MOLECULAR DYNAMICS SIMULATIONS OF FRICTION FORCE VERSUS LOAD

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Abstract: *The lubrication between materials in contact is important especially nowadays when requirements in engineering are continuously increasing. The development of computer simulation techniques, coupled with the experimental, provide a better understanding of atomic scale phenomena for nanotribology in thin films. Therefore, the molecular dynamics simulations is used to get an overview into the effects of film thicknesses, shear velocity and loading pressure on confined lubricant behavior.*

Keywords: *nanotribology, lubricants, molecular dynamic simulations, friction force*

1. Introduction

The word tribology, coined in 1966, derived from the Greek *tribos* meaning the science of rubbing, being an interdisciplinary field. In order to understand the complex phenomena that are appearing in interacting surfaces, knowledge of physics, chemistry, material science, mathematics, mechanical engineering and rheology are necessary. When two materials are brought together, separated by a few atomic layers of lubricant, the atomic processes that appear are needed to be analyzed. At this scale, we are now talking about nanotribology involved in magnetic storage devices studies, nanocomponents / nanotechnology and other applications. For example, in vehicle technology are studies related to friction control of machine elements on molecular level [1]. With the development of experimental and computer simulation for studying this phenomena at the atomic scale, the molecular mechanism of tribology come out. When two surfaces of materials are in contact, moved with respect to each other occurs many technological problems, like friction, lubrication, contact formation, wear, adhesion, asperities. Starting with the 90s, the investigations of this kind of process was done using particular microcopies, such as atomic force microscope (AFM), scanning tunneling microscope (STM) and surface force apparatus (SFA). The SFA was developed in 1981 in order to study the static and dynamic properties of molecularly thin films between two smooth surfaces, while the STM, developed in 1981 allows getting the imaging the lubricant molecules. Four years letter, in 1985, AFM provides methods for adhesion measurements, surface roughness and boundary lubrication [2, 3]. Traditionally, in physical systems, friction is analyzed using macroscopic experiments, considering the properties of bulk material. The problems starting to appear when the size of this kind of physical systems is increasingly smaller, so the macroscopic laws are now enable to apply.

Meanwhile, computer modeling and simulation methods are responsible for theoretical studies of these complex phenomena that appear in nanomechanics process. In our days, the thicknesses of lubricant films between two surfaces are increasingly smaller, being the order of a few nanometers. In this situation, the macroscopic laws are unable to provide proper explanations for the encountered phenomena. Thus appear the molecular dynamic (MD) simulation, as a

new approach to theoretical prediction. It is important to note that prediction of classical theories differs from the mechanical response of a nanometer-scale system. MD simulations emerge as a powerful tool in nano-technology, tracking the motion of atoms and molecules as a function of time. The idea is that motion of the particles follows the quantum mechanics theory, having a set of coupled differential equations,

$$m_i \frac{d^2}{dt^2} r_i = -\nabla_i E_{tot}(r_i), \quad i = \overline{1,n} \qquad (1)$$

where m_i is the mass of the ith particle in the system, r_i is the position of atom i (or coordinate vector of the particle), E_{tot} is potential energy and n is the number of atoms in system [4]. The trajectory of particles in phase-space can be analyzed if we know the forces that are acting on particles. The potential energy gives us information about intramolecular and intermolecular interactions. For example, in liquid simulation, widely used is the Lennard-Jones potential. The thickness of the present thin film between two surfaces, being now nanometric, we may say that we have few molecules. And, inside a molecule atoms are interacting on each other through chemical bonds. Coming back to the force field this is in the following form (AMBER force field [5]),

$$E_{tot} = \sum_{bond} K_r (r - r_0)^2 + \sum_{angle} K_\theta (\theta - \theta_0)^2 + \\ + \sum_{dihedrals} \frac{V_n}{2}[1 + \cos(n\Phi - \Phi_0)] + \qquad (2) \\ + \sum_{i<j} \left[\frac{A_{ij}}{R_{ij}^{12}} - \frac{B_{ij}}{R_{ij}^{6}} + \frac{q_i q_j}{\varepsilon R_{ij}} \right].$$

Therefore, exist stretching of bonds, bending of bond angles, potential of torsion angles, Lennard-Jones potential and electrostatic interaction. Between the atoms of nanometric film several types of force interact, thousands of steps of numerical integration of the equation of motion being necessary. Hence, the attention must be focused also on accumulated errors. Thermodynamic properties for different systems can be analyzed in NVE conditions (constant particle number, volume and total energy). Likewise, are in NVT and NPT conditions (temperature or pressure). As a complement, the analysis of the involved systems is made in Nonequilibrium Molecular Dynamics Simulations (NEMD), which is based on time-reversible equations of motion. The key to the nonequilibrium was that through internal control variables to replace the external thermodynamic environment [6]. In this way, the new variables can control, pressure, stress, energy or temperature, maintaining the nonequilibrium state. An important aspect on nanolubrication is type of lubricant thin films, the polymers being usually used. Lubricants such as perfluoropolyethers (PFPE) are sufficiently slippery, providing good surface wetting properties. Also, studies on PFPEs indicate shear stability and excellent lubricity under severe and normal conditions.

2. Simulation method

In this paper, the attention is focused on two thicknesses for the lubricant film, which is a perfluoropolyether lubricant (PFPE-Z). These are 2.1 nm and 1.5 nm respectively.

The sliding velocity ranges are from 3-9 m/s with a step of 1 m/s, the walls being moved in opposite directions (in the x-direction) and also when the bottom wall is at rest (Figure 1). The lubricant film is confined between two solid gold walls, each wall being formed by three layers, more accurate eight atomistic monolayers [7].

The upper side of the wall is made of three monolayers and is in contact with the lubricant film; the middle part is also made of three monolayers, but a Langevin thermostat is applied to the atoms, its role being to keep the system at constant temperature of 300 K. The cooling of the system is possible through the solid walls.

The thermostat is applied in the y-direction, perpendicular to the plane of shear.

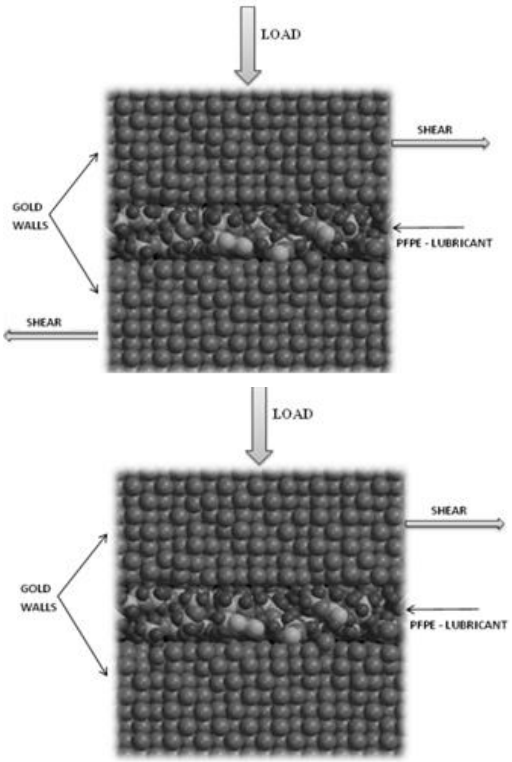


Figure 1: *Snapshot of the simulation cell*

The part which is kept rigid is formed by two monolayers. Both walls made of gold atoms present the same structure (Figure 2) [8, 9].

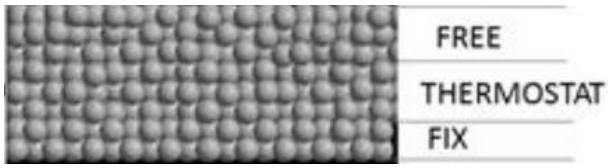


Figure 2: *The wall structure*

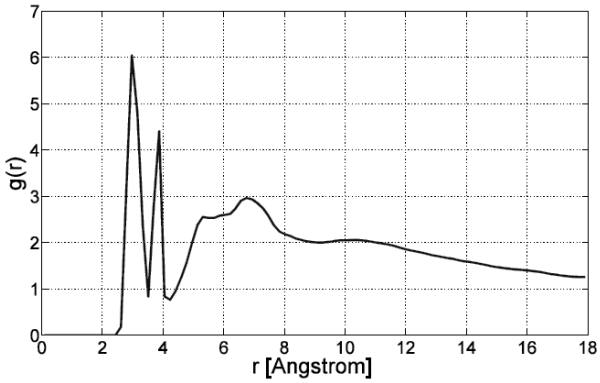
At the same time, the attention involves the loading pressure effect, the upper wall supporting six different loading pressures in the z-direction of 0.1, 0.5, 1.0, 1.5, 2.0 and 2.5 GPa [8, 9]. The simulations imply seven different values for sliding velocity and six loading pressure in condition of NVT-ensemble. The investigated thicknesses of the lubricant confined film is nanometric, so for 1.5 nm there is only 25 molecules while for 2.1 nm 50 PFPE-Z molecules (Figure 3, [9]) are present. The molecular simulations are performed using LAMMPS-MD code (Large Atomic/Molecular Massively Parallel Simulator) [10].

Figure 3: *The molecular model of PFPE-Z ($C_8F_{18}O_4$). Carbon atoms are gray (biggest balls), fluorine is white (small balls) and oxygen atoms are black*

This is a molecular dynamics code that models an ensemble of particles in different aggregation states, using boundary conditions and different types of force fields. It can be used for systems with a small number of particle and also for millions of particles, its versions being written in C++ and distributed by Sandia National Labs. So, the LAMMPS integrates the Newton's equations of motion for atoms and molecules that interact via forces considering the boundary conditions and initial conditions. The molecule structure was made using HyperChem v.8.8 [11], which is capable to draw and create any molecule.

3. Results

Information about the state of the confined thin lubricant film can be reached by examining the radial distribution function



(RDF), Figure 4.

Figure 4: Radial distribution function; 2.1 nm lubricant film thickness, v=4 m/s, 2.0 GPa loading pressure

Increasing the loading pressure, more accurate at high pressure, a second peak appears, which is related to the fact that the layers near the walls become like a solid. The second peak emergence show that the lubricant behavior is now as an amorphous solid, [7]. This phenomenon is related to the one of stick and slip phenomena described in previous papers [8]. Also the analysis of lubricant behavior is related to the friction force, which links the friction force to the applied load. The attention is focused on both cases, when both walls are moving in opposite directions [7] and when the bottom one is at rest, for both thicknesses involved, 2.1 nm and 1.5 nm respectively.

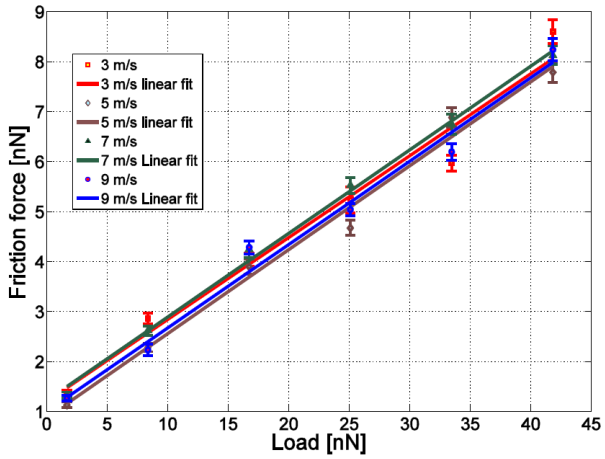


Figure 5: *The friction force as a function of load for 2.1 nm thickness of lubricant film; the bottom wall is at rest*

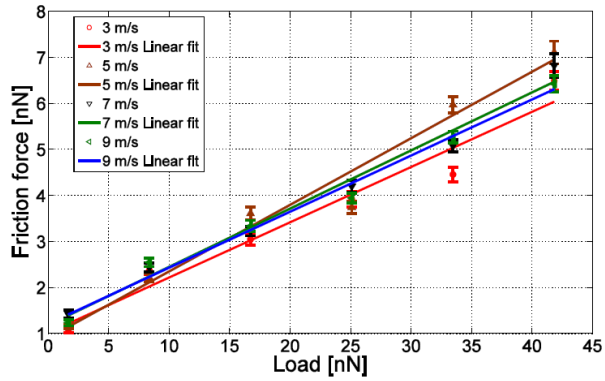


Figure 6: *The friction force as a function of load for 2.1 nm thickness of lubricant film; both walls are moving*

When only the upper wall is moving, it is done by the mentioned shear velocity, in the range of 3 to 9 m/s (step by 1 m/s), while when both walls are moving in opposite direction, each wall has half desired sliding speed from the mentioned above.

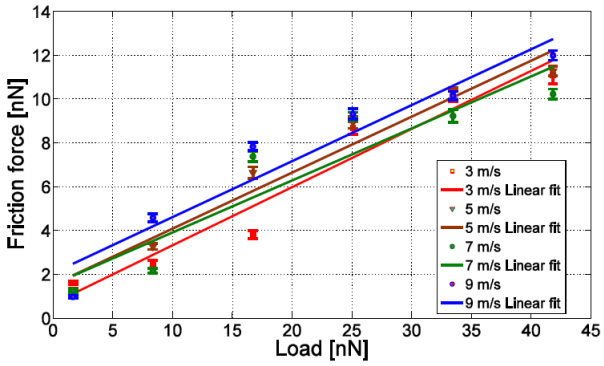


Figure 7: *The friction force as a function of load for 1.5 nm thickness of lubricant film; the bottom wall is at rest*

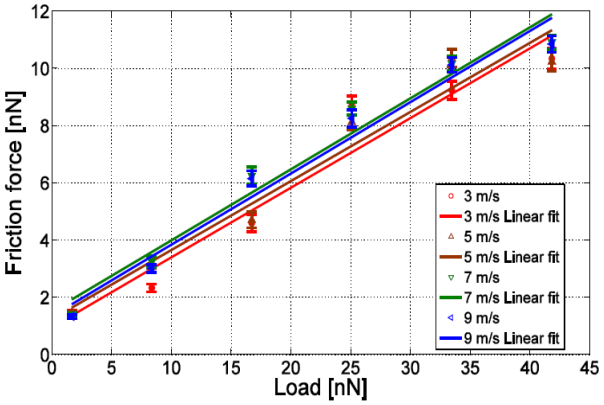


Figure 8: *The friction force as a function of load for 1.5 nm thickness of lubricant film; the both walls are moving*

Looking at the figures 5 and 6 it can be noticed that regardless of shear rate, the friction force is smaller when the both walls are moving. In the case of only 25 PFPE-Z molecules, the lubricant film behavior is the same; most likely the lubricant molecules are adsorbed to the walls, the lubricant film behaving like as an amorphous solid. Moreover, regardless of the system status (one or both wall is moving), when the lubricant thicknesses decrease to 1.5 nm, the friction force values increase.

4. Conclusions

In the present paper, a review article, the attention was focused on a confined thin lubricant film, a perfluoropolyether lubricant (PFPE-Z), also thanks to its good response in different mechanical situation. The thickness of the film is 2.1 nm and 1.5 nm, which corresponds to a few molecules. One molecule is consisting of 3 types of atom summing 30 atoms. The analysis was made using nonequilibrium molecular dynamics simulations (NEMD) via LAMMPS. Are investigated the cases when both gold walls, which confine the lubricant, are moving, and when only the upper wall is moving at different sliding velocities. It is important to note that during the each simulation the sliding velocity and loading pressure is constant. The analysis results is refer to friction force versus load, noticing that this drops when both walls are moving compared to when the bottom wall is at rest. And this is happening regardless of thicknesses of lubricant film.

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