Shear-Dependent Boundary Slip in an Aqueous Newtonian Liquid

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We report direct measurements of hydrodynamic drainage forces, which show clear evidence of boundary slip in a Newtonian liquid. The degree of boundary slip is found to be a function of the liquid viscosity and the shear rate, as characterized by the slip length, and is up to ~20 nm. This has implications for confined biological systems, the permeability of microporous media, and for the lubrication of nanomachines, and will be important in the microcontrol of liquid flow. We also show that current theories of slip do not adequately describe the experimental data.

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Fluid mechanics is one of the oldest and most useful of the "exact" sciences. For hundreds of years it has relied upon the assumption that when liquid flows over a solid surface, the liquid molecules adjacent to the solid are stationary relative to the solid [1,2]. This is the no-slip boundary condition and is applied successfully to model many macroscopic experiments. However this success may not always reflect the accuracy of the boundary condition but may in fact reflect the insensitivity of the experiment to a partial-slip boundary condition. Measurements using fine capillaries have been interpreted as indicating boundary slip [3]. Boundary slip will become important only when the length scale over which the liquid velocity changes approaches the slip length, that is only when the liquid is highly confined. The slip length, as defined by Brochard and de Gennes [4], is the distance behind the interface at which the liquid velocity extrapolates to zero. The slip boundary condition is suggested in several molecular dynamics simulations [5–8] and is acknowledged in non-Newtonian fluids [9–12], at the interface with a gas [13,14], and in the special case where a monolayer of C_{60} molecules is present at the interface [15]. Recently a study reporting slip at the interface with a hydrophobic surface in a nonaqueous Newtonian fluid has been published [16]. We demonstrate here, through direct measurement of the drainage force, that slip is also detectable in an aqueous Newtonian fluid bounded by relatively hydrophilic solid surfaces, and that the degree of boundary slip is shear dependent.

The hydrodynamic drainage force on a silica sphere (radius 10.4 ± 0.1 μm) approaching a flat wall (muscovite mica) perpendicularly in a viscous liquid has been measured using a Nanoscope III Atomic Force Microscope (Digital Instruments). Both the sphere and the mica are gold coated (15.1 ± 0.2 nm) using a layer of titanium (7.7 ± 0.2 nm) to promote adhesion. The gold surfaces (roughness 0.56 nm rms over 1000 nm × 1000 nm) are then treated with a mixture of 10 mM 11-mercapto-1-undecanol and 10 mM 1-dodecanethiol (20% dodecanethiol) in ethanol to produce a chemically bound self-assembled monolayer. The metal coatings and the self-assembled monolayers are depicted in the inset of Fig. 1 (not to scale). The resulting advancing and receding contact angles of water on these surfaces are $\theta_{\mathrm{adv}} = 70°$, $\theta_{\mathrm{rec}} = 40°$. This arrangement provides some control over the wettability and roughness of the surface. The sphere is attached to a fine cantilever spring ($0.115\ \mathrm{N\,m^{-1}}$) [17] following the method of Ducker *et al.* [18] enabling the drag force to be quantified. The drive rate and surface separation are accurately controlled using a piezoelectric transducer. The piezodrive rate is the velocity at which the substrate moves, and it is not equivalent to the approach rate of the surfaces. In fact the sphere is deflected away from the flat surface by the repulsive hydrodynamic drainage forces, so that the approach rate between the surfaces is progressively reduced (see inset, Fig. 3). Note that in Figs. 2–5 the theoretical curves are generated using the approach velocity derived from the experiments, so the noise in the theoretical curves is due to the noise in the approach velocity. Aqueous solutions of sucrose (BDH, AR) of varying concentration whose temperature has been equilibrated at 20 °C before each measurement are used as Newtonian viscous liquids.

We compare the experimental results to the existing theoretical models. The first is an exact calculation of

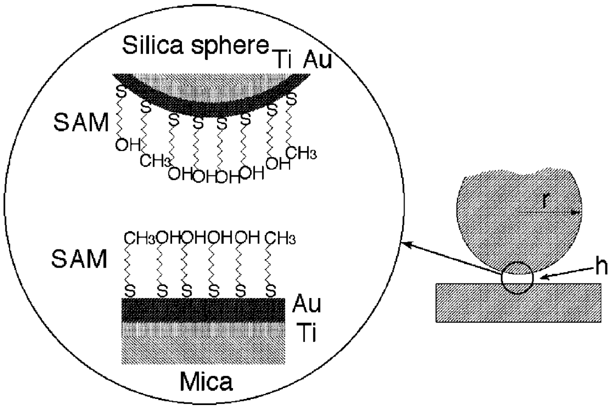

FIG. 1. Schematic representation of the employed sphere-plane system. The sphere of radius r is separated from the flat surface by h at the point of closest approach.

Brenner [19] for the no-slip boundary condition; the hydrodynamic force exerted on a sphere of radius r approaching a flat surface perpendicularly with a velocity V is given by $F_h = 6\pi\eta r V\lambda$, where η is the bulk dynamic viscosity and λ is a function of the ratio of the sphere radius (r) to the distance of its center from the flat surface [19]. The second is a calculation allowing for slip at the solid boundary by Vinogradova [20–22]. In this model the hydrodynamic drag force exerted on a sphere of radius r approaching a flat surface at a distance h (as depicted in Fig. 1) with approach velocity V is $F_h = \frac{6\pi r^2 \eta V}{h} f^*$, where f^* is the correction factor for slip for two surfaces with the same slip length b:

$$f^* = \frac{h}{3b}\left[\left(1 + \frac{h}{6b}\right)\ln\left(1 + \frac{6b}{h}\right) - 1\right]. \qquad (1)$$

This model is accurate for low Reynolds numbers and for small surface separations $(h < r)$. Both these approximations are valid for our measurements.

In using the Brenner model there are no adjustable parameters, as all the parameters (sphere radius, liquid viscosity, and spring constant) are known by independent measurement. In using the Vinogradova model we require a new parameter, the slip length. This is adjusted to give the best fit to the experimental data. In Fig. 2 the measured hydrodynamic drainage force is fitted with the Brenner theory and good agreement is found, indicating that the no-slip boundary condition is applicable. However, when the approach rate of the surfaces or the viscosity is increased the Brenner theory is unable to describe the experimental data. Typical experimental results, along with the theoretical models, are shown in Figs. 3 and 4. Note that in Fig. 3 the calculated maximum shear rate is 8000 s^{-1} at a separation of 40 nm and 160 s^{-1} at a separation of 700 nm; therefore the sucrose solutions behave as Newtonian fluids. The crucial point is that at higher viscosities and shear rates the no-slip theory does not fit the experimental results. The error bars in Fig. 3 are calculated for the no-slip theory allowing for an error of ±2 mPa s in the solution viscosity (i.e., about ±2 °C on the temperature of the solution) and an error of ±0.2 μm on the radius of the sphere. They illustrate how an improved fit of the no-slip theory cannot be made if the known parameters are made "adjustable." An improved fit to the data is obtained when slip is permitted. This is shown clearly in Fig. 5, where the force is plotted versus the inverse of the surface separation. This type of graph highlights the different behavior of the no-slip and the slip theories at small separations. The Brenner theory results in a nearly linear plot, while the Vinogradova theory and the experimental data show substantial deviations from linearity. We can conclude that there is evidence of boundary slip, and we can quantify this slip using the slip length which best fits the data. This slip length does not fully specify the state of the system, since the current theories are incomplete, but it does allow the general physical trends within our system to be determined. The slip lengths obtained for a number of approach speeds and viscosities are shown in Fig. 6. The main conclusion is that the slip length depends nonlinearly on the driving rate. In the theory of Vinogradova the drag force is proportional to the approach rate. Our experiments show this is not the case. A very recent report of slip [16] found no dependence on the shear rate, but this may be due to the limited accuracy with which the slip length can be determined. A complete theory of boundary slip would incorporate a shear-rate dependent term. Recent measurements of boundary slip in non-Newtonian liquids have led Horn *et al.* [9] to the same conclusion. Furthermore a dependence on the solution viscosity is also observed. This is in agreement with the approach of de Gennes [4] and Vinogradova. The occurrence of slip in aqueous Newtonian fluids considerably complicates flow predictions in confined Newtonian systems. We now need to know not

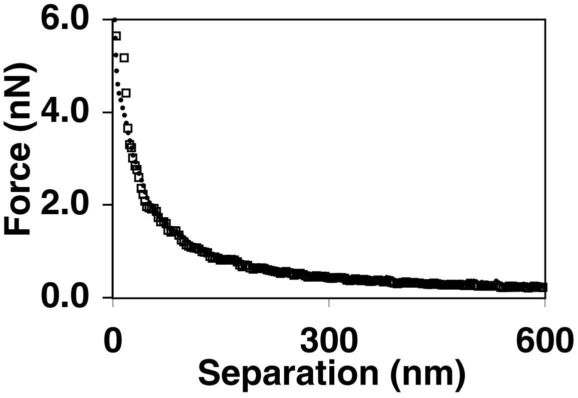

FIG. 2. Measurements of the hydrodynamic drainage force in a sucrose solution. The piezodrive rate is 2400 nm/s and the viscosity of the sucrose solution is 27.0 mPa s. The experimental data (circles) are presented together with the Brenner theory prediction (empty squares).

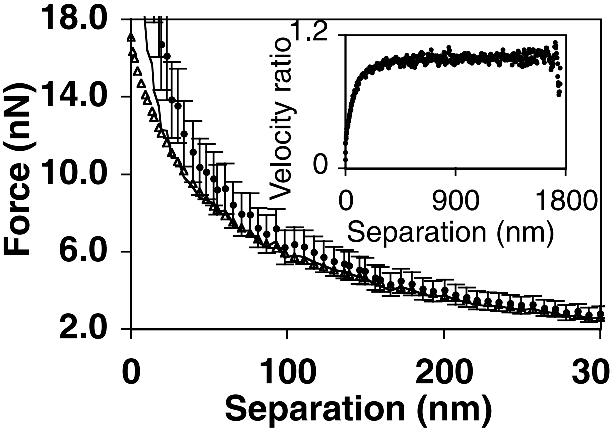

FIG. 3. Measurement of the hydrodynamic drainage force in a sucrose solution. The experimental data (empty triangles) are presented together with the no-slip theory (circles, with error bars) and the slip theory (line). The piezodrive rate is 21 600 nm/s and the viscosity of the sucrose solution is 19.2 mPa s. The fitted slip length is 5 nm. In the inset we report the ratio of the approach and drive velocity.

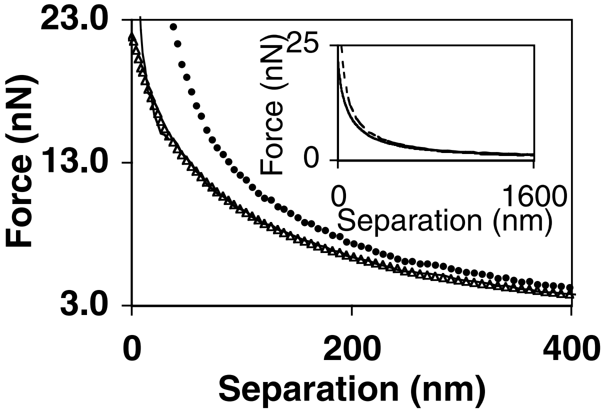

FIG. 4. Measurement of the hydrodynamic drainage force in a sucrose solution. The experimental data (empty triangles) are presented together with the no-slip theory (circles, with error bars) and the slip theory (line). The piezodrive velocity is 21 600 nm/s and the viscosity of the sucrose solution is 38.9 mPa s. The fitted slip length is 12 nm. In the inset the full scale experimental data (solid line) and the full scale Brenner theory (broken line) are presented.

just the viscosity but also some details of the surface-liquid interaction. This complication is the price that must be paid for accurate modeling of these systems.

In Fig. 7 we report the equilibrium surface forces in these systems, measured by employing slow surface approach velocities (400 nm/s) such that the hydrodynamic force is small. The measured surface forces are fitted using the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory, employing a published algorithm [23] to solve the nonlinear Poisson-Boltzmann equation. The DLVO force is calculated for a surface potential of 32 mV, Hamaker constant of 3.4×10^{-20} J (Ref. [24]), and Debye length of 27 nm for both the constant charge and constant potential boundary conditions. The surface charge regulates between these two extremes. The salt impurities in the sucrose are responsible for the low Debye length. The surface forces are well described by DLVO theory. The equilibrium forces are substantially smaller in magnitude and range than the dynamic forces. The dynamic measurements have not been corrected for the equilibrium forces, as over the range at which the slip length is fitted (greater than 50 nm), this correction is negligibly small. The DLVO surface interaction is not responsible for the deviation in force from the no-slip boundary condition. If the equilibrium forces were subtracted from the dynamic forces, the deviation of the experimental data from the no-slip theoretical force would increase.

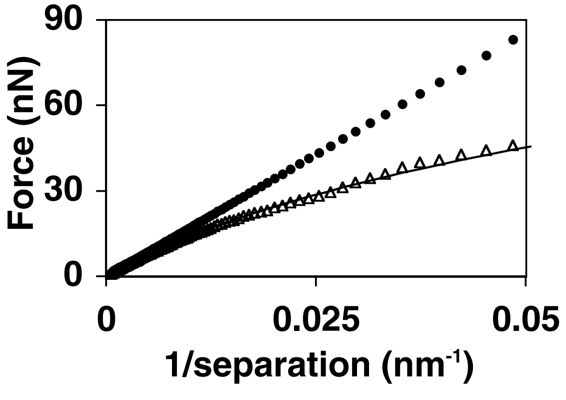

FIG. 5. Hydrodynamic force versus inverse of separation. The same data as in Fig. 4 are reported. The experimental force data are divided by the velocity ratio (see Fig. 3) to allow comparison with theories.

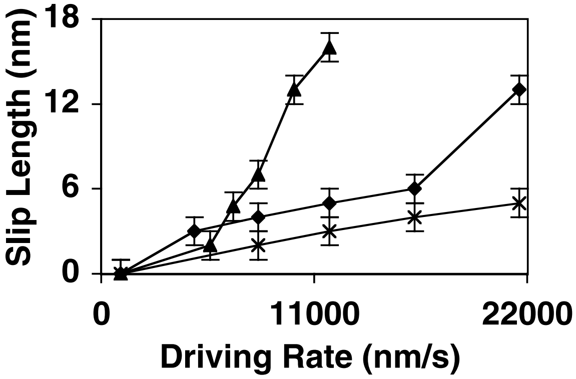

FIG. 6. Slip length versus driving rate. The sucrose solutions have viscosities of 19.2 mPa s (crosses), 38.9 mPa s (diamonds), and 80.3 mPa s (triangles). The lines are included to guide the eye.

Figure 6 demonstrates that the slip length is a function of the approach rate and shows why several previous careful measurements of confined liquids have not observed evidence for boundary slip [25–27]. Under the low approach rates previously employed we expect the slip length to be effectively zero and a no-slip boundary condition to be applicable.

It has been proposed that boundary slip in aqueous systems is favored by hydrophobic surfaces [3,8,20–22,28] as the attractive forces between the liquid and the solid are less than for hydrophilic surfaces and consequently the liquid-solid friction is decreased. Experimental evidence

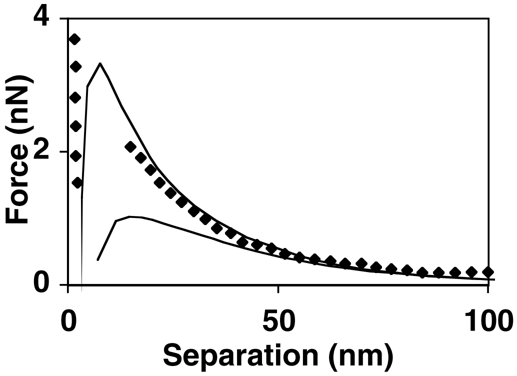

FIG. 7. Measurement of the typical equilibrium forces present in the system. The surface forces (diamonds), measured at low approach velocity in a 46% sucrose solution w/w, viscosity 10.2 mPa s, are fitted using the DLVO theory, for both the constant charge (upper curve) and constant potential (lower curve) boundary conditions.

for a relationship between surface properties and slippage exists [16], particularly in non-Newtonian systems [29]. Surface roughness may also play a role in boundary slip [30]. It has been predicted to both increase [31] the degree of slip and to decrease it [32]. Our system is ideally suited to examine boundary slip as a function of surface hydrophobicity and surface roughness. These studies are now being pursued.

The relationship between the slip length and the approach velocity of the surfaces determines the type of systems that will exhibit boundary slip. "Free" systems, such as a sphere approaching a wall under the action of a negative buoyancy force [33,34] or the approach of two colloidal particles, are unlikely to exhibit boundary slip as the drainage force acts to reduce the relative velocity of the surfaces considerably as the surface separation decreases. We have shown that low relative velocities will not result in boundary slip. Alternatively, "driven" systems, where the approach rate of the surfaces remains high at small separations, are more likely to exhibit slip. Generally, most unconfined systems are more likely to be free, and this may explain why boundary slip has not been previously revealed in studies of the bulk behavior of colloidal systems. Many systems can be described where boundary slip is likely to occur and the effects are important. For example our results suggest that red blood cells squeeze through narrow capillaries more easily and induce less shear stress on capillary walls due to boundary slip. An understanding of the role of wetting, surface roughness, and wearless friction in determining the degree of boundary slip has important consequences for the design of machines on the micro- to nanoscale.

In conclusion, hydrodynamic forces generated in an aqueous Newtonian fluid have been directly measured, revealing that partial boundary slip is occurring. The degree of slip is described by the magnitude of the slip length, and it is found to be a function of both surface approach velocity and fluid viscosity.

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