

# Liquid water can slip on a hydrophilic surface

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**Understanding and predicting the behavior of water, especially in contact with various surfaces, is a scientific challenge. Molecular-level understanding of hydrophobic effects and their macroscopic consequences, in particular, is critical to many applications. Macroscopically, a surface is classified as hydrophilic or hydrophobic depending on the contact angle formed by a water droplet. Because hydrophobic surfaces tend to cause water slip whereas hydrophilic ones do not, the former surfaces can yield self-cleaning garments and ice-repellent materials whereas the latter cannot. The results presented herein suggest that this dichotomy might be purely coincidental. Our simulation results demonstrate that hydrophilic surfaces can show features typically associated with hydrophobicity, namely liquid water slip. Further analysis provides details on the molecular mechanism responsible for this surprising result.**

Protein folding (1), micelle and cellular membrane formation (2), and frictionless flow of water through carbon nanotube membranes (3–5) are only some manifestations of hydrophobic effects. Flat surfaces are arbitrarily classified as hydrophobic when a water droplet yields a contact angle larger than 90°, hydrophilic otherwise. A now famous 2008 commentary by Granick and Bae (6) initiated a scientific discussion to identify the molecular signature of hydrophobic vs. hydrophilic surfaces. The question is whether or not molecular properties exist for interfacial water molecules that change with the surface “degree of hydrophobicity.” Identifying such properties could advance practical applications (e.g., designing self-cleaning surfaces) as well as fundamental scientific endeavors including understanding self-assembly (7).

Molecular simulations should allow the discovery of such molecular signatures because they allow a systematic variation of the properties of a surface, as well as of surface-water interactions (8). Although the resultant substrates may not be realistic, the results are useful to interpret nature and to design innovative materials. It has so far been possible to relate some macroscopic observables to the degree of hydrophobicity [i.e., contact angle to adsorption free energy (9)]. Garde and coworkers employed equilibrium molecular dynamics (MD) to determine a number of quantities, including local density, contact angle, and adsorption of small solutes for water near surfaces of varying degrees of hydrophobicity (10). Whereas the local water density provided unsatisfactory characterization, the probability of cavity formation was found to be large near hydrophobic and small near hydrophilic surfaces.

The present work focuses on the relation between one important macroscopic signature of hydrophobic surfaces, the hydrodynamic liquid slip, to molecular interfacial water properties. Large liquid slip on hydrophobic surfaces could reduce the drag in vessels navigating the seas, the pressure drop encountered by fluids flowing inside pipes, and even repel ice formation. Liquid slip seems to appear when a fluid does not wet a surface (11–15). Because the extent of slip varies systematically with the contact angle (16–18), in the case of water, slip should occur on hydrophobic surfaces (19). In the present study the extent of water slip is quantified at various solid interfaces. Equilibrium and nonequilibrium MD are employed to search for molecular-level hydrophobic signatures.

## Results and Discussion

The most important result presented herein is the demonstration that contact angles larger than 90° are not necessary to attain hydrodynamic slip. Instead, slip is determined by the distribution of water molecules at contact with the solid and by the strength of water–solid interactions. When favorable adsorption sites exist, but are separated from each other by well-defined subnanometer distances, no slip is observed. When favorable adsorption sites are present that are close to each other, liquid slip can occur, provided water–solid attractions are not too strong. Because hydrophobic surfaces, such as graphite, are typically characterized by uniform distributions of interfacial water molecules, whereas hydrophilic ones, such as crystalline silica, present isolated highly attractive adsorption sites that water molecules readily occupy and seldom leave (20), experiments typically show hydrodynamic slip on hydrophobic surfaces and no slip on hydrophilic ones. Our results suggest that such observations are just a coincidence: Should hydrophilic surfaces be manufactured with high density of adsorption sites close enough to each other to allow water molecules to easily migrate from one to the next, such hydrophilic surfaces could show liquid slip. Our interpretation is consistent with a recent simulation study for the thermal diffusion of carbon nanotube membranes (21), with the molecular mechanism proposed for liquid slip (22), and with experimental observations reported for alkanes (23). Our interpretation could also explain the experimental results by McCarthy and coworkers (24), according to which the contact angle hysteresis, and not the static contact angle, should be used, macroscopically, to determine the hydrophobic vs. hydrophilic character of a surface.

In Fig. 1 we show representative equilibrium simulation snapshots for water droplets of 1,000 water molecules on three surfaces. In all cases, water molecules are described using the single point charge/extended (SPC/E) model (25). The surface on the top is MgO, simulated by the CLAYFF force field (26), on which water dissociation is not permitted. The contact angle is approximately 47° indicating a hydrophilic surface. We arbitrarily modify the MgO surface following two protocols. In the first, we reduce the electrostatic interactions between water and the MgO atoms by a factor  $W$ , comprised between 0 and 1. When  $W = 1$  we recover MgO. When  $W = 0$  the surface interacts with water molecules only via weak dispersive interactions, and the contact angle becomes approximately 130° (Fig. 1, *Bottom Left*), characteristic of a hydrophobic surface. In the second modification protocol we maintain both dispersive and electrostatic surface-water interactions consistent with those of MgO, but we reduce the lattice parameter that separates Mg and O atoms by a factor  $D$ . When  $D = 1$  we recover MgO. As  $D$  decreases the surface atomic density increases. When  $D = 0.62$  (Fig. 1, *Bottom Right*) the contact angle is approximately 30°, consistent with a

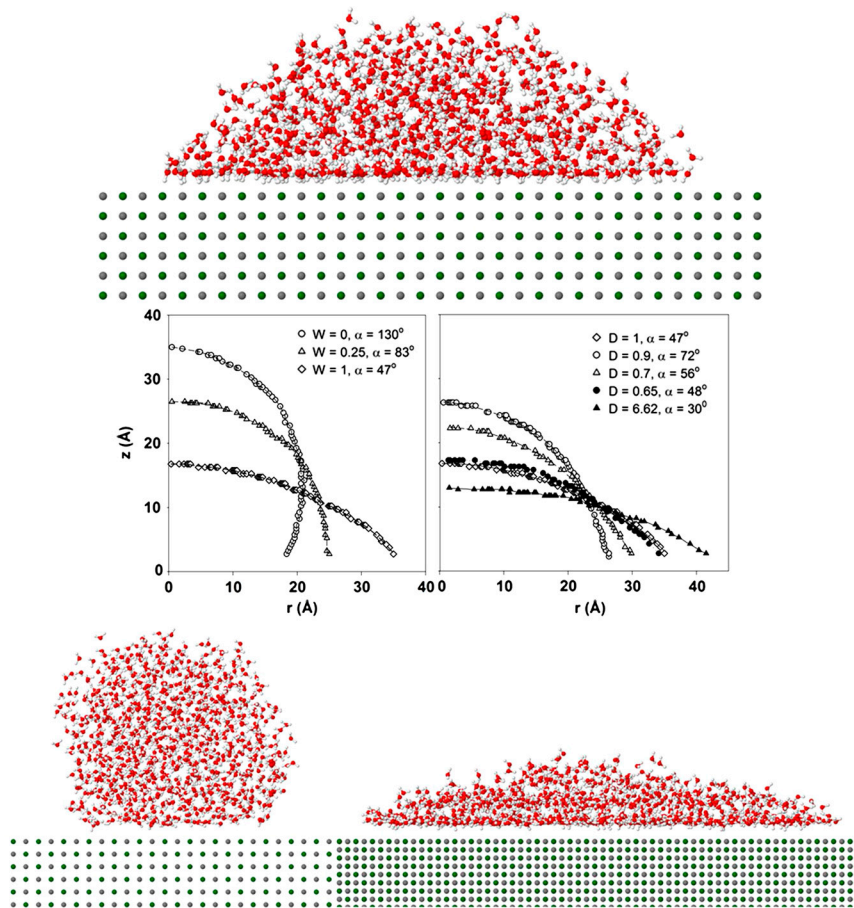
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**Fig. 1.** (Top) Simulation snapshot for one droplet of 1,000 SPC/E water molecules on MgO, showing that water wets the solid surface (water dissociation is not allowed). (Middle) Drop profiles obtained from simulation of water droplets on the various surfaces considered. As  $W$  decreases (Left) the contact angle systematically increases leading to hydrophobic substrates. As  $D$  decreases (Right) the contact angle changes, but not monotonically. In general the substrates remain hydrophilic, but when  $D = 0.62$  very hydrophobic surfaces are obtained. (Bottom) Simulation snapshots for the most hydrophobic (Left,  $W = 0$ , contact angle approximately  $130^\circ$ ) and the most hydrophilic (Right,  $D = 0.62$ , contact angle approximately  $30^\circ$ ) substrates considered herein.

very hydrophilic surface. It is worth mentioning that the distance between Mg and O atoms in MgO is 0.21 nm, less than the diameter of one SPC/E water molecule. Thus all surfaces considered here are atomically smooth.

In Fig. 1, Middle, we show the drop profiles used to calculate the contact angles from our simulations as  $W$  and  $D$  vary. Macroscopically, the MgO surface, originally hydrophilic, becomes hydrophobic when  $W$  decreases. The contact angle changes non monotonically as  $D$  decreases, although remaining in all cases lower than  $90^\circ$  (consistent with hydrophilic surfaces), and reaches approximately  $30^\circ$  when  $D = 0.62$ . The nonmonotonic dependence of the contact angle with changes in  $D$  is found to depend on the structure of interfacial water, as detailed in *SI Text, section 1*, consistently with MD results reported by Giovambattista et al. (27) and by Lee and Rosky (28) for water on various model surfaces.

In Fig. 2, Upper Left, we report one simulation snapshot to illustrate the protocol implemented for determining the presence/absence of liquid slip (details in Appendix). To investigate the presence/absence of liquid slip one could implement either the Couette or the pressure-driven Poiseuille flow. Hydrodynamic slip is independent of the flow type (29). Following Thompson and Troian (14), we simulate a Couette flow. Two parallel mirror-image solid surfaces are displaced along the  $Z$  axis. The bottom surface is maintained at a fixed location. The top surface is displaced along the  $X$  direction with a constant velocity,  $v_X = 100$  m/s. Admittedly, the resultant shear rate, which is limited by the current state-of-the-art computational resources, is much higher than shear rates typically explored experimentally (30), yet comparable to those

found in high performance lubrication applications such as rocket engines and computer disk drives (31). Nevertheless, important insights can be attained from simulations, as shown, for example, by Martini et al. (22). In most simulations reported here the atoms within the solid are maintained rigid. To ensure that this simplification does not introduce spurious effects (32), we conducted representative simulations in which the surface atoms vibrate, while maintaining the entire system at the desired temperature. No statistically significant differences were observed between the results obtained for MgO. It should also be pointed out that the Couette-type simulations are initiated after the thin film of water confined within the slit-shaped pores has been equilibrated at ambient conditions. Consequently, liquid water wets all surfaces considered in the nonequilibrium simulations discussed herein.

At steady states the water molecules confined in the gap between the two surfaces manifest a characteristic velocity profile  $[v_{w,X}(z)]$ . In Fig. 2, Upper Right, we show the oxygen atomic density profile and the velocity profile for water molecules as a function of their  $Z$  position. The reference  $z = 0$  is the center atomic position of the top layer of the bottom surface. The temperature is maintained at 300 K, as in all other cases. The surfaces considered are MgO. The results show that the contact water layer at  $z = 2.5$  Å has the same velocity as the immobile surface. This observation confirms that MgO shows no liquid slip, in qualitative agreement with the contact angle of approximately  $47^\circ$ , denoting hydrophilic properties. In Fig. 2, Lower, we compare the velocity profiles for confined water molecules as a function of their position within the slit-shaped pore when  $W$  (Left) and  $D$  (Right) de-









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