

Supporting Information: Water-Mediated Interactions between Hydrophilic and Hydrophobic Surfaces

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CONTENTS

A	Simulation details	1
B	Evaluating wetting coefficients	1
C	Interaction pressure at prescribed chemical potential	2
	C.1 Measuring chemical potential	2
	C.2 Thermodynamic extrapolation via particle number (N_w) adjustment	3
	C.3 Thermodynamic extrapolation via volume (V) adjustment	3
D	The relation between density profiles and pressure–distance curves	3
	References	4

A. SIMULATION DETAILS

We use the SPC/E water model¹ and united-atom parameters taken from the GROMOS forcefield for the chains.² The molecular dynamics simulations are carried out using the GROMACS simulation suite³ in the canonical constant-volume (N_wVT) ensemble with periodic boundary conditions at $T = 300$ K maintained by the Berendsen thermostat with a time constant of 1 ps⁴ and an integration time step of 2 fs. Lennard-Jones interactions are shifted by a constant offset such that they are zero at their cutoff distance $r_c = 0.9$ nm. Electrostatics

is treated using Particle-Mesh-Ewald (PME) methods^{5,6} with a 0.9 nm real-space cutoff. Prior to the production runs, the systems are equilibrated for at least 1 ns. Production runs for each separation have a duration of 60 ns. Simulations for the thermodynamic integration used for measurements of the Coulomb part of the water chemical potential have a cumulative duration time of 400 ns per surface separation.

B. EVALUATING WETTING COEFFICIENTS

We evaluate the wetting coefficients k_w of the surfaces via the Thermodynamic Integration (TI) technique as follows. Consider a system of two parallel surfaces separated by a large distance D in vacuum, such that they do not interact with each other. We transfer N_w water molecules from a hypothetical bulk water phase into the interlamellar region at fixed temperature. The corresponding free energy change of this transfer is $\mu(N_w)dN_w$, where $\mu(N_w)$ is the chemical potential of the water in the interlamellar region and depends on the number of water molecules. At the same time, we have removed dN_w water molecules from the bulk, which reduces the free energy of the bulk by $-\mu_0dN_w$, with μ_0 being the bulk water chemical potential. The total change in the free energy of the entire system after transferring N_w molecules from the bulk into the initially empty interlamellar region is

$$\Delta F = \int_0^{N_w} \mu(N'_w)dN'_w - N_w\mu_0. \quad (\text{S1})$$

The chemical potentials μ and μ_0 can be decomposed into their respective ideal and excess parts,

$$\mu(N_w) = k_B T \log \frac{N_w}{V} + \mu^{\text{ex}}(N_w), \quad (\text{S2})$$

$$\mu_0 = k_B T \log \rho_w + \mu_0^{\text{ex}}, \quad (\text{S3})$$

where $\rho_w = 33.0 \text{ nm}^{-3}$ is the density and $\mu_0^{\text{ex}} = -29.03 \text{ kJ/mol}$ the excess chemical potential of bulk water. Inserting these two expressions into eq S1 and carrying out the integration of the ideal parts, yields the expression for the free energy change

$$\Delta F = N_w k_B T \left(\log \frac{N_w}{V \rho_w} - 1 \right) + F^{\text{ex}}(N_w) - N_w \mu_0^{\text{ex}}. \quad (\text{S4})$$

Here, we have introduced the excess free energy of the interlamellar water consisting of N_w molecules,

$$F^{\text{ex}}(N_w) = \int_0^{N_w} \mu^{\text{ex}}(N'_w) dN'_w. \quad (\text{S5})$$

This term we evaluate via the TI procedure⁷ as follows. First, consider an empty interlamellar region, into which we hypothetically insert N_w molecules of an ideal gas. The ideal gas molecules interact only with the surface molecules via the repulsive Lennard-Jones interactions. The interlamellar pressure after this insertion rises from 0 to p and thus imposes a work of $(1/2)p\Delta V$ on the surfaces, with ΔV being the increase in the interlamellar volume due to compression of the surface layers. In the next step, we transform the ideal gas molecules into water molecules. Introducing a coupling parameter $\lambda \in [0, 1]$ that gradually switches the water interactions in the Hamiltonian $U(\lambda)$ from an ideal gas (for $\lambda = 0$) to liquid water (for $\lambda = 1$), the excess part of interlamellar water can be computed as

$$F^{\text{ex}}(N_w) = \int_0^1 \left\langle \frac{\partial U(\lambda)}{\partial \lambda} \right\rangle_\lambda d\lambda + \frac{1}{2} p \Delta V. \quad (\text{S6})$$

Here, the first term, stemming from TI, represents the dominant contribution. The pressure correction $(1/2)p\Delta V$ in the second term accounts in our case for less than around 0.1 of the final value of the wetting coefficients.

Performing the simulations with identical surfaces and obtaining the corresponding cavitation free energy ΔF , eq S4, the wetting coefficient for a given polarity is according to eq 3 in the main text given as $\Delta F/A = -2\gamma k_w$.

C. INTERACTION PRESSURE AT PRESCRIBED CHEMICAL POTENTIAL

Our simulations are all performed in the $N_w VT$ ensemble, where the number of water molecules is fixed. The water chemical potential and the pressure are state functions of the independent quantities, $p(N_w, V, T)$ and $\mu(N_w, V, T)$. While the simulation pressure can be measured via the virial as implemented in the GROMACS package, measuring the chemical potential represents a more demanding task, which we describe in the following.

C.1. Measuring chemical potential. In order to achieve a pressure accuracy of $\delta p \approx \pm 10 \text{ bar}$ at large surface distances, the chemical potential of water has to be determined with an accuracy of $\delta \mu = \delta p / v_\mu \approx \pm 0.02 \text{ kJ/mol}$, with $v_\mu = 0.03 \text{ nm}^3$ being the partial volume of a water molecule at given chemical potential, eq 7 in the main text, which is a challenging task. The chemical potential of water between the surfaces is composed of three contributions,

$$\mu = k_B T \log \rho(z) + \mu_C(z) + \mu_{\text{LJ}}(z). \quad (\text{S7})$$

The first term is the ideal contribution, where $\rho(z)$ corresponds to the density of interlamellar water at position z . The other two terms correspond to the excess Coulomb and Lennard-Jones (LJ) contributions, respectively. In thermodynamic equilibrium, the total chemical potential μ is independent of the position z , therefore it can be evaluated at an arbitrary position. The SPC/E water model, which we use in the simulations, has only one LJ interaction site, therefore it is convenient to evaluate μ_{LJ} by the Widom Test Particle Insertion method (TPI).⁸ Here it should be noted that for consistent evaluation of the LJ energies, the shifted LJ potentials should be used. The reason lies in the fact that the particle trajectories in MD are generated by computing the forces from potentials, and therefore any potential that is cut off behaves as being effectively shifted. This fact was disregarded in Ref. [9], which leads to tiny differences in the hydration pressures. The Coulomb interaction of a water molecule consists of three sites. Because of well-known convergence issues of the TPI method in this case, it is more efficient to determine μ_C by the Thermodynamic Integration (TI) method.^{7,10} Once the chemical potential in the simulation is known, its deviation from the reference chemical potential of bulk water μ_0 at ambient conditions can be quantified. Due to the chemical potential mismatch, the simulation normal pressure p does, of

course, not correspond to the desired interaction. The chemical potential in the simulations can be controlled in two ways, namely, by adjusting the number of water molecules N_w , or by adjusting the volume V of the simulation box. In either case, we are interested in the relation between the chemical potential $\mu(N_w, V, T)$ and the pressure $p(N_w, V, T)$. We now describe both possibilities. In the following, we discard all temperature dependencies from our notation.

C.2. Thermodynamic extrapolation via particle number (N_w) adjustment. The first possibility is to tune the chemical potential by changing the number of water molecules in the simulation. At fixed V and changing N_w , the quantities p and μ vary as

$$dp = \left(\frac{\partial p}{\partial N_w} \right)_V dN_w, \quad d\mu = \left(\frac{\partial \mu}{\partial N_w} \right)_V dN_w. \quad (\text{S8})$$

Eliminating N_w from the above relations, yields

$$\begin{aligned} dp &= \left(\frac{\partial p}{\partial N_w} \right)_V \left(\frac{\partial N_w}{\partial \mu} \right)_V d\mu \\ &= \left(\frac{\partial p}{\partial \mu} \right)_V d\mu = \frac{d\mu}{v_\mu}. \end{aligned} \quad (\text{S9})$$

This implies a relationship between the change in pressure and the change in chemical potential. The proportionality factor v_μ is the partial water volume at constant chemical potential,

$$\left(\frac{\partial p}{\partial \mu} \right)_V = \left(\frac{\partial N_w}{\partial V} \right)_\mu \equiv v_\mu^{-1}, \quad (\text{S10})$$

which is introduced by eq 7 in the main text and shown in Figure 5 in the main text.

The interaction pressure $p(\mu_0)$ at the prescribed chemical potential μ_0 can then be evaluated from the measured p and μ by linear extrapolation

$$p(\mu_0) = p + \frac{\mu_0 - \mu}{v_\mu}. \quad (\text{S11})$$

In general, the value v_μ is not a priori known, therefore, in order to evaluate the interaction pressure at given surface separation from the above relationship, at least two simulations with different N_w have to be performed. However, for large separations, where the partial volume v_μ is close to its bulk value, a single simulation often suffices.

The described TE approach via particle number adjustment, eq S11, is the method employed in this work.

C.3. Thermodynamic extrapolation via volume (V) adjustment. Another possibility to adjust the chemical potential is to change the volume V of the simulation box while leaving the number of water molecules unchanged. At fixed particle number N_w we can write

$$dp = \left(\frac{\partial p}{\partial V} \right)_{N_w} dV, \quad d\mu = \left(\frac{\partial \mu}{\partial V} \right)_{N_w} dV. \quad (\text{S12})$$

After eliminating V from both relations, we obtain

$$\begin{aligned} d\mu &= \left(\frac{\partial \mu}{\partial V} \right)_{N_w} \left(\frac{\partial V}{\partial p} \right)_{N_w} dp \\ &= \left(\frac{\partial \mu}{\partial p} \right)_{N_w} dp \\ &= v_p dp. \end{aligned} \quad (\text{S13})$$

Similarly as before, we obtain a linear relationship between the changes in p and μ , but this time with a proportionality factor being the partial water volume at constant pressure,

$$\left(\frac{\partial \mu}{\partial p} \right)_{N_w} = \left(\frac{\partial V}{\partial N_w} \right)_p \equiv v_p, \quad (\text{S14})$$

as already defined by eq 8 and shown in Figure 5 in the main text. As before, the interaction pressure at the prescribed chemical potential can be linearly extrapolated as

$$p(\mu_0) = p + \frac{\mu_0 - \mu}{v_p}. \quad (\text{S15})$$

In contrast to v_μ , the partial water volume at constant pressure v_p is technically simple to evaluate from MD simulations. Therefore, the interaction pressure $p(\mu_0)$ can in most cases be evaluated via eq S15 from a single measurement of chemical potential. This fact makes this approach, eq S15, advantageous over the previous one, eq S11.

D. THE RELATION BETWEEN DENSITY PROFILES AND PRESSURE-DISTANCE CURVES

At stiff surfaces, water molecules form ordered hydration layers, seen as oscillations in the density profiles in Figure 2a in the main text. The observed oscillatory nature of the water density profile can be described empirically in terms of a simple equation,

$$\rho(z) = \rho_0 + \rho_1 e^{-z/\lambda} \sin(kz + \delta z_p), \quad (\text{S16})$$

where ρ_0 , ρ_1 , λ , and δz_p are fitting parameters.

In Figure S1a we show the water density profile at a single type I surface with $\alpha = 1$ and the best fit of eq S16 by a red curve. The fit yields the decay length of the oscillatory density $\lambda = 0.19$ nm and the wave number $k = 26$ nm⁻¹. The corresponding oscillation period $2\pi/k = 0.24$ nm is of the size of a water molecule.

As has been shown in Ref. [9], the oscillations in the water density profiles imply on oscillatory behavior of the interaction pressure between two surfaces. The structure of the pressure–distance curve is rather complex, but for a simple comparison with the density profiles we assume the following form

$$p(z) = p_0 e^{-z/\lambda} \sin(kz + \delta z_p). \quad (\text{S17})$$

Adopting the fitting parameters λ and k from the density fit above, we now fit eq S17 with only p_0 and δz_p as free parameters to the pressure data points for $D > D_{\text{adh}}$ shown in Figure S1b.

As can be seen, the fitted pressure profile qualitatively follows the pressure data points. The density oscillation period satisfactorily matches the pressure oscillation behavior. The density decay length λ , on the other hand, does not describe well the decay length of the pressure.

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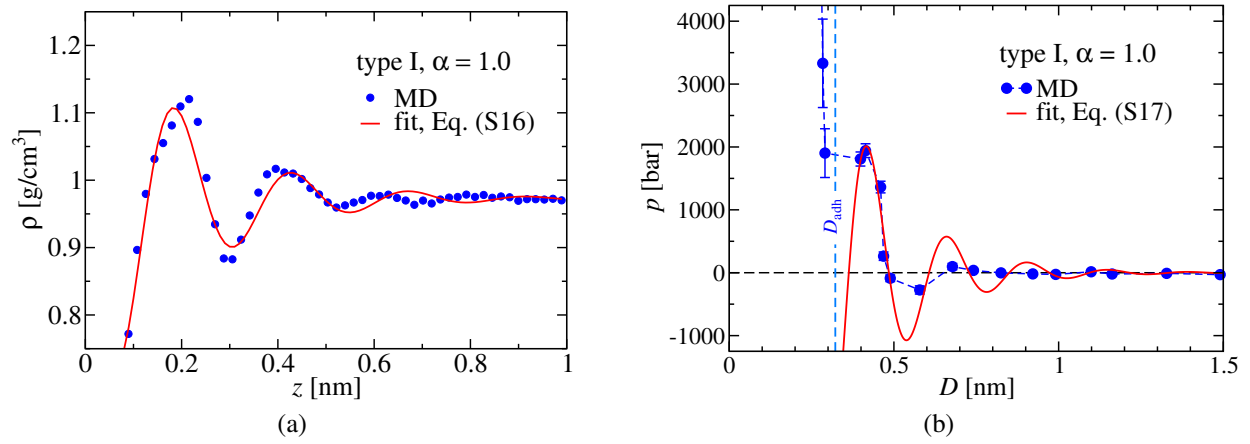


Figure S1: (a) Density profile of water at a stiff surface of type I with polarity $\alpha = 1$ (as in Figure 2a in the main text). The orange curve is the fit of eq S16 to the data points. (b) Interaction pressure between two identical surfaces of type I with polarities $\alpha = 1$ (as in Figure 3a in the main text). The red curve is the fit of eq S17 to the data points for $D > D_{adh}$, where the parameters λ and k are adopted from the density fit.