Velocity Profiles of Water Flowing Past Solid Glass Surfaces Using Fluorescent Nanoparticles and Molecules as Velocity Probes

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Measurements of the velocity profile of water flowing on a glass surface using fluorescent nanoparticles and single fluorescent molecules as velocity probes show that the no slip boundary condition holds down to at least 10 nm from the surface. For water flowing on a hydrophobic solid surface, silanized glass, the no slip boundary condition fails, and a slip length of 45 nm is measured. These velocity measurements are complemented with atomic force microscopy measurements of dissipation on a small sphere oscillating near the surface with results in agreement with the velocity profiles.

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The Navier-Stokes equations governing the flow of Newtonian fluids need to be complemented with sound boundary conditions. The widely used condition is that of no slip past the solid surface which was debated over a century ago and put to several tests in the past decade. The exact reasons for its validity remain somewhat controversial, but it is generally admitted that the interactions between the fluid and solid wall are at the heart of its existence. Numerical simulations have highlighted the role of the wetting properties of the fluid on the solid surface [1]. Two recent review articles highlight the main experimental results and bring forth some discrepancies [2,3]. For fluids not wetting the solid surface, a certain degree of slip exists with two distinct features: a nonzero velocity at the wall and a nonzero slip length which is the distance to which the velocity extrapolates to zero away from the wall. Slip lengths ranging from a few tens of nanometers to a fraction of a micron have been reported for different combinations of fluid and surface material with no particular correlation between the contact angle and the slip length, for example. Also, different techniques give different results [2,3]. Recent experiments have however presented strong evidence of the validity of the no slip condition for liquids wetting solid surfaces [4,5] and indicate the presence of slip, albeit with moderate values of the slip length (20 nm), for liquids not wetting solid surfaces [4]. This evidence is based on measurements of the dissipation as a small sphere or an atomic force microscopy (AFM) tip approaches a solid surface. Here, we present measurements of the velocity profile down to 10 nm from the surface.

We explore the flow properties of liquids near solid surfaces by using fluorescent nanoparticles or fluorescent single molecules as probes. Illumination of these objects floating in a liquid deposited on a glass slide by an evanescent wave delimits the observation region to spatial dimensions fixed by the penetration depth δ which can be of the order of 100 nm. The intensity of the evanescent wave decreases exponentially with the distance z to the surface: $I(z) = I_0 \exp(-2z/\delta)$ where I_0 is the intensity at the surface. In the linear regime (low excitation intensity), the fluorescence signal from the probes varies linearly with the incident intensity and can be used to infer the distance to the surface if I_0 and δ are known. Previous experiments have shown that such a scheme can provide direct information about the velocity in close proximity to the surface [6–9].

We use a small flow cell delimited from below by a thin plasma cleaned microscope slide and from above by a small piece of a similar slide attached to a piezoelectric transducer as shown in Fig. 1(a). The vertical oscillation of the transducer, driven by an amplified triangular or sinusoidal signal with different frequencies f and amplitudes A, gives rise to oscillations of the upper slide driving the flow of liquid between the two slides separated by a distance h. The system of slide and transducer was attached to a vertical translation stage and a mirror mount to control the tilt of the slide. The system is then mounted on another piezoelectric transducer for a fine control of the distance h. The system was mounted on an inverted fluorescence microscope equipped with an oil immersion 60× objective of high numerical aperture (1.45) allowing, in the Total Internal Reflection Fluorescence (TIRF) configuration, illumination with an evanescent wave of adjustable δ. A highly sensitive back illuminated CCD camera was used to collect the images. The liquid used is pure water with a small amount of fluorescent nanoparticles or fluorescent molecules. The fluorescent particles used are carboxylate modified and have diameters of 40 nm (Orange fluorescent nanospheres) or 20 nm (Nile Red fluorescent nanospheres). An estimate of the ionic strength of the nanoparticle laden aqueous solutions gives a Debye length of about 2 nm. The fluorescent molecules are Atto 647N in the shape of small rods of about 1 nm in length and a fraction of a nm in width. Considering that the rotational diffusion constant of these molecules is in the GHz range, they can be consid-

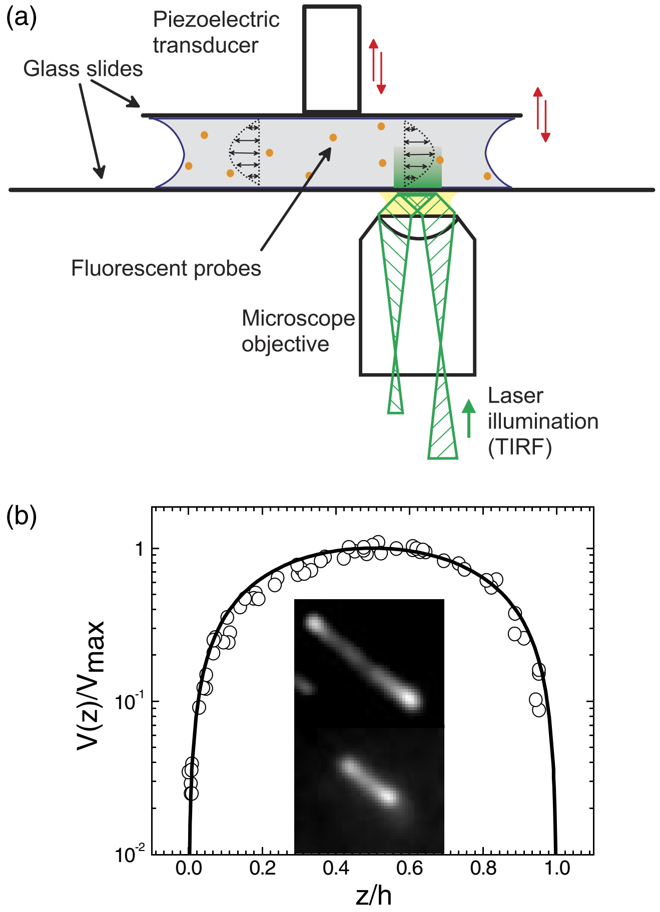

FIG. 1 (color online). (a) Schematic of the setup. (b) Velocity profile and a fit to a Poiseuille profile using 40 and 20 nm particles. Images of the 40 nm particles at 4 (lower) and 12 μm (upper) from the surface.

ered as small spheres. The depth δ was determined separately using a very thin glass fiber whose tip position from the surface could be controlled precisely with the second piezo transducer. The values of $\delta/2$ could be adjusted from about 1 μm to less than 100 nm.

First, we used direct illumination (no TIRF) to characterize the flow in our cell. Since the flow is oscillatory, the movement of the particles shows up as highly elongated strips. The exposure time for each image was kept low to minimize photo bleaching but slightly higher than the oscillation period so that the full strip is captured. The exposure time for the molecules was fixed between 10 and 20 ms. The length of the strip is proportional to the velocity. For a triangular oscillation signal, the velocity profile during a half period is given by $V(z) = V_{\max}[1 - (\frac{h/2-z}{h/2})^2]$ with $V_{\max} = \frac{3}{4} r \frac{A}{h} f$. During the second half period, the velocity switches sign and the particle travels back to its original position. The length of the major axis of the strip l_{maj} is given by $V(z)/2f$. Here, r is the distance from the center of the cell which varied between 1 and 3 mm. The height h was varied from 30 μm to 120 μm. The amplitude A was kept small with respect to h (a few percent) and varied from a fraction of a micrometer to 10 μm. The frequency varied from 60 Hz to a few kHz. At low frequencies, Brownian diffusion made the tracks of the probes deviate significantly from long strips, and only frequencies for which the tracks were well defined elongated strips with a well defined angle corresponding to the direction of the flow were considered. A velocity profile extracted from measuring l_{maj} is displayed in Fig. 1(b). The images in this figure were taken by focusing at different positions from the surface. As the distance to the surface increases, the length of the strips increases. Only the particles which were in focus were considered for this measurement. The distance z was measured with 2 μm precision. Only near the upper slide did the vertical oscillation make the strips difficult to measure. The velocity axis was divided by $V_{\max}$, and z was divided by h. The profile is well described by a Poiseuille profile.

To determine the velocity at very small distances to the surface, the illumination was switched to evanescent using the TIRF configuration. Now, the particles near the surface should appear bright with a small eccentricity since the velocity is small near the surface while particles far from the surface should have a large eccentricity and appear dim since the velocity is high and the excitation intensity is small. This is what we observe as shown in the images of Fig. 2. We take video images of the same flow so that the number of observed particles is large enough to be able to sample several distances from the surface. The images were analyzed using a home made program which extracts the major and minor axis ($l_{\min}$) as well as the integrated intensity I of the strips. The data is displayed in Fig. 2 for the 40 nm particles (over 13 000 particles were analyzed) and the single molecule probes (over 9000 molecules were analyzed). The plots show the eccentricity of the strips ($e = l_{\mathrm{maj}}/l_{\min} - 1$) versus the intensity I in a semi log plot. Zero eccentricity is indicative of circular dots and therefore zero velocity. High eccentricities indicate elongated strips or nonzero velocities. We expect $e(z)$ to vary linearly versus $\ln[I(z)]$ since for small values of z/h, $V(z)$

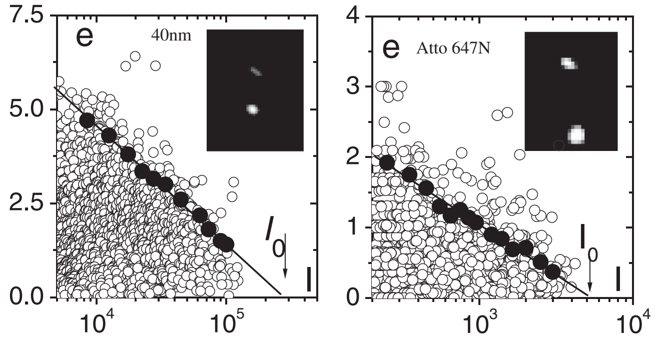

FIG. 2. $e(z)$ versus I: 40 nm particles ($\delta/2 = 1.1$ μm, $h = 124$ μm, $f = 1.1$ kHz, $e_{\max} = 40$) and Atto 647N ($h = 32$ μm, $f = 100$ Hz, $\delta/2 = 54$ nm, $e_{\max} = 110$). Black dots delimit the outer edge of the triangle. Solid line is the expected result. Insets: images of the probes.

$\sim 4V_{\max} z/h$ implies, using the relation between z and $I(z)$, that $e(z) \sim -4\frac{e_{\max}}{h}\frac{\delta}{2}\ln[I(z)/I_0]$. Note that for a fixed eccentricity, a multiplicity of intensities is measured. This multiplicity is due, for the single molecules, to their photophysics (blinking and photobleaching), and to their fast Brownian diffusion as they may explore different positions from the surface. For the fluorescent nanospheres, different intensities can be attributed to their size dispersion and fluorophore doping as well as to their Brownian motion. Polydispersity and Brownian motion are known to introduce a bias either in the measured intensity or in the estimated velocity [6,10]. However, all the data is contained within a well-defined triangular region. A conspicuous feature of this triangle is its outer edge which we determine as the best fit straight line going through $e(z)$ values corresponding to the 99.5% value of the cumulative probability of $e(z)$ in a fixed intensity interval [the black dots in Fig. 2(a) and 2(b)]. Along this line, $e(z) \propto V(z) \propto \ln[I(z)]$ as expected. The slope of this line turns out to be given by the expected value $4\frac{e_{\max}}{h}\frac{\delta}{2}$ and does not deviate from it by more than 10% for all the runs we have examined. Recall that $e_{\max}$, h, and δ are known beforehand for each run. This line intercepts zero at a well-defined value of the intensity which we identify as I_0. We therefore identify this outer edge determined by the black dots as the sought for velocity profile. As a check, we left $\delta/2$ unknown and estimated it from the slope of the line going through the outer part of the triangle determined as outlined above. The estimates gave 900, 200, and 90 nm instead of the measured 850, 180, and 87 nm. Despite the large spread in intensities, the data reveal the velocity profile as the outer edge of the triangle. The reason for this is that the brightest particles, those that were least affected by photobleaching or by Brownian diffusion, are the ones contributing to the outer edge of the triangle.

Figure 3(a) is a plot of $V(z)h/V_{\max}$ determined using the known values of $e_{\max}$, δ and I_0. The measured velocities, determined using the outer edge of the triangles, all lie on the same line for different runs using different particles at different concentrations, and different h, f, and δ values. This line is very close to $4z$ shown as a solid line which is expected for a Poiseuille flow. This is true for distances larger than 1 μm for which the velocity profile was determined separately [see Fig. 1(b) and the solid stars in Fig. 3(a)], and which validates our procedure, and down to 10 nm from the solid surface. Below 10 nm, the data is too scarce to reach a conclusion. Figure 3(b) shows all the data for this measurement as well as the outer edge determined as outlined above. Generally, the large diameter particles contribute to the large distances (> 100 nm) while the single molecules contribute to the smallest distances making the influence of the hydrodynamic interaction with the wall (which depends on the ratio of particle size to distance to the wall to the power 3) negligible [6]. According to this measurement, no detectable slip is observed in good agreement with some of the most recent measurements [4,5]. Figure 3(a) shows a comparison to a modified profile [7] with a slip length of 5 nm. The size of the points in this graph being smaller than the error, the data is better represented by the no slip hypothesis.

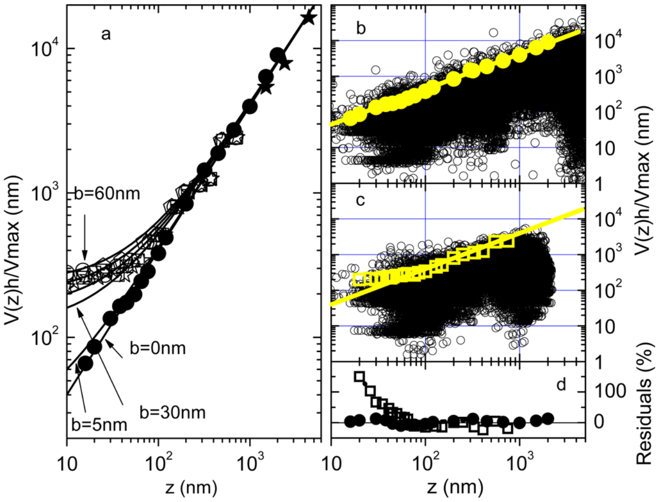

FIG. 3 (color online). (a) $Vh/V_{\max}$ versus z. dots: noncoated glass slides. solid lines: Poiseuille profile ($b = 0$) and modified profile ($b = 5$ nm). filled stars: measurements of Fig. 1(b). empty symbols: OTS covered slides $b = 30$ nm (stars), 40 nm (squares), 50 nm (circles), 60 nm (diamonds). solid lines: modified profiles. The error in z is at most 10%. The error for V is 15% for small z but less than 5% for large z. The size of the dots is greater than the error in z and in V. (b) noncoated slides. Data from different realizations with 40 nm and 20 nm particles, and Atto 647N. h: 22 μm to 120 μm, f: 60 Hz to 1 kHz, $\delta/2$: 54 nm to 1.1 μm, $e_{\max}$: 20 to 250, and the shear rate: 400 s^{-1} to 2000 s^{-1}. (c) OTS covered slides. Data using Atto 647N and 40 nm particles with h of 60 and 80 μm, f of 50, 100, 190, and 300 Hz, $e_{\max}$: 100 to 160, $\delta/2$: 76 to 500 nm, and shear rates: 300 to 2300 s^{-1}. solid lines represent the Poiseuille profile. (d) Difference between determined edge of graphs b (dots) and c (squares) and the Poiseuille profile.

Measurements using water and hydrophobic octadecyltrichlorosilane (OTS) coated glass slides with a contact angle of 90° were also carried out. Our measurements [Fig. 3(c)] show that the outer edge, determined as for the previous measurements, is given by a line close to $4z$. At values of z smaller than 100 nm, the value of $V(z)h/V_{\max}$ shows a saturation and does not extrapolate to zero as shown in Fig. 3(c). Figure 3(d) shows the difference between the measured values and the $4z$ dependence as a percentage of $4z$. While for the noncoated glass, the difference is close to zero, the difference for OTS coated glass seems slightly below zero for large z but greater than zero and increasing for smaller z ($z <$ 80 nm). *A priori*, in case a nonzero slip length b exists, $V(z)h/V_{\max} = 4b$ at $z = 0$. From the value of $V(z)h/V_{\max}$ at small z, we deduce b of about 50 nm as a first estimate. Now and because of slip, care has to be taken in evaluating the position of the interface. Indeed, our analysis extracts the maximal intensity I_0 and therefore the position of the solid surface by extrapolating to zero elongation. This amounts to fixing the position of the surface at the position where the velocity is zero. In the case where a slip length b exists, this amounts to estimating the surface at a distance b below its actual position. Figure 3(a) compares the data from the OTS coated slides to that of noncoated ones. The distance z is corrected by the corresponding value of b. While for $z > 100$ nm, the data from the two measurements differ little. For smaller z, the OTS covered slides give a saturation of the measured velocity on this log-log graph. By carefully comparing the extracted velocity profile to a modified Poiseuille profile [7], we estimate a slip length $b = 45\ \text{nm} \pm 15\ \text{nm}$. This value is larger than previously measured values [4] but remains modest and is in agreement with results obtained by measuring the dissipation as discussed below.

These results are complemented by measurements of the dissipation on a small sphere [4] oscillating near the solid surface both for the clean and OTS coated glass slides. To avoid electrostatic effects, we used 10 mM NaCl aqueous solutions. We use an AFM in dynamic mode working close to resonance. A glass sphere of 14 μm diameter was glued on the gold coated silicon nitride cantilever. A measurement of the amplitude of vibration of the cantilever is sufficient to extract the hydrodynamic damping coefficient [11] as the gap between the surface and the sphere diminishes. The surface approaches the sphere with a velocity of 0.2 μm/s with no noticeable effect on the cantilever mean deflection as shown in the inset to Fig. 4. The surface position was obtained by monitoring the mean deflection of the cantilever which is zero away from the surface and increases very rapidly at contact as shown in the inset. The resolution on the vertical approach distance is better than 2 nm. For a sphere at a distance z from a solid surface, the damping coefficient is given by $\gamma_s = 6\pi\eta R^2/z$. Figure 4 shows γ_0/γ_s for the two surfaces as extracted from the amplitude distance curve shown in the inset. The data for glass is fit assuming no slip on either the sphere or the surface giving a value of $6\pi\eta R^2/\gamma_0$ of 301 very close to the estimated value of 320 where γ_0 is the dissipation in the bulk of the fluid. This figure shows that γ_0/γ_s is a straight line intercepting the z axis at zero as expected for the no slip boundary condition. Deviation of the data at small gaps and therefore high dissipation is due to the breakdown of the simple harmonic oscillator model used to describe the cantilever. The results are consistent with the velocity profile data and previous measurements [4,5]. For the OTS covered glass slide, however, slip on the bottom surface needs to be taken into account. Indeed, extrapolation of the data to zero as shown by the dashed line intercepts the z axis at a value of about -50 nm. The hydrodynamic dissipation is in this case corrected by a factor $f^* = 1/4\{1 + 6z/4b[(1 + z/4b)\ln(1 + 4b/z) - 1]\}$ [7]. The inverse dissipation on the OTS covered surface can be fit as shown by the solid line to $(6\pi\eta R^2 f^*/z)^{-1}$ with $b = 50\ \text{nm} \pm 10\ \text{nm}$ which is in agreement with the velocity profile.

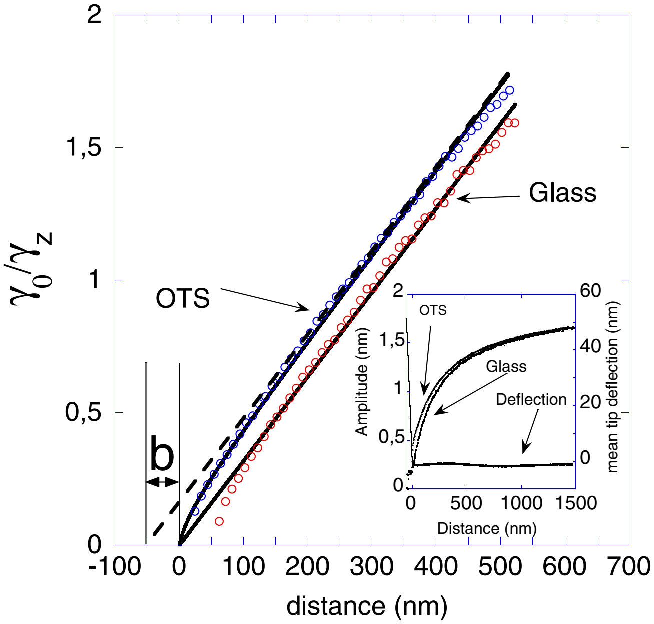

FIG. 4 (color online). γ_0/γ_s versus z from the vibration amplitude shown in the inset. Solid lines are fits using no slip (glass slide) and $b = 50$ nm (OTS covered slide). The dashed line extrapolates the data to zero.

We have shown that velocity profiles can be obtained by tracking single fluorescent nanoparticles and molecules. Despite the difficulty inherent in such a determination due to photobleaching, Brownian diffusion, and the polydispersity of probe sizes, the profile can be obtained down to 10 nm from the surface. Tests using clean glass and pure water show that the no slip boundary condition is valid. On a hydrophobic surface, water flows with a slip length of roughly 45 nm. These results are in agreement with measurements of the dissipation of a small sphere approaching the surface and with previous experiments.

[1] J. L. Barrat and L. Bocquet, Phys. Rev. Lett. **82**, 4671 (1999).
[2] C. Neto *et al.*, Rep. Prog. Phys. **68**, 2859 (2005).
[3] E. Lauga, M. P. Brenner, and H. A. Stone, *Handbook of Experimental Fluid Dynamics*, edited by J. Foss, C. Tropea, and A. Yarin (Springer, NY, 2005), Chap. 15.
[4] C. Cottin-Bizonne *et al.*, Phys. Rev. Lett. **94**, 056102 (2005).
[5] C. D. F. Honig and W. A. Ducker, Phys. Rev. Lett. **98**, 028305 (2007).
[6] P. Huang, J. S. Guasto, and K. S. Breuer, J. Fluid Mech. **566**, 447 (2006).
[7] O. Vinogradova, Langmuir **11**, 2213 (1995); D. Lumma *et al.*, Phys. Rev. E **67**, 056313 (2003).
[8] H. Li, R. Sadr, and M. Yoda, Exp. Fluids **41**, 185 (2006).
[9] S. Pouya *et al.*, Exp. Fluids **39**, 784 (2005).
[10] R. Sadr *et al.*, J. Fluid Mech. **577**, 443 (2007).
[11] C. Jai, T. Cohen-Bouhacina, and A. Maali, Appl. Phys. Lett. **90**, 113512 (2007).