## Supporting Information for "Long Range Effects of Confinement on Water Structure"

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## **Computational Details**

All simulations were carried out using Amber 9 program suite.<sup>1</sup> In the majority of simulations, NPT (constant number of particles, pressure, and temperature) ensembles were used (300 K, 1 atm) in association with periodic boundary conditions. The SHAKE algorithm<sup>2,3</sup> was used to constrain all bonds involving hydrogens and the time step was set to 2 fs. A 10.0-Å cutoff was applied for nonbonding interactions. The Particle Mesh Ewald method<sup>4,5</sup> was employed to treat the long-range electrostatic interactions. Two different types of hydrophobic surfaces, planar hydrophobic ones and those formed by aliphatic hydrocarbon monolayers, were employed to confine water in between. Three popular point-charge water models (SPC/E, TIP4P/ew, TIP5P) were tested with the most simulations performed using SPC/E.

For the hydrocarbon systems, a monomolecular layer of 100 tetracosanes ( $n-C_{24}H_{50}$ ) was placed in the middle of the simulation box and the water layer confined between the two surfaces of methyls in tetraconsanes (See Figure S1a) was adjusted to an original thickness *d* (in the z dimension) of 50, 100, 200, and 400 Å, respectively. These systems contains 3590, 7305, 14610 and 29220 waters, respectively. The hydrocarbon and the water layers were prepared separately. The tetracosanes were aligned and packed together and the x and y dimensions were determined according to its density of 0.797 g/cm<sup>3</sup>. After equilibrated for 5 ns with x and y dimensions carefully controlled to match those for the hydrocarbon layers at 300K and 1 atm, the water layer was attached to the hydrocarbon layer.

To further valid the simulation results, model planar hydrophobic surfaces were also used to confine water. For this model system, the interaction between the surface and water molecules takes the form (which is very close to *t*-butyl groups in alkanes and thus very hydrophobic),

$$v(r) = \varepsilon \left[ (r_m / r)^{12} - 2(r_m / r)^6 \right]$$
(1)

with  $r_m = 1.7767$  Å and  $\varepsilon = 0.1553$  kcal/mol for SPC/E water and with  $r_m = 1.487$  Å and  $\varepsilon = 0.0157$  kcal/mol for the planar hydrophobic surfaces. These parameters were used so that the attractive part of the potential is shallow and the walls are repulsive (very similar to the trimethyl plane in t-butyl or the phenyl plane). Different forms, such as the potentials with different  $\varepsilon$  used or even with the attractive term removed, of potential have been tested and no effects were found on the simulation results. In these simulations, effects of different boundary conditions were also tested: The simulations were performed with the model hydrophobic plates either positioned in the middle or the two ends of the simulation box (Figures S1b,c), and the x,y-dimensions were either  $27 \times 27$  or  $40 \times 40$  Å<sup>2</sup>. The thickness of each wall was set to 50 or 100 Å to test the effects of the nonbonding interactions across the walls and no difference was found from these simulation setups. The thickness d of the water film was taken as 50, 120, 160, 320, or 800 Å, resulting in systems containing 2355, 2483, 8049, 16098 and 22496 waters, respectively. The 8049-water system with a thickness of 160 was also simulated with TIP5P and TIP4P/ew models.

Figure S1. Cuboid boxes created to simulate water confined between linear alkane monolayers or flat planes with Lennard-Jones potentials. (a) 100 tetracosane molecules were positioned in parallel in the middle of the box and the C-11 and C-12 in tetraconsanes were fixed with a harmonic potential with a force constant of 10000 kcal/mol/Å<sup>2</sup>. The thickness of the water layer ( $d = z - z_a$ ;  $z_a$ : the thickness of the alkane monolayer) were set to approximately 50, 100, 200 or 400 Å and the x and y dimensions were about 50 Å; (b) Two flat planes with Lennard-Jones potential of  $r_0 = 0$  Å and  $\varepsilon =$ 0.0157 kcal/mol were fixed in the middle of the box. The thickness of the water layer ( $d = z - z_v$ ;  $z_v$ : the separation of the flat planes with a Lennard-Jones potential) were set to 50, 120, 160 or 320 Å while the separations between the planes were set to 50 or 100 Å; (c) similar to (b) except the flat planes were set on the ends of the box ( $z_w$  is the thickness *d* of the water film).



To further validate the simulation results of the NPT systems and in particular to avoid the usage of a pressure coupling algorithm, e.g., the weak-coupling<sup>6</sup> used in the NPT simulations, NVT (constant number of particles, volume, and temperature) ensembles were also used for the systems with the planar hydrophobic surfaces. In these simulations, the hydrophobic plates were positioned at the two ends of the simulation box, and the x,y-dimensions were set to be  $40 \times 50$  Å<sup>2</sup>. Two representative separation distances between these two plates, 50 and 160 Å, were used. The thickness of the walls was 50 Å, resulting in two systems with the sizes of about  $40 \times 50 \times 100$  and  $40 \times 50 \times 215$  Å<sup>3</sup> containing 3290 and 10663 waters, respectively (see Figure 1c).

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