Molecular dynamics studies on spreading of nanofluids promoted by nanoparticle adsorption on solid surface

Fengchao Wang\textsuperscript{a)} and Hengan Wu

CAS Key Laboratory of Mechanical Behavior and Design of Materials, Department of Modern Mechanics, University of Science and Technology of China, Hefei 230027 China

(Received 22 July 2013; accepted 13 August 2013; published online 10 September 2013)

Abstract  Spreading of nanofluids on solid substrate was studied via molecular dynamics simulations. Simulation models for two immiscible fluids (oil and water based nanofluids) confined in a slit between two planar solid walls were set up. The influence of the volume concentration of the nanoparticles on the three-phase contact line motion was investigated. We found that the larger volume concentration results in more visible nanoparticle adsorption on solid surface. This effect further induces an advancing displacement of the contact line compared with the meniscus profiles in low concentration case and that with the absence of nanoparticles. These findings are consistent with the previous experimental and theoretical results and provide the atomic-scale understanding on nanofluid spreading. © 2013 The Chinese Society of Theoretical and Applied Mechanics. [doi:10.1063/2.1305406]

Keywords: nanofluids, three-phase contact line, spreading, nanoparticles, molecular dynamics simulations

Nanofluids are suspensions containing evenly dispersed solid nanoparticles. Over the past decade, nanofluids have been reported to be very attractive as heat transfer fluids in many applications.\textsuperscript{1–3} More recently, Wasan and Nikolov\textsuperscript{4} have investigated the wetting behavior of nanofluids and proved that the wetting behavior changes if the liquid contains nanoparticles. It was reported that the disjoining pressure gradient drives further spreading of the nanofluids and it can be large enough to separate an oil droplet from the solid surface.\textsuperscript{5} These results suggest a new mechanism for enhanced oil recovery (EOR) and a new application prospect of nanofluids.\textsuperscript{6} Because the spreading of liquids on solid substrates is of interest to many practical applications and industrial processes, the dynamic motion of three-phase triple lines for nanofluids was studied both in experimental investigations and theoretical work.\textsuperscript{7} Actually, the dynamics of contact line is decided by the driven force due to the out of balance surface tension force, the adhesion force between solid and liquid phase and the resistant force due to viscosity.\textsuperscript{8} The presence of the nanoparticles would affect the interfacial phenomenon such as wetting, spreading and evaporation.\textsuperscript{9} Experimental studies and theoretical analysis show that a wetting wedge formed nearby the nanofluids/oil/substrate three-phase contact line.\textsuperscript{4} Compared with the position of the nominal contact line, there is also an advancing displacement of the contact line which increased with an increase in the nanoparticle volume concentration.\textsuperscript{5} This advancing displacement of the contact line was called the “inner contact line”, which was confirmed in the experiments using a microscope.\textsuperscript{5} However, a lack of microscopic understanding of how the nanoparticles influence on the contact line dynamics hinders the further application of nanofluids in EOR and detergency industry. Simulation studies aid the interpretation of experimental observations.\textsuperscript{10} As far as we are aware, the molecular dynamics (MD) simulations on the spreading of nanofluids are relatively few due to the complex modeling of this system.

In this letter, MD simulations were conducted to investigate spreading of nanofluids promoted by nanoparticle adsorption on the solid surface, using the classical parallel code LAMMPS.\textsuperscript{11} We built the simulation model for two immiscible fluids (oil and water based nanofluids) confined in a slit between two planar solid walls parallel to the $xy$ plane, as shown in Fig. 1. The nanofluids consist of water molecules and randomly distributed rigid nanoparticles with a diameter of approximately 0.7 nm. The multi-component oil was modeled as a ternary mixture of hydrocarbons: heptane, decane, and toluene.\textsuperscript{12} The initial configuration of the simulated system was built using Packmol.\textsuperscript{13} We also write a pre-processing program to convert the coordinate file to LAMMPS data file. The single point charge/extended (SPC/E) model was used to describe the water molecules.\textsuperscript{14}

The bond, angle, dihedral, van der Waals and electrostatic interactions among the hydrocarbon molecules were modeled by the CHARMM force field.\textsuperscript{15,16} The interactions between oil/solid walls, water/solid walls were described by the Lennard Jones (LJ) pairwise potential. A cutoff of 1.20 nm was used for the van der Waals interactions. The long-range electrostatic interactions were computed using the particle-particle particle-mesh (PPPM) algorithm, with a convergence parameter of $10^{-4}$. In the present study, we focus on the motion of the three-phase contact line on the lower solid wall. Thus the interactions between nanofluids and the upper wall were set to be equal to that between oil and the upper wall. The LJ parameter $\varepsilon$ for the

\textsuperscript{a)}Corresponding author. Email: wangfc@ustc.edu.cn.
nanofluids/lower wall interaction and for the oil/lower wall interaction was set to be 0.15 kcal/mol (1 kcal = 4.1868 kJ) and 0.05 kcal/mol. To model the nanoparticle adsorption on the solid surface, interactions between nanoparticles and the lower wall were enhanced. All the simulations were performed in the *NVT* ensemble (the number of particle (*N*), the volume (*V*), and the temperature (*T*) in the ensemble are constant, also referred as canonical ensemble). The temperature was set to 298 K using a Nosé–Hoover thermostat. The trajectories were collected in an interval of 1.0 ps for further analysis.

During the simulations, the distance between the two three-phase contact lines on the lower substrate *L* was calculated to characterize the spreading behavior of the nanofluids. We also monitored the center of mass (COM) position of oil along the *z* direction. These results were plotted in Fig. 2. We can observe that at the beginning of the simulation, spreading of the nanofluids/oil/substrate contact line is faster than that of the water/oil/substrate contact line. However, the spreading velocity of contact line decreases at *t* = 100 ps. The consequence is that *L* with *φ* = 5.0% is almost the same as *L* with *φ* = 0 at *t* = 500 ps. We also found that *L* with *φ* = 10.0% is smaller than *L* with *φ* = 5.0% and *L* with *φ* = 0. This indicates that in nanofluid spreading, the influence of nanoparticle adsorption on the solid surface becomes remarkable when a nanoparticle volume concentration is larger than 5.0%. We also calculated the distance between the two three-phase contact lines on the upper solid wall and found that there is no significant difference for the results of these three cases. Since we only focus on the motion of the three-phase contact line on the lower solid wall, the detachment of the oil droplet would be limited by the upper wall. As a result, the COM positions nanofluids seem to reach a steady value after a specific period of time, as shown in Fig. 2(b). However, in other modeling, the spontaneous detachment of the oil droplet from the solid substrate can be observed in charged nanoparticle suspensions.18

For liquid droplet spreading on the solid substrate, the radius of the contact line is a function of the spreading time, which was describe by the Tanner’s spreading law.19 From Fig. 2(a), variations of *L* as a function of *t* can be fitted with a modified spreading law, *L*(*t*) = *L*₀ − *A*/*t*ⁿ, where *L*₀ is the initial value and set to 10 nm. In the case of *φ* = 10.0%, the fitting parameters for *A* and *n* are 15.7 and 5.0, respectively. For *φ* = 5.0%, *A* and *n* are fitted to 11.7 and 4.5. While for the case with the absence of nanoparticles, *A* and *n* are 3.7 and 2.5, respectively. The fact that fitting parameters *A* and *n* increase with volume concentration of the nanoparticle shows that the spreading of the nanofluids is fast at the beginning, and the spreading velocity would become relatively low during the subsequent process. These results are consistent with the variation tendency of the COM position of oil in the *z* direction.
direction, as shown in Fig. 2(b). In the first 100 ps of the spreading process, the variations of COM position of oil with \( \phi = 10.0\% \) and \( \phi = 5.0\% \) are very close to each other. But for the last 100 ps of the spreading process, COM position of oil with \( \phi = 5.0\% \) is nearly equal to COM position of oil with \( \phi = 0 \), which are smaller than that in the case of \( \phi = 10.0\% \).

In Fig. 3, we plotted the MD snapshots of the simulated system at \( t = 0.5 \) ns. Due to the strong interactions between nanoparticles and the lower solid wall, the nanoparticle adsorption on the solid surface is obvious. We can find that the shapes of the nanofluids/oil interface are different for different nanoparticle volume concentration. As shown in Fig. 3(a), the shapes of the nanofluids/oil interface are not completely symmetrical. This discrepancy can be attributed to the difference of the local volume concentration of nanoparticles. Comparing the shapes of 3 nanofluids/oil interfaces on the left side of Fig. 3, we can see that the case of \( \phi = 10.0\% \) shows a trend of the advancing displacement, which forms the inner contact line as reported in the experimental observation and theoretical prediction. As the volume concentration of nanoparticles increased, the nanoparticles start to form agglomeration near the solid surface, which would enlarge the structural disjoining pressure gradient at the wedge.

To further investigate the effect of the nanoparticle adsorption on the spreading of nanofluids, we plotted the nanofluids/oil interface shape under different situations in Fig. 4. As the interactions between nanoparticles and the lower solid wall increase, we can see that the advancing displacement of the three-phase contact line becomes larger. By adjusting the volume concentration of nanoparticles or the nanoparticle adsorption effect, different spreading behavior of the nanofluids can be obtained.

In summary, spreading of nanofluids was investigated using MD simulations. The effect of the nanoparticle adsorption on solid surface on the spreading behavior of nanofluids was discussed. We found that the local volume concentration plays a significant role on the shape of the nanofluids/oil interface. Large nanoparticle concentration may enhance the effect of the disjoining pressure on the spreading of the nanofluid film. These findings may provide some insight into the basic understanding of the enhanced wetting behaviours of nanofluids. Besides the effect of nanoparticle concentration, the spreading behavior of nanofluids is sensitive to many parameters, such as particle size, particle charge and surface wettability of the nanoparticles.

Interdisciplinary studies to explore these problems should be undertaken in the future.

This work was supported by the National Natural Science Foundation of China (11172289, U1262103, and 11302218), Anhui Provincial Natural Science Foundation (1308085QA10), China Postdoctoral Science Foundation (2012M521243), and the Fundamental Research Funds for the Central Universities of China (WK2090050022 and WK20900050027).