# Supplementary Information: The effects of surface hydration on capillary adhesion under nanoscale confinement<sup>†</sup>

Sijia Huang,<sup>a</sup> Carlos E. Colosqui,<sup>\*a,b</sup> Y.-N. Young,<sup>c</sup> and Howard A. Stone<sup>d</sup>

## Supplementary Information

The supplementary information provides technical details of the molecular dynamics simulations performed in this work and results for nanoscale capillary bridges of different volume that verify the key assumptions in the theoretical model described in the main text.

## Molecular Dynamics simulations

The molecular dynamics (MD) simulations in this work are performed with the open-source code LAMMPS.<sup>1</sup> The simulations are performed in the NVT ensemble, with a fixed number of water molecules and simulation domain volume with the temperature regulated by a standard Berendsen thermostat. The water molecules are confined between two static walls that are separated at fixed height and fully bound the 3D simulation domain in the z-direction; periodic boundary conditions are applied in the x- and y-directions. Conventional Lennard-Jones (L-J) and Coulomb potentials determine the interactions between the modeled atomic species: (O) oxygen, (H) hydrogen, and (S) generic solid atoms. After an initial relaxation stage (1 ns) for which simulations are performed with a small timestep of 1 fs, the timestep is increased to 2 fs for the remaining 4 ns of the simulation.

The water molecules are modeled as a rigid assembly of oxygen and hydrogen atoms with a fixed dipole moment and dihedral angle using the conventional TIP4P/Ew model,<sup>2</sup> which at the simulated system temperature T = 300 K reproduces the p-n-T phase diagram and structural properties (e.g., radial correlation function) experimentally observed for bulk liquid water,<sup>3,4</sup> with a liquid mass density  $\rho = 964$  kg/m<sup>3</sup> that corresponds to a bulk number density  $n_b = 0.0322^{-3}$ , and a liquid-vapor surface tension  $\gamma = 65.4$  mN/m.<sup>5</sup>

The solid walls are modeled as a "frozen" crystalline structure of uncharged nonpolar atoms with an effective diameter  $\sigma_S = 0.281$  nm that are arranged in a face-centered cubic (fcc) lattice with constant spacing  $\Delta x = 0.35$  nm. The modeled oxygen atoms have a diameter  $\sigma_O = 0.3164$  nm that parameterizes the L-J potential while the H<sup>+</sup> ions are modeled as point-like charges. The effective diameter of the modeled water molecules is  $\Delta x_{OO} = 2^{1/6} \sigma_O = 1.015 \Delta x$  nearly equal to the fcc lattice unit of modeled solid surfaces. For the conditions modeled here, the L-J interaction energy between water molecules is  $\varepsilon_{OO} \simeq 0.27 k_B T$ , while the interaction energy between the solid and oxygen atoms  $\varepsilon_{SO} \simeq 0.83 k_B T$  is higher. The set interaction energies result in strong affinity of water molecules to the solid and hydrophilic behavior of the modeled solid surfaces.

In our MD simulations, the distance between the centers of the solid atoms that form the wall surfaces is  $h_{MD} = j\Delta x$ , where *j* is an integer number of lattice units. The solid-liquid interface in MD simulations (see Figure 1 in the main text) has a finite thickness  $\Delta x \simeq 2^{1/6}(\sigma_O + \sigma_S)/2$  that is approximately equal to one lattice unit and is determined by the effective diameters of the oxygen atoms in the water molecules and the solid atoms forming the walls. The height of the liquid bridge in the MD simulations is defined as  $h = h_{MD} - \Delta x$ , considering that in the sharp-interface continuum representation the top and bottom surfaces lie at the position of contact between the water molecules and solid atoms where  $|z| = z_w = h/2$  (cf. Figure 1b in the main text).

#### Number density and radius profiles

The bridge radius in the MD simulations is determined by a systematic algorithm that assumes a constant number density of water molecules within each slab. For a slab of height  $\Delta z$  centered at z and assuming that the number density n(z) inside each slab is constant the *k*-th order moment of area is

$$M^{(k)}(z) = n(z)\Delta z \int_0^{r(z)} s^k 2\pi s ds = \frac{2\pi}{k+2} n(z)\Delta z R^{k+2}(z)$$
(1)

where r(z) is the local radius of the bridge. For k = 0, 1, 2, we get:

$$M^{(0)}(z) = \pi n(z)\Delta z r^{2}(z)$$
  

$$M^{(1)}(z) = \frac{2}{3}\pi n(z)\Delta z r^{3}(z)$$
  

$$M^{(2)}(z) = \frac{1}{2}\pi n(z)\Delta z r^{4}(z)$$
(2)

The local number density and radius are thus obtained from solving the set of equations

$$n(z) = \frac{M^{(0)}(z)}{\pi\Delta z r^2(z)},$$
 (3)

and

$$r(z) = \frac{4M^{(2)}(z)}{3M^{(1)}(z)}.$$
(4)

The moments of area  $M^{(k)}$  (k = 0, 1, 2) in eqs. 3–4 are computed in MD simulations from the position of the oxygen atoms within each slab reported at every time step, and averaging during the final 2 ns of the full simulation.

<sup>&</sup>lt;sup>a</sup> Applied Mathematics & Statistics Department, Stony Brook University, Stony Brook, NY 11794, USA.

<sup>&</sup>lt;sup>b</sup> Mechanical Engineering Department, Stony Brook University, Stony Brook, NY 11794, USA; E-mail: carlos.colosqui@stonybrook.edu

 $<sup>^{\</sup>rm c}$  Department of Mathematical Sciences, New Jersey Institute of Technology, Newark, NJ 07102, USA.

<sup>&</sup>lt;sup>d</sup> Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, NJ 08544, USA.



Fig. 1 Number density profiles and height-dependent equilibrium contact angles. (a) Local number density profile modeled by eq. 5 in the main text and reported by MD simulations of nanoscale water bridges of height  $h=9\Delta x\simeq 3.2$  nm and three different volumes  $V/V_0=1$ , 2, and 3 ( $V_0=0.37$  zL). MD simulation results are indicated with markers (see legend). (b) Number density  $n_1$  and thickness  $\delta$  of the first hydration layer employed in analytical estimates for the height-dependent equilibrium contact angle  $\theta_Y(h)$  given by eq. 4 in the main text. The bulk density is  $n_b = 0.0322^{-3}$  for all the modeled conditions.

## Nanoscale water bridges with different volumes

The conditions studied in this work correspond to capillary bridges of nanoscale height *h* and sufficiently large volumes  $V \gg \pi h \sigma^2$  so that the local radius  $r(z) \gg \sigma$  is much larger than the molecular scale. Under these conditions the number density n(z) and height-dependent contact angle  $\theta_Y(h)$  given by analytical estimates are independent of the bridge volume. The MD simulations aim to model the conditions studied by the proposed analytical description (eqs. 1-5 in the main text).

We therefore performed MD simulations using a sufficiently large number of water molecules N = 12,000, 24,000, and 36,000 so that for the studied bridge heights h = 4-19  $\Delta x$  and water volumes  $V \simeq N/n_b = 0.37$ -1.11 zL, the characteristic bridge radius  $R = \sqrt{V/\pi h} > 10\Delta x$  is always larger than ten molecule diameters. As expected for the simulated conditions, the number density profiles obtained from MD simulations show no significant variation with respect to the bridge volume (cf. Figure 1a). The model parameters reported in Figure 1b can be thus employed to account for MD results for the three studied volumes, with the smallest simulated volume  $V_0 = 0.37$  zL corresponding to the lower bound for the validity of the analytical model assumptions.

The local radius profile r(z) and slopes  $\dot{r}(z)$  computed from MD simulations for the studied three different volumes and analytical estimates using the model parameters reported in Figure 1b are shown in Figure 2. The results reported in Figure 2 correspond to nanoscale bridges of heights as small as four water molecules and with volumes that are sufficiently large so that the neck radius  $r_0 \gtrsim 10\Delta x$  is larger than 10 water molecules even for the the case with the smallest volume (e.g., see Figure 2 in the main text). The MD results in Figure 2 are compared with predictions from the conventional YL equation (eq. 1 in the main text) for  $V = V_0$ and using the height-dependent contact angle predicted by eq.4 in the main text and reported in Figure 1b.



Fig. 2 Results for water bridges of different volume. (a) Dimensionless local radius variation  $\Delta \bar{r} = (r(z) - r_0)/h$ , where  $r_0 \equiv r(0)$  is the neck radius. (b) Local radius slope profile  $\dot{r}(z)$ . Markers indicate MD simulation results for water bridges of three different heights  $h/\Delta x = 4$ , 8, and 19 ( $\Delta x = 0.35$  nm) and volumes  $V/V_0 = 1$ , 2, and 3 ( $V_0 = 0.37$  zL). The dashed lines report numerical solutions of the YL equation (eq. 1 in the main text) with the height-dependent equilibrium contact angles  $\theta_Y(h)$  given by eq.4 in the main text.

### Notes and references

- 1 S. Plimpton, P. Crozier and A. Thompson, *Sandia National Laboratories*, 2007, **18**, 43.
- H. W. Horn, W. C. Swope, J. W. Pitera, J. D. Madura, T. J. Dick,
   G. L. Hura and T. Head-Gordon, *J. Chem. Phys.*, 2004, 120, 9665–9678.
- 3 H. W. Horn, W. C. Swope and J. W. Pitera, *J. Chem. Phys.*, 2005, **123**, 194504.
- 4 C. Vega, J. Abascal and I. Nezbeda, J. Chem. Phys., 2006, **125**, 034503.
- 5 C. Vega and E. De Miguel, J. Chem. Phys., 2007, 126, 154707.