

## ON THE WALLS-LUBRICANT FILM INTERFACE

Ana-Camelia Pirghie

*Stefan cel Mare University of Suceava, Department of Mechanics and Technology, camelia.pirghie@fim.usv.ro*

**Abstract:** *In the last 25 years, as a response to the intricate problems arise in engineering applications, molecular dynamics simulations manage to solve some of them. It is a computational method which assist to a better understanding about what is happening between surfaces separated by nanometric lubricant films. The response of the system, walls and film, is dependent on the type of walls, the properties of the lubricant and the external conditions.*

**Keywords:** *nanotribologies, molecular dynamic simulations, film layering, stick and slip motion*

### 1. Introduction

In many tribological applications the thicknesses of the lubricant film is nanometric, comparable to the fluid molecular size. Even so, at this nanometric scale the thin films have the ability to withstand the huge loads. Since 1981, using STM, has been possible to get imaging of lubricant molecules. The interactions between surfaces brought close together represent an important topic in tribology. More accurate, it is important to know how the presence of a lubricant film between the surfaces modifies these interactions. The presence of thin lubricants is responsible for a better wear resistance, providing hydrophobic properties [1]. It has been noticing that using different types of polymers, especially PFPE, the degradation of surfaces minimizes, reducing contact surfaces wear.

In literature there are analyses on friction, adhesion and durability between different types of lubricants. For example, the dewetting of Z-15 film results in higher adhesive force and poorer lubrication performance. Comparing to the water, the Z-15 has a higher viscosity, providing a higher resistance to motion and friction [1]. In the case of Z-DOL, another type of PFPE, its presence on the surfaces can reduce the adhesive force. A real

issue is the process of MEMS/NEMS lubrication (microelectromechanical /nanoelectromechanical systems). One way is Langmuir-Blodgett (LB) deposition, the other way being self-assembled monolayers (SAMs). Films produced by LB method are bonded to the substrate by van der Waals and weak forces, while those produced by SAMs are bonded through covalent bonds to the substrate [1].

The shape of molecules polymers influences the rheological properties of the lubricant films. And to determine it by experimental methods is quite a problem, molecular dynamic simulations being an alternative approach. This simulations help to understand how the lubricant molecules behave in different situations. In data storage devices, the lubricant is exposed to very large shear rate ( $10^9 \text{ s}^{-1}$ ). These conditions can be simulated via NEMD. So, the fluid structure of the lubricant film is a main topic in lubrication studies [2], together with the phenomena which occur to the walls. Accordingly, in polymer processing and lubrication, the rheological properties of thin films need to be well understood. It should be noted that shear response of thin films may differ significantly from the bulk films.

For instance, analyzing internal combustion engines, it can be seen that parts of it are subjected to very high shear rates, pressure and

temperatures [3]. In these conditions, the Reynolds theory of lubrication is no longer available. Consequently, for nanometric scale of the films and high shear rates molecular dynamics simulations are necessary, given a proper explanation to the phenomena.

In [3-5] for complex linear chain molecule the simulations reveals a strong layering near the wall, the films having a non-homogenous nature. Also, in [6, 7] it is reveal a strong layering between the surfaces. This fluid layering can be considered as a consequence of the increase in the effective viscosity [8], or as in [9, 10] because of roughness at atomic scale.

Closely linked to the lubricant structure, meaning also the layering of it, is the so called slip and stick at the solid walls. One explanation for this stick-slip is that friction decrease with velocity. Therefore, under conditions of very little shear, may occur the wall slip. In [8] it has been noticed that increasing the wall roughness amplitude the wall slip decreases. Analysis of confined films also was done by Yoshizawa and Israelachvili [11, 12], where they observed the stick and slip behavior related to the load, temperature and type of molecules. More, the authors suggest that is a critical temperature, dependent on film thickness, at which the stick and slip motion changes to a smooth one. Another factor that can influence the slip-stick motion seems to be the twist angle between surfaces, an angle around of  $10^0$  making that the slip-stick to disappear.

In the work of Manias [13], where it has been analyzed a confined polymer melt between two walls, which are moving in opposite directions, it come out that the velocity profile of film is linear in the middle part, with a density almost constant. Moreover, it has been observed a layering structure for the film, the first layer being stuck on the wall. Thus, in those simulations, increasing the shear rates or decreasing the film thickness, the slip increased. In the same article, an important conclusion was revealed, that the slip between the walls and the fluid and also between the layers of the film (interfacial and

the middle part) occurs in low-density areas. Studies on confined dodecane films between mica surfaces shows that the equilibration of the film leads to a highly layered film; applying the shear the order is destroyed, but the film reorders in the flow direction [14]. In the case of low shear viscosity the slip within the film is marked, distributed equally between layers [8].

Using alkane films, it has been notice that increasing wall roughness amplitude, the walls slip decrease [9]. Other simulations demonstrate that stick-slip behavior does not appear when thin film is water confined by graphene [15], in contrast with the case when the walls are mica. Therefore, the responses of the film are dependent on the thicknesses, molecular structure, topology, surface energy, relative orientation, crystallographic direction.

The slip and stick phenomenon is important given the application where lubricants are used to reduce friction and wear. The stick means that no-slip is present, or the lubricant particles stick to the surface of the wall, having zero velocity relative to the wall motion. In other words, the relative velocity between surface and fluid films is zero [16]. This lead to a boundary layer in the film where shear-thinning can be amplified. The no-slip was observed experimentally and through its consequences [17, 18].

## 2. Simulation method

In this paper, the attention is focused on two thicknesses for the PFPE-Z lubricant film.

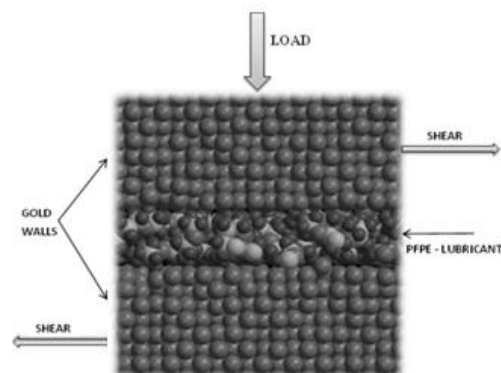
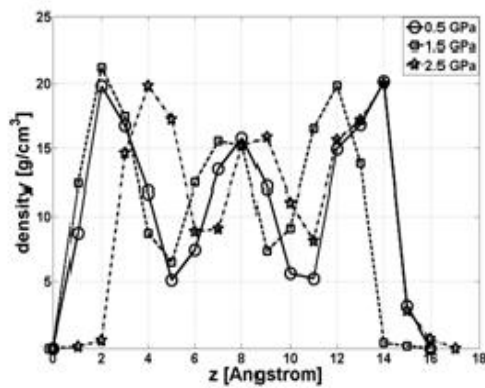


Figure 1: Snapshot of the simulation cell

These are 2.1 nm and 1.5 nm respectively. The lubricant is confined between two solid gold walls, the walls moving in opposite direction, each one at half the sliding speed. The simulation cell is presented in Figure 1 and well described in [19, 20]. The sliding velocities are 3 to 9 m/s (1 m/s step), the loading pressure being 0.1, 0.5, 1.0, 1.5, 2.0, and 2.5 GPa. The simulation method is well rendered in [19-21].

### 3. Results

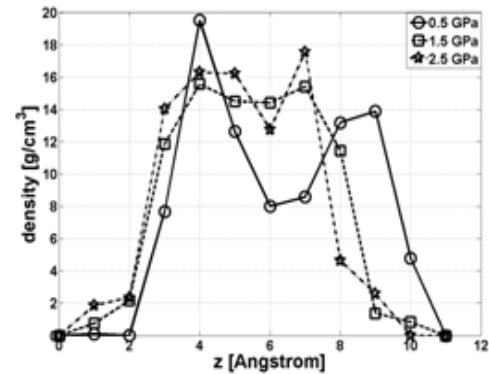
One of the local properties, such as density, can be measured using NEMD simulations. Observing the variation of density lubricant film is obviously related to the fact that we have thicknesses of nanometric scale, Figure 2 [19].



**Figure 2:** Density profile for 5 m/s sliding velocity, 2.1 nm lubricant film thickness

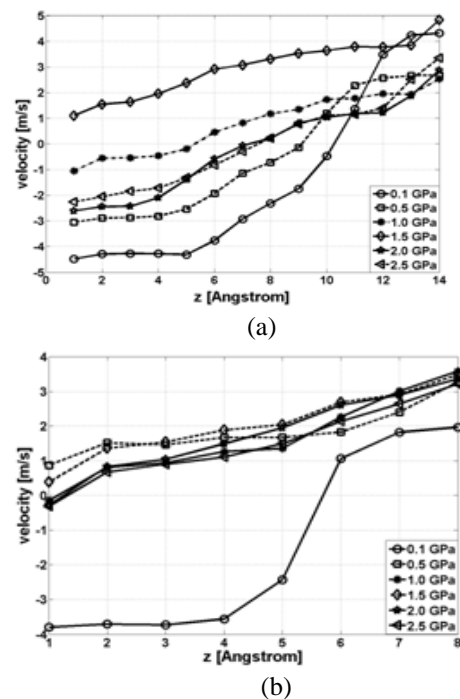
In [8] it is revealed the fact that if the atomic wall density is increasing, the fluid density profiles can be more sharpening. Looking to Figure 1 it can be seen three layers, and close to the walls density is higher than in the middle layer. In the work of Manias [13], where was investigated the confined polymer melts between walls that are moving also in opposite directions, the results showed also a higher density near the walls. The density variation was related to the flat orientation of the chains, in contact with the walls. Another explanation to a higher density of lubricant near the walls is based on a higher density of

the walls. If the surface energy of the walls is increasing, the adsorption of the lubricant molecules is higher [8]. When the thickness of lubricant film is smaller, the density profile shows only two layers for the lubricant, Figure 3 [19].



**Figure 3:** Density profile for 5 m/s sliding velocity, 1.5 nm lubricant film thickness

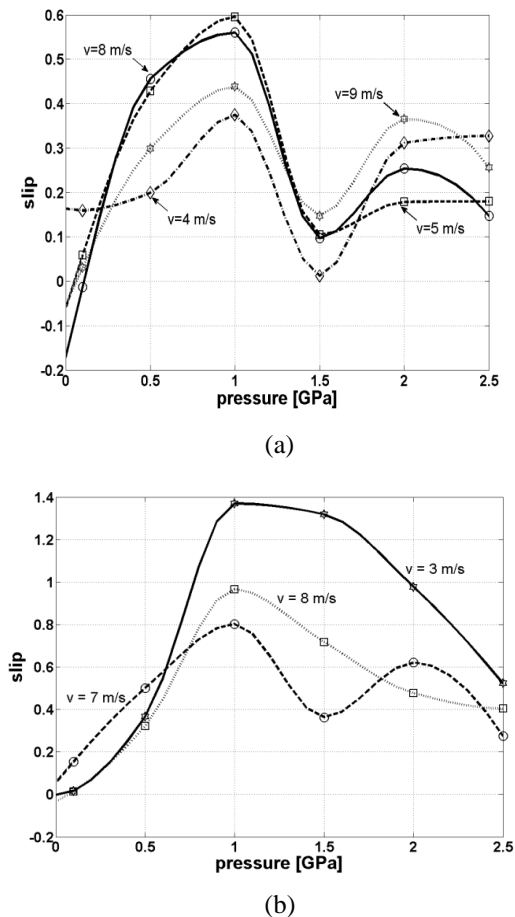
The velocity profiles of the lubricant films are correlated to the density profiles, Figure 4 [19], the lubricant behavior being different near the walls relatively into the middle of the lubricant.



**Figure 4:** Velocity profile at 9 m/s sliding velocity: (a) 2.1 nm lubricant film thickness; (b) 1.5 nm lubricant film thickness;

In [22] where it was investigated the behavior of a fluid in Poiseuille flow, comparing those two profiles, density and velocity, the authors obtained some information of temperature effect and heat-dissipation mechanism on the structure of the flow. So, increasing the driving force 10 times, the drift velocity also increase 10 times, which make that the second layer of the lubricant do not stick to the wall. In [23], while the sliding velocity is increasing the steady state of the film changes from high viscosity to lower viscosity.

Looking to the velocity profiles the slip-stick phenomena it can be noted, Figure 5, [19]. The slip was defined in [19], considering both, the velocity of the wall and the velocity of the lubricant near the wall.



**Figure 5:** Slip at the top (a)/bottom wall (b) as a function of pressure, different velocities for the wall, 2.1 nm lubricant film

As it can be observed at 1.0 GPa loading pressure the slip register the maximum value,

both the top and the bottom wall. Likewise, the slip at 7 m/s but for the bottom wall presents the same behavior as for the slip at the top wall.

#### 4. Conclusions

In the present paper, a review article, it is highlighted the importance of molecular dynamic simulations. In our days, new kinds of lubricant film are produced, as a response to the requirements of technologies. The advantage of MD simulations is that through its method the properties of this can be studied. The molecular structure of the films dictates the rheological and physical properties of it. These density variations of the confined lubricant film can be beneficial for the applications, not to mention the slip and stick motion at the walls.

It is emphasized that the response of the film depends on the combination film-wall. However, have to say that MD methods works best at high shear rates ( $>10^7 \text{ s}^{-1}$ ), below should be given a special attention to the results.

#### ACKNOWLEDGEMENT

The author would like to thanks to PrivDoz. Dr. rer.nat. Dipl.-Phys. András Vernes, Dipl.-Ing. Dr. techn. Georg Vorlaufer, DI Dr. Stefan Eder, Univ.-Prof. Dipl.-Ing. Dr. Friedrich Franek from Austrian Center of Competence for Tribology (AC<sup>2</sup>T research GmbH), and to PhD Phys. Lecturer Cristian Pirghie from Stefan cel Mare University of Suceava for their support and assistance.

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