

## Supporting information

# Displacement of Nanofluids in Silica Nanopores: Influenced by Wettability of Nanoparticles and Oil Components

Xiao Wang <sup>1</sup>, Senbo Xiao <sup>1</sup>, Zhiliang Zhang <sup>1</sup>, and Jianying He <sup>1,\*</sup>

<sup>1</sup> NTNU Nanomechanical Lab, Department of Structural Engineering, Faculty of Engineering, Norwegian University of Science and Technology (NTNU), 7491 Trondheim, Norway

\* Correspondence: [jianying.he@ntnu.no](mailto:jianying.he@ntnu.no) ; Tel.: +47-73594686

### S1. The force fields parameter of silica and oil components

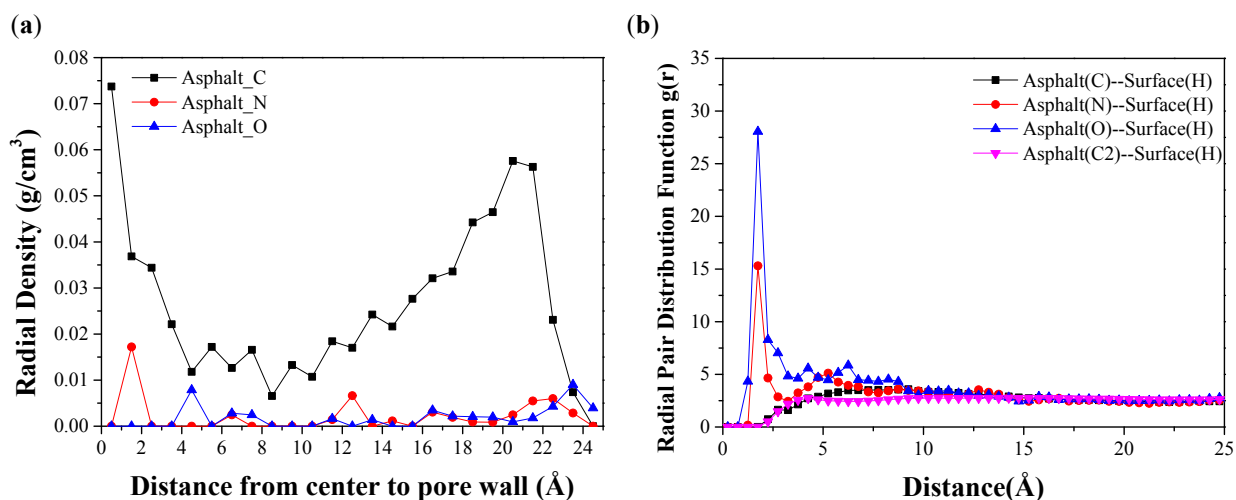
During the simulation, the CHARMM force field was used for organic oil molecules, while CLAY force field was used to describe the interactions of silica molecules. The detailed parameters are listed in Table S1.

**Table S1** Force field parameters for oil molecules and silica

Atoms	$\epsilon$ (Kcal/mol)	$\sigma$ (Å)	$q$ (e)
C(CH3)	0.0779	3.6349	--
C(CH2)	0.0560	3.5814	--
H (C-H)	0.0240	2.3876	--
C(C=C-C)	0.0699	3.5501	--
N (C=N-C)	0.0599	3.3676	--
C(C=O)	0.0699	3.5636	--
O (C=O)	0.1199	3.0291	--
Si	$1.8405 \times 10^{-6}$	3.3020	2.1
O (Si-O-Si)	0.1554	3.1655	-1.050
O (Si-OH)	0.1554	3.1655	-0.950
H(Si-OH)	0	0	0.425

### S2. Structural Information about Asphaltene

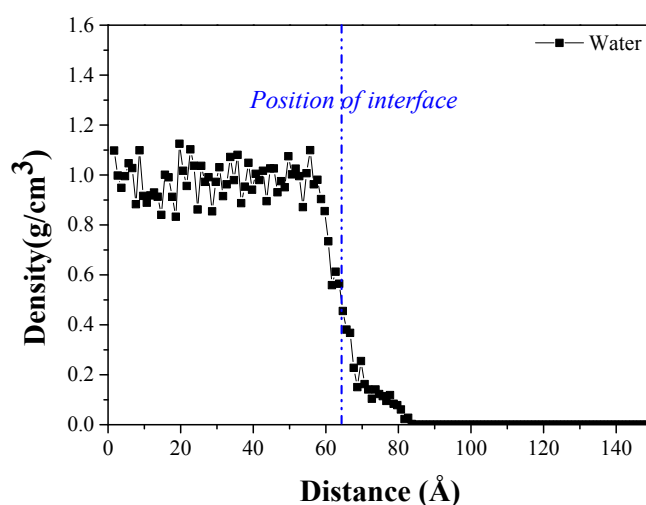
The radial density profiles and radial pair distribution profiles for different type of atoms in asphaltene are shown in Figure S1.



**Figure S1** (a) Radial density profiles for C, N and O atoms in asphaltene molecules; (b) radial pair distribution function between C, N, O in asphaltene and hydrogen in silica surface, respectively.

### S3. Density Profile of Water in the Capillary

Here, then density distribution of water along capillary at time 10.0 ns is selected, shown in Figure S2.

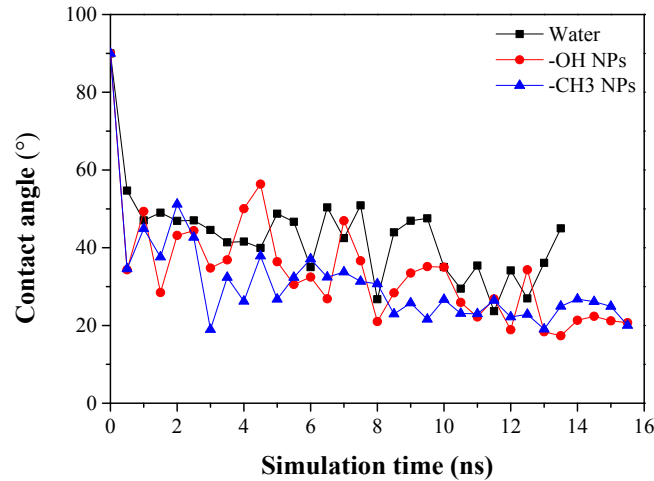


**Figure S2** The density distribution profiles of water phase along the capillary.  $x$  axis is the distance from the entrance of the capillary, and  $y$  axis is the density of the fluids.

### S4. Three-phase Contact angle

Three phases contact angle is analyzed to assess the wettability properties of capillary. According to our previous study <sup>1</sup>, contact angle will have large fluctuation and reach a dynamic equilibrium value during displacement. To determine the contact angle for three fluid, liquid in capillary is firstly divided into cylindrical shells, and then is subdivided by certain

thickness 1.5 Å. According to the density of fluids in each shell, the meniscus curves of fluid-fluid interface can be obtained approximately, then the contact angle can be calculated by fitting the profiles <sup>1</sup>.



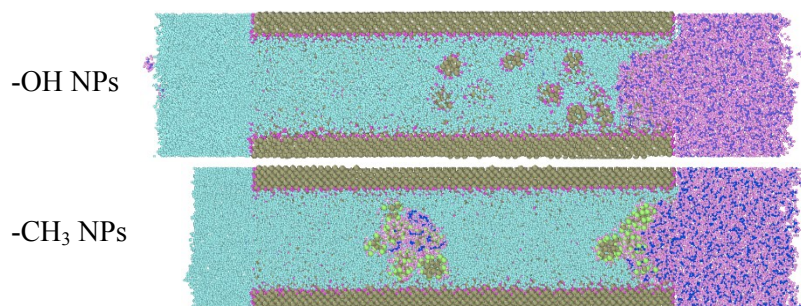
**Figure S3** Contact angle for different type of fluids

The calculated contact angles for different type of fluids during simulation time are shown in Figure S3. According to Figure S3, the value for all fluids is much smaller than 90°, indicating the water-wet property for capillary. Meanwhile, contact angles for all fluids will decrease initially due to the development of meniscus stage. Combing analysis of configuration and interfacial thickness, the fluids flow will keep stable after 10 ns simulation time. From Figure S3, the contact angle for fluids tends to dynamic equilibrium after 10 ns. The value for NP-free case is relatively higher than fluids with NPs during whole process, while contact angle for fluids with -CH<sub>3</sub> NPs is almost identical with the value of fluids with -OH NPs. The difference of contact angle for three kinds of fluids are very small during the dynamic equilibrium stage.

Based on the Lucas-Washburn equation, there is an inverse relationship between contact angle and displacement. Usually, the bigger the contact angle <sup>2</sup>, the smaller the displacement into the nanopore. As the small difference of three-phase contact angle for all three fluids, the wettability alteration of capillary is secondary effect factors for nanofluids transportation in silica nanopore.

## S6. Further Simulation on Displacement Process with NPs

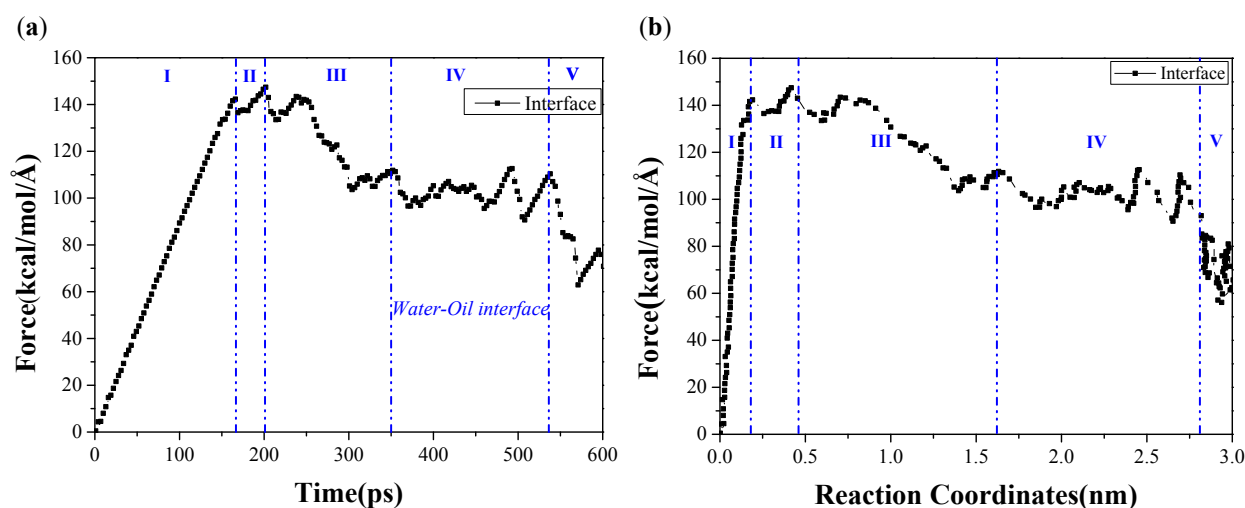
Here, the simulation with longer time was performed on two NPs systems to displace all oil molecules out from the silica nanopores. Therefore, 28.0 ns and 34.0 ns were employed for  $-OH$  NPs and  $-CH_3$  NPs, respectively. The final configurations are shown in Figure S4.



**Figure S4** Simulation configurations for systems with  $-OH$  NPs and  $-CH_3$  NPs at 28.0 ns and 34.0 ns, respectively.

### S6. Steered Molecular Dynamics Simulation for Nanoparticle

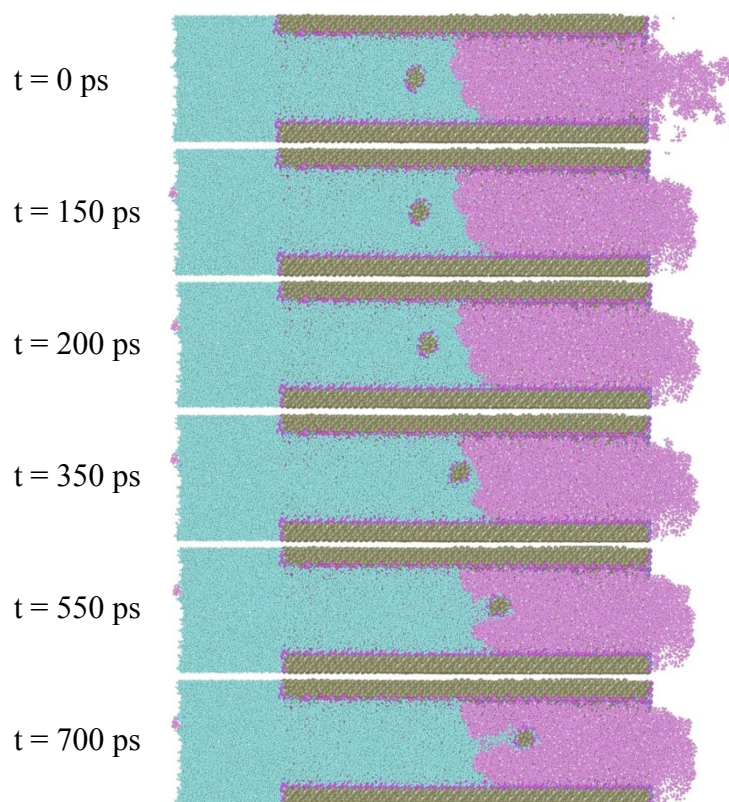
In order to briefly probe the resistance of fluid interface and oil phase to the hydrophilic NPs, the steered molecular dynamics (SMD) method<sup>3</sup> was adopted to mimic the migration of nanoparticles in the pore from water to the oil phase. An external force was applied on the center of one NP to horizontally drag it to the oil phase.



**Figure S5** External force profile for pulling a hydrophilic NP from the water to the oil phase by steered molecular dynamics simulation. (a) Force vs time; (b) force vs reaction coordinates.

The resistance experienced by NP is plotted with time evolution and reaction coordinates, shown in Figure S5. Combining the analyses of Figure S5 (a) and Figure S5 (b), the force can be divided into five stage. Initially, the force rapidly increases during the first  $\sim 150$  ps (Stage I), the NP moves very slowly but gains inertia at this stage. When the external force reaches certain value at simulation time of  $\sim 200$  ps (Stage II), the NP starts to move more significantly.

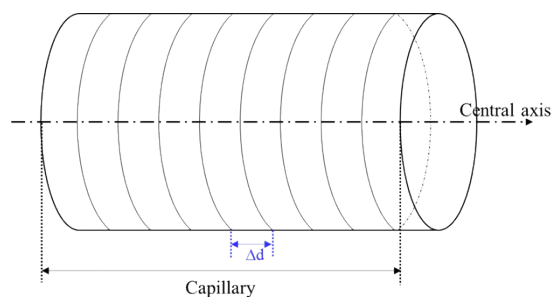
In Stage III, the NP starts to move to the water-oil interface, and the external force reduces to a stable value, until the NP passing through the fluid interface during simulation time from  $\sim 350$  to  $\sim 550$  ps (Stage IV). The external force further drops after the NP fully enter the oil phase owing to repulsion between NP and oil molecules (Stage V). During the passing of NP through the fluid interface, some water molecules are attached with NP and move together to the oil phase. The detailed SMD snapshots at different stages are shown in Figure S6.



**Figure S6** Simulation configurations about pulling one NP from water phase to oil phase by steered molecular dynamics.

### S7. Local pressure along capillary

To calculate the local pressure distribution along axial direction, simulation box was divided into layers with the thickness of  $\Delta d = 1.5 \text{ \AA}$  along y direction. For different layer, the pressure of individual atoms was calculated in LAMMPS, then the local pressure distribution was obtained by integrating the stress of atoms in each layer along axial direction. The schematic diagram is shown in Figure S7. The method has been well adopted in other literature<sup>4</sup>.



**Figure S7** Schematic diagram to calculate local pressure distribution along capillary.

### Reference

1. X. Wang, S. Xiao, Z. Zhang and J. He, Effect of Nanoparticles on Spontaneous Imbibition of Water into Ultraconfined Reservoir Capillary by Molecular Dynamics Simulation, *Energies*, 2017, **10**, 506.
2. G. Martic, F. Gentner, D. Seveno, D. Coulon and J. D. Coninck, A Molecular Dynamics Simulation of Capillary Imbibition, *Langmuir*, 2002, **18**, 7971-7976.
3. S. Park and K. Schulten, Calculating potentials of mean force from steered molecular dynamics simulations, *J. Chem. Phys.*, 2004, **120**, 5946-5961.
4. W. Li, W. Wang, X. Zheng, Z. Dong, Y. Yan and J. Zhang, Molecular dynamics simulations of water flow enhancement in carbon nanochannels, *Comput. Mater. Sci.*, 2017, **136**, 60-66.