Frictional Dynamics of Alkylsilane Monolayers on SiO₂: Effect of 1-n-Butyl-3-methylimidazolium Nitrate as a Lubricant

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The effect of 1-n-butyl-3-methylimidazolium nitrate ionic liquid (IL) on the shear dynamics and tribological properties of contacting ordered alkylsilane self-assembled monolayers (SAM) on SiO₂ surfaces was studied using molecular dynamics simulation. Use of the IL as a lubricant was found to reduce the friction between the contacting monolayers in the studied range of applied loads. At low applied loads, complex behavior in the dependency of the frictional force on the normal load in both lubricated and dry monolayers is observed and is shown to be due to the rearrangement of the SAM chains under shear. In contrast, this dependency was found to be linear at high normal loads. The simulations also indicate that the ordering of the SAM chains may be disrupted by penetrating lubricant molecules, suggesting that the IL could incorporate into a damaged area of the SAM coating and restore tribological properties. To our knowledge, this is the first simulation study of the effect of an IL lubricant on the frictional dynamics of SAMs.

I. Introduction

Nanoscale- (NEMS) and microelectromechanical (MEMS) devices that combine electrical and mechanical components at characteristic length scales of less than 100 nm (NEMS) and less than 1 mm but more than 100 nm (MEMS) have found use in a wide range of applications.1-4 Although MEMS technology has to date essentially focused on the fabrication (via photolithography) and laboratory demonstration of devices, with some commercial applications available (e.g., the acceleration sensor used in automobile air bags and the digital light processing (DLP) micromirror application technology, and cellular and molecular biology).1,2,6

As a result of the large surface-to-volume ratios in these devices, surface forces such as adhesion and friction can be detrimental to their reliability.1,2,6-10

Because MEMS are designed for small separations,3,17 as coatings to reduce the adhesion between the contacting surfaces.3,17 Therefore, understanding and controlling the forces acting in devices on the molecular level is of critical importance to the widespread commercial realization and successful operation of MEMS systems.5

To reduce the effects of adhesion and friction in MEMS, a number of engineering approaches have been suggested. For example, surface roughening at the contact interface was shown to reduce the adhesion pull-off force and friction coefficient significantly;18-23 however, this approach is not applicable on the nanometer scale. Attempts to employ solid diamondlike carbon films,11,22 silicon carbide films,22 and various oxides and nitriles11 as coatings to reduce the adhesion between the contacting surfaces have also been employed but suffer from problems with the deposition of uniform, conformal solid films on complex MEMS surfaces,1,2,11 as well as wear, and not being easily replenished without destroying the MEMS device. Studies of boundary liquid lubricants indicate that perfluoropolyether (PFPE) films,1,2,11,24-26 in particular, Z-dol1,2 and Z-tetraol25,26 with OH polar end groups, can also be used as lubricants in wear can also lead to device failure; for example, wear has an adverse effect on the performance of NEMS-based atomic force microscopy (AFM) data storage systems.15,16 As a result, commercially successful MEMS devices are primarily limited to those without interfaces in sliding contact and with large component separations.3,17

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MEMS devices; coating the Si(100) surface with partially and fully bonded Z-tetraol films reduced the adhesive forces and coefficient of friction measured by AFM and improved the durability of the coated surfaces, with the partially bonded lubricant showing the best tribological characteristics. However, the use of PFPE films also suffers from the difficulties associated with preparing a controllable uniform film and the aging of PFPE films on polysilicon and aluminum oxyfluoride surfaces.

An alternative strategy is the use of thin organic films prepared by self-assembly on the device surface. Several classes of organic films have been studied as boundary-layer lubricants, the most common being silane- and thiol-based self-assembled monolayers (SAMs), though these also suffer from the drawback of wear with operation and the inability to replenish the film without destroying the device. The use of binary lubricants composed of a SAM plus a mobile component (organic liquid) has been proposed in the literature as an effective method to reduce frictional coefficients and improve the longevity of performance in SAM systems. For example, Eapen et al. showed that the combination of a bound alcohol-based monolayer and a mobile (pentaerythritol tetraheptanoate) phase on Si(100) exhibited lifetimes that were at least an order of magnitude longer than the bound or mobile controls, and Satyanarayana and co-workers dip coated a perfluoropolyether (such as PFPE Z-dol 4000) top coat onto a SAM, which lowered the frictional coefficient and improved the wear life by over an order of magnitude compared to that of a bare substrate or a hydrophilic SAM; however, the performance was limited when the underlying SAM was hydrophobic, suggesting that the PFPE may be rubbed away because of poor adhesion with the SAM.

Low-viscosity room-temperature ionic liquids (ILs) have recently begun to attract attention as potential MEMS lubricants. Whereas their bulk-phase viscosity is comparable to that of traditional hydrocarbon lubricants, ILs have been shown to exhibit superior antiwear and friction-reducing properties in lubrication settings. ILs are synthetic salts with a bulky, asymmetric organic cation and a weakly coordinating anion, which frustrates packing and the formation of a stable crystalline structure. ILs are uniquely flexible compounds because their physical properties can be tuned by independently varying the cation or anion, yielding a wide variety of possible ILs (10^2–10^3 different liquids and binary and ternary mixtures have been predicted). Depending upon the ion combination, ILs can have negligibly low vapor pressure, be noncombustible, and have high thermal and electrochemical stability, a broad liquid range, and high thermal conductivity, which promotes heat dissipation during operation. Additionally, some ILs have been shown to be compatible with lubricant additives, and unlike conventional lubricants, ILs conduct electricity, which is important in some electrical applications.

Imidazolium-based ILs are the most commonly studied IL system to date because of their air and moisture stability, with BF_4 and PF_6 being common anions in early work. In particular, ILs based on the 1-alkyl-3-methylimidazolium cation with either the BF_4 or PF_6 anion are known to be effective lubricants, but the anions were later found to undergo complex tribochemical reactions and hydrolyze upon exposure to water, forming HF and other products. Several other imidazolium-based ILs have since been found to have good friction-reducing, antiwear, and load-carrying properties, as neat lubricants or lubricant additives, and outperformed conventional lubricants. Of particular relevance to the current work, Zhu et al. have shown that ultrathin films of 1-butyl-3-methylimidazolium triflate on surface-modified silicon wafers possess better tribological properties and antiwear properties than do the tetrafluoroborate and hexafluorophosphate films; however, better performance was achieved by increasing the alkyl chain length of the cation. Furthermore, tribological studies of ultrathin 1-butyl-3-methylimidazolium octylsulfate and hexafluorophosphate films on Si(100) surfaces indicated that longer alkyl chains on the anions also somewhat decrease the wear resistance of the IL films. In related studies, it was found that oxygen-rich anions provide better substrate wettability and lower wear compared to other imidazolium salts and that the wear life of ultrathin 1-alkyl-4-[5-(alkylsulfanyl)-1,3,4-oxadiazol-2-yl] pyridinium tetrafluoroborate-based IL films on silicon wafers increased when the alkyl chain length decreased. Therefore, ILs composed of 1-alkyl-3-methylimidazolium cations with moderate alkyl chain lengths and oxygen-rich anions are of interest as potential lubricants for MEMS devices.

In this work, we have performed molecular dynamics (MD) simulations of contacting alkylsilane SAMs on silica at full coverage, lubricated with a 1-butyl-3-methylimidazolium nitrate ([bmn][nitrate]) IL layer. This imidazolium-based IL

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contains cations with alkyl chains of moderate length and an oxygen-rich anion; therefore, ultrathin films are expected to show good friction-reducing and antiwear properties.25,36,46,49,53,54 The adhesion and frictional forces acting between the two lubricated SAM-coated SiO2 surfaces moving in opposite directions at constant velocities of 10 and 100 m/s have been determined from the simulations as a function of the separation between the surfaces. The remainder of the article is organized as follows: in section II, we provide details of the molecular models and simulation techniques used before discussing the results obtained in section III and conclusions and future work in section IV.

II. Model and Simulation Details

Snapshots of the simulations of contacting nonyl-silane SAMs on SiO2 with and without the [bmim][nitrate] IL lubricant are shown in Figure 1. The SiO2 surface is composed of 12 alternating Si and O atom layers and was obtained from the thermal equilibration of an ideal β-cristobalite crystal57,58 with a lattice constant of 7.116 Å at 300 K; the Si and O atoms are arranged in a layered hexagonal lattice composed of SiO4 tetrahedra alternatively pointing up and down that was cut above the outermost layer of O atoms at the top of the tetrahedra as in the work of Chandross and co-workers.55 The thickness of the SiO2 surface is 12.18 Å at 300 K. Each O atom was subsequently bonded to the Si atom in the Si(OH)2 terminal group of the alkylsilane chain to form a full-coverage SAM that satisfies both bonding and steric constraints.55,56 This bonding assumes that two of the chlorines in the nonyl-trichlorosilane molecules have reacted to become hydroxyl groups and the remaining Cl atom has reacted with the silicon oxide surface to form a chemical bond.55 Each surface contains 90 Si(OH)2(CH2)8CH3 chains. The thickness of each SAM is 11.61 Å at 300 K. The dimensions of the final surface were 43.88 Å × 45.60 Å, which has been shown to be sufficient to prevent the occurrence of system-size effects.55 with an area per chain of ∼22.2 Å2 that compares well with the experimental range of 22–25 Å2 for SAMs formed on amorphous silica at full coverage.23,59,60 For systems with an IL lubricating layer, 100 [bmim][nitrate] molecules were used.

In this study, the OPLS all-atom force field61 and its extension for the silicon oxide crystal62 are used to describe the interactions within the SAM-coated β-cristobalite surface. The transferable molecular force field of Maginn et al.63 is used to describe the [bmim] cations and [nitrate] anions. The interactions between and within the cations, anions, and the surface are represented according to the OPLS all-atom force field rules.61 Electrostatic interactions are computed using the damped shifted force method,64 which is based on the damped and cutoff-neutralized Coulombic sum originally proposed by Wolf et al.65 and has been shown to reproduce the energetic and dynamic characteristics of simulations employing lattice summation techniques, such as the Ewald method.64 For the electrostatic calculations, a damping parameter of 0.2 Å⁻¹ and a cutoff radius of 15 Å are used.64 A large cutoff distance of 13.5 Å is employed for accurate computation of the Lennard-Jones interactions.

MD simulations were performed using the multiple time step rRESPA66 algorithm with a 0.25 fs time step for bond, valence, dihedral, and improper angle forces and 1.0 fs for the intra- and intermolecular nonbonding forces. Two-dimensional periodic boundary conditions were employed during the simulations. Systems with various distances between the outermost layers of silicon atoms were prepared to model different normal loads applied to the SAM-coated surfaces and the fixed separations maintained by constraining the outermost silicon atoms in the SiO2 surface. All atoms (excluding the rigid Si atom layers of the surfaces) were coupled to a 300 K Berendsen thermal

Figure 1. Wireframe image of two opposing Si(OH)2(CH2)8CH3 SAMs on SiO2 surfaces: (a) without a lubricant and (b) with the [bmim][nitrate] IL lubricant. Oxygen is red, silicon is yellow, carbon is light blue, hydrogen is gray, and nitrogen is dark blue. Arrows indicate the direction in which the surfaces move during the simulations.
bath during an initial 200 ps equilibration period. Subsequently, the outermost silicon atoms were moved in opposite directions at a constant velocity, \( v \) yielding a relative shear velocity of 2\( v \) and were equilibrated for 300 ps to achieve a constant normal load for a given separation between the surfaces. In subsequent production runs of 0.4–1.2 ns, only the four atomic layers of each SiO\(_2\) surface adjacent to the rigid outer layer were connected to the 300 K thermostat. Values for the friction force, normal load, and thickness were determined as averages over blocks of 43.88 ps; the errors were then calculated as the standard deviation of these averages. For shear velocities of 10 m/s value, this block averaging time corresponds to the time it takes the surfaces to traverse 4.38 Å, which corresponds to one stick–slip cycle in the dry systems; for a shear velocity of 100 m/s, this corresponds to a distance of 43.88 Å. The statistical errors in the friction force were found to be smaller than 0.18 nN in the dry systems and smaller than 0.1 nN in the lubricated systems. For both systems, statistical errors for the normal load did not exceed 0.16 nN. The errors in the values of the thickness of the SAMs were found to be smaller than 0.1 Å.

### III. Results

1. Shear Dynamics of Ordered SAMs. After equilibration at 300 K, the alkylsilane chains of the SAM are found to be perpendicular to the silicon oxide surface. A similar perpendicular orientation for alkylsilane chains on SiO\(_2\) at 300 K was observed by Chandross et al.\(^{55}\) in their work on the friction between ordered alkylsilane monolayers with the MSI force field.\(^{68,69}\) In contrast, Irving et al.\(^{70}\) found an average tilt angle of 30° from the surface normal in simulations of octadecyltrichlorosilane SAMs at 300 K using the AMBER potential\(^{71}\) without electrostatic interactions; however, in this work, the silicon oxide substrate was not included in the model, and alkyltrichlorosilane molecules were instead arranged in a hexagonal lattice with an area per headgroup of 22 Å\(^2\). Although it still remains an open question as to whether the SiO\(_2\) substrate, the choice of the force field, or the presence of Cl atoms versus hydroxyl groups in the headgroups of the SAM chains has the most profound effect on the tilt angle of the chains, we note that the simulations with the OPLS force field\(^{61,62}\) used in this work and those of Chandross et al.\(^{55}\) with the MSI potential\(^{68,69}\) both predict a perpendicular orientation of the alkylsilane SAM chains on a SiO\(_2\) surface. Additionally, we note that hydrocarbon chains within alkylsilane monolayers on silicon are experimentally found to display a small (∼10 ± 2°) to zero tilt angle.\(^{72,73}\)

To understand the dynamics of alkylsilane chains under shear, the average thicknesses of the upper and lower monolayers was monitored as a function of distance between the outermost constrained Si atom layers of the two SiO\(_2\) surfaces. This distance was kept constant for a given MD trajectory and determines the actual separation distance between the SAMs and the normal load applied to the surfaces. At large separations between the surfaces, when their geometric structures are not compressed, the average length of the alkylsilane chains measured at 300 K (from the Si atom bonded to the oxygen in the β-cristobalite crystal to the C atom of the terminal methyl group) is \( l_0 = 11.61 \) Å. As the distance between the outermost Si atom layers of the upper and the lower SiO\(_2\) surfaces decreases, overall the chains in both SAMs tilt in the direction relative to the motion of the sliding surfaces (Figure 1); therefore, the thicknesses of the SAMs, \( l \), decreases. As can be seen in Figure 2a, the effect of shear on the SAM is complex; the chains of the lower SAM tilt as the distance between the outermost Si atoms decreases, resulting in a thinner, lower SAM layer, whereas the tilt angle (and therefore thickness) of the chains in the upper SAM remains essentially unchanged. The observed different response from the upper and lower SAMs to shear is associated with the positions of the hydroxyl groups at the base of the alkylsilane chains being oriented in the direction opposite to the direction of motion in the upper surface and in the direction of motion in the lower surface (Figure 1). As the distance between the outermost atomic layers is further decreased, a sudden drop in the thickness of the upper SAM associated with an increase in the chain tilt angle occurs and is accompanied by a restoration of the thickness of the lower layer. This behavior is observed at sliding velocities of both 100 and 10 m/s, although the tilt of the upper layer is observed at lower model thicknesses at 10 m/s. As shown in Figure 2a, at a shear velocity of 100 m/s, the thickness of the restored lower SAM almost reaches the original thickness.

With the further decrease of the distance between the outermost atomic layers, the thickness of both SAMs gradually decreases; however, the lower SAM remains thicker even at high applied loads. At the highest applied load studied, the tilt angle \( \theta \) (which can be evaluated as \( \theta = \arccos(l/l_0) \), where \( l \) is the steady-state thickness of the SAM at a given applied load and \( l_0 \), as defined above, is the thickness of the SAM at a given applied load and with the chains normal to the SiO\(_2\) substrate) of the chains in the upper SAM is 35.8° at both 100 and 10 m/s, and the tilt angle of the chains in the lower SAM is 34.1° at 100 and 32.7° at 10 m/s. The greater thickness of the SAM at the lower sliding velocity of 10 m/s can be explained by the fact that the slower-moving SAM chains have more time to relax and conform to the subnanometer-scale asperities of the opposite surface.

As can be seen in Figure 2b for the system with the [bmim] [nitrate] lubricant layer, a sudden decrease in the thickness of the upper SAM is also observed as the total thickness of the system decreases; however, it is not accompanied by a rapid increase in the thickness of the lower monolayer due to the buffering effect of the lubricant layer. As in the case of the system without a lubricant, the thickness of the lower monolayer remains higher than the thickness of the upper SAM at high normal loads.

2. Adhesion. Because adhesive forces between the two opposing SAM-coated silica surfaces depends on the relative positions of the alkylsilane chains in the upper and the lower monolayers, the average adhesive forces were determined as the surfaces were moved in opposite directions as a function of the distance between the outermost constrained Si atoms. The simulations are performed in a constraint ensemble in which at each time step normal constraint forces are applied to the outermost atomic layers of both surfaces in order to keep the distance between the surfaces fixed. Note that the instantaneous values of the constraint forces applied to the outermost atomic layers of the upper and lower surfaces may be different. This difference results in the instantaneous acceleration of the center of mass of the system in the direction normal to the surfaces. However, the average values of both constraint forces are equal. This constraint force is essentially the normal load on...
the system, so the averaged constraint force is equal to the average adhesive force acting between the contacting surfaces;\(^{74}\) negative adhesive forces correspond to forces of attraction acting between the surfaces, and positive adhesive forces correspond to repulsive forces. From the simulations, we observe complex behavior in the adhesion as a function of the thickness of the model, shown in Figure 3a, as a result of changes in the tilt angle of the SAM chains under shear. As can be seen from the figure, as the distance between the outermost atomic layers of the upper and lower surfaces decreases, the overall adhesion force increases; however, two drops or steps in the adhesion force profile are observed because of the rearrangement and tilting of the SAM chains in both the upper and lower surfaces in the direction relative to the motion. For a sliding velocity of 100 m/s, these steps are from 50.3 to 49.9 Å and from 49.5 to 49.1 Å; for a sliding velocity of 10 m/s, the steps are from 50.3 to 49.9 Å and from 48.7 to 48.3 Å. Note that the location of one step is common to both sliding velocities.

In Figure 3b, the actual separation distance between the SAMs, defined as the average distance between the plane of the methyl C atoms in the upper and lower surfaces, is shown as a function of the thickness of the model (i.e., the distance between the outermost atomic layers of the upper and lower surfaces). Beginning at the largest thickness (~51.3 Å), the actual separation distance decreases monotonically with decreasing model thickness, as would be expected intuitively. However, from 50.3 to 49.9 Å, corresponding to the common step in the adhesion, the actual separation distance increases (for 10 m/s) or remains constant (for 100 m/s) as the total thickness of the system decreases. This change from a monotonic decrease in the separation distance between SAMs is associated with the tilting of the chains in the lower surface and therefore with the decrease in its thickness exceeding 0.4 Å (Figure 2a). For both sliding velocities, there is a second sliding-velocity-dependent region of nonmonotonicity in Figure 3b that occurs at the same model thickness as for the steps in adhesion seen in Figure 3a (i.e., occurring as the thickness of the system decreases from 48.7 to 48.3 Å at a sliding velocity of 10 m/s and from 49.5 to 49.1 Å at 100 m/s). As the thickness of the system decreases by 0.4 Å, changes in the tilt of the chains in the upper and lower SAMs (Figure 2a) leads to a decrease in the combined thickness of both SAMs exceeding 0.4 Å and thus to an increase in the separation distance between the SAMs. Thus, nonmonotonicity in the separation distance between the SAMs as the total thickness of the model decreases yields the observed steps in the adhesion profile.

In the lubricated system, adhesive forces involve only interactions between the surfaces and the lubricant. Interactions between the monolayers are excluded because the smallest separation distance of 16 Å observed at the highest load studied exceeds both the cutoff in the van der Waals interactions of 13.5 Å and the cutoff in the electrostatic interactions of 15 Å. As can be seen in Figure 4, the adhesive force again increases as the thickness of the system decreases (Figure 2b). At a sliding velocity of 100 m/s, a drop in the adhesion profile was found as the distance between the outermost Si atoms in the upper and lower surfaces decreased.

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from 63.6 to 63.1 Å. This step in the adhesion profile is associated with the sudden decrease in the thickness of the upper monolayer due to tilting of the SAM chains. We note that this drop is less significant than the steps in the adhesion profile for the nonlubricated system (Figure 3a), since when sudden tilting of the SAM chains occurs in the lubricated system and the separation distance between the SAMs increases, the mobile IL layer expands to fill the gap between the monolayers and thus minimizes the changes in the adhesive forces acting between the SAMs and the IL.

3. Friction. The friction force was determined as a projection of the sum of all forces acting on all atoms of one particular surface due to all atoms of the other surface onto the direction of motion. The dependence of the frictional force on the normal load was determined for both models with and without the IL lubricant at sliding velocities of 10 and 100 m/s and is presented in Figure 5. Generally, the frictional force is seen to increase with increases in the normal load; however, at normal loads of less than 3 nN, several values of the frictional force were found to correspond to a single value of the normal load as a result of the complex rearrangement of the SAMs as discussed above.

At normal loads exceeding ~3 nN, the frictional force versus the normal load dependency can be approximated by

$$F = \alpha A + \mu L$$  

(1)

where $F$ is the frictional force, $\alpha$ is a constant, $A$ is the contact area, $L$ is the normal load, and $\mu$ is the microscopic friction coefficient. The parameters used to fit eq 1 to the data presented in Figure 5 are given in Table 1. For nonlubricated systems, the friction coefficient decreases by 55% as the sliding velocity decreases from 100 to 10 m/s. Chandross et al. found similar behavior for the friction coefficient when the sliding velocity was reduced from 10 to 1 m/s for contacting alkylsilane SAMs on SiO$_2$ with 6, 8, and 12 carbon atoms in the SAM chains at a pressure of 0.2 GPa; however, at a high pressure of 2 GPa, the coefficient of friction remained unchanged as the sliding velocity decreased from 10 to 1 m/s. Since we use the tribological characteristics of the nonlubricated system as a benchmark for the evaluation of lubricant performance, it is of interest to compare the microscopic friction coefficients computed in this work with the results of Chandross et al. obtained using the MSI force field. Taking into account that Chandross et al. defined the microscopic friction coefficient simply as the ratio of shear stress to applied pressure and noting that a normal load of 1 nN corresponds to 50 MPa in our simulations, simple computations using the fitting parameters from Table 1 for the nonlubricated SAM/SAM system at a sliding velocity of 10 m/s and a normal load of 4 nN yield a friction coefficient of 0.33. This value is in excellent agreement with the friction coefficients of 0.2–0.4 computed by Chandross et al. for SAMs with 6, 8, and 12 carbon atoms in chains.

The application of [bmim][nitrate] as a lubricating layer was found to reduce the friction coefficient by 50% at a sliding velocity of 100 m/s compared to that for the dry SAM system at the same sliding velocity. The friction coefficient, however, was found to be the same at 10 m/s in the lubricated and dry SAM systems. This is presumably due to the reduction in viscosity of the IL layer at higher sliding velocities (i.e., shear thinning behavior of the IL). Because the friction coefficient is the same in the dry and lubricated systems at 10 m/s, the observed lower frictional force for the lubricated system at a given load is due to the decrease in the $\alpha A$ intercept. We also note that friction between the SAM-coated surfaces exists even when forces of attraction act between the surfaces as shown in Figure 5.

During the sliding of the contacting ordered alkylsilane SAMs shown in Figure 1a, subnanometer-scale stick–slip behavior in the frictional force was observed. As an example, Figure 6a shows the frictional force as a function of sliding distance for the shear velocity of 10 m/s for which the stick–slip dynamics are clearly visible. The distance between the maxima in the frictional force is ~4.4 Å and corresponds to the distance between the rows of SAM chains in Figure 1. As shown in Figure 6b, the slow rise in the frictional force (sticking) is associated with periodic contractions in the thickness of the two SAMs. Note that these contractions occur every 8.8 Å in each SAM, with a frequency that is half of that of the peaks in the frictional force. Therefore, two adjacent peaks in the frictional force correspond to the contraction of one monolayer first and then the second monolayer. Thus, when the chains of two SAMs eclipse during sliding, one monolayer tilts, allowing the opposite SAM to pass, and

Table 1. Fitted Parameters Shown in Figure 5 for the Dependency of Frictional Force on Normal Load as Given by $F = \alpha A + \mu L$

<table>
<thead>
<tr>
<th>Simulation</th>
<th>$\alpha A$, nN</th>
<th>$\mu$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAM/SAM, 100 m/s</td>
<td>2.09</td>
<td>0.22</td>
</tr>
<tr>
<td>SAM/SAM, 10 m/s</td>
<td>0.93</td>
<td>0.10</td>
</tr>
<tr>
<td>SAM/IL/SAM, 100 m/s</td>
<td>0.77</td>
<td>0.11</td>
</tr>
<tr>
<td>SAM/IL/SAM, 10 m/s</td>
<td>0.34</td>
<td>0.09</td>
</tr>
</tbody>
</table>
during the next eclipse, the opposite monolayer tilts. We note that the stick–slip behavior of alkylsilane SAMs was observed previously in the MD simulations of Chandross et al. and in the AFM measurements of Kojio et al. Stick–slip dynamics require periodicity and commensurability of the structures of two sliding surfaces; therefore, this behavior is not observed in the lubricated systems because such commensurability is not characteristic of disordered systems.

In the case of the lubricated SAM-coated surfaces, the tilt angle of the SAM chains determines whether the lubricant molecules can incorporate between the chains and in turn can change the stiffness and tribological properties of the monolayer. A perpendicular orientation of the SAM chains with respect to the SiO₂ surface allows for a larger available volume between the chains and thus increases the probability of a lubricant molecule penetrating into the SAM. Because SAM chains are found to be perpendicular only at low normal loads, it is likely that the ions can penetrate between the SAM chains at low normal loads and during the transient period of establishing a shear motion when the chains are adjusting their tilt angle. Once the lubricant molecules are incorporated between the chains, the chains cannot change their tilt angle uniformly and orderly under shear until the lubricant molecules diffuse or are forced out of the SAM. Clearly, the tribological properties of lubricated contacts involving ordered monolayers and monolayers disrupted by penetrating lubricant molecules could be different. At a sliding velocity of 10 m/s, we noted several structures in which the ions of the [bmim][nitrate] lubricant were incorporated between the chains of the alkylsilane SAMs, causing disorder in the SAM chains, as shown in

![Figure 6](image1.png)  
Figure 6. (a) Evidence of the stick–slip dynamics in the friction force versus sliding distance dependency for the system shown in Figure 1. (b) Thickness of SAMs as a function of sliding distance for the upper (dashed) and lower (solid) surfaces.

![Figure 7](image2.png)  
Figure 7. Snapshot from the simulations of two opposing CH₃-terminated SAMs on SiO₂ surfaces lubricated with the [bmim][nitrate] IL. The image depicts the case when the IL ions penetrate within the upper SAM, causing its disorder. Colors have the same meaning as those in Figure 1, except the carbon atoms of the IL are shown in yellow for clarity.

![Figure 8](image3.png)  
Figure 8. Frictional force versus normal load dependencies for lubricated ordered (solid line) and disordered (dashed line) SAM contacts at a shear velocity of 10 m/s.

**IV. Concluding Remarks**

Molecular dynamics simulations have been performed to study how the use of 1-n-butyl-3-methylimidazolium nitrate ionic liquid as a lubricant affects the shear dynamics and tribological properties of ordered alkylsilane monolayers on silica...
surfaces. At low normal loads, in the regime of NEMS and MEMS operation, rearrangements of the chains in the monolayers under shear were found to cause steps in the adhesion force between the two monolayers as a function of separation distance. Rearrangement of the chains results in a complex dependency of the frictional force on the normal load for monolayers at low normal loads. At high normal loads, the frictional force versus normal load dependency can be approximated by a linear function of the contact area, normal load, and microscopic friction coefficient. Application of the ionic liquid lubricant decreases the frictional force between the contacting monolayers at a given normal load. This decrease is due to the reduction of both the microscopic friction coefficient and the intercept at a high sliding velocity of 100 m/s and a decrease in the intercept only at the lower sliding velocity of 10 m/s. The simulation studies also indicate that the ionic liquid may incorporate into the SAM chains at low normal loads and potentially “repair” a damaged area of the coating, thus restoring the tribological properties.

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