Molecular Dynamics Simulations of Elasto-hydrodynamic Lubrication and Boundary Lubrication for Automotive Tribology

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Abstract. Friction control of machine elements on a molecular level is a challenging subject in vehicle technology. We describe the molecular dynamics studies of friction in two significant lubrication regimes. As a case of elastohydrodynamic lubrication, we introduce the mechanism of momentum transfer related to the molecular structure of the hydrocarbon fluids, phase transition of the fluids under high pressure, and a submicron thickness simulation of the oil film using a tera-flops computer. For boundary lubrication, the dynamic behavior of water molecules on hydrophilic and hydrophobic silicon surfaces under a shear condition is studied. The dynamic structure of the hydrogen bond network on the hydrophilic surface is related to the low friction of the diamond-like carbon containing silicon (DLC-Si) coating.

1. Introduction
Computational physics or chemistry has been used for automotive tribology studies since the early 90s. One of the authors used molecular orbital calculations for determining the partial charges on the anti-wear agent molecules to study their adsorption property\cite{1}. When introducing the products of the molecular simulation such as molecular dynamics (MD) of nanotribology to automotive tribology, we are faced with a problem. That is, even though the technologies in nanospace are developed, the nonuniformity of time and space in the system are not on a nanoscale level. The size of engines and transmissions are on a sub-meter scale, while the oil film thickness and surface roughness at the contact area are of micrometer size. They are much larger when compared from the radius of the atoms. Therefore, in order to introduce computational physics for the development of car components from the viewpoint of tribo-material designing, we should be aware of the fact we can only select a tiny spacial area of the real lubricating surface. According to the Striebeck model, the lubricating state can be divided into (elasto) hydrodynamic lubrication, boundary lubrication, and mixed lubrication. In the hydrodynamic lubrication regime, although a number of properties can be explained by macroscopic theory, some properties, such as the origin of the traction force under high pressure is governed by intermolecular interactions. In the boundary lubrication regime, the macroscopic friction is determined by the friction in the real contact area which is governed by intermolecular forces. Therefore, we can apply a molecular dynamics analysis to the real lubricating phenomena.
of vehicles if we carefully treat the conditions of the simulation to conform to the outlook on Strubeck.

In this paper, we summarize our studies of the molecular dynamics simulations for automotive tribology and add some recent results from simulations related to boundary lubrication.

2. Simulations of elastohydrodynamic lubrication

Elastohydrodynamic lubrication is used in major part of automotive lubrication, including the valve system in the engine and the rolling surface of the transmission. In the traction type continuously variable transmission (CVT), the fluid under elastohydrodynamic lubrication transmits torque from the power disk to the roller. The traction properties of the fluids largely depend on the structure of the fluid molecules. In order to achieve a higher CVT capacity, improved fuel economy and protect the environment, the molecular design and development on a molecular level of high traction coefficients are needed. On the other hand, as the lubrication conditions, the molecular mechanism of the transmission of the force in a highly loaded fluid layer is not clearly known.

Therefore, we started our research using non-equilibrium molecular dynamics simulations of a traction fluid in a confined geometry [2, 3, 4, 5]. The fluid layer is confined between two solid Fe plates under high pressure. Traction simulations are performed by applying a relative sliding motion to the Fe plates. The mechanism of the traction due to the structure of the fluid molecules is then analyzed.

Because of the large difference in shear viscosity and oil film thickness, the simulations do not directly model the ball on disk type experiment which is used for measurements involving traction fluids. The shear rates in most experiments are below $10^6$ s$^{-1}$ and the film thicknesses are over 0.1 $\mu$m (III in Fig. 1). The shear rate regime in the simulations is far too high and the film thickness regime is far too thin. To solve this problem, we made non-equilibrium MD simulations which can treat a large number of fluid molecules up to a 10 nm film thickness using a supercomputer (I in Fig. 1, [2]). We then simulated the dynamics of hydrocarbon fluids under shear and high pressure. The effects of the film thickness and shear rate were studied [2]. In order to determine the condition that can qualitatively simulate the experiments, the dependence of the traction coefficients on the film thickness $z_0$ of 1 - 10 nm and on the shear rate of $10^7$ -
$10^9$ /s of n-hexane were calculated. Although our calculated traction coefficients show a higher value than the experimental ones over the entire simulation range, they decreased for both the decreasing shear rates and increasing film thickness, which provide a qualitative agreement with the experiments. In an ultra-thin film less than 2.5 nm, a large stick-slip-like motion caused by slip between the molecular layers is observed. These results suggest that a film thickness of at least 5.0 nm is needed to qualitatively simulate the experiments [2].

The traction force of a fluid has its origin in the translational momentum transfer across the fluid layer. From the viewpoint of the molecular dynamics scale, the traction force is generated by the concept of momentum transfer shown in Fig 2. At first, the external force, which is applied to the Fe plate as a constant sliding movement velocity and normal constant pressure, transfers to the fluid molecules by an intermolecular interaction. The molecules deform their shape due to this intramolecular interaction. The force transfers again to another molecule by an intermolecular interaction, and finally the force transfers to the other side of the Fe plate as a traction force. The heat produced during this process dissipates in each process. This process of momentum transfer of a molecular layer should be treated as a statistical mechanical process which is carefully extracted from the huge thermal noise.

The traction molecular dynamics simulations have been studied of hydrocarbon fluids which have a characteristic structure, including an industrial lubricant, and compared in the experiments [3, 4]. The relation between the traction coefficients and molecular structure were then analyzed by focusing on the inter- and intramolecular interactions. The molecular mechanism of the traction phenomena in a fluid layer was then presented.

![Figure 2. Concept of momentum transfer of EHL oil film and analytical procedures.](image)

The dynamic mechanism of the momentum transfer on layers of fluid molecules are analyzed by focusing on the intermolecular interactions (density profile, orientation factor, pair-correlation function) and intramolecular interactions (intramolecular interaction energy, conformation change of alicyclic ring) which are shown in Fig 2. These results are summarized in Fig 3. In contrast to the case of n-hexane, which shows a low traction due to a fragile chain-like interaction, other mechanisms are obtained in the high traction molecules of cyclohexane and dicyclohexyl. In cyclohexane, alicyclic rings face each other in a highly ordered molecular layer, and the motion of the conformational changes cooperates. In dicyclohexyl alicyclic rings, which distribute across the low ordered molecular layers, behave as a stiff bulky mass, and the momentum transfers to the end of the molecular axis. The traction mechanisms of nine hydrocarbon fluids were also obtained during the course of the analysis [4].

All-atom molecular dynamics simulations of an elastohydrodynamic lubricating oil film have been performed in order to study the effect of the oil film thickness (large spatial scale; thickness:
430 nm, MD time: 25 ns) and the effect of pressure (long time scale; thickness: 10 nm, MD time: 50 ns, external pressure: 0.1 to 8.0 GPa) [5]. Traction simulations were performed the same as the previous simulations. In a long spatial scale simulation, the mean traction coefficient was 0.03, which is comparable to the experimental value of 0.02. In a long time scale simulation, a transition of the traction behavior is observed around 0.5 GPa to 1.0 GPa which corresponds to a change from the viscoelastic region to the plastic-elastic region which have been experimentally observed. This phase transition is related to a suppressed fluctuation of the molecular motion [5].

Although our long spatial scale MD simulation reveal that the discrepancy between the simulations and the experiments disappear when calculating under the same condition on film thickness and shear rate, there remain two dimensions of nonuniformity which are unreasonable when using the all-atom MD. Recently, one of the authors derived a fundamental method for the dynamics of coarse-grained particles using a projection operator [6]. Such coarse-grained dynamics are promising for analyzing phenomena which have a three-dimensional nonuniformity such as a surface roughness effect.

3. Simulations of boundary lubrication
Diamond-like carbon (DLC) films possess the potential to reduce the friction coefficient which are expected when using both power-train and drive-train components. It is difficult to theoretically predict the friction properties of the DLC, however, they are affected by their mechanical properties, chemical properties, and the properties of base substrates such as surface roughness, sliding atmosphere and sliding conditions. Recently, one of the authors proposed a surface chemical mechanism of low friction which is observed in Si-containing DLC (DLC-Si) films [7, 8]. The influence of the silicon content of the DLC-Si films on the friction property of the films was examined by friction tests, and the low friction mechanism of the films was examined by analysis of the wear surface. The Si-OH (silanol) formation on the wear surface of the films was detected using derivatization-XPS [9, 10] which indicates that the low friction coefficients are attributed to the Si-OH formation. Also, the model measurements consisting of the Si-OH on the silicon wafer exhibit a low friction coefficient below 0.1. On both surfaces, an adsorbed water layer of 1 nm to 4 nm thickness was detected by spectroscopic ellipsometry [11]. The silicone on the surface of DLC-Si films produces Si-OH, then they adsorb the water in the atmosphere, eventually causing a friction reduction.

The existence of the water on the Si-OH surface was measured under static and unconfined conditions. The question then arises as to whether or not the surface water is stable on the confined geometry and under the shear. In this chapter, we report some of our recent results of

Figure 3. Mechanism of momentum transfer on the three types of traction fluid molecules.
molecular dynamics simulation of the water layer on the Si-OH surface under a sliding condition.

Figure 4 shows the model of water and Si substrates. TIP3P is used for the water molecules. The -OH base and -H base are placed on the dangling bonds on the (111) surface of the Si crystal. The bond and angle intramolecular interaction $E_{\text{bonds}}$ and $E_{\text{angles}}$ are treated by $E_{\text{bonds}} = K_r(r - r_{eq})^2$ for the bonds and $E_{\text{angles}} = K_\theta(\theta - \theta_{eq})^2$ for the angles. Where $r$ is the atom distance, $r_{eq}$ is the equilibrium distance, $\theta$ is the bond angle, $\theta_{eq}$ is the equilibrium bond angle, and $K_r$ and $K_\theta$ are the spring constants. The parameters are taken from the Amber force field [12] of a hydroxy group for simplicity. For the intermolecular interactions, the van der Waals are calculated by the OPLS type parameters [14], and the Coulomb interactions are calculated from the partial charges of each molecule. The partial charges on the Si-OH are set to $+0.4/e$, $-0.8/e$ and $+0.4/e$ on the Si, O and H atoms, and for the Si-H, $-0.1/e$ and $+0.1/e$ on the Si and H atoms, respectively, where $e$ is the elementary charge. The electrostatic interactions are truncated at half of the simulation cell. The vibrations inside the Si crystals are frozen. Although the reliability of the potentials for the Si substrates is currently under study using density functional theory calculations, the partial charges are within $0.12/e$ for each group and from the potential parameters for the bonds and angles, we can claim that the difference between the nature of the surfaces covered with the hydroxy group and terminated hydrogen can be distinguished from our method.

The substrates are placed in the center of the hexahedron simulation cell. On the $x$ and $y$ axes, the periodic boundary condition is adapted to the simulation cell. $x$ is the sliding direction and $z$ is the direction of the fluid thickness. The temperatures are controlled at 300 K using the Nose-Hoover formalism [13]. All the molecules are connected to a heat bath.

![Figure 4. Simulation models for water and Si-H, Si-OH terminated Si substrates.](image)

The constant shear states, i.e., constant pressure and constant velocity, are obtained in the following manner. First, a set of fluid molecules are arranged in a lattice configuration. The molecules are then moved by MD simulation under the periodic boundary condition in a direction at the constant temperature of 300K until a thermal equilibrium is obtained. Next, the sets of thermal equilibrium fluids are arranged in the direction between two solid plates. Fluid molecules are compressed by the MD simulation under the periodic boundary condition of the direction by adopting the constant pressure of 1 GPa on the plates. The film thickness $z_0$, which is defined as the length of the water molecules present in the direction, saturates to some fixed value. The shear in the $x$ direction is then applied by a relative sliding motion on the Si substrates by a constant velocity of 1 m/s.

Figure 5 shows snapshots of the layer of water molecules under steady shear. The water film thickness converged to 16.0 nm at the Si-H surface and 12.3 nm at the Si-OH surface. In the
Si-H surface, it is observed that the layer of water molecules repel from the surface. On the other hand, in the Si-OH surface, the layer of water molecules are strongly bound to the surface which suggests that a hydrogen bond network is made between the surface and the water layer. The thinning of the water film thickness on the Si-OH surface also suggests that the hydrogen bond networks are passed along the entire water layer.

(a) The Si-H surface.  
(b) The Si-OH surface.

Figure 5. Snapshots of the layer of water molecules under a steady shear.

Figure 6 and Figure 7 shows the trajectories of the oxygen atoms of the water molecules taken from the snapshots every nanosecond.

Figure 6. Trajectories of the oxygen atoms of water molecules on the Si-H surface.

Figure 7. Trajectories of the oxygen atoms of water molecules on the Si-OH surface.
Comparing Fig. 6 and Fig. 7, the water molecules are formed in a layered structure in the Si-OH, whereas they distribute as a more liquid-like structure in the Si-H.

The relation between the macroscopic friction and our MD results are discussed as follows. In contrast to the case of the Si-H surface from which the water layer is repelled from the surface, on the Si-OH surface, the water layer is strongly combined with the surface and may work as a boundary lubrication film, thus preventing direct contact with the other sides. As a result, the friction coefficient of the Si-OH yield is low in contrast to the Si-H case which makes real contact. This mechanism suggests that water of a few nm film thickness can act as a boundary lubricant like a Langmuir-Blodgett film. This property is not surprising since hydrogen bonds are 10 time stronger than van der Waals bonds in hydrocarbons. Further analysis of the water film is now progress.

4. Summary
Molecular dynamics studies of friction in two significant lubrication regimes are shown. For the elastohydrodynamic lubrication, although a discrepancy between the experiments and the simulations exists in the film thickness and shear rate, the mechanism of momentum transfer related to the molecular structure of the hydrocarbon fluids was able to be clarified by the simulations. The submicron thickness simulation of the oil film using a tera-flops computer showed that traction coefficients from the experiments could be reproduced by the simulation. For the boundary lubrication, dynamic behavior of water molecules on hydrophilic and hydrophobic silicon surfaces under a shear condition is studied. The dynamic structure of the hydrogen bond network on the hydrophilic surface is related to the low friction of the diamond-like carbon containing silicon (DLC-Si) coating.

5. References
[1] Ohmori T and Kawamura M 1990 J. Jpn. Soc. Tribologists 35 3 188 (in Japanese).
[2] Washizu H, Senda S, Ohmori T and Suzuki A 2006 J. Jpn. Soc. Tribologists 51 12 885 (in Japanese).
[3] Washizu H, Senda S, Ohmori T and Suzuki A 2006 J. Jpn. Soc. Tribologists 51 12 891 (in Japanese).
[4] Washizu H, Senda S, Hyodo S, Ohmori T, Nishino N and Suzuki A 2007 SAE Paper; transaction, 2007-01-1016.
[5] Washizu H, Senda S, Hyodo S, Ohmori T, Nishino N and Suzuki A 2006 Proc. 3rd Asia Int. Conf. on Tribology, Kanazawa 2 515.
[6] Kinjo T and Hyodo S, 2007 Phys. Rev. E 75 5 051109.
[7] Mori H, Takahashi N, K Nakanishi, Tachikawa H and Ohmori T 2007 SAE Paper; transaction, 2007-01-1015.
[8] Mori H and Tachikawa H 2002 Surf. Coat. Technol. 149 225.
[9] Takahashi N, Mori H, Kimoto Y. Ohmori T and Murase A 2005 J. Surf. Sci. Soc. 25 492 (in Japanese).
[10] Takahashi N 2006 R&D Review of Toyota CRDL 41 1 52.
[11] Kato N, Mori H and Takahashi N 2007 Proc. 4th Int. Conf. on Spectroscopic Ellipsometry, Stockholm 30.
[12] Cornell W D, Cieplak P, Bayly C I, Gould I R, Merz K M, Ferguson JR D M, Spellmeyer D C, Fox T, Caldwell J W and Kollman P A 1995 J. Am. Chem. Soc. 117 5179.
[13] Nose S 1984 J. Chem. Phys. 81 511.
[14] Jorgensen W L, Maxwell D S, and Tirado-Rives S 1996 J. Am. Chem. Soc. 118 11225

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