Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting information

Atomistic insights into the nanofluid transport through ultra-confined capillary

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S1. The selection of suitable characteristic energy of capillary

The spontaneous capillary displacement process would take place in the capillary only for wetting fluids. To ensure the spontaneous capillary displacement of water-oil fluid, the capillary should have stronger tendency to water than oil. In light of our previous simulation results [1] about spontaneous imbibition of water into capillary, two characteristic energy ε_{sw} 0.3 (mixed wet) and 0.6 kcal/mol (hydrophilic) for capillary were selected. The other simulation details were same as in our paper.

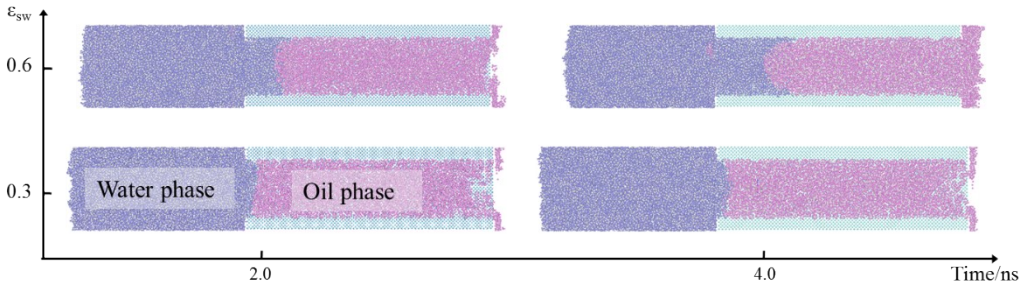

Figure S1. The snapshots of water-oil displacement in capillaries with different characteristic energy.

From Figure S1, it can be seen that for ε_{sw} = 0.3 kcal/mol, only a few water molecules diffuse into the capillary and displace oil molecules out of capillary. Furthermore, the shape of interface curvature shrink into the water phase, which means that it is difficult to trigger spontaneous water-oil

displacement into capillary at this characteristic energy. With an increase of characteristic energy to 0.6 kcal/mol, more water molecules could enter into capillary spontaneously. Here, three phase contact angle in capillary in dynamic equilibrium state are calculated and shown in Table S1. When ε_{sw} = 0.3 kcal/mol, the three phase contact angle is about 89.82±6.18°, indicating the mix-wet properties for capillary. With further increase of ε_{sw}, the contact angle becomes smaller, suggesting more water-wet properties.

Table S1 Three phase contact angle for fluids in capillary with different ε_{sw}.

Characteristic Energy ε_{sw} (kcal/mol)	0.30	0.6
Contact Angle (°)	89.82±6.18	19.05±2.06

The displacement curves vs time for water into two kinds of capillary are calculated in Figure S2. According to the displacement, it can be seen that the displacement curve almost kept stable after 500 ps for characteristic energy ε_{sw}=0.3 kcal/mol, claiming the difficulty for water displacement into the capillary spontaneously.

Based on discussion about the configuration and contact angle, characteristic energy ε_{sw} = 0.6 kcal/mol is chosen to study spontaneous displacement process.

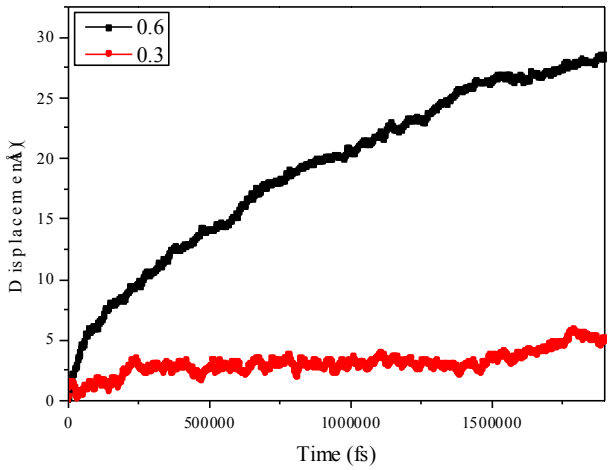

Figure S2. The displacement curves vs time for water into capillary at different characteristic energy ε_{sw}.

S2. The force fields parameters for nanoparticles

In order to study the influence of wetting properties of nanoparticles (NPs) on the displacement process, characteristic interaction energy ε_{nn} between NPs was set relatively small as 0.01 kcal/mol, and ε_{ns} between NP and solid capillary was chosen 0.7 kcal/mol, designating the stronger interaction

between NPs and solid capillary. To form different wettability of NPs, the detailed parameters are listed in Table S2.

Table S2 Force fields parameters for NPs with water ε_{nw}, oil ε_{no}, and capillary ε_{ns}.

Characteristic energy, kcal/mol	Water	Oil	Capillary
Hydrophilic NPs	0.6	0.05	0.7
Mixed NPs	0.3	0.3	
Hydrophobic NPs	0.05	0.6	

S3. Interaction energy for NPs with water and oil phases

The interaction energy between NPs and fluid is calculated to explore the potential mechanism of viscosity variation due to the dispersed NPs, shown in Figure S3.

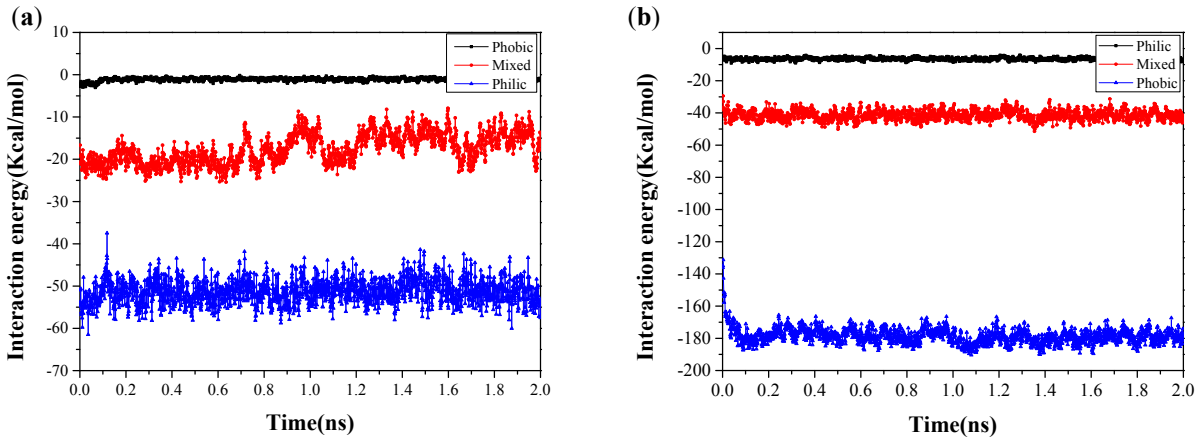

Figure S3. Interaction energy for NPs with water and oil phases: (a) water phase; (b) oil phase.

S4. Calculation of water-oil interfacial tension

The simulation systems (Figure S4) containing two phases: bulk water in the middle part (thickness was 83.0691Å), and two bulk oil phases (each was 45.5622Å) placed in the two sides of water phase were built to obtain the water-oil interfacial tension γ_{wo}. During simulation, all the parameters about water and oil molecules were the same as that in our paper. To obtain the equilibrium configuration, 4 ns constant temperature and pressure ensemble (NPT) were firstly carried out followed by 4 ns canonical ensemble (NVT) simulations. Then, 2 ns NVT MD simulation was performed for the statistical analysis. In the system, the total tension γ_{wo} of the system consisting of two water/oil interfaces can be derived by substracting mean tangential stress tensors and the normal one.

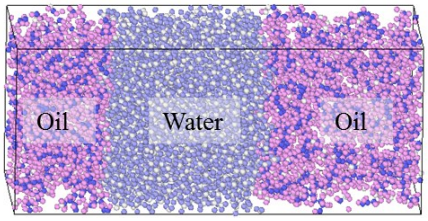

Figure S4. The model of water-oil interface to calculate interfacial tension.

S4. The mean square displacement (MSD) curve for water

The equilibrium simulation of bulk water was performed and the MSD curve was obtained, as shown in Figure S5.

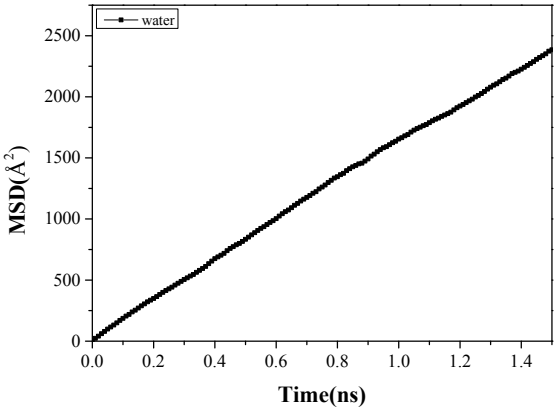

Figure S5. The MSD curves for water fluids.

References

1. X. Wang, S. Xiao, Z. Zhang and J. He, *Energies*, 2017, **10**, 506.