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# Frictional Dynamics of Fluorine-Terminated Alkanethiol Self-Assembled Monolayers

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Received April 7, 2004. In Final Form: August 25, 2004

The frictional dynamics of fluorine-terminated alkanethiol ( $\text{S}(\text{CH}_2)_8\text{CF}_3$ ) self-assembled monolayers (SAMs) on gold are studied using molecular dynamics simulations. The simulations treat the interactions between two SAMs on flat surfaces. The structure and frictional behavior are investigated as a function of applied pressure (200 MPa to 1 GPa) for a shear velocity of 2 m/s and compared to methyl-terminated alkanethiol SAMs. The maximum adhesive pressure between the SAMs is 220 MPa for both end groups. In agreement with experiments on the molecular scale, the shear stress and the coefficient of friction for  $\text{CF}_3$ -terminated alkanethiols are larger than for  $\text{CH}_3$ -terminated alkanethiols. The main source for the difference is primarily the tighter packing of the fluorinated terminal group resulting in a higher degree of order. The molecular scale coefficient of friction is correlated with the degree of order among all the systems.

## I. Introduction

Organic self-assembled thin films have been widely investigated during the past decade for a number of applications including chemical/biosensors, low friction and protective coatings for MEMS/NEMS, molecular overlays, and nanodots.<sup>1–3</sup> The majority of the research on self-assembled monolayers (SAMs) has focused on alkanethiols on gold, with additional work on alkylsilanes on silicon oxide.<sup>1,4</sup> For the alkanethiol SAMs, gold substrates are synthesized with large atomically flat regions, removing most issues and difficulties associated with rough surfaces. In addition, the strong headgroup–substrate interaction leads to densely packed chains in well-ordered domains.

Much research on SAMs has focused on the modification of surface properties and functionality through changes in the terminal group.<sup>5,6</sup> The interaction between two surfaces with various combinations of terminal groups has been studied, with particular attention on the influence of the terminal groups on the structure and dynamical properties of the SAMs. Different fundamental interactions, including van der Waals (vdW) and hydrogen bonding, have also been investigated with interfacial force microscopes using SAM-coated tips.<sup>5–7</sup> The properties of

SAMs that are related to the terminal groups, such as chemical composition, structure and reactivity (e.g., with water), are important parameters for controlling performance. In general, terminal groups can be categorized by their surface energy. Polar terminal groups, such as OH and COOH, have high surface energy and are hydrophilic, providing anchoring sites through hydrogen bonding. In contrast, nonpolar groups, such as  $\text{CH}_3$ , produce low-energy, hydrophobic surfaces. Recently, we have reported a simulation study of the terminal group and chain-length dependence of the adhesion and friction in alkanethiol SAMs on gold comparing  $-\text{CH}_3$ ,  $-\text{OH}$ , and  $-\text{COOH}$  terminations (denoted Paper 1 hereafter).<sup>8</sup> We found that both adhesion and friction depend strongly on the hydrogen bond capability of the terminal group.

In the current study, we extend our investigation to fluorine-terminated alkanethiol SAMs on gold. Fluorine-terminated alkanethiols have attracted much attention recently because of their chemical inertness, hydrophobicity, and low surface energy (15  $\text{mJ m}^{-2}$  for  $\text{CF}_3$ -terminated compared to 19  $\text{mJ m}^{-2}$  for  $\text{CH}_3$ -terminated SAMs<sup>9</sup>). These properties can be exploited, for example, to create lubricating layers for microelectromechanical systems (MEMS). In contrast to typical fluorinated films which have low friction, these  $\text{CF}_3$  SAMs have larger friction forces and coefficients than hydrocarbon SAMs at the nanoscale, as measured with AFM.<sup>9,10</sup> This intriguing difference in friction behavior is due to changing just the atoms in the endgroup. The  $\text{CF}_3$  group contains significant charges on the atoms, resulting in a polar group. This contrasts with  $\text{CH}_3$ , which is nonpolar and, at best,

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weakly charged. In addition, the  $\text{CF}_3$  group is larger, affecting the steric behavior of the system. These two fundamental aspects result, in some unknown manner, in the difference in friction behavior.

Here, we present the results of molecular dynamics (MD) simulations which investigated the chemical effects on the adhesion between methyl- and trifluoromethyl-terminated alkanethiol SAMs. We also considered the sliding friction between two SAMs. Using MD, we can simultaneously examine the interactions between the two surfaces as a function of separation and the structure of the SAM. In this sense, the current study is complimentary to previous experimental investigations by Kim et al.,<sup>11</sup> who studied the frictional properties of tridecanethiol ( $\text{CH}_3(\text{CH}_2)_{12}\text{SH}$ ) and 13,13,13-trifluorotridecanethiol ( $\text{CF}_3(\text{CH}_2)_{12}\text{SH}$ ) using atomic force microscopy (AFM) and found that wettability and friction are strongly influenced by the interfacial interaction.

To perform simulations on SAMs with  $\text{CF}_3$  end groups, we had to develop additional terms for the force field. In particular, the torsion potentials containing a single C atom bonded to F has not been determined. We performed the necessary quantum calculations to determine the intramolecular terms and the partial charges for the atoms. This force field is based on the alkane force field of Smith et al.<sup>12</sup>

The paper is organized as follows. In Section II, the details of the computational procedures are discussed briefly, including details of the new interaction potentials to treat the  $\text{CF}_3$  end group. More details are given in Paper 1 and ref 4. The adhesion and friction simulations are presented in Section III. In Section IV, we discuss the results. We present our conclusions in the final section.

## II. Computational Procedure

**A. Model Systems.** Our initial monolayer configuration was based on an equilibrated structure of alkanethiolate molecules on a gold (111) surface. Here, we study molecules  $\text{S}(\text{CH}_2)_n\text{X}$ , with  $\text{X} = \text{CH}_3$  or  $\text{CF}_3$ . In the following,  $\text{CH}_3(\text{CF}_3)$ -terminated alkanethiol SAMs will be referred to as CH-SAM (CF-SAM). Houssiau et al.<sup>13</sup> applied time-of-flight scattering and recoil spectroscopy to investigate the azimuthal orientation of SAMs. They found that alkyl chains are chemisorbed on the hollow sites of the gold (111) surface with the  $\sqrt{3} \times \sqrt{3} R30^\circ$  structure, tilted toward next-nearest neighbors with an angle of  $35^\circ$  from the surface normal. The ellipsometric data by Graupe et al.<sup>14</sup> reported that CH-SAM and CF-SAM both form densely packed and highly ordered monolayers. The packing densities of the two SAMs, as measured by AFM, have been found to be indistinguishable.<sup>10,9</sup> Pflaum et al.<sup>15</sup> reported that CH-SAM can have a domain size of 500 Å with a mixed phase of  $\sqrt{3} \times \sqrt{3} R30^\circ$  and  $(2\sqrt{3} \times 3)R30^\circ$  with a tilt angle of  $32.0 \pm 0.5^\circ$ . In contrast, in the CF-SAMs, the structural order is weaker with a maximum domain size of about 50 Å.<sup>15</sup> The molecules in CF-SAMs are more perturbed due to steric issues from the relatively large size of  $\text{CF}_3$ . The tilt angle for  $\text{S}(\text{CH}_2)_{10}\text{CF}_3$  is  $37 \pm 7.0^\circ$ .

In the simulations, all SAMs on both surfaces begin with the  $\sqrt{3} \times \sqrt{3} R30^\circ$  conformation, as in experiments.<sup>11,13</sup> Chains were constructed in the all-trans configuration, initially tilted by  $30^\circ$  from the normal ( $z$  axis) toward next-nearest neighbors. The lattice spacing for both SAMs is set to 4.9 Å, matching the

experimental values of 4.9 Å for  $\text{SH}(\text{CH}_2)_{12}\text{CH}_3$  and 4.8 Å for  $\text{SH}(\text{CH}_2)_{12}\text{CF}_3$ .<sup>11</sup>

For adhesion and friction studies, a second layer mirroring the first was added with a 10-Å initial vacuum gap. Each SAM contained 100 molecules on a  $(\sqrt{3} \times \sqrt{3})$  rectangular mesh (43 Å  $\times$  50 Å). These simulations are large enough to contain at least one domain. Recently, we reported that the effects of system size on adhesion and friction are small beyond a reduction in noise,<sup>4</sup> indicating that these systems are adequate for quantitative comparisons.

The sulfur atoms of the alkanethiol chains were assumed to be chemically bonded to the gold substrate at the hollow site and were kept frozen during the simulation. The bonding of thiolate groups to gold is strong, with a bond strength of 40 kcal mol<sup>-1</sup>.<sup>16</sup> Gold is a metal that is better modeled using the embedded-atom method, for example, than using organic force fields. Instead of attempting to mix force fields, we include the essential aspects of the gold surface. Particularly, for adhesion and friction between two SAMs, we expect the interaction to be dominated by the atoms in the SAMs. In this case, the gold surface mainly acts by determining aspects of the SAM structure, e.g., area per molecule and tilt angle.

Experimentally, alkanethiol chains tilt about  $30^\circ$  with respect to normal to maximize the vdW interaction between chains.<sup>2</sup> This was accounted for in the current simulations by the introduction of a ghost (i.e., noninteracting) atom at the hollow sites of the gold surface, with a harmonic ghost-sulfur-carbon angle. The equilibrium angle for this interaction was chosen to be  $119.65^\circ$  with a force constant of 146.06 kcal mol<sup>-1</sup>. Without this interaction, the calculated tilt angle was  $15^\circ$ . Other works have used effective surface-atom interactions by including a potential term that is the surface-integrated Lennard-Jones potential.<sup>17,18</sup> Our added angle potential effectively does the same thing and is designed to achieve the key physical effect, namely the correct tilt angle.

**B. Force Field.** The total potential energy of the system,  $U^{\text{tot}}(r)$  is represented as a sum of nonbonded interactions  $U^{\text{NB}}(r_{ij})$  as well as energy contributions due to the distortion of bonds  $U^{\text{BOND}}(r_{ij})$ , bends  $U^{\text{BEND}}(\theta_{ijk})$ , and torsions  $U^{\text{TORS}}(\phi_{ijkl})$  and is given by

$$U^{\text{tot}}(r) = U^{\text{NB}}(r_{ij}) + U^{\text{BOND}}(r_{ij}) + U^{\text{BEND}}(\theta_{ijk}) + U^{\text{TORS}}(\phi_{ijkl}) \quad (1)$$

where

$$U^{\text{NB}}(r_{ij}) = U^{\text{vdW}}(r_{ij}) + U^{\text{qq}}(r_{ij}) \quad (2)$$

$$U^{\text{BOND}}(r_{ij}) = \frac{1}{2}k^{\text{BOND}}(r_{ij} - r_0)^2 \quad (3)$$

$$U^{\text{BEND}}(\theta_{ijk}) = \frac{1}{2}k^{\text{BEND}}(\theta_{ijk} - \theta_0)^2 \quad (4)$$

$$U^{\text{TORS}}(\phi_{ijkl}) = \frac{1}{2}\sum k_t[1 + \cos(n\phi_{ijkl})] \quad (5)$$

The nonbonded energy  $U^{\text{NB}}(r_{ij})$  is a sum of two-body repulsion and dispersion energy terms,  $U^{\text{vdW}}(r_{ij})$ , plus electrostatic interactions,  $U^{\text{qq}}(r_{ij})$ . Here, a Buckingham potential is adopted for the former as

$$U^{\text{vdW}}(r_{ij}) = A \exp(-br_{ij}) - \frac{C}{r_{ij}^6} \quad (6)$$

and standard Coulomb interactions for the latter,

$$U^{\text{qq}}(r_{ij}) = \frac{q_i q_j}{r_{ij}} \quad (7)$$

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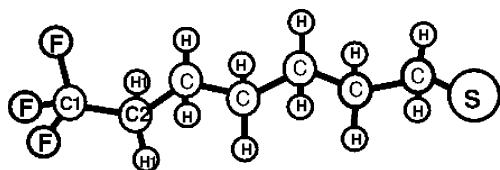
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**Figure 1.** One molecular chain of  $S(CH_2)_nCF_3$ . Note the atom types in Table 1.

**Table 1. Force Field Atom Types**

| atom type      | charge (e) |
|----------------|------------|
| F              | -0.216     |
| C <sub>1</sub> | 0.515      |
| C <sub>2</sub> | 0.153      |
| C              | 0.0        |
| H <sub>1</sub> | -0.01      |
| H              | 0.0        |

The force field for the CH-SAM is adopted from the Smith et al.<sup>12</sup> *n*-alkane force field and has no Coulombic interactions between atoms. Nonbonded interactions were included in all intermolecular interactions, as well as intramolecular interaction between atoms separated by three or more bonds, i.e., starting with 1-4 interactions.

When this work was started, no potential was available to treat alkanes with a  $CF_3$  terminal group. We have developed the necessary force field terms. The quantum-chemistry-based force field for the  $-CH_2-CH_2-CH_2-CF_3$  termination of the CF-SAM is developed in this work using 1,1,1-trifluorobutane (TFB) as a model compound. The methodology previously applied to force field development for ethers<sup>19</sup> is utilized. The quantum chemistry calculations were conducted using Gaussian98.<sup>20</sup> The force field development for the TFB is begun by the quantum chemistry calculation of the electrostatic potential on a grid of points around the trans and gauche conformers of TFB at the B3LYP/aug-cc-pvDz level. Partial charges for the force field are obtained by a fit that minimizes the mean-square deviation of the force field electrostatic potential from that obtained in the quantum calculation. Following Breneman et al.,<sup>21</sup> we excluded electrostatic potential grid points inside molecular vdW radii from the fit because the approach of any atom inside vdW radii is highly unlikely in MD simulations. The following vdW radii were used for carbon ( $r_{vdW}(C) = 2.5$  Å), fluorine ( $r_{vdW}(F) = 2.0$  Å), and hydrogen ( $r_{vdW}(H) = 1.8$  Å). The electrostatic grid points that were farther than 3.5 Å from any atom were also excluded from the fit, which allowed us to obtain a relatively homogeneous layer of electrostatic grid points around a molecule. The  $-CH_2-CH_3$  part of the TFB molecule was constrained to have zero partial charges in order to use the potential energy function for alkanes without partial charges. The resulting partial charges on the terminal  $-CH_2CF_3$  (see labeling in Figure 1), which are given in Table 1, described the electrostatic potential around the molecule with the mean-square error of 0.75–0.85 kcal mol<sup>-1</sup>.

Tables 2–4 show the nonbonded vdW parameters, bonding and bending force constants, and the torsional parameters that have been determined for the various interactions in these molecules. The equilibrium bond distance for the C–C and C–H bonds and the C–C–C, H–C–C, and H–C–H bending angles were also taken from the poly(vinylidene fluoride) force field.<sup>22</sup>

**Table 2. Nonbonded Force Field Parameters**

| nonbonded pair | A (kcal/mol) | b (Å <sup>-1</sup> ) | C (kcal mol <sup>-1</sup> Å <sup>-6</sup> ) |
|----------------|--------------|----------------------|---------------------------------------------|
| F–F            | 135782.0     | 4.5461               | 106.12                                      |
| F–C            | 45094.0      | 3.8181               | 260.77                                      |
| F–H            | 12300.0      | 4.1431               | 53.88                                       |
| C–C            | 14976.0      | 3.0900               | 640.80                                      |
| C–H            | 4320.0       | 3.4151               | 138.24                                      |
| H–H            | 2649.6       | 3.7400               | 27.36                                       |

**Table 3. Bond Force Field Parameters**

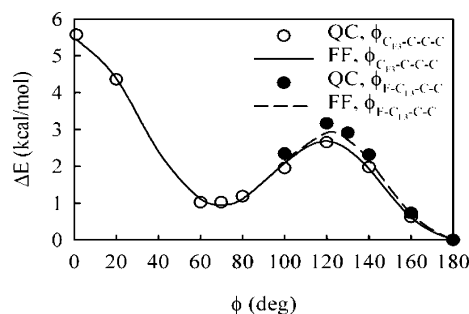
| bond type | $k^{\text{BOND}}$<br>(kcal mol <sup>-1</sup> Å <sup>-2</sup> ) | $r_0$<br>(Å) |
|-----------|----------------------------------------------------------------|--------------|
| F–C       | 722.0                                                          | 1.3600       |
| C–C       | 617.8                                                          | 1.5382       |
| C–H       | 655.2                                                          | 1.0850       |

| bend type | $k^{\text{BEND}}$<br>(kcal/(mol rad <sup>2</sup> )) | $\theta_0$<br>(deg) |
|-----------|-----------------------------------------------------|---------------------|
| F–C–F     | 240.0                                               | 104.84              |
| F–C–C     | 180.0                                               | 109.41              |
| C–C–C     | 160.0                                               | 118.24              |
| H–C–C     | 85.8                                                | 108.45              |
| H–C–H     | 77.0                                                | 109.27              |

**Table 4. Torsion Force Field Parameters**

| torsional type                      | $k_1$ (kcal mol <sup>-1</sup> ) | $k_2$ (kcal mol <sup>-1</sup> ) | $k_3$ (kcal mol <sup>-1</sup> ) |
|-------------------------------------|---------------------------------|---------------------------------|---------------------------------|
| C–C–C–C                             | -0.34                           | 0.0000                          | 0.630                           |
| F–C–C–C                             | 0.0000                          | 0.0000                          | 0.7300                          |
| C <sub>1</sub> –C <sub>2</sub> –C–C | 1.791                           | 0.676                           | 0.521                           |
| F–C–C–H                             | 0.0000                          | 0.0000                          | 0.000                           |
| C–C–C–H                             | 0.0000                          | 0.0000                          | 0.2340                          |
| H–C–C–H                             | 0.0000                          | 0.0000                          | 0.2340                          |

The equilibrium C–F bond distance and equilibrium F–C–F and F–C–C bending angles were fit to the quantum chemistry geometries of the trans and gauche conformers calculated at the B3LYP/aug-cc-pvDz level. The F–CF<sub>2</sub>–C–C torsional parameters were fit to obtain the best description of the CF<sub>3</sub>-group rotation in TFB, whereas the CF<sub>3</sub>–C–C–C torsional parameters were fit to obtain the best description of the conformational energies of the CF<sub>3</sub>–CH<sub>2</sub>–CH<sub>2</sub>–CH<sub>3</sub> torsion calculated using the MP2/aug-cc-pvDz energies at the B3LYP/aug-cc-pvDz geometries. The ability of the force field to capture the relative conformational energies of the CF<sub>3</sub>-group rotation and rotation around the CF<sub>3</sub>–CH<sub>2</sub>–CH<sub>2</sub>–CH<sub>3</sub> bond is shown in Figure 2.



**Figure 2.** The relative conformational energies for the  $CF_3-CH_2-CH_2-CH_3$  molecule from the developed force field (FF) and quantum chemistry calculations (MP2/aug-cc-pvDz/B3LYP/ aug-cc-pvDz level) (QC) for the  $CF_3$ -group rotation and rotation around the  $CF_3-CH_2-CH_2-CH_3$  torsion.

**C. Simulation Details.** Simulations were performed with the LAMMPS molecular dynamics code.<sup>23</sup> The temperature was set to 298 K with a Langevin thermostat. The damping was applied in the direction perpendicular to sliding and compression with a time constant of 0.01 fs<sup>-1</sup>. Integration was performed using rRESPA<sup>24</sup> with time steps of 0.3 fs for the bond forces, 0.6 fs for the other intramolecular forces and 1.2 fs for nonbonded

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interactions. The vdW interaction was cut off at 10 Å. The Coulombic interactions were cut off at 10 Å in all simulations, except the CF-SAM adhesion simulations in which a particle-mesh Ewald sum was used to calculate the Coulombic interactions. The majority of the simulations were run on 16 processors on Sandia's CPlant cluster.<sup>25</sup>

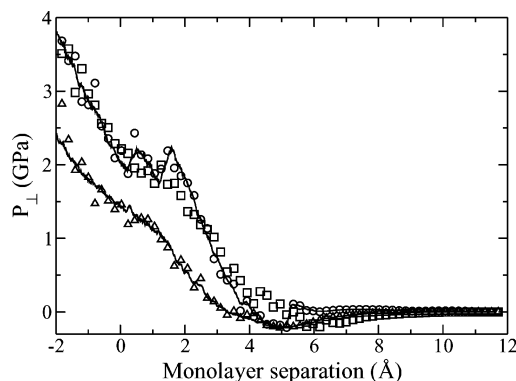
Adhesion simulations were carried out by compressing two SAMs at a constant velocity of 1.7 m s<sup>-1</sup> for all systems. We have monitored the change in structure and energetics during the simulations as a function of separation. For separations in which all the charged atoms in both monolayers are within the cutoff distance, we see nearly identical behavior between the particle-mesh Ewald sum and the cutoff method. However, at larger separations the cutoff introduces artifacts as charged atoms move beyond the cutoff distance. For this reason, we used the particle-mesh Ewald method.

The friction studies were conducted by applying a constant load to the system while two SAMs were sheared in opposite directions in the  $x$  direction ((210) and (210) directions) with a constant relative velocity of 2.0 m s<sup>-1</sup>. We note that is considerably larger than AFM measurement velocities which tend to be in the nm s<sup>-1</sup> to  $\mu$ m s<sup>-1</sup> range. This can be a source of differences between experiment and simulation. However, we expect that, for SAMs with the ideal or near ideal structures studied here, the results do not depend significantly on the shear velocity because the velocities of 2 m s<sup>-1</sup> and lower are sufficiently slow to allow the systems to relax for run times of about 10 ns. In earlier simulations of alkylsilanes, we found, at best, a logarithmic dependence of the friction coefficient on the shear velocity velocities in the range 0.01–10 m s<sup>-1</sup>.<sup>4</sup> However, for SAMs containing defects (most experiments), there are long time relaxations involving the domains. The dynamics of such domains is beyond present simulations. Any measurements that are significantly influenced by domain dynamics can produce results very different from the simulations results presented here. The best comparison between the present simulations and experiment is for SAMs that are as ideally ordered as possible.

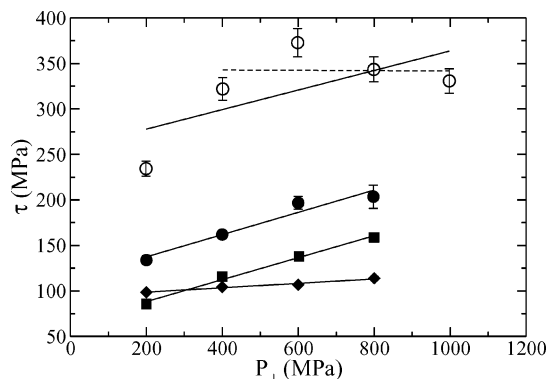
We calculate the 'friction coefficient',  $\mu$ , from the slope of the shear stress vs normal pressure curve.<sup>26</sup> The normal friction coefficient is the slope of the friction (shear) force vs normal load curve. Since we have parallel, flat surfaces in contact, the contact area is the same for all loads and the area can divide both the friction force and normal load to yield our 'pressure curves'. We note that this brings in the issue that our simulations with flat surfaces may yield different behavior than experiments (or simulations) with a tip. The stress distribution under a tip is nonuniform, while the flat surfaces have uniform distributions. The interaction between an uncoated tip and a SAM is different and may yield a different dependence of the friction force on load than two SAMs in contact. While modeling the complete nature of the experimental systems is an ultimate goal, treating simplified systems enables us to produce more clearly defined results and it lays a good foundation for further developments.

### III. Results

**A. Adhesion.** The adhesion curves between alkanethiol SAMs is given in Figure 3. Starting from the initial configuration with a 10 Å vacuum gap, the SAMs were compressed a total of 15 Å at a rate of 1.7 m s<sup>-1</sup>. At a separation of 10 Å, the end groups are beyond the interaction cutoff and the normal load is zero. As the separation is decreased, the normal load first becomes negative due to attractive vdW interactions and then becomes positive as repulsive interactions dominate at short separations. The minimum in the adhesive curve for the CH-SAMs is 220 MPa. In Paper 1, we used the COMPASS force field for which the minimum value was



**Figure 3.** Plot of the normal pressure,  $P_{\perp}$ , as a function of the SAM monolayer separation during compression at a rate of 1.7 m s<sup>-1</sup> for the CH-SAM ( $\Delta$ ), uncharged CF-SAM ( $\square$ ), and charged CF-SAM ( $\circ$ ). The lines are 25-point running averages for the charged CF-SAM and CH-SAM data.



**Figure 4.** Plot of the shear stress,  $\tau$ , as a function of applied pressure,  $P_{\perp}$ , for the CH-SAM ( $\diamond$ ), uncharged CF-SAM ( $\blacksquare$ ), low-shear-stress charged CF-SAM ( $\bullet$ ) and high-shear-stress charged CF-SAM ( $\circ$ ). For data points where the measured error is smaller than the representative symbol, error bars were omitted.

270 MPa.<sup>8</sup> The COMPASS vdW interaction has  $r^{-9}$  functional form for the repulsion term, which is weaker than the present force field (eq 6). The difference in the adhesive curves for the two force fields gives an indication of the level of accuracy in present force fields. For CF-SAM, the minimum is 220 MPa, the same as the hydrocarbon SAMs. Thus, we find no significant dependence of the maximum adhesive force on the end groups, but the charged F atoms do yield a repulsion at larger separations in the CF-SAM data that is not present in the CH-SAM data.

To better understand the origins of adhesion in the charged CF-SAMs, we performed additional adhesion simulations without Coulomb interactions by setting all charges to zero. The adhesive pressure (210 MPa) in the uncharged case was nearly unchanged; however, the maximum adhesion occurs at a monolayer separation of 6 Å compared with 5 Å for the charged case. At smaller separations, the general compression behavior is the same for the uncharged and charged cases. This shows that the dominant attraction is determined by the vdW term in the force field.

**B. Friction.** Figure 4 shows the measured shear stress,  $\tau$ , as a function of applied pressure,  $P_{\perp}$ , for the CH-SAM, CF-SAM, and uncharged CF-SAM systems. The stress values are determined by averaging the measured stress for 9 ns of steady-state behavior, after 9 ns of initial simulation to achieve the steady-state. In the case of the charged CF-SAM, two sets of data occur: one with a relatively high shear stress and one with low shear stress.

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**Table 5. Friction Coefficient,  $\mu$ , for CH-SAM, Uncharged CF-SAM, Low-Shear-Stress Charged CF-SAM, and High-Shear-Stress Charged CF-SAM**

| system                     | $\mu$           |
|----------------------------|-----------------|
| CH-SAM                     | $0.03 \pm 0.01$ |
| CF-SAM (no charge)         | $0.12 \pm 0.01$ |
| CF-SAM (low shear stress)  | $0.12 \pm 0.02$ |
| CF-SAM (high shear stress) | $0.10 \pm 0.07$ |

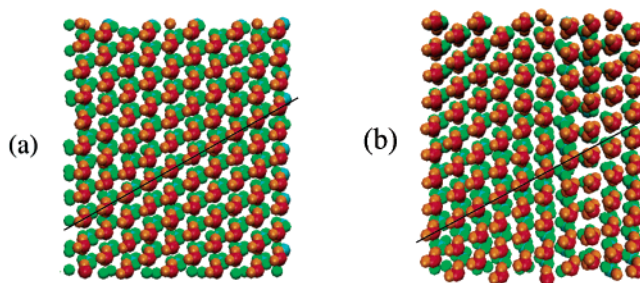
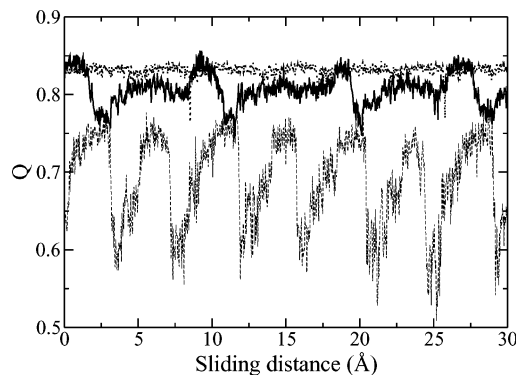
The solid lines represent fits to the different systems' data points that were determined using linear regression. The friction coefficient is then the slope of the equations for the curve fits, and the values are summarized in Table 5.

The CF-SAM simulations conducted at loads of 200, 400, and 600 MPa yielded relatively high shear stresses, while the simulation conducted at 800 MPa resulted in a measured shear stress in the low-shear-stress regime. These initial runs were all started from the same initial configuration and then brought to the desired load. The final configuration from the high-shear-stress  $P_{\perp} = 600$  MPa case was used as the starting state for simulations at  $P_{\perp} = 800$  MPa and 1 GPa, which yielded the high-shear-stress data. Similarly, the final configuration of the low-shear-stress  $P_{\perp} = 800$  MPa case was continued at  $P_{\perp} = 200, 400,$  and  $600$  MPa, resulting in low-shear-stress data at this  $P_{\perp}$ .

The CH-SAM has the lowest friction coefficient. Both the uncharged and low-shear-stress CF-SAM systems have the same friction coefficient ( $\mu = 0.12$ ). The effect of the included charges in the CF-SAMs is to increase the shear stress. This increase is not surprising since the Coulomb interactions are net repulsive which increases  $\tau$  (see Figure 8). The friction coefficient for the high-shear-stress data is not clear. A fit to the full data gives  $\mu = 0.10$ . However, considering only values for  $P_{\perp} \geq 400$  MPa, the high-shear-stress data gives a very low  $\mu$ , as shown by the dashed line with practically zero slope in Figure 4. As we will show, these systems have a high degree of order which yields a low friction coefficient.<sup>27</sup>

Before describing the difference between the high- and low-shear-stress systems, we briefly review the stick-slip dynamics of shearing SAMs.<sup>8</sup> Stick-slip motion is present in all the simulations here and generally occurs for ordered surfaces sliding over each other. For two SAMs sliding past one another, the terminal groups do not slide directly over each other. The terminal groups of one layer prefer to be in the 'valleys' between the terminal groups of the other layer and vice versa. However, inevitably, the path of the terminal groups must pass directly over each other (cf. Figure 5a). This yields the stick 'event' as the terminal groups collide. Ultimately, the terminal groups do not slide over each other. Instead, the chains tilt and the terminal groups slide around each other.

The high- and low-shear-stress data is due to a structural difference in the two systems. Figure 5 shows snapshots of the terminal carbons and attached fluorines of both the high- and low-shear-stress  $P_{\perp} = 600$  MPa CF-SAM systems under shear. The high-shear-stress CF-SAM system (Figure 5a) is well ordered, exhibiting a triangular lattice structure, and the terminal carbons in each monolayer maintain registry. The straight line shows that successive nearest neighbors are well aligned across the whole system. However, the low-shear-stress CF-SAM (Figure 5b) has a line defect (third column from the right) in one of the monolayers that formed spontaneously in the simulation. The black line in the figure shows that

**Figure 5.** Snapshots of the terminal carbons (top layer is cyan, bottom is red) and attached fluorines (top layer are green, bottom are orange) for the CF-SAM (a) high shear stress and (b) low shear stress under an applied pressure of 600 MPa. These systems are sheared at a constant relative velocity of  $2.0 \text{ m s}^{-1}$ .**Figure 6.** Plot of the hexatic order parameter  $Q$  as a function of sliding distance for the low- (solid curve) and high-shear-stress (dotted curve) CF-SAMs and the CH-SAM (dashed curve). In this case, the systems are under a constant  $P_{\perp} = 600$  MPa and the systems are sheared at a constant relative velocity of  $2 \text{ m s}^{-1}$ .

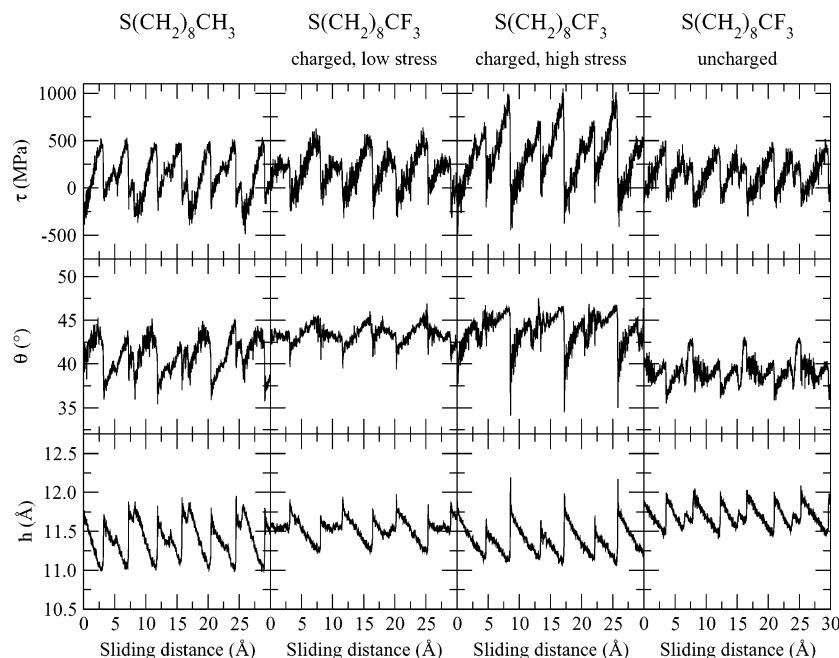
the line of terminal groups is no longer aligned throughout the system. As a consequence of this perturbed structure in one monolayer, the terminal carbons in these defect columns are forced to slide directly over the apposing terminal carbons in the apposite monolayer.

Given the structural differences, it is important to quantitatively characterize them, which can be done by calculating the hexagonal order parameter,  $Q$ ,

$$Q = \frac{1}{N_6} \sum e^{i6\theta} \quad (8)$$

Here,  $\theta$  is the angle between a (central) terminal carbon and each of two consecutive nearest neighbor terminal carbons. The sum is over  $N_6$  entries including all 6 angles per terminal C atom and over all terminal C atoms. For a perfect hexagon,  $\theta = 60^\circ$  and  $Q = 1$ . Figure 6 shows  $Q$  as a function of sliding distance for the low- and high-shear-stress CF-SAMs at  $P_{\perp} = 600$  MPa, as well as the CH-SAM. These curves show that the high-shear-stress CF-SAM is consistently more ordered than the low-shear-stress CF-SAM. The stick-slip dynamics are clearly evident in the  $Q$  data for the low-shear-stress CF-SAM. In the low-shear-stress case, comparison with the shear-stress data in Figure 6 shows that, at low shear stress,  $Q$  is low and vice versa. When there is a stick event, the low-shear-stress structure becomes as ordered as the high-shear-stress structure but afterward the order decreases significantly. In contrast, the high-shear-stress structure maintains a high degree of order throughout the sliding intervals (with some rare very quick drops in  $Q$ ). The CH-SAM has the lowest  $Q$  of all the cases with the largest fluctuations as a function of sliding distance. The larger

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**Figure 7.** End-group dependence of shear stress,  $\tau$ , tilt angle,  $\theta$ , and end-group height,  $h$ , for  $P_{\perp} = 600$  MPa and a relative shear velocity of  $2.0 \text{ m s}^{-1}$ .

F atom radius results in a more-ordered structure for the CF-SAMs.

The structural changes of the SAM molecules under shear are shown along with the shear stress as a function of the sliding distance in Figure 7 for all three cases at an applied pressure of 600 MPa. The data presented are only a short segment of the total run and represent the steady state which occurs after an initial transient of approximately  $180 \text{ Å}$ . The tilt angle of the chains is defined as the angle between the normal axis and odd numbered carbon atoms (starting from the substrate) averaged over all chains. The terminal-group height shown is the average height of the hydrogens (fluorines) in the terminal  $\text{CH}_3$  ( $\text{CF}_3$ ).

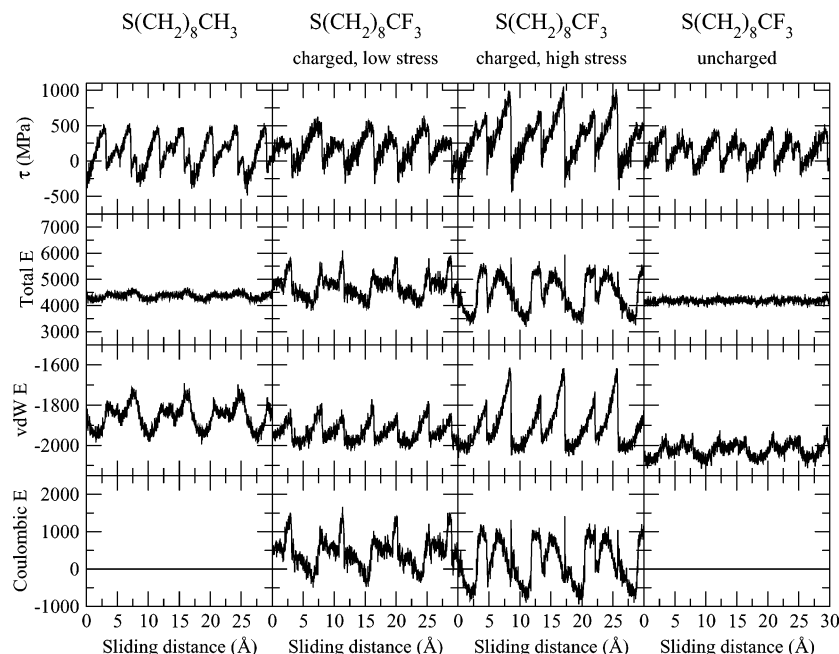
For each case, distinct stick-slip behavior occurs in all quantities. Two stick events typically occur in one period of the dynamics. A faster stick event with lower stress occurs when the terminal groups are sliding between two terminal groups on the apposite monolayer, and a slower stick event with larger stress occurs when the apposing terminal groups slide around each other. All but the uncharged CF-SAM have alternating shear distances of  $3.8$  and  $4.9 \text{ Å}$ , corresponding to the alternating times of the events. The uncharged CF-SAM shows a single period of  $4.4 \text{ Å}$ . While the periods observed in the high- and low-shear-stress CF-SAMs are the same, the stress peaks in each interval are considerably larger in the high-stress case than in the low-shear-stress case, which yields the high  $\tau$  values. Particularly, the stick events involving terminal groups sliding around each other result in a larger  $\tau$  for the ordered SAMs. The high degree of order forces each individual molecule at a stick event to simultaneously slide around the terminal group on the apposite monolayer. This coherent dynamic is a bit slow to occur, and the terminal groups collide with each other more strongly, yielding the larger  $\tau$ . For the low-shear-stress CF-SAM, the line defects push the apposed SAMs slightly further apart, reducing the stress on the molecules not in the line defect, although the local stress within the defect region should be larger. The net effect is a lower shear stress. The peak shear stresses in the CH-SAMs are about  $50$ – $100$  MPa lower than the low-shear-stress CF-SAM

peaks. While this is small relative to the fluctuation in  $\tau$ , it is large compared to the average and is a significant source of the difference between the two averages. The CH-SAM also has lower valleys in the shear stress. The smaller size of the CH-SAM terminal group and the weaker order makes it easier for the groups to slide around each other. The weaker order means that during the stick events a significant fraction of molecules are aligned *not* to collide with the terminal group on the apposite monolayer, yielding a lower  $\tau$ .

The stick-slip structural dynamics are reflected in the changes in tilt angle and the height of the terminal group. Except for the uncharged CF-SAM, the fluctuations in the tilt angle show clear correlation with the shear stress. In the uncharged CF-SAM, the tilt angle is noisier, though it exhibits some correlation. In the high-shear-stress CF-SAM, the tilt angle drops very sharply as the stress drops from a stick event. The molecules in this case are being squeezed so hard in sliding by the apposite terminal group that once past, the tilt angle snaps back beyond the equilibrium value. The fluctuations in the terminal-group height display the same stick-slip behavior seen in the stress. In fact,  $h$  is highly (inversely) correlated with the tilt angle, as it should be based on geometry. For the uncharged CF-SAM,  $h$  clearly shows the stick-slip dynamics while the tilt angle does not.

The contributions to the total system energy during shear are shown in Figure 8 for CH-SAM, low- and high-shear-stress CF-SAM, and uncharged CF-SAM as a function of sliding distance. As already determined for the CH-SAM, the nonbonded interactions dominate the energetics of the system.<sup>4</sup> While gauche defects certainly occur, the contribution to the variation in energy is negligible. The Coulomb energy is the dominant term in the charged CF-SAM systems, with fluctuations in the vdW energies about an order of magnitude smaller. In the uncharged systems, the total energy change comes only from vdW interactions; consequently, the total-energy fluctuations are much smaller in these cases. The main difference between the low- and high-shear-stress CF-SAMs is the larger vdW peaks at the stick events in the





**Figure 8.** Deconvolution of energy contributions to total energy (kcal mol<sup>-1</sup>).

latter. This is consistent with the structural picture described above.

Finally, we note that the shear stress depends strongly on the shear direction, since the two surfaces are commensurate.<sup>28</sup> Because of constraints of available simulation resources, we can only obtain data for multiple loads in one shear direction. We have performed two additional simulations for the low-shear-stress CF-SAM at  $P_{\perp} = 600$  MPa in different directions to assess the variability of  $\tau$  with direction. For shear in the  $y$  direction ((120) and (120) directions), the average shear stress is 98 MPa, compared with 197 MPa for shear in the  $x$  direction. In this direction, the lines of CF<sub>3</sub> groups can slide between each other and do not have to go around (over) terminal groups in the apposite SAM. Thus,  $\tau$  is lower in the  $y$  direction than in the  $x$  direction. In contrast, shearing at a 10° angle to the  $x$  direction yields an average shear stress of 374 MPa, which is larger than shearing in the  $x$  direction. In this direction, a CF<sub>3</sub> group must slide around (over) more terminal groups in the apposite SAM than it would if the shear direction was the  $x$  direction.

#### IV. Discussion

**A. Adhesion.** In general, adhesion between SAMs depends strongly on the chemical type of the terminal groups. In Paper 1, we reported on the adhesion between SAMs with three different functional groups, CH<sub>3</sub>, OH, and COOH. We found the adhesive interaction between COOH-terminated SAMs to be about five times larger than that between CH-SAM because of the hydrogen bonding in the former system. In the current study, the maximum attractive interaction between CF-SAMs is indistinguishable from CH-SAMs, but the CF-SAMs have a repulsive barrier at large separations not present in the CH-SAM data. The substitution of hydrogen with fluorine yields a larger atom with a nonzero partial charge for each fluorine atom in our force field. The electrostatic interactions have little net effect on the attractive part of the adhesion curve partly because the system is net neutral. The closest atoms are the F atoms on apposite

SAMs, which repel each other. Thus, the net electrostatic interaction tends to be repulsive, yielding the repulsive barrier and a shorter-ranged attractive well for the CF-SAMs. The attractive interactions come from the vdW interactions, which are similar in the two cases.

We note that the maximum attractive adhesion for CH-SAM from the current force field is almost the same as that from the COMPASS force field used in Paper 1.<sup>8</sup> The major difference in the adhesion behavior of the SAMs is in the repulsive region where the calculated normal load from the current force field shows a smaller repulsive stress at short separations. This is consistent with the different functional forms in the two force fields for the vdW core repulsion. The COMPASS force field is stiffer for separations below 2.7 Å for the C-C interaction.

**B. Friction.** The coefficient of friction for fluorocarbon SAMs has been found experimentally to be larger than that for hydrocarbon SAMs despite the low surface energy of the former.<sup>10,11,14</sup> In the current work, the friction coefficient for the low-shear-stress CF-SAM is also higher than that for the CH-SAM by about a factor of 3–4, as seen in Table 5. The low value of the CH-SAM friction coefficient makes the uncertainty in the ratio a bit large. This ratio is within the 2–3 range seen experimentally.<sup>10,11,14</sup>

Kim et al.<sup>11</sup> have summarized the factors that can influence friction: (i) chemical structure and composition of backbone, (ii) area/molecule and molecular order, (iii) defects such as gauche defects and vacancies, (iv) mechanical properties such as elastic constant, (v) terminal functional group, and (vi) surface dipole orientations. In addition, the packing density and structural order can influence the frictional behavior. For the case of just differing terminal groups, the backbones are identical. For the same reason, the mechanical properties of the SAM are similar. Given that the adhesive interactions are indistinguishable, the chemical nature of the two terminal groups does not explain the large difference in friction. The area/molecule for the two SAMs is identical even though the CF<sub>3</sub> terminal group is bulkier than the CH<sub>3</sub> group.<sup>11</sup> In the simulations, there are no defects due to wear (bond ruptures, pull-off chain) that may provide

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additional energy dissipation mechanisms. Thus, many of the possibilities are ruled out.

The main difference among all the systems in the simulations is the structure of the terminal-group layer which we quantified in terms of the order parameter  $Q$  (eq 8). The more the structure is ordered, the larger  $Q$  is. We find that the shear stress increases monotonically with  $Q$ . The well-ordered CF-SAM has the largest  $\tau$  and the largest  $Q$ . With the line defect in the CF-SAM, both  $\tau$  and  $Q$  decrease and the shear stress is larger than for the CH-SAM, which has the lowest  $Q$ . The dense packing of the CF-SAMs naturally leads to the high structural order. The smaller H atoms allow uncorrelated oscillations about the equilibrium position in the CH-SAM, resulting in a much lower  $Q$ . The high degree of structural order particularly forces the stick-slip motion to be highly coherent and has a large shear stress, particularly at the stick events. On the other hand, less order has less stress, as there is more play in the sliding structures.

As we noted in Section IIA, the AFM images of CF-SAMs show smaller domains than CH-SAMs. This is not in contradiction to the order as described by the quantity  $Q$  since  $Q$  is primarily a measure of local structural order. The order within the domains of CF-SAMs can be better than in CH-SAMs, but the domain size determined by nonlocal defects, such as the line defect found in these simulations, can be smaller in the CF-SAMs. The spontaneous formation of the line defect in the CF-SAM simulations is an interesting indication that such defects more easily form in the CF-SAMs. For these reasons, we consider the CF-SAM data with the line defect to be more representative of the experimental data.

With respect to which molecular interactions are most important, clearly the electrostatic interactions are domi-

nant in the CF-SAMs. Their fluctuations are much larger than the vdW. As seen from Tables 1–4, the dihedral forces involving CF<sub>3</sub> terminal group are much larger than those for CH<sub>3</sub>. However, the variation in the dihedral interactions is very weak in comparison to the electrostatic interactions. This contrasts with some earlier simulation work<sup>29</sup> which found that gauche defects played an important role. However, these simulations are for diamond on a CH-SAMs, not two CH-SAMs or CF-SAMs, and the loads are of order 10 GPa which, not surprisingly, yields more gauche defects.

## V. Conclusion

The frictional dynamics of methyl- and trifluoromethyl-terminated alkanethiol SAMs on gold were studied using molecular dynamics simulations. The maximum adhesion force between the SAMs is almost identical for the two end groups. The friction coefficient of CF<sub>3</sub>-terminated alkanethiol SAMs is 3–4 times larger than CH<sub>3</sub>-terminated SAMs, in agreement with experiment. The shear stress is also larger for the CF<sub>3</sub>-terminated SAMs. The source of this difference is primarily the tighter packing of the terminal group resulting in a higher degree of order.

**Acknowledgment.** Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

LA0491091

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