



## FRONTIERS ARTICLE

## Attraction between hydrated hydrophilic surfaces

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## ABSTRACT

According to common knowledge, hydrophilic surfaces repel via hydration forces while hydrophobic surfaces attract, but mounting experimental evidence suggests that also hydrophilic surfaces can attract. Using all-atom molecular dynamics simulations at prescribed water chemical potential we study the crossover from hydration repulsion to hydrophobic attraction for planar polar surfaces of varying stiffness and hydrogen-bonding capability. Rescaling the partial charges of the polar surface groups, we cover the complete spectrum from very hydrophobic surfaces (characterized by contact angles  $\theta \simeq 135^\circ$ ) to hydrophilic surfaces exhibiting complete wetting ( $\theta = 0^\circ$ ). Indeed, for a finite range  $\theta_{\text{adh}} < \theta < 90^\circ$ , we find a regime where hydrophilic surfaces attract at sub-nanometer separation and stably adhere without intervening water. The adhesive contact angle  $\theta_{\text{adh}}$  depends on surface type and lies in the range  $65^\circ < \theta_{\text{adh}} < 80^\circ$ , in good agreement with experiments. Analysis of the total number of hydrogen bonds (HBs) formed by water and surface groups rationalizes this crossover between hydration repulsion and hydrophilic attraction in terms of a subtle balance: Highly polar surfaces repel because of strongly bound hydration water, less polar hydrophilic surfaces attract because water–water HBs are preferred over surface–water HBs. Such solvent reorganization forces presumably underlie also other important phenomena, such as selective ion adsorption to interfaces as well as ion pair formation.

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## 1. Introduction

When immersed in water, particles and extended surfaces are subject to numerous mutual interactions, the two most important are the electric double layer force and the van-der-Waals force, summed up in the classical Derjaguin–Landau–Verwey–Overbeek (DLVO) theory. In situations when the surface charge is small and thus electrostatic interactions can be neglected, additional water-mediated interactions become important and have been at the focus of research for decades [1–4]. The nature of these water-induced non-DLVO interactions depends crucially on the surface polarity and is typically classified by the surface contact angle  $\theta$ .

For hydrophobic planar surfaces, that is, for contact angles  $\theta > 90^\circ$  according to the standard definition (which we adopt in this paper), the surface–water interfacial free energy  $\gamma_{\text{sw}}$  is higher than the surface–vapor interfacial free energy  $\gamma_{\text{sv}}$ : consequently,

for surface separations  $D$  smaller than a critical value  $D_{\text{cav}}$  the inter-surface water slab is unstable with respect to the cavitated state and in equilibrium vapor is expected to replace all liquid in between the surfaces [5–7]. Since, however, the kinetic barrier for this dewetting transition is prohibitively high [8–10], in careful experiments where contaminations and gas bubbles are avoided, the metastable water-filled state is observed for extended measurement times all the way down to separations of a few nanometers [11–13], much smaller than the equilibrium instability expected at  $D_{\text{cav}} \simeq 500$  nm for atmospheric pressure and a contact angle of  $\theta \approx 110^\circ$  characteristic of hydrocarbon–water interfaces. The concept of the hydrophobic force refers to all processes where hydrophobic molecules and particles aggregate in water and in particular is invoked as the driving force behind the ubiquitous processes of micellisation, oil–water demixing, and protein folding. It is not clear, however, whether and how the cavitation phenomena that occur between planar hydrophobic surfaces are connected to the mechanism of how single hydrophobic molecules aggregate [14,15]. Likewise, a good fraction of the literature discussion is concerned with contamination artifacts, secondary effects such as bubble formation and deformation, surface instabilities, as well as kinetic effects, see Refs. [11–13] for in-depth discussions. Recent theoretical research in this area focuses on various aspects of water

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structure and dynamics at hydrophobic surfaces and its influence on aggregation phenomena [16,17].

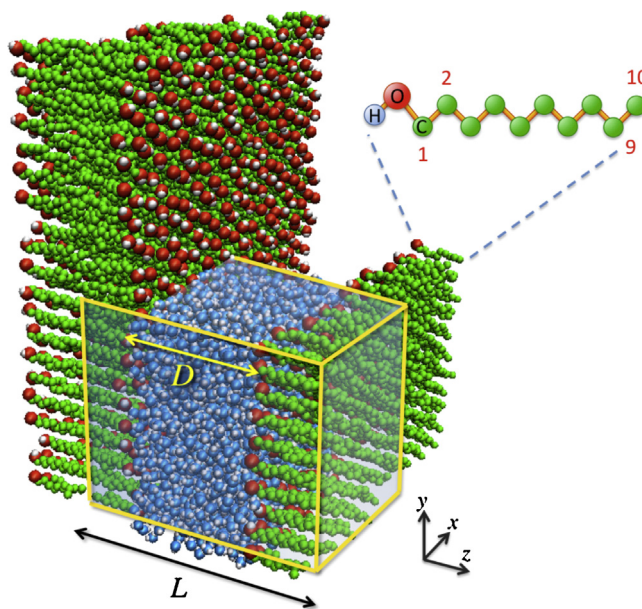
On the other side of the spectrum, hydrophilic surfaces that possess ample polar surface groups are characterized by contact angles  $\theta < 90^\circ$ , they frequently exhibit complete wetting behavior characterized by a vanishing contact angle  $\theta = 0^\circ$ . Such surfaces repel each other when immersed in water via the so-called hydration force, which becomes dominant at short separations on the nanometer range [1,4]. The probably best studied system is a stack of lipid bilayers, where the complete force–distance curve has been experimentally determined by measuring carefully the periodic bilayer repeat distance as a function of the applied osmotic or hydrostatic pressure [18]. In an often controversial discussion several different mechanisms for the so-called hydration repulsion were proposed: removal of surface-bound water molecules [1,19], reduction of the configurational entropy of surface groups [20,21], and the unfavorable overlap of interfacial water ordering profiles [22,23]. Recent simulation work suggests that more than one mechanism conspire for the case of the repulsion between DPPC bilayers [24].

The intense discussion on the underlying mechanism of the hydration repulsion, which is universally found to act between all different kinds of polar surfaces overshadowed a simpler and much more fundamental question: why do polar surfaces repel at all in water and why do they not form inter-surface hydrogen bonds (HBs) that would induce attractive forces? There are many examples of aggregation phenomena that are argued to be caused by inter or intramolecular HBs, such as nucleic base pairing or beta sheet and alpha helix formation in proteins, so why is it that surfaces covered by many polar groups tend not to form stabilizing HBs between themselves? As a matter of fact, a handful experiments demonstrated that even polar surfaces attract each other in a small range of contact angles above roughly  $\theta_{\text{adh}} \simeq 65^\circ$ . The first experiments were based on force measurements between symmetric self-assembled monolayers with contact angles finely tuned by adjusting the proportion of non-polar and polar surface groups [25–27], subsequent experiments considered the adsorption of proteins [28], single peptide chains [29], or the settlement of entire marine organisms [28] on surfaces with continuously varying contact angles. In all measurements, adsorption was found for surface contact angles above  $\theta_{\text{adh}} \simeq 65^\circ - 80^\circ$ ,  $\theta_{\text{adh}}$  is in some literature argued to constitute a universal threshold [30]. The question therefore is whether a regime of attraction between weakly hydrophilic surfaces in a finite contact angle range  $\theta_{\text{adh}} < \theta < 90^\circ$  universally exists and whether this attraction is more like a remnant hydrophobic attraction or due to the favorable interaction of polar surface groups.

Atomistic simulations including explicit water are well-suited to tackle this question. Our large scale MD simulations of the force–distance relation between different polar surfaces demonstrate that indeed an intermediate regime of hydrophilic attraction necessarily exists, the threshold angle  $\theta_{\text{adh}}$  and thus the width of this regime is determined by the adhesion free energy in vacuum. Our analysis reveals the hydrogen bonding capability of the polar surface groups as the microscopic mechanism behind the crossover between hydrophilic attraction and hydration repulsion: increasing the surface polarity strengthens the surface–water HBs more than the surface–surface HBs and therefore hydrophilic attraction occurs strictly above (and not below) a threshold contact angle  $\theta_{\text{adh}}$ .

## 2. Results and discussions

We simulate two surfaces, which consist of a total of  $N_s = 200$  hydroxyl-terminated alkane chains with periodic boundary conditions at different fixed box heights  $L$ , see Figure 1 for a snapshot of the simulation box. We use our thermodynamic extrapolation



**Fig. 1.** Simulation snapshot of surfaces type I for charge rescaling factor  $\alpha = 1$  at surface separation  $D = 2.7$  nm. The  $N_w = 2047$  water molecules are only shown in the primary simulation box indicated by yellow lines with the height  $L = 5.3$  nm. The periodically replicated surfaces are included and consist of a total of  $N_s = 200$  alkane molecules with hydroxyl head groups arranged in a hexagonal lattice, restraining potentials act on selected atoms, see Table 1 for details.

method to adjust the water molecule number  $N_w$  between the surfaces according to the prescribed chemical potential of bulk water at  $T = 300\text{K}$  and  $p_0 = 1\text{bar}$  [24]. We consider four surface types that are subject to different restraining potentials and thus differ in their stiffness and head group configurational freedom, rendering varying hydrogen-bonding capability (see Section 4 and Table 1). The type I surface is the stiffest and mimics a frozen structure, only for this surface we restrain the head-group hydrogen and thereby modify hydrogen bonding. Surface type III has a smaller head-group size and therefore is very efficient in forming surface–surface hydrogen bonds. Surface type IV has the smallest vertical restraining potential and is the softest surface, while surface II has intermediate properties. For each surface type, we consider a broad range of contact angles. In order to avoid complications due to inhomogeneous surface structures, we do not mix polar and non-polar surface groups; rather, we tune the surface polarity by scaling the polar surface group partial charges by a factor  $\alpha$ , following earlier work [31]. We thus consider a total of 28 different surfaces that reflect the wide range of experimental surface structures and chemistries. For each surface we calculate the complete force–distance relation and determine the contact angle  $\theta$  by thermodynamic integration of the intervening water slab, which gives higher numerical accuracy than the pressure tensor or droplet method (see SI for details).

### 2.1. Density profiles

Figure 2 shows water density profiles as well as surface oxygen distributions at large surface distance for (a) the softest surface type IV and (b) the stiffest surface type I, in each graph we compare the most polar surface (charge rescaling factor  $\alpha = 1$ ) and the completely non-polar variant ( $\alpha = 0$ ). The surface stiffness is characterized by the width  $\sigma_z$  of the oxygen head-group distribution, given by  $\sigma_z = 0.03$  nm for the stiff surface type I and  $\sigma_z = 0.18$  nm for the soft surface type IV and only mildly depends on  $\alpha$  as seen in Figure 2. Due to the high stiffness of surface type I, the water density exhibits pronounced layering, while for the soft type IV the water

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