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PFPE-Z lubricant thin films in molecular dynamics simulations – shear thinning and friction law

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A molecular dynamics simulation study has been conducted in order to point out the effect of steady shear and loading pressure on lubricant thin films. The model used in these simulations is composed of two solid walls and PFPE-Z lubricant. We apply steady shear by moving the walls in opposite directions while at the same time the upper wall exerts a constant load. The lubricant's properties are investigated focusing on the shear thinning phenomenon and friction law. The obtained results could be used to improve computer hard disk systems.

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1. Introduction

In our days, there exists a high need for understanding the lubrication by thin. The theoretical numerical approach in this work provides solid and necessary information to develop new high-performance nano-devices, for example computer hard disk systems. In this respect, better magnetic materials, new and improved read/write heads, the tribology of the head/medium interface, are all responsible for a dramatic increase in the areal density in both disk and storage devices.

In the case of aluminum disks, the existing carbon layer is lubricated with a thin film of perfluorinated polyether for wear protection whose thickness is between 1 and 2 nm [1]. Patterned lubricant films on magnetic hard disks provide longer durability, protecting the disk surface in the case of the slider-disk contact [2]. When one reduces the magnetic space, the protection offered by the combination of the diamond-like carbon layer (DLC) and the perfluoropolyether (PFPE) lubricant film deteriorates. Current requirements include thinner DLC layers, therefore the nanometric lubricant film needs to be more robust in order to provide the same tribological protection. There exists an optimum thickness of the lubricant film for a specific disk, since the stability of the flight height is affected by the stiction, caused by the presence of too much lubricant [3]. On the other hand, it is not possible to obtain the desired protection if too little lubricant is involved. To achieve what is required, we have to consider the fact that the lubricant molecules need to be bound to the surface in order to provide shear resistance, and at the same time some lubricant molecules must remain mobile to flow back into the contact zone for self-healing. In other words, optimum lubrication of a hard disk is controlled by the amount of lubricant molecules at the head–disk interface after a certain number of contacts. As we said above, the most commonly used disk lubricants are perfluoropolyethers (PFPE), which are a family of fluorinated synthetic fluids. They are sufficiently slippery, and the long chain structure provides good surface wetting properties. Also, PFPEs are well suited for demanding environments as they possess numerous advantages such as shear stability and excellent lubricity under normal and severe conditions [4].

At the nano scale, with the lubricant film thickness in the range of 1-2 nm, we approach the molecular scale. For a proper analysis of the encountered phenomena, especially when experimental information is not available, computer simulations are very useful for providing us with some physical explanations. This regime has been extensively studied using Non-Equilibrium Molecular Dynamics (NEMD) simulations [5-7], which has proven to be a very useful tool for investigating lubrication by thin films.

It is important to point out that in the field of thin film lubrication we have to develop well-known theories which are applicable on larger scales. For example, instead of viscosity, we should rather talk about shear viscosity, being expressed by the ratio of shear stress (τ) and shear rate ($\dot{\gamma}$). This dependence of the viscosity on the shear rate is known as the shear thinning phenomenon, which has been studied intensively from an experimental point of view [8] and, no less important using molecular simulations [9, 10]. Some authors treat it in simulations at constant load [11], or at constant thicknesses for the lubricant film [12]. The shear thinning phenomenon is dependent on the simulated system and, very importantly, on the type of lubricant [13]. In [14] the authors focus on the effect of the shear rate on the viscosity of polymer fluids, using a FENE potential function and defining nominal viscosity as well as actual viscosity.

The PFPE lubricant's behavior was investigated using several types of force field, for example a united-atom potential [15, 16], a consistent valence force field [17], or a universal force field [9].

2. Simulation method

In this paper our attention is focused on perfluoropolyether lubricants (PFPE-Z), a thin film of which is confined between two solid gold walls. The apparent surface of each wall is 40.9 × 40.9 Å², consisting of 1600 Lennard-Jones atoms arranged in three layers of an fcc lattice structure. The thin lubricant film is thus confined by parallel walls in the *z*-direction.

The investigated thicknesses of the thin lubricant film were 2.1 nm and 1.5 nm. We mention that we measure these thicknesses before the loading pressure is applied, the thickness of the lubricant film decreasing with increasing loading pressure. The 2.1 nm thickness of the lubricant has 50 PFPE-Z molecules, while for 1.5 nm we have only 25 molecules of PFPE-Z. In this paper, all molecular simulations were performed with the Large Atomic/Molecular Massively Parallel Simulator (LAMMPS) MD code [18], the force field being AMBER (Assisted Model Building and Energy Refinement). This force field is described by

$$U = \sum_{bond} K_r (r - r_{eq})^2 + \sum_{angle} K_\theta (\theta - \theta_{eq})^2 + \sum_{dihedrals} \frac{V_n}{2}[1 + \cos(n\Phi - \Phi_{eq})] + + \sum_{i<j} \left[\frac{A_{ij}}{R_{ij}^{12}} - \frac{B_{ij}}{R_{ij}^{6}} + \frac{q_i q_j}{\varepsilon R_{ij}} \right], \quad (1)$$

where the first term refers to bond stretching, the second one to angle bending, and the third term designates the torsional (dihedral) intramolecular interactions. The last part represents van der Waals and Coulombic term. Since the lubricant consists of C, O, and F atoms, the bond stretching component involves CC, CO, and CF terms. Angle bending parameters are defined for the CCO, CCF, COC, FCF, and OCF triples, while COCC, OCCO, FCCF, COCF, and FCCF refer to bond torsional components.

For this paper, the molecular structure optimization, which implies the minimization of energy, was obtained from HyperChem v.8.8 [19]. One molecule of this type of lubricant film consists of 30 atoms ($C_8F_{18}O_4$). The wall-molecule potential is given by the Lorentz-Berthelot mixing rules [20]. Each wall we modeled as being formed by three "layers". These three "layers", in turn, consist of atomistic monolayers. The upper "layer" of the wall, which is in contact with the lubricant film, is free to move according to the interaction potentials and formed by three monolayers. The middle "layer" of the wall also contains three monolayers, but here a Langevin thermostat is applied to the atoms, its role being to keep the system at constant temperature (300 K). This type of thermostat meets the requirements since the maximum shear velocity is 9 m/s [21].

Nevertheless, in the simulations, the temperature of the investigated system increases due to viscous heating, but cooling of the system is possible through the solid walls. When the temperature of the lubricant film has equilibrated, the steady state of the simulation is reached. In analogy to [22], we mention that this thermostat is applied only in the *y*-direction, perpendicular to the plane of shear. In this way we are able to remove the influence of shear (in the *x*-direction) and compression (in the *z*-direction). Finally, the lowest "layer" of the wall, formed by two monolayers, is kept rigid. Both walls, the upper and the lower one, exhibit the same structure. The simulation cell is periodic in the *x*- and *y*-directions, ,while the boundary in the *z*-direction is being formed by the walls.

The minimum slider (wall) velocity is 3 m/s, the maximum is 9 m/s, the step size being 1 m/s. In this way, we investigate seven different values for the sliding velocity. In this paper we apply a steady shear by moving both walls in opposite directions (in the *x*-direction) each one at half the desired sliding speed.

Furthermore, our attention was focused on the loading pressure effect. In this respect, on the upper wall we apply six different loading pressures (0.1, 0.5, 1.0, 1.5, 2.0 and 2.5 GPa). This constant loading pressure is applied to the rigid part of the top wall in the *z*-direction (see Fig. 1). The NEMD simulations were performed at constant system temperature, volume and number of particles (NVT-ensemble).

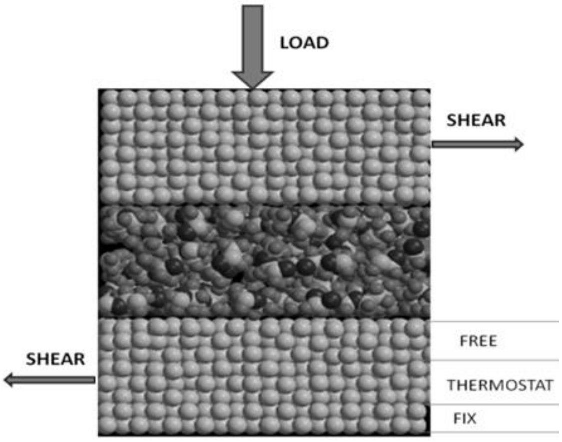

Fig. 1. Snapshot of the simulation cell.

3. Results

The shear viscosity η of the thin lubricant film is given by the ratio between the shear stress, τ_{xz} and, effective shear rate, $\dot{\gamma}$,

$$\eta = \frac{\tau_{xz}}{\dot{\gamma}}. \quad (2)$$

In order to evaluate the shear rate we used two different assumptions. The first one is Newtonian behavior for the thin lubricant film, considering the slope of the linear part for the velocity profile (dashed line in Fig. 2).

In the second case, we are interested in the slope that takes into account the entire lubricant film thickness (solid line in Fig. 2). In our non-equilibrium simulations, moving the walls in opposite directions, we produce a shear rate of about $10^9\,s^{-1}$.

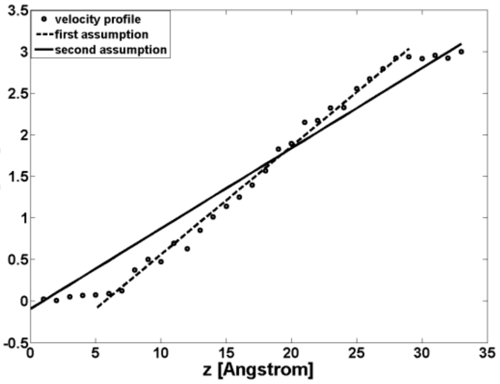

Fig. 2. Assumptions for evaluating the shear rate.

As we already know, the Barus law, $\eta = \eta_0 e^{\alpha p}$, gives us the dependence of viscosity on the pressure. We represented this dependence for these two investigated thicknesses of the confined thin lubricant film with 2.1 nm thickness (Fig. 3) and 1.5 nm thickness (Fig. 4).

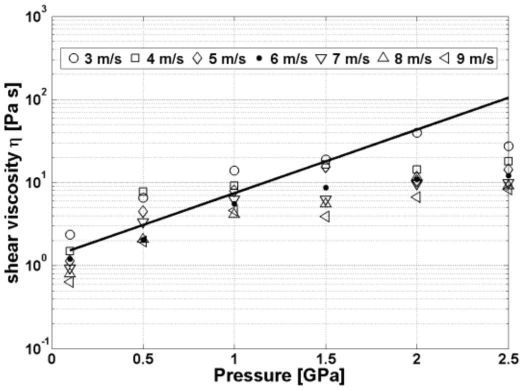

Fig. 3. Shear viscosity as a function of pressure,
2.1 nm thickness.

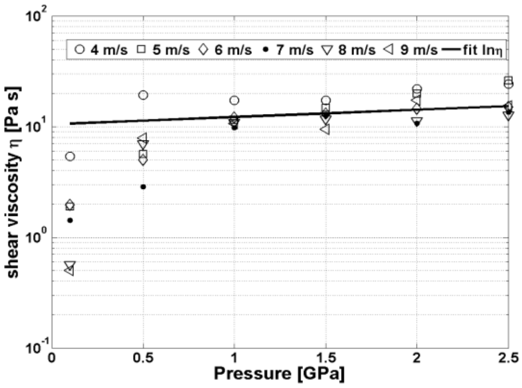

Fig. 4. Shear viscosity as a function of pressure,
1.5 nm thickness.

Going further, as in [10], the shear viscosity can be described by a power law

$$\eta\alpha\dot{\gamma}^{-\beta}, \qquad (3)$$

the constant β depending on the investigated system and on the type of lubricant film, generally with a value lower than one. In Fig. 5 and 6 we highlighted shear thinning phenomena for thin lubricant films with 2.1 nm and 1.5 nm thicknesses.

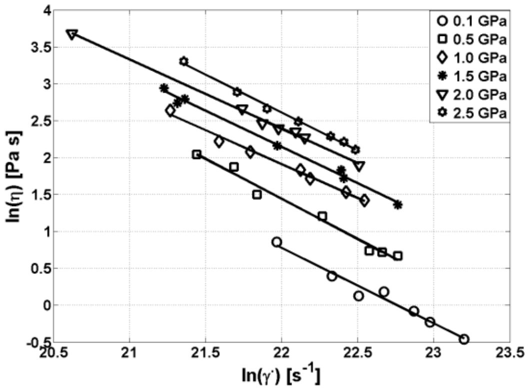

Fig. 5. Shear viscosity as a function of shear rate for
2.1 nm thickness of lubricant film (solid lines are fit lines).

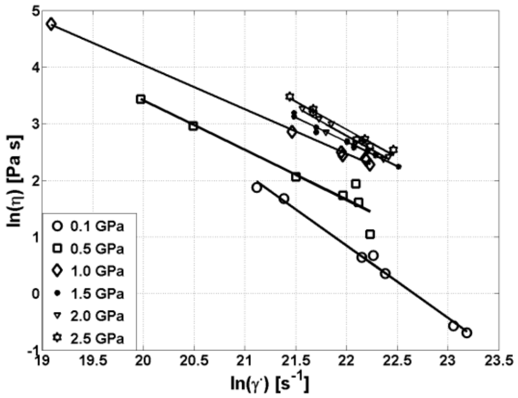

Fig. 6. Shear viscosity as a function of shear rate for
1.5 nm thickness of lubricant film.

Another important aspect of characterizing lubricant behavior is the friction law which links the friction force to the applied load. In this respect, for an accurate interpretation of the phenomena, we had to compare our results with those obtained when only the upper wall is moving (at full sliding velocity) while the bottom wall remains at rest. In Figs. 7 and 8 we represent the friction force as a function of load only for the situation when both walls are moving in opposite directions.

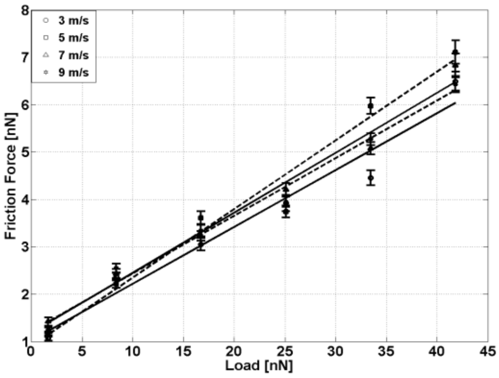

Fig. 7. The friction force as a function of load for 2.1 nm thickness of lubricant film.

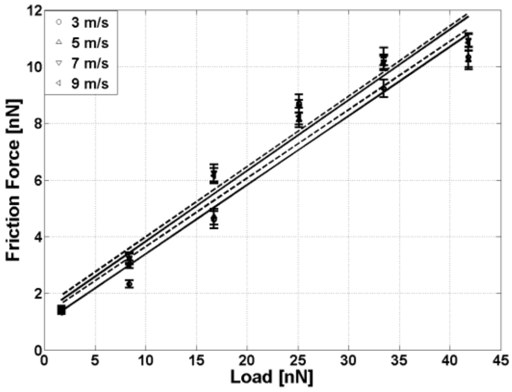

Fig. 8. The friction force as a function of load for 1.5 nm thickness of lubricant film.

4. Discussion

The shear thinning phenomenon depends on the investigated scale, and in our case of thin film lubrication we encounter large shear rates. For example, in [17] shear viscosities several orders of magnitude larger than those in bulk systems were reported. After a proper analysis, we are able to say, comparing errors obtained using our two assumptions for evaluating the shear rate, that the first assumption (Newtonian behavior) is better than the second one. We have this difference between errors because in the second assumption we also include the stick-slip phenomenon. These phenomena, among others, will be discussed in another article.

The Barus law analysis in our cases shows that at 2.1 nm thickness for the lubricant film and low pressure, the law is respected, while it is violated at high pressure (Fig. 3). On the other hand, for 1.5 nm film thickness, the Barus law does not hold at low pressures (Fig. 4).

The shear viscosity of the shearing films is well described by the power law in Eq.(3) for 2.1 nm film thickness (Fig. 5), while for 1.5 nm, the law is not in good agreement with the simulation results (Fig. 6). We explain this behavior considering the interactions between lubricant atoms and wall atoms. In the initial state, when no pressure is applied, decreasing the thickness of the film will increase these mentioned interactions. Applying pressure on the upper wall, the lubrication gap will decrease, resulting in significant deformation of the lubricant molecules.

The Barus law was obtained for a thickness of the lubricant larger than several micrometers. On the nanometric (or smaller) scale of the lubricant film, there was no data to confirm or disprove this law. Our simulations indicate it for a nanometric lubricant film, with the above observations.

Also, we point out that for 2.1 nm film thickness, when both walls are moved in opposite directions, the friction force is higher than when the bottom wall is at rest. This behavior was observed regardless of the shear rate. When the thickness of the lubricant film is 1.5 nm, the number of the lubricant molecules is smaller, and the friction force is independent of the walls' motions, most likely because all lubricant molecules are adsorbed to the walls. In this condition the layers of lubricant behave as an amorphous solid. This behavior is sustained by the radial distribution function (RDF) profiles, which will be discussed in an upcoming publication in further detail. Maintaining the same relative velocity of the walls, we can see that the friction force increases with decreasing thickness of the lubricant film in both investigated cases.

If there is no direct contact between the walls during the experiment (the asperities of the walls are smaller than the lubricant gap), the friction force as a function of load is given by [21]

$$F_f = F_0 + \mu L, \qquad (4)$$

where F_0 is a load-independent force offset, μ is the friction coefficient and L the applied load. In Figs. 7 and 8 we notice that the offset is dependent on lubricant thickness, between 1 and 1.5 nN for 2.1 nm, and from 1.5 to 2 nN for 1.5 nm. Generally, decreasing the lubricant gap increases the offset values. Also, we can see that the friction coefficient is the same in both cases. We suppose that changes which appear in the offset values are determined by the deformation of the molecules when the lubricant thickness is small. These molecular deformations lead to new properties of the lubricant and can cause changes to various properties of the walls (for examples magnetic properties, if the walls are built from ferromagnetic materials).

5. Conclusion

In this paper we investigated the behavior of a confined thin PFPE-Z lubricant film using molecular dynamics simulations. The total number of lubricant molecules was 50 and 25, respectively. Simulations were done moving the confining walls in opposite directions, evaluating seven shear velocities and six values for loading pressure. An analysis of the lubricant yields some interesting behavior: for 1.5 nm lubricant film thickness, the Barus law is respected for loading pressures higher than 0.5 GPa. Beginning with this pressure, the viscosity of the lubricant is approximately constant. Also, shear thinning phenomena can be observed for both simulated lubricant film thicknesses. A friction analysis shows that decreasing the thickness of the lubricant film leads to a friction force increase.

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