No-Slip Boundary Condition Switches to Partial Slip When Fluid Contains Surfactant

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Physisorbed surfactant can change the hydrodynamic boundary condition of oil flow from "stick" to "partial slip", provided that the shear stress on the wall exceeds a threshold level that decreases with increasing surface coverage of surfactant. To demonstrate this, Newtonian alkane fluids (octane, dodecane, tetradecane) were placed between molecularly smooth surfaces that were either wetting (muscovite mica) or rendered partially wetted by adsorption of surfactant (0.2 or 0.1 wt % hexadecylamine). The surface spacing was vibrated at spacings so large that the fluid responded as a continuum. The resulting hydrodynamic forces agreed with predictions from the no-slip boundary condition when flow rate, peak velocity normalized by surface spacing, was low but implied partial slip when it exceeded a critical level. In other words, the "slip length" depended on reduced velocity. When the reduced velocity was sufficiently high, a plateau shear stress was observed, $\approx$1.3 N m^{-2} for 0.2 wt % hexadecylamine, but also showing some dependence on the fluid, being $\approx$20% higher when the fluid was octane rather than tetradecane. In other words, adsorbed surfactant molecules appeared to act as a somewhat rougher surface, the smaller the adjoining molecules of fluid. The magnitudes of the slip lengths were considerably less than in experiments with chemically modified surfaces of equivalent smoothness. This study points to a possible mechanism by which "friction modifiers" operate in oil and gasoline.

Introduction

One hardly questions that a jet of fluid flows through air with small frictional loss but that this is impossible for flow through a pipe. Textbooks and the mathematical descriptions of fluid flow assign the difference to boundary conditions; the jet "slips" through air but "sticks" to the pipe, in the sense that fluid molecules immediately at the wall have no net velocity tangent to it.[1]

There is a long history in which exceptions to this have been considered, especially by investigating the pressure drop of fluids in capillaries.[1−5] Most recently, when flow occurred over methylated surfaces or over surfaces that were rendered hydrophobic by the adsorption of cetyltrimethylammonium bromide (CTAB) solutions, the reduced pressure drop in the presence of the partially wetted surface was interpreted as owing to slip.[5] In such experiments, the magnitude of "slip" was interpreted to be constant, not depending on the magnitude of pressure or flow rates.

Using different approaches, recent experiments[6−14] and simulations[15−18] show that Newtonian fluids appear to slip when they flow past rigid molecularly smooth surfaces and that this is velocity dependent. It occurs only provided that the flow rate exceeds a system-specific necessary level.[8,9,14,17] In most studies, the surface was imperfectly wet by the flowing fluid. Parenthetically, we note that the mechanism of slip remains unclear; it may be that it is related to the presence on the solid surfaces of adsorbed gases and to the observation that the long-range "hydrophobic" attraction disappears when water and hydrophobic surfaces are rigorously degassed.[19]

This also holds when water flows past water-wetted surfaces[13,14] and when various fluids, aqueous or not, flow past wetted surfaces that carry surface-attached polymer chains.[20,21]

Prior studies from this laboratory concerned situations where surfaces were rendered hydrophobic by self-assembled monolayers, a laborious matter. The chemical composition of the walls was fixed and their wettability was controlled by chemical surface modification to produce a large contact angle and a robust condition of partial wetting. It is also interesting to ask if the flow boundary condition can be effectively controlled by physisorption of surfactant, as has been done for the pressure-driven flow through capillaries.[5]

Here we show experimentally that the simple strategy of dissolving surface-active molecules at dilute concentration in oils (short alkanes) can cause stick boundary conditions to break down. Although the magnitude of the slip length is lessened compared to the case of surface

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modification by chemisorption, this strategy to control surface wettability has the advantage of ease of implementation and does not require chemical surface modification. Rapid enough flow rates can cause desorption of the surfactant to occur, however.

This suggests an explanation of the success of "friction modifiers" in engine oils and gasoline[21,22] and points to a versatile new strategy for diminishing energy losses when fluid flows past a solid surface, provided that it is sufficiently smooth.

Experimental Section

The linear alkanes, $C_{14}H_{30}$ (Aldrich, 99% pure), contained 0.2 wt % of 1-hexadecylamine, $CH_3(CH_2)_{15}NH_2$ (Aldrich 99% pure), except for a control experiment in which 0.1 wt % hexadecylamine was used. They were dried over molecular sieves (Aldrich; pore size, 5 Å) before use, and then the hexadecylamine was dissolved by agitation in a hot water bath and then in an ultrasonic bath. Static force−distance profiles show zero static surface forces when tetradecane is squeezed between hexadecylamine adsorbed onto mica, except when the surface spacing was considerably smaller than that studied below.[23] Therefore the findings described below originated not from static surface forces but from dynamical interactions between fluid and solid surface.

The adsorbed amount was estimated from the dry thickness after a 0.2 wt % solution of hexadecylamine was allowed to adsorb onto mica from hexane. With the assumption that the dry layer had the density of 1 g cm^{-3}, we estimate the surface coverage as 0.5 mg m^{-2}, amounting to roughly 50% of close-packed monolayer coverage. Furthermore, the advancing contact angle of tetradecane droplets placed on the monolayers decayed by about 26° over a period of 10 min, from around 38° to a stable value around 12°, which indicates that the adsorbed hexadecylamine was only physisorbed to the surface, as expected. Experiments commenced after 30 min when the amount adsorbed had equilibrated.

The modified surface forces apparatus used for these flow experiments was described in detail elsewhere[24−30] and is the same one used in our earlier studies of stick and slip boundary conditions.[9,11,31] The geometry was cylindrically shaped surfaces with a radius of curvature of 2 cm that were oriented at right angles to one another. The film thickness was measured using optical interferometry, and the dynamic forces were measured using piezoelectric methods. The apparatus provided a means to place freshly cleaved, atomically smooth surfaces of muscovite mica, with fluid placed between, at controlled and measurable spacing with a resolution of ±0.5 nm while pumping them in the normal direction with small-amplitude oscillatory modulations of film spacing and measuring the resulting dynamic forces. The amplitude and frequency of oscillatory modulation were controlled independently, as will be described in results presented below, thereby making it possible to vary the effective mean velocity of translation over a wide range without a concomitant large change of the film thickness.

Bearing in mind that particulate matter is deposited when cleaved mica sheets are prepared in a manner that is customary when using the surface forces technique,[32] a modified technique was employed. Rather than braise each sheet of mica on all four sides using a red-hot platinum wire,[32] a large sheet was cleaved and silvered, and afterward smaller pieces were cut from it using a sharp scalpel. This is the method employed by this laboratory since the earliest experiments.[24]

Experimental Approach and Data Analysis. The same methods of data analysis were used previously in earlier papers from this laboratory. Here for completeness we describe them in detail in a single place.

The top surface was held fixed, and the bottom surface, fixed to a double cantilever spring comprised of two piezoelectric bimorphs, was pumped in the normal direction with small-amplitude oscillatory force (corresponding to displacements of 5−10 Å). The methods to analyze the dynamic mechanical data were the same as for shear experiments, described in detail elsewhere.[24−27] The main point is that a sinusoidally oscillating force is applied to a "sender" piezoelectric bimorph, and the damping and phase shift of oscillation are detected by a symmetrically placed "receiver" piezoelectric bimorph. The damping and phase shift of the oscillation can be related to the elastic and viscous force constants, respectively, as follows:

$$\omega b = K_{sp} A_0 \sin(\theta)/A \tag{1}$$

$$k = K_{sp}(A_0 \cos(\theta)/A - 1) \tag{2}$$

Here A is the displacement in the presence of liquid, A_0 is the maximum displacement when surfaces are separated in air, θ is the phase difference between the output when the surfaces are separated in air and that in the presence of liquid, and K_{sp} is the effective spring constant of the normal force assembly. Equations 1 and 2 hold for measurements below the resonance frequency of the normal force assembly, and this was the case for all experiments in this paper. For the pumping experiments presented here, $K_{sp} = 1920$ N/m (determined from the resonance frequency of the spring assembly and its known mass). In other experiments from this laboratory, the spring constant has varied, sometimes stiffer, sometimes weaker; it is a simple matter to construct bimorph assemblies of different spring stiffness and we do so frequently.

Not only the mechanical response of the test sample but also apparatus compliance, which we call the "glue", contributes to the measured forces. To separate these respective contributions, the response of the sample (a serial combination of complex device impedance, Z_G, the glue, and complex liquid impedance, Z_L) acts in parallel with the stiffness of the piezoelectric bimorphs.[25,26,28,29] The contribution of Z_G to a measurement is small only when $Z_G \ll Z_L$, the sample impedance. Inspection shows that the contribution of glue impedance is a nonlinear function,

$$\frac{1}{Z} = \frac{1}{Z_L} + \frac{1}{Z_G} \tag{3}$$

Each of these impedance terms has an elastic part, in phase with the driving force (k), and a viscous part, 90° out of phase with the driving force and proportional to angular frequency ω (ωb). Thus, for example, the glue impedance, $Z_G \equiv k_G + i\omega b_G$, has a predominant elastic contribution (the former term) and also a viscous contribution (the latter term), and similarly for Z_L. This terminology originates in the viscoelastic study of bulk polymers.[33]

Although the model was originally developed in order to make this separation when shear forces were measured,[28,29] later we found that the same parallel model describes experiments in which hydrodynamic forces are measured by oscillations of the surface−surface separation,[25,26] as in the present experiments. The apparatus compliance term, Z_G, can be deduced in two ways. One way is to consider the uncorrected measurements of a Newtonian fluid at separations so large that the liquid could show no real elasticity; the apparent elasticity in the data reflects the magnitude of the glue response.[25] Alternatively, Z_G is readily calibrated by making measurements when the opposed surfaces are placed in adhesive contact.[25] In the measurements described below, we employed the first method, calibrating the device compliance in each experiment separately.

Although elsewhere we attributed Z_G to the glue that is used to fasten mica sheets to the apparatus, it now appears that the

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compliance also includes contributions from other portions of the apparatus, perhaps the glue used to shape the piezoelectric bimorphs themselves. This does not affect the analysis.

Consider now how the ideas just described apply to the present experiments. If one assumes the stick boundary condition, solids of mean radius of curvature R, at spacing D, encounter a hydrodynamic force F_H when they approach one another (or retreat from one another) dynamically in a liquid medium. This force F_H is proportional to the rate at which spacing changes, dD/dt (t denotes time), is inversely proportional to D, and furthermore is proportional to the geometrical factor $6\pi R^2$ times the viscosity (η). High-order solutions of the Navier–Stokes equations essentially confirm this expression, known as the Reynolds equation:[1,2]

$$F_H = 6\pi R^2 \eta (1/D)(dD/dt) \quad (4)$$

When the surface spacing is vibrated, the prediction is analogous.[6,9] A sinusoidal oscillatory drive generates an oscillatory hydrodynamic force whose peak we will denote as $F_{H,peak}$. This experimental approach enabled us to determine (a) F_H, from the product of the measured viscous force constant and the oscillatory amplitude; (b) the peak dD/dt, from the product of oscillatory frequency and the oscillatory amplitude, and (c) the absolute value of D, from optical interferometry employing the customary surface forces techniques. As the oscillatory amplitude was kept small relative to D, by judicious changes of oscillatory frequency the value of dD/dt could be varied over a wide range at a fixed film thickness.

Consider how the device compliance affects these experiments. In a given experiment, an oscillatory force of a certain amplitude is generated at the lower surface by applying a given voltage. There results a certain oscillatory deformation amplitude. This is calibrated in two alternative fashions, either by an optical microscope[27] or by optical interferometry with nanometer-level displacements,[30] and direct comparison shows agreement.[30] The product of frequency and amplitude is the applied peak velocity, what it would be in response to the applied force if there were no resistance from the sample. Hydrodynamic drag reduces the amplitude, and the induced velocity is inferred after taking into account the hydrodynamic drag and compliance of the device in the manner just described, using eq 4. It is like the distinction between "acting stress" and "responding stress" described by this laboratory several years ago.[29] A recent publication from this laboratory confusingly failed to distinguish between the applied and induced velocity.[34]

Consider, finally, how surface forces affect these experiments. It is true that when the separation between two surfaces is changed at constant velocity, the forces that resist this originate only partly in the flow of fluid; they also result from equilibrium forces between the surfaces. In such experiments, repulsive surface forces increase the resistance to flow, and attractive surface forces decrease it. The issue is more subtle when the changes in surface separation are sinusoidal, as in the present experiments. Surface forces are in phase with deformations. As the experiments analyzed below concerned the viscous forces and considered the out-of-phase component only, the equilibrium surface forces did not contribute.

Results

Experiments with Tetradecane. We observed quantitative agreement with eq 4 when pure tetradecane was studied, as illustrated in Figure 1. The hydrodynamic force, $F_{H,peak}$, needed to cause drainage under conditions specified in the figure caption is plotted against film thickness. This behavior was known from prior experiments by others,[35–37] and its observation here lends credibility to

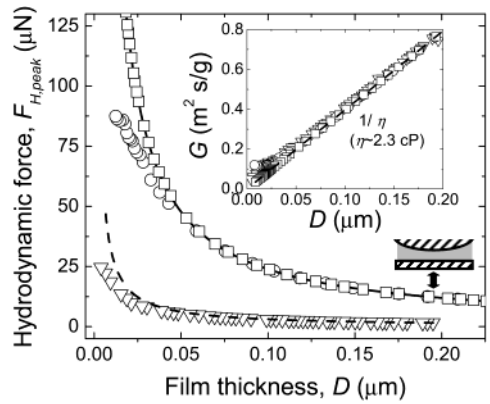

Figure 1. The hydrodynamic force $F_{H,peak}$ is plotted as a function of film thickness D for pure tetradecane (squares, for vibration frequency 63 rad s^{-1} and applied amplitude 2 nm) and for tetradecane containing 0.2 wt % 1-hexadecylamine (circles) between two crossed cylinders in a modified surface forces apparatus. A schematic diagram of the experiment is shown in the bottom right. The data are compared to the hydrodynamic force expected from the Reynolds equation (dashed lines), $F_{H,peak} = (6\pi R^2\eta/D)(dD/dt)$, where R is the mean radius of curvature of the two cylindrical surfaces, D is the closest spacing, η is the viscosity of the liquid in between, and dD/dt is the time rate of change in D. The peak velocity of vibration was $v_{peak} = d\omega$ where d is vibration amplitude and ω is the frequency of vibration. In the inset panel, the damping function $G = 6\pi R^2 v_{peak}/F_{H,peak} = D/\eta$ is plotted against D. The reciprocal of the slope at large film thickness gives the known viscosity of tetradecane, $\eta = 2.3 \pm 0.2$ cP at 25 °C. Data presented in succeeding figures also show that results depended upon dD/dt in addition to D itself. To illustrate this with raw data, the triangles show tetradecane measured at a lower frequency, 16 rad s^{-1}, and a smaller applied amplitude (1 nm).

the present experiments. The new results concern behavior when hexadecylamine surfactant was added. One sees in Figure 1 that the hydrodynamic forces at spacing $D < 40$ nm were systematically less than predicted and also depended on flow rate. To show this more clearly, the inset of Figure 1 shows a linearization of eq 4. A quantity proportional to $1/F_{H,peak}$ is plotted against D. Whereas the data obtained at the largest spacings extrapolate linearly to the origin in classical fashion, at $D < 40$ nm they deviated and showed curvature with negative deviations from linearity. For the purpose of subsequent analysis, the experimental data were described empirically as $F_{H,peak} = f^*K(1/D)(dD/dt)$, where K denotes the factors referred to in eq 4 and f^* was a dimensionless number that quantified the deviation. Note that although f^* lacks units, it does depend on dD/dt and on D, as shown below.

If $f^* = 1$, the Reynolds equation, eq 4, is obeyed quantitatively. The magnitude by which $f^* < 1$ is less than we observed using mica surfaces that were chemically modified to be nonwetting,[9] but it is systematic and exceeds experimental uncertainty.

Next we varied the effective velocity over a wide range at several levels of film spacing and found that the quantity f^* appeared to scale systematically with the quotient of velocity and film thickness, as also found for surfaces that were chemically modified to be nonwetting.[9,11] Here the peak velocity of vibration was defined as $v_{peak} = d\omega$ where d is vibration amplitude and ω is the radian frequency of vibration. It was varied by orders of magnitude, from $v_{applied} = 6$ to 1000 nm s^{-1}, as described in the caption of Figure 2, at levels of film spacing that varied by a factor of nearly 8, from 8 to 60 nm, with measurements made in the

(34) In ref 9, the velocity plotted in Figure 2 is the "applied velocity" (the fictitious velocity referring to the absence of a sample that resisted it) and the velocity in Figure 3 is the true velocity after taking glue compliance and hydrodynamic drag into account, the "induced velocity." The distinction was not made clear in the text.

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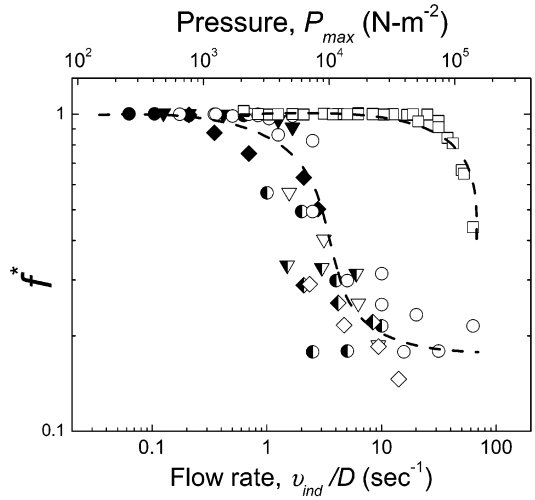

Figure 2. The parameter f^* plotted against the logarithmic reduced flow rate (bottom abscissa) or equivalently the calculated logarithmic peak wall pressure (top abscissa) for tetradecane containing 0.2 wt % 1-hexadecylamine. Here f^* is the ratio of measured F_H to the value expected from eq 4. The measurements were made in the sequence of ascending velocity. The reduced flow rate is the induced velocity, v_{ind}, of liquid flow normalized by film thickness. Also shown is the flow rate dependence of the f^* parameter at the three film spacings of 60 nm (circles), 24 nm (triangles), and 8 nm (diamonds) upon varying applied v_{peak} from 6 to 1000 nm s^{-1} by controlling the vibration amplitude and frequency independently. The amplitude of applied vibration varied from 0.6 to 4 nm. The pumping frequency was 16 rad s^{-1} (filled), 63 rad s^{-1} (semifilled), or 252 rad s^{-1} (open). The data of control experiments with tetradecane containing 0.1 wt % 1-hexadecylamine responding to the same range of applied vibration velocity (6−1000 nm s^{-1}) are shown in open squares. The dashed line is a guide for the eye.

sequence of ascending velocity. Here $v_{applied}$ is the applied peak velocity, what it would be in response to the applied force if there were no resistance from the sample. Hydrodynamic drag reduces the amplitude, and v_{ind}/D in Figure 2 refers to the induced velocity after taking into account hydrodynamic drag and compliance of the device.[34]

Although more studies are needed to establish the functional form, it is remarkable that the data appear to collapse on the single curve in Figure 2. It is important to appreciate that the oil studied here is a simple Newtonian fluid over the range of flow rates studied in this experiment. Therefore, the sensitivity to flow rate reflects subtle variations of the interaction of the bulk liquid with the solid past which it flows.

The bottom abscissa of Figure 2 shows logarithmic values of the flow rate, v_{ind}/D. Parenthetically we remark that *under the assumption of stick*, the maximum shear rate experienced by the flowing fluid scales as $D^{-3/2}$ (see eq 6 below). Instead, we observe the weaker D dependence illustrated in Figure 2 and also found in our earlier studies.[9,11,31]

Figure 2 also suggests that desorption of the surfactant appeared to occur when the flow rate was sufficiently high; this is distinctly different from the pattern observed using chemically modified mica surfaces,[8] in which case f^* decreased monotonically with increasing flow rate, whereas here f^* leveled out to a plateau at $f^* \approx 0.2$. Note also that whereas the magnitude of decrease of f^* using a chemically modified surface could exceed 2 orders of magnitude,[8] the magnitude of decrease in Figure 2 did not exceed a factor of ≈9.

An equation given by Vinogradova allows one to calculate the maximum pressure on the coincident apex

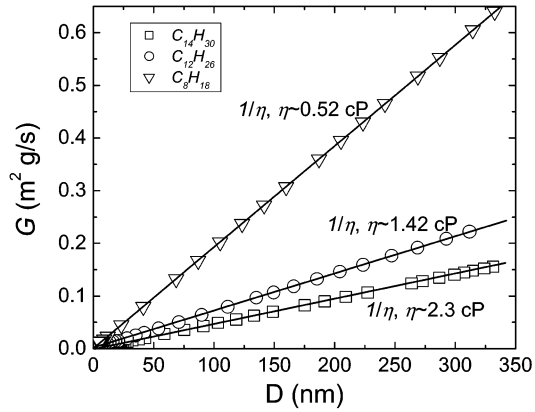

Figure 3. The damping function, $G = 6\pi R^2 v_{peak}/F_{H,peak} = D/\eta$, is plotted as a function of film thickness D for tetradecane (squares), dodecane (circles), and octane (triangles) all containing 0.2 wt % 1-hexadecylamine between two atomically smooth mica surfaces at a vibration frequency of 63 rad s^{-1} and an applied amplitude of 2 nm.

of crossed cylinders undergoing relative displacement in the direction normal to one another even in the presence of partial slip;[38,39] owing to its complexity, we do not reproduce it here. In this view, one may consider that the transition from stick to partial slip in Figure 2 was pressure controlled, as one may see from the top abscissa of Figure 2. This representation shows more clearly that partial slip began at the pressure of $(2.5 \pm 0.8) \times 10^3$ N m^{-2} and that f^* dropped abruptly, with increasing wall pressure, from $f^* \approx 1$ to $f^* \approx 0.2$.

The threshold stress increased when the surfactant's surface coverage decreased. In a control experiment in which the surfactant concentration in solution was halved to 0.1 wt %, resulting in less adsorption, the threshold pressure increased by more than an order of magnitude, to $\approx 1 \times 10^5$ N m^{-2}, as shown in Figure 2.

Comparison with Dodecane and Octane. The data just described (Figures 1 and 2) may be expressed as shear rate controlled, or equivalently as stress controlled. Seeking to determine experimentally which way of thinking is more fundamental, we performed parallel experiments with alkanes of shorter length, dodecane and octane. In this homologous series, the chemistry of the fluid was the same and the concentration of hexadecylamine surfactant was the same (0.2 wt %), but the viscosity of the alkane was varied.

Figure 3 shows linearization of the hydrodynamic forces. A quantity proportional to $1/F_{H,peak}$ is plotted against surface separation. On this scale, the data are linear and the inverse slope, which should give the viscosity according to eq 4, is consistent with the known viscosity of these fluids. Alternatively, Figure 4 plots F_H as a function of the ratio v_{ind}/D, suggested by eq 4. For low values of v_{ind}/D, the finding of linear dependence is equivalent to the finding that $f^* = 1$ in Figure 2. However, this representation has the advantage of showing that decided deviations appeared at a similar level of F_H in all three fluids.

It was desirable to normalize the plateau hydrodynamic force with an effective area so that the magnitude of the threshold shear stress could be considered. To do this, we adopted the expedient of considering the shear stress *if* stick boundary conditions held, since the equations to make that calculation are known. An equation of Spikes[40,41] allows one to express the stress on the coincident apex of

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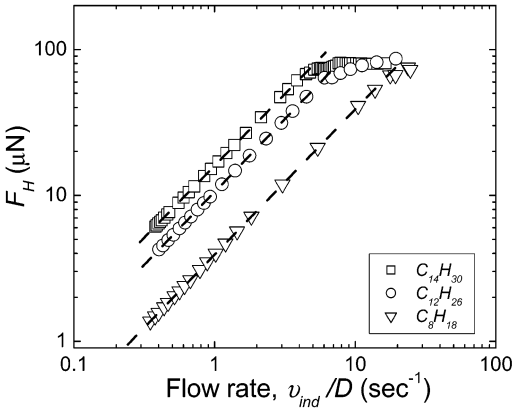

Figure 4. The hydrodynamic force $F_{H,peak}$ is plotted against the logarithmic reduced flow rate, v_{ind}/D for tetradecane (squares), dodecane (circles), and octane (triangles) all containing 0.2 wt % 1-hexadecylamine between two atomically smooth mica surfaces.

two crossed cylinders as a function of the radius of curvature R, the viscosity η, the separation D, and v_{ind}:

$$\sigma_{peak} = \frac{1.378\eta R v_{peak}}{D^{3/2}} \tag{5}$$

In this way, by extrapolating the dotted lines in Figure 4 until they crossed the threshold $F_H \approx 9 \times 10^{-5}$ N, we obtain 1.3, 1.5, and 1.6 N m^{-2} for tetradecane, dodecane, and octane, respectively. For comparison, the critical shear rate acting between the crossed cylinders under the assumption of stick can also be estimated by a equation given by Vinogradova,[38,39]

$$\dot{\gamma}_{max} = A\sqrt{\frac{R}{D}}\frac{v_{ind}}{D} \qquad \text{where } A = (27/128)^{1/2} \tag{6}$$

and, from the levels of v_{ind}/D at which the threshold F_H was attained, one obtains the shear rates 1.2×10^3, 2.7×10^3, and 7.2×10^3 s^{-1} for tetradecane, dodecane, and octane, respectively. Although the conclusion must be considered tentative because the viscosity of these fluids differed by a factor of only 4, it seems that the phenomenon of saturation of the hydrodynamic force was a more fundamental quantity than shear rate. Simply put, a higher shear rate was needed to attain the threshold shear stress, the lower the fluid viscosity.

An alternative interpretation of this same data in terms of surface roughness should also be considered. In this view, the adsorbed surfactant acts as a rougher surface, the smaller the fluid molecule that is in contact with it. Indeed, increasing surface roughness is known to increase the flow rate at which deviation from stick boundary conditions is observed.[11] It also increases the critical shear stress.[11,41] Discussion of the previous paragraph showed that the critical shear stress did increase systematically as the size of the alkane fluid decreased. Especially the level for tetradecane fluid was significantly less than for the other two fluids.

Another alternative interpretation would consider that the adsorbed amount of surfactant may have differed, depending on the fluid from which it adsorbed. On physical grounds, we do expect higher affinity adsorption, the larger the fluid molecules, and less wettability in consequence. Although we have not been able to obtain an in situ measurement of the amount adsorbed in the nonvolatile fluids, dodecane and tetradecane, using the methods available in this laboratory, the argument should be taken seriously. It is consistent with the fact that deviations from stick boundary conditions were observed at lower flow rates, the longer the alkane chain length. But it does not explain why roughly the same plateau shear stress appeared to be observed regardless.

(41) The expression used to calculate peak shear stress at the onset of apparent slip (Figure 4 in ref 11 was erroneous and should read as given in eq 5). The difference is significant as it indicates that apparent slip occurred at even lower shear stresses than were stated in ref 11. We are grateful to Hugh Spikes for pointing out the error.

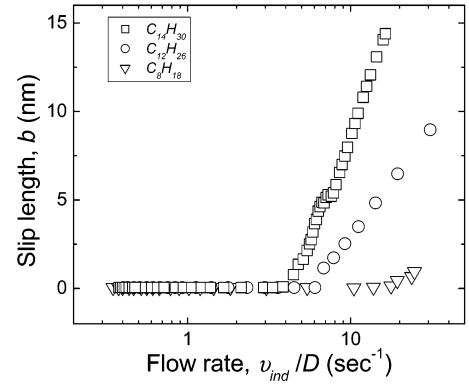

Figure 5. The inferred slip length, b, is plotted against the logarithmic reduced flow rate, v_{ind}/D, for three systems, tetradecane (squares), dodecane (circles), and octane (triangles). Slip length was numerically calculated from eq 7 given in the text.

Considerations of the Slip Length. There is a tradition in fluid dynamics to infer the "slip length", the fictive distance inside a solid boundary at which the stick flow boundary condition would hold. Mathematical manipulation shows that deviations from eq 1 can be quantified from the equation

$$f^* = 2\frac{D}{6b}\left[\left(1 + \frac{D}{6b}\right)\ln\left(1 + \frac{6b}{D}\right) - 1\right] \tag{7}$$

where b is the slip length.[38,41] For the same data considered above, Figure 5 shows the implied slip length plotted against logarithmic v_{ind}/D. The slip length was zero for the flow of pure tetradecane but increased monotonically, in the presence of dissolved surfactant, when the flow rate was sufficiently large, and similarly for the other alkane fluids.

To find that the slip length was variable contrasts with the common theoretical assumption that the slip length of low-viscosity fluids is a constant number. These observations of rate-dependent slip are qualitatively consistent with findings concerning chemically modified surfaces[7−11] and also with computer simulations by Thompson and Troian[17] that preceded these experiments. The magnitudes of the slip lengths in Figure 5 are considerably less than in experiments with chemically modified surfaces of equivalent smoothness,[9,11] however.

Summary and Prospects

The observation of rate-dependent slip, slip only when a threshold of shear rate or shear stress is exceeded, confirms a pattern that has now been observed by several research laboratories, our own laboratory and also laboratories in Australia and Germany.[8,9,11,13] The new point in the present study is that the solid surface was naturally wet by the fluids that we studied; only the adsorption of dilute dissolved surfactant rendered it partially nonwetting.

These observations cannot be explained away by appeal to modification of the fluid viscosity itself owing to shear thinning, since the case of tetradecane between mica at comparable levels of thickness (complete wetting) presents a counterexample to that. The experiments were performed at least 6 orders of magnitude below the very high shear rates at which shear thinning of small alkane molecules is anticipated based on computer simulations, so shear thinning is hardly credible.

The magnitudes of the slip effects that we report here are less than those that we have found previously for surfaces chemically modified to be nonwetting.[9,11] If we considered only those studies, it would have been possible to argue that those slip effects stemmed from the adsorption of adventitious small amounts of contaminant within the fluids. But in the present study, "contaminant" in the form of surfactant of known concentration was added intentionally. The systematically softened effects reported here, relative to the effects of chemisorption, suggest strongly that the earlier results from this laboratory, in which the surfaces were prepared by chemisorption and even larger flow anomalies were observed, should not be dismissed as owing to the presence of adventitious contaminants.

The observation of modified friction when surfactant molecules spontaneously adsorb from dilute solution qualitatively confirms earlier findings using pressure-driven flow through capillaries[5] and points to a new, versatile method to control energy loss during fluid flow. Looking to the future, this study shows that the simple expedient of causing a loose-packed monolayer to physisorb to a solid surface from dilute solution in a flowing fluid can change the boundary condition of fluid flow from "stick" to "partial slip" and furthermore suggests that slip occurs at a point dictated by the shear stress on the wall.

At the same time, several important issues are left unresolved by this study and left for future work. First, the connections remain unclear between a flow rate when surfaces approach one another or retreat from one another (present study) and the shear rate when surfaces slide parallel to one another while separated by a constant thickness.[7] The present curved geometry is ambiguous because only a portion of the viscous drag results from the points where the crossed cylinders approach most closely; indeed, for the simplest case of the stick boundary condition, it is on the order of only one-half of the total hydrodynamic drag.[43] We anticipate the situation studied in this paper to be more complex: partial slip near the points of closest approach, but stick at points farther removed.

Second, the matter of how the slip phenomenon depends on surface coverage of the surfactant remains unclear; only a single surfactant surface coverage has been studied to date. A third point of uncertainty concerns the interplay between partial slip (promoted by surfactant adsorption) and the stick boundary condition (promoted by flow-induced detachment of the surfactant).

In imagination of practical consequences, of course it is true that the molecularly smooth surfaces studied here comprised model systems. The massive amount of drag reduction reported here, up to 90% reduction of the hydrodynamic forces from that predicted by textbook expectations, should not be expected in the case of rougher surfaces, as roughness reduces the tendency toward slip.[11] Nonetheless, a point of principle has been established. From the standpoint of fuel economy in automobiles, for example, an improvement of even a few tenths of a percent is worthwhile when one integrates over the economics of a national or global economy.

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