Molecular-Dynamics Study Examines Effect of Nanoparticles on Oil/Water Flow

Experiments on oil/water/nanoparticle flow behavior in confined clay nanochannels were conducted with molecular-dynamics simulations. Three sizes of nanochannels and different numbers of nanoparticles were 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. 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 in the transport of oil in nanoscale porous media.

Introduction

One of the more promising applications of nanotechnology in the field of oil and gas, in particular for enhanced oil recovery and drilling, is the creation of a new generation of fluids. Nanofluids are a class of fluids engineered by dispersing nanoparticles (nanofibers, nanotubes, nanowires, or nanodrops) in base fluids. Nanofluids were first recognized because of their thermal properties.

The most commonly studied nanoparticles for enhanced oil recovery are the spherical silica nanoparticles with a diameter in the range of several to tens of nanometers. Functionalized nanoparticles can form a highly stable emulsion to determine the oil-saturation situation, improve the oil-flow mechanism, and identify the location of bypassed oil. Although the exact interface mechanisms are still unclear, it is generally expected that silica nanoparticles will also reduce the surface tension between oil and rock and enhance the depletion of oil from porous media. Before full-scale deployment of silica nanoparticles occurs, many issues remain to be resolved, such as how the particles behave in a reservoir and how to design the appropriate silica nanoparticles.

This study focused on the fundamental understanding of the role of silica nanoparticles in the oil/water binary mixture in a confined nanochannel.

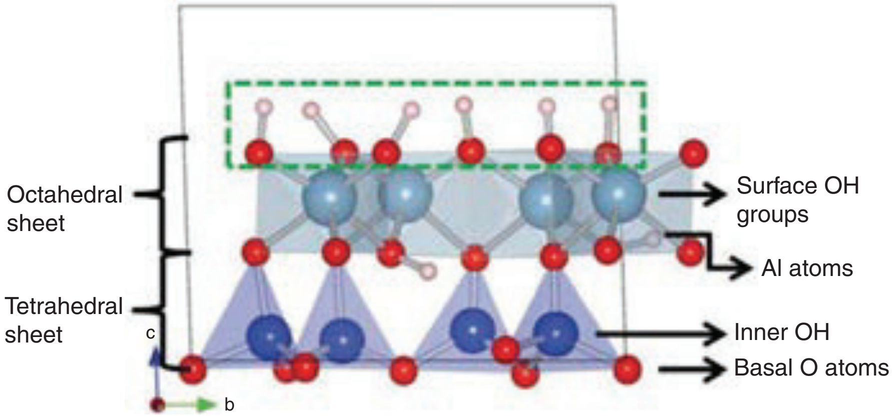

Fig. 1—Crystal structure of a unit cell of kaolinite.

Structure and Simulation Details

Rocks that are rich in kaolinite are known as kaolin clay. Kaolinite has the chemical composition $Al_4Si_4O_{10}(OH)_8$ **(Fig. 1).** Kaolinite is a layer clay with neutral charge, and the asymmetric structure allows the formation of hydrogen bonds between consecutive layers.

To construct the molecular-dynamics simulation models, a cuboid-shaped simulation cell was first created by converting the original triclinic cell into an orthogonal cell possessing both basal octahedral and tetrahedral surfaces. To investigate the oil/water/clay/nanoparticle system, a simulation cell containing 1,200 kaolinite unit cells (10×12×10) from the converted orthogonal cell with 51.5×107.2×69.5 Å was generated and the middle eight layers were deleted with residual top and bottom kaolinite slabs to create a 54-Å-thick interlayer. Then, the water and hexane molecules were added randomly into the left part and right part of the interspace to obtain a three-phase system **(Fig. 2a).** To study the pressure-driven water and oil flow through a nanochannel, another model with a scale of 51.5×268.0×69.5 Å was constructed, which consisted 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 region. The pressure was introduced by moving the kaolinite to the right.

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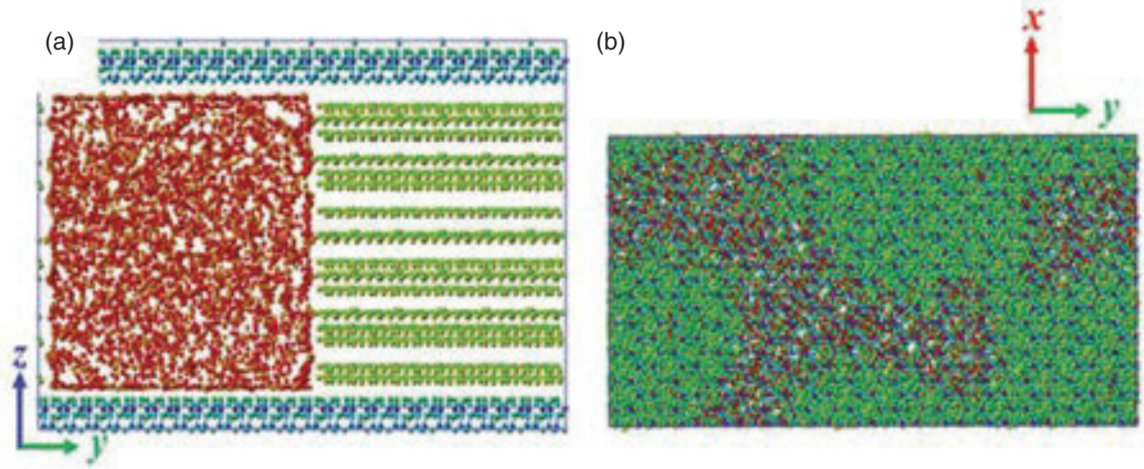

Fig. 2—Representative side views of a clay/oil/water-system simulation box. (a) Initial configuration of a clay/oil/water system. Top and bottom are the kaolinite layers. Middle left is the oil (red), and middle right is the water (green). (b) Top-view equilibrium snapshot of a clay/oil/water system.

Large-scale molecular-dynamics simulations were performed. A constant temperature of 300 K is maintained for the water, hexane, and particles, and the atoms of kaolinite clay layers were fixed during the entire simulation. Periodic boundary conditions are applied to all three directions of the simulated boxes. To enforce a pressure-driven flow of the oil/water binary mixture through the nanochannel, the kaolinite membrane was given a constant velocity of 10 m/s toward the right reservoir. The radius distribution functions (RDFs) describing how the density varies as a function of the distance from a reference point were obtained by averaging the values collected every 10 picoseconds and the density profile was obtained from the values collected every 100 picoseconds. For the dynamical properties, the mean square displacement, which is associated with atomic diffusivity as a function of time, was calculated.

Results and Discussion

Oil/Water/Clay System. First, an oil/water binary mixture in a confined nanochannel without nanoparticles was considered as a reference to study the dynamical properties before discussing the effect of the nanoparticles. Fig. 2 shows the representative side views of the clay/oil/water multiphase system. After simulation time of 5 nanoseconds, the cuboid shape of the oil and water in a confined nanochannel changed to disordered shapes because of thermodynamics and a smooth interface between the oil and water, as shown in Fig. 2b.

Oil/Water/Clay/Nanoparticle Systems. To study the effect of nanoparticles on the flow of an oil/water mixture in a confined clay nanochannel, a nanoparticle was placed either in oil or in water as well as in the combined liquids. **Fig. 3** shows initial and equilibrium configuration snapshots of a clay/oil/water/nanoparticle multiphase system. Nanoparticles were placed in the middle of both oil and water. After a simulation time of 4 nanoseconds, nanoparticles moved toward and stuck to the clay wall because of van der Waals and Coulombic forces between the nanoparticles and the clay. This implies that the presence of nanoparticles changes the surface properties between aqueous fluid and clay because of a new surface formation between nanoparticle and clay. The same phenomenon was observed for the cases with nanoparticle placed only in oil or only in water. The presence of nanoparticle in this multiphase context also influences the dynamical properties of the components in a confined nanochannel. The water in the system with the nanoparticle placed in oil possesses the lowest motion. It was concluded that the nanoparticle placed in the oil phase promoted the self-diffusion of oil while restraining that

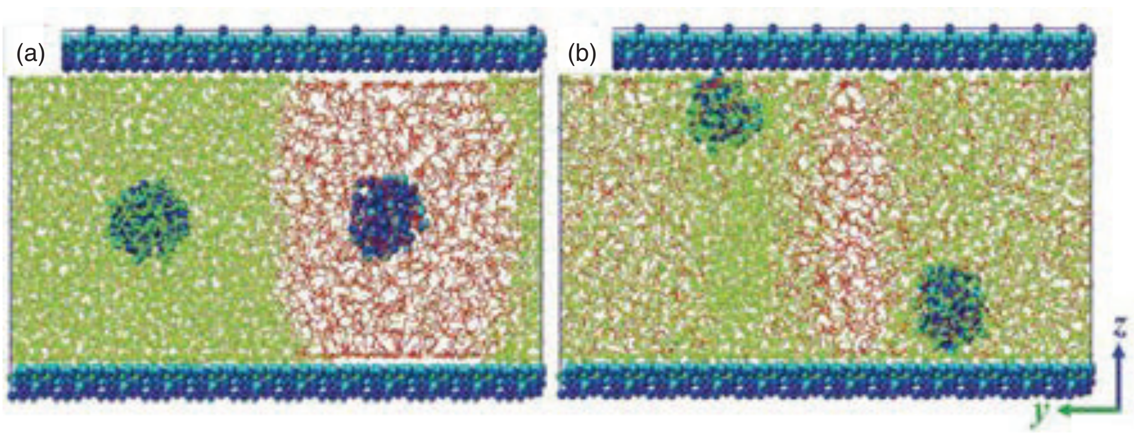

Fig. 3—Representative side views of a clay/oil/water/nanoparticle multiphase-system simulation box. (a) Initial configuration, one nanoparticle in oil and one in water. (b) Equilibrium configuration, two nanoparticles stick to the clay wall and in a water-surrounded environment.

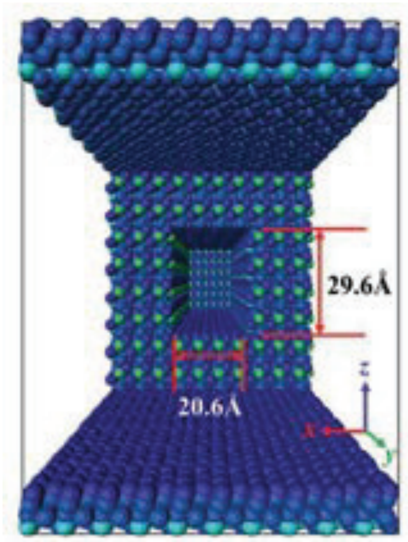

Fig. 4—A perspective view of nanochannel system with a 29.6×20.6-Å cross-sectional area in compound side view.

of water. For the case of one nanoparticle in oil and one in water, the movability of the nanoparticle was as strong as it was in the case of the nanoparticle in water. It is found that the nanoparticle first tries to be in a water-surrounded environment and sticks to the clay wall because of its hydrophilic surface properties.

Nanoparticle-Free Oil/Water Flow Through Nanochannel. A perspective view of a framework model with a nanochannel with a 29.6×20.6-Å cross-sectional area in compound side view is shown in **Fig. 4.** This nanochannel is connected to the reservoirs along the *y* direction. Three sizes of nanochannel were built to investigate the size effect on the pressure-driven oil/water binary-mixture flow through nanochannels. It was seen clearly that pressure difference dramatically increased for the system with the smaller nanochannel, especially in the large displacement range. The main reason was that the diameter of hexane is too large to flow easily through the small nanochannel. With the increase of size of the nanochannel, the pressure for pushing the oil/water binary mixture flow through the nanochannel significantly decreased. For the case of the large channel, a relatively small pressure was required to move the membrane. Generally, it was found that the pressure gradually increased for pushing the oil/water-mixture flow through the nanochannel.

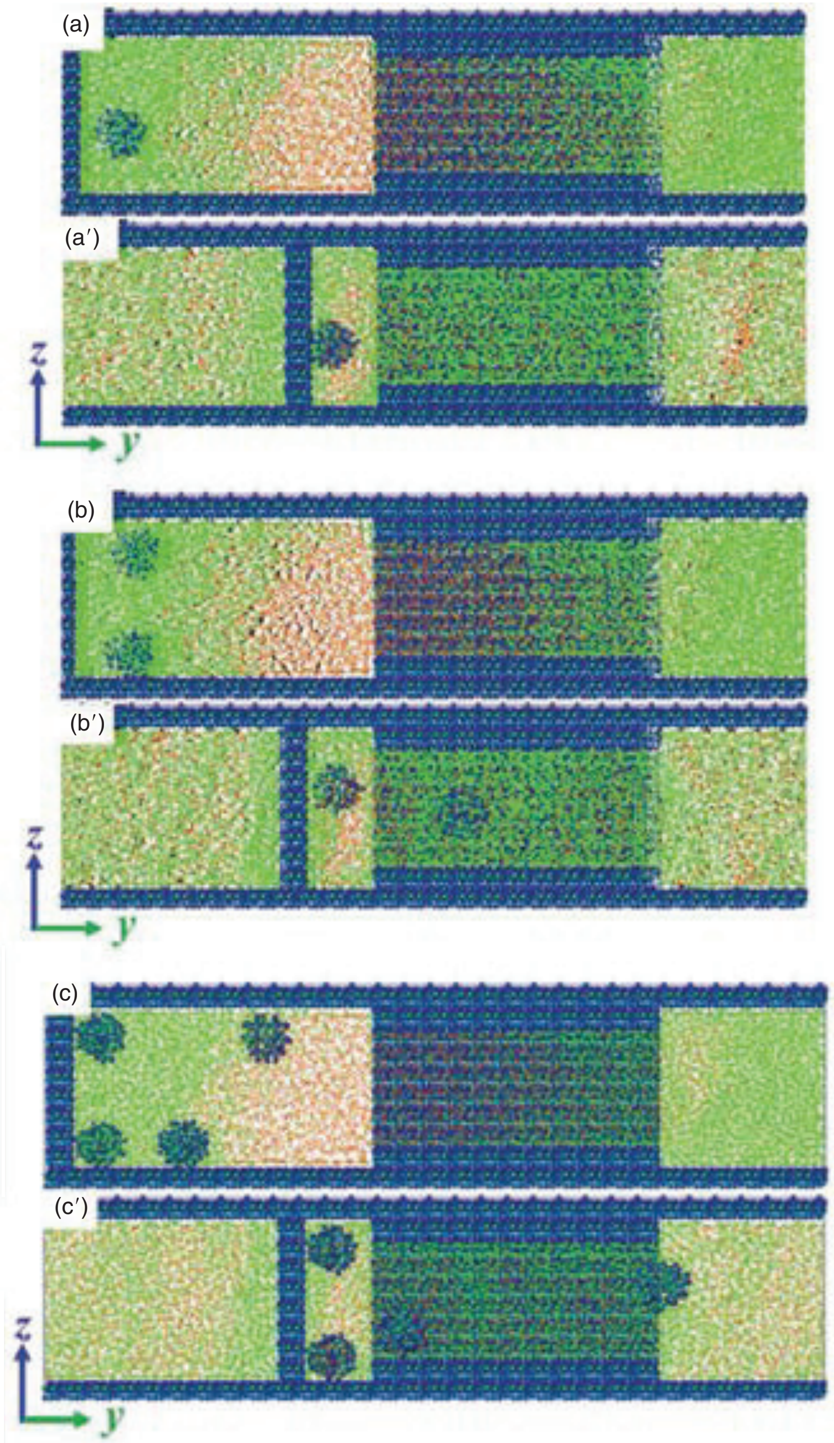

Fig. 5—Representative side views of pressure-driven oil/water/nanoparticle flow through a confined clay nanochannel. (a), (b), and (c) show the initial membrane placed between the reservoirs with one, two, and four nanoparticles mixed with the oil/water system, respectively. (a′), (b′), and (c′) show the 8-nm membrane placed between the reservoirs with one, two, and four nanoparticles mixed with the oil/water system, respectively. Water is green in the left reservoir where the nanoparticles are mixed, and oil is red.

Nanoparticle/Oil/Water Flow Through Nanochannel. To investigate the effect of nanoparticles on the oil/water flow through the nanochannel, three cases—one, two, and four nanoparticles placed in the water phase of the left reservoir—were studied. In contrast to the nanoparticle-free case, the pressure decreased during the flow process when a small amount of nanoparticles was added, whereas a large amount of nanoparticles in the aqueous injection introduced large pressure difference. It was observed that two nanoparticles placed in water led to a larger pressure decrease compared with the case of one particle. This suggests that there was a critical concentration of nanoparticles in the oil/water binary-mixture flow through the nanochannel. Preliminary work showed that a large number of nanoparticles in this confined nano interlayer will result in a self-aggregation of nanoparticles. A close watch of the flow process for the one-nanoparticle case indicates the nanoparticle was rotating and moving forward before sticking to the membrane. For the double-nanoparticle case, two nanoparticles were rotating and moving forward along the clay wall. Then, the lower nanoparticle moved to the middle and met with the upper nanoparticle. The upper nanoparticle escaped from the clay wall because of a stronger interaction with the lower nanoparticles. Upon approaching the nanochannel, the lower nanoparticle became free from the bondage of self-aggregation and entered into the nanochannel. The upper nanoparticle was not able to escape the membrane because of strong interactions. For the case of the four-nanoparticle system, two left-side nanoparticles always stuck to the clay wall and membrane without rotation. This suggests that two significant pressure drops do not result from the breaking of the hydrogen bond between nanoparticles and clay wall during the movement of membrane. A close inspection at the first lowest point revealed that the upper-right nanoparticle reached the corner and stayed there for approximately 70 picoseconds; but, it rotated to climb the "mountain" to enter the nanochannel. This was responsible for the increase of pressure during this stage. The lower-right nanoparticle first rotated and moved toward the nanochannel. Then, the two lower nanoparticles stuck together because of the nonbond force, which led to the lower-right nanoparticle crawling to the nanochannel without rotating. As it approached the nanochannel, the nanoparticle could not maintain this motion. It started rotating again and ultimately fled to the nanochannel. **Fig. 5** shows the two stages (before propelling and after propelling) of the pressure-driven oil/water/nanoparticle system.

Conclusions and Outlook

The oil/water flow through a confined kaolinite nanochannel system has been investigated by classical-molecular-dynamics simulations. Regardless of whether they are oil-surrounded or water-surrounded, hydrophilic silica nanoparticles move toward and stick to the kaolinite wall because of van der Waals forces to minimize surface energy. The flow pressure of an oil/water mixture with nanoparticles through the confined nanochannel is found to be strongly channel-size dependent. The presence of nanoparticles 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 potentially be used for enhanced oil recovery. **JPT**