Supporting Information: Role of Spatial Ionic Distribution on the Energetics of Hydrophobic Assembly and Properties of the Water/Hydrophobe Interface

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I. VELOCITY DISTRIBUTION

Here we compare the velocity distributions of water molecules in the bulk water region (WAT_{bulk}) and near the plates (WAT_{plates}). Based on the energy minimization of a single TIP4P-FQ water interacting with a plate and the water density profile along the z-coordinate (shown in Figure 2(a) of the main paper), we choose $z = 3.6$ Å relative to the z-component of the plate center of mass as the cutoff and the radius $r = 8.0$ Å about the center of the plate to define the cylindrical volume sampled for WAT_{plates}; this particular choice of cutoffs selects the first layer of water molecules near the plates. In order to sample a comparable number in the bulk, we choose the cylinder with the same radius and relative length with z between 19.0-22.0 Å from the plate; this is sufficiently far from both water-plate and water-air interfaces. Figure 1 shows the velocity distribution of the WAT_{bulk} (black filled circles) and WAT_{plates} (red hollow squares). Here v_x, v_y and v_z are the x, y, z components of the TIP4P-FQ oxygen atom velocities. v represents the total velocity of the oxygen atom:

$$v = \sqrt{v_x{}^2 + v_y{}^2 + v_z{}^2} \tag{1}$$

From Figure 1a-c all the velocity distributions are Gaussian with the center at zero. There is no evident difference between WAT_{bulk} and WAT_{plates} with respect to velocity distributions.
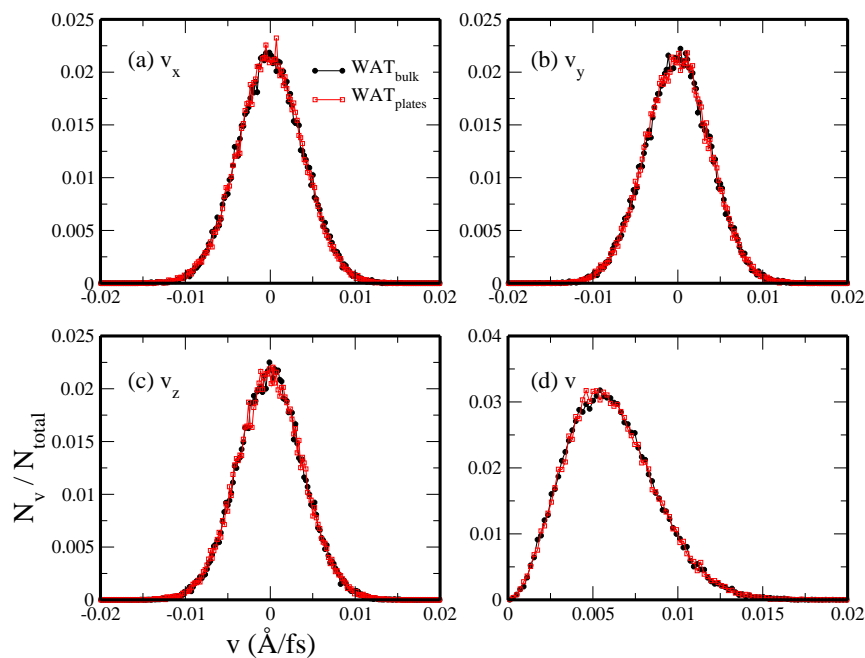
FIG. 1: Velocity distribution of water molecules in the bulk (black filled circles) and near the plates (red hollow squares). (a) is showing the distribution of the x component of velocities, while (b), (c) and (d) correspond to the y, z velocity components and the total velocities, respectively.

II.   THERMOSTAT IN THE VICNITY OF PLATES

The kinetic energy (KE) of a homogeneous system can be written as

$$KE = \frac{1}{2} \sum_N \left(\sum_j \sum_\alpha m_j v_{j,\alpha}^2 \right) = N\rho \frac{k_B T}{2} \qquad (2)$$

where N is the number of molecules, m_j is the mass of j_{th} atom, $v_{j,\alpha}$ is the α_{th} component of j_{th} atom ($\alpha = x, y, z$), k_B is the Boltzmann constant, and T is the system temperature. ρ is the number of degrees of freedom for a single molecule. In the present case, since the M-site of TIP4P-FQ is massless, we can consider $\rho = 3N_{nuclear} - 3 = 6$; the three constraints in each molecule correspond to the three bond length constraints, one between the two hydrogen atoms, and the second two between the oxygen atom and the two hydrogen atoms to which it is bonded. Consequently, we obtain the temperature of a specified region by computing the total kinetic energy of the molecules in that region. Figure 2 shows the temperature profiles of WAT_{bulk} and WAT_{plates} versus time. Water in both regions is shown to oscillate about an average value of $T = 300$ K (the target temperature). As shown in Figure 3, the temperature distributions of WAT_{bulk} and WAT_{plates} do not have significant differences, suggesting the constraints on the plates do not significantly affect the thermostating of water in different environments.
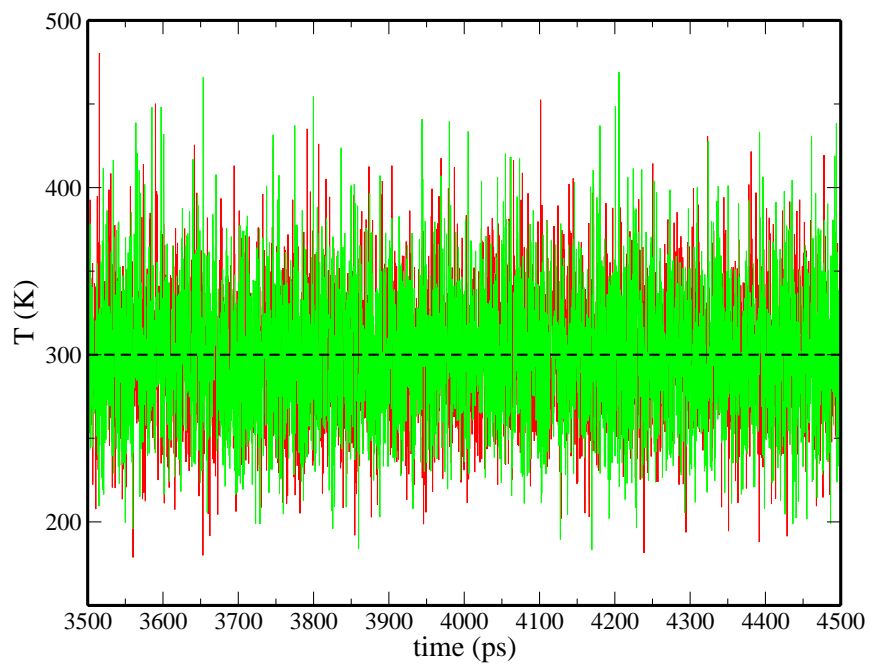
FIG. 2: Temperature profile for WAT_{bulk} (red) and WAT_{plates} (green) as functions of time. Black dashed line represents the temperature ($T = 300$ K) using Nosé-Hoover thermostat in our system.
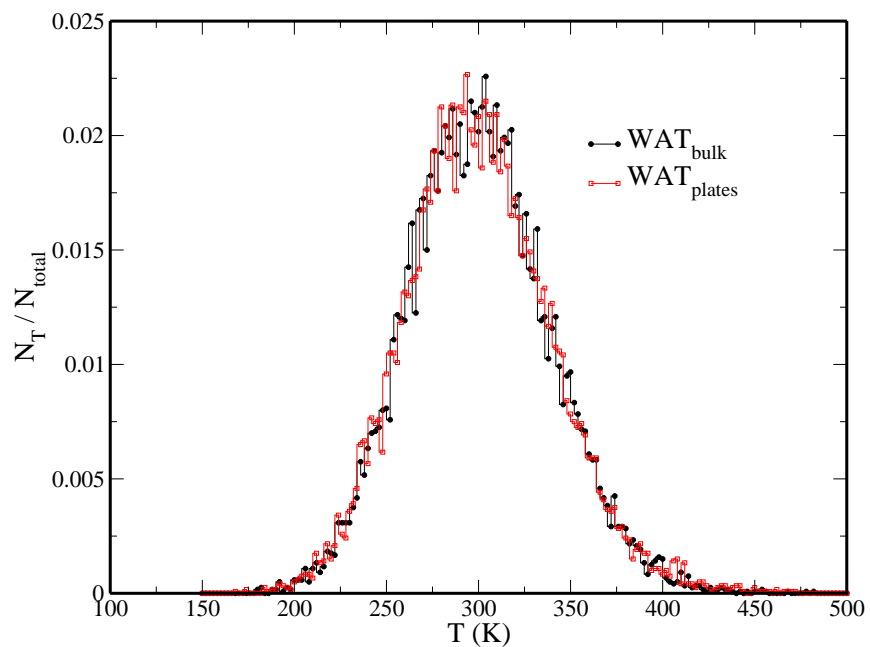

FIG. 3: Temperature distribution of WAT_{bulk} (black filled circles) and WAT_{plates} (red hollow squares).