Superlubricity: A Paradox about Confined Fluids Resolved

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Using the method of Frantz and Salmeron to cleave mica [Tribol. Lett. **5**, 151 (1998)] we investigate alkane fluids in a surface forces apparatus and confirm several predictions of molecular dynamics (MD) simulation. An oscillatory force-distance profile is observed for the methyl-branched alkane, squalane. Boundary slip is inferred from the frictional sliding of molecularly thin fluids and also from the hydrodynamic flow of thicker films. These findings resolve the paradox that prior experiments disagreed with these aspects of MD predictions, and demonstrate that exceptionally low energy dissipation is possible when fluids move past solid surfaces that are sufficiently smooth.

Fluids commonly move past solid surfaces. If the surface is sufficiently rough, then the ''no-slip'' boundary condition holds: fluid at the moving surface takes the same net velocity as that surface [1,2]. We are concerned here with the converse situation when surfaces are extremely smooth—a situation potentially relevant to boundary lubrication, to microfluidics and to nanofluidics. Common sense suggests that if a surface could be prepared so uniform that the fluid-surface potential of interaction were everywhere the same, this should be observable as very low friction when solids, separated by fluid, move past one another.

This intuitive expectation [3] has been confirmed by numerous molecular dynamics (MD) simulations during the past 15 years [4–8]. Very low friction is also observed experimentally when solids slide on incommensurate solids [9,10] and, in atomic force microscopy (AFM) experiments, when fluid films of macroscopic thickness are squeezed between two surfaces whose separation is changed dynamically, even when the surfaces are wetted by the fluid [11,12]. Slip has also been inferred by other experimental methods [13,14].

Paradoxically, other experiments cast doubt on the generality of these conclusions. Experiments using the surface forces apparatus (SFA) report that when nonpolar fluids are confined between atomically smooth mica sheets to a thickness of <5–10 molecular dimensions, the effective shear viscosity increases to the point that the frictional response turns solidlike [15–17]. It was at first supposed that the fluids might be commensurate with the mica surface lattice, thus pinning near-surface fluid molecules [6]. This cannot be reconciled with the fact that confinement-induced solidification has been reported using a large family of confined fluids of different chemical structures and therefore different length scales. How to resolve the paradox? Here, we present experiments showing that the condition of exceptionally low dissipation can be realized experimentally, using simple alkane fluids and very smooth surfaces.

Inspiration for this work comes from the pioneering study of Frantz and Salmeron [18], who used mica sheets that were cleaved and mounted in the experimental apparatus using the standard protocol in this field of study [19] but then recleaved immediately before an experiment. They found that the adhesion was systematically larger by a factor of 50% than when using the standard [19] protocol. The Frantz-Salmeron method was followed in the present study. Muscovite mica (ASTM V-2 grade) was silvered on the back side and glued onto a cylindrical disc using the usual protocol for surface forces experiments, then adhesive tape was placed onto it and detached [18]. A drop of fluid was added rapidly. This produces freshly cleaved mica and has the further advantage that exposure to ambient air is shorter, reducing potential exposure to airborne contaminants. The surfaces were mounted in crossed cylinder geometry and oriented to be free of steps at their contact. Separation was subsequently calculated by optical interferometry. The reference ''zero'' thickness was the thickness of two sheets in adhesive contact in air. In the present experiments, the wavelengths of four adjacent interference fringes were analyzed to deduce the surface-surface separation. Experiments were performed at $25\,^{\circ}\mathrm{C}$, with P_2O_5 (a highly hygroscopic chemical) inside the sealed sample chamber. The samples of squalane and tetradecane (Fluka, purum grade >99%) were used after being dried over molecular sieves and filtered. The radius of curvature of the mica sheets was ≈ 2 cm, giving a slitlike geometry when the surface separation was molecularly thin.

This field of study has seen singular attention to comparing fluids of linear and branched alkanes. A survey of the literature shows no consensus. Figure 1 shows the force-distance profile for squalane, a branched alkane with a C_{24} backbone and six symmetrically placed methyl groups. Force, normalized by mean radius of curvature of the surfaces, is plotted against surface separation. As the surfaces were squeezed together, squalane drained smoothly until oscillatory forces of alternating attraction
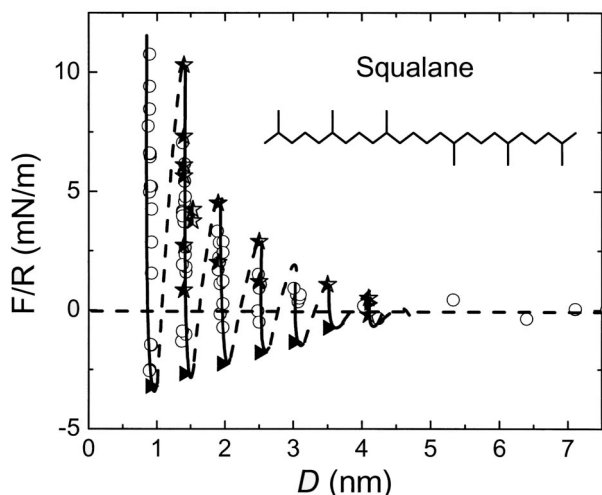
FIG. 1. Static force-distance profile of squalane at room temperature, 25 °C; the confining mica surfaces were cleaved using the method of Frantz and Salmeron [18]. Static force F normalized by the mean radius of curvature, R (≈ 2 cm) of the crossed cylinders using the Derjaguin approximation in which F/R between curved surfaces is proportional to energy per unit area between parallel surfaces at the same closest separation [27], is plotted against surface separation, D. The circles show data measured without shear and the stars show that measurements were unaffected by concomitant oscillatory shear at 256 Hz with shear amplitude 0.5 nm. The triangles indicate outward jumps, which reflected instability when the gradient of attractive force exceeded the elastic force constant of the measuring device. The dashed lines (guides to the eye) represent regions inaccessible to measurement because the force gradient exceeds the apparatus spring constant. The inset shows the chemical structure of this fluid, squalane.

and repulsion were first detected at thickness ≈ 4 nm. This reflects the tendency of squalane to form layers parallel to the solids; application of pressure caused it to drain in discrete steps corresponding to squeezing out of successive layers. The liquid could ultimately be squeezed to ≈ 0.9 nm, twice the thickness of the chain backbone. These data resemble strikingly the molecular dynamics simulations of Gao, Luedtke, and Landman [20] and also recent AFM experiments by Lim and O'Shea [21]. There is agreement even in the details—the magnitudes of the force maxima exceed the magnitudes of the force minima [20] and the magnitudes of the force maxima grow more strongly with decreasing separation than the magnitudes of the force minima [20]. Prior experiments had reported that oscillatory forces with period of the chain width, characteristic of *linear* alkanes, disappear with the addition of a single methyl group [22] or the addition of numerous methyl groups, as for squalane [23,24]. Possible reasons for dependence of surface forces experiments on the method of surface preparation have been debated in the literature without agreement [18,19,25,26], and we will not address them here. The main point is that, using the Frantz-Salmeron

method to prepare mica [18], the inconsistency between simulation and experiment is now removed.

We now consider the interplay between layering and friction, which is another problem that had seen no prior consensus in the literature. The same system (squalane, the model branched alkane) was considered. To apply shear, small-amplitude sinusoidal shear forces were applied to one piezoelectric bimorph, the resulting displacement was monitored by a second bimorph, and a lock-in amplifier decomposed the output into amplitude and phase. Linear viscoelastic response was confirmed [17]. The slowest, quasistatic quenches to a given thickness (compression at $<10^{-2}$ nm sec^{-1}) were produced by slow mechanical drifts in the apparatus. Figure 2 shows the frequency (ω) dependence of the linear viscoelastic dissipative and elastic shear moduli $G''(\omega)$ and $G'(\omega)$ for squalane nominally two layers thick (0.9 nm) produced in this quasistatic manner. One sees that $G''(\omega) \sim \omega$; this signifies that these highly confined films responded to shear deformation in the manner of a viscous fluid, with viscosity $\eta \approx 10$ Pa sec. In other experiments (not shown), this pattern of viscous response was confirmed using ethylene glycol (a hydrogen-bonded fluid) and isododecane (a glass former), so it appears to be general. This agrees with recent studies of the globular-shaped molecule, octamethylcyclotetrasiloxane (OMCTS) [25,26], but contrasts with the confinement-induced solidification reported by other experiments [15–17,23,24].
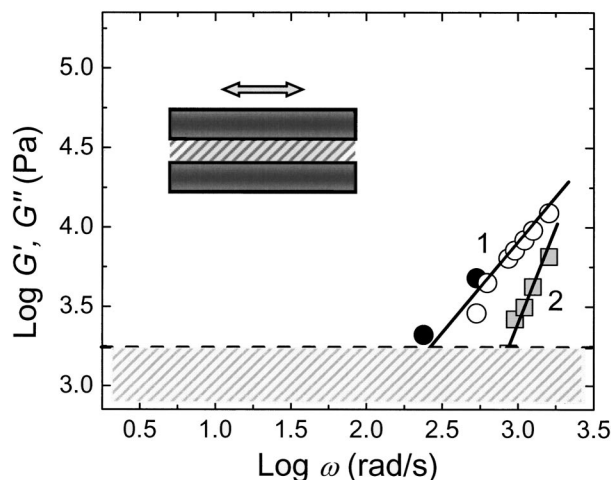

FIG. 2. Shear measurements of squalane, a model branched alkane, confined to thickness 0.9 nm between mica cleaved using the method of Frantz and Salmeron [18]. The effective viscous and elastic shear moduli $G''(\omega)$ (circles) and $G'(\omega)$ (squares), respectively, are plotted against radian frequency (ω) after quasistatic quench to thickness 0.9 nm without shear during the quench process (solid symbols) or with accompanying small-amplitude oscillatory shear at 256 Hz (open symbols). The pressure, normal force normalized by contact area of the flattened crossed cylinders, was 3 MPa. The shaded area shows the minimum resolvable numbers. The inset shows schematically this shear experiment.

A limitation of the recent experiments with OMCTS [25,26] was that the unusual cyclic structure of this fluid left uncertain the generality of those conclusions. The present experiments demonstrate this for the important class of alkane fluids, which possess the complexity of chain architecture characteristic of oils widely used in science and engineering.

Other experiments (not shown) confirmed the phenomenon of exceptionally low friction, also when the shear displacements were much larger than the film thickness. The conclusion therefore appears to be general.

We hypothesized that fluidity observed here—which contrasts qualitatively with solidification reported in the literature [15–17]—resulted from low surface disorder using the Frantz-Salmeron [18] method of surface preparation. If so, it should be possible to produce disorder in the same chemical system by the converse strategy of introducing disorder in the fluid, simply by allowing less equilibration of that fluid. Exploring this idea, next we performed other experiments in which these same solid surfaces were brought together more quickly. It is striking that after these faster quenches, friction was observed starting at larger separation and was considerably enhanced. In Fig. 3, the effective viscosity is plotted against film thickness for an experiment in which the compression rate was 500 times faster, $0.5-1$ nm sec^{-1} (note that this was still sufficiently slow that hydrodynamic forces were too small to flatten the curved surfaces). In control experiments, we reproduced slow-quench findings after making fast-quench measurements, thus demonstrating that the surfaces were not damaged. Tentatively, we imagine that rapid quench nucleated less perfect layering of density waves parallel to the solid surfaces. Then friction resulted as multiple layers jammed against one another, as indicated also by a viscosity enhancement. Easy slip of layers past one another (produced by quasistatic formation of the confined layers) was impeded. This suggests that slip is not strictly between wall and fluid but rather between wall-induced layers of fluid molecules.

Next, we turned to hydrodynamic flow. Physically, this signifies that the volume of fluid was altered by changing the surface separation dynamically, rather than keeping the surface separation constant but changing laterally the relative positions of the constraining surfaces, as in the experiments reported in Figs. 2 and 3. Thickness of the fluid was so large that a continuum description should hold. Tetradecane was selected because linear alkanes were the focus of earlier pertinent data showing "stick" [2,27].

In this situation, "slip"—a limit to stress buildup when oils flow past solid surfaces—has been predicted from molecular dynamics simulations [5] concerning smooth surfaces and has been observed in AFM and other experiments [2,3,11–14]. As implemented here, the main idea was that two solids of mean radius of curvature R, at spacing D, experience a hydrodynamic force F_H as they approach one another (or retreat from one another) in a
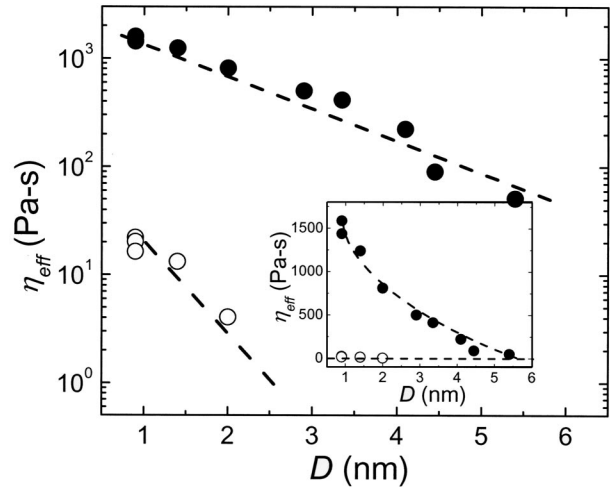
FIG. 3. Logarithmic effective dynamic viscosity, $\eta'_{\text{eff}} \equiv G''(\omega)/\omega$ is plotted against film thickness for squalane (a model branched alkane), confined between mica sheets prepared using the method of Frantz and Salmeron [18]. The data contrast results obtained after rapid quench at shear frequency $f = 1.3$ Hz (open circles) and after quastistatic quench at $f = 256$ Hz (filled circles). The inset shows this same data on linear scales.

liquid medium. The force F_H is proportional to rate at which spacing changes dD/dt (t denotes time), proportional to viscosity η, and inversely proportional to D. The no-slip boundary condition combined with the Navier-Stokes equations gives to first order the following expression, known as the Reynolds equation:

$$F_H = f^* \frac{6\pi R^2 \eta}{D} \cdot \frac{dD}{dt} \qquad (1)$$

The deviation of the dimensionless number f^* from unity quantifies the deviation from the no-slip prediction. A sinusoidal oscillatory vibration of the surface spacing generates an oscillatory hydrodynamic force whose peak we denote as $F_{H,\text{peak}}$. The peak velocity is $v_{\text{peak}} = d \cdot \omega$ where d is vibration amplitude and ω the radian frequency. Studies show that when the frequency and amplitude are varied, results depend on their product v_{peak} and that deviations from Eq. (1) depend on v_{peak}/D [2]. According to Eq. (1), the conventional stick prediction [2,27] ($f^* = 1$) corresponds to a horizontal line. The main part of Fig. 4 shows decided deviations from this idea provided that v_{peak}/D was sufficiently large, i.e., that the hydrodynamic forces were sufficiently large.

To analyze this from another point of view, in the inset of Fig. 4 a quantity proportional to $1/F_H$ (see figure caption for the prefactors) is plotted against D. Whereas the data obtained at the larger spacings extrapolate linearly to the origin with slope proportional to $1/\eta$, which is expected for the stick boundary condition, they deviate decidedly when the spacing was sufficiently small. Yet these smaller spacings were still so large that continuum
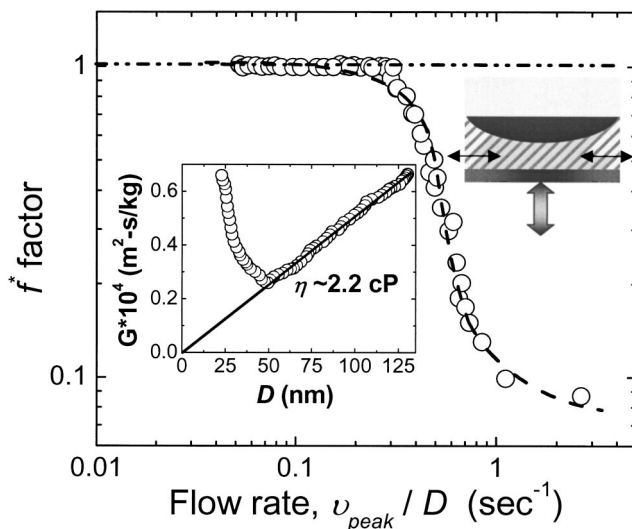
FIG. 4. Hydrodynamic experiments (in which the surface separation was varied dynamically) involving the model linear alkane, tetradecane. The graph contrasts expectations if the conventional stick boundary condition held ($f^* = 1$) with actual data. Specifically, on log-log scales f^* (the ratio between observed hydrodynamic force, $F_{H,peak}$, and that predicted from the no-slip boundary condition) is plotted against the ratio of peak velocity to surface separation D for crossed mica cylinders separated by tetradecane and undergoing 1 nm vibrations at 10 Hz. Inset. The damping function $G = \frac{6\pi R^2 v_{peak}}{F_{H,peak}} = \frac{D}{\eta}$, is plotted against surface separation, D. The reciprocal of the slope in the linear portion of the inset gives the known viscosity of tetradecane. Given the no-slip boundary condition and a Newtonian fluid, G should extrapolate to the origin. The observed curvature implies breakdown of the no-slip boundary condition. An inset shows a schematic diagram of the experiment.

viscosity must be expected. Therefore, the observed nonlinearity indicates slip [2,3,11,12]—when the hydrodynamic forces exceeded a threshold level, the resistance to flow of the fluid was less than would be predicted from a stick boundary condition. This conclusion disagrees with some prior mica-based experiments involving different surface preparation [2,27]. But it is in gratifying agreement with experiments and computer simulations showing that slip occurs even for wetting fluids, provided that the surfaces are sufficiently smooth [2].

In summary, these experiments show exceptionally low energy dissipation. Slip appears to be not strictly between wall and fluid but rather between wall-induced layers of fluid molecules. These experiments concern not only shear flow, in which the volume was constant, but also hydrodynamic flow, in which the volume changed dynamically. It is gratifying to see this resolution of the persistent disagreements described in the introduction. However, the present mica sheets were surely not themselves perfectly orderly, as they had been exposed to ambient air and also possessed a random distribution of

surface potassium ions after cleavage. An agenda for the future will be to understand the amount and type of disorder that a system can tolerate without pinning fluid to a solid surface resulting in high friction. The proof-of-concept presented here, that superlubricity [9,10] can exist in a realistic laboratory situation involving fluid lubrication, holds evident possibilities for nano- fluidics, nanofabrication, and related applications where exceptionally low energy dissipation may be desired.

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