Molecular dynamics simulations of friction in self-assembled monolayers

Kenneth J. Tupper*, Donald W. Brenner

Surface Chemistry Branch, Code 6170, Naval Research Laboratory, Washington, DC, 20375-5342, USA

Abstract

Molecular dynamics simulations were performed to study friction in self-assembled monolayers of alkanethiols on gold. The simulations yield a frictional force that is proportional to the applied load, consistent with Amontons' second law for macroscopic systems. It is further demonstrated that the chain length of the alkanethiols and the load under which the surfaces interact has an effect on the structure of the monolayer film during compression. The simulations suggest, however, that these changes in structure have little effect on the friction properties of the monolayer film. Also, the mode of energy dissipation in both this system and a system in which two monolayer films interact is examined.

Keywords: Computer simulation; Monolayers

1. Introduction

Several factors can effect the wear rates observed for organic thin films, such as film thickness and applied load [1]. An understanding of the relationship of these factors to the frictional properties of thin films is therefore essential for the design of low friction protective coatings [2, 3]. While techniques such as the surface force apparatus [4], atomic force microscopy [5], interfacial force microscopy (IFM) [6], and scanning tunneling microscopy [7] are providing information on the atomic scale regarding the characteristics of thin films, results are sometimes difficult to interpret owing to an incomplete understanding of the processes which occur at the atomic level. For this reason, computer simulations of atomic processes often provide a valuable method for interpreting experimental results and explaining new phenomena.

In a previous study [8], molecular dynamics simulations were used to examine the effect of compressing a monolayer film of hexadecanethiol $(CH_3(CH_2)_{15}SH)$ chemisorbed on a gold (111) surface. A compression-induced structural transition was observed in which the sulfur head groups rearrange from a hexagonal to an oblique packing in the plane of the surface. The simulated force profile was compared with recent IFM measurements [6] and suggests that the transition is observable experimentally. Recent work by Chen and Israelachvili [9] further suggests that phase transitions can be experimentally observed in monolayer films. In the present study, the effect of chain length was examined with respect to the compression-induced structural transition. It is demonstrated that the chain length can have an effect on the observed transition. Also, the compressing surface was slid at various loads in order to compute the friction coefficient as a function of load. Although the compression studies clearly indicate that a change in structure of the monolayer films has occurred, no change in the friction coefficient is observed at the transition point. Finally, the interaction of two monolayers of hexadecanethiol was examined as the films were compressed together and slid.

2. Model

The model used in this study was derived from the model for the study of alkanethiols on gold proposed by Hautman and Klein [10]. The alkanethiol chains were modeled using pseudoatoms representing the sulfur head groups, CH_2 groups, and the CH_3 tail groups. Bond

---

*Current address: Applied Research Corporation, 8201 Corporate Drive, Landover, MD 20785, USA.

bending terms were modeled using a harmonic potential, and torsional terms were modeled using a power series expansion of the dihedral angle. Intrachain interactions for pseudoatoms four or more atoms apart and interchain interactions were modeled using a Lennard-Jones 6–12 potential. The model proposed by Hautman and Klein was modified to include harmonic bond stretching terms to account for possible shortening of the bonds during compression. Further, the continuum aproximation used by Hautman and Klein to model the chain surface interactions was replaced with an explicit surface atom model. This modification was made to account for the fact that, during compression, the sulfur head groups bound at the three-fold hollows on the gold (111) surface can move from the binding sites. It is important to note that the gold surface is modeled as a single gold (111) layer, as the purpose of the modification is to include explicit binding sites on the surface and not to model the bulk properties of the gold surface. The explicit surface atom model was fit so as to give the same results as the continuum model. A description of the modified model used for the compression studies is presented elsewhere [8].

The monolayer films used for this study were composed of 64 chains of hexadecanethiol ($CH_3(CH_2)_{15}SH$) or heneicosanethiol ($CH_3(CH_2)_{20}SH$) chemisorbed to a gold (111) surface composed of 192 atoms. An infinite system was modeled using periodic boundary conditions. The equations of motion were integrated using a third-order predictor–corrector algorithm with a constant step size of 0.25 fs. Non-equilibrium equations of motion suggested by Hoover [11] were used to perform NVT dynamics at a constant temperature of 300 K. The monolayer films were equilibrated for 50 ps prior to compression. The potential energy and average tilt angle were monitored to assure that the system had reached equilibrium. In agreement with recent ab initio calculations [12], the sulfur head goups bind at the three-fold hollow sites on the gold (111) surface. The films were then compressed by moving a gold (111) surface towards the substrate at a constant velocity of 0.1 nm ps^{-1} until a load of 1.8 μN was obtained. The loads were computed by summing the forces on the compressing surface normal to the surface. This method gives the same result as taking the numerical derivative of the total energy. The bare gold (111) indenting surface and maximum load of 1.8 μN were chosen to allow for comparison with the IFM experiments previously reported by Joyce et al. [6]. For the friction simulations of a monolayer film, the gold (111) surface used to compress the monolayer was slid in the [110] direction at a velocity of 0.1 nm ps^{-1} for a distance of 1.5 nm under different loads. This distance corresponds to approximately 3 unit cells. Sliding the gold (111) surface for longer distances did not change the computed friction coefficients. Finally, a friction simulation

for the interaction of two monolayer films was performed by compressing two monolayer films to a load of 0.10 μN and then sliding the upper gold surface at a constant velocity of 0.1 nm ps^{-1}. In all of the above simulations, the compression and sliding speeds of 0.1 nm ps^{-1} were chosen to give a reasonable timescale for the molecular dynamics simulations. Compression speeds of 0.5 nm ps^{-1} and 0.01 nm ps^{-1} gave the same results as those reported here.

3. Results

The simulated force profiles (SFP) for hexadecanethiol and heneicosanethiol are shown in Figs. 1(a) and 1(b) respectively. For the hexadecanethiol film, at approximately 0.36 μN, a change in the slope of the force profile is observed. This change in slope is accompanied by a change in the head group positions on the
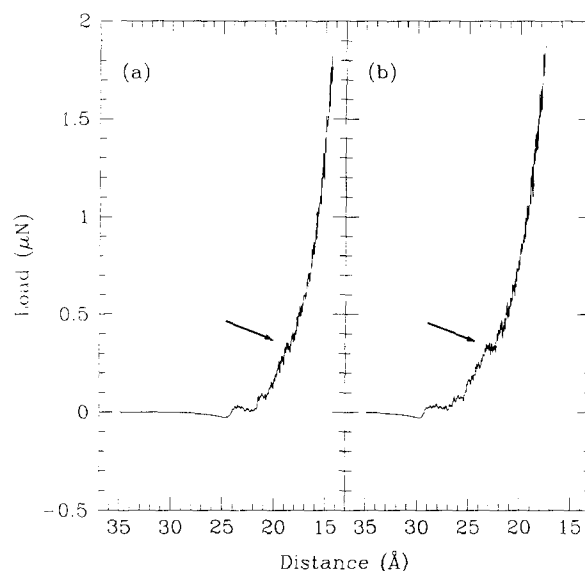

Fig. 1. The simulated force profiles for the compression of (a) hexadecanethiol and (b) heneicosanethiol. The distance corresponds to the separation between the two gold surfaces. Transition points are marked with arrows.
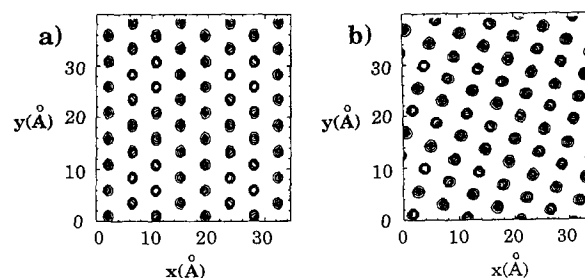

Fig. 2. Calculated average positions for the sulfur head group at a load of (a) 0.18 μN and (b) 1.80 μN; X direction [110], Y direction [112].

surface. Fig. 2 represents the average head group positions at loads of 0.18 μN and 1,80 μN respectively. As seen in Fig. 2, at the higher load the head groups on the surface have rearranged from a hexagonal packing commensurate with the three-fold hollows on the gold (111) surface to an oblique packing where some of the head groups reside over bridge sites. The change in compressibility of the film is thus most probably the result of the change in packing of the hexadecanethiol chains which results during this transition. The compression-induced structural transition observed in this system is discussed in detail elsewhere [8].

For the heneicosanethiol system, a discontinuity in the SFP is seen at approximately the same load as the change in slope for the hexadecanethiol system (Fig. 1(b)). It is interesting to note that the discontinuity in the force curve which is observed for this system is not observed for the smaller chain length. A possible explanation for this can be deduced by examining the structure factors for the sulfur head group and methyl tail groups. The structure factors for the head group and tail group positions in the plane of the gold surface can be calculated using [13]

$$S(Q) = \frac{1}{N} \left| \sum_{j=1}^{N} e^{(iQ \cdot R_j)} \right|^2 \qquad (1)$$

where Q is the reciprocal lattice vector over the box length in intervals of 2π, R_j are the components of the positions in the surface plane, and the sum is over the number of head or tail groups. $S(Q)$ can be plotted as a function of Q_x and Q_y to obtain the equivalent of a diffraction pattern for the head group or tail group positions. The sum of the peak heights in this diffraction pattern for peaks not shared by the hexagonal and the oblique packing can be used to determine both the point at which the transition occurs and the extent to which the head and tail group positions deviate from the hexagonal and oblique packing. For the purpose of this discussion, the transition point will be defined as the point at which the curve for the hexagonal packing begins to fall off. The sums of the structure factors for the head and tail groups for both the hexadecanethiol and the heneicosanethiol systems are shown in Fig. 3. For the hexadecanethiol system, the transition begins at a surface separation of 1.9 nm, which is also when the change in slope in the SFP is observed. The transition in both the head groups and the tail groups begins at the same distance, and approximately 40% of both the head and tail groups occupy positions which are commensurate with the oblique structure following the transition. For the heneicosanethiol system, the transition begins at approximately 2.4 nm for the CH_3 tail groups and approximately 2.3 nm for the sulfur head groups. Thus, the difference in the two systems is that, for the system containing longer chains, the tail groups can begin to rearrange prior to the head groups. While the
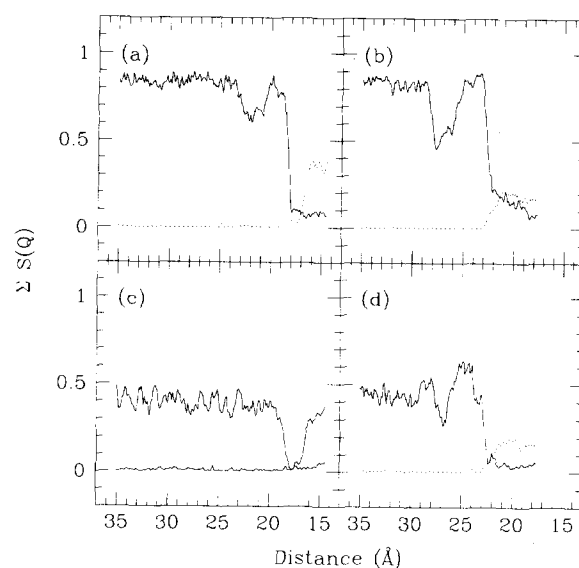

Fig. 3. Sum of the structure factors for the peaks not shared by the hexagonal and oblique packings for (a) the sulfur head groups in hexadecanethiol, (b) the sulfur head groups in heneicosanethiol, (c) the CH_3 tail groups in hexadecanethiol, and (d) the CH_3 tail groups in heneicosanethiol; —— hexagonal packing, - - - oblique packing.

points at which the transitions begin are only approximate, the above explanation does account for the differences seen in the force profiles for both systems. Following the transition, only about 20% of both the head group and tail group positions are commensurate with the oblique structure, suggesting that the system containing the longer chains is also more disordered.

Previous molecular dynamics simulations performed by Glosli and McClelland [14] to examine friction in a model Langmuir–Blodgett film identified a low temperature mode of energy dissipation which was a 'plucking' of the chains as the sliding interfaces passed over potential energy maxima. At higher temperatures, the chains contained sufficient vibrational excitation so that energy flow readily occurred as the chains passed over potential maxima, which decreased the observed friction. Harrison et al. [15] have also characterized the modes of energy dissipation for sliding diamond interfaces. Again the mode for energy dissipation was found to be a plucking motion for the case of hydrogen-terminated surfaces. It was determined that, for the diamond surfaces, the friction coefficient was strongly dependent on the direction of sliding, the average applied load, and the structure of the surface groups.

In the present study, the frictional forces were examined as a function of the applied load for a self-assembled monolayer of hexadecanethiol on a gold (111) surface compressed by a gold (111) surface. Fig. 4 shows the frictional force as a function of the applied load. The frictional force is seen to be linearly dependent on the applied load for this system. Because the friction coefficient is defined as $\langle F_x \rangle / \langle F_z \rangle$, the average
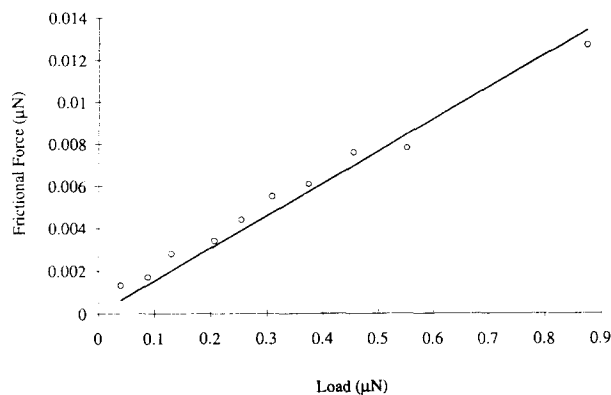
Fig. 4. Frictional force as a function of applied load for the hexadecanethiol system.

Fig. 5. Change in tilt angle observed during friction simulations for two interacting monolayer films of hexadecanethiol.

frictional force over the average applied load, the above suggests that the friction coefficient for this system should be a constant regardless of the applied load. This result is consistent with Amontons' law [16], which states that the friction coefficient should be independent of the applied load.

It is important to note that for these simulations the distance between the compressing surface and the substrate was kept constant, as opposed to maintaining a constant load. The effect of this constraint is that the frictional force and applied load oscillate as a function of time. The oscillations have a period equal to the distance between gold atoms in the sliding direction. Thus, in agreement with the simulations performed by Glosli and McClelland, the sliding surface passes over a potential energy maximum. The tilt angle also oscillates; however, the oscillations are out of phase with the frictional force and applied load. The energy dissipation is thus most probably associated with a 'vibrational' mode, similar to the plucking motion observed by Glosli and McClelland, in which the tilt angle of the monolayer film oscillates. It can be assumed that, if these simulations had been performed at constant load instead of constant surface separation, the mode of energy dissipation would have been an oscillation in the tip height as a function of time. This conclusion is currently being explored.

To examine further the mode of energy dissipation in these systems, a simulation was performed in which two monolayer films of hexadecanethiol were compressed together to a load of 0.10 μN. The upper gold surface was then slid in the [110] direction at 0.1 nm ps^{-1} (see Fig. 5). It is important to note that only the upper gold surface was given an initial velocity. Several important observations were made during this study. First, the chains do not entangle as the two monolayers approach—the preferred mode of relaxation during compression is an increase in the tilt angle for the timescale and load examined in this simulation. The chains also do not entangle as the monolayers are slid across one
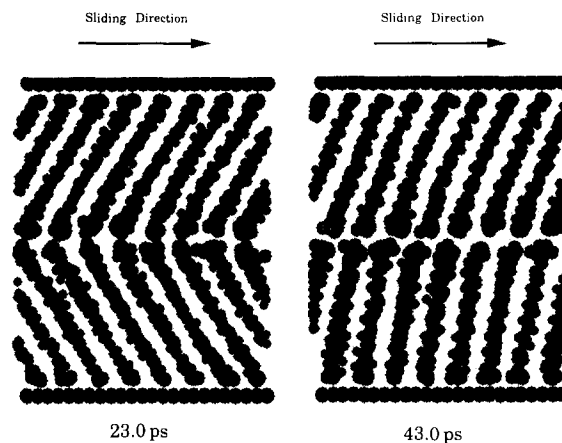
another. Second, the sulfur head groups of the upper surface remain bound in a hexagonal lattice as the upper gold surface is slid. Thus, the binding energy is sufficient to prevent slipping of the upper gold surface across the chemisorbed head groups. Finally, the chains in the lower monolayer rearrange as the upper layer slides. The rearrangement is best classified as a change in the azimuthal angle of 180°. The rearrangement takes over 20 ps to occur, which is much longer than the timescale expected for any energy dissipation mode at the sliding speed examined here. Thus, some other mode of energy dissipation must be responsible for the observed frictional force. The same oscillations in the tilt angle which were observed for the monolayer compression studies were also observed for both the upper and lower monolayer in this study. Thus, it can be deduced that energy dissipation in this system is again due to the oscillations in the tilt angle.

4. Conclusion

The simulations reported in this study suggest that several interesting tribological and structural properties can be observed for self-assembled monolayers. The simulations demonstrate that a structural transition can occur during compression of a monolayer film. This result is supported by recent IFM measurements by Joyce et al. [6] as well as measurements by Chen and Israelachvili [10]. Also, the simulations suggest that the frictional force observed for these types of systems should be proportional to the applied load, in agreement with Amontons' law. Finally, the simulations suggest that, for both the case of a monolayer film compressed by a flat surface and the interaction of two monolayer films, the mode of energy dissipation during sliding is an oscillation of the tilt angle of the chains.

Acknowledgments

References

[1] V. Novotny, J. D. Swalen and J. P. Rabe, *Langmuir*, 5 (1989) 485.

[2] A. Ulman, *An Introduction to Ultrathin Organic Films*, Academic Press, Boston, MA, 1991.

[3] I. L. Singer, in D. Dowson, C. M. Taylor, T. H. C. Childs, M. Gopdet and G. Dalmaz (eds.), *Dissapative Processes in Tribology*, in press.

[4] J. Israelachvili, *Intermolecular and Surface Forces*, Academic Press, San Diego, CA, 1985.

[5] C. Binning, C. F. Quate and Ch. Gerber, *Phys. Rev. Lett.*, 56 (1986) 930.
C. A. Alves, E. L. Smith and M. D. Porter, *J. Am. Chem. Soc.*, 114 (1992) 1222.

[6] S. A. Joyce, R. C. Thomas, J. E. Houston, T. A. Michelske and R. M. Crooks, *Phys. Rev. Lett.*, 68 (1992) 2790.

[7] C. Binning, H. Rohrer, Ch. Gerber and E. Weibel, *Phys. Rev. Lett.*, 49 (1982) 57.

[8] K. J. Tupper and D. W. Brenner, *Langmuir*, 10 (1994) 2335.

[9] Y.-L. Chen and J. Israelachvili, *J. Phys. Chem.*, 96 (1992) 7752.

[10] J. Hautman and M. L. Klein, *J. Chem Phys.*, 91 (1989) 4994.

[11] W. G. Hoover, *Molecular Dynamics*, Springer, Berlin, 1986.

[12] H. Sellers, A. Ulman, Y. Shnidman and J. E. Eilers, in G. Pacchioni (ed.), *Cluster Models for Surface and Bulk Phenomena*, Plenum, New York, 1992, p. 441.

[13] J. Harris and S. A. Rice, *J. Chem. Phys.*, 89 (1988) 5898.

[14] J. N. Glosli and G. M. McClelland, *Phys. Rev. Lett.*, 70 (1993) 1960.

[15] J. A. Harrison, C. T. White, R. J. Colton and D. W. Brenner, *J. Phys. Chem.*, 97 (1993) 6573.

[16] F. P. Bowen and D. Tabor, *The Friction and Lubrication of Solids*, Clarendon Press, Oxford, 1950.