Supporting information for:

On the Thermodynamics and Kinetics of

Hydrophobic Interactions at Interfaces

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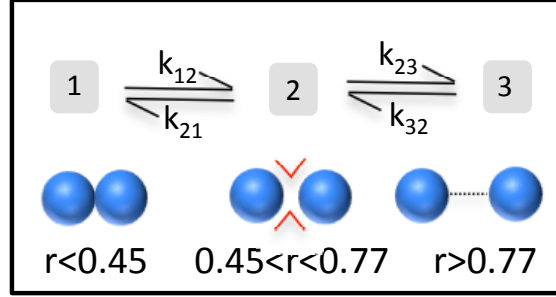
I. Kinetics: Rate Equations

Figure S1: A schematic defining the three states for a pair of hydrophobic solutes: state **1**: contact; state **2**: solvent-separated; state **3**: dispersed.

The rate equations for the above process are as follows

$$\frac{d[1]}{dt} = k_{21}[2] - k_{12}[1] \tag{1}$$

$$\frac{d[2]}{dt} = k_{12}[1] + k_{32}[3] - [2](k_{21} + k_{23}) \tag{2}$$

$$\frac{d[3]}{dt} = k_{23}[2] - k_{32}[3] \tag{3}$$

where, k_{ij} is the rate constant for '**i**' to '**j**' transition and [i] is the concentration of the state '**i**'. At equilibrium,

$$\frac{k_{12}}{k_{21}} = \frac{\tau_{21}}{\tau_{12}} = \frac{[2]_{eq}}{[1]_{eq}} \tag{4}$$

$$\frac{k_{32}}{k_{23}} = \frac{\tau_{23}}{\tau_{32}} = \frac{[2]_{eq}}{[3]_{eq}} \tag{5}$$

$$k_{21} + k_{23} = \frac{k_{12}[1]_{eq} + k_{32}[3]_{eq}}{[2]_{eq}} \tag{6}$$

where $[i]_{eq}$ is the equilibrium concentration of the state 'i' and τ_{ij} is the mean first passage time for 'i' to 'j' transition, which is also equal to the inverse of k_{ij}.

We obtained equilibrium concentrations of states **1**, **2**, and **3** as well as the τ_{ij} for all the relevant transitions (see Table S1). Table S2 shows that the equilibrium relations (Equations 4, 5, and 6) are indeed satisfied by our data, confirming that our trajectories are sufficiently long and that there are no non-ergodicity or sampling problems.

Table S1: Equilibrium concentrations and mean first passage times (in picoseconds)

SAM	[1]	[2]	[3]	$\tau_{12} = \frac{1}{k_{12}}$	$\tau_{21} = \frac{1}{k_{21}}$	$\tau_{23} = \frac{1}{k_{23}}$	$\tau_{32} = \frac{1}{k_{32}}$
near -OH	0.043	0.104	0.853	5.89	14.30	7.18	58.35
near -CH_3	0.078	0.108	0.813	2.64	3.65	3.48	26.12

Table S2: Validating equilibrium

SAM	$\frac{k_{12}}{k_{21}} = \frac{\tau_{21}}{\tau_{12}}$	$\frac{[2]_{eq}}{[1]_{eq}}$	$\frac{k_{32}}{k_{23}} = \frac{\tau_{23}}{\tau_{32}}$	$\frac{[2]_{eq}}{[3]_{eq}}$	$k_{21} + k_{23}$	$\frac{k_{12}[1]_{eq}+k_{32}[3]_{eq}}{[2]_{eq}}$
near -OH	2.42	2.42	0.12	0.12	0.21	0.21
near -CH_3	1.38	1.38	0.13	0.13	0.56	0.56

II. Including the Jacobian of transformation in the PMFs

To account for the Jacobian of transformation (i.e., the relative volume of the states), we plot, $W_2^J(\mathrm{r}) = W(\mathrm{r})$ - kTln(r), in Figure S2. The PMFs are arbitrarily zeroed at the contact-minimum (CM). Inclusion of the Jacobian term shows that the barrier heights for **2**→**1** and **1**→**2** transitions are approximately equal near the -OH surface. This fact and that state **2** can transition to either state **1** or state **3** qualitatively accounts for the relative differences in τ_{12} and τ_{21} near the -OH surface. Similar factors are in play for transitions near the -CH_3 surface.
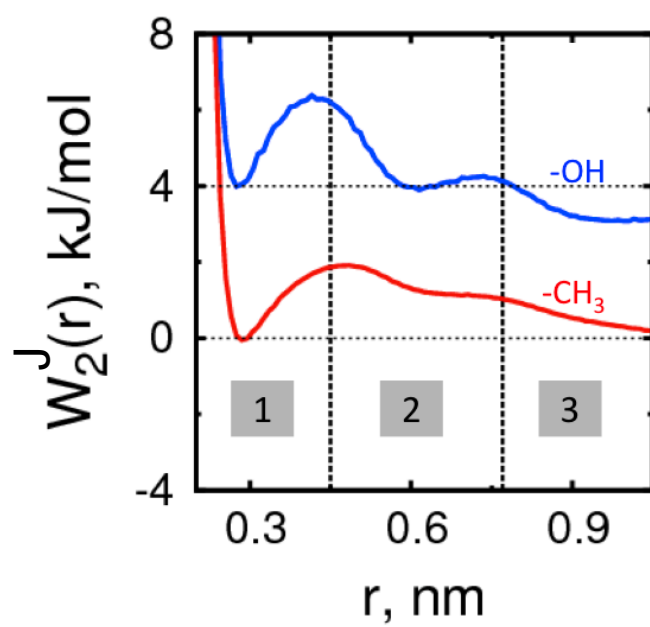
Figure S2: PMF between the solutes with Jacobian of transformation included. (red = near -CH$_3$; blue = near -OH)