Slippery questions about complex fluids flowing past solids

Viscous flow is familiar and useful, yet the underlying physics is surprisingly subtle and complex. Recent experiments and simulations show that the textbook assumption of 'no slip at the boundary' can fail greatly when walls are sufficiently smooth. The reasons for this seem to involve materials chemistry interactions that can be controlled — especially wettability and the presence of trace impurities, even of dissolved gases. To discover what boundary condition is appropriate for solving continuum equations requires investigation of microscopic particulars. Here, we draw attention to unresolved topics of investigation and to the potential to capitalize on 'slip at the wall' for purposes of materials engineering.

STEVE GRANICK*, YINGXI ZHU AND HYUNJUNG LEE

Department of Materials Science and Engineering, Chemistry and Physics, University of Illinois, Urbana, Illinois 61801 USA.
***e-mail: sgranick@uiuc.edu**

I wear eyeglasses (you may too) and blow on them when they are dusty. The large dust particles blow off easily but the small particles do not. But why not? This familiar occurrence illustrates the no-slip boundary condition of fluid flow past a solid surface, which states that flowing fluid (air, in this example) comes to rest just at the point where it meets the solid surface. There is no relative motion of the fluid to the impenetrable boundary that it flows past; molecules at the boundary move on average with the same velocity as that boundary, and is therefore zero at a solid (the normal velocity component is also zero but physically trivial). We therefore realize that small dust particles do not extend far enough beyond an adsorbing surface to experience a large enough airflow to be blown off. Schematically, this is illustrated in Fig. 1.

The same situation arises elsewhere in everyday life. When we take a shower, wash our hands, wash dishes… it's difficult to wash soap off simply by rinsing. To remove soap from the surfaces on which it sits, it's much more effective to scrub with a washcloth. A less mundane example is the energy lost to pump fluids. One hardly questions that a jet of fluid flows through air almost without frictional loss but that this is impossible for flow through a pipe. Why? Why, as we age, does fatty detritus tend to accumulate on our arteries?

This is a core concept in fluid mechanics — 'no slip at the wall'. It forms the basis of our understanding of the flow of simple low-viscosity fluids and comprises a springboard for much sophisticated calculation. Although it is true that at some level of detail this continuum description must fail and demand description at the molecular level, it is tremendously successful as the basis for continuum-based calculations. As expressed in a prominent fluid dynamics textbook[1]:

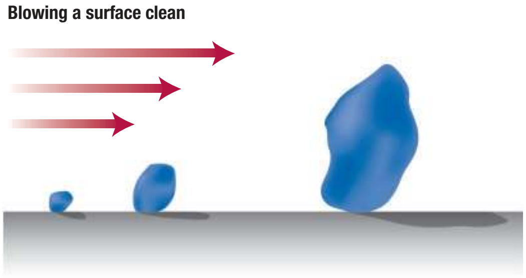

Figure 1 Blowing a surface clean of dust particles. The large particles are removed easily but very small particles cling tenaciously. They cannot be blown off because the speed of moving air, denoted by length of the arrows, comes to zero at the surface.

> In other words there is no relative motion between the fluid and the solid. This fact may seem surprising but it is undoubtedly true. No matter how smooth the solid surface or how small the viscosity of the fluid, the particles immediately adjacent to the surface do not move relative to it. It is perhaps not without interest that Newton's term for viscosity was 'defectus lubricitatis' - 'lack of slipperiness'. Even for a fluid that does not 'wet' the surface this rule is not violated.

Is it necessarily so? These issues were controversial for centuries to those who developed the foundations of fluid mechanics[2,3]. The compelling rational arguments — for and against — were decided by the pragmatic observation that predictions agreed with experiments. The possibility of slip was discussed in mainstream literature only in the context of the flow of polymer melts[4–6], although over the years persistent doubts were expressed[2,3,7–9]. But experimental capability and technical needs have changed — especially so with the emerging interest in microfluidics and MEMS (micro-electromechanical system)-based devices.

The situation has changed but the enormous and enduring success of the no-slip assumption for modelling must be emphasized. It works beautifully

Flow over walls of variable roughness

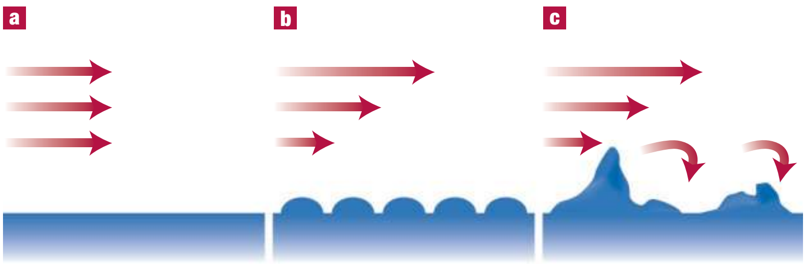

Figure 2 Surface roughness promotes stick. This figure compares flow past **a**, an absolutely smooth wall; **b**, a wall with corrugation at the atomic level in the surface potential such that fluid molecules are preferentially attracted to particular sites on the surface; and **c**, a surface whose roughness, larger than the molecules of fluid, creates irregularities of near-surface fluid flow. In **a**, nothing pins the fluid to the wall. In **b**, the fluid is pinned to the wall by corrugation of the wall potential, except if the fluid–fluid cohesive forces exceed the fluid–wall attraction. In **c**, the fluid is pinned to the wall by flow irregularities, even if the fluid wets the wall only partially. Velocity of the moving fluid is indicated by the length of the arrows. Although the sketches in this figure show topographical irregularity, different chemical make-up can also produce wall irregularity.

provided that certain assumptions are met: a single-component fluid, a wetted surface, and low levels of shear stress. Then careful experiments imply that the fluid comes to rest within 1–2 molecular diameters of the surface[10–12]. But the necessary assumptions are more restrictive, and their applicability is more susceptible to intentional control, than is widely appreciated.

THE ENDURING EXCEPTIONS

Widely appreciated by practitioners, exceptions to the central dogma have made their way too little into the textbooks, but are documented abundantly in the engineering literature. In some situations, engineers work hard to prevent exceptions when they deal with suspensions in fluids — they routinely roughen the surfaces of their test instruments and verify that their measurements do not depend on the sample thickness[13]. In other instances, engineers take advantage of exceptions to reduce viscous drag — as in the flow of suspensions, foodstuffs and emulsions[14] or the addition of so-called processing aids to facilitate the flow of plastics through moulds[15]. These commonplace aspects of wall slip are not widely enough appreciated outside a small community of engineers. They are endemic when the fluid has more than one component and one of them has lower viscosity than others, as may happen when non-adsorbing polymers are dissolved in fluids of lower viscosity.

Exceptions in cases of partial wetting — for example, the flow of water past hydrophobic walls — have been occasionally reported for many years[2,3,7–9]. These reports seem never to have been widely considered trustworthy, but the idea behind these observations has been put on a firm quantitative basis (see below).

Finally, there is the 'weak link' argument that whenever the rate of flow is sufficiently strong, something must break down. If a fluid is sheared at some rate, a force will resist this. If the shear rate is raised by a factor of (say) ten, the resisting force will rise by the same amount. This cannot continue without limit because if so, eventually the fluid would sustain forces larger than can be withstood by even the strongest material. Something must give, either at the wall ('slip') or within the fluid itself.

This review will not consider all exceptions to the no-slip boundary condition. Beyond the cases discussed here, these include viscous polymers[4–6], gas flowing past solids whose spacing is less than a few mean-free paths[16], superfluid helium, and contact lines when liquid droplets move on solids. Recently much interest has also been given to slip in sheared films of molecularly thin simple liquids, but those interesting anomalies disappear for films thicker than 5–10 molecular dimensions[17], and therefore are relevant mainly to friction.

THE MECHANISMS THAT CONTROL SLIP IN LOW-VISCOSITY FLUIDS

Partial slip of so-called newtonian fluids, such as alkanes and water, is predicted by an increasing number of computer simulations[18–23] and, in the laboratory when forces are measured, systematic deviations from the predictions based on no-slip are found[24–34]. Some sense of urgency comes from potential practical applications. Typical magnitudes of the slip length reported in the literature are submicrometre, so small that the practical consequence of slip would be minimal for flow in channels whose size is macroscopic. But if the channel size is very small, the potential ramifications in microchannels and nanochannels are major.

The simulations must be believed because they are buttressed by direct measurements. In the past, all laboratory reports of slip were based on comparing mechanical measurements of force to fluid mechanics models, and hence were indirect inferences. Optical methods have been introduced to measure fluid velocity directly. For example, Léger and co-workers photobleached tracer fluorescent dyes, and from the time rate of fluorescence recovery — measured in attenuated total reflection to focus on the region within an optical wavelength of the surface — the velocity of

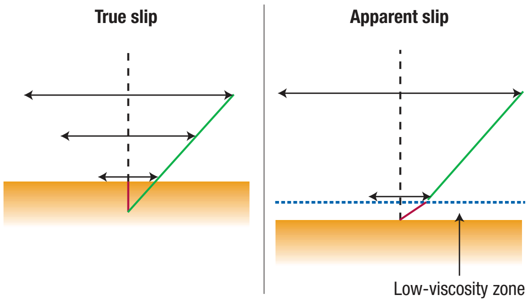

Figure 3 Slip of fluid past a surface can be apparent or real. This figure distinguishes between true slip (left) and apparent slip (right) in oscillatory flow. In both cases the velocity of the moving fluid extrapolates to zero at a notional distance inside the wall and is finite where it crosses the wall. For true slip, this is literally so. It may also happen that a low-viscosity component in the fluid facilitates flow because it segregates near the surface. The velocity gradient is then larger nearest the surface because the viscosity is smaller. When specific real systems are investigated, structural and chemical materials analysis at the microscopic scale are needed to distinguish between these possibilities. The blue dashed line shows the boundary between the majority fluid and a near-surface zone of exceptionally low viscosity. The speed of the fluid, denoted by the length of arrows, seems to extrapolate to zero below the surface (green line) but in fact does not (red line).

flow near the surface was inferred[26]. They reported slip of hexadecane near an oleophobic surface provided that it was smooth, but not when it was rough. Tretheway and Meinhart used laser particle image velocimetry of tracer latex particles to infer the velocity of water flow in microchannels[34] — they reported slip when the surface was hydrophobic but no-slip when it was hydrophilic. Callahan and co-workers demonstrated the feasibility of using NMR velocity imaging, though this method has been used to date only for multicomponent fluids[35].

An important hint about mechanism comes from the repeated observation that the amount of slip depends on the flow rate, in measurements using not only the surface force apparatus[28–31] but also atomic force microscopy[27,32]. The main idea of all of these experiments is that two solids of mean radius of curvature R, at spacing D, experience a hydrodynamic force $F_{\rm H}$ as they approach one another (or retreat from one another) in a liquid medium, thereby squeezing fluid out of (or into) the intervening gap. This force $F_{\rm H}$ is proportional to the rate at which spacing changes, $\mathrm{d}D/\mathrm{d}t$ (where t denotes time), is proportional to the viscosity, (η, assumed to be constant), and is 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[3]:

$$F_{\rm H} = f^{*}\,\frac{6\pi R^2\eta}{D}\cdot\frac{\mathrm{d}D}{\mathrm{d}t} \qquad (1)$$

The deviation of the dimensionless number f^{*} from unity quantifies the deviation from the classical no-slip prediction. The classical prediction is analogous when the surface spacing is vibrated. In that case a sinusoidal oscillatory drive generates an oscillatory hydrodynamic force whose peak we denote as $F_{\rm H,peak}$. The peak velocity of vibration is $v_{\rm peak} = d\omega$ where d is vibration amplitude and ω the radian frequency of vibration. Studies show that when the frequency and amplitude of oscillatory flow are varied, results depend on their product, $v_{\rm peak}$, and that deviations from equation (1) depend on $v_{\rm peak}/D$.

Box 1

WHY DOES THE CENTRAL DOGMA WORK SO WELL?

For many years it was observed that the no-slip boundary condition is not intuitively obvious. A pantheon of great scientists — among them, Bernoulli, Coulomb, Navier, Poisson, Stokes, Taylor, Debye, de Gennes — has worried about it. It has seemed doubtful to so many of them[2,3,7] that one must inquire why it appears to work so well. There are two answers.

In a general sense one may argue from the fact that fluid molecules are stuck to walls by intermolecular forces. Because nature abhors a discontinuity, these molecules move with the same velocity as the wall, and molecules nearby with nearly the same velocity, and so forth. Of course this is not absolutely true; individual molecules hop on and off the wall by brownian motion at rates much more rapid than the rate of fluid flow. It is so statistically[21], just as the surface of a glass of water is well defined in spite of the heavy, rapid traffic of molecules between surface and bulk air above it. But this explanation is not entirely satisfying because it might happen that cohesive forces between the fluid and solid are weaker than within the bulk fluid; this would be so if the contact angle were large enough. Then the main issue would be whether the fluid molecules attract the surface or the fluid more strongly[2,3,18–20,25–31,33,34].

Furthermore, what about fluid that contains more than a single component such that the components might not be evenly distributed between the bulk and the wall region? This is so for many engineering fluids (foodstuffs, plastics, suspensions of particles in fluids…). Why then does the no-slip boundary condition hold so generally?

The second school of microscopic explanation argues that because most surfaces are rough, the viscous dissipation as fluid flows past surface irregularities brings it to rest, regardless of how weakly or strongly molecules are attracted to the surface[29,36–38]. In this view, slip would occur at featureless walls. Molecular dynamics simulations confirm slip past surfaces that lack any lateral corrugation of the potential of interaction with the fluid; the fluid glides like a skater over ice, but this situation is hypothetical. In a real world, the argument goes, the surface pins the flowing liquid. Realistic walls do possess structure and those points of localized preferential attachment produce stick. Schematic diagrams of the effects of topographical irregularity on fluid flow, resulting in pinning to the surface, are sketched in Fig. 2. In fact, the irregularity may also be chemical.

The roughness argument explains convincingly the ubiquitous success of the no-slip boundary condition central dogma in so many engineering situations: rough walls, single-component fluids. Its Achilles heel is to leave open the question of how much wall roughness is enough to matter.

HOW TO QUANTIFY SLIP

The formal idea of a slip length is common. Slip signifies that in the continuum model of flow, the fluid velocity at the surface is finite (the slip velocity, $v_{\rm s}$) and increases linearly with distance normal to it. The slip velocity is assumed to be proportional to the shear stress at the surface, $\sigma_{\rm s}$:

$$\eta v_{\rm s} \equiv b\,\sigma_{\rm s} \qquad (2)$$

where η is viscosity and b, the slip length, is the notional distance inside the surface at which the velocity equals zero, if the velocity profile is extrapolated inside the surface until it reaches zero. Fig. 3 illustrates the distinction schematically. In much of the literature, the slip length has been assumed to be a constant that characterizes the material response of a given fluid–surface pair, but evidence of additional dependence on velocity is discussed below.

It is unreasonable to expect this continuum description to yield microscopic information. One example of this was already given — the appearance of no-slip when the microscopic reason is that flow irregularities pin the fluid to the wall (see Fig. 2)[29,36–38]. Another example is apparent slip when a low-viscosity component in the fluid facilitates flow because it segregates near the surface[14,15]. When conventional continuum mechanics contends with situations that are more complex than the model allows, one should resist the temptation to interpret literally the parameters in which the continuum mechanics model is couched. These examples emphasize instances where the notions of stick and slip are numerical conveniences not to be interpreted literally in terms of molecular mechanism. The appearance of slip owing to surface segregation of a low-viscosity component is illustrated in Fig. 3.

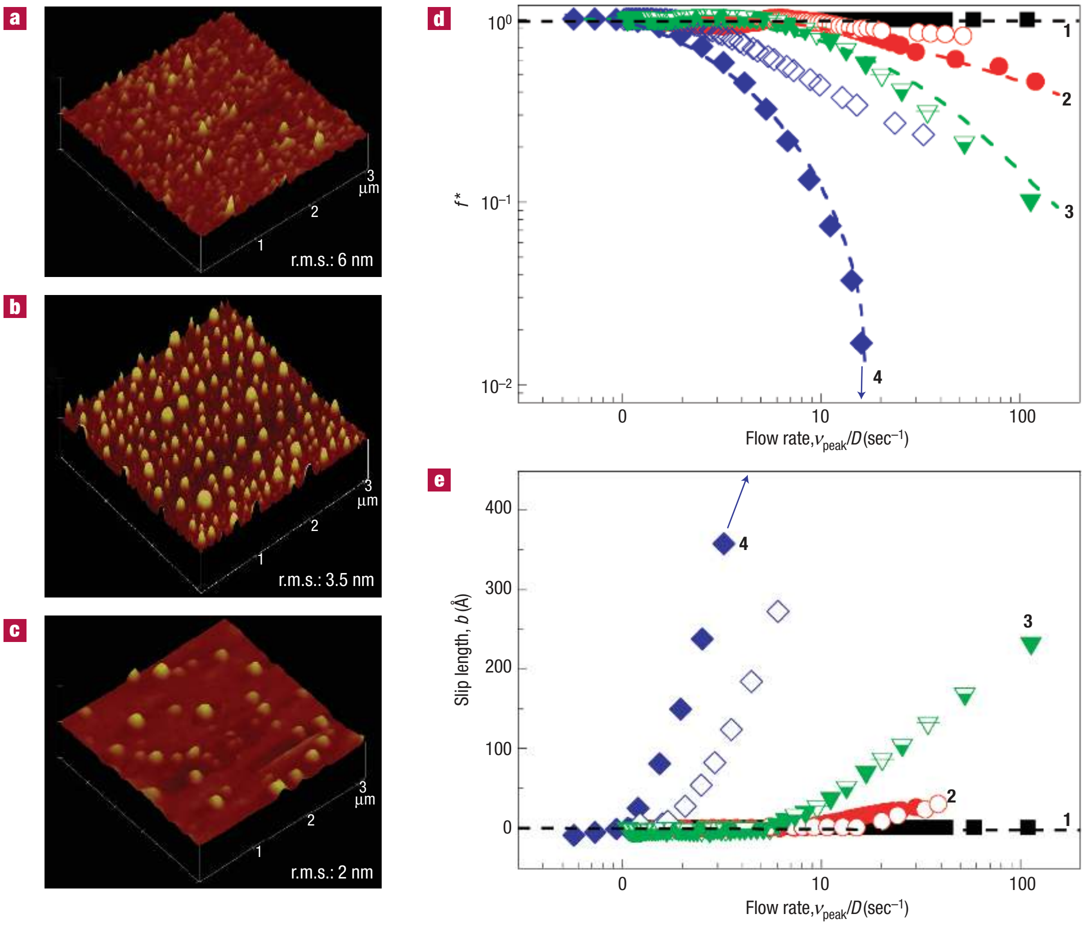

Figure 4 Influence of wall roughness on flow past partially wetted surfaces. **a–c**, Atomic force microscope images in which the roughness was varied to the indicated root-mean-square (r.m.s.) level as described previously[29]. Each image concerns an area 3 µm × 3 µm. **d**, **e**, show, as a function of logarithmic flow rate, v_{peak}/D, f^* (**d**; f^* is defined in equation (1)) and the equivalent slip length (**e**), for deionized water (filled symbols) and tetradecane (open symbols) between surfaces of different levels of r.m.s. surface roughness, specifically: 6 nm (case 1; squares), 3.5 nm (case 2; circles), 2 nm (case 3; triangles), atomically smooth (case 4; diamonds). The data were taken at different amplitudes in the range 0.3–1.5 nm and frequencies in the range 6.3–250 rad-sec^{-1}; not all data points are shown. To illustrate the successful collapse of data taken at different frequencies, case 3 for water distinguishes data taken at 6.3 rad-sec^{-1} (crossed triangles) and 31 rad-sec^{-1} (semi-filled triangles). Adapted from ref. 29.

This ratio, the flow rate, is the ratio is suggested by the form of equation (1).

PARTIALLY WETTED SURFACES WITH VARIABLE ROUGHNESS

According to equation (1), the 'stick' prediction is $f^* = 1$. One observes in Fig. 4 that deviations from this prediction decreased systematically as surface roughness increased. In addition, deviations from the predictions of the no-slip boundary condition are alternatively often represented as the slip length discussed in Box 1 ('How to quantify slip?'), the imagined distance inside the solid at which the no-slip flow boundary condition would hold; the equivalent representation of this data in terms of the slip length is included in Fig. 4. It had been known that a very large amount of roughness is sufficient to generate no-slip[36–38], however, an experimental study in which roughness was varied systematically[29] succeeded in quantifying how much roughness was needed in a real system. The critical level of 6 nm considerably exceeded the size of the fluid molecules.

Observation of rate-dependent slip suggests that fluid is pinned up to some critical shear stress, beyond which it slips. However, some laboratories report slip regardless of flow rate[24–26,33]. Perhaps, as Hugh Spikes (Imperial College, London) has suggested, the essential difference is that the magnitude of shear stress is larger in the latter experiments, such that the critical shear stress was exceeded over all of the flow rates that were studied[39]. In cases where slip is rate-dependent, this affords a potential strategy by which to effect purposeful mixing in a microfluidic device. The idea would be to simply make some patches on the surface hydrophobic and other patches hydrophilic, so that when flow was slow enough it would be smooth, but when it was fast enough, mixing would result from jerkiness at the hydrophobic patches.

Although it is true that slip at smooth surfaces is predicted based on computer simulations[18–23], the shear rate of molecular dynamics simulations so much exceeds shear rate in those laboratory experiments that the direct connection to experiment is not evident. To quantify the influence of surface roughness, Fig. 5 shows the limit up to which predictions based on the classical no-slip boundary condition still describe the data in Fig. 4. Because the no-slip boundary condition still holds in this situation, it was valid[29] to calculate the shear rate and shear stress by known equations. The data show that deviations from the no-slip prediction began at very low levels of hydrodynamic stress — of the order of only 1 to 10 Pa. Beyond this point, in some sense the moving fluid was depinned from the surface. (Note that the calculation of peak shear stress at the onset of apparent slip was erroneous in the original publication[29] and should read as given in the caption of Fig. 5 here, though the qualitative conclusion is not affected. We are grateful to Hugh Spikes, Imperial College, London, for pointing this out.)

Slip need not necessarily be predicated on having surfaces coated with self-assembled monolayers to render them partially wetted, though this was the case in most of the studies cited so far. The no-slip boundary condition switches to partial slip when the fluid contains a small amount of adsorbing surfactant[25,31].

DISSOLVED GAS MODULATES SLIP

When experimental observations deviate from expectations based on the no-slip boundary condition, there are at least two alternative scenarios of microscopic interpretation. The first would not be realistic; for newtonian fluids, it is not reasonable physically to suppose that the fluid viscosity changes. Why then do experimental data seem to undergo shear thinning with increasing values of the ratio v_{peak}/D, if it is unreasonable to suppose that the viscosity really diminished? Inspection shows that the data for smooth surfaces at high flow rates are consistent with a two-layer-fluid model in which a layer <1 nm thick, but with viscosity 10–20 times less than the bulk fluid, adjoins each solid surface[28]. A possible mechanism to explain the genesis of this layer was discussed by Vinogradova[3] and recently formalized by de Gennes[40], who conjectured that shear may induce nucleation of vapour bubbles; once the nucleation barrier is exceeded the bubbles grow to cover the surface, and flow of liquid is over this thin gas film rather the solid surface itself. Indeed, it is likely that incomplete air removal from the solid surfaces can profoundly influence findings in these situations where surface roughness is so low. It is identified by recent research as a likely source of the miss-named 'long-range hydrophobic attraction'[41,42]. Gases also appear to influence the sedimentation rate of small particles in liquid[43].

Accordingly, this laboratory has performed experiments in which the surface force apparatus was used to measure hydrodynamic forces of newtonian fluids that had been purged with various gases. It emerges that dissolved gas strongly influences hydrodynamic forces, in spite of the fact that gas solubility is low.

Figure 6a illustrates experiments in which a simple non-polar fluid (tetradecane) was placed between a wetted mica surface on one side, and a partially wetted methyl-terminated surface on the other, using methods described in detail elsewhere[29]. The surface–surface spacing of 10–100 nm substantially exceeded the size of the fluid molecules, therefore the fluid responded as a continuum. The spacings were vibrated with small amplitude and the magnitude of hydrodynamic force was measured as a function of the ratio v_{peak}/D suggested by equation (1). The experiments showed that whereas textbook no-slip behaviour[2] was obeyed when the tetradecane had been saturated with carbon dioxide gas, massive deviations from this prediction were found when the tetradecane was saturated with argon. This makes it seem likely that argon segregated to the solid walls, creating a low-viscosity boundary layer, in this way greasing the flow of fluid past that surface. Presumably, the amount of segregation is a materials property of the fluid, the chemical makeup of the surface, and the chemical identity of the dissolved gas. In this example, the fact that argon possesses low solubility in tetradecane may have made it more prone to segregate to the surfaces.

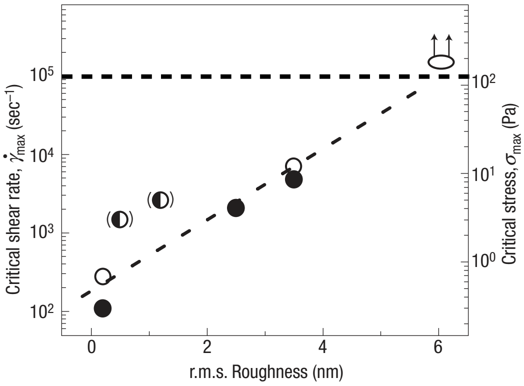

Figure 5 Illustration that deviations from the traditional no-slip boundary condition depend systematically on surface roughness. Here the critical shear rate for onset of slip (left ordinate) and critical shear stress (right ordinate) are plotted semilogarithmically against r.m.s. surface roughness for flow of deionized water (solid symbols) and tetradecane (open symbols and semi-filled symbols as identified in ref. 29). The two semi-filled data in parentheses show the asymmetric situation of partially wetted surfaces with r.m.s. roughness 0.5 nm and 1.2 nm on one side and smooth wetted mica surface on the other (as discussed in ref. 29). The line through the data is a guide to the eye. Maximum shear rate and shear stress on the surfaces were calculated using known relations based on continuum hydrodynamics from ref. 3. Specifically,

$$\dot{\gamma}_{max} = A \cdot \sqrt{\frac{R}{D} \cdot \frac{\upsilon_{peak}}{D}} \qquad (3)$$

and $\sigma_{peak} = 1.378 \eta R^{1/2} v_{peak}/D^{3/2}$. The datum with arrows (top right) is above the experimental resolution (dashed horizontal line) and represents a lower bound; the arrows indicate that the actual value may be even larger. Figure adapted from ref. 29.

Indeed, it has been suggested[44] that when a solid wall is hydrophobic and immersed in water, thermodynamics may assist forming a vapour phase near the wall. Recent thin-film shear force measurements support this idea[45].

We remark parenthetically that gas at a surface need not take the form of bubbles; that idea would be inconsistent with the enhanced solubility that is expected according to the Kelvin equation when the radius of curvature is very small. It is more likely that it is a subtler effect. Segregation of gas to the near-surface region seems to facilitate some kind of low-density surface excitations, but their nature is not well understood at this time.

SLIP PAST WETTED SURFACES

The influence of dissolved gas (discussed above) casts doubt on a traditional assumption of work in this field, which is that slip arises because fluid–fluid intermolecular interactions are stronger than those between fluid and surface, that is, that the surface must be wetted only partially. For several years, there have been prominent counterexamples, showing 'slip' past wetted surfaces[26,32]. Recent experiments from this laboratory have quantified that dissolved gases can mediate apparent slip even for solid surfaces that are fully wetted by the flowing fluid, provided that the wetted surfaces are sufficiently smooth.

To illustrate this, Fig. 6b summarizes experiments in which deionized water was placed between wetted surfaces of mica and the surface–surface spacing of 10–100 nm was vibrated with small amplitude in the manner described previously[28–31]. On log–log scales, hydrodynamic force is plotted against the ratio, v_{peak}/D. It is obvious that the prediction based on equation (1), a straight line on the log–log plot with a slope of unity, was violated systematically when the hydrodynamic force reached a critical level. An intriguing point is that initial findings were at first found to be irreproducible (they varied within the range marked by the hatched lines in the graph) but became reproducible when the water was first deliberately saturated with gas.

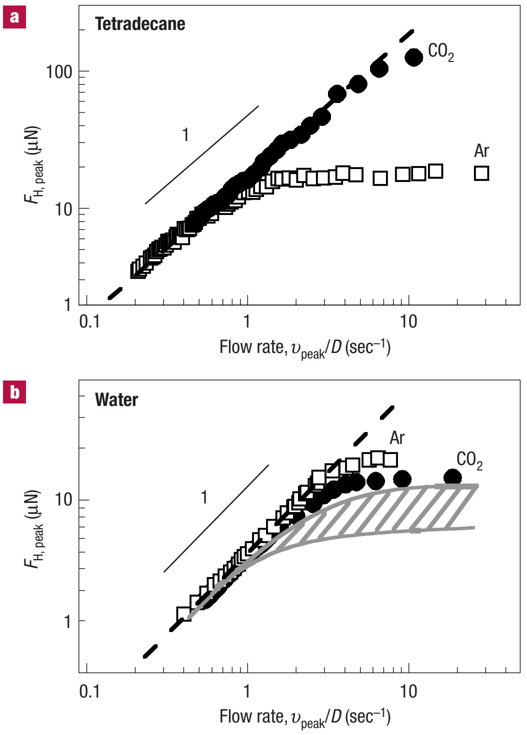

Figure 6 Illustration that the onset of 'slip' depends on dissolved gas, when simple newtonian fluids flow past atomically smooth surfaces, either wetted or partially wetted. On log–log scales, the hydrodynamic force $F_{H,peak}$ is plotted against reduced flow rate, v_{peak}/D such that a straight line of slope unity would indicate 'no-slip' assumed by equation (1). The fluid was saturated with carbon dioxide (filled symbols) or argon (open symbols). The vibration frequency was 9 Hz; other experiments at larger v/D (not shown), performed at similar D but higher frequency, verified saturation of hydrodynamic force. **a**, Tetradecane flowing between the asymmetric case of a wetted mica surface on one side, a partially wetted surface of methyl-terminated self-assembled monolayer on the other side, prepared as described elsewhere[29]. **b**, Deionized water flowing between mica surfaces that are wetted by this fluid. The hatched region of the graph shows the range of irreproducible results obtained using deionized water such that gases dissolved in the water were not controlled.

One observes that water saturated with argon seemed to 'slip' at a slightly higher level of shear stress than water saturated with carbon dioxide, and that in both cases the limiting hydrodynamic force was larger than when the nature of the dissolved gas was not controlled.

This rich and complex sensitivity to detailed materials chemistry of the system disappears when surfaces are so rough that the 'stick' boundary condition is produced trivially by the influence of surface roughness[29,36–38]. Therefore for scientific and practical reasons alike, these issues of flow past nearly smooth surfaces comprise fertile ground for future work.

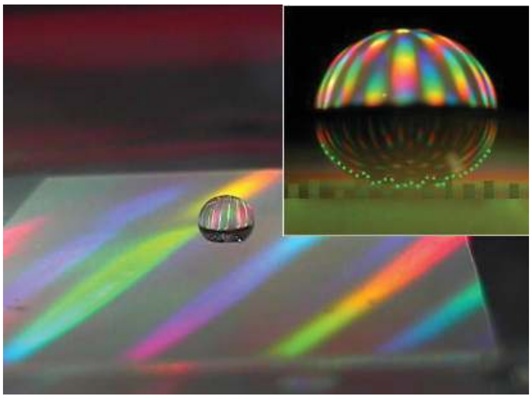

Figure 7 Illustration of what happens when contact of a water droplet with a solid surface is minimized by making the surface very rough. The rough surface traps pockets of air between the drop and the surface, resulting in a 'pearl drop' with an unusually large contact angle approaching 180°. Viscous friction is expected to be unusually small when water flows past such a surface[49].

Photo courtesy of Aurélie Lafuma and David Quéré, Collège de France, Paris.

THE PURPOSEFUL GENERATION OF SLIP

Inspired by these ideas to design new engineering structures, one might strive to 'grease' the flow of liquids past solid surfaces by altering the boundary condition. One strategy is to make the surfaces ultra-smooth[28,29]. Another (mentioned already) is to add processing aids that segregate to the surface[15,25,31]. A third way is to purposefully use multicomponent fluids to generate concentration gradients and differential wetting to generate slip, as can occur even if there is no velocity gradient in the fluid[23]. These methods could potentially be used in nanomotors or nanopumps.

Alternatively, one may seek to maximize contact with air, which is exceedingly solvophobic. Readers will have noticed that water ubiquitously forms beads on the leaves of plants. Some plants can display a contact angle that approaches 180°, even though water at a smooth surface of the same chemical make-up as the leaf displays a much lower contact angle. A recent series of experiments from the Kao Corporation in Japan provided insight into why[46] — the surfaces are rough on many length scales[47,48] and trap air beneath them. Readers will have noticed that if one tilts a leaf, a drop of water on it rolls smoothly; this is because it rides mainly on a cushion of air. This, the Lotus Leaf effect, is illustrated in Fig. 7. It is the principle of an ingenious method introduced recently to lower the viscous drag when fluids are caused to flow through pipes whose diameter is macroscopic[49]. Of course, given a long enough period of time, it is likely that the trapped gas would dissolve into the flowing fluid, but perhaps this effect could be enhanced by placing air nozzles along the walls of the tube and replenishing the trapped gas with a stream of inlet air.

A final method by which flow of a newtonian fluid past surfaces may be facilitated is to 'ciliate' the surfaces by coating with chain molecules — polymers, proteins or sugars. Experiments using a surface force apparatus suggest a similar (but less dramatic) rate-dependent slip in this case also[30]. This is possibly related to fluid flow in biological organs whose surfaces are also extensively ciliated, such as blood vessels and the kidney[50].

OUTLOOK

The textbook presentation of engineering fluid mechanics is often of a subject thoroughly understood, but recent experiments and simulations using smooth surfaces show behaviour that is richer and more complex than had been supposed. The correct boundary condition appears to depend on physical and chemical properties of the solid–liquid interface that are susceptible to rational control.

doi: 10.1038/nmat854

References

1. Massey, B. S. *Mechanics of Fluids* 6th edn Section 5.6 (Chapman and Hall, London 1989).
2. Goldstein, S. *Mechanics of Fluids* Vol. II 677–680 (Clarendon, Oxford, 1938).

3. Vinogradova, O. I. Slippage of water over hydrophobic surfaces. *Int. J. Miner. Process* **56,** 31–60 (1999).
4. Schowalter, W. R. The behavior of complex fluids at solid boundaries. *J. Non-Newton. Fluid* **29,** 25–36 (1988).
5. Léger, L., Raphael, E. & Hervet, H. Surface-anchored polymer chains: their role in adhesion and friction. *Adv. Polym. Sci.* **138,** 185–225 (1999).
6. Denn, M. M. Extrusion instabilities and wall slip. *Annu. Rev. Fluid Mech.* **33,** 265–287 (2001).
7. Debye, P. & Cleland, R. L. Flow of liquid hydrocarbons in porous Vycor. *J. Appl. Phys.* **30,** 843–49 (1958).
8. Ruckenstein, E. & Rajora, P. On the no-slip boundary condition of hydrodynamics. *J. Colloid Interface Sci.* **96,** 488–493 (1983).
9. Churaev, N. V., Sobolev, V. D. & Somov, A. N. Slippage of liquids over lyophobic solid surfaces. *J. Colloid Interface Sci.* **97,** 574–581 (1984).
10. Chan, D. Y. C. & Horn, R. G. The drainage of thin liquid films between solid surfaces. *J. Chem. Phys.* **83,** 5311–5324 (1985).
11. Israelachvili, J. N. Measurement of the viscosity of liquids in very thin films. *J. Colloid Interface Sci.* **110,** 263–271 (1986).
12. Georges, J. M., Millot, S., Loubet, J. L. & Tonck, A. Drainage of thin liquid-films between relatively smooth surfaces. *J. Chem. Phys.* **98,** 7345–7360 (1993).
13. Wein, O. & Tovchigrechko, V. V. Rotational viscometry under presence of apparent wall slip. *J. Rheol.* **36,** 821–843 (1992).
14. Barnes, H. A. A review of the slip (wall depletion) of polymer solutions, emulsions and particle suspensions in viscometers: its cause, character, and cure. *J. Non-Newton. Fluid* **56,** 221–251 (1995).
15. Achilleos, E. C., Georgiou, G. & Hatzikiriakos, S. G. Role of processing aids in the extrusion of molten polymers. *J. Vinyl Addit. Technol.* **8,** 7–24 (2002).
16. Noever, D. A. Diffusive slip and surface transport-properties. *J. Colloid Interface Sci.* **147,** 186–191 (1991).
17. Granick, S. Soft matter in a tight spot. *Phys. Today* **52,** 26–31 (1999).
18. Thompson, P. A. & Robbins, M. O. Shear flow near solids: epitaxial order and flow boundary condition. *Phys. Rev. A* **41,** 6830–6839 (1990).
19. Thompson, P. A. & Troian, S. A general boundary condition for liquid flow at solid surfaces. *Nature* **389,** 360–362 (1997).
20. Barrat, J.-L. & Bocquet, L. Large slip effect at a nonwetting fluid-solid interface. *Phys. Rev. Lett.* **82,** 4671–4674 (1999).
21. Brenner, H. & Ganesan, V. Molecular wall effects: are conditions at a boundary 'boundary conditions'? *Phys. Rev. E.* **61,** 6879–6897 (2000).
22. Gao, J., Luedtke, W. D. & Landman, U. Structures, solvation forces and shear of molecular films in a rough nano-confinement. *Tribol. Lett.* **9,** 3–134 (2000).
23. Denniston, C. & Robbins, M. O. Molecular and continuum boundary conditions for a miscible binary fluid. *Phys. Rev. Lett.* **87,** 178302 (2001).
24. Campbell, S. E., Luengo, G., Srdanov, V. I., Wudl, F. & Israelachvili, J. N. Very low viscosity at the solid-liquid interface induced by adsorbed C-60 monolayers. *Nature* **382,** 520–522 (1996).
25. Kiseleva, O. A., Sobolev, V. D. & Churaev, N. V. Slippage of the aqueous solutions of cetyltriimethylammonium bromide during flow in thin quartz capillaries. *Colloid J.* **61,** 263–264 (1999).
26. Pit, R., Hervet, H. & Léger, L. Direct experimental evidence of slip in hexadecane-solid interfaces. *Phys. Rev. Lett.* **85,** 980–983 (2000).
27. Craig, V. S. J., Neto, C. & Williams, D. R. M. Shear-dependent boundary slip in aqueous Newtonian liquid. *Phys. Rev. Lett.* **87,** 54504 (2001).
28. Zhu, Y. & Granick, S. Rate-dependent slip of Newtonian liquid at smooth surfaces. *Phys. Rev. Lett.* **87,** 096105 (2001).
29. Zhu, Y. & Granick, S. Limits of the hydrodynamic no-slip boundary condition. *Phys. Rev. Lett.* **88,** 106102 (2002).
30. Zhu, Y. & Granick, S. Apparent slip of Newtonian fluids past adsorbed polymer layers. *Macromolecules* **36,** 4658–4663 (2002).
31. Zhu, Y. & Granick, S. The no slip boundary condition switches to partial slip when the fluid contains surfactant. *Langmuir* **18,** 10058–10063 (2002).
32. Bonaccurso, E., Kappl, M. & Butt, H.-J. Hydrodynamic force measurements: boundary slip of water on hydrophilic surfaces and electrokinetic effects. *Phys. Rev. Lett.* **88,** 076103 (2002).
33. Baudry, J., Charlaix, E., Tonck, A. & Mazuyer, D. Experimental evidence of a large slip effect at a nonwetting fluid-solid interface. *Langmuir* **17,** 5232–5236 (2002).
34. Tretheway, D. C. & Meinhart, C. D. Apparent fluid slip at hydrophobic microchannel walls. *Phys. Fluids* **14,** L9–L12 (2002).
35. Britton, M. M. & Callaghan, P. T. Two-phase shear band structures at uniform stress. *Phys. Rev. Lett.* **78,** 4930–4933 (1997).
36. Nye, J. F. A calculation on the sliding of ice over a wavy surface using a Newtonian viscous approximation. *Proc. Roy. Soc. A* **311,** 445–467 (1969).
37. Richardson, S. On the no-slip boundary condition. *J. Fluid Mech.* **59,** 707–719 (1973).
38. Jansons, K. M. Determination of the macroscopic (partial) slip boundary condition for a viscous flow over a randomly rough surface with a perfect slip microscopic boundary condition *Phys. Fluids* **31,** 15–17 (1988).
39. Spikes, H. A. The half-wetted bearing. Part 2: potential application to low load contacts. *Proc. Inst. Mech. Eng. Part J* **217,** 15–26 (2003).
40. de Gennes, P.-G. On fluid/wall slippage. *Langmuir* **18,** 3413–3414 (2002).
41. Tyrrell, J. W. G. & Attard, P. Atomic force microscope images of nanobubbles on a hydrophobic surface and corresponding force-separation data. *Langmuir* **18,** 160–167 (2002).
42. Ishida, N., Inoue, T., Miyahara, N. & Higashitani, K. Nano bubbles on a hydrophobic surface in water observed by tapping-mode atomic force microscopy. *Langmuir* **16,** 6377–6380 (2000).
43. Boehnke, U. C. *et al.* Partial air wetting on solvophobic surfaces in polar liquids. *J. Colloid Interface Sci.* **211,** 243–251 (1999).
44. Lum, K., Chandler, D. & Weeks, J. D. Hydrophobicity at small and large length scales. *J. Phys. Chem. B* **103,** 4570–4577 (1999).
45. Zhang, X., Zhu, Y. & Granick, S. Hydrophobicity at a Janus interface. *Science* **295,** 663–666 (2002).
46. Onda, T., Shibuichi, S., Satoh, N. & Tsuji, K. Super-water-repellent fractal surfaces. *Langmuir* **12,** 2125–2127 (1996).
47. Bico, J., Marzolin, C. & Quéré, D. Pearl drops. *Europhys. Lett.* **47,** 220–226 (1999).
48. Herminghaus, S. Roughness-induced non-wetting. *Europhys. Lett.* **52,** 165–170 (2000).
49. Watanabe, K., Udagawa, Y. & Udagawa, H. Drag reduction of Newtonian fluid in a circular pipe with a highly water-repellent wall. *J. Fluid Mech.* **381,** 225–238 (1999).
50. Bechert, D. W., Bruse, M., Hage, W. & Meyer, R. Fluid mechanics of biological surfaces and their technological application. *Naturwissenschaften* **87,** 157–171 (2000).

Acknowledgements.

For discussions, we are indebted to John Brady, Michel Cloître, Jack Douglas, Steve Meeker, Hugh Spikes, Jan Vermant and Norman Wagner. This work was supported in part by a grant to H.L. by the postdoctoral fellowship program from Korea Science & Engineering Foundation (KOSEF). This work was supported by the U.S. Department of Energy, Division of Materials Science, under Award No. DEFG02-91ER45439 through the Frederick Seitz Materials Research Laboratory at the University of Illinois at Urbana-Champaign.
Correspondence and requests for materials should be addressed to S.G.

Competing financial interest

The authors declare that they have no competing financial interests.