Interfacial Water at Hydrophobic and Hydrophilic Surfaces: Slip, Viscosity, and Diffusion

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The dynamics and structure of water at hydrophobic and hydrophilic diamond surfaces is examined via non-equilibrium Molecular Dynamics simulations. For hydrophobic surfaces under shearing conditions, the general hydrodynamic boundary condition involves a finite surface slip. The value of the slip length depends sensitively on the surface water interaction strength and the surface roughness; heuristic scaling relations between slip length, contact angle, and depletion layer thickness are proposed. Inert gas in the aqueous phase exhibits pronounced surface activity but only mildly increases the slip length. On polar hydrophilic surfaces, in contrast, slip is absent, but the water viscosity is found to be increased within a thin surface layer. The viscosity and the thickness of this surface layer depend on the density of polar surface groups. The dynamics of single water molecules in the surface layer exhibits a similar distinction: on hydrophobic surfaces the dynamics is purely diffusive, while close to a hydrophilic surface transient binding or trapping of water molecules over times of the order of hundreds of picoseconds occurs. We also discuss in detail the effect of the Lennard–Jones cutoff length on the interfacial properties.

Introduction

For many applications in microfluidic technology and almost all situations in the biological domain, the behavior of interfacial water is of prime importance. The geometric constraint of a solid surface, as well as the interactions between water molecules and the substrate, lead to structural changes of water compared to its bulk properties. Surfaces can be divided into two classes according to their affinity to water: hydrophilic, water attracting, and hydrophobic, water repellent. Since water molecules interact favorably with surface charges, surfaces which bear electric charges or polar groups typically are hydrophilic. In contrast, non polar surfaces are generally hydrophobic since the water molecules suffer a loss of hydrogen bonding partners at the interface. This classification into hydrophobic and hydrophilic surfaces has profound bearing on diverse situations such as interacting colloidal particles, protein folding, and adsorption of molecules or more complex structures on surfaces.

Over the past years it has become increasingly clear that the no-slip boundary condition, that is, the condition of zero interfacial fluid velocity, does not necessarily hold at nanoscopic length scales.1–3 In fact, the hydrodynamic boundary condition at the liquid/solid interface is of particular importance for microfluidic applications4,5 or biological nanoscale scenarios, such as the transport through membrane channels.5 But even in seemingly unrelated areas such as the automobile industry the importance of surface slip effects is acknowledged. As an example, mechanical components which are coated with hydrophobic, diamond-like carbon exhibit favorable friction properties,7,8 which could be put to good use in ball bearings and gear boxes to increase efficiency. Likewise, surface slippage amplifies the flow rate for pressure driven flow, which enhances fluid transport in narrow channels. Clearly, a noticeable increase of fluid transport is only obtained if the slip length is comparable to the channel dimension. For electrically driven flow, on the other hand, even small slip lengths in the nanometer range lead to a considerable increase in flow.9,10 All these examples demonstrate that a profound and microscopic understanding of the flow boundary condition at surfaces is necessary.

In this paper we analyze the structure and dynamics of interfacial water via molecular dynamic (MD) simulations. To set the stage, we first consider equilibrium properties of water in contact with a hydrophobic diamond-like surface. By variation of the surface water affinity, the hydrophobicity of the surface is controlled and quantified by the contact angle. Here we also discuss the influence of the Lennard–Jones cutoff length on the interfacial water interaction strength and the surface roughness; heuristic scaling relations between slip length, contact angle, and depletion layer thickness are proposed. Inert gas in the aqueous phase exhibits pronounced surface activity but only mildly increases the slip length. On polar hydrophilic surfaces, in contrast, slip is absent, but the water viscosity is found to be increased within a thin surface layer. The viscosity and the thickness of this surface layer depend on the density of polar surface groups. The dynamics of single water molecules in the surface layer exhibits a similar distinction: on hydrophobic surfaces the dynamics is purely diffusive, while close to a hydrophilic surface transient binding or trapping of water molecules over times of the order of hundreds of picoseconds occurs. We also discuss in detail the effect of the Lennard–Jones cutoff length on the interfacial properties.
nanometers for water, but in the past values up to micrometers have been reported. A collection of experimental and theoretical results can be found in ref 2. As a possible explanation for the large slip lengths in experiments the presence of a thin gas layer at the surface was considered. However, in simulations of a Lennard–Jones liquid it was found that the slip length is only moderately increased in the presence of dissolved gas. Using our realistic water model and gas parameters, we also observe only a modest enhancement of the slippage in the presence of surface groups compared to the bulk value within a layer of a few angstroms. We do not find evidence for a layer of frozen water or surface groups compared to the bulk value within a layer of a few angstroms. The analysis is then extended to polar, hydrophilic surfaces. From the velocity profile in the interfacial region we obtain zero slip and extract the surface viscosity, which is taken as the surface mobility of a hydrocarbon molecule adsorbed on inert gas. The analysis is then extended to polar, hydrophilic surfaces. From the velocity profile in the interfacial region we obtain zero slip and extract the surface viscosity, which is taken as the surface mobility of a hydrocarbon molecule adsorbed on inert gas.

### Molecular Dynamics Simulations

In MD simulations, the system is modeled on an atomistic scale, and the trajectories of all constituent particles are calculated using Newton’s equations of motion. Particles interact via bond interactions, typically harmonic springs and cosine torsional potentials, and non-bonded Coulomb and dispersion interactions, as well as Lennard–Jones interactions specified in eq 1.

\[
\epsilon(r) = 4 \sigma_{AB} \left[ \left( \frac{\sigma_{AB}}{r} \right)^{12} - \left( \frac{\sigma_{AB}}{r} \right)^6 \right]
\]

In most of our simulations, all Lennard–Jones interactions are truncated at a radius \( R_0 = 0.8 \) nm, as is customarily done to speed up the simulations. The effect of varying values of \( R_0 \) on the water contact angle is discussed in detail below. Long ranged electrostatic interactions are calculated with the Particle-Mesh Ewald (PME) method. For all simulations, we use the SPC/E water model.

### Hydrophobic Surface

We first consider a hydrophobic, hydrogen terminated diamond surface. The diamond slab is modeled by 2323 carbon atoms, arranged in a double face-centered-cubic lattice with lattice constant \( a = 3.567 \) Å. The surface normal of the (100) plane points in the direction. The lateral extension of the slab is \( 3 \times 3 \) nm\(^2\), its thickness 1.5 nm. Carbon atoms are connected by harmonic bonds and are subject to angular and torsional potentials of the GROMOS96 version 53A6 force field. The surface layer of the diamond is reconstructed and terminated by H atoms. Carbon atoms and water molecules interact via the Lennard–Jones potential in eq 1 with interaction parameters given in Table 1. Except for the Ne–O\(_1\) and O–O\(_1\) interactions and for the interactions involving O\(_2\) gas, the combination rules \( e_{AB} = (e_{AA} + e_{BB})^{1/2} \) and \( \sigma_{AB} = (\sigma_{AA} + \sigma_{BB})^{1/2} \) are used. For the simulations with the diatomic oxygen gas

| Lennard–Jones GROMOS Forcefield Parameters for Carbon, SPC/E Water and Noble Gases as Defined in Equation 1 |
|---------------------------------|---------|------------------|
| atom types | \( \sigma \) [nm] | \( \epsilon \) [kJ/mol] |
| H–H | 0.0 | 0.0 |
| C–C | 0.3581 | 0.2774 |
| O\(_1\)–O\(_1\) | 0.3166 | 0.6502 |
| C–O\(_1\) | 0.3367 | 0.4247 |
| Ne–Ne | 0.3136 | 0.6398 |
| Ne–O\(_1\) | 0.3293 | 0.4951 |
| Ne–C | 0.3351 | 0.4213 |
| Ar–Ne | 0.3410 | 0.9964 |
| Ar–O\(_1\) | 0.3285 | 0.8049 |
| Ar–C | 0.3494 | 0.5257 |
| O\(_2\)–O\(_2\) | 0.3030 | 0.4016 |
| O\(_2\)–O\(_1\) | 0.3098 | 0.5110 |
| O\(_2\)–C | 0.3306 | 0.3338 |
| O–O | 0.2760 | 1.2791 |
| O–C | 0.3144 | 0.5957 |
| O–O\(_1\) | 0.3017 | 0.8070 |

*The parameters for gaseous oxygen \( O_2 \) are taken from ref 37. O\(_1\) denotes aqueous oxygen while O denotes the COH group of a hydrophilic surface.

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the modified combination rule \( \sigma_{AB} = 0.5(\sigma_{AA} + \sigma_{BB}) \) for the Lennard–Jones diameter is used.\(^{37}\) The \( \text{Ne}–\text{O} \) and \( \text{O}–\text{O} \) parameters are explicitly given in Table 1.

There are different methods to change the hydrophobicity of a surface in simulations, for example, by adding hydrophilic groups or by rescaling the surface polarity.\(^{39–42}\) Within a certain range, the hydrophobicity of the surface can also be tuned with the liquid/solid interaction energy \( \varepsilon_{CO} \) between surface atoms and water molecules, which we varied in the range between \( \varepsilon_{CO} = 0.11 \) to 0.72 kJ/mol, while keeping the Lennard–Jones diameter \( \sigma_{O} \) constant. Decreasing the liquid/solid interaction energy increases the hydrophobicity since water molecules are less attracted by the solid and the water density close to the interface goes down, as shown in Figure 1a. These density profiles are obtained in simulations of the diamond surface in contact with 1850 water molecules in a 3.0 \( \times \) 3.0 \( \times \) 8.0 nm\(^3\) simulation box in the N\(A\)P\(T\) ensemble. For not too low values of \( \varepsilon_{CO} \), water layering is found and the density profile is non-monotonic. For the standard GROMOS value \( \varepsilon_{CO} = 0.42 \) kJ/mol, listed in Table 1, the water density in the first layer is roughly twice the bulk density. Lowering the interaction energy decreases the height of the density maximum. The density profile for the lowest interaction energy has no maximum at all and is similar to the density profile of the air/liquid interface.\(^{43}\) Therefore, by tuning the interaction energy, a smooth transition from a liquid/solid to a liquid/vapor-like interface is obtained.

We also considered surfaces with different degrees of nanoroughness, shown in Figure 1. Surface \( \text{R}_1 \) is constructed by erasing every third pair of rows of surface atoms, and surface \( \text{R}_2 \) is obtained by the deletion of every second pair of rows. For the construction of \( \text{R}_3 \), every second single row of carbon atoms is deleted. The roughest surface, \( \text{R}_4 \), is generated by removing carbon atoms down to the fourth surface layer. One should note that these nanorough surfaces are very different from so-called superhydrophobic surfaces, for which the surface structuring occurs on a much larger length scale. From the density profiles in Figure 1b it is seen that on the rough surfaces water molecules fill the voids left by the deleted surface atoms.

Hydrophilic Surface. Hydrophilic surfaces are constructed based on the smooth diamond surface by substituting every fourth \( x_{OH} = 1/4 \) or every eighth \( x_{OH} = 1/8 \) surface carbon atom by a \( \text{C}–\text{O}–\text{H} \) group with standard angular and torsional force potentials. The bond angle at the oxygen atom is 108° and the partial charges are set to \( q_0 = -0.674 e \), \( q_{\text{H}} = 0.408 e \) and \( q_{\text{C}} = 0.266 e \), while the standard GROMOS value \( \varepsilon_{\text{CO}} = 0.42 \) kJ/mol is used. These parameters are taken from the GROMOS96 forcefield for serine, the Lennard–Jones parameters are those of the GROMOS96 version 53A6 forcefield, see Table 1. Figure 3 shows the top view of the two studied hydrophilic surfaces. Torsional rotations around the \( \text{C}–\text{O} \) bond are in principle possible but severely inhibited by the large activation energies, so the OH rotational degrees of freedom are effectively quenched.

As can be seen in Figure 1a, the water is closer to the hydrophilic surface compared to the hydrophobic interface, and the first water peak is more pronounced and has a smaller width. Only minor differences are present between the two hydrophilic surfaces (data not shown): For the larger OH density, the first water peak is slightly higher and closer to the interface.

Contact Angle. One experimentally easily accessible parameter characterizing the surface hydrophobicity is the contact angle which ranges from 180° (for a hypothetical substrate with the same water affinity as vapor) down to 0° for a hydrophilic surface. On smooth hydrophobic surfaces, contact angles up to 130° are experimentally observed.\(^ {44} \) Even higher contact angles can be reached with patterned surfaces. In MD simulations, the contact angle can be determined either by the simulation of a nanodroplet on the surface\(^ {45} \) or by the calculation of the surface tension of a flat interface (as used in this study). Via Young’s law,\(^ {46} \) the contact angle is given by

\[
\cos \theta = \frac{\gamma_{ls} - \gamma_{lv}}{\gamma_{lv}}
\]

and depends on the surface tensions of the liquid/solid (ls), solid/vapor (sv), and liquid/vapor (lv) interfaces. In the simulations, the surface tension is obtained from the diagonal components of the virial tensor,\(^ {47} \)

\[
\gamma = (1/(2A)\!\mathbf{\Pi}_{ii} - (\mathbf{\Pi}_{xx} + \mathbf{\Pi}_{yy})/A, \quad A \text{ denotes the surface area and the virial tensor is given as } \mathbf{\Pi}_{ii} = \sum_q (r_i^q F_i^q)^2 \text{ and depends on the positions } r_i \text{ and forces } F_i \text{ of all single particles.}
\]

For the calculation of the virial tensor, the surface atoms are frozen and all interactions between the surface atoms are switched off, which directly yields the difference \( \gamma_{ls} - \gamma_{lv} \). Freezing the surface atoms also avoids subtle problems with substrate stress contributions.\(^ {47} \) To calculate the surface tension of the air–water interface, a water slab of up to 1807 molecules is simulated in a 3.0 \( \times \) 3.0 \( \times \) 12.0 nm\(^3\) box in the N\(T\) ensemble, yielding a surface tension of \( \gamma_{lv} = 0.0543 \pm 0.002 \) N/m. The substantial deviation from the experimental value of \( \gamma_{lv} = 0.072 \) N/m is a well-known deficiency of the SPC/E water model\(^ {1} \) and means that one has to be careful when comparing interfacial energies with experiments. The systems first were equilibrated for at least 200 ps with subsequent production runs of 5 ns.

Figure 4a shows the contact angle for a hydrophobic diamond surface as a function of the water-surface interaction strength \( \varepsilon_{CO} \) using the pressure tensor method (circles), compared to the results obtained from the simulation of a nanodroplet on the surface (triangles). The data fall on a straight line that reaches \( \theta = 180° \) for vanishing interaction strength. Whereas the limiting behavior as \( \varepsilon_{CO} \rightarrow 0 \) is as expected, the linear behavior \( 180° - \theta \sim \varepsilon_{CO} \) is not obvious and will be later discussed in connection with a depletion layer occurring at the interface. The data for the droplet method

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are taken from ref 43 and are in excellent agreement with the method used in this work except at large contact angles where line tension and cutoff effects influence the droplet data. The contact angle at the diamond surface with the standard GROMOS forcefield, $\epsilon_{CO} = 0.42$ kJ/mol, is 106°. In Figure 4b, we plot the results for the contact angle as $1 + \cos(\theta)$ as a function of the liquid/solid interaction energy $\epsilon_{CO}$. Here again a reasonable description is obtained with a linear function that however is shifted by an offset of the order of $\epsilon_{CO} \approx 0.14$ kJ/mol. Note that the two linear laws in Figure 4, panels a and b, are incompatible with each other, since $1 + \cos(\theta) \sim (180° - \theta)^2$ as $\theta \sim 180°$, and indeed a slight deviation of the data from the straight line for small values of $\epsilon_{CO}$ is observed in Figure 4b. The offset in $\epsilon_{CO}$ as $1 + \cos(\theta) \rightarrow 0$ in Figure 4b is especially troublesome, since it erroneously points to a drying transition at a finite value of the surface water Lennard–Jones attraction, which is unreasonable, as will be discussed further below.

The linear dependence $1 + \cos(\theta) \approx \epsilon_{CO}$ on the other hand follows from a simplified calculation of the surface tension. Although in this derivation one assumes constant liquid and solid densities and neglects the presence of a depletion layer, which play an important role as will be discussed later, the derivation which we will now sketch is quite useful conceptually. The surface tension of the liquid/solid interface is related to the work $H_{12}$ per surface area which is necessary to separate the liquid and solid slabs, defined as:

$$H_{12} = \gamma_l + \gamma_v - \gamma_{lv}$$

It can be easily calculated approximately assuming homogeneous solid and liquid densities $\rho_l$ and $\rho_v$ and neglecting any electrostatic or interfacial entropy contributions. For that we define the interaction energy of a single liquid molecule at a distance $z$ from the interface with the solid phase as

$$\eta(z) = 2\pi \rho_v \int_{r_z}^{R_0} dr \int_{z_r}^{z_z} d\epsilon_0 (\cos \theta) r^2 u(r)$$

where the intermolecular liquid/solid interaction potential is $u(r)$ and $R_0$ denotes the upper cutoff. Considering the Lennard–Jones potential in eq 1, which has a short ranged repulsive and a long ranged attractive part, the water film will exhibit a thin depletion layer of width $z^*$ that is defined by the condition $\eta_d(z^*) = 0$ and is (in the limit $R_0 \rightarrow \infty$ explicitly given by

$$z^* = a \left( \frac{2}{15} \right)^{1/6}$$

The work term $H_{12}$ contains the interactions of all water molecules with the surface and is given by

$$H_{12} = -\rho_l \int_{z_r}^{R_0} dz \eta_v(z) = -\pi \rho_v \int_{z_r}^{R_0} dz z(z - z^*)^2 u(z)$$

With the linear dependence of the Lennard–Jones potential in eq 1 on $\epsilon_{CO}$, $H_{12}$ turns out to be a linear function of the water-surface interaction energy $\epsilon_{CO}$ as well. From Young’s equation, eq 2, it follows that the cosine of the contact angle should be linearly dependent on the interaction energy.

$$1 + \cos \theta \sim \gamma_{lv} \frac{\gamma_v - \gamma_{lv}}{\gamma_{lv}} = \frac{H_{12}}{\gamma_{lv}} \sim \epsilon_{CO}$$

This linear relation gives a fair description of the simulation results in Figure 4b but, as we have noted before, would suggest a vanishing of the expression $1 + \cos \theta$ at a finite liquid solid interaction energy $\epsilon_{CO}$. Such a drying transition would not be expected on theoretical grounds since the entropic repulsion of a confined interface that is governed by surface tension is very
short-ranged, and the attraction between water molecules and the substrate should keep the depletion layer at a finite width. This follows from theories that incorporate the intrinsic coupling between interfacial fluctuations and interactions between substrate and liquid, according to which interfacial fluctuations (that give rise to a fluctuation pressure that decays exponentially with depletion layer thickness) are dominated by the attraction between the water film and the substrate as long as the decay is power-law-like (which is the case for van-der-Waals type interactions).

However, the situation is complicated by the fact that in MD simulations all interactions are cut off at a length $R_0$ which on the other hand makes the attraction between water and substrate also very short-ranged (an issue that will be considered in the next section). So our conclusion regarding the validity of eq 7 is that although at first sight the fit to the simulation data in Figure 4b seems reasonable, we argue that depletion effects and density profile variations not included in the derivation of eq 7 will be discussed further below considering the additional effects of a depletion layer.

**Cutoff Dependence.** In MD simulations, all Lennard–Jones interactions are usually truncated at an upper cutoff $R_0$. In the above simulations, the cut off radius was set to $R_0 = 0.8$ nm. It turns out that the value of the cutoff sensitively influences the resulting contact angle, an issue only recently considered in simulations. In Figure 5a, the contact angle at a hydrophobic diamond surface is shown as a function of the liquid/solid interaction energy $\epsilon_{CO}$ and for different cutoff radii $R_0$. The liquid–vapor surface tension was similarly calculated for different cutoff radii in simulations of a water film of 1807 water molecules in the $NVT$ ensemble in a $3 \times 3 \times 12 \text{ nm}^3$ simulation box. The liquid–vapor surface tension slightly increases with increasing cutoff radius $R_0$ and shows no statistically significant dependence on the number of water molecules, see Table 2, in agreement with previous simulations. In fact, the main contribution to the interfacial tension stems from Coulomb interactions which are fully taken into account via Ewald summation.

As seen in Figure 4a, for the most hydrophobic surfaces, that is, large contact angles, a variation in the cutoff radius only leads to minor changes of the contact angle. This is an important fact, as it shows that the spurious drying transition suggested when plotting the data as in Figure 4b is not caused by too small a cutoff radius $R_0$. In contrast, for the less hydrophobic surfaces, that is, for small contact angles, the cutoff radius substantially influences the contact angle. Increasing the cutoff radius leads to smaller contact angles. This effect can be understood from the density profiles, see Figure 5, panels b and c. As $R_0$ increases, the interfacial water density goes up, thus decreasing the substrate-water interfacial tension. This effect is more pronounced for large values of the interaction strength $\epsilon_{CO}$. The dependence of the contact angle on the cutoff radius $R_0$ can be rationalized by a simple model calculation. Again assuming constant liquid and solid densities and neglecting interfacial entropy, the interfacial work $H_{12}$ as defined in eq 6 can for large $R_0$ be written as

$$H_{12} = 2\pi\epsilon_{CO} \rho_0 \rho_l \left[ \frac{1}{8} \left( \frac{15}{2} \right)^{1/3} \left( \frac{a}{R_0} \right)^2 + \left[ \frac{a}{R_0} \right]^{3/2} \right]$$

where we have used the intermolecular potential eq 1 and the result for the depletion layer width eq 5. It is seen that the smaller $R_0$ becomes, the weaker the interfacial attraction and thus the contact angle increases. Figure 5d shows the contact angle as a function of the cutoff radius for a diamond surface with fixed $\epsilon_{CO} = 0.57$ kJ/mol from simulations (circles) and from eq 8 (triangles). This is the largest value of $\epsilon_{CO}$ considered by us, for which the cutoff dependence of the contact angle is very dramatic. In the calculation, the bulk water and diamond densities are used for $\rho_l$. The trend in the simulations is well captured; considering the very approximate character of the scaling Ansatz leading to eq 8, the agreement is surprisingly good. For all subsequent simulations, we use a cutoff radius of $R_0 = 0.8$ nm. It is important to keep in mind that, especially for large surface water interaction strengths, the contact angle and thus all other interfacial properties, exhibit a pronounced dependence on the value of the cutoff radius $R_0$ employed in the simulations. It follows that whenever simulations of interfacial systems are performed, not only must the interaction strength be reported, but also the cutoff radius. This is important also since the water force-field parameters have been optimized for a certain finite Lennard–Jones cutoff and deviations from the desired water bulk properties will occur if the cutoff length deviates drastically from that value. Ideally, one should always determine the contact angle, which is the only experimentally meaningful parameter that characterizes the surface hydrophobicity.
Figure 6. Snapshot of the sheared hydrophobic diamond system with \( D = 4 \) nm gap size (left). Not shown is the second water film. The diamond slabs are 1.5 nm thick and have 3.0 \( \times \) 3.0 nm\(^2\) lateral extension. In the middle, the water density profile is shown. The right figure shows the solvent velocity profile for diamond velocity \( v_0 = 0.02 \) nm/ps and the definition of the slip length \( b \). The vertical lines denote the surface velocity \( \pm v_0 \). The Lennard–Jones parameters are the standard GROMOS values given in Table 1 which leads to a contact angle of 106\(^\circ\) at the diamond surface.

**Shear at Hydrophobic Surfaces**

At a hydrophobic surface, the partial slip boundary condition holds, which quantifies the amount of slippage by the slip length \( b \). This length is defined via the normal gradient of the tangential fluid velocity field \( v(z) \):

\[
(v_0 - v)_{z=z_0} \equiv b(\partial v/\partial z)_{z=z_0}
\]

where \( v_0 \) and \( z_0 \) denote the velocity and position of the surface, see Figure 6.

The simulation setup consists of two diamond blocks which are separated by two SPC/E water slabs of typical thickness \( D \approx 4 \) nm each. This corresponds to roughly 1000 water molecules in each water slab. In Figure 6, we show a snapshot of half the simulation system, where only one of the two water slabs is shown. As was done in previous simulation setups, \( \mu \) Couette shear flow is induced by attaching harmonic springs with spring constants \( k = 1000 \) kJ mol\(^{-1}\) nm\(^{-2}\) to the upper and lower surface. The upper spring is pulled with a velocity of typically \( v_0 = 0.02 \) nm/ps in the \( x\)-direction and the lower spring is pulled with the same speed in the opposite direction such that the net momentum input vanishes. The motion of the diamond blocks induces a linear velocity profile for the solvent flow, see Figure 6. The shear rate follows as \( \gamma = (v_0 - v)_{z=2D} \), where \( D \) is the water slab thickness. Using the definition of a partial slip boundary condition at the position of the surface in eq 9, the slip length \( b \) is obtained by extrapolating the velocity profile. For that purpose, the velocity profile is fitted to a linear function. The location of the surface at which the slip boundary condition is applied is defined by the center of the topmost layer of surface atoms. The systems are equilibrated for \( 200 \) ps and then subsequent production runs of up to \( 30 \) ns are performed. Several simulations with the same parameters are performed and all trajectories are used for further analysis.

The used Berendsen weak-coupling thermostat is in principle critical for shear simulations. We checked this issue by performing two benchmark simulations, where a Berendsen thermostat with velocity scaling in all Cartesian directions and a Nose-Hoover thermostat with velocity scaling only in the direction perpendicular to the shear direction and perpendicular to the surface normal were applied, during otherwise identical simulations.\(^{13}\) We found no difference between these different simulation protocols, meaning that the type of thermostat does not influence the slip-length results.

Since experimental shear rates are substantially lower than the rates used in MD simulations, a careful examination of the influence of the applied pulling velocity on the resultant slip length is necessary.\(^{52}\) Therefore, shear flow simulations at different shear rates are performed to rule out artifacts that have to do with deviations from the linear-response behavior. Up to shear rates of \( 10^{10} \) s\(^{-1}\), the slip length \( b \) is almost independent of the shear rate and independent of the water film thickness which was varied between \( D = 2 \) and 8 nm, see Figure 7. To obtain reliable data at acceptable computational cost a shear rate of \( \dot{\gamma} = 10^9 \) s\(^{-1}\) is utilized for all subsequent shear simulations, with a water-slab thickness of \( D = 4 \) nm.

In Figure 8a we show the slip length as a function of the surface energy parameter \( \varepsilon_{CO} \) for the four different surface topologies shown in Figure 2. For decreasing interaction energies, that is, for more hydrophobic surfaces, the slip length increases. For the lowest interaction energy, the slip length is of the order of \( 20 \) nm. The slip length for the rough surfaces is always smaller than for the smooth diamond surface. At the roughest surface \( R_4 \), the slip length is smallest. Increasing surface roughness leads to smaller values for \( b \), since the friction at the liquid/solid interface is enhanced by the stronger corrugation of the liquid/solid interaction potential. A similar dependence of the slip length on the surface interaction strength was seen in simulations on polymeric melt systems\(^{53,54}\) and in simulations of liquid–liquid interfaces.\(^{55}\)

To rationalize the dependence of the slip length on static surface properties, especially on the interaction energy \( \varepsilon_{CO} \), we follow an argument of Bocquet and Barrat.\(^{56,57}\) who related the slip length of a fluid with viscosity \( \eta \) at a surface with surface area \( A \) to the friction forces \( F_x \) exerted by the fluid on the solid

\[
F_x/A = \frac{\eta}{b} v_x(z = z_0) = \eta v_x(z = z_0)
\]

The friction coefficient \( \lambda \) is defined as \( \lambda = F_x/(v_x(z = z_0)A) \), which together with eq 10 yields \( b = \eta/\lambda \). The Green-Kubo relation for

\[(51)\] Thompson, P. A.; Robbins, M. O. Science 1990, 250, 792–794.


the friction coefficient reads \( \lambda = \int_0^\infty dt \langle F_x(0)F_x(t)\rangle/(k_BT) \), which for many systems can be simplified to \( \lambda \approx \tau \langle F_x^2 \rangle/(k_BT) \) where the relaxation time \( \tau \) has been defined and \( \langle F_x^2 \rangle \) is the mean-squared lateral force acting between the substrate and the liquid phase. For the relaxation time we write \( \tau \sim \sigma^2/D \) where \( \sigma \) is a characteristic length scale and \( D \) is the diffusion coefficient of a fluid particle. The mean squared lateral surface force comes from force fluctuations, and in the thermodynamic limit scales as \( \langle F_x^2 \rangle \sim C_L(\varepsilon_{CO}/\sigma^2)A \) where \( C_L \) is a geometric factor that accounts for roughness effects. The rougher the surface, the larger \( C_L \). Putting everything together, we arrive at the scaling expression

\[
b \sim \frac{\sigma^2 \eta D k_B T}{C_L \varepsilon_{CO}} \tag{11}
\]

which incorporates a number of drastic approximations and simplifications but on the other hand constitutes an easily testable relation between slip length and surface energy \( \varepsilon_{CO} \). In Figure 8a, the slip length is plotted as a function of \( 1/\varepsilon_{CO} \) for the different roughnesses considered. The agreement with the straight lines verifies the above scaling considerations. Also, the rougher the surface, the smaller the slip length, again in agreement with the scaling in eq 11 if one takes the coefficient \( C_L \) as a measure of the degree of surface roughness.

Together with the linear dependence of the cosine of the contact angle on the liquid/solid interaction energy, eq 7, a simple relation between the slip length and contact angle is obtained,\(^{13}\)

\[
b = 0.63 \text{ nm} \cdot (1 + \cos \theta)^{-2} \tag{12}
\]

where the numerical prefactor is obtained from a fit to the data, broken line in Figure 8b. We hasten to add that the alternative and more physically sound relation \( \varepsilon_{CO} \sim 180^\circ - \theta \), as suggested by Figure 4a, gives the modified scaling relation

\[
b = 12 \mu \text{m} \cdot (180^\circ - \theta)^{-2} \tag{13}
\]

which in fact gives a comparable description of the data, solid line in Figure 8b. The effects of roughness on \( b \) on the one hand and on \( \theta \) on the other hand partially cancel out: Increasing roughness leads to decreasing slip lengths because of the enhanced friction (by increasing the factor \( C_L \)), see Figure 8a. On the other hand, since the liquid/solid contact area is increased on a rough surface, the liquid/solid interaction energy becomes larger which leads to decreasing contact angles, see Figure 4b. The influence of roughness on the scaling plot in Figure 8b is thus reduced. Despite the rough estimates leading to eq 11, the simulation results follow nicely the predicted scaling. The dependence of the slip on the contact angle shows the same dependence also for different surface structures such as fcc(100) Lennard–Jones surfaces or alkane chains.\(^{13}\) This quasi-universal relation between contact angle and slippage is of particular interest, since the contact angle is an experimentally easily accessible quantity.

**Slippage and Depletion Layer.** An alternative theory for the slippage at the liquid/solid interface is based on the existence of a thin depletion layer between the surface and the water with thickness \( \delta \). The viscosity \( \eta_0 \) of this layer is assumed to be substantially lower than the bulk water viscosity \( \eta_s \), which gives rise to an apparent slip length\(^{21,23,54}\)

\[
b = \delta \left( \frac{\eta_0}{\eta_s} - 1 \right) \tag{14}
\]

which is linearly dependent on the depletion width. To test this prediction, we used two different definitions of the depletion layer width \( \delta \): (i) the position where the water density is half its bulk value, \( \delta' \), and (ii) the integrated density deficit of the water layer\(^{41,58}\)

\[
\delta = \int_0^\infty dz \left[ 1 - \frac{\rho(z)}{\rho^b_0} \right] \tag{15}
\]

as visualized in Figure 9. Here \( \rho^b_0 \) are the bulk densities of the liquid and solid phase. Both depletion lengths can be directly calculated from the density profiles of the simulations. For both definitions, we do not find a linear dependence of the slip length on the depletion width, see Figure 10c. Therefore, unless one postulates a parametric dependence of the depletion-layer viscosity \( \eta_0 \) on the depletion width \( \delta \) the data do not support the prediction eq 14 of the two-viscosity model. In addition, the depletion length is less than a molecular diameter which makes the definition of an effective viscosity for such a thin layer awkward.

In Figure 10a, the depletion length is plotted as a function of the liquid/solid interaction energy, which suggests the scaling

\[
\delta^{-2} \sim \varepsilon_{CO} \tag{16}
\]

Combining this with the relation eq 11, one immediately obtains a quartic dependence of the slip length on the depletion length,

\[
b \sim \delta^4 \tag{17}
\]

---

which is nicely confirmed by the data in Figure 10c (broken line). On the other hand, combining eq 16 with eq 7 one obtains the scaling relation

$$\delta^{-2} \sim 1 + \cos \theta$$

(18)

which is compared with the simulation data shown in Figure 10b. The agreement is fair, but note that the line for the smooth diamond surface extrapolates to a finite depletion length for \(\theta \rightarrow 180^\circ\), which is at odds with the expectation that the interaction between the water and diamond slabs vanishes only when \(\delta \rightarrow \infty\). This is the same problem one encounters when applying eq 7 to the simulation data in Figure 4b. We can in fact bring out the shortcomings of eq 7 more clearly: Taking into account the presence of a depletion layer of width \(\delta\) between the solid and the liquid phase (which amounts to replacing the lower integration boundary \(z^*\) in eq 6 by \(\delta\)), the interfacial energy is given by

$$H_{12} \sim \rho_0 \rho_s \delta^2 \epsilon_{CO}/\delta^2$$

(19)

Naive application of Young's equation, eq 2, and using the definition of \(H_{12}\) in eq 3 gives the relation \(1 + \cos \theta \approx \epsilon_{CO}/\delta^2\), which cannot be simultaneously satisfied with eq 16 and eq 18, as noted before.\(^{13}\) A simple way out of this apparent dilemma is to postulate a second contribution to the interfacial energy,

$$-H_{12} \sim a/\delta^m - \rho_0 \rho_s \delta^2 \epsilon_{CO}/\delta^2$$

(20)

with at first an arbitrary exponent \(m\) and prefactor \(a\). In fact, the relation eq 16 follows from eq 20 by minimizing \(-H_{12}\) with respect to \(\delta\) if one chooses \(m = 4\); at that minimum one finds \(H_{12} \sim \epsilon_{CO}^2\), in contrast to the naive scaling result in eq 7. Indeed, using \(H_{12} \sim \epsilon_{CO}^2\) together with eqs 2 and 3 yields \(\epsilon_{CO} \sim (1 + \cos \theta)^{1/2} \sim 180^\circ - \theta\) which gives an equally sound description of the data, as shown in Figure 4a. Finally, combining \(\epsilon_{CO} \sim 180^\circ - \theta\) with the result eq 11 gives the modified scaling law \(b \sim (180^\circ - \theta)^{-2}\), which describes the data in Figure 8b equally well as the form proposed in eq 12.

We conclude that the quality of the numerical data does not allow to firmly distinguish between the conflicting scaling forms for the dependence of the contact angle \(\theta\) on \(\epsilon_{CO}\), as suggested by the straight lines in Figure 4, panels a and b. The scaling relation \(b \sim \epsilon_{CO}^{-2}\), shown in Figure 8a, and the relation \(\delta^{-2} \sim \epsilon_{CO}\), shown in Figure 10a, seem more robust and in fact are fully consistent with the scaling result eq 11 and the modified interfacial free energy scaling form in eq 20. Taken together, these relations lead to the striking result \(b \sim \delta^4\), which is presented in Figure 10c.

There are a number of effects that could lead to the postulated repulsive contribution \(a/\delta^m\) with \(m = 4\) in eq 20 with well-studied consequences on the wetting and dewetting behavior.\(^{29}\) One possible candidate, the repulsion due to confinement of the interface fluctuations, is by itself quite complicated\(^{38-50}\) and displays a distance-dependent crossover from being dominated by interfacial tension (at large length scales) to being dominated by interfacial bending rigidity (at short length scales).\(^{50}\) On the other hand, the water density profile changes as a function of the Lennard–Jones parameter \(\epsilon_{CO}\) which also gives rise to sizable corrections to \(H_{12}\). Finally, the modification of the electrostatic interactions between water molecules in the interfacial layer because of the presence of the solid substrate will also contribute to the interfacial free energy. At this stage, we can only state that a consistent description of the data is possible with an ad-hoc modified interfacial free energy as in eq 20, the microscopic origin of which is left for future investigation.

**Slippage and Dissolved Gas.** To examine the effect of dissolved gas on the slip length, shear flow simulations on hydrophobic diamond surfaces are performed with added gas particles. In most simulations, 10 gas particles are inserted in each of the two water slabs. We examine different types of gas particles. Species X \((m_x = 12.01 u)\) interacts equally with all other atoms present in the system via a purely repulsive potential,

$$V_X(r) = 4\epsilon_{\chi} \left( \frac{\rho_X}{\sigma_X} \right)^{12}$$

(21)

with \(\rho_X = 0.3581\) nm and \(\epsilon_{\chi} = 0.2774\) kJ/mol, the Lennard–Jones parameter of carbon. GROMOS force field parameters are used to model the noble gases Ne \((m_{Ne} = 20.18 u)\) and Ar \((m_A = 39.95 u)\). For the diatomic oxygen gas O\(_2\) \((m_O = 16.00 u)\), we use the Lennard–Jones parameters from ref 37 with a bond length of 1.21 Å. The interaction parameters for all considered gas types are summarized in Table 1. For the simulations with argon and gas type X, we consider variations of the surface hydrophobicity, while for oxygen and neon only the standard diamond parameters are used. For the simulations with argon, all interaction energies involving the surface atoms are recalculated by \(\epsilon_{CC} = (\epsilon_{CC} + \epsilon_{CA})^{1/2}\) and \(\epsilon_{CO} = (\epsilon_{CO} + \epsilon_{CC})^{1/2}\), while for the simulations with gas type X, only the liquid/solid interaction energy \(\epsilon_{CO}\) is varied, while the gas/solid interaction \(\epsilon_{\chi}\) is unchanged and given by eq 21.

Figure 11 shows the density profiles obtained within shear flow simulations, which in fact are indistinguishable from density profiles obtained in equilibrium simulations. The densities are averaged over all four interfaces in the simulation cell. As expected, the gas atoms accumulate at the hydrophobic interface, as was previously observed in MD simulations of Lennard–Jones fluids\(^{24}\) and in grand canonical


The density of neon, argon, and oxygen gas at the interface is increased by a factor of roughly 20–60 compared to the density in the bulk of the waterslab. The gas adsorption is restricted to one monolayer of gas particles, there is only one narrow peak present in the density profiles shown in Figure 11. The density of the purely hydrophobic gas type X at the interface is increased by a factor of more than 150. All X atoms are mostly present on one surface and the formation of a large cluster of gas atoms can be seen in the simulations, see Figure 12. This strong clustering is reflected in the shoulder of the X-density profile in Figure 11. The other gases do not exhibit such a clustering and they are more or less equally distributed on the two interfaces.

A variation of the surface hydrophobicity does not lead to qualitative changes in the density profiles. The accumulation of argon atoms is strongest at the most hydrophobic surface ($\varepsilon_{CO} = 0.26$ kJ/mol). This effect is also observed for gas type X. Pronounced interfacial gas accumulation is not seen in simulations of dissolved gas between the hydrophilic surfaces, as shown for argon in Figure 11b. Here, the gas density at the surface is only twice the bulk value.

Although the gas particles Ne, Ar, and O$_2$ are strongly attracted to the interface, they frequently desorb from the interface as seen in the snapshot, Figure 12a. The gas accumulation at the interface is not because of the Lennard–Jones attraction between the surface and the gas atoms, since also gas type X with a purely repulsive potential exhibits an increased density at the surface. Rather, the hydrogen bonding network is less perturbed if the gas particles are at the interface which favors gas adsorption at a hydrophobic surface.

A mole fraction of $0.25_{/C^2}10^{-4}$ Ar-molecules ($0.23_{/C^2}10^{-4}$ for O$_2$) is soluble in water at a partial gas pressure of 1 atm and $T = 298.15$ K. In the simulations, the total pressure is fixed at 1 bar $\approx$ 1 atm. Since the partial pressure of water vapor at room temperature is roughly 0.02 atm, the partial gas pressure in the simulation is comparable to the experimental situation, $p_{gas} \approx (1 - 0.02)$ atm $\approx$ 1 atm. From the density profiles, we deduce that the mole fraction of dissolved argon gas in the bulk liquid has a

value of about $5 \times 10^{-3}$ (similarly, for oxygen the mole fraction in the bulk is about $4 \times 10^{-5}$) and is thus much higher than the maximally soluble mole fraction (the gas bulk concentration is determined from all gas molecules that have a surface separation of at least 1 nm). However, we do not observe phase separation of argon or oxygen in the simulations, which is related to the very large nucleation barrier for gas bubble formation in such small systems. We nevertheless checked whether the unphysically large gas concentration in the simulations leads to spurious effects. For this we performed one simulation with only four oxygen molecules per water slab. In the normalized density profiles in Figure 11a, no difference is seen between the two different oxygen concentrations; we conclude that for all gases except the artificial gas type X (for which the solubility presumably is even lower than for the other gases considered) the simulation results approximately reflect the situation of a saturated solution of gas in water.

The surface adsorption of gas particles enhances the slip length only slightly, see Table 3 and Figure 13. The largest relative change in slip length $b$ because of gas adsorption is seen for the highest liquid/solid interaction energy (i.e., for the smallest contact angle). There, the slip length roughly doubles when, for example, Ar atoms are added to the water. Dissolved gas only moderately amplifies the slip length for large contact angles, which remain in the range of only a few nanometers. Thus, we conclude that large slip lengths as measured experimentally are not caused by surface adsorbed thin gas layers. However, experimental measurements suggest the formation of gas-nanobubbles at the liquid/solid interface. The lateral dimension of these bubbles is in the order of 100 nm, with a height of several nanometers which could significantly enlarge the slip length. These gas cavities are much larger than simulation box sizes one can possibly study and are therefore out of reach for present computer simulations.

Shear Flow Simulations at Hydrophilic Surfaces

We now examine the hydrodynamic boundary condition and the viscosity of water close to polar, hydrophilic surfaces. Experiments report on viscosities for confined water between mica surfaces at room temperature, which are comparable to the bulk viscosity. Sub-nanometer confinement was shown to lead to an increase in viscosity of approximately 80 times the bulk viscosity in simulations. Other experiments and simulation studies report on a strong increase in viscosity of several orders of magnitude for highly confined water films. Besides from these conflicting results for the viscosity in confined water layers, also the structure of water at hydrophilic surfaces is under debate. Spectroscopy experiments and computer simulations find an ice-like structure of thin water films. These crystal-like structures are identified via a sharp drop in the diffusion constant, a substantially increased shear viscosity, and can sustain shear stress. At hydrophilic interfaces, in contrast, this ice like water structure is not observed. A critical summary of simulation work on confined water has recently been published.

To clarify the structure and properties of water at hydrophilic surfaces, we perform NEMD simulations of water at polar, hydrophilic surfaces with relative large water slab thickness. In the non equilibrium shear flow simulations, the shear viscosity profile of interfacial water is obtained from the fluid velocity profiles. Via this method, we are able to locally probe the shear viscosity of water close to interfaces without introducing additional effects due to confinement. The velocity profiles, Figure 14, differ qualitatively from those obtained for the hydrophobic surfaces: close to the surface, the gradient of the velocity profile is smaller than in the middle of the water slab. In contrast, the gradient of the velocity profiles at the hydrophilic surfaces is constant, even close to the interface, see Figure 6. At the hydrophilic surface, the water molecules at the interface are dragged along with the surface. The region over which this dragging of water molecules occurs roughly corresponds to the extent of the first water layer. This feature is due to the strong interaction between the hydroxyl surface groups and the water molecules. These findings are in agreement with velocity profiles obtained from simulations of sheared water films between mica surfaces.

Since the shear viscosity is linearly related to the inverse of the velocity gradient, it is possible to define two different viscosities in the system. One in the surface region, $\eta_{\text{s}}$, and the other one in the bulk region, $\eta_{\text{b}}$. To obtain the shear rates in the two regions, the
A change in viscosity is moderate and does not support an ice-like viscosity. The less hydrophilic surface exhibits an interfacial viscosity that is larger by a factor of 4 compared to the bulk region used in the fitting.

The ratio of the two viscosities, the force acting on the diamond slabs is needed. In the simulation, the two solid slabs are attached to harmonic springs which are pulled with constant velocities \( v_0 \).

From the average displacement of the slabs with respect to the minimum of the spring potential, the average force \( F \) acting on the slabs is determined. The bulk and surface viscosities are given by \( \eta_0 = F(2A\gamma_0) \) and \( \eta_s = F(2A\gamma_s) \) with surface area \( A \) (the factor 2 in the expressions for the shear viscosities arises because each diamond slab is connected to two water slabs). From the shear rates \( \dot{\gamma}_0 \) and \( \dot{\gamma}_s \), obtained from the velocity profiles, and the average force \( F \) measured in the simulations, the viscosities given in Table 5 are thus obtained. The bulk viscosity \( \eta_0 \) in the inner region of the water film is similar for the hydrophilic and hydrophobic surfaces. The moderate confinement of 4 nm does not lead to strong deviations from the bulk viscosities, that is, our estimates for the bulk viscosity of the water film are in good agreement with the literature value \( \eta = 0.642 \text{ cP}^{76} \) for the SPC/E water model, obtained in non-equilibrium simulations at 300 K (note that the SPC/E water model considerably underestimates the viscosity of real water, \( \eta = 0.851 \text{ cP}^{77} \)).

Since the used shear rates \( \dot{\gamma} \sim 10^{-10} \text{ s}^{-1} \) are much larger than those typically used in experiments, it is crucial to check if the linear response regime is reached for the hydrophilic surface. We account for this issue by performing two benchmark simulations with double and half of the diamond pulling speed. Since neither the measured bulk viscosities nor the slip length changed with different pulling speed, see Table 5, we infer that the system is still in the linear response regime.

### Diffusion

The viscosity \( \eta \) of a liquid directly affects the diffusion constant for a particle with radius \( a \), which is given by the Stokes–Einstein relation \( D = k_B T/6\pi \eta a \) for the no-slip case or \( D = k_B T/4\eta a \) for the perfect-slip case. In this section we seek to understand the relation between the increased surface-viscosity at a hydrophilic surface, and the diffusivity of water molecules themselves. Not much is known for water dynamics at a single surface. Recent polarization-resolved pump–probe spectroscopy studies showed that water around small hydrophobic methyl groups is effectively immobilized,\(^{7,8}\) but the dynamics on planar surfaces is less clear. Simulations studied the diffusion of water molecules at various surfaces,\(^{79–82}\) In the present work, we shall be mainly interested in the difference of the diffusivity perpendicular to hydrophobic and hydrophilic surfaces. In simulations, diffusion constants are typically determined from the mean square displacement or from the velocity autocorrelation function. This leads to difficulties for

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**Table 4. Shear Rate and Viscosities for the Bulk (\( \gamma_0, \eta_0 \)) and Interfacial Region (\( \gamma_s, \eta_s \)) and the Corresponding Slip Length, Obtained from the Velocity Profiles of the Non-Equilibrium MD Simulations**

<table>
<thead>
<tr>
<th>( x_{OH} )</th>
<th>( \dot{\gamma}_0 ) [1/ns]</th>
<th>( \dot{\gamma}_s ) [1/ns]</th>
<th>( \eta_s/\eta_0 )</th>
<th>slip length [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/4</td>
<td>13.4</td>
<td>3.6 ± 0.8</td>
<td>3.7 ± 0.9</td>
<td>-0.32 ± 0.01</td>
</tr>
<tr>
<td>1/8</td>
<td>12.8</td>
<td>5.9 ± 1.0</td>
<td>2.2 ± 0.4</td>
<td>-0.29 ± 0.01</td>
</tr>
</tbody>
</table>

\(^{a}\) The slip length \( b \) is defined with respect to the layer of oxygen atoms of the surface C–O–H groups.
the determination of a local diffusion constant. Another route to obtain diffusion constants is to consider the time-correlation of a function $f(z)$ which is unity if the particle is inside a certain layer and zero otherwise,

$$f(z) = \begin{cases} 
1 & \text{if } z_0 < z < z_0 + \Delta z \\
0 & \text{else} 
\end{cases}$$

(22)

The autocorrelation function (ACF) of $f(z)$ is given by

$$C(t) \equiv N^{-1} \int_{z_0}^{z_0 + \Delta z} \int_{z_0}^{z_0 + \Delta z} dz' \int_{z_0}^{z_0 + \Delta z} dz'' p(z', t) f(z') f(z'') \rho(z'')$$

(23)

where the function $p(z', t)$ is the probability that a particle is at $z$ at time $t$, given that it was at $z'$ at $t = 0$ and the liquid density is given by $\rho(z)$. The normalization constant $N$ assures that $C(0) = 1$. $p(z', t)$ is the solution of the one-dimensional diffusion equation for a particle in an external potential $W(z)$,

$$\partial_t p(z', t) = \partial_z \left\{ D(z) \left[ \frac{1}{k_B T} (\partial_z W(z)) + \partial_z^2 \right] p(z', t) \right\}$$

(24)

$$p(z', 0) = \delta(z - z')$$

(25)

For bulk water with zero external potential and position independent diffusion constant, $D$, the solution is given by

$$p(z', t) = (4\pi D t)^{-1/2} \exp \left( -\frac{(z - z')^2}{4Dt} \right)$$

(26)

with the boundary condition $p(z', t) \to 0$ for $|z - z'| \to \infty$. Since for bulk water, the density $\rho(z)$ is constant, the normalization constant in eq 23 is given by $N = \int dz' \int dz'' \rho(z'') f(z') f(z'') \rho(z'') = (\Delta z) \rho_0$. The integrals in eq 23 can be performed and the autocorrelation function is given by

$$C(t) = \int_{z_0}^{z_0 + \Delta z} dz \int_{z_0}^{z_0 + \Delta z} dz' [4\pi D t (\Delta z)^2]^{-1/2} \exp \left( -\frac{(z - z')^2}{4Dt} \right)$$

$$= \frac{4D t}{\pi (\Delta z)^2} \left[ \exp \left( -\frac{(z - z')^2}{4Dt} \right) + \text{erf} \left( \frac{\Delta z}{\sqrt{4Dt}} \right) \right]$$

(27)

With the asymptotic behavior of the Error function, the asymptotics are $C(t) \approx (\Delta z^2)/(4\pi D t)^{1/2}$ for long times $t \gg (\Delta z)^2/D$ and $C(t) \approx 1 - (2/(\Delta z^2)/D) t^{1/2}$ for short times $t \ll (\Delta z)^2/D$.

We first calculate autocorrelation functions in bulk (in the absence of a substrate) from simulations for an NAP, T ensemble of 6000 water molecules in a $3 \times 3 \times 20.5$ nm$^3$ box. As for the other simulations, the system is coupled to a temperature of 300 K. The obtained autocorrelation functions are shown in Figure 15 together with the exact expression eq 27 for four different values of the correlation-slab thickness $\Delta z$. The only free parameter is the diffusion constant, for which we fit the value $D = 2.70$ nm$^2$/ns. This value is in good agreement with previous publications for the SPC/E water model, where the diffusion constant was determined to be $D = 2.70 - 2.79$ nm$^2$/ns.83 Experiments on the self-diffusion of real water yield a value of $2.30$ nm$^2$/ns at 298 K.84,85

The agreement between the data and eq 27 is excellent all the way from tens of femtoseconds to nanoseconds. This means, not unexpectedly, that in bulk the water dynamics is purely diffusive. The upper panel shows the data on a logarithmic time scale. The lower panel shows the data on a linear time scale; here some deviations are observed in the time window below one picosecond: in fact, water seems to diffuse faster than predicted by its long-time diffusion constant. The microscopic reason for this interesting behavior is at present unclear. We also note that in the lower panel, one is tempted to erroneously fit a straight line to the data for short times, from which one could extract a time constant of the order of 500 fs (with a spurious dependence on the correlation-slab thickness $\Delta z$). Only the comparison with the exact expression eq 27 shows that this is a non-sensical procedure, as the behavior is purely diffusive down to the smallest time scales with no typical time constant present in the data.

For water molecules close to the solid/liquid interface, the solution of the diffusion equation, eq 24, is much more complicated. Generally, the liquid particles experience a non-zero surface potential $W(z)$ and in addition the mobility of a single water molecule depends on its distance from the surface because of hydrodynamic boundary effects. In fact, the diffusion tensor even becomes anisotropic with different components for motion laterally and normal to the surface: simulations have shown that the water molecules are more mobile along the lateral direction.79 More sophisticated models are necessary to calculate the diffusion constant in the interfacial layer under the presence of a surface potential.90 As a crude approximation, we consider the solution of the diffusion equation at an interface assuming a position-independent diffusion constant and vanishing external potential. Since there is no flux of particles across the interface, the first derivative of the probability distribution must be zero at the location of the surface, $z = 0$. The solution of eq 24 that satisfies this no-flux boundary condition is given by

$$p_s(z, z', t) = (4\pi D t)^{-1/2} \left[ \exp \left( -\frac{(z - z')^2}{4Dt} \right) + \exp \left( -\frac{(z + z')^2}{4Dt} \right) \right]$$

(28)

<table>
<thead>
<tr>
<th>$\xi_{\text{OH}}$</th>
<th>$v_0$ [nm/ps]</th>
<th>$\eta_0$ [10^{-3} N s/m^2]</th>
<th>$b$ [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/4</td>
<td>0.02</td>
<td>0.75 ± 0.03</td>
<td>2.7 ± 0.7</td>
</tr>
<tr>
<td>1/8</td>
<td>0.02</td>
<td>0.71 ± 0.01</td>
<td>1.5 ± 0.3</td>
</tr>
<tr>
<td>0</td>
<td>0.02</td>
<td>0.66 ± 0.06</td>
<td>0.28</td>
</tr>
<tr>
<td>$\eta_\text{eff}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1/4</td>
<td>0.01</td>
<td>0.71 ± 0.03</td>
<td>0.31 ± 0.01</td>
</tr>
<tr>
<td>1/8</td>
<td>0.04</td>
<td>0.722 ± 0.005</td>
<td>0.317 ± 0.004</td>
</tr>
</tbody>
</table>

8 The errors of the viscosities are calculated from the uncertainties of the measured spring force and of the shear rate. Also the results of two benchmark simulations at half and double pulling speed $v_0$ are shown (for which the interfacial viscosity is not calculated because of shorter simulation runs and the considerable statistical fluctuation in the velocity profile).


The surface autocorrelation function decays with the inverse square root of time as
\[ C_s(t) = \frac{\Delta z}{\sqrt{\pi Dt}} \left( e^{-t^2/4Dt} - 2e^{-2t^2/4Dt} + e^{-t^2/(4Dt)} \right) \]

for long times \( t \gg (\Delta z)^2 / D \). In contrast to the bulk solution in eq 27, the prefactor is larger by a factor of 2, which is caused by the reflecting boundary condition. The autocorrelation functions, shown in Figure 16, are obtained from the simulation of one solid surface in contact with 1830 water molecules in a 3.0 × 3.0 × 8.0 nm box in the NPT ensemble. The region of the water slab considered for the estimation of the diffusion constant is depicted in Table 6 and corresponds to a \( \Delta z = 0.1 \) nm wide layer centered around the maximum of the density in the first water peak. For the hydrophobic surface, the lowest curve in Figure 16, the expression eq 29 gives a good description of the data over the complete time range, provided the diffusion constant is fitted to a value \( D = 0.85 \text{nm}^2/\text{ns} \), which is reduced by a factor of about three compared to the bulk case (note that \( D \) is the diffusion coefficient normal to the surface). This decrease is not surprising, as the hydrodynamic self-mobility of a particle at a surface is reduced compared to the bulk case. The correlation-slab width is taken as \( \Delta z = 0.1 \) nm as used in the simulations, the correlation-slab position is fitted as \( z_0 = 0.03 \text{nm} \) which is in rough agreement with the actual distance between the correlation slab and the point where the water density approaches zero (note that the actual position of the reflecting boundary is not well-defined within the simulation, which means that this is actually a free parameter in the theoretical description). For the hydrophilic surface data shown in Figure 16 (middle and upper curves), the expression eq 29 cannot fit the data, in fact, the functional form of the data suggests an exponential process that has to do with transient binding or trapping of water at polar surface groups. The simplest model for such a trapping process is one where initially a fraction \( \phi \) of water molecules is bound to the surface, then exponentially released, and only after release subject to diffusion. Neglecting rebinding of water molecules to surface sites, the autocorrelation function that allows for trapping thus reads
\[ C_s^*(t) = (1 - \phi)C_s(t) + \phi \left( e^{-t/\tau} + \int_0^t \frac{df}{\tau} C_s(t - \tau)e^{-\tau/\tau} \right) \]

Keeping the same diffusion constant \( D \) as on the hydrophobic surface for both hydrophilic surfaces, we can successfully fit the data with two fitting parameters, namely, binding fraction \( \phi \) and binding time \( \tau \), see Table 6. That the diffusion constant is at least very similar for all three hydrophobic and hydrophilic considered surfaces is suggested by the fact that for long times beyond one nanosecond the curves are seen to converge. The most interesting property is the time scale \( \tau \) over which a water molecule is bound to the polar surface groups, which turns out to be \( \tau = 210 \text{ps} \) for the \( x_{\text{OH}} = 1/8 \) surface and \( \tau = 340 \text{ps} \) for the \( x_{\text{OH}} = 1/4 \) surface. These are long times on simulation time scales, which means that equilibrating polar surfaces takes a long time. The fact that the time scale on the \( x_{\text{OH}} = 1/4 \) surface is larger than on the \( x_{\text{OH}} = 1/8 \) surface points to the presence of cooperative effects, meaning that...
on the $\chi_{\text{OH}} = 1/4$ surface a water molecule presumably binds to two OH surface groups simultaneously or into a network of other surface-bound water molecules. The fraction of bound water molecules, $\phi = 0.33$ and $\phi = 0.51$ on the two surfaces, is rather high and close to saturation. The fact that the $\chi_{\text{OH}} = 1/4$ surface does not bind twice as many water molecules as the $\chi_{\text{OH}} = 1/8$ surface again points to some cooperative (i.e., saturation) effects. The fact that our decay times are rather sensitive to the surface hydrophilicity is in contrast to the results in ref 79, where the residence time is insensitive to the surface hydrophilicity. The longer residence time at the hydrophilic surface is due to the fact that the water molecules are strongly attracted to the polar surface groups, whereas on the hydrophobic surface no binding is observed at all but purely diffusive behavior is seen when compared with the exact prediction from the diffusion equation. Note that water density fluctuations close to hydrophobic spherical cavities display a somewhat different behavior that suggests short-time exponential decay.\textsuperscript{82} In bulk water, see Figure 15, the behavior is also purely diffusive down to time scales as short as 20 fs, which is shorter than the lifetime of a single hydrogen bond $t_{\text{H}} \sim 1$ ps.\textsuperscript{86}

Care has to be taken with the interpretation of the obtained (normal) surface diffusion constant because of our crude assumptions. The neglect of a surface potential and of a position dependent mobility and the assumption of a constant water density in the surface region most likely lead to changes in the fitting of the surface diffusion constant, but recent results on Lennard–Jones fluids suggest that the changes are small.\textsuperscript{87}

### Conclusion

The structure and dynamics of liquid water close to interfaces is examined. We use nonpolar hydrophobic, as well as polar hydrophilic, substrates. In shear flow simulations we find slip lengths of only a few nanometers at hydrophobic surfaces with realistic contact angles. Via variation of the surface hydrophilicity, we obtain a heuristic scaling of the slip length with the contact angle of the surface, which is backed up by some simple scaling arguments. We also find a strong dependence of the slip length on the water depletion thickness at the hydrophobic surfaces. Dissolved gas is found to strongly adsorb to the hydrophobic surfaces but only moderately increases the slip length. In contrast, at the hydrophilic surfaces, no major gas accumulation at the interface is observed. From the velocity profiles obtained from shear flow simulations at the polar, hydrophilic substrates, we infer that the viscosity of water in the interfacial region is increased by a factor of 2 to 4, compared to the bulk viscosity, depending on the surface fraction of hydroxyl groups. From the decay of the autocorrelation function, the dynamics of water molecules at hydrophobic and hydrophilic surfaces is obtained. On hydrophobic surfaces, the dynamics is found to be purely diffusive, with no sign of surface binding or trapping. On hydrophilic surfaces, on the other hand, exponentially decaying surface trapping with typical decay times of hundreds of picoseconds is found. It is this transient water binding that most likely causes the effectively increased surface viscosity on hydrophilic surfaces in the shear flow geometry.

Even for contact angles as large as $\theta = 140^\circ$, the slip length obtained in our simulations is only of the order of $b = 18$ nm, see Figure 9b, whereas recent experiments consistently yield larger slip lengths, of the order of 20 nm at a contact angle of $105^\circ$.\textsuperscript{17,18} The reason for this disagreement is at present not clear. However, our simulations and scaling arguments give evidence for a strong dependence $b \sim \delta^4$ of the slip length $b$ on the depletion length $\delta$. Thus, a small deviation in depletion length between experiment and theory would lead to a much amplified disagreement between slip length in experiment and theory. Indeed, compared to experiments for silanized surfaces, the simulations underestimate the depletion length typically by a few angströms.\textsuperscript{23}

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**Table 6. Parameters Obtained from Fitting the Autocorrelation Function in Bulk\textsuperscript{a} to the Analytic Expression Equation 27 and the Autocorrelation Function on the Hydrophobic and Hydrophilic Surfaces\textsuperscript{b} to the Analytic Expression Equation 29 without Surface Trapping (for the Hydrophobic Surface) and to the Expression Equation 30 with Surface Trapping for the Hydrophilic Surfaces\textsuperscript{c}**

<table>
<thead>
<tr>
<th>$\chi_{\text{OH}}$</th>
<th>$\Delta \zeta$ [nm]</th>
<th>$z_0$ [nm]</th>
<th>$D$ [nm$^2$/ns]</th>
<th>$\phi$</th>
<th>$\tau$ [ps]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.10</td>
<td>0.03</td>
<td>0.85</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>1/8</td>
<td>0.10</td>
<td>0.03</td>
<td>0.85</td>
<td>0.33</td>
<td>210</td>
</tr>
<tr>
<td>1/4</td>
<td>0.10</td>
<td>0.03</td>
<td>0.85</td>
<td>0.51</td>
<td>340</td>
</tr>
<tr>
<td>bulk</td>
<td>0.10</td>
<td>-</td>
<td>2.70</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

\textsuperscript{a}See Figure 15. See Figure 16. Here, $\chi_{\text{OH}}$ is the surface fraction of OH groups, $\Delta \zeta$ is the correlation slab thickness, and $z_0$ its distance from the hydrodynamic boundary (see graph on the right which shows the water density at a hydrophilic substrate with standard $C_{176}$ parameter and arbitrarily shifted origin of the $z$-axis), $D$ is the fitted diffusion constant, $\phi$ is the fraction of initially surface-trapped water molecules, and $\tau$ is the characteristic release time of those bound water molecules.