# Direct Experimental Evidence of Slip in Hexadecane: Solid Interfaces

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The boundary condition for the flow velocity of a Newtonian fluid near a solid wall has been probed experimentally with a novel setup using total internal reflection–fluorescence recovery after photobleaching leading to a resolution from the wall of the order of 80 nm. For hexadecane flowing on a hydrocarbon/lyophobic smooth surface, we give what we think to be the first direct experimental evidence of noticeable slip at the wall. We show that the surface roughness and the strength of the fluid-surface interactions both act on wall slip, in antagonist ways.

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When solving Navier-Stokes equations, it is usually assumed that the relative fluid-solid velocity is equal to zero. This is the so-called nonslip boundary condition (NSBC) [1]. Strong experimental evidences do support this assumption at *macroscopic* scales [2,3], but it is not supported by strong physical arguments at *microscopic* scales. Consequently, much research has been devoted to the investigation of adhesion and friction of liquid molecules at solid interfaces, since the pioneering work by Coulomb [4] who, based on experiments with a poor experimental resolution, concluded that the NSBC was true even at microscopic scales [2,5]. Several indications however (both from experiments [6,7] and from molecular dynamic (MD) simulations [8,9]) suggest the possibility of slip at the wall for a simple liquid on a "weakly bonding" surface [4–6,8–16].

In case of a finite relative velocity between the fluid and the wall, $v_s$, the shear stress at the solid/liquid interface, $\sigma_{\mathrm{S/L}}$, can be expressed as [5] $\sigma_{\mathrm{S/L}} = -k_{\mathrm{FV}} v_s$, introducing the friction coefficient $k_{\mathrm{FV}}$. It is convenient to define the extrapolation length of the velocity profile to zero, or slip length $b$, as $b = v_s/\dot{\gamma} = \eta/k_{\mathrm{FV}}$, with $\dot{\gamma}$ the shear rate near the wall and $\eta$ the bulk viscosity of the liquid. If slip at the wall develops in a flow cell with a thickness $d$, the flow characteristics are the same as for a cell with a thickness $d + b$ and no slip at the wall. Slip at the wall thus leads to corrections of the order of $b/d$ in shear stresses or capillary flow rates. For entangled polymers, slip lengths larger than 1 $\mu$m have been reported [17]. For simple liquids, if slip exists, $b$ should be smaller than for polymers, and cells with a thickness in the micron range or below have to be used to allow slip to be detected through flow rate or shear stress measurements. Water flow in thin hydrophobic quartz capillaries (1 $\mu$m radius) has been investigated [6]. Slip at the wall had to be postulated to recover the viscosity of water. The corresponding slip length remained however poorly determined, due to the difficulty of controlling the surface quality (roughness and hydrophobic treatments) in such thin capillaries. The surface force apparatus (SFA) should allow one to encompass these difficulties, but the sensitivity of the present apparatus is too weak to allow for shear stress measurements for gap sizes larger than 10 nm [18]. At smaller spacing, confinement induced ordering occurs in the fluid, complicating the investigation of the boundary condition for the fluid velocity. The question of probing directly wall slip in simple fluids on controlled surfaces thus appears as still open, due to the lack of adapted experimental techniques.

In the present paper, we report experimental evidence of slip at the wall for a simple liquid, hexadecane, obtained by directly probing the fluid velocity within 80 nm from the solid surface. This velocity is averaged over a small surface (diameter $\Phi = 60$ $\mu$m). The technique is adapted from an experimental setup used to study wall slip in polymers [19] and has been described elsewhere [20]. We briefly present here the principle of the technique and of the data analysis. Results obtained for hexadecane on various modified sapphire surfaces will then be described and discussed.

The liquid is sheared between two parallel disks and confined by capillarity on a corona (mean radius $R =$ 32 mm, width $\Delta R = 5$ mm) where the gap between the two disks, 190 $\mu$m, is thinner than everywhere else, as shown schematically in Fig. 1(a). This geometry allows one to impose a constant shear rate (within $\pm\Delta R/2R =$ 8%) to the whole stream of fluid. The 190 $\mu$m gap is large enough to avoid confinement induced effects. The shear rate may be varied between $10^2$ and $10^4$ s$^{-1}$ by rotating one disk while the other one is maintained immobile. For all experiments discussed here the Reynolds number is well below 50 so that the flow is laminar. The shear rate is always small compared to the inverse natural relaxation time of the fluid ($1/\tau \sim 10^{10}$ s$^{-1}$, [21]) which thus behaves as a simple Newtonian fluid. Fluorescent probes, similar in size to the liquid molecules, are used as flow tracers. A short pulse of an intense focused laser beam (waist at focal point $\Phi = 60$ $\mu$m) photobleaches part of the probes within a cylinder normal to the disk's surfaces. The fluorescence close to the immobile solid surface, at the base of the bleached cylinder, is probed with an evanescent wave (penetration depth $\Lambda = 80$ nm; waist at focal point $\Phi = 60$ $\mu$m) obtained by total internal reflection

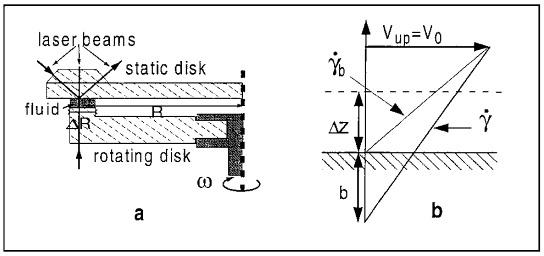

FIG. 1. (a) Schematic of half the flow cell; (b) equivalence between slip and shear rate.

(TIR) at the solid/liquid interface. Immediately after the bleaching pulse, the fluorescence intensity is low (photobleached probes are inside the illuminated area), and it progressively recovers due to the transport of nonbleached probes into the evanescent wave. The kinetics of fluorescence recovery after photobleaching (FRAP) reflects the fluid velocity close to the solid wall. If diffusion is negligible compared to convection, the relation between FRAP and $v_s$ is straightforward [17,19]: With slip at the wall, the base of the photobleached cylinder is translated at the velocity $v_s = b\dot{\gamma}$, while in case of NSBC, fluorescent probes only penetrate into the illuminated zone because the bleached cylinder is tilted by the flow. The fluorescence recovery is then more rapid for slip than for no slip at the wall. For simple liquids such as hexadecane, diffusion is fast and strongly competes with convection complicating the quantitative analysis of the FRAP curves, while the above qualitative trends are still observed. The diffusion coefficient of hexadecane is too large to be directly measured by FRAP techniques but an estimate through the Stokes formula gives $D = 10^{-10}$ m$^2$/s, with a 50% accuracy. Characteristic diffusion times can be evaluated using the Einstein-Stokes equation, $z^2 = 2Dt(z)$, for the various characteristic lengths of the experiment. Diffusion blurs out the photobleached cylinder in $t(\Phi/2) \sim 4.5$ s, while the diffusion time over the penetration depth of the evanescent wave is $t(\Lambda) \sim 50$ $\mu$s. The first time is large compared to the experimental fluorescence recovery time, $\tau$, ($\tau < 100$ ms for the whole range of $\dot{\gamma}$ investigated). The second time, $t(\Lambda)$, is short compared to $\tau$, meaning that the velocity gradient normal to the surface will be totally blurred through diffusion during the fluorescence recovery experiment [22,23]. The fluorescence recovery is thus sensitive to an average of all velocities within a thickness $\Delta z = (2D\tau)^{1/2}$: $\overline{v} = \dot{\gamma}(\Delta z/2 + b)$ [Fig. 1(b)]. This average velocity, $\overline{v}$, remains sensitive to slip and allows one to measure $b$ as long as $\Delta z/2$ is not much larger than $b$.

As illustrated in Fig. 1(b), the same $\overline{v}$ may be obtained with a no slip BC, replacing the imposed shear rate $\dot{\gamma}$ by an effective shear rate $\dot{\gamma}_b = 2\overline{v}/\Delta z$. The fluorescence recovery time $\tau$ can be estimated as the time necessary for a probe to cross the bleaching beam diameter at the velocity $\overline{v}$: $\tau = 2(\Phi^2/4D)^{1/3}\dot{\gamma}_b^{-2/3}$. All curves can thus be scaled on a single master curve through the time scaling: $t' = t\dot{\gamma}_b^{2/3}$. This provides an experimental determination of the effective shear rate, $\dot{\gamma}_b$, and thus of the slip length: $b = \Delta z/2 \times (\dot{\gamma}_b - \dot{\gamma})/\dot{\gamma}$. Clearly, $\Delta z$ and thus $b$ depend on the value of the diffusion coefficient $D$. This is anyhow a weak dependence ($D^{1/2}$), and the poor accuracy in the estimate of $D$ results only in a systematic uncertainty of 20% in the $b$ values.

The diffusion length during $\tau$ gives an upper limit for $\Delta z$: $\Delta z^{\max} = 2(D\Phi/2\dot{\gamma}_b)^{1/3}$. For hexadecane, $\Delta z^{\max}$ is of the order of a micrometer, a value that we have obtained independently by solving numerically the convection-diffusion equations for a two-dimensional modeling of the experiment. This agreement between experimental and simulated $\Delta z$ values means that if numerical prefactors exist in the relation defining $\Delta z$, they remain of the order of 1 and should not drastically affect the estimated $b$ values. It is important to notice that the experiment is sensitive to the BC at a distance $\Lambda = 80$ nm though the measured velocity is averaged over a micrometer: The FRAP experiment appears quite analogous to a thin capillary flow experiment (diameter in the micron range), but it allows a better control of the quality of the solid surface.

We have examined the flow behavior of hexadecane, a model lubricant with a rather high surface energy ($\gamma_L = 27.4$ mJ/m$^2$ at 20 °C). The fluorescent probe, NBD dihexadecylamine at 5 ppm, showed no preferential adsorption on any of the investigated surfaces. The solid surface was sapphire $\alpha$-Al$_2$O$_3$ {0001} with a rms roughness of 0.4 nm as determined by x-ray reflectivity. It has been treated in four ways: (a) an UV/ozone cleaning [24] yielded a surface totally wetted by hexadecane ($\gamma_s > 72$ mJ/m$^2$); two controlled lyophobic surfaces were obtained by grafting a self-assembled monolayer of (b) octadecyltrichlorosilane (OTS: $\gamma_s = 21$ mJ/m$^2$) and (c) perfluorodecanetrichlorosilane (FDS: $\gamma_s < 13$ mJ/m$^2$) following a procedure similar to that used for silica [25,26]; (d) adsorption of stearic acid (octadecanoic acid) from the hexadecane solution produced an *in situ* surface modification within the flow cell. Wetting characterizations of surface (c) suggested that the FDS monolayer was incomplete, leading to a chemically inhomogeneous surface made of FDS islands, in a way similar to what has been seen by atomic force microscopy (AFM) on incomplete OTS surfaces [27].

Typical fluorescence recovery curves at different imposed shear rates are reported in Fig. 2 for two different surfaces: FDS (closed symbols) and bare sapphire (open symbols). The use of a normalized relative intensity $\Delta I/I$, with $\Delta I$ the decrease in fluorescent intensity due to the photobleaching, and $I$ the average intensity after fluorescence recovery, allows one to get rid of experimental conditions such as photobleaching intensity, concentration in fluorescent probes, duration of the bleaching period, intensity of the evanescent reading beam, .... In such normalized intensity units the fluorescence recovery curves are characteristic of one shear rate and of one surface. It is clear in Fig. 2 that the fluorescence recovery kinetics are faster on bare sapphire than on the FDS surface, whatever

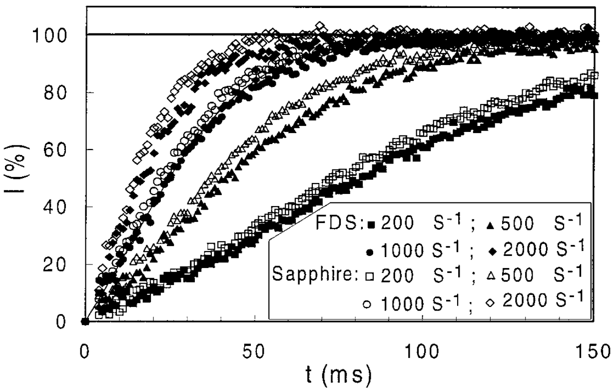

FIG. 2. FRAP curves for hexadecane flowing over a bare sapphire surface and over an incomplete FDS monolayer.

the shear rate, revealing different boundary conditions for the flow velocity (same fluid and same imposed shear rate). Using the time scaling method described above to analyze the data, all curves obtained on the FDS surface can be superimposed to form a master curve, using the imposed shear rate to scale the time axis ($\dot{\gamma}_b = \dot{\gamma}$), as shown in Fig. 3. This means that no slip at the wall is detectable on this FDS surface. To get a similar scaling of the fluorescence recovery curves on the bare sapphire and superimpose them on the master curve of Fig. 3, effective shear rates $\dot{\gamma}_b$ different from the imposed shear rates need to be introduced. This means that, contrary to what had been assumed previously [20], hexadecane slips on bare sapphire. The corresponding slip length is 175 nm (±50 nm), and appears independent of the applied shear rate within the accuracy of the analysis.

The fluorescence recovery is clearly much faster on a fully methylated surface as seen by comparing the curves obtained on a dense OTS surface to the FDS curves (Fig. 4). Again the scaling of these curves needs to introduce effective shear rates, and the corresponding slip length is 400 nm (±100 nm) for shear rates between 200 and 2000 $s^{-1}$.

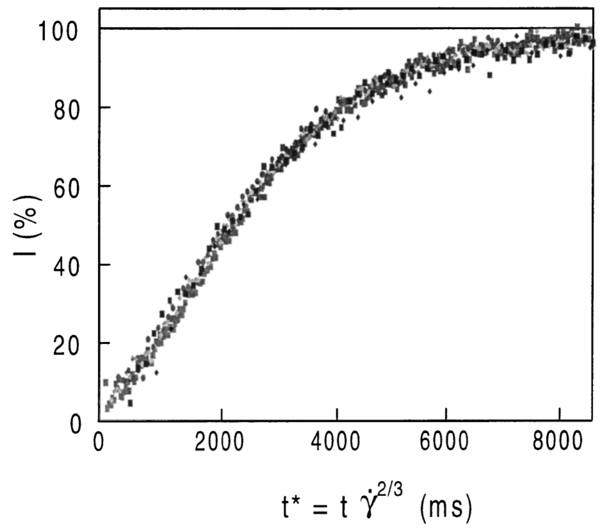

FIG. 3. Scaling of all FRAP curves obtained on the FDS surface, through the time scaling, $t' = t\dot{\gamma}^{2/3}$, using the imposed shear rate.

The wall slip BC appears however very sensitive to the exact molecular structure of the monolayer: On a slightly incomplete OTS monolayer, the fluorescence recovery is much slower, with a slip length of "only" 100 nm (±50 nm). This suggests that the corrugation of the surface plays an important role in determining the BC, as has been emphasized by MD studies [9].

*In situ* adsorption from a solution of 1% stearic acid (SA), a classical additive to lubricants, provides an easy method to modify the sapphire surface from bare to densely covered by methyl groups, in a continuous manner. Spontaneous adsorption of stearic acid has been widely investigated [28], and it has been shown that a complete monolayer forms within a time varying between a few seconds to several days depending on the surface reactivity. The effect of SA adsorption on the velocity BC, investigated through TIR-FRAP, has already been reported [20]. The BC varies with the time of incubation, i.e., with the degree of SA adsorption. At short contact times (less than 1 h), the FRAP curves are comparable to those on bare sapphire, with a slip length of 150 nm (±50) (notice that in [20] the bare sapphire was assumed to be a nonslip surface, a plausible assumption as long as we did not have the data on the FDS surface). As stearic acid self-assembles on the surface, the slip length increases to reach 350 nm (±100 nm) at adsorption equilibrium.

All the above results clearly demonstrate that the velocity BC for a simple liquid is not always a no slip BC. The obtained slip lengths are not inconsistent with macroscopic experiments or previous estimates [6] although they are much larger than those obtained by MD simulation in confined liquids. The substantial pressure often imposed in simulations may be at the origin of this discrepancy, as it can modify wetting properties and affect the flow BC. Our results appear in sharp contrast with SFA experiments by Georges *et al.* [29] who interpreted their results for

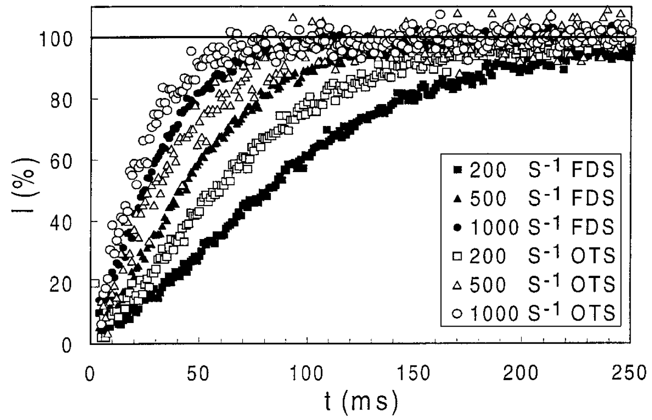

FIG. 4. FRAP curves for hexadecane flowing over a dense OTS surface and, for comparison, curves obtained on the FDS surface.

hexadecane on a bare mica surface with a no slip BC. It would certainly be interesting to check directly the BC through fluorescence recovery in this particular system.

Friction may generally be related to two basic parameters: adhesion and roughness. The former parameter can be adjusted by chemically modifying the solid surface. We find that this leads to important slip for hexadecane on a dense methylated surface (OTS or SA layer at adsorption equilibrium). Our results on incomplete FDS or OTS monolayers demonstrate that roughness at scales of molecular dimensions can however strongly inhibit slip. It is indeed reasonable to consider that a corrugated surface can transfer momentum, increasing the effective friction, as soon as some liquid molecules near the surface can be trapped inside the holes of the monolayer. Since the modified surfaces could not be analyzed through AFM (the disk diameter is too large), we cannot, in the present state of the experiments, gain more specific information on the mechanisms of liquid-solid friction.

To conclude, we have used TIR-FRAP to directly probe the velocity of a simple liquid within 80 nm from a solid wall. A series of experiments with hexadecane sheared against various modified sapphire surfaces shown that the boundary condition for the fluid velocity depends both on the interfacial energy and on the surface roughness at molecular scales, in agreement with intuition [5] and MD simulations. The liquid-solid friction appears larger on an incomplete fluorinated monolayer than on any other surface we have investigated, while the surface energy is the lower. The data are compatible with a no slip BC on this fluorinated surface, while slip lengths of the order of 400 nm are obtained on smooth lyophobic surfaces. Further work with different liquids such as squalane (apolar and spherical) or water (polar) is ongoing.

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