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Molecular dynamics simulation on the friction properties of nanofluids confined by idealized surfaces

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ABSTRACT

We performed molecular dynamics simulations to study friction property differences between base fluids and nanofluids in shear flow field. The results show that with the increase of load, liquid–solid transitions take place for both base fluids and nanofluids. Specifically, the transition pressure for nanofluids is higher than that of the base fluid and the nanofluids show excellent friction-reducing properties when the load is high (exceeds the transition pressure of base fluid). Additionally, nanofluids have a greater load-carrying capacity than base fluids. In this work, we explained the mechanisms responsible for the nanoparticles' favorable friction properties, and to verify these mechanisms we additionally studied the effect of nanoparticle radius on friction behaviors.

1. Introduction

Friction is one of the main causes of energy loss in mechanical systems. In fact, machine elements usually fail due to excessive wear. To improve the efficiency of energy utilization and the reliability of mechanical systems it is essential to provide superior lubrication.

Lubrication is an effective way of reducing the friction and decreasing the erosion in mechanical systems. Nanoparticles have excellent physical and chemical properties due to their small size and large specific surface area that differentiate them from conventional bulk materials. Recently, several studies have investigated the tribological properties of nanoparticles used as liquid lubricant additives. The anti-wear and low friction behaviors of a variety of nanoparticles used as oil additives, including metal (e.g., Zn, Cu, Ni, Fe, Co, Pd, and Au), metal oxides (e.g., Al_2O_3, CuO, ZnO, ZrO_2, and TiO_2), sulfides (e.g., WS_2, MoS_2, CuS, and ZnS), nonmetal (e.g., diamond, SiO_2, and fullerenes), inorganic oxythiomolybdates (e.g., $Cs_2MoO_2S_2$, $ZnMoO_2S_2$) have been extensively reported [1–25]. To promote the applications of nanoparticle-added lubricating oil, we should study the mechanisms of dispersing nanoparticles in lubricants that result in lower friction and erosion. Several mechanisms have been proposed in literatures: (a) nanoparticles can change the sliding friction to rolling friction [11–16], (b) nanoparticles can act as spacers preventing metal–metal contact between the surfaces of asperities [5,17], (c) surface protective film [1,3,6,7,16,18], (d) self-repair effect [19–21], and (e) third body material transfer [12,22]. However, these mechanisms are all speculated based on the experimental phenomena with a lack of theoretical support, and the essence of the mechanisms is still not well known. To obtain a better understanding of the anti-wear and friction reduction mechanisms of nanoparticle-added lubricating oil, the rheological properties (e.g., velocity profile, film thickness, motion characteristics, etc.) of lubricant under certain conditions (e.g., load bearing and shear) should be studied. Because of the small scale of lubricant films, it is difficult to study the rheological properties in experiments. Fortunately, the methods of Molecular Dynamics (MD), which are based on computational implementations of solutions to Newton's equations of motion for molecular systems, provide an effective approach to study micro-flows and mechanical behaviors of lubricant films. By considering the dynamic and energetic behavior in atomic detail, MD simulations become useful in the design of lubricants [26]. To date, several MD simulations to study the frictional characteristics of lubricants have been performed. Specifically, Thompson et al. [27] tried to understand how solid walls affect the structure and dynamics of a contacting fluid. The simulations showed that as the film thickness decreases, there are modifications on its structure that can result in phase transitions to a crystalline or glassy state. Tamura et al. [26] investigated the dynamic behavior of hydrocarbon molecules under shear conditions describing the frictional behaviors of several olefin films. Hu et al. [28] examined the rheological properties of ultra-thin lubricant film in Poiseuille flow. They concluded that the rheological performance of lubricant can become film thickness-dependent and that a liquid–solid transition can be induced when

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the wall spacing decreases to a few molecular diameters. Jabbarzadeh et al. [29] investigated the effect of wall roughness on slip and rheological properties of thin liquid films. They found that the wall roughness has important influences on the wall slip, film viscosity, and pressure. Capozza et al. [30] found that the frictional properties of thin lubricant film are significantly affected by the presence of nanopatterned surfaces. Berro et al. [31] studied the tribological performance of a lubricant mixture containing a hexadecane base oil and zinc dithiophosphate (ZDDP) under molecular confinement conditions. The results showed that the migration of ZDDP molecules and their adsorption onto the solid surface result in a remarkable suppression of mechanical slip. MD simulations also enable exact calculations on nanofluids. Specifically, there have been several studies on strengthening the heat conduction [32–34] and flow characteristic of nanofluids [35–38]. However, investigations on the frictional behaviors of nanoparticle-added lubricating oil are scarce. Lv et al. [39] studied the friction behaviors of Cu–Ar nanofluids between two solid plates by MD methods. They found that with the increase of pressure, nanoparticles show an obvious aggregation phenomenon and provide support for the two plates. However, the study mainly focused on the motion states of nanoparticles and ignored the rheological properties of the lubricant film.

The speculations leading to the existing mechanisms of friction-reduction and anti-wear of nanoparticles in lubricant are based on changes of the worn surface morphology. If the effects of the morphology of friction pairs on the lubricant characteristics are not considered, the differences of the friction characteristics between base oil and nanoparticle-added lubricating oil (called nanofluids for short) are not clear. To understand the tribological behaviors of nanofluids, first we should study the friction behavior of nanofluids when the morphology of friction pairs remains unchanged, and then consider the changes of the morphology of friction surfaces caused by the addition of nanoparticles. Therefore, this paper will study the friction behaviors of nanofluids confined by smooth surfaces with MD methods. Particularly, we will study the interaction mechanisms between nanoparticles and base fluids. This work aims to understand the physics behind the friction and load-carrying capacity of nanofluids and base fluids. In this manuscript, we consider smooth confining surfaces and we will not study the effect of surface morphology on friction.

2. Model and simulation details

2.1. Model setup

All the simulations were performed using the classical open source MD LAMMPS code [40]. The friction properties of base fluids and nanofluids were studied by all-atom simulations. The simulation systems are shown in Fig. 1. Periodic boundary conditions were imposed in the x- and z-directions. Initially, the two simulation boxes were both $6 \times 8.8 \times 6$ nm^3 in size, and the liquid height, h, was 6.2 nm. The vibrations of the lowest layer of the lower plate and the highest layer of the upper plate are frozen. The lower plate was kept still and the upper plate slid along the z-direction at velocity v. The y-dimension was allowed to vary (shrink wrapped) when the simulations were performed under imposed normal load (P) thus allowing the fluctuation of the film thickness. The nanofluid model contained one nanoparticle with a diameter of 2 nm. When there was no load, the nanoparticle volume concentration was 1.87%. The nanoparticles and walls were made of copper (Cu). To simplify the calculations we selected liquid argon (Ar) as base fluid. Several studies have demonstrated that this simplified form can be used to explore the physical properties of nanofluids [35–38]. The total amounts of atoms were 11,165 and 11,417 for the base fluid and the nanofluids models, respectively. Initially all liquid Ar atoms, the Cu nanoparticle, and walls were arranged as a face-centered cubic lattice (FCC).

2.2. Molecular dynamics

In our simulations, the interatomic interactions between Ar atoms and between Cu and Ar atoms were described by a Lennard-Jones potential [35]:

$$U(r_{ij}) = 4\varepsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right] \tag{1}$$

where ε and σ are the energy parameter and the length scale, respectively, and r_{ij} is the intermolecular distance between atoms i and j. For Ar, $\varepsilon_{Ar} = 1.67 \times 10^{-21}$ J and $\sigma_{Ar} = 0.3405$ nm, and for Cu, $\varepsilon_{Cu} = 65.625 \times 10^{-21}$ J and $\sigma_{Cu} = 0.23377$ nm. We used the Lorentz–Berthelot mixing rule [41] to determine the parameters between Ar and Cu atoms:

$$\varepsilon_{sl} = \sqrt{\varepsilon_{ss}\varepsilon_{ll}} \tag{2}$$

$$\sigma_{sl} = \frac{\sigma_{ss} + \sigma_{ll}}{2} \tag{3}$$

where s and l denote solid and liquid, respectively. Therefore, σ and ε between Ar and Cu are 0.2871 nm and 10.4153×10^{-21} J, respectively.

For the nanoparticle lower and upper plate, the more precise embedded atom method potential [42] shown in Eq. (4) was used to represent interactions between Cu atoms:

$$U = \sum_i F_i\left(\sum_{j \neq i} \rho_i(r_{ij})\right) + \frac{1}{2}\sum_{j \neq i} \phi_{ij}(r_{ij}) \tag{4}$$

where F_i is the embedding energy which is a function of the atomic electron density ρ, ϕ is a pair potential interaction, and i and j represent atoms i and j, respectively.

2.3. Simulation procedure

We arranged the atomic initial positions in a regular FCC lattice; therefore, the two systems needed to be relaxed adequately to let the systems reach an equilibrium state. During the relaxation, the temperature of simulation was set to 86 K to keep the low-boiling liquid Ar in liquid state. In this study, the two systems were relaxed for 400 ps and both systems reached an equilibrium state. Then, we applied a uniformly distributed load P to the upper plate of each system and subsequently we equilibrated the systems again at 86 K for 400 ps. We performed sliding simulations by smoothly moving the upper plates at velocity v in the z-direction followed by another relaxation for 400 ps. Finally, to collect data for the calculation of the physical properties we simulated each system for 6000 ps. We applied the Nose–Hoover thermostat [43] to keep the systems at a temperature of 86 K. The cutoff radius for the potential used in this work was $2.5\sigma_{Ar}$. The simulation time step was 0.002 ps. In this study, we used the velocity Verlet algorithm to calculate the atomic motions [44].

Shear stress (S) is defined as $S = F/A$, where F and A are, respectively, the total lateral force needed for the upper plate to move at a constant velocity and the action area. The concept of compression ratio was introduced to characterize the load-carrying capacity of the lubricant film. It is expressed as $\eta = (H_0 - H_p)/H_0 \times 100\%$, where H_0 is the height of the system under the unloading condition, H_p is the height after loading, and η is the compression ratio. Lower values of η are equivalent to a good compression resisting property and a higher load-carrying capacity.