Hydrodynamic boundary condition of water on hydrophobic surfaces

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By combining total internal reflection fluorescence cross-correlation spectroscopy with Brownian dynamics simulations, we were able to measure the hydrodynamic boundary condition of water flowing over a smooth solid surface with exceptional accuracy. We analyzed the flow of aqueous electrolytes over glass coated with a layer of poly(dimethylsiloxane) (advancing contact angle $\Theta = 108^\circ$) or perfluorosilane ($\Theta = 113^\circ$). Within an error of better than 10 nm the slip length was indistinguishable from zero on all surfaces.

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A fundamental problem in physics is to understand the flow of a liquid near a solid surface. To describe such a flow quantitatively, one needs to know the hydrodynamic boundary condition. This is characterized by the slip length $b$, which is obtained from extrapolating the liquid velocity parallel to the interface ($v_x$) beyond its position $z = 0$ according to $v_x(z = 0) = b \frac{\partial v_x}{\partial z} \bigg|_{z=0}.$

Here, $z$ and $x$ are coordinate axes oriented, respectively, normal and parallel to the interface. Traditionally, the no-slip boundary condition, which approximates $b$ by the value zero, has been successfully used to describe macroscopic flow of Newtonian liquids. However, for micro- or nanosized channels this may not be precise enough. Some theoretical studies and simulations indicated that a significant amount of slip may exist, in particular, in the case of weak solid-liquid interactions [2–9], i.e., a large contact angle [4,5,7,8]. Molecular simulations are, however, carried out at extremely high shear rates of typically $10^9$–$10^{10}$ s$^{-1}$. Furthermore, other parameters such as the presence of dissolved gases, the lyophilicity of the interface, or its roughness may also affect slip [10,11]. Thus, theoretically the situation is far from being resolved.

From the experimental side, even less consensus has been reached about the degree of slip and the conditions under which slip occurs. In particular, for water on hydrophobic surfaces values from 0 to more than 1 $\mu$m have been reported [12–29]. This controversy can be resolved only by developing accurate and surface sensitive methods to measure the flow profile of a liquid at a solid surface with nanometer resolution and at high shear rates. Unfortunately, most surface sensitive methods, e.g., colloidal probe techniques, provide only indirect information on the flow properties [23–34]. Direct visualization of the flow profile is possible with tracer-based methods such as particle image velocimetry (PIV) [17–19] or fluorescence correlation spectroscopy (FCS) [20,35–37]. These methods, however, suffer from the fact that they are not sufficiently surface sensitive; the slip length can only be determined with accuracy on the order of 100 nm. To improve the surface sensitivity of PIV, the method has been combined with total internal reflection (TIR) illumination. In TIR-PIV, the tracers are illuminated by an evanescent wave produced by TIR of a laser beam on the interface between the solid surface and the flowing liquid. The evanescent light intensity decreases exponentially in the liquid, with a typical decay length of 100 nm. This way only tracers that are close to the solid-liquid interface are illuminated and monitored. Using TIR-PIV the velocity of tracer particles close to the wall can be probed [16,21,22,38,39]. Such experiments with aqueous electrolytes indicated a slip of up to 60 nm on hydrophobic surfaces. Little or no slip was found on hydrophilic surfaces [16,18,22,39].

Such studies, however, suffer from one fundamental difficulty. As pointed out by Huang et al., the tracer particles do not follow the flow lines perfectly, but rather also diffuse randomly [40]. To estimate the influence of Brownian motion let us consider a typical situation, i.e., a tracer particle of $R = 20$ nm radius and a shear rate of $\dot{\gamma} = 1000$ s$^{-1}$. The diffusion coefficient of the particle is $D = k_B T/6\pi \eta R$ ($k_B$ is Boltzmann’s constant, $T$ is the temperature, and $\eta$ is the viscosity of the liquid). For water at 25 $^\circ$C with $\eta = 8.9 \times 10^{-3}$ Pa s we have $D = 1.22 \times 10^{-11}$ m$^2$/s$^{-1}$. To diffuse a distance of, say, $r = 100$ nm, the particle needs $\tau = r^2/6D = 137$ $\mu$s. The flow velocity at 100 nm away from the surface (assuming zero slip) is $0.1$ mm/s. In $137$ $\mu$s the particle would thus be carried only 14 nm by the flow, i.e., its movement is strongly influenced by diffusion. Suppressing this effect by using larger particles is not advisable, since the tracers should be small compared to gradients in the flow velocity, such that they may be considered as point particles. Large particles average over many flow lines and also influence the flow field, i.e., they hydrodynamically interact with the wall.

To overcome these problems we have recently developed total internal reflection cross-correlation spectroscopy (TIR-FCCS) [41] as a method to measure flow velocities near solid surfaces (Fig. 1, Refs. [41,42]) This method combines the speed, statistical accuracy, and sensitivity of FCS with a high normal resolution of TIR excitation. TIR-FCCS allows studies of...
at high shear rates using small tracer particles. In order to obtain quantitative values for the slip lengths we developed an algorithm based on Brownian dynamics to simulate and fit the outcome of a TIR-FCCS experiment, taking diffusion into account [43].

Here, we employ this combination of surface sensitive experiments and precise data evaluation to systematically measure the slip length for water flow over two types of hydrophobic surfaces. First, microscope cover glasses were coated with a covalently linked monolayer of (1H, 1H, 2H, 2H-perfluorooctyltrichlorosilane) [42]. Perfluoroalkyls are known to form the highest contact angle with water. Second, cover glasses were coated with poly(dimethylsiloxane) (PDMS). PDMS is fluid at room temperature and is known to lead to low contact angle hysteresis [44].

We used TIR-FCCS to study the flow of water in 5-cm-long, 4-mm-wide, and 100-μm-high channels, prepared by sandwiching a 100 μm adhesive polymer film between two glass slides as described earlier [41,43]. TIR excitation was accomplished at the bottom wall of the channel, a borosilicate cover slide with a thickness of 150 μm. The surface of this cover slide was either kept hydrophilic by cleaning with different solvents and argon plasma or made hydrophobic by covalently attaching a monolayer of perfluorosilane (PFS) and polydimethylsiloxane (PDMS). The last two columns show the statistical error of the data. The fits (continuous lines) were generated with our Brownian dynamics and Monte Carlo based simulation algorithm. Note that the shown cross-correlation curve is the difference between the downstream (G_{12}) and upstream (G_{21}) correlation function.
between simulated and experimental data plays the role of a Hamiltonian, while the magnitude of the statistical error bars is analogous to temperature. This provides the optimum parameter values together with their statistical error bars. The statistical uncertainty of the results comes mainly from the statistical error bars of the experiment. A statistical uncertainty of the simulation data is, in principle, present as well, but is, in practice, negligible compared to the experimental contribution. Furthermore, there are also systematic errors, mainly as a result of imperfect modeling of the observation volumes. Their effect is difficult to assess (and they are therefore not reported), but previous studies, in which we varied the optical model, indicated that the systematic error of the slip length is unlikely to be more than 5 nm [43]. To further improve the accuracy of the determined slip length, for each experiment the shear rate $\dot{\gamma}$ at the channel wall was independently determined by measuring the entire flow velocity profile in the channel with confocal FCS [36,43] and its value was kept fixed during the Monte Carlo fitting procedure (see Ref. [43] for an explanation). Since $\dot{\gamma}$ from the independent measurement is only known with finite accuracy, we ran different simulations with different $\dot{\gamma}$ values within the interval given by the error bar. This resulted in a variation of slip length by a maximum $\pm 5$ nm (Table I) that should be viewed as a contribution to the systematic error.

Using the combination of surface sensitive TIR-FCCS experiments and precise data analysis, we measured the slip lengths for water flowing over 13 different samples with either hydrophilic or hydrophobic surfaces (Table I). Averaging the values measured on similar types of surfaces results in slip values measured on similar types of surfaces results in slip lengths of 1.6 nm for the hydrophilic glass surfaces, 3.8 nm for water flowing over 13 different samples with either hydrophilic or hydrophobic surfaces (Table I). Averaging the values for water on both hydrophilic and hydrophobic smooth surfaces. No significant adsorption of tracers to the surfaces was observed. In summary, TIR-FCCS was applied for direct characterization of water flow profiles in proximity to smooth hydrophilic and hydrophobic surfaces. The high sensitivity of the method allowed studies at high shear rates using small tracers. TIR-FCCS combined with careful fitting of the measured correlation curves by means of Brownian dynamics and Monte Carlo simulations of a theoretical model allowed estimating the slip length with a statistical error of better than 5 nm, while our analysis shows that the systematic error is not significantly larger. Within this error the slip length for water flowing with a shear rate as high as 4000 s$^{-1}$ on smooth hydrophilic and hydrophobic surfaces is indistinguishable from zero.