Short Communication

Macroscopic No-Slip Boundary Condition Confirmed in Full Atomistic Simulation of Oil Film

Hitoshi Washizu^{1,2)*}, Shi-aki Hyodo¹⁾, Toshihide Ohmori¹⁾, Noriaki Nishino³⁾ and Atsushi Suzuki³⁾

¹⁾Toyota Central R&D Labs., Inc.
Nagakute, Aichi 480-1192, Japan

²⁾Elements Strategy Initiative for Catalysts and Batteries (ESICB), Kyoto University
Katsura, Kyoto 615-8520, Japan

³⁾Toyota Motor Corporation
1 Toyota-cho, Toyota, Aichi 471-8572, Japan
*Corresponding author: h@washizu.org

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The no-slip boundary condition widely used in the macroscopic fluid mechanics has not been explained from the molecular level. This letter describes all atom molecular dynamics simulation to study boundary slip of hydrocarbon oil film under shear of a submicron thickness confined between solid walls. The large time-space scale simulation under the realistic interactions of fluid atoms, solid-fluid interaction and sliding speed has shown the no-slip of the oil film. The difference between the nanoscale film and the submicron thick film is explained from the viewpoint of the anisotropic viscosity rise in the vicinity of the solid wall and the correlation length of the momentum up to several tenths of nanometers. The results of the present simulation coincide with the experiments of fluid flow through nanometer-scale channels.

Keywords: tribology, no-slip boundary condition, molecular dynamics, elastohydrodynamic lubrication

1. Introduction

The relative motion of a liquid on a surface is one of the fundamental problems in physics, chemistry, biology and engineering [1,2]. Fluid mechanics has been the most powerful tool to treat these phenomena for two hundred years [3]. Macroscopic studies of fluid mechanics rely upon the assumption that when a liquid flows over a solid surface, the liquid molecules adjacent to the solid are stationary relative to the solid [3,4]. This no-slip boundary condition has been successfully applied to describe macroscopic experiments. For example, in the classical theory of hydrodynamic lubrication, Reynolds used the assumption that the liquid adjacent to the solid is stationary relative to the solid [5].

This assumption has not been confirmed on a molecular level mainly because of the limitation of computational resources when attacking this problem by molecular simulation. When the film thickness is on a nanoscale, the breakdown of this no-slip boundary condition [1] is found using a surface force apparatus [6] or atomic force microscopes [7]. Based on the molecular picture at the interface, the relative motion of fluid molecules should be expressed by the characteristics of the intermolecular interaction with the solid surface

atoms. The molecular dynamics (MD) simulation is the most accurate tool to simulate the nanoscale problem. For a single atom fluid under nanoscale confinement, the slip length saturates with a decrease in the shear rate, and slips are generally observed except that the wall-fluid interaction energy is a maximum [8]. In general, a fluid consisting of molecules which have an internal degree of freedom, are studied using the united-atom model [9,10].

According to the MD simulation [10], the slip motions occur when the fluid-wall surface interactions are weaker than the fluid-fluid interactions, or the entanglement action between fluid molecules is strong though the above fluid-wall surface, or fluid-fluid interactions are equal and when the film thickness is small. Though the decrease in the slip length with an increase in the film thickness was found, the slip length did not saturate until the thickness was 20 nm, since the increase in the film thickness means an increase in the simulation cost, thus the discussion of the mechanism has been limited [10]. Experiments of fluids including hydrocarbons, water and silicone oil, flowing through nanometer-scale channels have shown that the transition of slip to no-slip are found below a thickness of about 100 nm [11]. The border between the nano and the macro seems to be exist around this film thickness. On the other

hand, recent experiments based on fluorescence recovery after photo-bleaching [12] and the statistical mechanical theory [13] have indicated that slip will occur even on fully wettable surfaces at any thickness.

A key question is whether or not we can extrapolate the film thickness dependence on a nanometer scale [10] to the macroscopic phenomena. This is what we first need to confirm. The next question is if the no-slip boundary condition holds in a macroscopic fluid from the atomistic point of view, then what is the mechanism of disappearance of slip which is observed both in the nano-experiments and the molecular simulations [14]? We examined the all atom molecular dynamics simulation of a lubricating oil film confined between solid walls under shear condition in order to analyze the boundary slip when the macroscopic fluid dynamics theory is used.

2. Simulation

The number of required atoms is about a half million to simulate the submicron thick oil film. *n*-Hexane is chosen as the fluid molecule so that the general behavior of the fully wettable surfaces of hydrocarbon oils are simulated. The related sliding speed of the solid walls is set to $2v_{wall} = 0.1$ m/s which is the usual driving condition in the macroscopic machine elements (shear rate $\dot{\gamma} = 10^5$). The bcc crystal solid wall-fluid interaction is set to very weak and the vibration of the solid atoms is frozen in order to simulate the easiest condition to produce the boundary slip [10].

In the molecular dynamics simulation, the hydrocarbon fluid molecules are dynamically treated using the AMBER force field [15]. On the *x*, *y* and *z* axes, the periodic boundary condition is adapted for the hexahedron simulation cell, where *x* is the sliding direction and *z* is the direction of the fluid thickness. The temperatures are controlled at 350 K using the Nosé-Höover formalism [16]. All the molecules are connected to a heat bath. While this has been shown to affect the rheology of confined fluids at shear rates above $\dot{\gamma} = 0.2$ (in reduced Lennard-Jones units), the low shear rates here, a maximum of $\dot{\gamma} (\epsilon/mR^2)^{1/2} \approx 0.004$, suggest that such artifacts should be negligible [17,18]. Each simulation step corresponds to 0.5 fs and the time integral due to the motion of the atoms is calculated by the rRESPA (Reversible Reference System Propagator Algorithm) [19] method. The solid plate of an alpha-ferrous crystal is modeled as a solid atom layer with a lattice of $10 \times 10 \times 3$ in the directions and the lattice parameter is 2.87 Å. Due to the restriction of the computational resource the size of the solid film layer are restricted. Although the periodic boundary condition means infinite width of the solid atom layer, the size effect should be discussed in future. The fluid-solid interface is the (1 0 0) surface, and the vibrations of each Fe atom are suppressed. The Lennard-Jones (LJ) parameter is then set to 0.1214 kcal/mol for solid atom.

The well depth between solid atom and hydrogen or carbon atoms are determined by mixing rule. The parameter is comparable to the LJ parameter 0.066 kcal/mol for carbon atom used. The temperature and pressure are set to compare with our previous simulation results [14,20] which is chosen from the running condition of continuously variable transmissions. Under high pressure of 1 GPa, the oil film is under elasto-hydrodynamic lubrication (EHL) regime, which the temperature in the contact area rises dozens of degrees from room temperature [21]. Constant shear states under constant pressure and constant velocity are obtained in the following manner. A set of fluid molecules is first arranged in a lattice configuration. The molecules are then moved by MD simulation under the periodic boundary condition in the *x*, *y* and *z* directions at the constant temperature of 350 K until a thermal equilibrium is obtained. Next, the sets of thermal equilibrium fluids are arranged in the *z* direction between two solid plates. The number of the *n*-Hexane molecules is 25,920 and the average thickness of the oil film obtained in equilibrium state is 428.8 nm. Fluid molecules are compressed by the MD simulation under the periodic boundary condition in the *x*, *y* direction by applying a constant pressure, $P_{ext} = 1$ GPa on the plates. Stress on the plates is in the *z* direction. The shear in the *x* direction is then applied by a relative sliding motion on the solid plates by the constant velocity, v_{wall} . The steady state is determined from the saturation of the oil film thickness and the friction coefficient [20]. In this simulation, the steady state trajectory is obtained after the MD run for more than 50 ns.

3. Results and discussion

The oil film structure and dynamics in the vicinity of the solid wall are plotted in Fig. 1. The periodic density distribution of carbon atoms near the wall is shown in Fig. 1(a). Although the fluctuation of the velocity in this area shown in Fig. 1(b) is large compared to the sliding speed of the solid wall v_{wall} , the velocity at the peak of the density shows a positive value, and the average of the entire region is $0.96(\pm 0.10) v_{wall}$. This means that there is no slip under the submicron thick oil film, although the sliding of the fluid is discrete, which corresponds to the discrete distribution of the fluid molecules, from the viewpoint of the average. In the statistical mechanical theory of the boundary slip based on a combination of the linear response theory and equilibrium molecular theory of solvation [13], Kobryn and Kovalenko pointed out that the use of the molecular dynamics simulation for the macroscopic oil phenomena may lead to questionable, nonphysical results. They employed the calculation of Petravic and Harrowell [22] which is based on the linear response theory for molecular dynamics. The interfacial friction coefficient of the Navier type λ is described as $\lambda = \eta / (L + \delta_1 + \delta_2)$, where η is the bulk viscosity, *L* is the film thickness, and δ_1 , δ_2 are the slip length on each solid

Fig. 1 Profiles of carbon atom density ρ normalized by the average density ρ_{average} (a), velocity normalized by the sliding speed of the wall v_{wall} (b), and partial viscosity $\eta(z)$ (c) of submicron thick oil film. Square points in (b) (c) are added for visual guide which denotes the three representative points around the peaks in each period of the carbon atom density profiles (a)

wall, and λ is related to the surface shear stress σ and liquid velocity v_s by $\sigma = \lambda v_s$. This equation lead to the near zero friction when the oil film thickness is large which is not true in the fluid dynamics measurements of realistic fluids. In our simulation, the friction coefficient calculated by dividing the transverse stress on the solid wall by the normal pressure is $\mu = 0.0178$ which is comparable to $\mu = 0.02$ obtained by the experimental measurements using the ball on disk apparatus [14].

Fig. 2 Snapshots of the fluid molecules adjacent to the solid wall. a ($t = 0$ ns), b ($t = 13.5$ ns), c ($t = 27$ ns). The green part of the rod is carbon atom and the gray part of the rod is hydrogen atom. The orange (A) and blue (B) molecules are samples of the motion of the fluid molecules. The red atom of solid wall is a visual guide

Therefore, in order to understand the experimental phenomena and our result of the non-equilibrium molecular dynamics simulation, the modification of the theories based on a linear response and on the fluctuation of the physical variable in the equilibrium state are needed.

We next considered the suggestion by Navier in about 200 years ago [23], who claimed that a thin liquid layer

adjacent to a flat surface could exhibit a viscosity with a value quite different from that of the bulk liquid. We then calculated the partial viscosity which is related to the momentum correlation functions [24] as a function of the distance from the solid wall z as $\eta(z) = \left\langle \sum p_{xi} p_{xj} [z_i - z_j]^2 \right\rangle_z$ where p_{xi} , p_{xj} denotes the momentum of carbon atoms i , j and $\langle \rangle_z$ denotes the time average of the molecules i in the coordinate $z = z_i$. $\eta(z)$ plotted in Fig. 1c that shows a positive value much larger than the $\eta_{center} = \langle \eta(z) \rangle$ in the center of the oil film.

Here $\langle \rangle$ denotes the average at the center region. This means that the anisotropic increase in the partial viscosity is found which Navier had suggested. Figure 2 shows the characteristic motion of fluid molecules adjacent to the solid wall. Since the atoms are inhibited to penetrate the solid wall, the segment motions of the molecules are restricted to move on the x , y plane or translational motion in the z direction converts to rotational motion. Translational motions in the x , y direction are less found due to the high density in the vicinity of the wall shown in Fig. 1(a). In Fig. 2, the orange molecule A flips its tail while the other end is bound on the surface and the blue molecule B turns on the surface. Note that during the segment motion of the molecules, the center of mass of each molecule moves almost at same sliding speed with the solid wall. This constrained segment motion (C-C bond motion) is the origin of the increase of the partial viscosity. This can be found only in the simulation which consider the internal degree of freedom in each molecules, which are not treated in a simulation of sphere atoms. For the same solid wall-fluid interaction strength, the boundary slip occurs in the nm thick oil film and not in the submicron thick one. The partial viscosity curves in the submicron thick oil film shows the same tendency with the curves of the no slip in the oil films [25]. This would be explained by the correlations of the momentum. Figure 3 shows the

Fig. 3 Momentum correlation function $C(r)$ of the carbon atoms in the vicinity of the wall

momentum correlation function $C(r)$ of the carbon atoms in the vicinity of the wall. $C(r) = \left\langle \sum m^2 (v_{xi} - \bar{v}_{xi0})(v_{xj} - \bar{v}_{xj0}) \right\rangle_r$ where m denotes the mass of the carbon atoms, v_{xi} , v_{xj} denotes the velocity of the carbon atoms i , j , $\bar{v}_{xi0}$ and $\bar{v}_{xj0}$ denote the average of velocity in the x direction of the carbon atoms i , j at the corresponding z , and $\langle \rangle_r$ denotes the time average of the molecules i of distance r of molecules x , y . The correlation of momentum has two slopes. The first slope is from 1.0 to 1.5 nm which corresponds to 3 times the diameter of the hydrocarbon segments. This means that the momentum directly transfers to 3 surrounding hydrocarbon molecules, the momentum correlation length. The second slope saturates from about 50 to 80 nm. This length is comparable to the experimental transition thickness of 100 nm [11]. A schematic illustration of the mechanism which shows the relation between correlation length and the boundary slip between the nano-scale film (a) and the submicron thick film (b) is shown in Fig. 4. The momentum correlation length in the fluid layer would depend on the pressure and the temperature which is the same in the nm thick system and submicron meter thick system. The length from one solid wall to the other side, however, is much greater in the submicron system, thus the degree of motion of the fluid molecules which would follow the motion of the nearest solid wall is greater in the submicron system ($v_i \approx v_{wall}$) than in the nm thick system ($v_i < v_{wall}$).

Our all atom molecular dynamics simulation of fully wettable simple hydrocarbon oil film showed that the no-slip phenomenon, which is one of the simplest boundary conditions held under sliding speed of $2v_{wall} = 0.1$ m/s, which is a realistic condition of some applications of mechanical engineering, such as hydrodynamic lubrication of automotive machine elements, very weak solid-fluid interactions and a very thick film thickness of 0.43 micron. This result is consistent with the assumption of macroscopic fluid

Fig. 4 Schematic illustration of relation between correlation length and the boundary slip for the nano-scale film (a) and the submicron thick film (b)

dynamics theories, and with the experiments of nanometer-scale channels [11], and verified the suggestion of the molecular dynamics simulation [10]. Our simulation still includes 4% statistic error for the complete “no slip” condition. For the realistic system, however, include thermal vibration of the solid atoms and surface roughness which both lead to suppress the slip. Therefore we think our results show no slip condition within error margin. Although the further validation of this mechanism is needed, the concept of momentum transfer described by the momentum correlation functions $C(r)$ is based on the reasonable physics of entanglement of the segment of hydrocarbon molecules so that the well-thought-out single-particle model [8] can hardly be treated. We believe that we have successfully reproduced the fundamental feature of a molecular liquid adjacent to a solid wall. Precise analyses and applications are now in progress.

4. Conclusion

All atom molecular dynamics simulation is used to study boundary slip of hydrocarbon oil film under shear of a submicron thickness confined between solid walls. The no-slip boundary condition of the oil film is confirmed by the molecular simulation. The origin of the difference between the nano-scale films which are studied in previous simulations and the submicron thick film under study is related to the momentum correlation length.

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