Effect of Nanoparticles on Oil-Water Flow in a Confined Nanochannel: a Molecular Dynamics Study
Jianyang Wu, Jianying He, Ole Torsæter, Zhiliang Zhang, Norwegian University of Science and Technology (NTNU), Norway

Abstract

Nanotechnology has contributed to the technological advances in various industries, such as medicine, electronics, biomaterials and renewable energy production over the last decade. Recently, a renewed interest arises in the application of nanotechnology for the upstream petroleum industry; such as exploration, drilling, production and distribution. In particular, adding nanoparticles to fluids may drastically benefit enhanced oil recovery and improve well drilling, such as changing the properties of the fluid, wettability alternation of rocks, advanced drag reduction, strengthening sand consolidation, reducing the interfacial tension and increasing the mobility of the capillary-trapped oil. In this study, we focus on the fundamental understanding of the role of nanoparticles on the oil-water binary mixture in a confined nanochannel. A series of computational experiments of oil-water-nanoparticle flow behaviour in confined clay nanochannels are carried out by molecular dynamics simulations. Three sizes of nanochannels and different numbers of nanoparticles are considered. The results show that the pressure to drive the oil-water binary mixture through a periodic confined channel increases dramatically with the reduction of the channel size. In the absence of nanoparticles the pressure increases with the propelled displacement. Interestingly, an opposite behavior is observed in the oil-water system mixed with a small amount of nanoparticles: the pressure decreases with the increase of the displacement. The findings from molecular dynamics simulations may elucidate the role of nanoparticles on the transport of oil in nanoscale porous media, although the exact mechanisms remain to be further explored.

Introduction

World-wide research and development of nanotechnology have primarily focused on application to renewable energy and sustainability; nanoelectronics based information and communications technology; stronger and lighter materials with improved properties; biomedical devices and nanomedicine et al. In Norway, possibly also in other countries, application to petroleum industry was excluded from the previous nanotechnology research program. With the passing of the era of easy oil and the increasing difficulty of finding new resources, attention of the traditional oil and gas industry has been directed to extract more resources from existing oil fields (enhanced oil recovery) and from the fields exposed to extremely harsh environments by using new technologies and solutions. Nanotechnology bears the promise and has received great attention recently from the petroleum industry and there is a general perception that more than a decade’s nanotechnology hype may become nano reality in the oil field (Rassenfoss 2012; Amanullah 2010).

One of the most promising applications of nanotechnology to the oil and gas fields, in particular for enhanced oil recovery and drilling, is the new generation fluids based on nanofluids and nanoparticles (NP). Nanofluids are a class of fluids engineered by dispersing NPs (nanofibers, nanotubes, nanowires, nanodrops) in base fluids. Nanofluids were first known because of their thermal properties. Since the introduction of “nanofluid” (Choi and Eastman 1995) for carbon and metal-based NPs, research has intensified on their enhanced thermal-physical properties and heat transfer performance. A large amount of experimental work has demonstrated that the increase of thermal conductivity with increasing volume fraction of NPs can be significantly larger than predicted by the effective mean theory (Fam and Wang 2011, Saidur et al. 2011, Yu and Xie 2012). The discrepancy between the prediction by the conventional theory and the observations in many experiments has inspired
efforts in identifying the mechanisms of enhanced thermal physical properties of nanofluids based on a variety of experimental observations and numerical simulations (Yu and Xie et al. 2012, Evans et al 2006). The exact heat transfer mechanisms are still under debate, however, three major mechanisms responsible for the reported conductivity enhancement have been proposed in the literature: 1) liquid-layering, 2) particle aggregation and 3) particle motion. The liquid-layering mechanism was proposed based on the idea that liquid molecules near the solid-liquid interface are more orderly organized and such ordered layer may act as a bridge to generate more effective thermal transport across the interface (Choi et al. 2001). Molecular dynamics simulations have revealed that the solid-liquid interface strength (wetting versus non-wetting) determines the interfacial thermal resistance. Stronger interaction results in thicker layer and lower thermal resistance and vice versa (Xue et al. 2003). Particle aggregation to form chain structures have been confirmed in experiments. Because the chain structure facilitates the heat transport along the direction of heat flux, the heat conduction can be enhanced due to particle aggregation (Hong et al. 2006). The thermodynamical effects of Brownian motion (random collisions of the surrounding liquid molecules) of NPs in nanofluids may increase the heat transport among particles. However, the thermal diffusivity of the base fluid is usually two or three orders larger than the particle, molecular dynamics simulation has shown that the Brownian motion of NPs play an insignificant role on the thermal conductivity of nanofluids (Evans 2006).

The finding by Wasan and Nikolov (2006) about the polystyrene NPs has drawn great attention from the oil industry. When the NPs meet an oil drop, it will concentrate around the drop and forming a thin wedge film between the surface and the oil drop. The NPs will diffuse into the wedge film, causing an increase in local concentration and subsequently an increase in disjoining pressure in the film region. With this dynamic spreading process, an oil drop can finally detach from the surface completely. The phenomenon which results in reduction of interfacial tension and increased spreading detergent effect does not limit to the polystyrene NPs and inspires the search of other NPs. The most commonly used NPs for enhanced oil recovery study are the spherical silica NPs with a diameter in the range of several to tens of nanometers. Various lab scale experimental studies have been carried out to understand the transport behavior of NPs through porous media (Rodriguez et al. 2009, Skauge et al. 2010) and to explore the potentials of silica NPs to form stabilized oil-in-water and/or water-in-oil emulsions (Zhang et al. 2010). Functionalized NPs can form a high stable emulsion to determine the oil saturation situation, improve the oil flow mechanism and identify the location of bypassed oil. Rodriguez (2009) et al. have shown that silica NPs move through the rocks in a way similar to colloid with weak attachment to the wall. The van der Waals force is probably responsible for the observed attachment of NPs to the wall. Although the exact interface mechanisms are still unclear, it is generally expected that silica NPs will also reduce the surface tension between oil and rock and enhance the depletion of oil from the porous media. Before full scale deployment of silica NPs, there are many issues to be resolved, such as how the particles behave in a reservoir and how to design the appropriate silica NPs.

In this study, we focus on the fundamental understanding of the role of silica NPs on the oil/water binary mixture in a confined nanochannel. Molecular dynamics simulation is a powerful tool to understand the deformation and flow behavior of nanomaterials and its link to the atomistic structures (Wu et al. 2011). A series of computational experiments in which hydrophilic silica NPs mixed with an oil-water system confined in clay nanochannels is performed by molecular dynamics simulations. First, we examine the effect of NP on a clay-oil-water system without a driving pressure; such as the mobility of hydrophilic silica NPs mixed with an oil-water system confined in clay nanochannels. Molecular dynamics simulation is a powerful tool to understand the deformation and flow behavior of nanomaterials and its link to the atomistic structures. Structure and simulation details

Rocks that are rich in kaolinite are known as kaolin clay. Kaolinite with chemical composition Al₂Si₂O₅(OH)₄ is the most common 1:1 phyllosilicate consisting of a gibbsite octahedral sheet and a silicon oxide tetrahedral sheet. Kaolinite is a layer clay with neutral charge, and the asymmetric structure allows the formation of hydrogen bonds between consecutive layers. A silicon tetrahedral sheet is linked through oxygen atoms to an octahedral sheet of alumina. Thus each layer has two different surfaces. One basal surface is made of the oxygen atoms of the six-membered silicate rings and the other is of hydroxyl groups which are tied to the hexacoordinated Al atoms of the four-membered aluminates rings. There are aslo hydroxyl groups located within the shared plane of the octahedral/tetrahedral sheet. The silicate and aluminate layers are kept together to be a bulk structure via hydrogen bonds formed between basal oxygen atoms of the six-membered silicate rings and hydroxyl groups of the alumina octahedral of the adjacent layer. The triclinic crystal structure of kaolinite is show in Figure 1, based on the data by Young and Hewat (Young and Hewat 1988), which has space group P1 symmetry with the lattice parameters: \(a = 0.5149\) nm, \(b = 0.8934\) nm, \(c = 0.7384\) nm, and \(\alpha = 91.93^\circ, \beta = 105.04^\circ, \gamma = 89.79^\circ\).

To construct the molecular dynamics simulation models, a cuboid-shaped simulation cell is first created by converting original triclinic cell into an orthogonal cell possessing both (001) basal octahedral and tetrahedral surfaces. To investigate the oil-water-clay-(NP) system, a simulation cell containing 1200 kaolinite unit cells \((10 \times 12 \times 10)\) from the converted orthogonal
cell with $51.5 \times 107.2 \times 69.5 \, \text{Å}^3$ is generated, and the middle 8 layers are deleted with residual top and bottom kaolinite slabs to create a 54 Å thickness interlayer. Then the water and hexane molecules are added randomly into the left part and right part of the interspace to obtain a three phase system (Figure 2a). To study the pressure-driven water and oil flow through a nanochannel, another model with $51.5 \times 268.0 \times 69.5 \, \text{Å}^3$ which consists of a 10 nm long cuboid nanochannel with different side length connected to a water-hexane filled reservoir in the left side, a water filled reservoir in the right side and a kaolinite membrane in the leftmost, is constructed. The pressure is introduced by moving the kaolinite rightwards. The rectangle-shaped cross-section of nanochannel is utilized to ensure a charge neutral system which is modeled to give pH independent results. For preparing the silica NP, a spherical NP with about 1.5 nm diameter is carved out from an amorphous glass bulk. Then unsaturated silica atoms are removed from the surface and the non-bridging oxygen atoms are saturated with hydrogen atom. The silica NP contains 141 atoms ultimately.

The CLAYFF forcefield developed by Cygan et al (2004) is employed to describe the kaolinite and silica NPs, and it has been widely used to simulate the clay miner and organoclay systems (Zhu et al. 2011; Croteau et al. 2010; Fan et al. 2011). In this forcefield, the interaction between metal and oxygen is described by a short range Lennard-Jones functions known as the van der Waals term and a long range Coulombic function expressed in a form of pairwise interacting atomic charges, whereas the only bonded interaction within the hydroxyl groups OH are described by a harmonic bond which is based on the single point charge water model (Berendsen et al. 1981). The total configuration energy of kaolinite system is give by the sum of Coulombic and Lennard-Jones functions:

$$E_{\text{total}} = E_{\text{Coul}} + E_{\text{vdW}} = \frac{e^2}{4\pi\varepsilon_0} \sum_{i<j} \frac{q_i q_j}{r_{ij}} + D_{0,i,j} \left[ \left( \frac{R_{0,i,j}}{r_{ij}} \right)^{12} - 2 \left( \frac{R_{0,i,j}}{r_{ij}} \right)^6 \right]$$

(1)

where the first Coulombic terms, $q_i$ and $q_j$ are partial atomic charges from quantum chemistry calculation, and $r_{ij}$ is the distance between atoms $i$ and $j$. $e$ and $\varepsilon_0$ represent the charge of electron and the dielectric permittivity of vacuum, respectively. The second van der Waals energy term, defined by a common Lennard-Jones (12-6) function, represents a short-range repulsive and a long-range attractive dispersion energy. $D_{0,i,j}$ and $R_{0,i,j}$ are the depth of potential well and the finite distance at which the interaction energy is zero. The parameters of van der Waals interaction between atoms $i$ and $j$ are calculated according to the arithmetic combination rule:

$$D_{0,i,j} = \sqrt{D_{0,i} D_{0,j}}$$

(2)

$$R_{0,i,j} = (R_{0,i} + R_{0,j}) / 2$$

(3)

In a description of water model, the single point charge model is implemented to model water as hydroxyl groups OH in CLAYFF forcefield. For the hexane molecules, a united atom forcefield (Pant et al. 1993; Capaldi et al. 2004) is employed to model hexane to reduce the computational resource. In addition to LJ and Coulumbic functions, in order to keep a stable structure of silica NP, the CVFF forcefield (Dauber-Osguthorpe et al. 1988) is employed to model the harmonic bond and angle in the silica NPs. The atoms of water and hexane interact with each other and with kaolinite also via dispersive and electrostatic forces as described above. Tables 1 and 2 show the forcefield parameters for all nonbonded and bonded interactions in the systems, respectively.

Large-scale molecular dynamics simulations are performed using LAMMPS simulation package (Plimpton et al. 2007) under the NVT ensemble (constant numbers of atoms, volume, and temperature). A constant temperature of 300 K for water, hexane and particles is controlled by a Nosé-Hoover thermostat, and the atoms of kaolinite clay layers are fixed during the entire simulations. The Verlet velocity algorithm is used to numerically integrate Newton’s equation of motion with a timestep of 1 fs. Periodic boundary conditions (PBC) are applied to all three directions of the simulated boxes. The Particle-Particle-Particle-Mesh method (PPPM) (Hockney, 1981) is used to correct the long-range Coulombic electrostatic interaction. The cutoff for all interactions is set to 1.0 nm. For the first model, the system with NP-free is equilibrated for 1 ns, followed by 4 ns of flow simulation, while the systems with NP is given a 20 ps relaxation time to examine the NPs’s dynamical behaviors in three phase clay-oil-water system. For the second model, a dynamics run of 200 ps is performed to give a relaxation for the two reservoirs system. To enforce a pressure-driven flow of the oil-water binary through the nanochannel, the kaolinite membrane is given a constant velocity of 10 m/s toward the right reservoir. The driving pressure is calculated by the sum of force of molecules in the system acted on the membrane along the direction from one reservoir to another divided by area of $xz$ plane of the membrane. The radius distribution functions (RDF) describing how the density varies as a function of the distance
from a reference point are obtained by averaging the collected values of every 10th ps and the density profile from the values of every 100th ps. For the dynamical properties, the mean square displacement (MSD) which is associated with atomic diffusivity as a function of time is calculated by:

\[
\langle X^2(t) \rangle = \frac{1}{N_m N_t} \sum_m \sum_{t_0} \left[ X_i(t + t_0) - X_i(t_0) \right]^2
\]

where \( N_m \) is the number of diffusing molecules, \( N_t \) is the number of time origins used in calculating the average, and \( X_i \) is the coordinate of the center of mass of molecule \( i \).

Results and discussion

Oil-water-clay-system
First, we consider an oil-water binary mixture in a confined nanochannel without NP as a reference to study the dynamical properties prior to discussing effect of NP. Figure 2 shows the representative side-views of the clay-oil-water multiphase system. The initial model is shown in Figure 2(a). After simulation time of 5 ns, the cuboid-shaped oil and water in a confined nanochannel change to disordered shapes due to thermodynamics and a smooth interface between oil and water is observed as shown in Figure 2(b), as expected. Figure 3 shows the MSDs of water and oil molecules during the last 4 ns simulation time. The MSDs-time curves are linear, which suggests the water-oil binary mixture in this multiphase system is already in an equilibrium state. A small value of MSDs for both water and oil in \( z \) direction is observed due to a confinement of the movement in \( z \) direction. Large value of MSDs for both water and oil in \( y \) direction is related to the changes of interface between oil and water by preferred moving of aqueous along \( y \) direction.

Oil-water-clay-nanoparticle-systems
To study the effect of NPs on the flow of oil-water mixture in a confined clay nanochannel, NP is placed either in oil or water aqueous as well as in both liquids. Figure 4 shows initial and equilibrium configuration snapshots of a clay-oil-water-NP multiphase system. NPs are placed in middle of both oil and water aqueous. After a simulation time of 4ns, NPs move towards and stick to the clay wall due to both vDW and Coulombic force between NPs and clay. This implies that the presence of NPs changes the surface properties between aqueous and clay due to a new surface formation between NP and clay. The same phenomenon is observed for the cases with NP placed only in oil or in water. To quantify the effect of NPs in this clay-oil-water multiphase system, the MSDs of each component are calculated. Figure 5 shows the MSDs of water and oil molecules as a function of simulation time with or without NPs. For the water component, the self-diffusion coefficient of water with NP-free defined by the slope of the late linear part of curves divided by 6 (Berne 1971) is the largest, whereas the oil is opposite. This means that the presence of NP in this multiphase also influences the dynamical properties of the components in a confined nanochannel. The water in the system with NP placed in oil possesses lowest motion. It is concluded that NP placed in oil phase promotes the self-diffusion of oil while restrains that of water. It is also of importance to give a quantification of dynamical properties of NP in this multiphase system. Figure 6 shows the MSDs of NP as a function of time. It is shown that the NP will rapidly move toward the clay wall from the \( z \) direction curve in Figure 6(a). The time required for reaching and being a stable state on the clay wall is around 1.3 ns. After that time, a flat curve in \( z \) direction is observed, suggesting a static state of NP in \( z \) direction owing to stable and strong interaction between NP and clay. Meanwhile, the NP also moves along \( y \) direction before it reaches a favorable energy state, while the NP almost does not move in \( x \) direction except in the beginning. It is observed that NP placed in oil has largest total MSD value, which means the travelling distance of this NP is relatively long. From 0 – 0.5 ns, a linear curve with small slope observed represents the NP is trying to escape the oil-surrounded environment. Then after reaching a water-surrounded environment, it moves rapidly towards the clay wall due to relatively weak hindrance as other cases. For the case of one NP in oil and one in water, the movability of NP is as strong as the case of NP in water. It is found that the NP first tries to be in a water-surrounded environment and sticks to the clay wall due to its hydrophilic surface properties.

With regard to structure properties, analysis of RDFs can help one understand microscopic behavior of molecules in this multiphase confined system. A series of RDFs are displayed in Figure 7. It is clearly shown that, from Figure 7(a), first peaks around 3.0 \( \text{Å} \) in \( g_{O-O}(r) \) are a clear indication of the existence of stable hydrogen bonding. It is also found that a peak around 3.8 \( \text{Å} \) in \( g_{O(H2O)-CH3(oil)}(r) \) is a structure surface property between oil and water, which may be relative to the interfacial tension between oil and water. A bulb and low peak around 3.8 \( \text{Å} \) in \( g_{O(H2O)-CH3(oil)}(r) \) implies a relatively stable surface between oil and clay. In Figure 7 (b) and (c), we show radial distribution functions regarding NP in this system. One of the additional RDFs \( g_{O(H2O)-CH3(oil)}(r) \) is demonstrated, in which a first peak around 3.0 \( \text{Å} \) also represents strong hydrogen bonding forms between clay and NP. A NP with large surface/volume ratio placed in oil-water introduces a new structural property among this system which gives a possibility to modify the wettability of rocks.
Nanoparticle-free oil-water flow through nanochannel

The preliminary work shown above indicates that NP participated in the oil-water-clay system could change the dynamical and structural properties of the system. A further study that a set of simulations of pressure-driven oil-water binary mixture flow through a confined nanochannel are performed to study the effect of NP. A perspective of framework model with a 29.6 × 20.6 Å² cross-section area nanochannel in compound side-view is shown in Figure 8. This nanochannel connects to the reservoirs along y direction. Three sizes of nanochannel are built to investigate the size effect on the pressure-driven oil-water binary mixture flow through nanochannels. In consideration of non-equilibrium systems, a short 25 ps time is given to relax the systems. Figure 9 shows the pressure difference on the membrane in y direction as a function of propelled displacement for various nanochannels. It is clearly shown that pressure difference drastically increases for the system with the smaller nanochannel, especially in the large displacement range. The main reason is that the dynamical diameter of hexane is too large to flow easily through the small nanochannel. With the increase of size of nanochannel, the pressure for pushing oil-water binary mixture flow through the nanochannel significantly decreases. It is observed that, from the Figure 9(b), the pressure increases with the increasing displacement of the membrane in the region from 0–20 Å, and a relatively flat curve follows in the middle range. Then a peak at 20 Å indicates a strong resistance for aqueous flow to another reservoir. For the case of large channel, a relatively small pressure is required to move the membrane (Figure 9(c)). A linear function (y = 0.007787 x + 0.19457) is obtained by curve fitting. Generally, it is found that the pressure gradually increases for pushing the oil-water mixture flow through the nanochannel.

Nanoparticle-oil-water flow through nanochannel

To investigate the effect of NPs on the oil-water flow through the nanochannel, three cases with one, two and four NPs placed in water phase of left reservoir are studied. We focus on the largest nanochannel model. The corresponding volume of NPs is carved out from the water phase to eliminate the densification. Figure 10 show the pressure on the membrane as a function of amount of NPs are placed, whereas large amount of NPs in the injection aqueous introduces large pressure difference. It is observed that, from Figure 10(a) and (b), two NPs placed in water lead to a larger pressure decrease compared with the case of one particle. This suggests that there is a critical concentration of NPs on the oil-water binary mixture on the flow through the nanochannel. Our preliminary work (unpublished) shows that large number of NPs in this confined nano-interlayer will result in a self-aggregation of NPs. Two significant pressure drops are observed in the Figure 10(c), which is strongly linked to the motion of NPs. A close watch of the flow process for the one NP case indicates the NP is rotating and moving forward before sticking to the membrane. For the double NP case, two NPs are rotating and moving forward along the clay wall. Then the lower NP moves to the middle and meet with the upper NP. The NP escapes from the clay wall due to a stronger interaction with the lower NPs. Upon approaching the nanochannel, the lower NP frees from the bondage of self-aggregation and then enters into the nanochannel. The upper NP is not able to flee from the membrane due to strong interactions. For the case of four NPs system, we observed two left side NPs are always stick to the clay wall and membrane without rotation. This suggests that two significant pressure drops are not from the break hydrogen bond between NPs and clay wall during the movement of membrane. From a close inspection at the first lowest point, it is found that the upper right NP reaches to the corner. Then it sits at this corner for around 70 ps, but it is rotating to climb the “mountain” to enter into the nanochannel, which is responsible for the increase of pressure during this stage. The lower right NP first rotates and moves towards the nanochannel. Then the two lower NPs stick together due to the nonbond force, which leads to the lower right NP crawl to the nanochannel without rotating. With approach the nanochannel, the NP can not maintain this motion. It starts rotating again and flies to the nanochannel ultimately. Figure 11 shows the two stages (before propelling and after propelling) snapshots of pressure-driven oil-water-NP system. It is observed that one NP stays at the nanochannel from Figure 11(b). From the Figure 11(c), it is found that one NP stays at the nanochannel while another reaches to another side window of reservoir. Figure 12 displays the density profiles of water and oil of nanochannel systems along y direction at two stages. It is found that the distributions of water and oil components in the NP-free system are smoother instead of numbers of peaks after a relaxation time. Obviously, the diffusion of water and oil in the case of NP is faster than that of NP-free, which is consistent with the above Oil-water-clay-(NP)-systems. For the density profiles of water, two sharp peaks appear at the ends of the nanochannel due to an adsorbed layer at the window edge and an abrupt diameter change of the flow channel. In the gray covered region, linear curves are seen which suggest a pressure gradient inside the nanochannel. The pressure gradient boosts the flow of nanoparticle through the nanochannel in spite of relatively strong interaction between clay and nanoparticle as Figure 11(c’) presents. The pressure gradient decreases with the increased propelled distance. A large pressure gradient for both water and oil in the NP-free system compared to NP-placed system is observed. This strongly implies that the presence of NP promote the flow of oil-water binary mixtures through clay nanochannel. RDFs of pairwise of O(water), O(clay) and O(NP) are shown in Figure 13. Besides peaks observed in gO(clay)-O(water)(r), gO(NP)-O(water)(r) and gO(water)-O(water)(r) around 3-3.5 Å, several sharp peaks also in gO(clay)-O(NP) around 2-4 Å mean that there is also a strong hydrogen bonding exists between clay and NPs.

Conclusions and outlook

The oil-water flow through a confined kaolinite nanochannel systems has been investigated by classical MD simulations based on the CLAYFF forcefield. Independent of environment, oil-surrounded or water-surrounded, hydrophilic silica nanoparticles
move towards and stick to the kaolinite wall due to vdW interaction in order to minimize surface energy. The flow pressure of oil-water mixture with nanoparticle through the confined nanochannel is found to be strongly channel size dependent. The presence of nanoparticle not only changes the dynamical and structural properties of oil-water-clay systems, but also enhances the oil-water flow through the nanochannel at a small nanoparticle concentration, which implies that nanoparticles can be potentially utilized for enhanced oil recovery. While the nanoparticle-free oil-water flow behaves in laminar flow manner, with the increase concentration of nanoparticle the flow tends to change from laminar to turbulent type. The nanoparticle first slides along the clay wall in a local low velocity with the process of breaking and forming hydrogen bonds, whereas it rotates forwards in a local high velocity aqueous environment, and escapes from the attractive clay wall ultimately to enter into the nanochannel.

Although it is limited by the simulation scale, our study provides valuable information about flow behavior in porous media and optimization of nanoparticle concentration. At the same time, this study has raised up a number of key topics for future work: (1) the effect of hydrophobic silica and Janus silica nanoparticles on the wettability alternation and oil-water flow behavior through nanochannels; (2) design of nanoparticles with improved performance and reliability in harsh environments; and (3) experimental verification and further development of nanoparticle based flow.

Acknowledgements

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Table and caption

Table 1 Nonbond parameters of CLAYFF forcefield, and hexane.

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<th>definition</th>
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Table 2 Bond parameters of CLAYFF, CVFF forcefield, and hexane.

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Figures and captions

Figure 1 Crystal structure of a unit cell of kaolinite.

Figure 2 Representative side-views of a clay-oil-water system simulation box. (a) initial configuration of a clay-oil-water system, top and bottom are the kaolinite layers. Middle left is the oil (red), and middle right is the water (green). (b) Top-view equilibrium snapshot of a clay-oil-water system.
Figure 3 MSDs (x, y, and z directions, and total) of (a) water molecules and (b) oil molecules as a function of time in a multiphase clay-oil-water system at 300 K.

Figure 4 Representative side-views of a clay-oil-water-NP multiphase system simulation box. (a) Initial configuration, one NP in oil and one in water. (b) Equilibrium configuration, two NPs sticks to the clay wall and in a water-surrounded environment.

Figure 5 MSDs of (a) water molecules and (b) oil molecules as a function of time in clay-oil-water-NP multiphase systems at 300 K.

Figure 6 MSDs of silica nanoparticle as a function of time in clay-oil-water-NP multiphase systems at 300 K. (a) MSDs of (x, y, and z directions, and total) for one NP in water, (b) total MSDs for NP mixed with different liquids.
Figure 7 RDFs of (a) pairwise of O(water), O(clay) and CH₃(oil) for NP-free, (b) pairwise of O(water), O(clay), O(NP) and CH₃(oil) for NP mixed with water, and (c) pairwise of O(water), O(clay), O(NP) and CH₃(oil) for NP mixed with oil.

Figure 8 A perspective of nanochannel system with a $29.6 \times 20.6$ Å² cross-section area in compound side view.
Figure 9 Pressure difference on the membrane as a function of propelled distance for (a) $15.7 \times 11.3 \, \text{Å}^2$, (b) $29.6 \times 20.6 \, \text{Å}^2$ and (c) $43.4 \times 36.9 \, \text{Å}^2$ cross-section area nanochannels clay-oil-water multiphase systems at 300 K.
Figure 10 Pressure difference on the membrane as a function of propelled distance for possessing $43.4 \times 36.9 \text{ Å}^2$ cross-section area nanochannels in clay-oil-water-NP multiphase systems with (a) one, (b) two and (c) four NPs.
Figure 11 Representative side-views of pressure-driven oil-water-NP flow through a confined clay nanochannel. (a), (b) and (c) show that the initial membrane placed between the reservoirs with one, two, four NPs mixed with oil-water system, respectively. (a'), (b') and (c') show that 8 nm membrane placed between the reservoirs with with one, two, four NPs mixed with oil-water system, respectively. Water is colored with green in left reservoir where NP is mixed, and oil is colored with red.
Figure 12 Density profiles of water and oil along the y direction (flow direction) in clay-oil-water-(NP) multiphase systems for (a) and (b) with NP-free, (c) and (d) with one NP, (e) and (f) with two NPs, (g) and (h) with four NPs.
Figure 13 RDFs of pairwise of O(water), O(clay) and O(NP) in clay-oil-water-NP multiphase systems (a) with one NP, (b) with two NPs and (c) with four NPs by MD simulations at 300 K.