showed any break in the smoothly exponential line down to mean surface separations of 0.3–0.5 nm.[2,3,6,7,29] With the present interpretation this paradox disappears: viz., the so-called steric force was always there right from the start. Note, too, the predicted steep upturn of the force at very small D (Figure 2), as has also been observed.[29]

It is likely that, in a first approximation, the protrusion force is additive with other forces such as double-layer, van der Waals, undulation, hydration, and hydrophobic forces. However, in some cases these forces may be coupled; e.g., the protrusion force may be supressed between charged surfaces, as is the undulation force.[30]

Clearly, more rigorous experimental and theoretical analyses are needed than given here to explore the full nature and implications of this type of interaction. Thus, computer simulations should include any motional degrees of freedom of molecular groups at interfaces, head-group tilting, etc., while experiments should consider which surface-bound groups are mobile and which are immobile.

Finally, on the conceptual level, our findings imply that more careful thought must be given before using terms such as "structured water", "hydration layer", "head-group hydration", "water binding", etc. For example, it is no longer obvious that the amount of water uptake per head-group during the swelling of a lamellar phase can be directly associated with the "structured water" or "hydration" of that group.

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The Origin of Static Friction in Ultrathin Liquid Films

John Van Alsten and Steve Granick*

Department of Materials Science and Engineering, University of Illinois, Urbana, Illinois 61801

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We study the solid-like shear response (the static friction) of liquid films of both compact and chain geometry, whose thickness approaches molecular dimensions. The nonpolar liquids were confined between parallel plates (step-free single crystals) of muscovite mica. The finite shear stress required to produce sliding increased with measurement time over intervals from minutes to hours, at temperatures above the bulk melting temperature or the bulk glass transition temperature. This loss of fluidity may reflect a vitrified state imposed by the liquid's confinement.

Introduction

The physical behavior of confined fluids can differ remarkably from that in the unconstrained bulk. This has implications in many areas, from biology to tribology. Much progress has been made in understanding static equilibrium, and it has become well-established that packing requirements near a solid boundary impose order on the fluid near this solid boundary—the local density shows decaying oscillations normal to the surface with a period of about one particle diameter.[1] However, little is known about relaxation and diffusion within such interfacial regions. In earlier studies,[2-4] we performed measurements to explore the dynamic shear response of nonpolar fluids confined as a sandwich between ultrasmooth parallel surfaces that were close together (a discrete number of molecular layers) but not quite touching. Two varieties of mechanical response were found: liquid-like, but with a rate of viscous energy dissipation enhanced by orders of magnitude over that for the isotropic liquids, and solid-like, meaning that sliding did not occur unless a certain shear stress (or "yield stress") was attained. At a given film thickness, liquid-like behavior degraded into solid-like behavior with increasing net normal pressure. Such yield stress behavior is familiar but not understood. It is the well-known fact of life, static friction.

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In this paper, we study the magnitude and evolution of the yield stress. We show, for what we believe to be the first time, that this stress is time-dependent, a result which has implications regarding the molecular origin of static friction in liquid films. We propose that this loss of fluidity may reflect a vitrified state imposed by the fluid's confinement, despite being found to occur at temperatures above the melting temperature T_m or the glass transition temperature T_g.

Experimental Section

The experimental apparatus and procedure closely resemble that described previously.[2,3] Purified and dried fluids were confined between atomically smooth, step-free single crystals of muscovite mica.[2] Changes in surface separation (±1–2 Å) were measured by optical interferometry between the back sides of the mica sheets, just as in the usual force balance experiment. Shear forces were applied, and the resulting motion was detected by using piezoelectric bimorphs.[2,3]

The usual force balance experiment involves mica sheets that are curved everywhere. However, as the cylinders separated by a liquid droplet are pressed together, the liquid in the final few molecular layers resists being squeezed out.[1–7] In the present experiments, a soft glue (*sym*-diphenylcarbazide) underneath the mica sheets deformed instead. This resulted in a region of constant thickness between the mica sheets, the thickness of the liquid between the mica sheets adjusting to the external normal pressure. The zone of contact is this situation is circular to the extent that the radii of curvature of the crossed cylinders are the same near the point of contact. In the experiments reported below, pains were taken to ensure circular contact area. The contact diameter was measured (±5 μm) by viewing the flattened interference fringes in two orthogonal directions through an optical microscope. Typically, the contact diameter was on the order of 100 μm. We discuss below the empirical evidence that parallel plate geometry was achieved.

External forces in the normal direction were applied, just as in conventional surface forces instruments, by deflection of a double cantilever spring to the tip of which the bottom surface was mounted. The spring constant of the double cantilever spring was approximately 700 N m^{-1}. The normal pressures reported here were calculated as the normal load (W) divided by the measured area (A) of contact: $P = W/A$. In fact, it should be recognized that there is a distribution of pressure within the contact circle, as discussed in standard textbooks. It is well-known that if adhesive forces are small compared to external forces, the classical equations for Hertzian (nonadhesive) contact apply. The pressure is then zero at the circle periphery and is $(3/2)P$ at the center.[8]

The enclosed apparatus was purged with dry nitrogen, and a beaker of phosphorous pentoxide was kept inside to scavenge rogue moisture. To check the absence of surface contamination, the sheets were brought together at a slow rate in N_2 atmosphere to verify the expected jump into contact resulting from attractive van der Waals forces. In the event this attraction was not observed, the experiment was aborted. A droplet of liquid (freshly distilled, stored over type 4A molecular sieves, and filtered through a 0.5-μm PTFE filter immediately before use[9]) was placed between the surfaces. The presence of oscillatory structural forces as a function of separation, characteristic of dry liquids at <100 Å separation, was also verified routinely except for the siloxane polymer samples, which were so viscous that reliable static measurements are not feasible.[10] The temperature was 23 ± 1 °C.

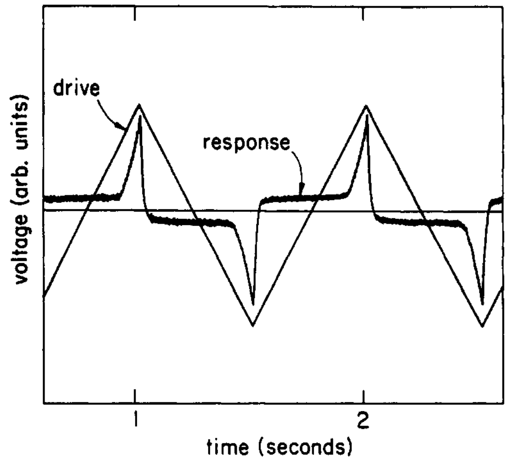

Figure 1. Oscilloscope trace of the drive and response voltages used to determine yield stress, as described in text. The drive is proportional to shear force, and the response is proportional to resulting velocity. Spikes in the response curve correspond to macroscopic slip between the solid surfaces. Data are for hexadecane: thickness 8 Å and net normal pressure 3.0 MPa.

The experiment was performed under conditions designed to minimize surface contamination (mica was cleaved in a laminar flow cabinet, experiments were performed in a sealed enclosure containing phosphorous pentoxide and dry nitrogen). Surface separations refer to the zero which was measured in dry nitrogen atmosphere; we note that others[5–7,11,12] define zero slightly differently, as the closest approach of two sheets of mica in the presence of water, a convention which gives a zero 4–8 Å less than that used here (J. N. Israelachvili, private communication). This admitted uncertainty regarding the zero, which we discuss elsewhere,[13] of course does not affect the relative distances reported below. To anticipate later discussion, we note that although the film thickness was constant during these experiments within the experimental resolution (±1–2 Å), strictly speaking the experiments were conducted at fixed net external normal pressure and not at fixed film thickness.

The lateral distances traversed in this oscillatory experiment were a small fraction, always less than 1%, of the diameter of the contact. Therefore, the region of flattened contact was essentially fixed; the rheology of the glue beneath the flattened mica sheets made a negligible contribution to these measurements, as will be reported in detail elsewhere.

Results

Figure 1 shows an example of the raw shear data. Every nonpolar liquid we studied responded in a qualitatively similar fashion; this example is for hexadecane, as described in the figure caption. The oscillatory force–distance profile of hexadecane is known.[11] Traces from an oscilloscope are shown. The triangular wave form, which shows a voltage proportional to the driving shear force, rose and fell linearly with time. The second wave form shows a voltage proportional to the resulting velocity. The nonzero velocity at low driving shear force reflects the mechanical compliance of the contact point; the top surface was stuck when the shear force was low. The abrupt onset of slip occurred at a well-defined critical shear force, beyond which the top surface accelerated. When the rate of change of shear stress changed direction, the flow stopped, and

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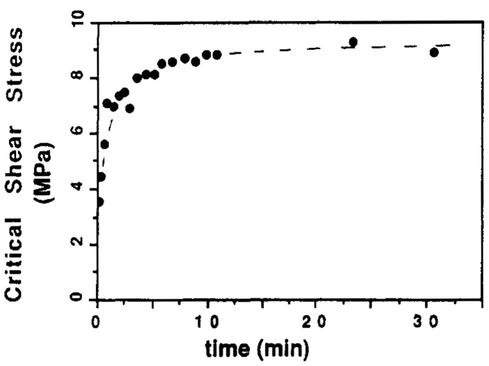

Figure 2. Yield stress of octamethylcyclotetrasiloxane (OMCTS) plotted against elapsed time of the experiment. Film thickness was 9 Å, and net normal pressure was 0.8 MPa.

subsequent flow was not observed until the critical shear stress was reached in the opposite direction. This behavior repeated each cycle, as illustrated in Figure 1.

The experimental design is believed to have ensured parallel plate geometry. This is also supported by measurement showing the film thickness was constant within the experimental uncertainty across the contact diameter and by measuring the same critical shear force in the two opposite directions of motion. Dividing the shear force by the area of contact, which was measured continually during the experiment, gave the critical shear stress.

First we discuss the observation that the critical shear stress built up over remarkably long times in the course of repetitive cycles of oscillation. These times were minutes to hours, which is many orders of magnitude slower than the picoseconds to nanoseconds characteristic of relaxation in these unconstrained liquids at these temperatures and pressures. Figure 2 illustrates this buildup for a compact molecule of roughly globular shape, octamethylcyclotetrasiloxane (OMCTS). Force–distance profiles of this liquid are known.[12] The thickness was 9 Å, approximately a single molecular layer, throughout the duration of the experiment. The net external normal pressure was 0.8 MPa (a low pressure, equivalent to approximately 8 atm). The first measurement of σ_c was approximately 3.5 MPa, but this value increased over the space of 10 min to 9 MPa before the experiment was terminated. Buildup of this kind repeated itself when the mica surfaces were pulled apart and then brought back together at the same spot, a control experiment which suggests that the buildup did not result from chemical degradation of the fluid or from wear of the mica. Note that the yield stress of 3.5 MPa corresponds to an energy density that is physically reasonable for mechanically activated motion, approximately $(1/3)kT$/molecule.

The buildup in σ_c was slower for the siloxane chain molecules than it was for hexadecane or for molecules of compact shape. The times required to reach the plateau in σ_c were observed to vary from several minutes (OMCTS, *p*-xylene) to several hours for longer siloxane chain molecules (poly(phenylmethylsiloxane), poly(dimethylsiloxane)). This difference is illustrated in Figures 2 and 3 for OMCTS and poly(phenylmethylsiloxane), respectively. In the course of the buildup of σ_c, the film thickness was constant within the experimental resolution (±1–2 Å), which suggests that the number of molecules within the films did not change. The slower kinetics for the chains than for the compact molecules is consistent with a process involving packing and crowding of many segments.

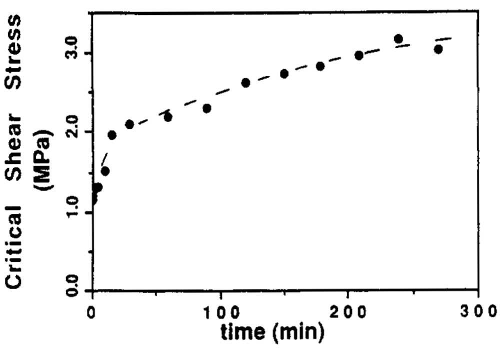

Figure 3. Yield stress of a glass-forming liquid, poly(phenylmethylsiloxane) (PPMS), plotted against elapsed time of the experiment. Film thickness was 20 Å, and net normal pressure was 0.8 MPa. The polydispersity of the liquid (ratio of weight-average to number-average degree of polymerization) was 1.11.

To test the possibility that the yield stress phenomenon stemmed from surface-induced crystallization (perhaps epitaxial crystallization as has been suggested by Monte Carlo calculations),[14,15] a glass-forming liquid was studied. This was an atactic siloxane oligomer, poly(phenylmethylsiloxane) (number-average degree of polymerization 20.8, glass transition temperature T_g = −20 °C).[16] The film thickness was 20 Å, approximately six segment diameters, and the net normal pressure was 0.8 MPa. Yield stress was observed for this glass-forming fluid also, as shown in Figure 3, demonstrating that the capacity to crystallize in the bulk is not necessary for yield stress behavior.

The onset of solid-like behavior occurred at thicknesses up to approximately six layers. However, thick films of the siloxane chain molecules were the more stable; when attempts were made to measure $\sigma_c(t)$ over extended times for films six layers thick of OMCTS, hexadecane, and *p*-xylene, the liquids drained out, leaving a thinner film behind.

Sensitivity to experimental detail was noted with respect to both the film thickness at solidification and the precise kinetics during the rise in σ_c. When the external normal pressure was applied at a particularly slow rate or when the levels of vibration in the laboratory room were particularly high, the film thickness at solidification was less and the rise in σ_c was faster. This may be related to recent measurements of surface forces between mica surfaces separated by nonpolar fluids,[10] which showed that the levels of adhesion in the normal direction were enhanced by agitation of the fluid during the experiment, which in turn suggested that agitation enhanced the layering of the fluid. This sensitivity to experimental detail is an important feature of these experiments because it raises important questions about what physical behavior of ultrathin liquid films is equilibrated and what behavior is metastable—a question that is not usually considered.

We now discuss the dependence on the pressure squeezing the plates together. The yield stress rose markedly with increasing net normal pressure, with a pressure dependence far stronger than even for bulk solids. In Figure 4, the yield stress after 30 min of equilibration is plotted against the net normal pressure for a hexadecane film 8 Å thick (approximately two molecular layers). The relationship is approximately linear with the large slope of

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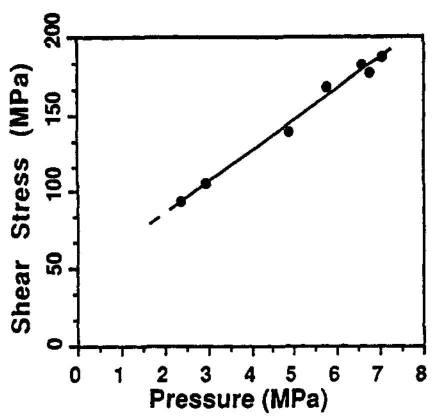

Figure 4. Yield stress of hexadecane after 30 min of equilibration at each pressure, plotted against net normal pressure. Film thickness was 8 Å.

20. From such data, it is customary to calculate an activation volume.[17,18] If an activation volume is calculated from the data in Figure 4, it is unphysically large (10^7 nm^3/molecule!), which at least suggests that the unit process for slip is larger than the volume of any single molecule. Studies of the energy dissipated in sinusoidal oscillation in the liquid-like state also show a large dependence on pressure,[2] indicating the generality of the phenomenon.

It is known from previous work that confined liquids of small molecules have some compressibility, in the sense that force–distance profiles show alternating minima and maxima;[1,11,12] this compressibility may be larger than in the unconstrained disordered liquid. This shows up experimentally as small adjustments in the film thickness with increasing normal pressure, as one climbs from the force minimum of a given layer toward the force maximum.[1,11,12] Such adjustments in thickness, although too small to measure in our experiments (less than 1–2 Å), could have been a significant fraction of the total thickness and could have produced significant changes in the average densities. The time and pressure effects we observe may in part reflect changes in the average density. A reviewer has noted that on this basis one would expect the yield stress to rise more rapidly, the less the film thickness. Preliminary experiments support this expectation, but further experiments are still in progress.

It is worthwhile to contrast this study with another recent study, in which a related technique was used to investigate dynamic friction during travel at constant velocity.[5–7] That experimental setup was significantly different from the present one; the solid surfaces were swept over much larger distances, so fresh liquid constantly entered the zone of contact. Pressure-dependent and time-dependent σ_c values were not observed. In the present study, the distances traversed were always less than 1% of the diameter of the contact; slow equilibration of the compressed thin liquid film then occurred, as described above.

Discussion

These findings have implications for understanding the organization of molecular fluids in restricted geometries. First, the observation of a yield stress which evolves with time is a new empirical phenomenon, whose origin is presently not understood. We have speculated above about its possible physical origin in the compressibility of an ultrathin liquid film. Whatever the eventual molecular explanation, it seems that nonequilibrium structures need to be taken into account for a complete description even of these fluids of very low bulk viscosity and that trapped structures of some kind are long-lived. Further work will be needed to disentangle the effects of confinement from those of possible shear-induced orientation.

What underlying structure is responsible for the observation of a yield stress? Does the existence of a yield stress reflect surface-induced crystallization? This is unlikely in the present systems. To have observed yield stress behavior even for a glass-forming liquid, at a temperature well above the bulk glass transition temperature T_g, suggests that yield stress need not necessarily involve epitaxial crystallization of the liquid, even though computer simulations show that surface-induced crystallization can play a role in some systems.[14,15] In addition, from still another point of view, coincidental commensurability of the liquid microstructure with that of the mica lattice[14,15] is an unlikely explanation of these observations when one considers that the solid-like response was observed for a variety of molecular liquids, of various segmental sizes.

Instead, we suggest that increasing the external normal pressure may squeeze out orientational degrees of freedom to the point that accommodation to slip is not thermally activated and can only be activated mechanically. In this sense, these experiments suggest the possibility of a laterally disordered state, imposed by confinement of the liquid. The origin of such behavior in the loss of orientational degrees of freedom is reminiscent of bulk vitrification.

These observations also have implications for understanding static friction and lubrication. Empirically, it has long been known that static friction usually increases with time when solids are left in contact. It is traditional to belive that this results entirely from the flattening of asperities and resulting increases in the true area of contact.[19] The present experiments, in which the true area of contact was measured directly, suggest that this is not the whole story. It seems that the buildup of static friction can also be an intrinsic phenomenon: slow rearrangements of liquid molecules trapped between two solid surfaces can also contribute to a significant extent.

Implications also exist for understanding the pressure dependence of static friction. Classical theories of friction suppose that the shear stress σ_c is a constant in a given system.[19] But empirically, it has long been known that this is not strictly true: σ_c increases with applied normal pressure.[17,18,20] The coefficient of pressure found in previous friction studies was weaker than in this one, only 0.05–0.8, but already much larger than for shear of the corresponding bulk materials over similar ranges of pressure.[17,18,20] These differences in pressure dependence are intuitively reasonable since surface-induced density profiles of condensed gases (refs 17, 18, and 20) or of liquid (this study) should be smeared out near a rough surface as compared to near a smoother one. In friction, a smoother substrate seems to make the critical shear stress more dependent upon the applied normal pressure.

In summary, ultrathin films of nonpolar fluids displayed a yield stress in response to shear between parallel plates, despite being at temperatures above the bulk melting temperature T_m or the glass transition temperature T_g. The magnitude of the yield stress (static fric-

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tion) built up over long times and also increased strongly with increasing net normal pressure. It is suggested that these remarkable effects can be rationalized on the basis of the compressibility of an ultrathin film near a solid boundary and an eventual vitrified state imposed by low levels of external normal pressure. Much more study, both experimental and theoretical, will be needed to understand the associated trapped structures which appear to evolve with time, the nature of the defects which accommodate the ultimate sliding motion, and the structure of these layers during the times that they do accommodate sliding. This study of fluids in intimate contact with solid boundaries emphasizes the profound influence that a boundary can have on the structure and dynamics of molecular fluids, leading to loss of fluidity when the fluid is sufficiently thin.

Acknowledgment. We thank I. Bitsanis and J. N. Israelachvili for discussions and comments and S. J. Clarson and A. J. Semlyen for providing the PPMS sample. This work was supported by the National Science Foundation, Grants MSM-88-19796 and NSF-DMR-86-12860, with generous assistance from the IBM, Eastman Kodak, and 3M Corporations.

Fluorescence Studies of the Interaction of Sodium Dodecyl Sulfate with Hydrophobically Modified Poly(ethylene oxide)

Yong-Zhong Hu, Cheng-Le Zhao, and Mitchell A. Winnik*

Department of Chemistry and Erindale College, University of Toronto,
Toronto, Canada, M5S 1A1

Pudupadi R. Sundararajan

Xerox Research Centre of Canada, 2660 Speakman Dr., Mississauga, Canada, L5K 2L1

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A poly(ethylene oxide) (PEO, $M = 8000$), 1, containing pyrene (Py) groups at both ends attached via ether linkages has been prepared (1), and the fluorescence properties of its aqueous solutions have been examined. These solutions show a weak excimer emission which is at first strongly enhanced and then suppressed by adding increasing amounts of sodium dodecyl sulfate (SDS) to the solutions. From the sharp onset of enhanced excimer emission and a correspondingly sharp change in the vibrational structure of the locally excited Py emission, we infer the formation of mixed micelles with an apparent cmc of 8×10^{-4} M. SDS–polymer interaction occurs at concentrations well below that of SDS with either Py itself or PEO itself, indicating that in the hydrophobically modified polymer 1 the chain and end groups act cooperatively to promote interaction with the surfactant. At low SDS concentrations, the chains tend to cyclize to put both Py groups in the same micelle.

Introduction

There has been a long-standing interest in the interaction of water-soluble polymers with small amphiphilic molecules.[1-7] Part of this interest derives from the importance of these interactions in various applications as diverse as paints and enhanced oil recovery. Perhaps the best studied system of this genre is that of poly(ethylene oxide) (PEO) in water interacting with the anionic surfactant sodium dodecyl sulfate (SDS).[5-7] SDS itself in water associates into micelles containing approximately 60 molecules at concentrations above 8×10^{-3} M (its critical micelle concentration (cmc)). In the presence of PEO, this association takes place at somewhat lower amphiphile concentration. The critical concentration for this aggregation is essentially independent of PEO concentration and its molar mass. Chain length effects only appear for chains much shorter than $M = 10^4$.

The SDS–PEO aggregate has all the characteristics of a mixed micelle: a localized ensemble of SDS molecules incorporating the polymer chain into its structure. For long polymers, many of these aggregates adhere to a given

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