

## Surface roughness and hydrodynamic boundary conditions

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We report results of investigations of a high-speed drainage of thin aqueous films squeezed between randomly nanorough surfaces. A significant decrease in the hydrodynamic resistance force as compared with that predicted by Taylor's equation is observed. However, this reduction in force does not represent the slippage. The measured force is exactly the same as that between equivalent smooth surfaces obeying no-slip boundary conditions, but located at the intermediate position between peaks and valleys of asperities. The shift in hydrodynamic thickness is shown to be independent of the separation and/or shear rate. Our results disagree with previous literature data reporting very large and shear-dependent boundary slip for similar systems.

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It has recently been well recognized that the classical no-slip boundary condition [1], which has been applied for more than a hundred years to model macroscopic experiments, is often not applicable at the submicro-, and especially, nanoscale. Although the no-slip assumption seems to be valid for molecularly smooth hydrophilic surfaces down to a contact [2–6], it is now clear that this is not so for the majority of other systems. The changes in hydrodynamic behavior are caused by an impact of interfacial phenomena, first of all hydrophobicity and roughness, on the flow. A corollary from this is that a theoretical description based on the no-slip condition has to be corrected even for simple liquids. What, however, still remains the subject of hot debate is how to correct the flow near the interface, and what would be the amplitude of these corrections.

The simplest and most popular way to model the flow is to use a slip-flow approximation [7], which assumes that the slip velocity at the solid wall is proportional to the shear stress, and the proportionality constant is the so-called slip length. Such an assumption was justified theoretically for smooth hydrophobic surfaces [8–10] and was confirmed by the recent surface force apparatus (SFA) [6,11] and the atomic force microscope (AFM) [5] dynamic force experiments. Despite some remaining controversies in the data and the amount of slip (cf. [12]), the concept of the hydrophobic slippage is now widely accepted.

For rough surfaces, a situation is much less clear both on the theoretical and on the experimental sides. One point of view is that roughness decreases the degree of slippage [12–14], unless the surface is highly hydrophobic, so that trapped nanobubbles are formed to accelerate the flow [15,16]. An opposite conclusion is that roughness generates extremely large slip [17].

We believe our paper entirely clarifies the situation with flow past rough surfaces, highlights reasons for existing controversies, and resolves apparent paradoxes.

We use a specially designed homemade AFM-related setup [18–20] to perform dynamic force experiments on a nanoscale (Fig. 1). Glass spheres of radius  $R \sim 20 \pm 2 \mu\text{m}$  (Duke Scientific, Palo Alto, CA) were attached with UV glue on the top of the rectangular tipless cantilevers (length  $L = 450 \mu\text{m}$ , width  $w = 52 \mu\text{m}$ , spring constants  $k \sim 0.22 \text{ N/m}$ ). The spheres were then coated with a gold layer (50 nm) using a layer of chromium (3 nm) to promote adhesion. For the planar substrate, we used silicon wafers coated with a gold layer (50 nm). Both surfaces were then treated with a 1 mM solution of 11-amino-undecane thiol ( $\text{SH}-(\text{CH}_2)_{11}-\text{NH}_2$ ) for 24 h to produce a chemically bound self-assembled monolayer (SAM). The advancing and receding water contact angle on the thiolated planar surfaces were measured with a commercial setup (Data Physics, Germany), and were found to be  $(69 \pm 1)^\circ$  and  $(63 \pm 1)^\circ$ , respectively. These values are close to those for the surfaces used in [21]. Imaging of thiolated surfaces with a regular AFM tip revealed the root-mean-square roughness over  $1 \times 1 \mu\text{m}^2$  is in the range 10–11 nm for a sphere and 0.5–0.8 nm for a plane. The maximum peak-to-valley difference is less than 45 nm for a sphere (Fig. 2) and less than 2.5 nm for a plane. This (nearly smooth against rough) geometry of configuration allows us to avoid large scatter in the data at separations of the order of or smaller than the roughness size. Such a scatter would be unavoidable for two rough surfaces (depending on whether the rough sphere is falling on a tip or in a valley of a rough plane). Cantilevers were then fixed in a

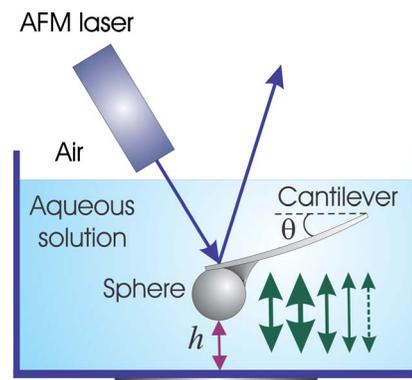


FIG. 1. (Color online) Schematic of the dynamic AFM force experiment.

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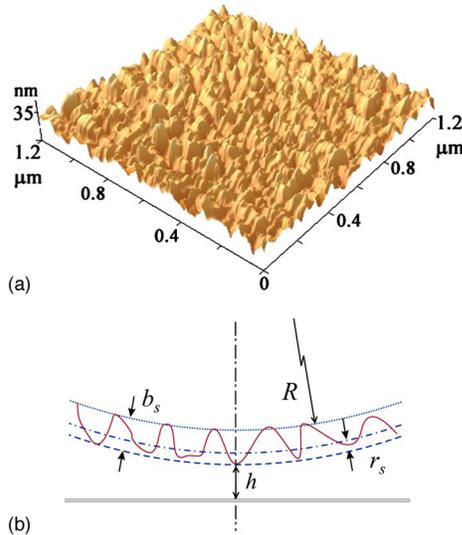


FIG. 2. (Color online) An AFM image of an apex of a gold-coated sphere (a) and a schematic of a rough sphere-plane interaction near the point of a contact (b).

holder with the variable tilt angle, and the intermediate position with the angle  $\theta=(10\pm 2)^\circ$  was chosen. A planar substrate was placed onto the bottom of a Teflon cuvette, which was filled with 1 mM NaCl (99.99%, Aldrich) aqueous solutions. Water for solutions was prepared using a commercial Milli-Q system containing ion-exchange and charcoal stages. The de-ionized water had a conductivity less than  $0.1 \times 10^{-6}$  S/m and was filtered at  $0.22 \mu\text{m}$ . To measure force-vs-position curves, the cuvette was moved toward the particle with a  $12 \mu\text{m}$  range piezoelectric translator (Physik Instrumente, Germany). This translator was equipped with integrated capacitance position sensors, which allows to avoid any creep and hysteresis and provided the position with an accuracy of 1 nm in the closed-loop operation. During the movement, the deflection of the cantilever was measured with an optical lever technique. Therefore, the light of a laser diode (1.5 mW, 670 nm) was focused onto the back of the gold-coated cantilever. After reflection by a mirror, the position of the reflected laser spot was measured with a position sensitive device (United Detectors, U.K., active area  $30 \times 30 \text{ mm}^2$ ). The total force was calculated by multiplying the instantaneous cantilever deflection with the spring constant. The distance  $h$  between surfaces was calculated by adding the piezodisplacement to the deflection of the cantilever, so that  $h=0$  corresponds to the contact [of the tips of the sphere's asperities with a plane] (see Fig. 1). We stress, that since our plane is smooth enough, we have no ambiguity in determining this zero of separation.

The AFM force balance incorporates both (concentrated) force on the sphere and the drag on the cantilever [5] (Fig. 1), so that the total force measured in the AFM dynamic experiment is

$$F_t = \frac{-1 + 3 \cos \theta}{2} (F_s + F_h) + F_c, \quad (1)$$

where  $F_s$  and  $F_h$  are the surface and hydrodynamic forces, respectively, acting on a sphere, and  $F_c$  is the force due to the distributed hydrodynamic drag on the cantilever.

The total force  $F_t$  is proportional to the instantaneous deflection of the end of the spring from its equilibrium position multiplied by the spring constant  $k$  [2]:

$$F_t = k[h - (h_0 + vt)], \quad (2)$$

where  $h_0$  is the initial separation between surfaces, and  $v$  is the driving speed of the piezodisplacement (negative speed corresponds to approach).

The hydrodynamic force  $F_h$  between a sphere and a plane can be written as [22]:

$$F_h = -\frac{6\pi\mu R^2}{h} \frac{dh}{dt} f^*, \quad (3)$$

where  $\mu$  is the dynamic viscosity and  $-dh/dt$  is the relative velocity of the surfaces. To finalize the description of  $F_h$ , we should define the expressions for a correction function  $f^*$ , which will be discussed later. Note that when  $f^*=1$ , Eq. (3) transforms to the famous G. I. Taylor's formula (which, however, never appeared in any of G. I. Taylor's publications as discussed in [23]).

The drag force on a cantilever  $F_c$  is given by [5]:

$$F_c = -\frac{v\mu L}{2} \left[ \left( \frac{w}{2R+h} \right)^3 \gamma^* + B \right] \quad (4)$$

with

$$\gamma^* = \gamma \left[ 1 - \frac{3\gamma}{2} + 3\gamma^2 - 3\gamma^3 \ln \left( 1 + \frac{1}{\gamma} \right) \right], \quad (5)$$

where  $\gamma=(2R+h)/(L \sin \theta)$ .  $B$  is a constant, which reflects the contribution from the Stokes flow to the cantilever deflection, and represents an adjustable (dimensionless) parameter to the model.

The surface force  $F_s$  is assumed to be unaffected by the relative motion of the surfaces, and was taken to be the equilibrium force being a function of only  $h$ . It was obtained from low-speed (below  $1 \mu\text{m/s}$ ) force measurements. At distances larger than 20–25 nm, no interaction was detected. In other words, no electrostatic contribution can be seen despite a relatively large (9.6 nm) Debye length in a 1 mM NaCl solution. This suggests that the surfaces are uncharged. Similar observations have been made before for other classes of thiols [24]. The range of the jump distance was always  $15 \pm 2$  nm. The contribution of contact deformation to the jump distance was estimated using the experimental values for the pull-off force  $0.70 \pm 0.05$  mN/m (with the correction to the hydrodynamic interaction) and the values of Young's modulus of the UV glue (3 GPa), as it was the softest material in our system. We also ignore the possible plastic flattening of the gold (50 GPa) asperities. For these parameters, the central displacement due to a contact deformation is of the order of 0.1 nm, so that it can safely be ignored. We have fitted the experimental results by assuming  $F_s = -AR/6h^2$ , taking the Hamaker constant,  $A$ , as an adjusting parameter. The value  $A=5.4 \times 10^{-20}$  J is obtained from fitting and was further used in all calculations.

Figure 3 shows the hydrodynamic resistance force calculated by subtracting  $F_s$  and  $F_c$  from the total force measured. Theoretical curves obtained by a numerical solution of differential Eq. (1) in the assumption  $f^*=1$  are also included.

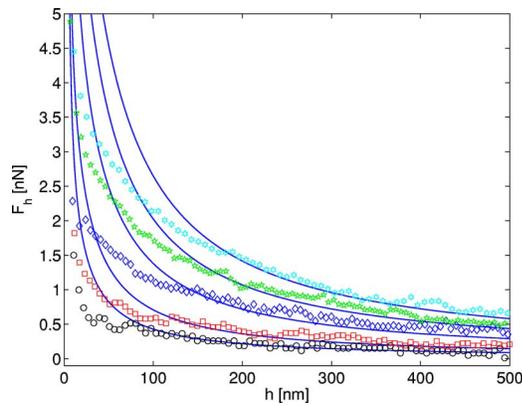


FIG. 3. (Color online) Hydrodynamic force acting on a sphere at a high speed of approach. Only each second point is shown. From bottom to top are data (symbols) obtained at the driving speed  $-6$ ,  $-10$ ,  $-20$ ,  $-30$ , and  $-40$   $\mu\text{m/s}$ . Solid curves show the calculation results obtained for the same speed, by assuming  $f^* = 1$ .

Note that cantilever contribution was found to be neither small nor negligible. The adjusting parameter  $B$  reflecting a Stokes-like flow on a cantilever was about 30–34 for our geometry of configuration and varied slightly from one experiment to another. Measured  $F_h$  is much smaller than predicted by Taylor's theory. The deviations from theory are clearly seen at distances 100–200 nm and depend on the driving speed. One can conclude, therefore, that there is a clear impact of roughness on the film drainage.

In Fig. 4, the hydrodynamic force measured at the driving speed  $-30$   $\mu\text{m/s}$  is compared with Taylor's equation (solid curves). The force is plotted vs the inverse of the surface separation. Note that even Taylor's equation does not result in a linear plot. This would be expected only at a constant approach velocity, which is not the case due to forces acting on the sphere. However these deviations from linearity, caused by a decrease of  $dh/dt$ , are much smaller than required to fit the experimental data. The general analytical solution for rough interfaces does not exist in the literature, probably since such a problem is outside the scope of a lubrication approximation. Below we analyze some approximate models.

We have calculated the force expected between smooth slippery surfaces. The slip length is assumed to be roughly equal to zero for a plane and to the height of asperities  $b_s$  (as defined in Fig. 2) for a sphere, which is close to its definition. In this case, the correction for slippage takes the form [22]:

$$f^* = \frac{1}{4} \left\{ 1 + \frac{3h}{2b_s} \left[ \left( 1 + \frac{h}{4b_s} \right) \ln \left( 1 + \frac{4b_s}{h} \right) - 1 \right] \right\}. \quad (6)$$

An improved fit to the data is obtained when slip is permitted (dashed curve in Fig. 4). For this speed of approach, the best fit to Eq. (6) was found with  $b_s = 48$  nm. Equation (6) provides an excellent fit at distances larger than  $\sim 100$  nm. However, since data still deviate from theoretical predictions at smaller separations, it is clear that slippage does not necessarily represent the roughness.

Therefore, we further assumed that stick boundary conditions remain valid, but are applied to a surface defined at a distance  $r_s$  toward a center of the sphere:

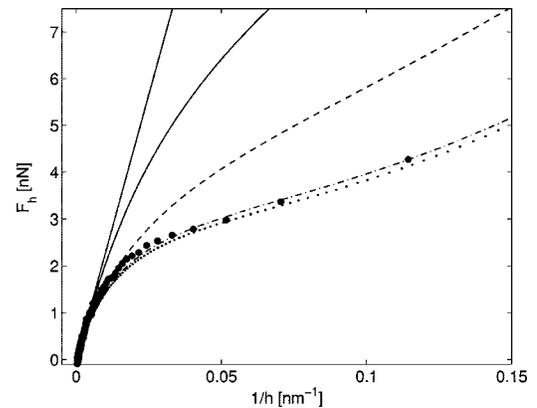


FIG. 4. Hydrodynamic force vs the inverse of separation obtained at the driving speed  $-30$   $\mu\text{m/s}$ . Symbols represent experimental data. Solid curves show the theoretical results obtained within Taylor's formula. Upper line shows the calculation results in the assumption of a constant speed of approach. Lower curve corresponds to the real approaching speed. Dashed curve is the calculation results within the model described by Eq. (6) with  $b_s = 48$  nm, and the dotted curve—by Eq. (7) with  $r_s = b_s = 48$  nm. The approximation (7) with  $r_s = 45$  nm provides the best fit to the data.

$$f^* = \frac{h}{h + r_s}. \quad (7)$$

By adjusting the value of  $r_s$ , we found that the hypothesis of a shift in separation gives a perfect coincidence between data and theoretical predictions (dash-dotted curve in Fig. 4, obtained with  $r_s = 45$  nm). We remark and stress that Eq. (7) provides an excellent description of the data even when  $h$  is much smaller than  $r_s$ . [Another point to note is that the values of  $r_s$  seem to be slightly larger than would be expected from the AFM imaging, which is likely connected with the fact that the AFM tip has a finite size and cannot go into grooves. This can also be due to some non-zero roughness of the plane ignored in our analysis.]

Thus, we conclude that the description of flow near the rough surfaces has to be corrected, but this is not the relaxation of no-slip boundary conditions, but the correction for separation with its shift to larger distances within the asperities size. (Remark, however, that in case of a single nanoasperity the model becomes more complicated [28]). It has to be stressed that similar ideas were justified theoretically at macroscale for a shear flow along a periodically corrugated wall [25] and recently for a far-field motion of a sphere toward such a wall [26]. They are also consistent with molecular-dynamic simulations on simple model systems [27]. We provided accurate experimental data showing that the concept can be applied for a randomly rough surface and at the nanoscale, down to a contact. Note that so far Eq. (7) has not received any theoretical justification for short, i.e., of the order of or smaller than the size of asperities, separations. This is probably because this situation escapes from the framework of the lubrication approximation, since two length scales of the problem become comparable. The applicability of Eq. (7) at the short distances probably reflects the fact that the height of the roughness elements is much smaller than the sphere radius, so that even when separation is getting small, the plane "sees" many roughness elements

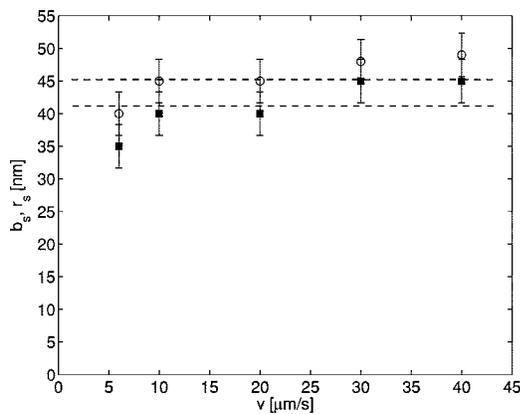


FIG. 5. A hydrodynamic height of asperities  $b_s$  (open circles) and a hydrodynamic shift  $r_s$  (filled squares) obtained at a different speed of approach.

at the same time and fluctuations are averaged out. This hypothesis remains the subject for further theoretical work.

This conclusion remains valid for all driving speeds, and results are summarized in Fig. 5. One can see that  $r_s$  remains roughly the same at all speeds, although it shows some weak tendency to increase with the rate of approach. However, this increase is within the error of experimental data, so it remains an open question for future research. The same remarks are true for  $b_s$ , which is included for completeness since the slip model is applicable at large separations.

Note that our results clarify the reason for apparently contradictory reports suggesting that roughness increases [14] and decreases [17] the drag force. In our opinion, these different conclusions only reflect that in these papers, the wall location was defined differently. It follows from our results that if an equivalent smooth surface is defined as coinciding with the location of the valleys of asperities (which corresponds to experimental techniques used in [14]), the measured force is larger than expected for an equivalent surface (cf. dotted curve in Fig. 4). If, however, it is defined on the peaks of asperities (experimental techniques used in [17]), then the measured force is smaller (cf. dashed curve in Fig. 4). Clearly, both results [14,17] physically mean that roughness increases the dissipation in the system, and that an

equivalent surface is located at the intermediate position. Note that in [12], which reports the increase in force with roughness, the equivalent surface is also defined on the peaks of asperities. We do not have any explanation of this result.

Our data and conclusions do not confirm results obtained with similar, but “smooth” surfaces, where shear-rate-dependent slippage was detected [21]. In our opinion, the reduction in the hydrodynamic resistance force might indicate that their gold-coated thiolated sphere was in reality rougher than expected. Reasons for a shear dependency could probably be connected with some errors in the experimental determination of  $dh/dt$ , since the piezotranslator used in [21], and later in [17], is not suitable for highly dynamic force measurements due to its nonlinearity. Another reason for a significant rate dependence is the use of binary mixtures [21]. Clearly, both confinement and shear might lead to their stratification and a formation of a thin low viscosity lubricant layer [10]. It is well known and has been proven experimentally [23] that such a layer leads to rate-dependent phenomena (normally expected only at a very large shear rate [29]) even at a low speed. We suspect that this effect of the stratification of a binary mixture, enhanced by roughness, is responsible for a very large reduction in the force observed in [17]. Finally, we would like to stress that since the force balance represents a differential equation, even small  $F_c$  could implicate the results by decreasing  $dh/dt$ , and therefore,  $F_h$ . The similar remark concerns  $F_s$ , which cannot be excluded from analysis. Both  $F_s$  and  $F_c$  are not present in the force balance specified in [17,21], which might cause a further inaccuracy in their results.

In summary, by performing a high-speed drainage experiment with nanorough hydrophilic surfaces, we demonstrate that their interaction is similar to that between equivalent smooth surfaces located at some position between the peaks and valleys of asperities. Thus, our results are in favor of no-slip assumptions for a hydrophilic surface valid down to a contact.

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