

Molecular dynamics simulations of friction between alkylsilane monolayers

Vivek Kapila¹, Pierre A Deymier and Srini Raghavan

Department of Materials Science and Engineering, University of Arizona, Tucson, AZ 85721, USA

E-mail: vkapila@email.arizona.edu

Received 15 July 2005, in final form 16 January 2006

Published 17 February 2006

Online at stacks.iop.org/MSMSE/14/283

Abstract

Alkylsilane monolayer films are used in the fabrication of microelectromechanical systems (MEMS) as anti-stiction coatings. Recently, these films are also being considered as anti-friction coating for MEMS parts that operate under conditions of friction, such as gears, motors, etc. Study of frictional behaviour of these films is of significant interest from the performance point of view. In this work we use the method of molecular dynamics (MD) to study the friction between two rigid silica substrates coated with alkylsilane monolayers. The friction coefficient, friction force and normal force on the films are obtained as a function of separation between the substrates, temperature of the films and velocity of the substrates. The results of simulations are compared with the thermal activation model of Briscoe and Evans (1982 *Proc. R. Soc. Lond. A* **380** 389). The frictional behaviour of the films as a function of separation between the substrates follows the thermal activation model. The MD simulations in the present work show that the normal force (or pressure) on the films is dependent on the temperature and the substrate velocity. This is in contrast to the thermal activation model in which the pressure on the films is assumed to be independent of these variables. The simulation results are seen to be in agreement with a modified thermal activation model which takes into account the dependence of pressure on the temperature and substrate velocity.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Microelectromechanical systems (MEMS) are rapidly becoming an important part of many modern equipments and devices. The surface micromachining technology used in the

¹ Author to whom any correspondence should be addressed.

fabrication of MEMS has gained immensely from the advances made in the silicon microelectronics industry. Poor tribological properties of silicon are still an area of concern when the surfaces of MEMS are subjected to significant friction. For example, the useful life of rotating devices such as pinwheels and microturbines is rendered very short as they are frequently subjected to wear related failure [1] after a few minutes of operation that may generate surface contamination. The short functional life of these devices is attributed to the excessive wear rate of silicon induced by high friction and low cohesive energy density of the material [2–4]. Practical MEMS devices must be designed to overcome these limitations. Since silicon micromachining is such a well-established technology, the most logical solution is to leave the silicon micromachining in place but devise methods of improving or modifying the surface properties of silicon and polysilicon.

Several studies have been conducted to develop solid and liquid lubricants and hard films to minimize friction and wear in MEMS. The use of tungsten films as wear resistant coatings for silicon based MEMS has been investigated by Mani *et al* [5,6]. Self-assembled monolayer films of alkylsilanes have also been investigated as lubricants on smooth silicon surfaces [7–9]. The lifetime of alkylsilane monolayer coated silicon surfaces is seen to increase with an increase in chain length of the alkyl substituent. Friction and wear studies of self-assembled monolayer films have been done using pin on disc technique and friction force microscopy (FFM). Pin on disc [7] are macroscale friction experiments that cannot provide insight into the actual contact phenomena encountered at MEMS interfaces. Macroscopic samples with different morphologies than their microscale counterparts can obscure the importance of intrinsic surface forces, and the tribology of the macrosystem may be dominated by particulate contamination [10]. AFM [11–13] has been used to study adhesion, friction and wear properties of SAM coatings at load levels that are encountered in the operation of MEMS.

Computer simulations play a critical role in understanding tribological processes. Unlike laboratory experiments, the computer simulations enable the analysis of friction/wear problem at the atomic scale. Tremendous advances in computing hardware and methodology have enabled many computational studies [14–21] in the area of tribology over the last decade.

Molecular dynamics (MD) simulations have been carried out on a number of systems of interest to wear resistant coatings. Wenning and Muser [14] have studied the effect of surface curvature on the law relating frictional forces to normal load as a function of surface symmetry, adhesion and contamination. MD simulations have proved useful in gaining a better understanding of the atomic stick-slip phenomenon commonly observed in the surface measurements using atomic force microscopy [15]. The friction behaviour of confined thin films under shear has been investigated as a function of molecular chain length [17]. An MD study of model diamond–copper sliding system has revealed that wear and friction mechanisms involve four different regimes of deformation, namely no-wear regime, adhering regime, ploughing regime and the cutting regime [18]. MD simulations of two hydrogen and alkyl group terminated diamond surfaces in sliding contact have predicted the possibility of occurrence of tribochemical reactions [19]. Also, the third body effects (contaminant particles, wear-debris) on the friction and wear properties of diamond surfaces have been investigated [20]. The MD simulations allow measurement of average frictional force between contacting hydrogen-terminated diamond surfaces in sliding motion as a function of applied load, crystallographic sliding direction and the presence of chemisorbed groups on the diamond surface. The friction properties of monolayer lubricants, chemically bound to a diamond surface, have recently been studied by Tutein *et al* [20]. The role of defects in the hydrocarbon monolayers consisting of 8, 13 and 22 carbon atoms has been examined on the compression, friction and energy dissipation processes. Recently, Mikulski and Harrison [21] have reported on the effect of packing density on the friction of n-alkane monolayers.

The frictional behaviour of the molecularly thin films in the experimental/simulation studies is often determined in terms of the friction coefficients of the deposited films as a function of separation between the probe and the coated surface and also as a function of velocity of the moving surfaces. Simulations have also been used to investigate the frictional behaviour of films under the environments of different hydrophobicities [22].

In this work, a simple model is developed to study the frictional behaviour of the alkylsilane monolayer films deposited on a silica substrate. The friction coefficient of the model alkylsilane films is determined as a function of separation between the films, velocity of the moving rigid substrates and temperature. A similar work by Glosli and McClelland [23] has reported on the frictional behaviour of organic films. These authors have shown that the frictional behaviour of their model films follows a thermal activation model due to Briscoe and Evans [24]. The thermal activation model provides functional relations between the pressure (P), substrate velocity (V), frictional force (τ) and temperature (T) of the films. In the original thermal activation model pressure (P) on the films is assumed to be independent of substrate velocity and temperature of the films. The results in the present work illustrate that the frictional behaviour of the model alkylsilane films still follows the thermal activation model. However, in contrast to the original thermal activation model, the pressure on the films is found to be a function of substrate velocity and temperature of the films under friction.

The paper is organized as follows. In section 2 the structural models for the alkylsilane films and the silica substrates are presented along with the potential model used to simulate the dynamics of this system. Also, a description of the thermal activation model of Briscoe and Evans is given in section 2.2. The results from these MD simulations are presented and discussed in section 3. The paper ends with the conclusions drawn from this study in section 4.

2. Models

2.1. The MD model

The alkylsilane films on the practical MEMS structures are typically deposited on an amorphous silica substrate. However, in MD simulations it is convenient to model alkylsilane films bonded to a crystalline substrate while keeping the surface density of chain molecules similar to what is seen in the experimental films. In the current work, an α -cristobalite structure is used to model the silica substrate. The unit cell for this structure has dimensions of $(4.97 \times 4.97 \times 6.92) \text{ \AA}^3$. The silica surface for monolayer deposition is constructed from a $(10 \times 10 \times 2)$ array of the unit cells of cristobalite, leading to surface dimensions of $(49.7 \times 49.7) \text{ \AA}^2$ in the simulation cell. The silica substrate in this work is considered to be rigid, i.e. the real dynamics of the substrate atoms is not simulated. Therefore, effectively, this substrate structure serves the purpose of providing the sites for alkylsilane chain attachment and a means to slide the films against each other.

The alkylsilane films in the experimental MEMS structures are chemisorbed to the Si atoms on the silica substrate via an Si–O–Si linkage (figure 1). Also, the head groups ($\text{Si}(\text{OH})_3$) of the alkylsilane chains are known to crosslink, leading to a very rigid alkylsilane–substrate interface structure. Because of this rigid interface, it is convenient not to simulate the real dynamics of these ($\text{Si}(\text{OH})_3$) head groups. Therefore, a simplified model is used with the hydrocarbon tail of alkylsilanes attached to the terminal Si groups on the cristobalite substrate. The united atom model is used to represent CH_2 and CH_3 groups as a single entity in the hydrophobic tail of the alkylsilane. Such coarse graining of the complex molecules is widely accepted in the MD simulations and describes the properties accurately when coupled with appropriate potential models. The structure of the model substrate provides one site per unit cell for the

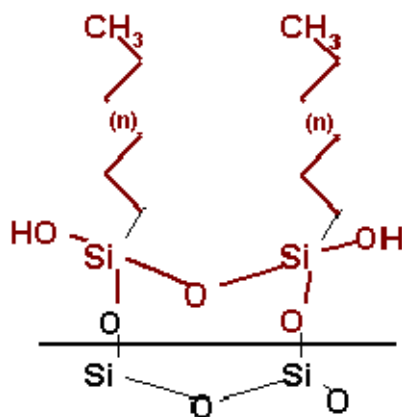


Figure 1. A simplified representation of alkylsilane films on a silica substrate.

alkylsilane chains. Therefore, the simulation cell consists of 100 alkylsilane chains on each substrate. This structure results in a density of 24.7 \AA^2 per chain that is consistent with the density of alkylsilane films seen in experiments on amorphous silica substrates.

In the model developed here, the alkyl chains are attached to the terminal Si atoms of the α -cristobalite surface keeping the bond angles and bond lengths as specified in table 1. A mirror image of the bottom substrate and film is then used to generate the top substrate and film at a given distance from the bottom film. A schematic representation of the two alkylsilane coated α -cristobalite substrates is shown in figure 2. The substrates are made infinite in the X and Y (perpendicular to XZ plane) directions by employing two-dimensional periodic boundary conditions. To simulate the friction between films, the top and bottom rigid substrates are set in motion at a constant velocity in the opposite directions. The structure of alkylsilane films then evolves following Newton's equations of motion. An MD time step of 1 fs is used in solving the equations of motion. The temperature of the films is maintained at the desired value by utilizing the Nose–Hoover thermostat [26].

A molecular mechanics potential model is used to describe the interactions between different species in the simulation cell. The potential model includes intra-chain bond stretching and bond bending potentials and also inter-chain and intra-chain 12–6 LJ potential. The intra-chain LJ potential is used for groups that are separated by three or more bonds. The interactions between the alkyl tails and the silica substrate are modelled as 12–6 LJ potential. The total potential energy of the system is given by the equation

$$U(r) = \sum_{\text{bonds}} \frac{k_i}{2} (l - l_0)^2 + \sum_{\text{angles}} \frac{k_i}{2} (\theta_i - \theta_0)^2 + U(r)_{LJ}. \quad (1)$$

The interaction parameters for the various potential terms are taken from a universal force field (UFF) [27] and are summarized in table 1.

The frictional behaviour of alkylsilane films in this work is characterized in terms of the friction coefficient of these films at different conditions. The friction coefficient in macroscopic experiments is defined as the ratio of the forces in the sliding direction F_x , and in the direction normal to sliding F_z , and is expressed as

$$\mu = \frac{F_x}{F_z}. \quad (2)$$

In the MD simulations performed here, the sliding and normal forces on the film are computed as the sum of the respective force components on atoms comprising a film and its corresponding

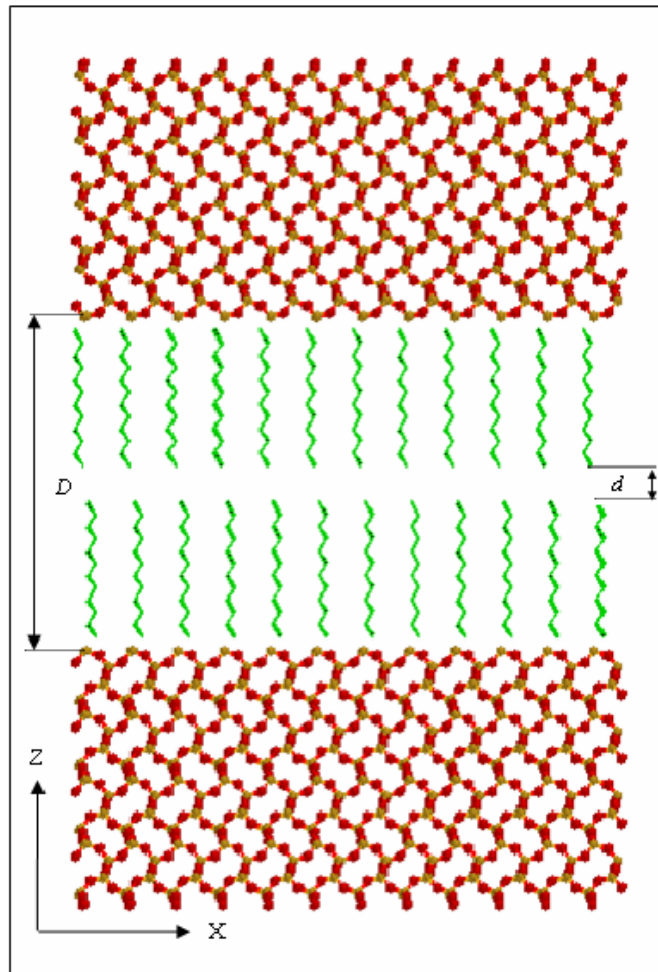


Figure 2. A schematic representation of the initial structure of the alkylsilane films on α -cristobalite substrates used in the friction simulations.

substrate. The instantaneous force values are recorded during the course of the simulation, and the friction coefficients are determined as the ratio of the time average of the sliding force ($\langle F_x \rangle$) and normal force ($\langle F_z \rangle$)

$$\mu = \frac{\langle F_x \rangle}{\langle F_z \rangle}. \quad (3)$$

The time averages of the sliding and normal forces are computed by taking block averages (for block size of at least 2 ps) of the force values, and the standard deviation of the average force values is calculated as the standard deviations of the block averages.

2.2. Thermal activation model

The results of friction simulations obtained in this work are described using a thermal activation model for friction due to Briscoe and Evans [24], which is presented next. The thermal activation model assumes that the plastic deformation in solids takes place by discrete processes

Table 1. Parameters for harmonic bond stretching and bond bending potentials and LJ interactions.

| Bond length (Å) | | |
|---|----------------------------|--------|
| CH ₂ -CH ₂ | 1.545 | |
| CH ₂ -CH ₃ | 1.545 | |
| Si-CH ₂ | 1.910 | |
| Bond bending | | |
| | K (K/radian ²) | Angle |
| CH ₂ -CH ₂ -CH ₃ | 62545.1 | 114.6 |
| CH ₂ -CH ₂ -CH ₂ | 62545.1 | 114.6 |
| Si-CH ₂ -CH ₂ | 96223.2 | 109.7 |
| Lennard-Jones parameters | | |
| | σ (Å) | ε (K) |
| CH ₂ -CH ₂ | 3.905 | 88.06 |
| CH ₂ -CH ₃ | 3.905 | 72.31 |
| Si-CH ₂ | 3.865 | 133.52 |
| CH ₃ -CH ₃ | 3.905 | 59.38 |

involving a small number of molecules. The motion of a particular molecule during the deformation is restricted because of potential barriers due to the neighbouring molecules. The height of these potential barriers increases by increasing the pressure (or normal force) and decreases by the application of a shear stress (or friction force). Representing the potential barrier as Q' , the applied pressure as P and the shear stress as τ , the average time t' for a molecule to pass over the potential barrier can be expressed as a product of a Boltzmann factor and the effective vibration frequency f_0 of the molecule:

$$1/t' = f_0 \exp\{-(Q' + P\omega - \tau\phi)/kT\}, \quad (4)$$

where $\{-(Q' + P\omega - \tau\phi)\}$ is the effective height of the potential barrier under the application of a normal load and shear stress. The factors ω and ϕ are termed pressure activation volume and the stress activation volume, respectively. The stress activation volume is interpreted as the size of the segment that moves in a unit shear process, and the pressure activation volume is the change in local volume necessary to permit motion to occur. Considering a regular series of such barriers separated by a distance b , and allowing transitions in both directions (forward and backward motion), the average velocity v of the molecules down the potential gradient is given by

$$v = 2f_0b \exp\{-(Q' + P\omega)/kT\} \sinh(\tau\phi/kT). \quad (5)$$

In a friction experiment, the sliding velocity V of the substrate is considered to be proportional to the velocity of the rate controlling process v , allowing the equation (5) to be re-expressed as

$$V = 2V_0 \exp\{-(Q' + P\omega)/kT\} \sinh(\tau\phi/kT), \quad (6)$$

where V_0 is an unknown velocity term. Equation (6) is treated as the basic equation in the thermal activation model of friction. In the work of Briscoe and Evans ($\tau\phi/kT > 1$), permitting equation (6) to be re-written as

$$V = V_0 \exp\{-(Q' + P\omega - \tau\phi)/kT\}. \quad (7)$$

The following functional relations between P , τ , T and V and are then derived from equation (7) considering that P , T and V are independent of each other:

$$\tau = \tau_0 + \alpha P, \quad (8)$$

where

$$\begin{aligned}\tau_0 &= \frac{1}{\phi} \left\{ kT \ln \left(\frac{V}{V_0} \right) + Q' \right\}; & \alpha &= \frac{\omega}{\phi}, \\ \tau &= \tau'_0 - \beta T,\end{aligned}\tag{9}$$

where

$$\begin{aligned}\tau'_0 &= \frac{1}{\phi} (Q' + P\omega); & \beta &= -\frac{k}{\phi} \ln \left(\frac{V}{V_0} \right), \\ \tau &= \tau''_0 + \theta \ln V,\end{aligned}\tag{10}$$

where

$$\tau''_0 = \frac{1}{\phi} (Q' + P\omega - kT \ln V_0); \quad \theta = \frac{kT}{\phi}.$$

3. Results

In this section, the frictional behaviour of the alkylsilane films deposited on a silica substrate is presented as a function of (a) the separation between the films, (b) the substrate velocity and (c) the temperature of the films. For the simulation of friction between the films, two alkylsilane-coated substrates are slid against each other at constant velocity, temperature and separation between the films. The flexible hydrocarbon tails of the alkylsilane molecules are very mobile and tilt during the sliding friction, making it difficult to define the separation between the films as the distance between the terminal CH₃ groups of the chains in the two films. Therefore, the separation between the films is defined as the distance D between the fixed (rigid) Si head groups of the films (figure 2).

The results of the MD simulations of friction of alkylsilane monolayers are presented next and are discussed in the context of equations (8), (9) and (10).

3.1. Compression of alkylsilane films

As described in the model section, to generate the initial configuration of the alkylsilane films the alkyl chains are anchored to the terminal Si groups of the α -cristobalite substrate with the length of the chain normal to the substrate. Before performing the sliding friction, this initial structure of the films is allowed to relax for 5 ps at zero substrate velocity. This is followed by a compression run at 2 \AA ps^{-1} to obtain several configurations at different separation distances for use in the subsequent simulations of sliding friction.

The initial separation between the films, D , is set at 43.47 \AA during the relaxation run. This corresponds to a separation of $d = 12 \text{ \AA}$ between the terminal CH₃ groups of the chain molecules of top and bottom substrates. The initial separation between the films is beyond the cut-off range of L-J interactions ($\sim 10 \text{ \AA}$); therefore, there is no interaction between the films initially. Following relaxation, the films are seen to tilt slightly from the normal direction, indicating that the natural structure of these alkylsilane films on the substrate is not perpendicular to the substrate. This tilting of chains is not random: instead the chains seem to have a preferred orientation. A similar tilting of chains has been observed by Zhang *et al* [25] in their MD study of alkyl monolayers and by the experimental studies referenced therein.

Next, the upper alkylsilane coated substrate is moved downwards at the above stated compression rate. The configurations of the system are recorded every 500 compression steps (or every 1 \AA) for use in the subsequent friction simulations. During the compression runs, the normal force on the films is recorded as a function of time. A plot of this data (figure 3)

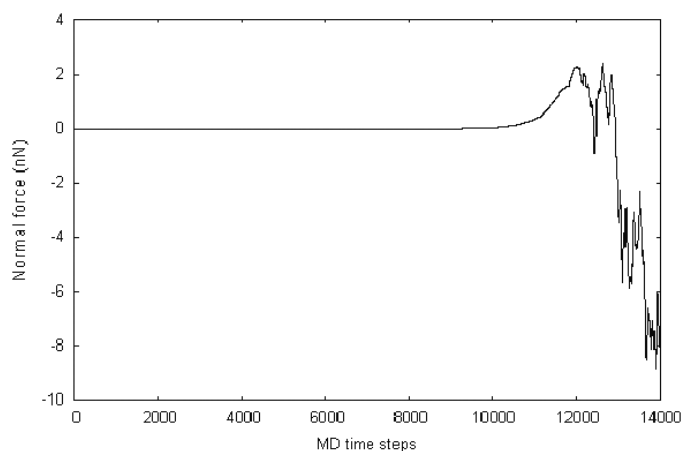


Figure 3. Instantaneous force on the films during compression at a rate of 2 \AA ps^{-1} as a function of MD time steps (one time step corresponds to 1 fs).

shows that the normal force on the film is zero for the first ~ 9500 MD steps corresponding to separations (D) greater than 23.27 \AA . The normal force on the alkylsilane films on the bottom substrate then increases to positive values, reaches a maximum and then decreases to the negative values. A compression of 20 \AA of these films would correspond to the overlap of $\sim 8 \text{ \AA}$ of films ($d \sim -8 \text{ \AA}$) if the alkylsilane chains were to remain normal to the substrate. The minimum in the inter-film L–J potentials occurs at $d \sim 4.5 \text{ \AA}$. The films should, therefore, experience a large repulsive force at these compressions if they were to remain perpendicular to the substrate. However, because of their flexibility, the films are able to accommodate these repulsive forces by tilting with respect to the surface normal. On further compression the films start interacting with each other. The nature of this interaction is attractive at first that becomes increasingly repulsive on increasing levels of compression. Also, in the plot of force versus displacement (figure 3), the compressive force (negative) on the bottom film is seen to oscillate at large compressions. As this plot is showing the instantaneous values of the normal load as a function of compression, it appears that these force values are not the steady state values and time scale for film relaxation is greater than the rate of compression.

3.2. Sliding friction as a function of separation between the films

Following the compression of the films, MD simulations are performed for selected configurations, saved during the compression runs. The criterion for the selection of configurations is to choose those configurations that are under compressive force. The films on the bottom substrates are under compression when the net normal force on the film is negative. As mentioned earlier, the configurations obtained from the compression simulations are not the steady state configurations. Therefore, before starting the sliding friction simulations, the films are allowed to relax for 5 ps at the zero substrate velocity. During the relaxation run the normal force on the films is found to relax to a lower value. The substrate velocity is then ramped up in the next 1000 MD steps to 1 \AA ps^{-1} . Further relaxation of the normal force takes place during the substrate velocity ramp up and then the normal load acquires a steady state value in the next 1–2 ps. The force components in the sliding and the normal direction are averaged for the next 10 ps. The friction coefficient for the sliding friction of the alkylsilane

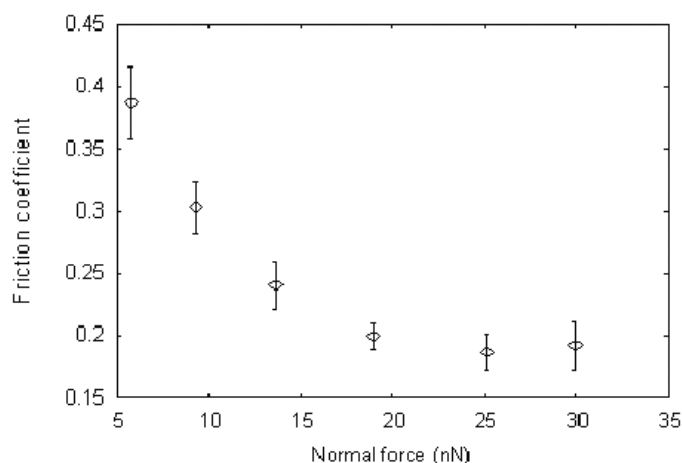


Figure 4. Friction coefficient as a function of normal force.

monolayers is calculated by taking the ratio of time average of the lateral force (F_x) on the films to the time average of the normal force (F_z).

The data from these simulations is used to plot friction force as a function of normal force, and also friction coefficient as a function of normal force. The friction coefficient in figure 4 is seen to decrease non-linearly with increasing normal force. As seen in equation (8) from thermal activation model, the frictional force $F_F = F_0 + \alpha F_N$; therefore friction coefficient can be expressed as

$$\mu = \frac{F_F}{F_N} = \frac{F_0}{F_N} + \alpha. \quad (11)$$

The friction coefficient μ in equation (11) does show a non-linear relationship with normal force, and data from the MD simulations is consistent with equation (8) of thermal activation model.

In figure 5, the friction force is plotted as a function of normal force on the film. A linear fit to the data points is used to obtain the parameters F_0 and α as follows:

$$\begin{aligned} F_0 &= 1.50 \pm 0.18 \text{ nN}, \\ \alpha &= 0.13 \pm 0.01. \end{aligned} \quad (12)$$

3.3. Friction as a function of temperature

Next, the frictional behaviour of the alkylsilane films is examined as a function of temperature. The sliding friction simulations have been performed at the temperatures of 200, 300, 400 and 500 K. A plot of friction coefficient as a function of temperature is shown in figure 6.

From figure 6 it is seen that the friction coefficient decreases non-linearly with increasing temperature. Normally, in macroscopic solid surfaces the friction coefficient is a constant, implying that in order for sliding motion to occur, a larger frictional force would need to be applied at higher normal loads. However, for the sliding friction of alkylsilane monolayers examined in this work, it is seen that although the normal force on the films increases with increase in temperature (figure 7), there is no appreciable change in the frictional force (figure 8). This, therefore, results in a decrease in the frictional coefficient with increasing temperatures (figure 6). An explanation for this decrease in the friction coefficient is offered

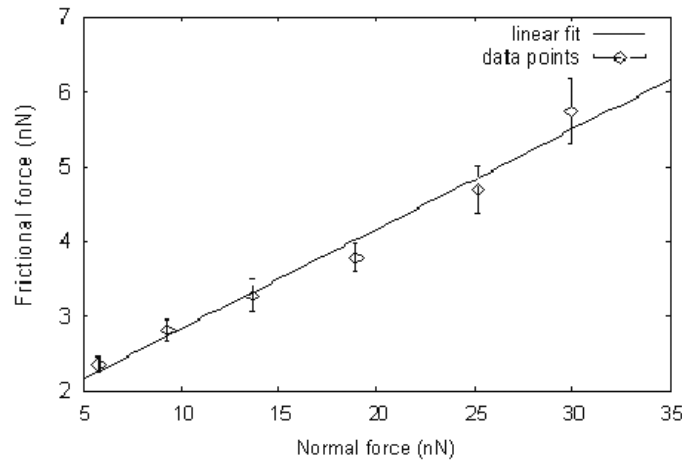


Figure 5. Friction force as a function of normal force on the films.

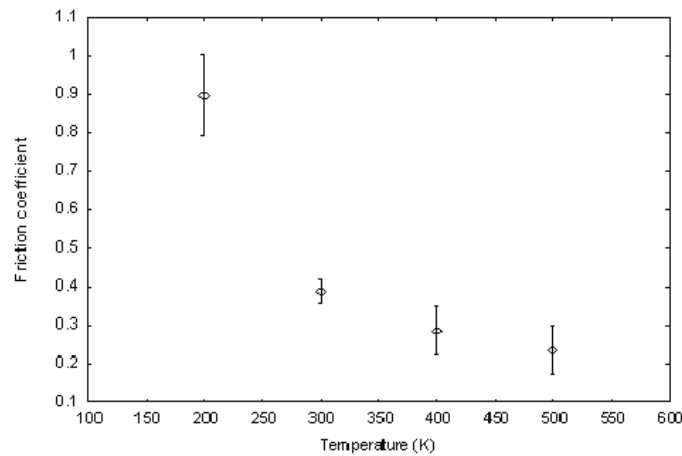


Figure 6. Variation of friction coefficient as a function of temperature.

on the basis of the work of Glosli and McClelland [23]. According to these authors, the films on the substrates can be treated as a collection of harmonic oscillators. At low temperatures, when the system is very weakly excited, the films behave harmonically. As the temperature is increased, the system becomes anharmonic. As the system becomes anharmonic, the amplitude of vibrations increases and the system can jump the surface potential barriers more easily. We also add here that a thermal expansion results from anharmonicity of the potential in a confined space leading to an increase in pressure or normal force.

By fitting their friction data to a thermal activation model proposed by Briscoe and Evans [24], Glosli and McClelland [23] predict a linear relationship between the temperature and friction force. While these authors observe a drop in the frictional force at increasing temperatures, the frictional force in this work shows little variance as a function of temperature (a linear fit to the data in figure 8 yields a slope of 0.0071 nN K^{-1}). This discrepancy can be explained by incorporating the functional dependence of pressure on temperature in equation (9). The data obtained from simulations in the current work (figure 7) shows a

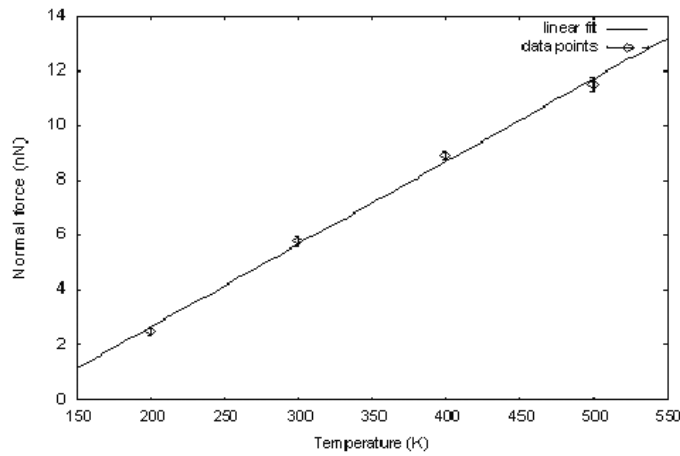


Figure 7. Normal force on the films as a function of temperature.

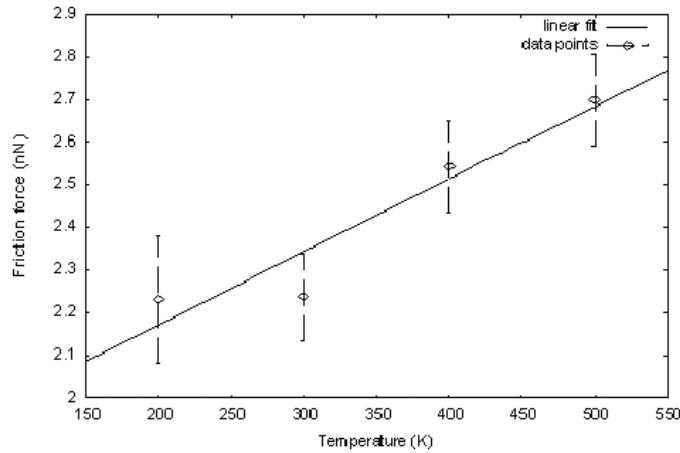


Figure 8. Friction force as a function of temperature.

clear dependence of the normal force (or load) on temperature. A linear fit to the data gives the following relationship ($F_N(T) = -3.39874 + 0.0302047T$). Inserting this temperature dependent load term in equation (9) and fitting the friction force versus temperature data to a linear function, the following parametric values are obtained:

$$\begin{aligned} Q' &= 9.24 \times 10^7 \text{ J m}^{-3}, \\ \frac{k}{\phi} \ln \left(\frac{V}{V_0} \right) &= -9.38 \times 10^4 \text{ J m}^{-3} \text{ K}^{-1}. \end{aligned} \quad (13)$$

Incorporating the temperature dependence of pressure in equation (9), we get

$$\tau = \frac{1}{\phi} \{Q' + P(T)\omega\} - \beta T. \quad (14)$$

The relative insensitivity of the friction force on temperature in the current work is now evident from equation (14) which suggests that, in the present simulations, the effect of increase in the temperature is balanced by the increase in pressure. The simulations in the current work,

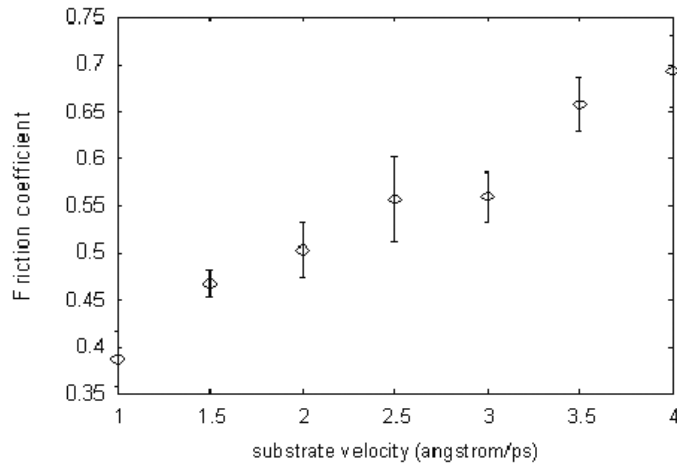


Figure 9. Friction coefficient as a function of substrate velocity.

therefore, appear to have brought out the proper physics of the system undergoing sliding friction.

Friction coefficient can now be re-expressed as

$$\mu = \frac{\tau}{P(T)} = \frac{1}{\phi} \left\{ \frac{Q'}{P(T)} + \omega \right\} - \beta T \frac{1}{P(T)}. \quad (15)$$

From figure 7, it can be said that because P and T have a linear relationship, the last term in equation (15) is independent of temperature. However, because the first term is inversely proportional to the temperature, the friction coefficient will decrease with increasing temperatures.

3.4. Friction as a function of substrate velocity

The frictional behaviour of the alkylsilane films is also investigated as a function of substrate velocity at 300 K for a separation of 24.47 Å between the films. The friction coefficient, normal force and friction force on the films are plotted as a function of substrate velocity in figures 9, 10 and 11, respectively.

It is seen from figure 9 that the friction coefficient increases with the increasing substrate velocity. This increase in the friction coefficient is a consequence of the increase in friction force with the increasing substrate velocity (figure 11). The frictional behaviour of the alkylsilane films as a function of substrate velocity is compared with equation (10) of the thermal activation model. In contrast to equation (10), which predicts a linear relation between τ and $\ln V$, data obtained from simulations in the current work shows a non-linear relation between friction force and $\ln V$ as seen in figure 11. Again, it is noted that in equation (10), the load P is assumed to be independent of the substrate velocity, whereas it is evident from figure 10 that the normal force (or load) is a function of substrate velocity. This modifies equation (10) as follows:

$$\tau = \left(\frac{Q'}{\phi} - \frac{kT}{\phi} \ln V_0 \right) + \frac{\omega}{\phi} P(V) + \frac{kT}{\phi} \ln V. \quad (16)$$

The simulation data is fit to a linear function that relates normal force and the substrate velocity as $F_N(V) = 6.3396 - 0.319081V$. Inserting the substrate velocity dependence of normal force

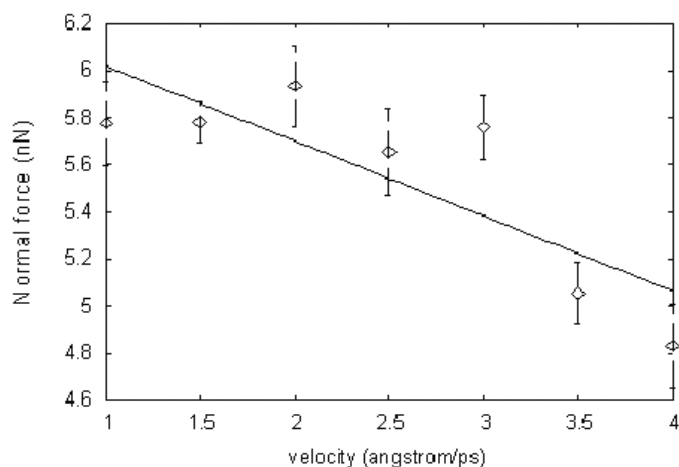


Figure 10. Normal force as a function of substrate velocity.

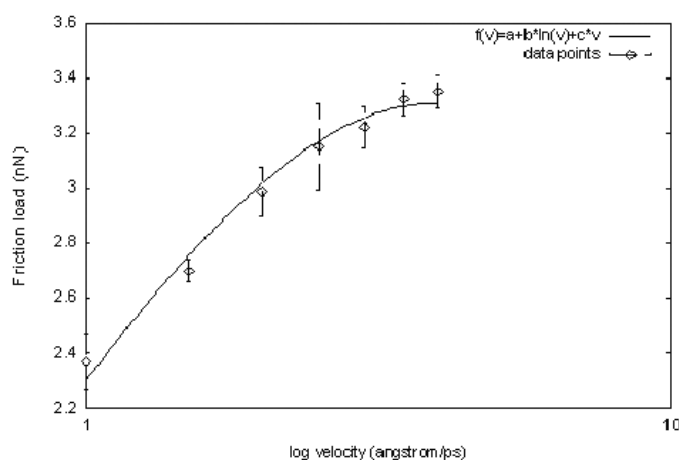


Figure 11. Friction force as a function of the log of substrate velocity ($\ln V$).

in equation (15) gives the following parameter values:

$$\begin{aligned} \frac{kT}{\phi} \ln V_0 &= 2.87 \times 10^7 \text{ Pa}, \\ \frac{kT}{\phi} &= 2.95 \times 10^7 \text{ Pa}. \end{aligned} \quad (17)$$

Solution of equations (12), (13) and (17) gives the following values of the various parameters: $\phi = 140.54 \text{ \AA}^3$, $\omega = 18.73 \text{ \AA}^3$, $V_0 = 3.37 \text{ m s}^{-1}$ and $Q' = 7.83 \text{ KJ mole}^{-1}$.

The value of stress activation volume (ϕ) is consistent with the periodicity of the lattice to which the alkylsilane head groups are attached, and the value of pressure activation volume (ω) is lower than the value of ϕ which is consistent with the results of Briscoe and Evans, as is the value of Q' . However, the value of V_0 is inconsistent with equation (13) that indicates a value of V_0 greater than the substrate velocity $V = 100 \text{ m s}^{-1}$. This discrepancy appears to be due to the simple linear relationship assumed between F_N and V .

4. Conclusions

The friction behaviour of model alkylsilane films is investigated as a function of separation between the films, temperature and the velocity of the substrate. The frictional behaviour of these model films is found to follow the thermal activation model of Briscoe and Evans [24]. While the frictional behaviour of the films in the experiments is examined as a function of load (normal force) on the film, the current work examines frictional behaviour of the film at fixed separations between the films. One of the justifications for such an approach is that in the actual MEMS devices, e.g. gears, it is the separation between the alkylsilane-coated surfaces that is fixed. As a consequence, the normal force on the films in these simulations becomes a function of separation between the films, temperature and the substrate velocity. Therefore, performing the simulations at a fixed distance between the films in this work allows the determination of the functional dependence of the normal force on temperature and velocity. Additionally, by taking into account this dependence of the normal force on these various parameters, the apparent discrepancy in the dependence of friction force on the temperature between this work and that of Glosli and McClelland [23] is successfully resolved. The friction simulations in this work are performed at extreme conditions of velocity. The minimum substrate velocity used in this work is 1 \AA ps^{-1} or 100 m s^{-1} . Although, this is an order of magnitude larger than the velocities used in friction experiments of alkylsilane films with AFM, the velocities used in this work are in the operating range of actual MEMS devices. The simulations of alkylsilane friction with the substrate velocity in the range of AFM probes would require much longer time and will be the focus of future work. However, it is notable that the results of the simulations are in agreement with the thermal activation model even at the extreme conditions of this work.

References

- [1] Lee A P, Pisano A P and Lim M G 1992 Impact, friction and wear testing of microsamples of polycrystalline silicon *Mater. Res. Soc. Symp. Proc.: Smart Mater. Fabrication Mater. Microelectromech. Syst.*
- [2] Tai Y C and Muller R S 1990 Frictional study of Ic-processed micromotors *Sensors Actuators A—Phys.* **21** 180
- [3] Gabriel K J, Behi F, Mahadevan R and Mehregany M 1990 *In situ* friction and wear measurements in integrated polysilicon mechanisms *Sensors Actuators A—Phys.* **21** 184
- [4] Gardos M N 1996 Tribological behavior of polycrystalline and single-crystal silicon *Tribol. Lett.* **2** 355
- [5] Mani S S, Fleming J G, Sniegowski J J, De Boer M P, Irwin L W, Walraven J A, Tanner D M and Dugger M T 2000 Chemical vapor deposition coating for micromachines *Mater. Res. Soc. Symp. Proc.: Methods, Mechanisms and Models of Vapor Deposition* **616** p 21
- [6] Mani S S, Fleming J G, Sniegowski J J, De Boer M P, Irwin L W, Walraven J A, Tanner D M and La Van D A 2000 Selective W for coating and releasing MEMS devices *Mater. Res. Soc. Symp. Proc.: Mater. Sci. Microelectromech. Syst. (MEMS) Devices II* **605** p 135
- [7] DePalama V and Tillman N 1989 Friction and wear of self-assembled trichlorosilane monolayer films on silicon *Langmuir* **5** 868
- [8] Ando Y and Ino J 1996 Friction and pull-off force on silicon surface modified by FIB *Sensors Actuators A—Physical* **A57** 83
- [9] Ruhe J, Novotny V J, Kanazawa K K, Clarke T and Grest G B 1993 Structure and tribological properties of ultrathin alkylsilane films chemisorbed to solid-surfaces *Langmuir* **9** 2383
- [10] Komvopoulos K 1996 Surface engineering and micro-tribology for microelectromechanical systems *Wear* **200** 305
- [11] Bhushan B, Kulkarni A V, Koinkar V N, Boehm M, Odoni L, Martelet C and Belin M 1995 Microtribological characterization of self-assembled and Langmuir–Blodgett monolayers by atomic and friction force microscopy *Langmuir* **11** 3189
- [12] Liu Y H, Wu T and Ewans D F 1994 Lateral force microscopy study on the shear properties of self-assembled monolayers of dialkylammonium surfactant on mica *Langmuir* **10** 2241

- [13] Liu H W, Bhushan B, Eck W and Stadler V 2001 Investigation of the adhesion, friction and wear properties of biphenyl thiol self-assembled monolayers by atomic force microscopy *J. Vac. Sci. Tech. A—Vac. Surf. Films* **19** 1234
- [14] Wenning L and Muser M H 2001 Friction laws for elastic nanoscale contacts *Europhys. Lett.* **54** 693
- [15] Shimizu J, Eda H, Yoritsune M and Ohmura E 1998 Molecular dynamics simulation of friction on the atomic scale *Nanotechnology* **9** 118
- [16] Koike A and Yoneya M 1998 Chain length effects on frictional behavior of confined ultrathin films of linear alkanes under shear *J. Phys. Chem. B* **102** 3669
- [17] Zhang L and Tanaka H 1997 Towards a better understanding of wear and friction on the atomic scale—a molecular dynamics analysis *Wear* **211** 44
- [18] Harrison J A and Brenner D W 1994 Simulated Tribochemistry: an atomic-scale view of the wear of diamond *J. Am. Chem. Soc.* **116** 10399
- [19] Perry M D and Harrison J A 1996 Molecular dynamics studies of the frictional properties of hydrocarbon materials *Langmuir* **12** 4552
- [20] Tutein A B, Stuart S J and Harrison J A 2000 Role of defects in compression and friction of anchored hydrocarbon chains on diamond *Langmuir* **16** 291
- [21] Mikulski P T and Harrison J A 2001 Packing density effects on the friction of n-alkane monolayers *J. Am. Chem. Soc.* **123** 6873
- [22] Zhang L, Wesley K and Jiang S 2003 Molecular simulation study of nanoscale friction for alkyl monolayers on Si(111) immersed in solvents *J. Chem. Phys.* **119** 765
- [23] Glosli J N and McClelland G M 1993 Molecular dynamics study of sliding friction of ordered organic monolayers *Phys. Rev. Lett.* **70** 1960
- [24] Briscoe B J and Evans D C B 1982 The shear properties of Langmuir–Blodgett layers *Proc. R. Soc. Lond. A* **380** 389
- [25] Zhang L, Wesley K and Jiang S 2001 Molecular simulation study of alkyl monolayers on Si(111) *Langmuir* **17** 6275
- [26] Nose S 1984 A molecular dynamics method for simulation in the canonical ensemble *Mol. Phys.* **52** 255
- [27] Zhang L and Jiang S 2002 Molecular simulation study of nanoscale friction for alkyl monolayers on Si(111) *J. Chem. Phys.* **117** 1804