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Slip and depletion in a Newtonian liquid

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Abstract – Despite the fact that the magnitude of surface slip, which may occur for a liquid flowing past a solid wall, was quantified by different experimental techniques, the microscopic origin of this effect remains unclear. In the present article we present a neutron reflectivity study for a Newtonian liquid, hexadecane, in contact with solid walls at rest and under shear. In this system slip is not explained by a depleted liquid layer.

The solid-liquid interface introduces anisotropy to a fluid and represents a singularity that may result in distinct properties as compared to the volume. Usually, in fluid mechanics flow is described by the Navier-Stokes equation in the bulk and a no-slip boundary condition at the solid interface [1], which is in agreement with many macroscopic experimental observations [2]. First evidence for deviations from this assumption have been reported more than a hundred years ago [3]. Starting in the 80's, with improved detection techniques a systematic study of anomalous boundary effects became possible, and since then both experiments and theory have confirmed that on a microscopic scale liquids may undergo significant slip at a solid wall [4].

To have a quantitative measure of the discontinuity at the solid-liquid interface the slip length has been defined as distance from the solid interface, at which the velocity profile extrapolates to zero: $b = u(0)(\partial u(z)/\partial z)^{-1}$, where u denotes the velocity of the liquid and z is the distance from the interface. It turns out that boundary slip becomes important at length scales comparable to the slip length. Several experimental methods are available for the direct or indirect measurement of boundary slip, like capillary methods [5], particle image velocimetry (PIV) [6], or fluorescence recovery after photobleaching (FRAP) [7], which yield either a slip length or the flow field of a fluid. Additionally, (dynamical) surface force apparatus (SFA) [8,9] and atomic force microscopy (AFM) [10] allow the determination of the forces between the fluid and the interface and quantities like the slip length can then be calculated. These techniques are essential to decide in which systems slip occurs and to determine its magnitude.

Although now admitted that an intrinsic slip length on a smooth homogeneous solid-liquid interface exists in many systems, there is not yet a quantitative understanding of the relation between the structure of the liquid-solid interface and its friction properties. The microscopic origin of surface slip remains unclear as none of the experimental methods named above gives insight into the near surface structure of a liquid. One possible explanation for slip might be a density decrease in the interfacial layer of the liquid [11,12]. The influence of shear rate [9,13,14] and roughness of the solid surface [15–17] are under discussion. An alternative explanation was given by assuming a change in the local structure of a liquid in the vicinity of a non-wetting surface without a change in the density [18]. Relating to this fact it has been shown that the molecular shape has an influence on slip [19]. It was found that the anomaly at the interface is more pronounced for elongated molecules than for spherical ones. For most liquids, the short length scales important for slip effects are difficult to probe directly and non-destructively.

Neutron reflectivity measurements (NR) [20] have made an important contribution to the problem by showing that nano-bubbles previously observed in water close to a hydrophobic surface by AFM [21] are not intrinsic but

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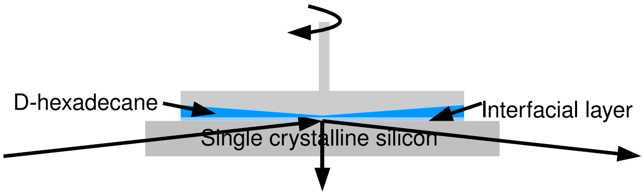

Fig. 1: Scattering geometry used for the experiment.

introduced by the AFM-tip moving in tapping mode. However, the extension of the depletion layer in water has been probed and yield different results [20,22–24]. Recently, it has been shown that depletion can be generally assumed for liquids in contact with a non wetting surface [25]. A density decrease leads to a reduced viscosity of the fluid in this layer [11] which might be related to the slip length [12].

At present sparse experimental information on how the amount of surface slip relates to the molecular structure or dynamics is available. This is the missing link to either attribute slip phenomena to depletion or reject this model. As flow could possibly influence the thickness of a depleted layer shear-rate–dependent measurements are desired. In the present article we will fill in this gap. We demonstrate that from neutron reflectivity measurements no effect of shear on the depleted layer is found for a system, hexadecane in contact with non-wetting surfaces, which is known to show surface slip. We quantitatively relate the depletion length extracted from our data to the slip length reported earlier [7]. It turns out that the amount of surface slip cannot be attributed to depletion. Additional changes in the local structure or dynamics, at constant density, of the liquid close to the interface have to be considered.

The experiments were conducted on the NG-7 reflectometer at the National Institute of Standards and Technology (NIST) center for Neutron Research, Gaithersburg (USA). This instrument has a vertical scattering geometry and allows reflecting from the bottom of the sample surface (see fig. 1). A variable incident beam collimation was chosen resulting in a footprint of the beam on the sample of 39 mm. In order to allow for the shear experiment we mounted a rheometer type shear device with cone-plate geometry on the sample stage (see fig. 1). The neutron beam impinges on the sample from the bottom after entering a block of silicon, size $70 \cdot 70 \cdot 10\,\mathrm{mm}^3$, on the narrow side. This geometry has the advantage that no sealing is needed, which may due to wear contaminate the sample, but limits the accessible Q-range to $0.12\,\text{Å}^{-1}$.

Table 1: Result of the fitting parameters for the bare substrates measured in air.

Wafer	Piranha solution	Native oxide	HMDS
Silicon:			
$\mathrm{SLD}_{\mathrm{Si}}$ $[(10^{-6}\,\text{Å}^{-2})]$	2.07 ± 0.05	2.07 ± 0.05	2.07 ± 0.05
Roughness [Å]	5.5 ± 1	5.5 ± 1	5.5 ± 1
SiO_2:			
Thickness [Å]	15 ± 2	15 ± 2	14 ± 2
$\mathrm{SLD}_{\mathrm{SiO}_2}$ $[(10^{-6}\,\text{Å}^{-2})]$	3.26 ± 0.07	3.26 ± 0.07	3.20 ± 0.07
Roughness [Å]	4.0 ± 0.5	4.0 ± 0.5	3.0 ± 0.5

As liquid deuterated hexadecane, purchased from Polymer Source[1] (Montreal, Canada) and used without further characterization, was investigated in contact with three polished and differently treated silicon surfaces. The first silicon wafer was cleaned by treatment with a freshly prepared Piranha solution[2] (70/30, v/v, concentrated H_2SO_4 mixed with 30% aqueous H_2O_2) at 90–100 °C for 1 h and was then rinsed with deionized water and dried with a stream of high-purity N_2. Finally the substrate was UV/ozone treated for 10 min. The second wafer was used as received with a layer of native oxide and the third one was coated by HMDS (1,1,1,3,3,3-hexamethyldisilazane) after cleaning with Caros acid and by subsequent exposure for 24 h to a HMDS atmosphere. The surfaces were characterised by measuring the contact angle for a water droplet on the different surfaces. The respective values are $\theta < 10°$, $55 \pm 2°$ and $90 \pm 2°$.

First the bare wafers have been measured (up to $Q = 0.2\,\text{Å}^{-1}$, reflectivities not shown) and the parameters obtained (see table 1, $\mathrm{SLD}_{\mathrm{Si}}$ and $\mathrm{SLD}_{\mathrm{SiO}_2}$ denotes the scattering length density for neutrons for Si and SiO_2) from the fit have then been fixed for extracting the depletion effect in the measurements with d-hexadecane. The errors given were estimated from a 20% increase in the standard deviation of the fit. We find a 15 Å thick oxide layer covering the silicon substrates and a roughness of 4 Å and 5.5 Å at the Si-SiO_2 interface and at the air surface, respectively. The HMDS coating, providing a small contrast with respect to air, is not visible in the reflectivity.

Figure 2 shows the result of the reflectivity measurements taken with d-hexadecane in contact to the silicon wafers for the static sample (open circles) and with an applied shear rate of $1000\,\mathrm{s}^{-1}$ (crosses). The error bars for the respective data points are not shown as they are smaller than the markers. For clarity the reflectivities for the HMDS-coated wafer and the wafer with native oxide are shifted by a factor of 10^4 and 10^2, respectively. For each sample two separate measurements were taken under shear and an additional at rest before and after shearing to check

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[1] Commercial materials, instruments and equipment are identified in this paper in order to specify the experimental procedure as completely as possible. In no case does such identification imply a recommendation or endorsement by the National Institute of Standards and Technology nor does it imply that the materials, instruments, or equipment identified are necessarily best available for the purpose.

[2] Piranha etching includes using hydrogen peroxide and sulfuric acid, which can be dangerous. Acid-resistant gloves, protective goggles, and lab coats must be worn when handling the piranha solution.

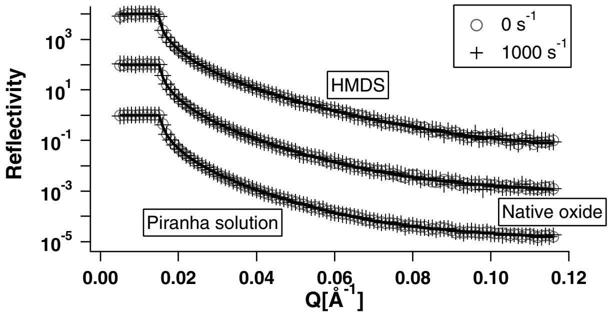

Fig. 2: Reflectivity of d-hexadecane in contact with silicon surfaces with different surface treatments without shear (open circles) and for a shear rate of $1000\,\mathrm{s}^{-1}$ (crosses). The solid line shows the fit to the data. Measurements for different surface energies are shifted by a factor of 100 for clarity.

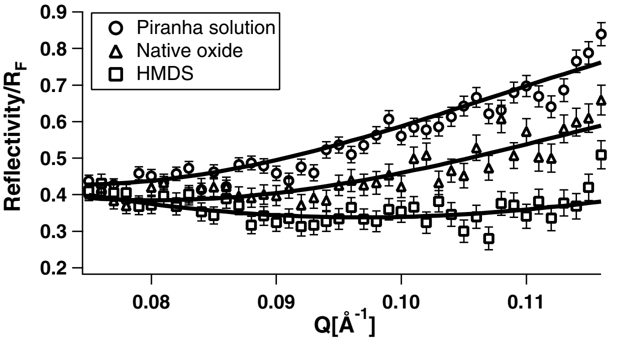

Fig. 4: High-Q reflectivities, normalized to the Fresnel reflectivity, measured with d-hexadecane in contact to differently treated silicon interfaces. The solid lines represent the fit to the data.

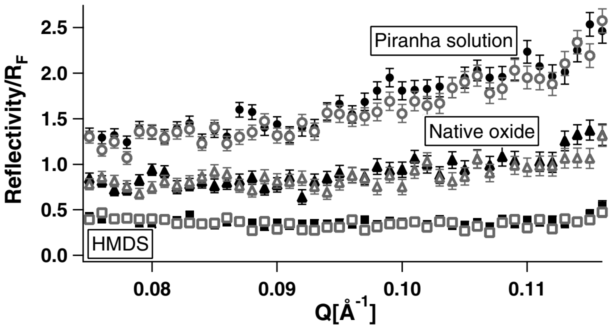

Fig. 3: High-Q reflectivities, normalized to the Fresnel reflectivity, measured with d-hexadecane in contact with interfaces with different surface treatments. The open and closed symbols represent data taken without shear and for a shear rate of $1000\,\mathrm{s}^{-1}$.

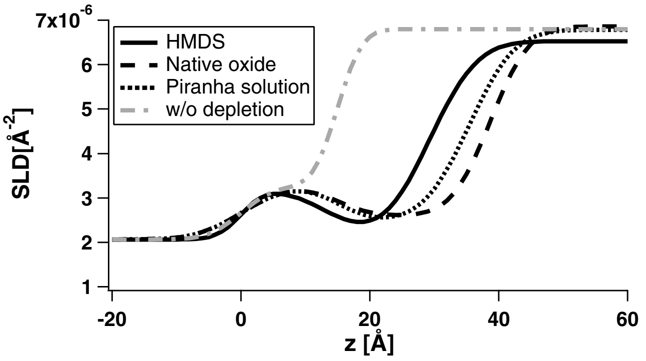

Fig. 5: Scattering length density profiles extracted from the fit to the reflectivities for d-hexadecane in contact with silicon wafers with different surface treatments. For comparison the scattering length density profile for an interface showing no depletion is shown.

the reproducibility of the results. Figure 3 shows a zoom into the large-Q region for the reflectivities, normalised to the Fresnel reflectivity for the silicon–d-hexadecane interface, taken for the sample in contact to the three differently treated interfaces without shear and for a shear rate of $1000\,\mathrm{s}^{-1}$ (open and closed symbols). The reflectivities are shifted by a factor of 2 and 3 for clarity. From this representation it becomes clear that within the experimental error bars the scattering length density of d-hexadecane close to the three interfaces is not altered by a shear rate of $1000\,\mathrm{s}^{-1}$. From the Q-range ($Q_{max} = 0.12\,\text{Å}^{-1}$) probed in the present experiment this holds at least for length scales down to 50 Å. However, the difference in the data at large Q-values can be, as shown later by the fitting, attributed to changes on a smaller length scale and the sensitivity of the measurements is about 2 Å. This is an important result for the discussion of slip as it implies that shear has no influence on the depleted layer of a Newtonian liquid, hexadecane, close to a solid interface.

Figure 4 shows a zoom into the high-Q regime of the data, normalized to the Fresnel reflectivity for a silicon–d-hexadecane interface, but now plotted on the same scale for the three different surface treatments. With decreasing hydrophobicity the intensity at large Q becomes increased even though hexadecane is totally wetting on the oxidized wafers and only partially wetting on the HMDS coated one. However, this effect is just above the error bars (as later seen from the fitting) and might be related to the non-polar d-hexadecane molecules close to a polar surface. For a quantitative analysis of the depletion layer the data have been fitted by using of the Parratt formalism [26]. The scattering length density profiles extracted from the fits are shown in fig. 5 and the fitted reflectivities are depicted in figs. 2 and 4 as solid lines. For all substrates, the depletion layer has been modeled using a single-box model with Gaussian roughness. The parameters extracted from the fit are summarized in table 2. For comparison the simulation of the scattering length density profile without depletion is shown in the panel. The values extracted for the scattering length density of the d-hexadecane are slightly smaller than the calculated value of $6.9 \cdot 10^{-6}\,\text{Å}^{-2}$. This fact could be due to an imperfect deuteration. Remaining hydrogen atoms in the sample of concentration less than 1% are of no importance for the discussion of depletion manifesting at large Q-values

Table 2: Result of the fitting parameters for the substrates in contact with d-hexadecane.

Wafer	Piranha solution	Native oxide	HMDS
Depleted layer:			
Thickness [Å]	23.7 ± 1	20.4 ± 1	15.6 ± 1
SLD_{hexdep} $[(10^{-6}\,\text{Å}^{-2})]$	2.61 ± 0.07	2.50 ± 0.07	2.10 ± 0.1
Roughness [Å]	4.8 ± 0.5	5.6 ± 0.5	5.8 ± 0.5
d-hexadecane:			
SLD_{hex} $[(10^{-6}\text{Å}^{-2})]$	6.86 ± 0.06	6.78 ± 0.07	6.53 ± 0.05

whereas the scattering length density of the d-hexadecane defines the value of the critical momentum transfer.

By taking the difference of the fit and the simulation for no depletion normalised to the bulk scattering length density of d-hexadecane the local concentration close to the interface can be calculated:

$$c_{hex}(z) = \frac{\mathrm{SLD}_{hexundep}(z) - \mathrm{SLD}_{hexdep}(z)}{\mathrm{SLD}_{hexbulk}}. \tag{1}$$

Where c_{hex} denotes the concentration of d-hexadecane at the interface, $\mathrm{SLD}_{hexundep}$ is the scattering length density of the simulation for undepleted d-hexadecane, SLD_{hexdep} is the result from the fit and $\mathrm{SLD}_{hexbulk}$ is the bulk value. By integrating $1 - c_{hex}$ along z the depletion length can be extracted and is found to be 14.3 ± 0.4 Å, 13.0 ± 0.3 Å and 10.0 ± 0.4 Å for the wafer treated with Piranha solution, the one with native oxide and the HMDS-coated one, respectively. These values are high as compared to the numbers found for water in contact with hydrophobic surfaces [11,20,22,25]. However, for the present experiment the liquid has not been degassed prior to the experiment and the measured values give the upper limit for the depletion length.

To quantitatively relate the depleted layer to the value of the slip length according to the two-fluid model the local viscosity of the liquid close to the interface has to be calculated. By assuming the particle-particle interaction to be independent of the concentration, the kinematic viscosity ν is constant and the dynamic viscosity η can be calculated: $\eta = \rho\nu$, where ρ denotes the mass density. For extracting the slip length from the viscosity of the liquid at the interface the following equation has been proposed [12]:

$$b = \int \mathrm{d}z \left(\frac{\eta_{bulk}}{\eta_{int}(z)} - 1 \right). \tag{2}$$

This transforms to

$$b = \int \mathrm{d}z \left(\frac{\rho_{bulk}}{\rho_{int}(z)} - 1 \right) = \int \mathrm{d}z \left(\frac{1}{c_{hex}(z)} - 1 \right). \tag{3}$$

The subscripts *bulk* and *int* denote bulk and interface values, respectively. For the present measurements a slip length of 31 ± 3 Å, 27 ± 2 Å and 19 ± 3 Å is calculated for the wafer treated by Piranha solution, the one with native oxide and the HMDS-coated one, respectively. These numbers are much smaller than the numbers reported earlier, between 1100 ± 500 Å and 3500 ± 500 Å for comparable or smaller surface energies measured by FRAP [19]. In this experiment hexadecane was investigated on a bare sapphire, a SiH and an OTS substrate. The longer OTS chains are known to form a denser packed and flatter surface as compared to the HMDS coating. However, one would expect an increasing depletion length and a decreasing slip length for increasing surface roughness. Considering this, our measurements provide an upper limit for the slip length and it is clear that surface slip is not fully explained by depletion. A depleted layer of thickness large or density low enough[3] to explain a slip length of 1100 Å would have been visible in our data. Note, that in our experiment we measure a depletion layer and do not get a direct information on the velocity profile in the liquid. For hexadecane slip should rather be attributed to conformal or dynamical changes at the interface than to depletion. Both possibilities will be probed by diffuse and grazing incident neutron diffraction and spectroscopy in future experiments. This is in contrast to results obtained for water [11]. In this case slip was related to the depleted layer. However, recent careful measurements have shown that for a freshly prepared surface the depletion effect vanishes [22] but no data for the liquid under flow are available.

In summary, we have shown that there exists no effect of shear on the depleted layer for a Newtonian liquid, hexadecane, which is known to show surface slip. We have quantitatively related the depletion length extracted from our data to the slip length reported earlier [7]. It turns out that the amount of surface slip cannot be attributed to depletion but has either to be explained by changes in the local structure or dynamics, at constant density, of the liquid close to the interface.

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