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Supplemental Material: Solute Adsorption at Air-Water Interfaces and Induced Interface Fluctuations: The Hydrophobic Nature of Ions?

Shu-Ching Ou, Di Cui, and Sandeep Patel*

Department of Chemistry and Biochemistry, University of Delaware, Newark, Delaware 19716, USA

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*Corresponding author. E-mail: sapatel@udel.edu

I. POTENTIAL OF MEAN FORCE: CONVERGENCE AND UNCERTAINTY

Figure S1 shows the comparison of potentials of mean force between nonpolarizable (with TIP3P) and Drude polarizable (with SWM4-NDP) force fields. The parameters were retrieved from CHARMM36 all-atom force field for simulations with TIP3P[1]; parameters for simulations using Drude Oscillator Model were from Ref[2]. For the same molecule, deeper minima are found using polarizable force fields; however, the values of $\Delta G_{\mathrm{vapor}} - \Delta G_{\mathrm{bulk}}$ (hydration free energy) are similar.

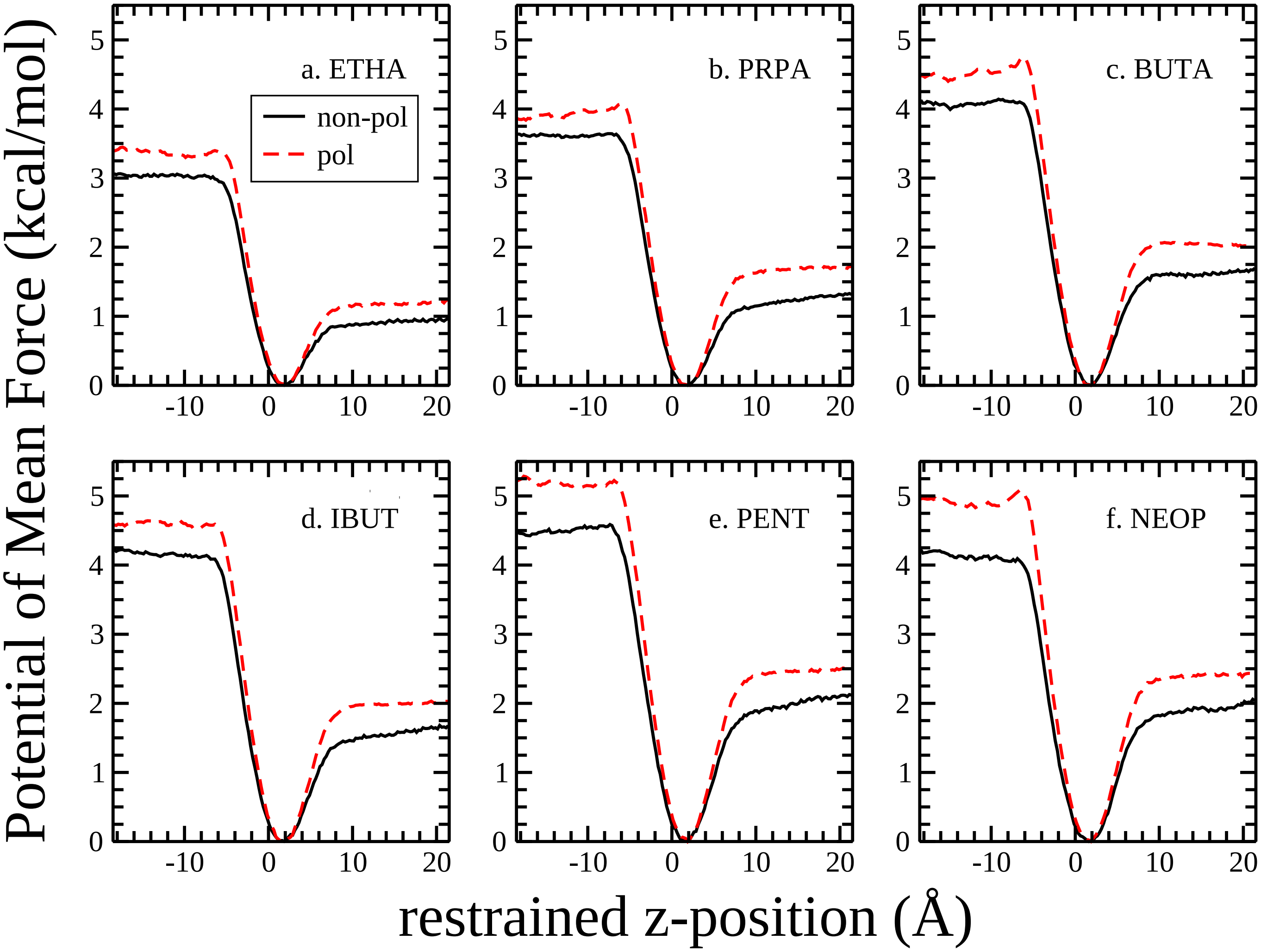

FIG. S1: Potential of mean force as a function of the z-position of a single alkane along the direction normal to the water surface.

The uncertainties in potentials of mean force are determined using the approach of Zhu and Hummer[3]:

$$\mathrm{var}[G(\xi_{\mathrm{N}})] \approx \sum_{i=1}^{N} \mathrm{var}[K\Delta\xi\bar{z}_{\mathrm{i}}] \tag{S1}$$

where $\bar{z}_{\mathrm{i}}$ is the mean position of z in the i_{th} window, which can be obtained from block averages[4]. K is the force constant. The corresponding standard deviation $\sigma[G(\xi_{\mathrm{N}})]$ is then the square root of $\mathrm{var}[G(\xi_{\mathrm{N}})]$. In this case, the alkane in the vapor ($z_{\mathrm{restrained}}$ = 22.0 Å) is set to be the reference state, therefore the window $z_{\mathrm{restrained}}$ = -18.0 Å is expected to have the largest uncertainty. Figure S2 shows the PMF along with the uncertainty of each window for single pentane in TIP3P. The largest uncertainties for the systems are approximately 0.15 kcal/mol. The inset shows the time profile of $\Delta G_{\mathrm{vapor}}$. As the collective sampling increases, $\Delta G_{\mathrm{vapor}}$ converges to the value of -2.09 kcal/mol.

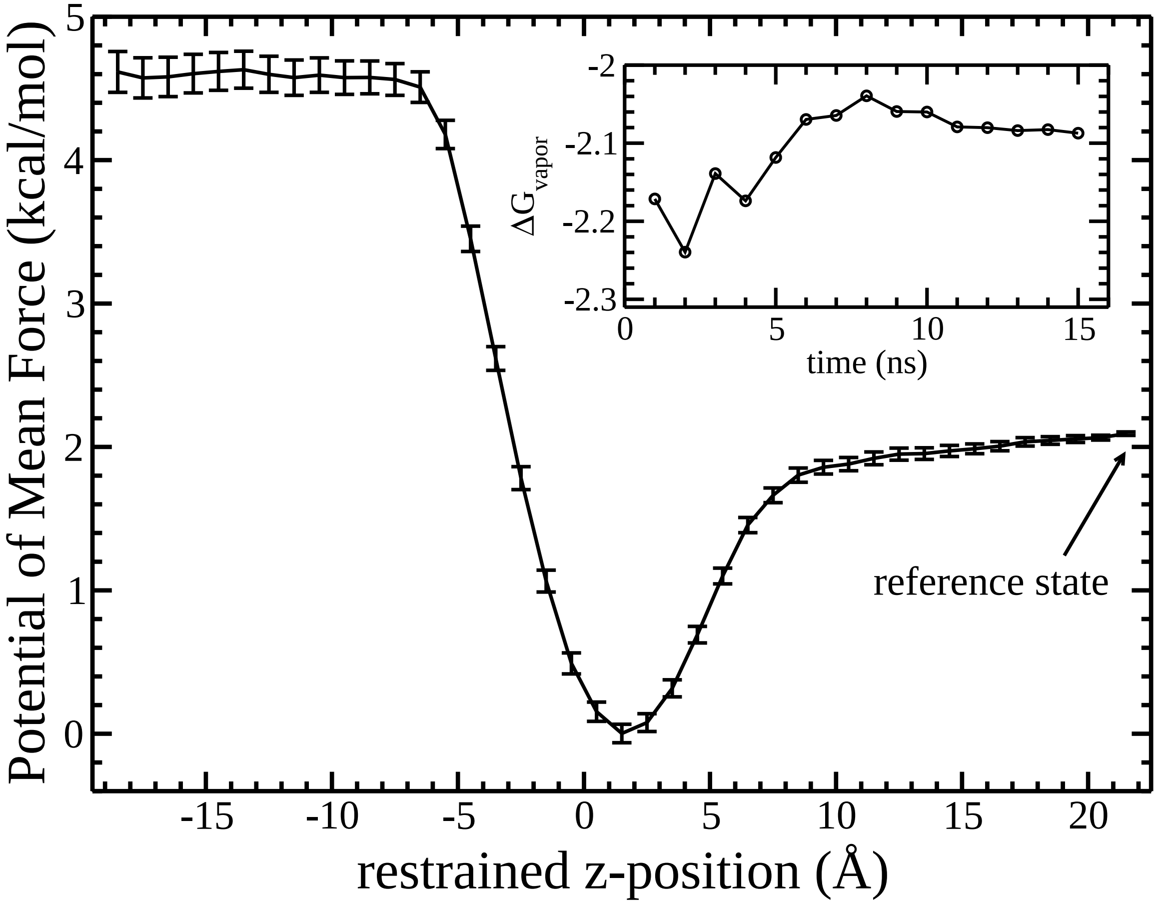

FIG. S2: Potential of mean force for single pentane along the direction normal to the water surface, using TIP3P water model. The inset shows the time profile of $\Delta G_{\mathrm{vapor}}$.

II. SINGLE IODIDE

Figure S3 shows the potential of mean force and the coordination number for single iodide along the direction normal to the water surface, using TIP4P-FQ water model. For simulation detail, refer to Reference[5]. From Figure S3a, iodide shows a lower free energy state when it resides at the bulk side. Even when the ion is restrained 25 Å away from GDS, there are still water surrounding the single iodide ion.

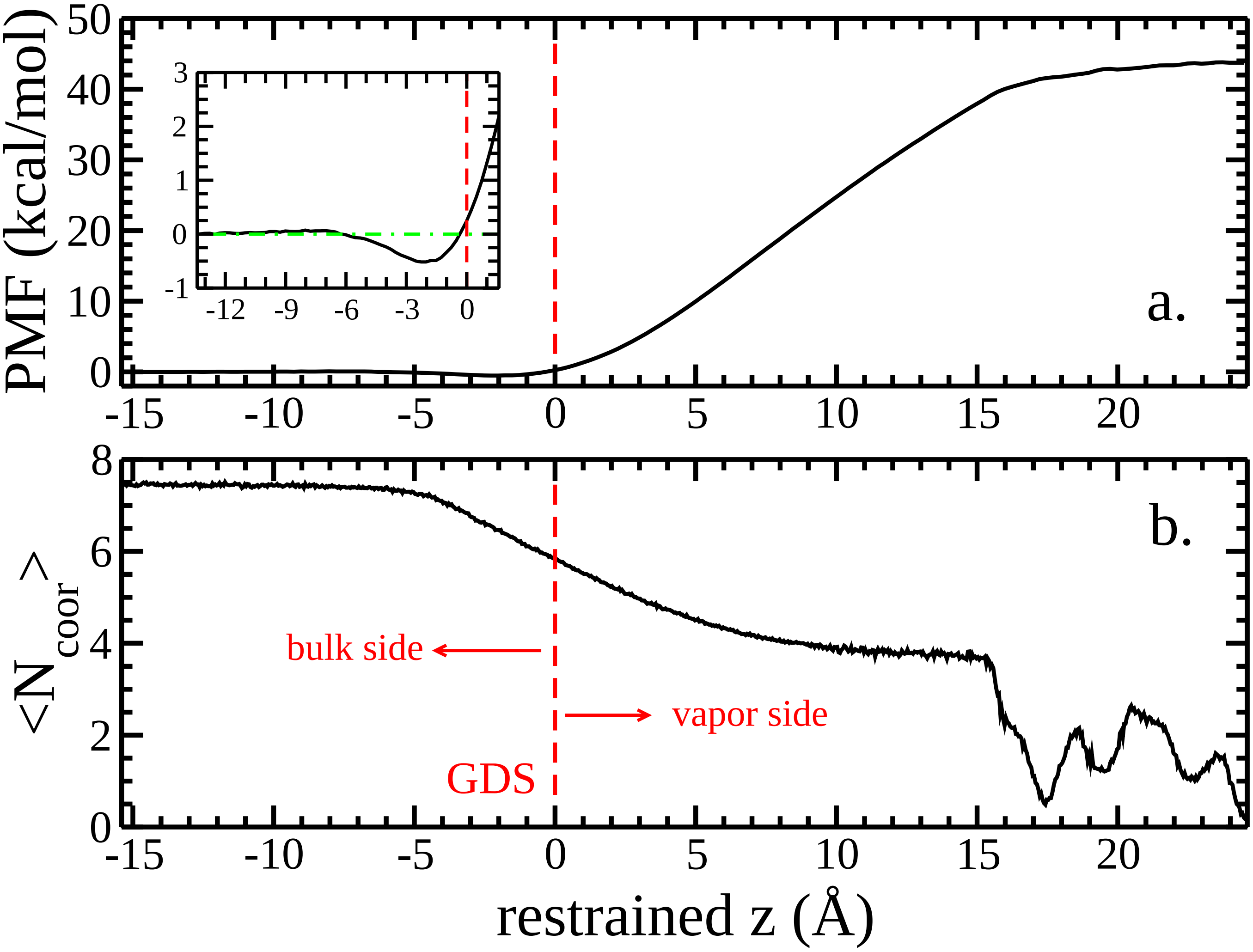

FIG. S3: (a) Potential of mean force for single iodide along the direction normal to the water surface, using TIP4P-FQ water model. Inset shows the profile near the PMF minimum. (b) The corresponding average coordination number.

III. FLUCTUATION PROFILES: SINGLE PENTANE

Figure S4 displays the height fluctuations (unnormalized) induced by single n-pentane at simulation windows z = -18.0, -6.0, -5.0, 0.0 Å. When z = -18.0 Å, the solute is too far from the air-water interface to induce any fluctuation, thus it gives a value that characterize the inherent fluctuation of pure TIP3P water (1.27 Å^2). When z = 0.0 Å, i.e., pentane is at the water surface, the fluctuation is suppressed. The geometry of the fluctuation profile $\langle \delta h^2(x,y) \rangle$ possesses radial symmetry. The convergence of fluctuation is displayed in Figure S5. The uncertainty can be estimated via block average[4]; the decorrelated uncertainty is less than 0.1 Å^2.

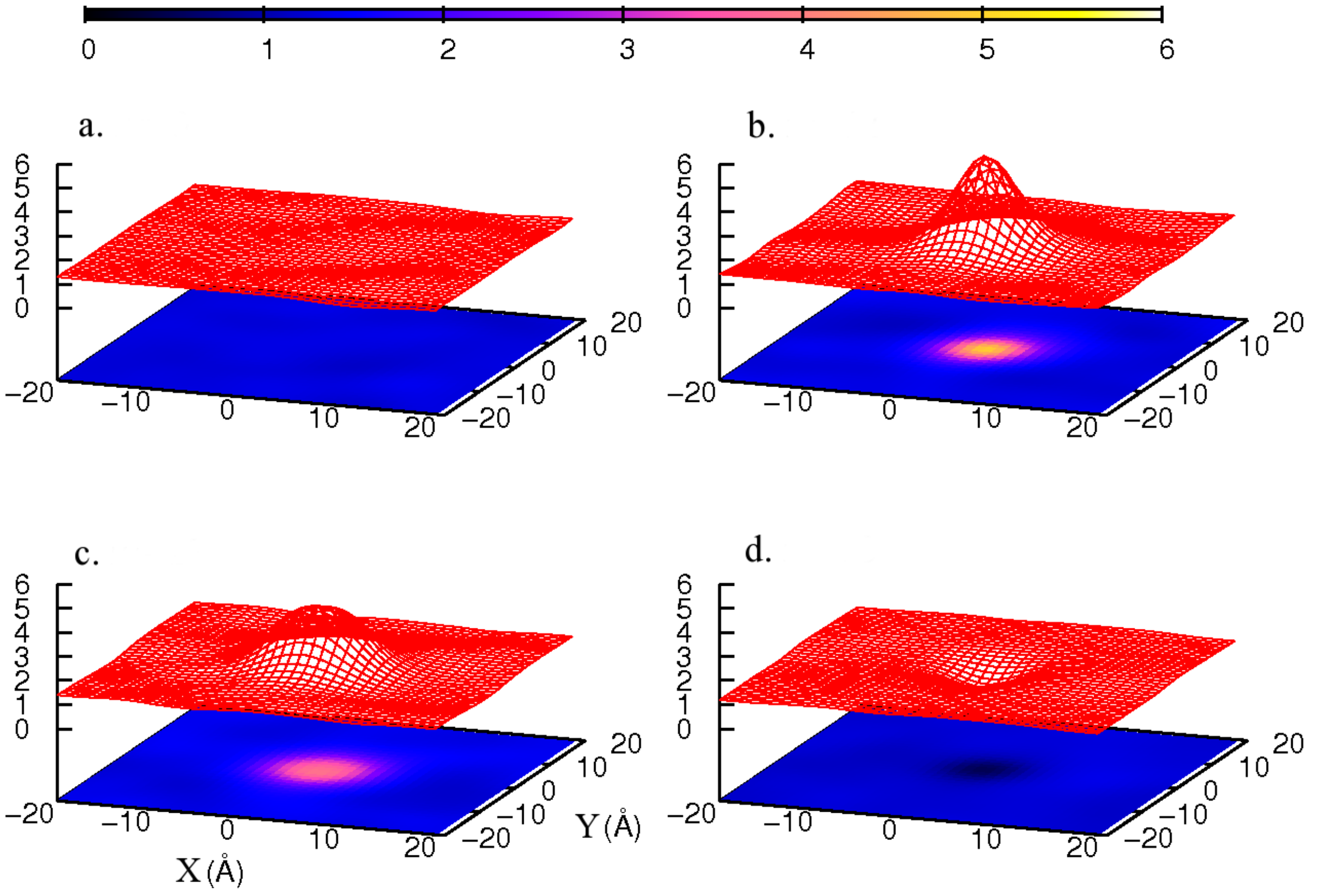

FIG. S4: Fluctuation profiles for single pentane (in TIP3P) at simulation windows z = -18.0, -6.0, -5.0, 0.0 Å. The unit is Å^2.

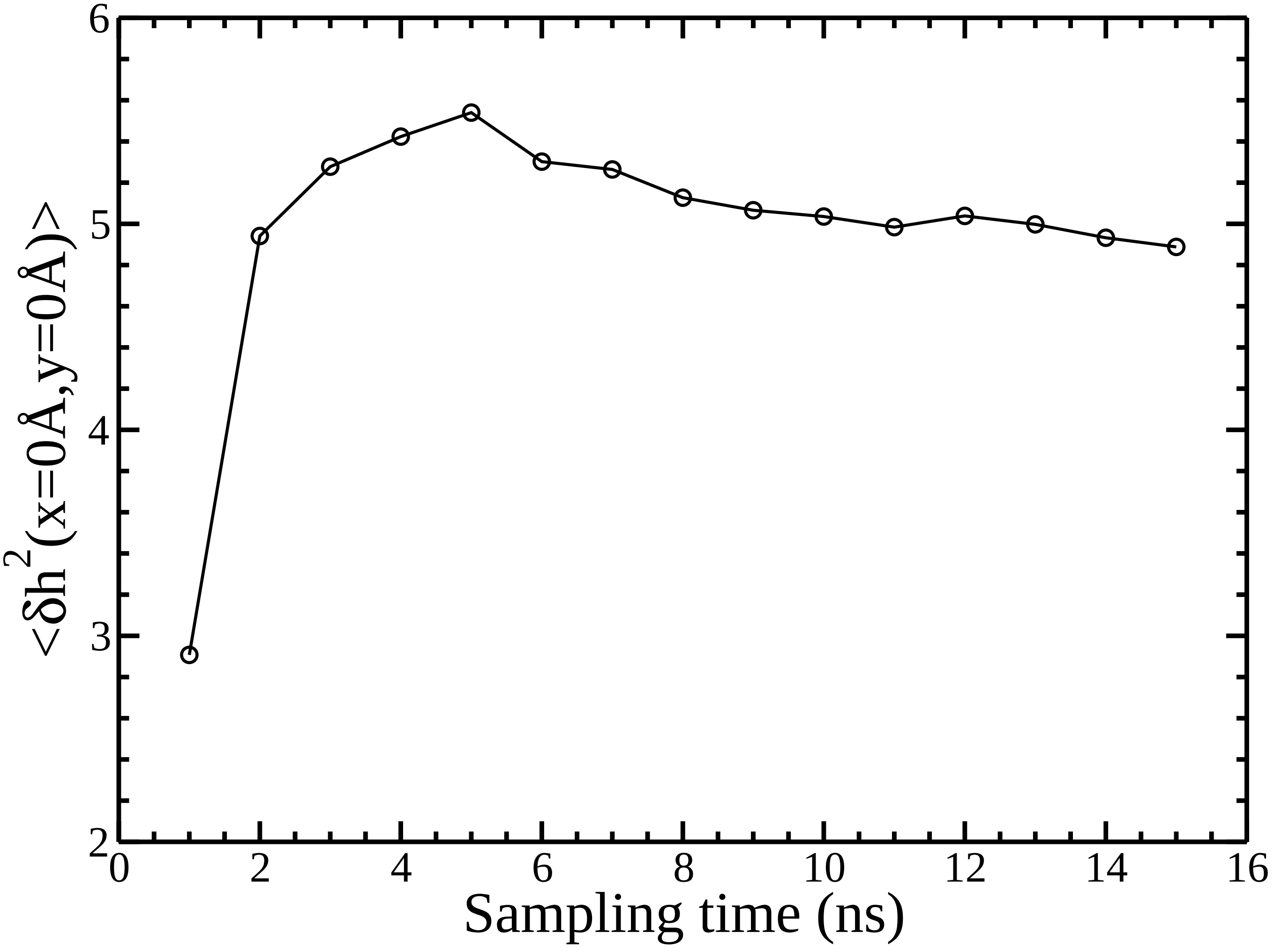

FIG. S5: Convergence of the characteristic fluctuation $\left\langle \delta^2(x=0,y=0)\right\rangle$ for single pentane at z = -6.0 Å.

IV. ESTIMATION OF SURFACE ENTROPY USING SURFACE HEIGHT FUNCTION

For a random variable x with continuous density $f(x)$, the entropy can be written as[6]

$$S(f) = -\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\cdots\int_{-\infty}^{\infty} \ln[f(x)]f(x)dx \tag{S2}$$

where $x = (x_1, x_2, \cdots, x_{\mathrm{N}})'$. The density function of the multivariate normal distribution is given by

$$f(x) = \frac{1}{|2\pi\Sigma|^{1/2}} exp\{-\frac{1}{2}(x-\mu)'\Sigma^{-1}(x-\mu)\} \tag{S3}$$

Σ is the covariance matrix, $\Sigma_{\mathrm{ij}} = cov(x_{\mathrm{i}}, x_{\mathrm{j}}) = E[(x_{\mathrm{i}} - \mu_{\mathrm{i}})(x_{\mathrm{j}} - \mu_{\mathrm{j}})]$, where $\mu_{\mathrm{i}} = E(x_{\mathrm{i}})$ is the expected value of the i_{th} entry of x. We can therefore rewrite the entropy as

$$\begin{aligned} S &= \frac{1}{2}\{N + N\ln(2\pi)\ln + \ln|\Sigma|\} \\ &= \frac{1}{2}\{\ln e^N + \ln(2\pi)^N + \ln|\Sigma|\} \\ &= \frac{1}{2}\ln\{(2\pi e)^N|\Sigma|\} \\ &= \frac{N}{2}\ln(2\pi e) + \frac{1}{2}\ln|\Sigma| \end{aligned} \tag{S4}$$

where $|\Sigma|$ is the determinant of covariance matrix Σ. The surface entropy can therefore be estimated with surface height function $\delta h = h - \langle h\rangle$. The covariance matrix (χ) is then defined as $\chi_{\mathrm{ij}} = \delta h_{\mathrm{i}}\delta h_{\mathrm{j}}$. The $\frac{N}{2}\ln(2\pi e)$ term is then constant for different windows with the same resolution of grid points (which, in other words, same N). Consequently, we get the entropy described by the fineness of the resolution of grid points, and can be written as:

$$S = constant + \frac{k_{\mathrm{B}}}{2}\ln|\chi| \tag{S5}$$

where k_{B} is the Boltzmann constant.

In the main text, the resolution we used along x and y-dimensions is 1.0 Å. For each snapshot we therefore have 40×40 surface height values, resulting in a covariance matrix with 1600×1600 elements. However, from the aspect of estimating surface entropy, the resolution of 1 Å may be too fine and computational resource consuming. In practice, we use a coarser resolution of 2.0 Å (in x and y) to construct the covariance matrix (400×400 elements) and estimate the surface entropy. In Figure S6, we present the time profile of calculated surface entropy for single methane (using CHARMM36) at solvent bulk, the window that generates largest fluctuations, and at the interface. For this analysis, the accumulated average of the covariance matrix (χ) is calculated every 50 ps; the estimated entropies converge after 8 ns. The difference of entropies can be calculated as $\Delta S_{\mathrm{largest}} = S(z=-4) - S(z=-18) = 82.5k_{\mathrm{B}}$, $\Delta S_{\mathrm{interface}} = S(z=0) - S(z=-18) = -34.7k_{\mathrm{B}}$, while $\Delta S_{\mathrm{largest}}$ and $\Delta S_{\mathrm{interface}}$ refer to the increment/reduction of entropies when the methane is placed at the position that generates the largest fluctuation or at the interface. For the case of pentane, these values are $\Delta S_{\mathrm{largest}} = 184.1 k_{\mathrm{B}}$ and $\Delta S_{\mathrm{interface}} = -37.1 k_{\mathrm{B}}$, respectively.

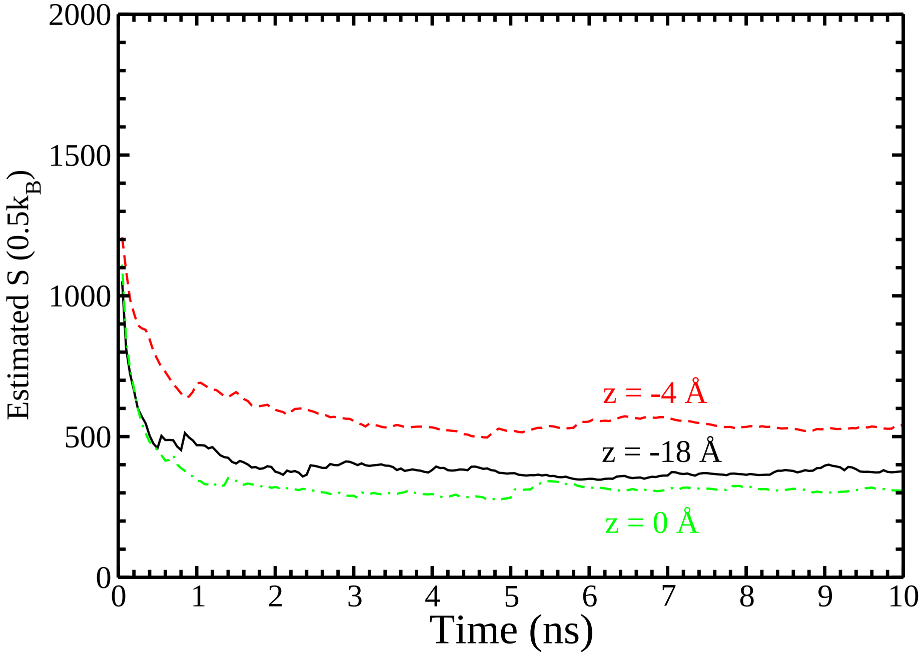

FIG. S6: Time profile of the estimated entropy.

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