Supporting Information

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SI Text

Here, we describe the details of the solvation model used in the main text.

Interface Description. We describe the liquid–vapor-like interface next to the model surface by a periodic height function $h(\mathbf{a})$, with $\mathbf{a} = (x,y)$ and $-D/2 \le x,y < D/2$. This function is sampled discretely at a resolution Δ, at points satisfying

$$\mathbf{a} = (n_x\Delta, n_y\Delta), \qquad -\frac{D}{2\Delta} \le n_x, n_y < \frac{D}{2\Delta}.$$

This choice results in N^2 discrete sampling points $\{\mathbf{a}\}$, with $N = D/\Delta$. In the following, sums over $\mathbf{a}$ denote sums over these N^2 sampling points. We have used $D = 60$ Å and $\Delta = 1$ Å.

The discrete variables $\{h_\mathbf{a}\}$ represent the interface height at each sample point $\mathbf{a}$, so that

$$h_\mathbf{a} = h(\mathbf{a}), \quad \text{for } \mathbf{a} = (n_x\Delta, n_y\Delta).$$

This notation clearly distinguishes between the N^2 height variables $h_\mathbf{a}$ and the continuous height function $h(\mathbf{a})$ that they represent.

The discrete Fourier transform of $\{h_\mathbf{a}\}$ is denoted by $\{\tilde{h}_\mathbf{k}\}$ and is defined at wavevectors $\mathbf{k} = (2\pi/L)(m_x, m_y)$, with $-N/2 \le m_x, m_y < N/2$. We use the symmetric normalization convention throughout for Fourier transforms.

Energetics. The essential property of the liquid–vapor-like interface is its surface tension, which results in the following capillary-wave Hamiltonian (1) for a free interface,

$$H_0[\{h_\mathbf{a}\}] \approx \frac{\gamma\Delta^2}{2} \sum_\mathbf{a} |\nabla h_\mathbf{a}|^2 \approx \frac{\gamma\Delta^2}{2} \sum_\mathbf{k} k^2 |\tilde{h}_\mathbf{k}|^2,$$

where $\nabla h_\mathbf{a}$ is a finite-difference approximation to $\nabla h(\mathbf{a})$.

Using an appropriate definition of an instantaneous water–vapor interface (2), the power spectrum of capillary waves in the Simple Point Charge Extended (SPC/E) model of water has been found to agree with the spectrum predicted by the above Hamiltonian for wavevectors smaller than about $2\pi/\ell$, but is substantially lower for higher wavevectors (Fig. 5 of main text). This result is consistent with the liquid–vapor-like interface being sensitive to molecular detail at high wavevectors (3). At $T = 300$ K, we have found that $\ell \approx 9$ Å. We thus constrain all Fourier components $\tilde{h}_\mathbf{k}$ to be zero for high $\mathbf{k}$—i.e.,

$$\tilde{h}_\mathbf{k} = 0, \quad |\mathbf{k}| > 2\pi/\ell. \qquad \text{[S1]}$$

In our model, the liquid–vapor-like interface interacts with a model surface via a potential that depends on $\{h_\mathbf{a}\}$. As discussed below, it is also convenient to introduce additional umbrella potentials to aid in sampling. The Hamiltonian of the interface subject to this additional potential energy $H'[\{h_\mathbf{a}\}]$ is

$$H[\{h_\mathbf{a}\}] = \frac{\gamma\Delta^2}{2} \sum_\mathbf{k} k^2 |\tilde{h}_\mathbf{k}|^2 + H'[\{h_\mathbf{a}\}]. \qquad \text{[S2]}$$

When expressed as a function of the Fourier components $\{\tilde{h}_\mathbf{k}\}$, we denote the Hamiltonian by $\tilde{H}[\{\tilde{h}_\mathbf{k}\}]$ and the external potential by $\tilde{H}'[\{\tilde{h}_\mathbf{k}\}]$, so that

$$\tilde{H}[\{\tilde{h}_\mathbf{k}\}] = \frac{\gamma\Delta^2}{2} \sum_\mathbf{k} k^2 |\tilde{h}_\mathbf{k}|^2 + \tilde{H}'[\{\tilde{h}_\mathbf{k}\}].$$

Dynamics. We calculate thermal averages of interface configurations by introducing a fictitious Langevin dynamics and replacing thermal averages by trajectory averages. We first assign a mass per unit area μ to the interface. The Lagrangian in real space is

$$L[\{h_\mathbf{a}, \dot{h}_\mathbf{a}\}] = \frac{\mu\Delta^2}{2} \sum_\mathbf{a} \dot{h}_\mathbf{a}^2 - H[\{h_\mathbf{a}\}].$$

The corresponding Lagrangian in Fourier space is

$$\tilde{L}[\{\tilde{h}_\mathbf{k}, \dot{\tilde{h}}_\mathbf{k}\}] = \frac{\mu\Delta^2}{2} \sum_\mathbf{k} |\dot{\tilde{h}}_\mathbf{k}|^2 - \tilde{H}[\{\tilde{h}_\mathbf{k}\}].$$

Because all $h_\mathbf{a}$ are real, the amplitudes of modes $\mathbf{k}$ and $-\mathbf{k}$ are related, $\tilde{h}_\mathbf{k} = \tilde{h}_{-\mathbf{k}}^*$. Taking this constraint and Eq. S1 into account, the Euler–Lagrange equations yield equations of motion in Fourier space. To thermostat each mode, we add Langevin damping and noise terms. The final equation of motion has the form

$$\mu\Delta^2 \ddot{\tilde{h}}_\mathbf{k} = -\gamma\Delta^2 |\mathbf{k}|^2 \tilde{h}_\mathbf{k} - \frac{\partial \tilde{H}'[\{\tilde{h}_\mathbf{k}\}]}{\partial \tilde{h}_\mathbf{k}} - \eta\dot{\tilde{h}}_\mathbf{k} + \tilde{\xi}_\mathbf{k}(t), \quad (|\mathbf{k}| < 2\pi/\ell).$$

$$\text{[S3]}$$

The Langevin damping constant η is chosen to decorrelate momenta over a timescale τ, so $\eta = \mu\Delta^2/\tau$. The zero-mean Gaussian noise terms $\{\tilde{\xi}_\mathbf{k}(t)\}$ have variance such that

$$\langle \tilde{\xi}_\mathbf{k}^*(t)\tilde{\xi}_\mathbf{k}(t') \rangle = 2\eta k_B T \delta(t-t').$$

As with $\tilde{h}_\mathbf{k}$, $\tilde{\xi}_\mathbf{k}$ satisfy the related constraint $\tilde{\xi}_\mathbf{k} = \tilde{\xi}_{-\mathbf{k}}^*$. Hence, for $\mathbf{k} = \mathbf{0}$, the noise is purely real and its variance is twice that of the real and imaginary components of all other modes.*

We propagate these equations of motion using the Velocity Verlet algorithm. At each force evaluation, we use a fast Fourier transform (FFT) to calculate $\{h_\mathbf{a}\}$ from $\{\tilde{h}_\mathbf{k}\}$. We then calculate $\partial H'[\{h_\mathbf{a}\}]/\partial h_\mathbf{a}$ in real space and perform an inverse FFT to obtain the force $\partial \tilde{H}'[\{\tilde{h}_\mathbf{k}\}]/\partial \tilde{h}_\mathbf{k}$ on mode $\tilde{h}_\mathbf{k}$ due to $H'[\{h_\mathbf{a}\}]$. We then add the forces due to surface tension, Langevin damping, and thermal noise, as in Eq. S3.

For the Velocity Verlet algorithm to be stable, we choose a timestep equal to 1/20th of the typical timescale of the highest-frequency mode of the free interface, $\Delta t = \frac{1}{20}\sqrt{\mu\ell^2/\gamma}$. To equilibrate the system quickly but still permit natural oscillations, we choose the Langevin damping timescale so that $\tau = 100\Delta t$. Finally, we choose a value of μ close to the mass of a single water layer, $\mu = 100$ amu/nm^2.

This interface dynamics is entirely fictitious. However, it correctly samples configurations of the interface Boltzmann weighted by the Hamiltonian $H[\{h_\mathbf{a}\}]$, regardless of the exact values of μ, Δt, and τ, so our choices have no effect on the results in the main text. We have simply chosen reasonable values that do

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*The constraint on the magnitude of **k** ensures that no Nyquist modes (i.e., modes with k_x or k_y equal to $\pm\pi/D$) are ever excited. If they were included, these modes would also be purely real, and the variance of the real component of their noise terms would likewise be twice that of the real component of the interior modes.

not lead to large discretization errors when solving the system's equations of motion.

Surface-Interface Interactions. The liquid–vapor-like interface interacts with the model surface via a potential $H'_{\text{surf}}[\{h_{\mathbf{a}}\}]$. In the atomistic simulations, the self-assembled monolayer (SAM) sets up an interaction potential, $U(\mathbf{r})$, felt by the atoms in the water molecules. Below, we use the notation $\mathbf{r}$ and (x,y,z) interchangeably. To model this interaction potential, we smear out the atomistic detail of the SAM and replace it with three elements:

- A uniform area density μ_{head} of Lennard–Jones sites (with length and energy scales σ_{head} and ϵ_{head}) in the $z = 0$ plane to represent the SAM head groups.
- A uniform volume density ρ_{tail} of Lennard–Jones sites (with length and energy scales σ_{tail} and ϵ_{tail}) in the half-space $z < -\zeta$ to represent the SAM tail groups.
- Coarse-graining the head-group atoms into a uniform area density results in a softer repulsive potential allowing the interface to penetrate far deeper into the model surface than would be possible in the actual SAM. To rectify this artifact, we apply a strongly repulsive linear potential in the half-space $z < R_0$, where R_0 is the radius of the head-group's hard core. The repulsive potential is chosen to be 1 $k_{\text{B}}T$ when 1 nm^2 of interface penetrates the region $z < R_0$ by a "skin depth" δ.

The head groups are thus modeled by the following potential acting on a water molecule at position $\mathbf{r}$:

$$U_{\text{head}}(x,y,z \geq R_0)$$
$$= \mu_{\text{head}} \int_{-\infty}^{\infty} dx' \int_{-\infty}^{\infty} dy' u_{\text{LJ}}(|\mathbf{r}-\mathbf{r}'|; \epsilon_{\text{head}}, \sigma_{\text{head}})|_{z'=0},$$

where $u_{\text{LJ}}(r; \epsilon, \sigma) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6]$ is the Lennard–Jones pair potential. Similarly, the effect of the tail groups is captured by

$$U_{\text{tail}}(x,y,z \geq R_0)$$
$$= \rho_{\text{tail}} \int_{-\infty}^{\infty} dx' \int_{-\infty}^{\infty} dy' \int_{-\infty}^{-\zeta} dz' u_{\text{LJ}}(|\mathbf{r}-\mathbf{r}'|; \epsilon_{\text{tail}}, \sigma_{\text{tail}}).$$

Finally, the repulsive wall is modeled by the potential

$$U_{\text{wall}}(x,y,z < R_0) = 2\rho_\ell^{-1} \cdot (1\,k_{\text{B}}T / 1\,\text{nm}^2)(R_0 - z)/\delta,$$

where $\rho_\ell = 0.03333$ Å^{-3} is the number density of liquid water. These smeared interaction potentials depend only on z, not on x or y. As described in the main text, we also scale the head-group interaction by a parameter η. Putting everything together, we obtain an explicit expression for the surface-interface interaction potential,

$$H'_{\text{surf}}[\{h_{\mathbf{a}}\}] = \rho_\ell \Delta^2 \sum_{\mathbf{a}} h'_{\text{surf}}(h_{\mathbf{a}}),$$

where

$$h'_{\text{surf}}(h_{\mathbf{a}}) = \int_{h_{\mathbf{a}}}^{\infty} dz\, \eta U_{\text{head}}(z) + U_{\text{tail}}(z) + U_{\text{wall}}(z),$$

$$= \begin{cases} \eta \pi \epsilon_{\text{head}} \mu_{\text{head}} \sigma_{\text{head}}^3 \left[\frac{4}{45}(\sigma_{\text{head}}/z)^9 - \frac{2}{3}(\sigma_{\text{head}}/z)^3 \right] \\ \quad + \pi \epsilon_{\text{tail}} \rho_{\text{tail}} \sigma_{\text{tail}}^4 \left[\frac{1}{90}(\sigma_{\text{head}}/[z+\zeta])^8 - \frac{1}{3}(\sigma_{\text{head}}/[z+\zeta])^2 \right], & z \geq R_0, \\ h'_{\text{surf}}(R_0) + \rho_\ell^{-1} \cdot (1k_{\text{B}}T / 1\,\text{nm}^2)([R_0 - z]/\delta)^2, & z < R_0. \end{cases}$$

To model the $-\text{CH}_3$ SAM in this paper, we chose the following values for the parameters:

- The head groups are modeled as Optimized Potential for Liquid Simulations (OPLS) united-atom CH$_3$ groups interacting with SPC/E water, so $\sigma_{\text{head}} = 3.5355$ Å and $\epsilon_{\text{tail}} = 0.68976$ kJ/mol.
- The tail groups are modeled as OPLS united-atom CH$_2$ groups (sp^3 hybridized) interacting with SPC/E water, so $\sigma_{\text{tail}} = 3.5355$ Å and $\epsilon_{\text{tail}} = 0.5664$ kJ/mol.
- The tail region is inset from the plane of the head groups by a distance equal to a CH$_2$-CH$_3$ bond length (1.50 Å), minus the van der Waals radius of a CH$_2$ group (1.9525 Å), so $\zeta = -0.4525$ Å.
- The head-group density is known from the atomistic SAM geometry to be $\mu_{\text{head}} = 0.0462$ Å^{-2}. The mass density of the SAM tails was estimated to be 935 kg/m^3 (4), resulting in a CH$_2$ group number density of $\rho_{\text{tail}} = 0.0402$ Å^{-3}.
- The equivalent hard sphere radius R_0 of a $-\text{CH}_3$ group at room temperature was estimated to be 3.37 Å (5). It has a small temperature dependence, which we neglect.
- The wall skin depth δ was set to 0.1 Å, which is small enough so that the repulsive potential is essentially a hard wall at $z = R_0$, but large enough that we can propagate the interfacial dynamics with a reasonable timestep.

Umbrella Sampling. Calculating $\mu^{\text{ex}}(V)$ from Eq. 5 of the main text as a thermal average $\langle P_v(0) \rangle$ over Boltzmann-weighted configurations of $h(\mathbf{a})$ is impractical for large V. The configurations that dominate this average simply have a vanishingly small Boltzmann weight. To solve this problem, and in analogy to what we do in atomistic simulations, we perform umbrella sampling on the size of the subvolume v of the probe cavity V that is above the interface.

We begin by defining the volume V corresponding to a probe cavity of dimensions $L \times L \times W$ as the set of points satisfying $|x|, |y| \leq L/2$ and $R_0 \leq z \leq R_0 + W$. We then define $v[\{h_{\mathbf{a}}\}]$ as the size of the subvolume of V that is above the interface. Using umbrella sampling and the multistate Bennet acceptance ratio method (6), we calculate the probability distribution for v, $P(v)$, down to $v = 0$. We use quadratic umbrellas defined by a center $\bar{v}$ and width $(\delta v)^2$, which result in the addition to the Hamiltonian of

$$H'_{\text{umb}}[\{h_{\mathbf{a}}\}] = k_{\text{B}}T \frac{(v[\{h_{\mathbf{a}}\}] - \bar{v})^2}{2(\delta v)^2}.$$

During each umbrella run, we also record the configurations $\{h_{\mathbf{a}}\}$, which yield each observed value of v. We then approximate the right-hand side of Eq. **5** in the main text by summing over these configurations with appropriate weights, and we obtain

$$\mu^{\text{ex}}(V) \approx -k_{\text{B}}T \ln \frac{\sum_{\{h_{\mathbf{a}}\}} P_v(0) P(v[\{h_{\mathbf{a}}\}])}{\sum_{\{h_{\mathbf{a}}\}} P(v[\{h_{\mathbf{a}}\}])},$$

where, as in the main text, the term $P_v(0)$ depends on the interface configuration $\{h_{\mathbf{a}}\}$, and the sum $\{h_{\mathbf{a}}\}$ is over all interface configurations in all the different umbrellas. To evaluate $P_v(0)$, we implement discrete versions of the integrals defining $\langle N \rangle_v$ and σ_v as was done in ref. 7.

1. Buff F, Lovett R, Stillinger FH (1965) Interfacial density profile for fluids in the critical region. *Phys Rev Lett* 15:621–623.

2. Willard AP, Chandler D (2010) Instantaneous liquid interfaces. *J Phys Chem B* 114:1954–1958.

3. Sedlmeier F, Horinek D, Netz RR (2009) Nanoroughness, intrinsic density profile, and rigidity of the air-water interface. *Phys Rev Lett* 103:136102.
4. Godawat R, Jamadagni SN, Garde S (2009) Characterizing hydrophobicity of interfaces by using cavity formation, solute binding, and water correlations. *Proc Natl Acad Sci USA* 106:15119–15124.
5. Patel AJ, Varilly P, Chandler D (2010) Fluctuations of water near extended hydrophobic and hydrophilic surfaces. *J Phys Chem B* 114:1632–1637.
6. Shirts MR, Chodera JD (2008) Statistically optimal analysis of samples from multiple equilibrium states. *J Chem Phys* 129:124105.
7. Varilly P, Patel AJ, Chandler D (2011) An improved coarse-grained model of solvation and the hydrophobic effect. *J Chem Phys* 134:074109.