Supporting Information

Effect of Nanoparticles on Spontaneous Imbibition of Water into Ultraconfined Reservoir Capillary by Molecular Dynamics Simulation

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S1. The Selection of Suitable Characteristic Energy of Capillary

In order to ensure the spontaneous imbibition of water into the capillary, the capillary should be hydrophilic solid. Herein, the characteristic energy ε_{so} is varied from 0.25 to 0.4 kcal/mol to create different wettability. The other simulation details are the same as in our paper.

From Figure S1, it can be seen that for ε_{so} = 0.25 kcal/mol, only a few water molecules diffuse and enter into the capillary with time elapse of 4.0 ns, which means that water molecules are difficult to transport into the capillary spontaneously at this characteristic energy. With an increase of characteristic energy, more water molecules could enter into the capillary spontaneously.

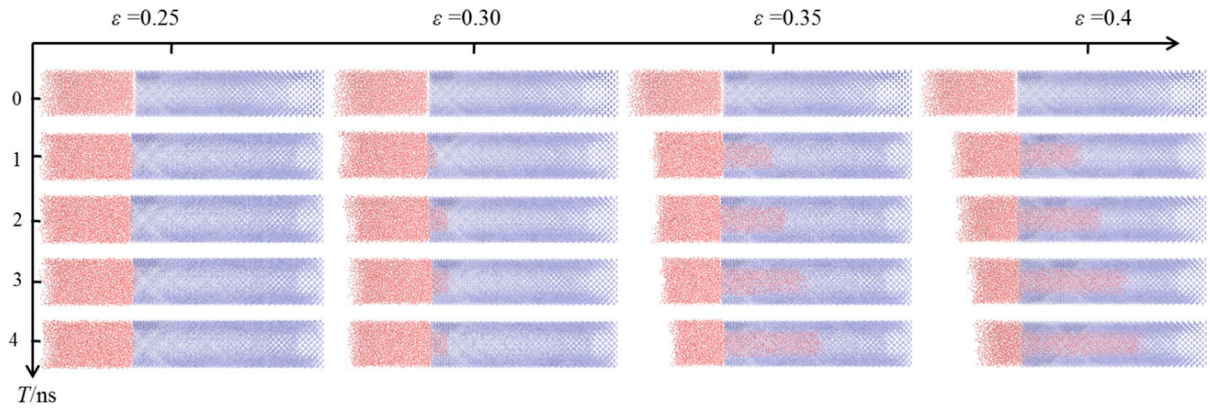

Figure S1. The imbibition simulation snapshots of water into the capillary at different characteristic energy with time.

Herein, the contact angles of fluids in the capillary at equilibrium state are calculated and shown in Table S1. When ε_{so} = 0.25 kcal/mol, the contact angle of fluids in the capillary is 116.69° and the capillary shows hydrophobic property. It can be seen that when ε_{so} increases to 0.3 kcal/mol, the fluid starts to permeate into the capillary. The corresponding contact angle is around 90°, which indicates that this capillary is mix-wet. With a further increase of ε_{so}, the contact angle becomes smaller, suggesting that the wettability of the capillary would alter from hydrophobic to hydrophilic property. The hydrophilicity of the capillary would promote much more water entering into the capillary spontaneously.

Table S1 The water contact angle in the capillary with different ε_{so}.

Characteristic Energy ε_{so} (kcal/mol)	0.25	0.30	0.35	0.4
Contact Angle (°)	116.69	89.97	63.98	53.20

Based on the configuration and contact angle of water in the capillary, the characteristic energy ε_{so} above 0.3 kcal/mol should be chosen to study the spontaneous imbibition phenomena.

S2. Validation of Simulation Results with Lucas–Washburn Equation

In order to validate the reasonability of systems, displacement curves based on the well-known Lucas–Washburn equation are compared with our simulation results. The Lucas–Washburn equation is listed as follows [1].

$$l = \sqrt{\frac{\gamma R \cos\theta}{2\eta}} \cdot \sqrt{t} \tag{1}$$

where l and t are displacement distance and time, respectively. According to the Lucas–Washburn equation, surface tension (γ), liquid viscosity (η), contact angle of water on the capillary wall (θ) and the radius of the capillary (R) should be specified to get the relationship of l and t. Herein, the contact angle of water on the characteristic energy 0.35 kcal/mol capillary is adopted in the equation, and other parameters are obtained from experiments [2]. The comparison curves are plotted in Figure S2, which shows a good agreement between simulation results and calculated results based on the Lucas–Washburn equation.

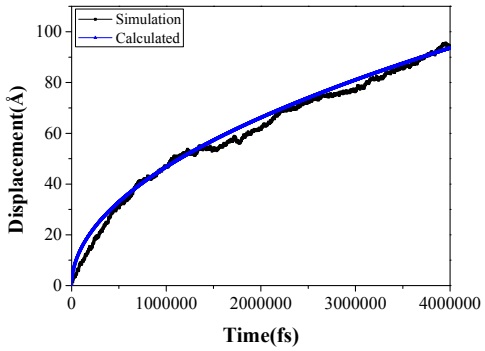

Figure S2. Comparison curves for displacement vs simulation time between simulation results (black line) and calculated results (blue line) based on the Lucas–Washburn equation.

S3. The Method to Obtain Displacement Value from Density Profiles

The same method as previous studies [3–5] is adopted to get displacement. Firstly, the density of water as a function of the distance in the capillary is calculated. Then, the density is fitted using the following hyperbolic tangent function for the liquid–vapor or liquid–liquid interface:

$$\rho(y) = 0.5\rho_{liquid} - 0.5\rho_{liquid} \tanh\left(\frac{2(y - y_0)}{d}\right) \tag{2}$$

where ρ is the density, y_0 is the position of the interfacial front, and d is the adjustable parameter related to the interfacial thickness. The extremity position of liquid is defined as where its density falls to a ratio of 0.5.

References

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