

Dipole-Dependent Slip of Newtonian Liquids at Smooth Solid Hydrophobic Surfaces

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We present atomic force microscopy observations of the “effective” slippage of various nonpolar and polar liquids on alkylsilane coated glass surfaces. For small contact angle nonpolar liquids, the slip length decreases as one approaches a wetting transition. However, for large contact angle polar liquids it is found that the slip length is primarily influenced by the dipole moment, rather than the wettability of the liquid for the surface, where the slip length decreases with increasing dipole moment.

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A common assumption, which has been successfully used to describe many macroscopic fluid dynamic experiments over the centuries, is that when fluids flow across solid surfaces a no-slip boundary condition holds at the solid-fluid interface such that the fluid velocity, relative to the solid, is zero precisely at the solid surface. Although there were a number of hints that perhaps this was not necessarily true [1], especially for partially wettable surfaces, nevertheless, the no-slip boundary condition has served its purpose well because many macroscopic fluid experiments are not particularly sensitive to the precise condition assumed at the solid/liquid interface. However, in micro- or nanofluidic systems, the boundary condition will play a very important role in determining the fluid flow behavior. Recent experiments [2–7] and computer simulations [8,9] indicate that on a microscopic scale there is frequently slip at solid boundaries where the amount of slip can depend upon many different factors such as the wettability of the surface [2,4,9], shear rate [3,4], viscosity of the fluid [3], surface roughness [2,4,6], presence of dissolved gases [7], or amount of in-plane ordering near the surface [8]. A quantity called the slip length provides a useful qualitative measure of the amount of slip at any given surface. The slip length represents the extrapolation distance into the solid at which the fluid velocity would be zero. Hence, no-slip boundary conditions correspond to zero slip length.

Evidence for boundary slip has been most prevalent in driven systems where two surfaces, with a liquid in between, are driven together at a high rate. A hydrodynamic repulsive force acts between these two surfaces where the actual rate of approach is slowed because it takes a finite amount of time to drain the fluid from between the surfaces. For a spherical solid, of radius a , approaching a molecularly flat surface the hydrodynamic force is given by [10]

$$F_h = \frac{6\pi a^2 v \eta}{h} \psi. \quad (1)$$

This condition is valid for small separation distances

$h \ll a$, where $v = dh/dt$ is the approach velocity, η the liquid shear viscosity, and for no-slip boundary conditions $\psi = 1$. If slip should occur at the two surfaces, then the hydrodynamic force is less (i.e., $\psi < 1$) and the liquid can more easily drain from between the surfaces where for hydrophobic surfaces

$$\psi \simeq \frac{h}{3b} \left[\left(1 + \frac{h}{6b} \right) \ln \left(1 + \frac{6b}{h} \right) - 1 \right], \quad (2)$$

and the slip length b is assumed to be identical at both surfaces.

In the colloidal probe atomic force microscopy (AFM) technique [11], a colloidal sphere of radius a is attached to an AFM cantilever, and the interaction force $F = kx$ is measured as a function of separation distance h , where k and x are, respectively, the cantilever spring constant and deflection due to the presence of the interaction. The probe and substrate are driven towards each other at a fixed frequency f (and constant drive velocity). For low frequencies, the van der Waals, electrostatic, and structural forces dominate the interaction, while for sufficiently high f the hydrodynamic force provides the dominant contribution. In the hydrodynamic regime, a comparison of the variation of F_h versus h [Eqs. (1) and (2)] with experimental data (F versus h) allows a determination of the slip length b .

The prevailing assumption in this field [1,9] (however, see [8b]), which agrees with a number of measurements in [2,4], is that the slip length b increases as the surface becomes less wettable, namely as the contact angle θ for droplets on the surface increases. In this publication, we demonstrate that this general rule does *not* necessarily hold, especially for highly polar liquids.

In order to be able to quantitatively compare the slip behavior of many different liquids, we have used a colloidal probe attached to a Nanoscope IIIa AFM where, as much as possible, we have used the same borosilicate surface, borosilicate colloidal sphere, and AFM cantilever. Both the surface and colloidal sphere were coated

TABLE I. Liquid parameters and slip lengths at piezodrive of $42 \mu\text{m/s}$.

Classes	Liquids	σ_{lv} (erg/cm ²)	θ (°)	η (mPas)	p (D)	b (nm)
I	Octane	21.1	13.5	0.5	0	0
	Dodecane	24.9	32.0	1.5	0	0
	Tridecane	25.6	35.3	1.9	0	10
	Tetradecane	26.1	37.0	2.3	0	15
	Pentadecane	26.6	39.1	2.7	0	10
	Hexadecane	27.1	39.4	3.3	0	20
II	Cyclohexane	24.7	25.5	1.0	0	10
	Benzene	28.2	32.5	0.6	0	50
III	Aniline	42.1	64.1	4.2	1.13	50
	Water	72.0	97.5	1.0	1.85	30
	Benzaldehyde	38.0	61.8	1.5	3.00	20
	Nitrobenzene	43.5	63.2	2.0	4.22	10
	2-nitroanisole	45.7	69.8	3.4	4.83	0

under similar preparation conditions with a hexadecyltri-chlorosilane layer using a standard wet chemistry procedure. Hence, the wettability and slip length for both surfaces is expected to be the same. Both surfaces also exhibited a low rms surface roughness of ~ 0.3 nm over a $1 \times 1 \mu\text{m}^2$ area; therefore surface roughness [2,4,6] is not expected to play a role in our measurements. The borosilicate colloidal probe (Mo-Sci Corp.) of large radius $a \approx 28.5 \mu\text{m}$ enabled liquids of relatively low viscosity η to be measured with high precision. This probe was attached using chemically resistant Norland 61 UV epoxy to a standard Veeco V-shaped contact mode silicon nitride cantilever with a measured spring constant of $k \approx 0.56$ N/m (using the technique in [12]). The measurement protocol in [11] was followed where the zero of separation ($h = 0$) could be determined to within a few nm or better.

A variety of nonpolar and polar liquids of varying surface tension σ_{lv} are studied (Table I). Nonpolar class I liquids consist of the n -alkanes, class II liquids were nonpolar “ring shaped” molecules, while class III liquids consisted of polar liquids of either a benzene derivative or water. All of the liquids possessed a purity of $\sim 99\%$ and were used as received. A Zisman plot [13] of $\cos\theta$ versus σ_{lv} (Fig. 1, inset) is remarkably linear and provides an excellent measure of the wettability of each liquid for the surface. Class I and II liquids are useful for examining the variation in the slip length b as one approaches a wetting transition for $\theta \rightarrow 0^\circ$. Class III liquids are useful for examining the variation in the slip length b as one moves away from the wetting transition.

Prior work [3,4] has shown that the slip length in general increases with increasing approach velocity. Here we mainly concentrate on a single piezodrive velocity of $42 \mu\text{m/s}$. The behavior of the slip length for the different liquids is listed in Table I, where Fig. 2 provides a visual summary. For both class I and II nonpolar liquids, the slip length decreases as one approaches a wetting transition [Fig. 2(a)]; however, the rate of decrease is

different for these two categories of liquids which could be an indication of different layering effects against the solid surfaces thus leading to a different perceived slip length [8]. A no-slip boundary condition was a reasonable approximation for both octane and dodecane even though these liquids possess a finite nonzero contact angle with $\theta = 13.5$ and 32° , respectively. The slip behavior exhibited in Fig. 2(a) for class III liquids, where θ is large, is unexpected. The benzene derivatives possess rather similar contact angles ($\theta \sim 60^\circ - 70^\circ$) and therefore one might expect the slip lengths to be similar with a magnitude much larger than the low contact angle class I and II liquids. This is certainly not the case and, in fact, there is no obvious dependence upon the contact angle for these class III liquids. Even for water (a class III polar liquid),

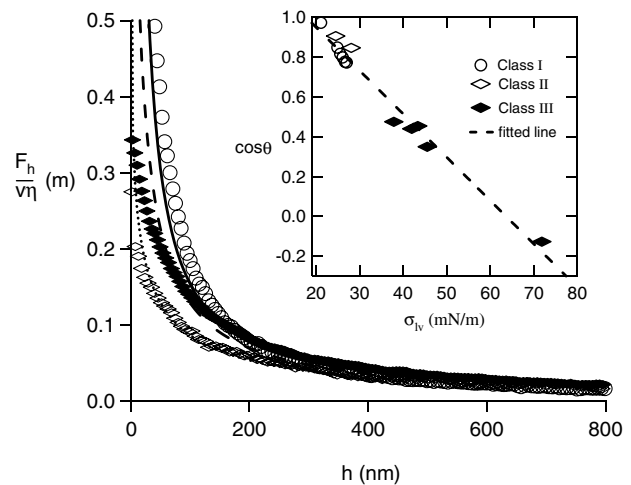


FIG. 1. Comparison of the slip behavior for dodecane (circles), benzene (open diamonds), and 2-nitroanisole (solid diamonds) at a piezodrive speed of $42 \mu\text{m/s}$. The solid, dashed, and dotted lines correspond to theoretical calculations for 2-nitroanisole with slip lengths of 0, 10, and 50 nm, respectively. Inset: Zisman plot of $\cos\theta$ versus σ_{lv} for all liquids.

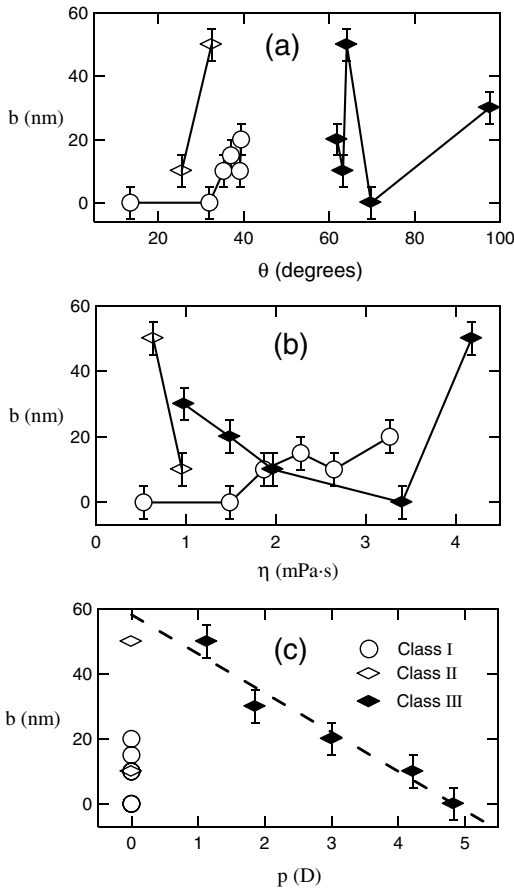


FIG. 2. Comparison of the slip length b for all classes of liquids, measured at a piezodrive velocity of $42 \mu\text{m/s}$, as a function of (a) contact angle θ , (b) viscosity η , and (c) dipole moment p .

which possesses the largest contact angle for our system ($\theta \sim 100^\circ$), its slip length ($b \sim 30$ nm) is considerably smaller than either benzene (class II, $b \sim 50$ nm) or aniline (class III, $b \sim 50$ nm) which possess contact angles of, respectively, 32.5° and 64° .

What physical parameter determines the slip length for these large contact angle liquids? This property must be a property of the liquid rather than of the solid because our solid substrate and colloidal sphere remained essentially unchanged. In previous work on highly viscous sucrose solutions [3], where the viscosity was a factor of 10 larger than for systems studied here, the authors noted a dependence of the slip length upon viscosity. For our low viscosity liquids, there is no systematic dependence upon the viscosity [Fig. 2(b)]. Finally, if the slip length is plotted as a function of the dipole moment [Fig. 2(c)], a correlation is immediately obvious for the class III liquids. The slip length decreases, essentially linearly, with increasing dipole moment where the small dipole moment limit, for aniline [upper solid diamond, Fig. 2(c)] with a dipole moment of $1.13D$, is in approximate agreement with the nonpolar benzene result (upper open dia-

mond). Note, however, that the “slip length” is a useful but nevertheless oversimplified measure of the general slip behavior [4]. In our case, it describes the approximate boundary conditions that hold for large separation distances, $1.2 \mu\text{m} \gtrsim h \gtrsim 0.1 \mu\text{m}$.

A useful illustration, which highlights the behavior in Fig. 2(c), is to compare $F_h/\nu\eta$ as a function of h for dodecane (circles, Fig. 1), benzene (open diamonds), and 2-nitroanisole (solid diamonds) which have, respectively, 0, 50, and ~ 0 nm slip lengths where, as noted above, the small slip lengths for dodecane and 2-nitroanisole originate from different physical mechanisms. In Fig. 1, the solid, dashed, and dotted lines depict the theoretical behavior calculated for 2-nitroanisole for slip lengths of, respectively, 0, 10, and 50 nm. This theoretical behavior is accurate when comparing it with the 2-nitroanisole data, but only illustrative when comparing it with benzene and dodecane. In comparison with theory, both dodecane and 2-nitroanisole exhibit very small slip lengths b (0–10 nm), whereas benzene exhibits a very large slip length (~ 50 nm) for $h \gtrsim 0.1 \mu\text{m}$. At smaller separations ($h < 0.1 \mu\text{m}$), the liquids start to exhibit much larger slip lengths as noted earlier [4]; this is particularly evident for the 2-nitroanisole data.

Why should polarity influence the slip length? Before speculating on this question, we first examine the low frequency behavior of the highly polar 2-nitroanisole liquid which perhaps sheds some light on the physical structuring at the surface. For a very slow piezodrive speed of $0.3 \mu\text{m/s}$, the force F exhibits an unusual repulsive interaction during both approach (solid line, Fig. 3) and retraction (heavy dashed line). At this speed, the hydrodynamic (light dashed line) and nonretarded van der Waals (dotted line) forces are negligible compared with this large static repulsive interaction. What is the physical origin for this large repulsive interaction? The dipole-image dipole energy $U = p^2(\epsilon_l - \epsilon_s)(\cos^2\theta + 1)/16\epsilon_l(\epsilon_l + \epsilon_s)z^3$ [14] for dipole moment p , at depth z and angle θ (relative to the \hat{z} axis), where ϵ_l and ϵ_s are the static dielectric constants of the liquid and substrate, respectively. In our situation, $\epsilon_l > \epsilon_s$ and the energy is a minimum for $\theta = \pi/2$ or $3\pi/2$ and the dipole preferentially has its axis oriented parallel to the surface where the dipoles tend to be repelled from the interface because U is positive. We believe that this dipole-image dipole interaction forms the fundamental origin of the large repulsive interaction exhibited in Fig. 3. The dipole-dipole interaction will also have a strong influence on the structure of the liquid in the vicinity of the surface where, in order to minimize this energy, a structured “surface lattice” (schematically depicted in the Fig. 3 inset) will form for a sufficiently large dipole moment. This surface orientational order will decay with increasing depth into the liquid. How would the presence of such a structured liquid adjacent to the solid surface influence the slip behavior? In order for the liquid to

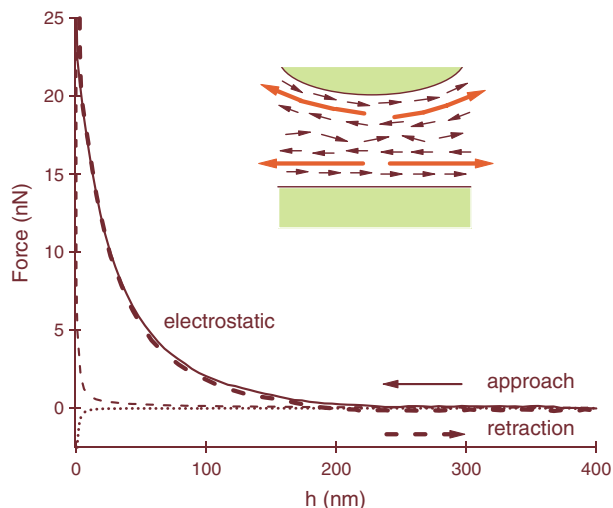


FIG. 3 (color online). Electrostatic repulsive force for 2-nitroanisole (approach, solid line; retraction, heavy dashed line) at a slow piezodrive speed of $0.3 \mu\text{m/s}$. The hydrodynamic force (light dashed line) and nonretarded van der Waals force (dotted line) are negligible compared with this repulsive force. Inset: dipolar “surface lattice structure”; large arrows indicate the direction of shear flow in the colloidal probe geometry.

exhibit surface slip in this colloidal sphere geometry, the lattice structure adjacent to the surface must be sheared apart, in *opposite* directions (large left and right pointing arrows in the Fig. 3 inset). However, this lattice structure in the first few monolayers adjacent to the surface will possess a very large cohesive energy, which will make it more difficult to shear this lattice structure apart [15]. Therefore, with *increasing dipole moment* the surface cohesive energy of the lattice structure increases; thus, the shearing of the lattice structure becomes more difficult which will show up as a *decreasing slip length b* , in agreement with the experimental results depicted in Fig. 2(c).

In summary, we examined the slip behavior of a large number of liquids at alkylsilane coated solid surfaces using the colloidal probe AFM technique. For nonpolar liquids (classes I and II) possessing small contact angles ($\theta \sim 10^\circ\text{--}40^\circ$), the slip length b decreased with decreasing contact angle [Fig. 2(a)]. For polar liquids (class III) possessing large contact angles ($\theta \sim 60^\circ\text{--}100^\circ$), there was no obvious correlation between the slip length b and either the contact angle θ [Fig. 2(a)] or the viscosity

η [Fig. 2(b)]; instead, the slip length for these polar liquids is controlled by the dipole moment p [Fig. 2(c)]. We believe the dipole-dipole and dipole-image dipole interactions, in the vicinity of the surface, generate a surface lattice structure (Fig. 3 inset), and it is the cohesive energy of this lattice structure (which opposes the disruption of this lattice) that generates the observed slip behavior for these liquids.

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- [15] The dipole-dipole interaction leads to an *in-plane* antiferroelectric structure adjacent to the surface; hence, even if the shear direction is in some arbitrary direction [rather than in the dipole direction as in Fig. 3 (inset)], this surface lattice structure will always exhibit a large cohesive energy.