

Nanotribology and Lubrication at Nanoscale: Molecular Dynamics Simulation Studies

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ABSTRACT

Increasing technological advances to make devices and processes at the nanoscale, have made it necessary to effectively minimize the friction and adhesion of moving mechanical assemblies, such as those in micro- or nano-electromechanical (MEMS/NEMS) devices. Lubrication and frictional properties of such systems are complex and often do not obey established laws of macroscale lubrication and friction. Two aspects of the problem are extremely important, for such systems. How the properties of the surfaces and the type of the lubricant affect the lubrication and interaction of the contacting surfaces. In this work, a review of the results of large scale molecular dynamics simulations will be presented to demonstrate, how the properties of confined lubricant can be affected and controlled by manipulating the structure, roughness, and type of the substrate. Two types of lubricants, including freely moving molecules [1]-[4] and self assembled monolayers [5]-[6] will be described in this work. It will be shown by simply manipulating the characteristics of the contacting surfaces, one can change the rheological state of the film and as a result the tribological properties of the contact. Self assembled monolayers (SAMs) will be shown to have diverse mechanical, tribological and thermal properties, and should be employed by understanding such considerations.

Keywords: molecular dynamics simulations, nanotribology, low friction, adhesion, surface effects, gold substrate

1 INTRODUCTION

Miniaturization of the devices in the form of nano/micro electromechanical (NEMS/MEMS) systems requires working with extremely small parts whose adhesion/mass ratio is significantly larger than those in macro-scale applications. So it is of great interest to the industry to understand friction at the nanoscale and to devise strategies that effectively reduce friction. Strategies based on traditional lubrication, that is with a layer of protective liquid lubricant may not work, as the friction at this length scales is far from simple. Experiments have shown that properties of liquid lubricants are altered significantly when confined and squeezed to only a few nanometer thick films. They show enhanced viscosity, several orders of magnitude

larger than their bulk value [7]. This means very high friction, something that must be avoided. The structural origin of such remarkable alterations in the properties has been found through comprehensive molecular dynamics simulations [1]-[4]. Transition to rigidity has been shown to occur when the film solidifies and forms ordered molecular structures. Despite this limitation, simulations have also shown that the solid structure that forms could be avoided by carefully modifying the surface characteristics. This involves either using surfaces of different crystalline structure or, using surfaces that destroy the ordered structures leading to a film that has a resistance to shear of the same order of the unconfined bulk lubricant. Another strategy that has a good potential and application for lubrication at the nanoscale is to coat the surfaces in contact by self assembled monolayers. These monolayers can be easily deposited onto a substrate by submerging them into a solution of precursor molecules. Other deposition methods such as vapour deposition techniques are also possible. Such coatings are commonly used to modify adhesion and frictional properties of a surface. However an understanding of the structural properties of SAMs and their response to operating conditions such as temperature, load, and sliding velocity is very important. Alkanethiols, $[\text{CH}_3(\text{CH}_2)_n\text{-SH}]$, are among the simplest thiol-based SAMs and these systems on gold surfaces have been widely studied through both experimental and simulation techniques. Such studies have shown that these systems could provide a low friction surface, however they are sensitive to the choice of material, and the length of molecules. It is shown that these systems are sensitive to the number of monomers on the backbone being odd or even [5][6].

In this paper a summary of findings from molecular dynamics simulations are presented that should help with the choice of material, substrate, and lubrication strategy at the nanoscale for NEMS/MEMS systems.

2 SIMULATION METHODS

Molecular dynamics simulation methods are used to simulate confined systems of alkanes and also the alkanethiol systems on (111) planes of exposed flat gold substrates. Various surfaces including, crystalline model mica, amorphous surfaces, gold surfaces of different crystalline order are used. All simulations are done by

algorithms and a program that was developed by the author [8]. Three types of simulations are done, simulations of bulk lubricants, simulations of unconfined SAMS, simulation of confined lubricant systems under a certain load, and simulation of confined lubricants under shear. For all systems the structural, thermal, physical, and tribological properties are calculated by standard statistical methods used in MD simulations.

2.1 Modelling the Lubricant Molecules

Both alkanes ($\text{CH}_3(\text{CH}_2)_n\text{CH}_3$) and thiol based alkanethiol ($\text{CH}_3(\text{CH}_2)_{n-1}\text{SH}$) [n =number of carbon atoms] molecules are simulated by a united atom model [9] in which CH_2 , SH and CH_3 groups are treated as single interaction sites. Such a model has been successfully used in our research group to study crystallization,[10],[11] confinement induced phase transitions, [1] and lubrication with gold surfaces [12]. Henceforth for brevity, in this paper, these alkanes or alkanethiols will be referred to by their number of carbon atoms (e.g. C16 for hexadecanethiol) in each molecule. The alkane systems are equilibrated in the bulk form and then are confined and equilibrated under *NPT* conditions. The configuration of the SAM molecules, at the startup is upright and all trans with sulphur group attached to the threefold position on gold surface atoms. As a result, the sulphur atoms form a hexagonal configuration giving a packing density of $21.6 \text{ \AA}^2/\text{chain}$. Periodic boundary conditions are applied in the lateral (X and Y) directions. The interaction between sulphur atoms and gold substrate is governed by a harmonic potential (eq. (1)) with an equilibrium distance of $r_0=0.244 \text{ nm}$.

2.2 Modelling of the Surfaces

The substrates are modelled by using an explicit atomic structure. The mica and gold have crystalline structure. Crystalline surface of gold is made from four layers of either (111) or (100) faces of fcc (face centred cubic) lattice structure. Gold has a density of 19.32 g/cm^3 and an atomic weight of 196.97 amu. Au(111) surfaces are formed out of individual gold atoms which are placed in a crystalline structure with a lattice constant of 0.408 nm and the nearest neighbor distance of 0.288 nm . Dimensions of the confining surfaces, depending on the confined system, ranged from 5 to 9 nm in the lateral (xy) directions. Snapshots of various surfaces are shown in Figure 1, and their corresponding roughness calculated by a method described in [4] are listed in Table 1. As we can see from this table the roughness of all the surfaces is only a fraction of nanometer, however the Au(111) has the lowest roughness and the amorphous surface has the largest roughness here. We will see, despite these rather small differences in the roughness, the resulting effect on the lubricant film rheology and friction is very significant.

2.3 Potential Model

The model included stretching, bond angle, and dihedral potentials given by equations 1, 2 and 3. The van der Waals interactions were modelled via a 6-12 Lennard-Jones potential, given by eq. 4, cut off at $r_c=1 \text{ nm}$. The initial random velocity for each atom was assigned to give a Maxwell-Boltzman distribution corresponding to the target temperature of 300K which is kept constant unless stated otherwise. The confined systems are simulated under *NPT* conditions where the number of atoms, normal load and temperature are kept constant. The equations of motion were integrated using the velocity Verlet algorithm with a time step of 2.35 fs. A parallel algorithm [8] with link cell and neighbor list methods was used in order to reduce the computational time and effort.

$$\phi(r) = \frac{1}{2}k(r - r_0)^2 \quad (1)$$

$$\phi(\theta) = \frac{1}{2}k_\theta(\cos\theta - \cos\theta_0)^2 \quad (2)$$

$$\phi(\varphi) = \sum_i^s C_i(\cos\varphi)^i \quad (3)$$

$$\phi_{LJ}(r) = 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r} \right)^{12} - \left(\frac{\sigma_{ij}}{r} \right)^6 \right] - \phi_{shift}, \quad (4)$$

$$\phi_{shift} = 4\epsilon \left[\left(\frac{\sigma}{r_c} \right)^{12} - \left(\frac{\sigma}{r_c} \right)^6 \right]$$

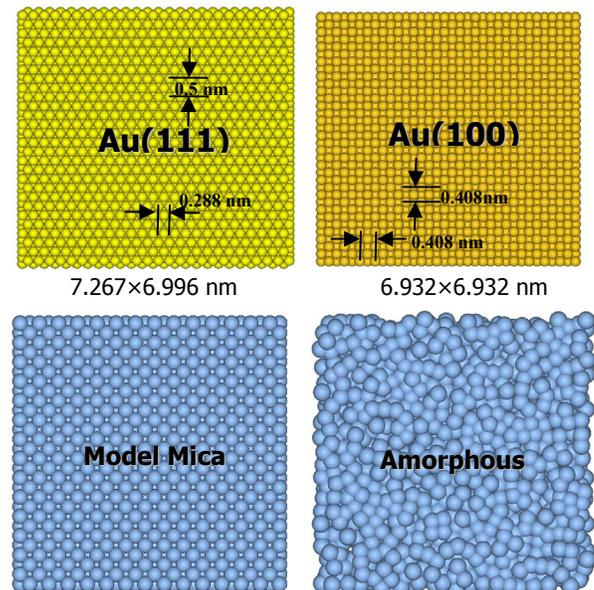


Figure 1 Crystalline and amorphous atomic models for hard surfaces of Au(111), Au(100), model mica, and a disordered amorphous surface. The size of the lattice and the lateral dimensions of the gold surfaces are also shown.

<u>Wall type</u>	<u>Roughness, R_{rms} (nm)</u>
AU(111)	0.008
AU(100)	0.012
Model mica fcc(100)	0.020
Amorphous	0.064

Table 1 The rms roughness of the various type surfaces shown in Figure 1.

The interactions of the surface atoms and lubricant united atoms are also governed by the 6-12 Lennard Jones potential (eq. 4). The interaction parameters of Au are chosen by fitting the calculated and experimental desorption data of alkanes from metal surfaces. These values are ($\epsilon_s/k_B=939$ K) and $\sigma_s=0.2655$ nm, which yield energy and length parameters for the interaction of CH_2 and Au of about four times that of $\text{CH}_2\text{-CH}_2$, LJ interactions. So that substrate- CH_2 interaction parameters are $\epsilon_{sf}=1.795$ kJ/mol= $4.59\epsilon_{\text{CH}_2}$ and $\sigma_{sf}=0.328$ nm. Other potential parameters are given elsewhere in [9], [8], [1] and [13].

3 RESULTS

3.1 Complex Rheology of Alkane Films Confined by Au(100) Gold Surfaces

The rheology of the confined film can be altered by many factors including the type of lubricant, film thickness, and type of the surface. The shear viscosity versus shear rate for various alkanes (C10-C16), with film thickness in the range of 0.85-5 nm, over shear rates of 3.16×10^7 - 10^{11} s^{-1} under constant atmospheric pressure is plotted in Figure 2. For all systems the confining surfaces are Au(100) and the temperature is kept constant at 300K. We can see up to 2 orders of magnitude difference in the shear viscosity at lower shear rates, depending on the type of lubricant and film thickness. The variations in the lubricant film viscosity and friction is the result of changes in the structure of the molecular film induced by the confining film (Figure 3). The critical film thickness for transition to an ordered structure (high viscosity) however could be altered by size of the lubricant molecule and type of the surface.

3.2 Surface and Shear Induced Rheology Alterations

Shear viscosity is calculated for confined films of dodecane confined by various surfaces over a wide range of shear rates 10^8 - 10^{11} s^{-1} . The results that are plotted in Figure 4 show remarkable phenomena. The shear viscosity of the film shows variation by up to 3 orders of magnitude across the various states. At one end of the spectrum there is a film with ultralow viscosity where the viscosity of the film is

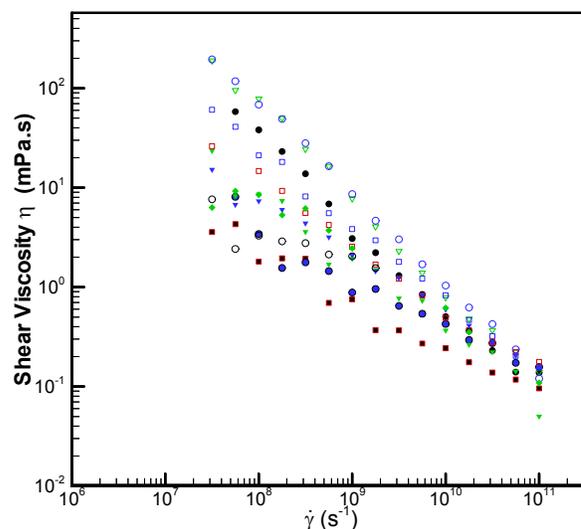


Figure 2 Shear viscosity versus applied shear rate for a various alkane films (C10, C12, C14, C16) of various thicknesses in the range of 0.85-5 nm confined by Au(100) surfaces. Note up to 2 orders of magnitude variation in the viscosity at the lower shear rates.

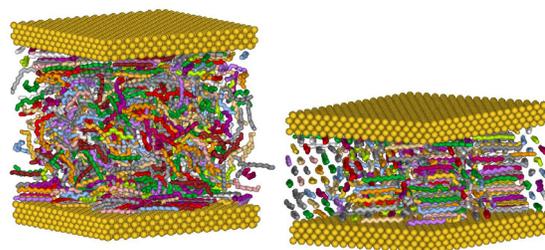


Figure 3 Snapshots of 6.4nm (left) and 3.23nm (right) thick dodecane films confined by Au(100) surfaces; showing the liquid and disordered structure for the thicker film and ordered and solid-like structure for the thinner film.

even lower than the bulk value. This is a film whose molecules are aligned in the shear direction [3]. At the other end of the spectrum the film exhibits ultrahigh viscosity enhanced by two orders of magnitude over that of the bulk [1]. The extrapolation to lower shear rates would show an even larger enhancement in the viscosity of up to 6 orders of magnitude, similar to that reported by the experiments [7]. In both cases the films are confined by the same model mica surfaces and the effect is due to shear driven structural changes in the molecular alignment of lubricant molecules. If the two mica surfaces are twisted by 45° with respect to one another, the lubricant viscosity drops significantly. Here the reason is developing a slip plane within the film due to mismatch of the surfaces [2]. Replacing the confining crystalline surfaces of model mica by two amorphous surfaces whose atomic size, density and interaction energy are the same as the model mica, results in significant decrease in the viscosity. Here the ordered structure is destroyed leading to a liquid like behaviour and

only moderate enhancement of the viscosity [4]. If Au(100) surface is used as the confining surface we do see enhancement in the viscosity and a non-Newtonian behaviour, however the enhancement is much smaller than with the model mica [12]. This is due to easier slip at the interface of the lubricant and solid surface.

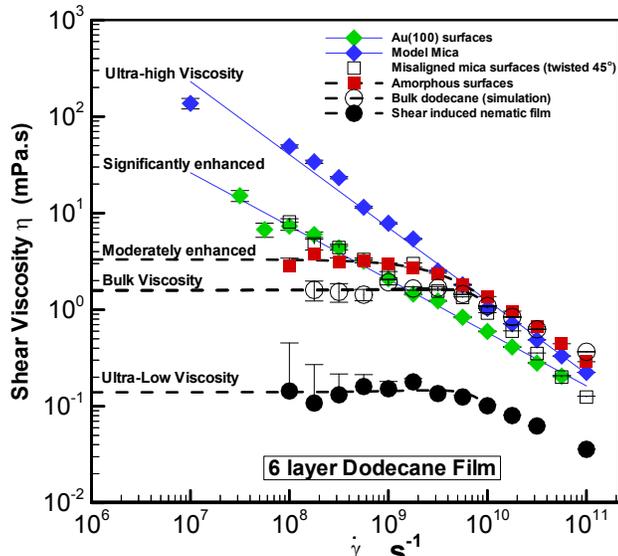


Figure 4 shear viscosity versus applied shear rate for a 6-layer film of dodecane confined under different conditions; note alterations in the viscosity due to surface or shear induced effects.

3.3 Self Assembled Monolayers as Lubricants

Self assembled monolayers (SAMs) are potentially good lubricants offering friction coefficients as low as $\mu=0.01$. Their friction coefficient however is sensitive to the length of molecule, and whether one or both surfaces are coated by SAMs. The adhesion force plays a major role in the overall friction and this force shows some dependence on the length of molecule especially at lower normal loads. There are abundant signs of odd-even effects (Figure 5), where friction and adhesion forces show dependence on the n (number of carbons) in the molecule being odd or even.

CONCLUSIONS

Some of the advances in the molecular dynamics simulations of friction and lubrication at the atomic scales are reported for organic lubricants and self assembled monolayers. It is shown that the rheology of lubricant film and ensuing friction force at these scales is greatly influenced by complex parameters and by controlling these parameters one is able to control the friction at the nanoscale.

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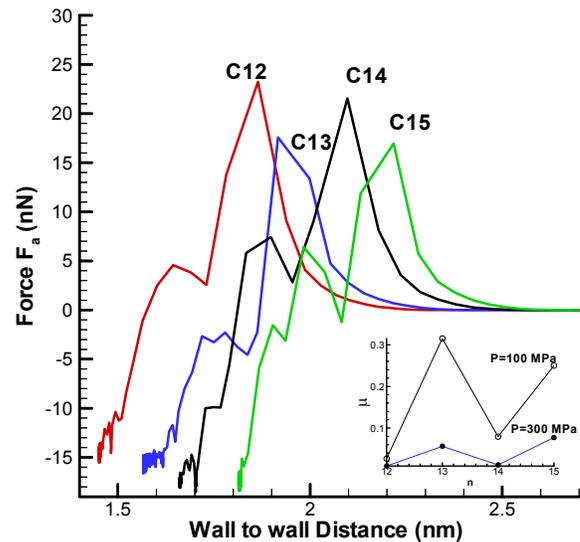


Figure 5 The force applied on the alkanethiol SAMs during the approach of an Au(111) surface to another Au(111) surface coated by alkanethiol SAMs of various lengths. The peak in the force is indicative of the adhesion force; inset shows friction coefficient vs. n for two loads.

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