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# Simulations of Self-Assembled Monolayers under Compression: Effect of Surface Asperities

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Molecular dynamics simulations are used to probe the response of a self-assembled monolayer of hexadecanethiol chemisorbed on a gold(111) surface to compression with a flat surface and a surface with atomic-scale roughness in the form of surface asperities. The film responds elastically with only a uniform change in tilt angle upon compression to low loads with the flat surface. In contrast, our results show that the asperities are able to get closer to the substrate relative to the flat surface at comparable loads without completely disrupting the film and that at higher loads the monolayer film disorders by creating a large number of gauche defects in order to accommodate the asperity. The findings presented in this work support conclusions based on recent scanning tunneling microscopy studies on self-assembled monolayers that imaging occurs at surface asperities which penetrate the film.

Techniques such as scanning tunneling microscopy (STM),<sup>1</sup> atomic force microscopy (AFM),<sup>2</sup> and interfacial-force microscopy (IFM)<sup>3</sup> have been important in the study of organic molecules adsorbed to surfaces,<sup>4,5</sup> in that these techniques allow one to examine the structure of the adsorbates at the atomic level. However, interpretation of results is sometimes difficult due to a lack of understanding of the fundamental processes involved in these techniques. One such phenomenon is the unexpected imaging of long chain organic molecules in self-assembled monolayers (SAMs) and Langmuir-Blodgett films observed during tunneling experiments.<sup>6-8</sup> The problem, simply stated, is how it is possible to tunnel through an insulating film which is over 2 nm thick. Recently, Dürig and co-workers examined monolayer films of mercaptohexadecanol on a gold(111) surface by STM combined with interaction-force-gradient sensing.<sup>9,10</sup> Based on the force-gradient experiments, it was concluded that the proximity of the tip to the surface during tunneling is close enough to elastically compress the monolayer film. Based on the tunneling images, which had a resolution of 1.0 nm, and a calculated contact diameter of 5.0 nm for the tip, it was concluded that only a small portion of the tip area which is in contact with the film contributes to tunneling and that tunneling occurs through atomic-scale asperities on the tip that penetrate the film. Similar ideas have also recently been suggested by Salmeron and co-workers.<sup>2c</sup> The present calculations support this picture, show the kind of forces involved, and show the way in which the film is disturbed during compression.

In this study, molecular dynamics simulations are used to probe the response of a model SAM film of hexade-

cane-thiol chemisorbed on a gold(111) surface to compression. The molecules are 2.0 nm long from the sulfur head group to the CH<sub>3</sub> tail group and adsorb at the 3-fold hollow sites in a hexagonal array on the gold(111) surface with an average tilt angle of 28° with respect to the surface normal. The simulations suggest that the film responds elastically with a uniform change in tilt angle when compressed to low loads by a flat surface. Only a jump-to-contact during the initial stages of compression, and adhesion of the monolayer film to the compressing surface during the final stages of withdrawal, keep the compression from being totally reversible. Similar results have been obtained by Monte Carlo simulation performed by Siepmann and McDonald.<sup>11</sup> In contrast, additional simulations presented in this study predict that compression to low loads using a surface with atomic-scale roughness in the form of asperities allows the asperities to come closer to the substrate relative to the flat surface at comparable loads. Hence, in the STM scenario, a tip with no asperity would exert a much higher loading force on the film while trying to tunnel. The force could potentially disrupt the film and alter the image.

The model used in this study was derived from the model proposed by Hautman and Klein<sup>12</sup> for the study of alkanethiols on gold. The hexadecanethiol chains were modeled using pseudoatoms representing the sulfur head group, CH<sub>2</sub> groups, and CH<sub>3</sub> tail group. The intramolecular potential contains a harmonic term for bond bending and a power series expansion of the cosine of the dihedral angle as the torsional term. Interchain and intrachain interactions between pseudoatoms separated by four or more atoms were modeled using a Lennard-Jones 6-12 potential. In the original model, intramolecular bonds were held rigid using the SHAKE<sup>13</sup> algorithm and the surface was modeled as a continuum using a 3-12 potential. However, in simulations involving compression of the monolayer film where the possibility of distorting the film exists, one would expect that compression of the bonds, packing of the head groups on the substrate, and the lateral mobility of the head groups on the substrate would become important factors. Thus, the original model<sup>12</sup> was modified in the following manner. First, a harmonic potential was included for bond stretching with parameters derived from molecular mechanics.<sup>14</sup> Second, the chain-to-surface interactions were modeled

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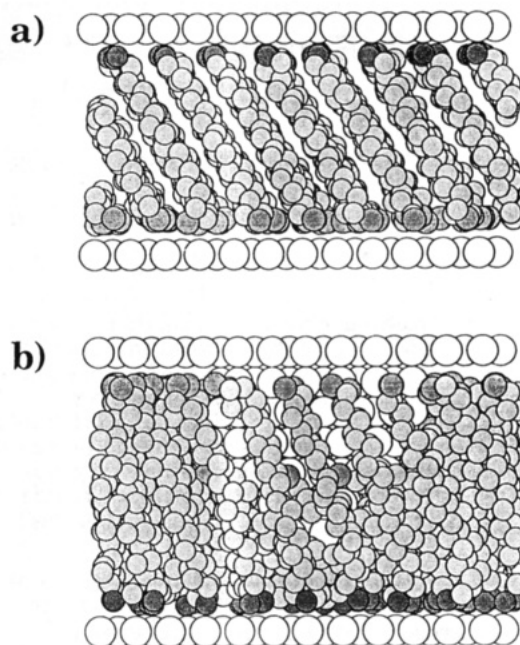
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using a Lennard-Jones 3-12 potential with explicit surface atoms included in the simulation. This potential was fit to give the same chain-to-surface potential energy and head-group-to-surface distance as the continuum model proposed by Hautman and Klein.<sup>12</sup> For a single chain interacting with the surface, the explicit surface atom model gives a binding energy of 1.28 eV (29.5 kcal/mol), while the continuum model gives a binding energy of 1.21 eV (27.9 kcal/mol). The experimental binding energy for this system has been measured as 28 kcal/mol.<sup>15</sup> Parameters for this model are given elsewhere.<sup>16</sup>

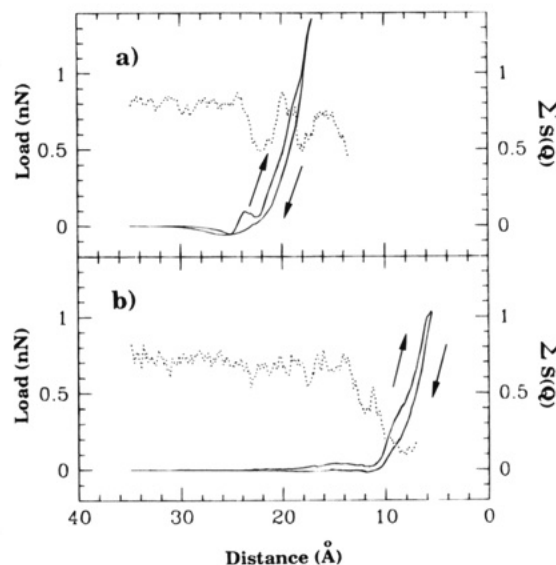
The molecular dynamics simulations were performed on a monolayer consisting of 64 chains adsorbed to a gold-(111) surface composed of 192 atoms. An infinite system was simulated using periodic boundary conditions. The flat compressing surface was simulated using a gold(111) surface also composed of 192 atoms. The surface containing the asperity was modeled using a flat surface composed of 192 atoms to which a six layer tip approximately 1.5 nm in length was attached. The asperity was one-fourth the size of the flat surface at the point of contact with the flat surface and was tapered to include only three atoms at the apex. The equations of motion were integrated using a velocity Verlet algorithm<sup>17</sup> with a constant step size of 0.25 fs. A constant temperature of 300 K was maintained throughout the simulation by scaling the velocities every 20 time steps. Prior to compression the films were annealed for 50 ps, and the potential energy, tilt angle, and orientation of the chains were monitored to assure that the systems had attained equilibrium. The resulting films were highly ordered, with the sulfur head groups in the film binding at the 3-fold hollow sites in a hexagonal array with a nearest-neighbor distance of 4.99 Å. This is in agreement with experimental measurements<sup>18</sup> and *ab initio* calculations.<sup>19</sup> Following equilibration, the films were compressed by moving the upper surface toward the substrate at 1.0 Å/ps (see Figure 1). All atoms in the surfaces were otherwise held rigid during the simulations. The films were compressed to a load of approximately 1.0 nN per molecule, at which time the compressing surface was withdrawn. The potential energy, load, and average tilt angle of the molecules were recorded during the simulation.

The simulated force profiles for compression of the monolayer film with both a flat surface and a surface containing an atomic-scale asperity are shown in Figure 2. The force profiles were calculated by summing the forces on the compressing surface in the direction of compression. One can see that the asperity (Figure 2b) is able to come much closer to the substrate at comparable loads than the flat surface (Figure 2a). This supports the notion that a small asperity on the end of the tip may come within tunneling range of the substrate without totally disrupting the film. The penetration of the asperity into the film is not without consequence, however, and will be examined next.

One concern is that the structure of the underlying film may be lost during compression and tip penetration. Three distinct structural changes are observed during these simulations for the compression of the monolayer film with the flat surface. First, there is a reversible change in the tilt angle of the chains normal to the surface. At no load, the chains are tilted uniformly at an angle of 28°



**Figure 1.** Monolayer film of hexadecyl mercaptan on a gold-(111) surface compressed to a load of 1.0 nN per molecule by (a) a flat gold(111) surface and (b) a gold(111) surface containing an asperity. At this load, the monolayer compressed by the flat surface remains ordered, while a defect forms in the monolayer film to support the asperity.



**Figure 2.** Simulated force profiles (solid line) and the sum of the peaks in the structure factors (dashed line) for compression of a monolayer film of hexadecyl mercaptan on a gold(111) surface with (a) a flat gold(111) surface and (b) a surface containing an asperity. The arrows indicate the direction of compression. The distance is defined as the separation between the leading edge of the flat surface or asperity with respect to the substrate. The figure suggests that the asperity is capable of approaching closer to the substrate at comparable loads before structure is altered.

with respect to the surface normal. As the film is compressed to a load of 1.0 nN per molecule, following the jump-to-contact where the tilt angle decreases to approximately 20°, there is a uniform change in the tilt angle to a maximum of 48°. No hysteresis is observed in the tilt angle upon withdrawing the tip until the film begins to lose contact with the compressing surface. At final contact the film has an average tilt angle of 0° before returning to the equilibrium value of 28°. Second, as shown in Figure 3a, for the film compressed with the flat surface the average chain length of the hexadecanethiol molecules in

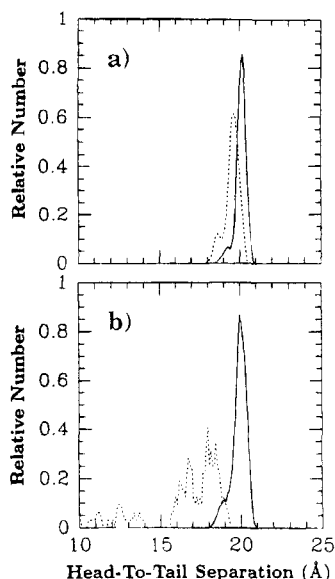
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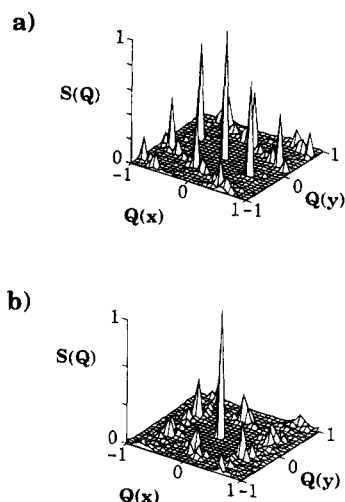
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**Figure 3.** Sulfur head-group to  $\text{CH}_3$  tail-group distance distribution for (a) a monolayer compressed by a flat surface and (b) a monolayer compressed by a surface containing an asperity: solid line, load = 0.0 nN; dashed line, load = 1.0 nN.



**Figure 4.** Structure factors for (a) compression to 1.0 nN per molecule with a flat surface and (b) compression to 1.0 nN per molecule with a surface containing an asperity.

the monolayer film changes from approximately 2.0 nm at no load to 1.9 nm at a load of 1.0 nN per molecule. Examination of the distribution of bond lengths, angles, and dihedrals shows that the shift in chain length is primarily due to a compression of the bonds in the chains, and that few gauche defects are formed. Finally, at higher loads, the sulfur head groups rearrange to occupy both 3-fold hollow and 2-fold bridge sites on the gold(111) surface. To examine the order within the films, structure factors<sup>20</sup> for the head groups in the fully compressed monolayers were calculated using

$$S(\mathbf{Q}) = \frac{1}{N} \left| \sum_{j=1}^N e^{i(\mathbf{Q} \cdot \mathbf{R}_j)} \right|^2 \quad (1)$$

where  $\mathbf{Q}$  is a wave vector given as multiples of  $2\pi$  divided by the box length and  $\mathbf{R}_j$  values are the components of the positions of the head groups in the surface plane. The values of  $S(\mathbf{Q})$  are shown in Figure 4. For the monolayer film compressed by the flat surface (Figure 4a), the head groups go from a hexagonal packing to an oblique packing. This change in packing is also observed for the  $\text{CH}_3$  tail

groups, suggesting that the structural change is uniform throughout the chains. Both the sharp peaks in the structure factor and the uniform change in average tilt angle upon compression suggest that this new structure is also ordered. This compression-induced structure change is discussed elsewhere.<sup>16</sup>

In contrast, the film compressed using the surface containing the asperity (Figure 4b) shows a large amount of random changes in the structure of the monolayer film, with the monolayer film disordering at high loads. The average tilt angle changes nonuniformly during compression, varying between  $20^\circ$  and  $30^\circ$ . The steady increase in tilt angle observed for compression with the flat surface is not observed in this case. Further, the distribution of chain lengths, shown in Figure 3b, is much broader for compression with the surface containing the asperity. Examination of the distribution of bond lengths, angles, and dihedrals for the monolayer suggests that, in addition to the decrease in bond lengths observed for compression with the flat surface, the average bond angle also decreases and a large number of gauche defects are formed in the chains. Finally, the structure factors for the monolayer film compressed by the surface containing the asperity (Figure 4b) suggest that the head groups are disordered at a load of 1.0 nN per molecule and that no rearrangement to the oblique packing observed for compression with the flat surface is obtained.

Because a loss of structure is not observed at the loads associated with STM experiments, the question arises at what load or size of the asperity does the underlying structure of the monolayer film deform. Figure 2 shows the sum of the peaks in the structure factors, minus the central ( $\mathbf{Q} = 0$ ) specular peak, with respect to the tip-to-surface distance. For compression with the asperity, the monolayer film does not begin to disorder until the tip is approximately 1.4 nm from the surface. This result, combined with the results from the force profiles, shows that an asperity can approach the substrate much closer than the flat surface before disrupting the film. This supports Dürig's and co-workers<sup>9,10</sup> and Salmeron and co-workers<sup>2c</sup> conclusions that surface asperities that penetrate the film may play a crucial role in tunneling experiments in these systems. However, as also noted previously,<sup>2c,6-9</sup> the distance between the tip and substrate is still too large for vacuum tunneling. Thus, the structural defects induced in the film by the asperity must also contribute to the tunneling conduction mechanism.

In conclusion, we have used molecular dynamics simulations to examine the effect of an asperity on a tip when compressing a self-assembled monolayer film. Our results show that asperities are able to get closer to the substrate without completely disrupting the film relative to a flat surface and that the monolayer film disorders by creating a large number of gauche defects in order to accommodate the asperity. The findings presented in this work support conclusions based on recent scanning tunneling microscopy studies on self-assembled monolayers that imaging occurs at surface asperities which penetrate the film.<sup>2c,6-9</sup>

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