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The Atomic-Scale Investigation of Friction at Hydrocarbon Interfaces via Molecular Dynamics Simulations
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In this digest, we briefly review our current molecular dynamics (MD) simulations that utilize both the reactive empirical bond order potential (REBO) and the adaptive intermolecular REBO (AIREBO) potential energy functions. The AIREBO potential includes intermolecular interactions, so that self-assembled monolayers, and liquids, can be modeled. We have examined the mechanical and tribological properties of model self assembled monolayers and amorphous carbon films. Self-assembled monolayers are modeled by covalently bonding hydrocarbon chains to diamond substrates. Because the REBO potentials can model chemical reactions, specific compression and sliding induced chemical reactions were identified.

Keywords : self-assembled monolayers, hydrocarbons, molecular dynamics simulations, friction, amorphous carbon

1. INTRODUCTION

A number of groups have examined the frictional properties of alkanethiols on Au and alkylsilane monolayers (or self-assembled monolayes) on various substrates using scanning probe microscopies [1-7]. These self-assembled monolayers (SAMS) may ultimately prove to be useful as boundary layer lubricants in the construction of microlelectromechanical systems with low friction, reduced stiction, and desirable wear properties [8].

Recently, we have used MD simulations to examine the friction of SAMs composed of hydrocarbon chains of various lengths and packing densities [9]. We have also examined the friction and wear of amorphous carbon films [10]. Mechanical and tribological properties of these systems were examined via compression of the monolayers and sliding of the counterface over the monolayers, respectively. In the SAMS systems, we have examined the effects of chain length, packing density, and chain hybridization on friction. The effects of amorphous carbon film thickness and structure on mechanical and tribological properties have also been examined.

In this digest, we present a short summary of some of our recent simulations. For more detailed analyses of our simulations, the reader is referred to our previous publications [9,10].

2. METHODS AND PROCEEDURES

The simulation systems consist of a counterface, or probe, that is used to compress the films of interest. Configurations are extracted from the compression runs to use as starting configurations for the sliding simulations. In most of our simulations, the counterface is a hydrogen-terminated diamond (111) surface. The SAMS are modeled with hydrocarbon chains covalently bound to a (111) diamond substrate (Fig. 1) in the (2 x 2) arrangement (or 1 chain for every 4 carbon atoms in the substrates top layer). The amorphous carbon films are also attached to diamond (111) substrates (Fig. 2).

The outer layers of both the counterface and the diamond substrate that contains the film are held rigid. The rigid layers of the counterface are moved at constant velocity closer to (or parallel to) the opposing film to simulate compression (or sliding).

Periodic boundary conditions are applied in the plane horizontal to the films. Langevin thermostats [11] are applied to the layers adjacent to the rigid layers in both the probe and the counterface to maintain a constant temperature. All remaining atoms are free to move according to classical dynamics. Standard numerical techniques, such as the velocity Verlet algorithm, are used to integrate the equations of motion for non-rigid atoms [12].

The interaction potential utilized for the model SAM systems is the adaptive intermolecular reactive empirical bond-order (AIREBO) potential [13], which is based on Brenner's reactive empirical bond-order (REBO) potential [14]. The REBO potential is used to model amorphous carbon films. The AIREBO potential introduces long-range non-bonded interactions without compromising the potential's ability to model chemical reactions.

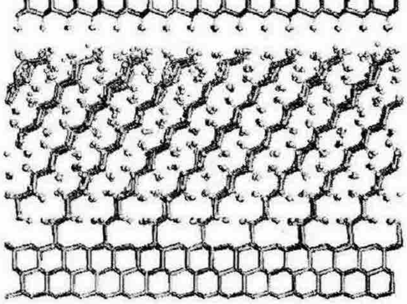

Fig. 1 Typical starting configuration for hydrogen-terminated diamond (111) counterface and a model SAM system composed of C_{16} n-alkane chains on diamond (111) [9]. Carbon-carbon bonds appear in heavy wire frame.

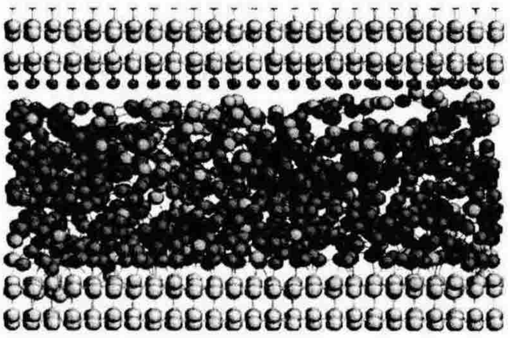

Fig. 2 Amorphous carbon film attached to diamond (111). Sp^3-, sp^2-, and sp-hybridized carbon atoms are colored blue, red, and yellow, respectively. Carbon atoms in the diamond counterface and substrate are gray. Hydrogen atoms are green. This is the thin-film system of Ref [10].

3. SUMMARY OF RESULTS

Extensive compression and sliding studies have been conducted on the systems shown in Figs. 1 and 2 (and related systems [15]). In what follows, we summarize some of the work done on the systems shown in Figs. 1 and 2. More detailed analyses were presented in Refs [9] and [10].

Friction versus load data for several systems are shown in Fig. 3.

It is clear from analysis of Fig. 3 that in amorphous carbon films, with comparable surface structures, the thickness of the film has no affect on friction. Gao *et al.* [10] also showed that even at light loads, chemical reactions occurred within the films during sliding. These reactions grow more numerous as the load is increased. At some critical load, around 300 nN for the thick- and thin-film systems, chemical reactions occur between the counterface and the film. This type of chemical reaction can lead to increased adhesion between the probe and the film and a concomitant increase in the frictional force.

The adhesive contribution to friction was examined more specifically by repeating the simulations done on the thin-film system with two additional counterfaces. These two counterfaces had 10% (or 90% terminated) and 20% of the hydrogen atoms removed. Removing hydrogen atoms from the counterface increases the number of chemical reactions between the counterface and the film (increasing adhesion between the probe and the film). These simulations clearly show that the increased adhesion between the probe and the counterface increases the friction at a given load.

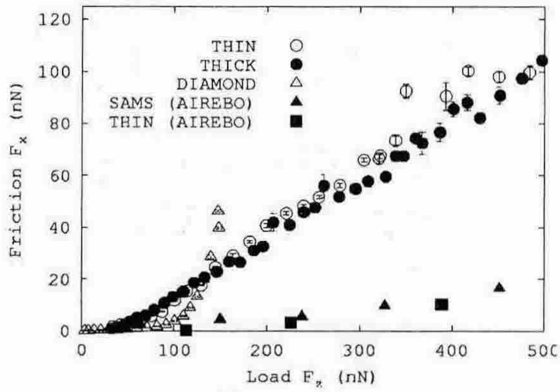

Fig. 3 Friction versus load data from Ref [10]. Thin-film (open circles, filled squares) system shown in Fig. 2. System labeled SAMS (filled triangles) is the system shown in Fig. 1.

The data in Fig. 3 also demonstrate the effect of long-range potential interactions on the measured friction. Simulations on the thin-film system (Fig. 2) were done with both the REBO and the AIREBO potential energy functions. At a given load, the friction calculated with the AIREBO potential is always lower. The long-range LJ interactions present in the AIREBO function cause the counterface to be farther from the film at a given load when the AIREBO is used. This results in lower friction.

We have also examined the friction of the system shown in Fig. 1 and a system with fewer alkane chains of the same length. That is, a system where the packing density of chains is less. Our simulations demonstrated that systems with more loosely packed chains, less order, have higher friction at moderate to high loads. This finding agrees with published atomic force microscope data on spiroalkanedithiols [2]. Simulations were able to link differences in the friction in these systems to bond length fluctuations during sliding.

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