

## Monte Carlo Simulation of the Mechanical Relaxation of a Self-Assembled Monolayer

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Monte Carlo calculations have been used to study the mechanical relaxation of a monolayer of  $\text{CH}_3(\text{CH}_2)_{15}\text{SH}$  admolecules on a gold substrate when subjected to indentation caused by a nanometer-scale force-microscope tip. An almost elastic response is observed to forces that compress the monolayer by about 25% of its original thickness. Jump to contact on approach of the tip is signaled by an abrupt change in the mean molecular tilt, and the subsequent compression leads to very substantial but reversible changes in the conformations of the molecules. Comparison is made with results obtained by interfacial-force microscopy.

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Recent research on the properties of Langmuir-Blodgett films and self-assembled monolayers (SAMs) has been largely motivated by their potential technological importance. Particular interest has been shown in the use of the techniques of force microscopy for the study of mechanical properties of substrate-supported, organic monolayers: the results of such experiments are relevant to applications involving lubrication, adhesion, and wetting [1, 2]. Unfortunately, the interpretation of the experimental data is complicated by the fact that the relationship between the observable effects and the microscopic properties of the monolayer is usually indirect. It follows that this is an area of work where simulation by molecular dynamics (MD) or Monte Carlo (MC) methods [3, 4] can make an important contribution to an understanding of the fundamental processes involved. Here we present the results of a MC simulation of the microindentation of a SAM in which the interfacial forces and structural relaxation of hexadecyl mercaptan,  $\text{CH}_3(\text{CH}_2)_{15}\text{SH}$ , chemisorbed on a gold substrate [5] have been studied as functions of the separation between the supporting and the force-microscope surfaces. The choice of system was dictated by two considerations: first, the mechanical properties of the same physical system have recently been probed [6] by interfacial-force microscopy (IFM); second, simulations of the structural properties of the monolayer in the absence of any probe have already been carried out with both MD [7] and MC [8] methods, and good agreement has been found with a range of experimental data.

The interaction model used to describe the monolayer is the same as that adopted in the MD simulations of Hautman and Klein [7] (their model I) and in our own earlier MC calculations [8] (model  $C_S$ ). The admolecules are represented by chains of 17 pseudoatoms ( $\text{CH}_2$ ,  $\text{CH}_3$ , and S) connected by rigid bonds but with allowance made for bond bending and torsional motion. The pseudoatoms interact with each other via Lennard-

Jones 12-6 potentials and with the substrate via a 12-3 potential. The restricted lateral mobility characteristic of chemisorption is mimicked by an increase in the Lennard-Jones parameters for the interaction between headgroups. The force-microscope tip is modeled in the same way as the supporting surface, i.e., as a flat gold surface without atomistic detail. This provides a fair approximation to the tungsten tip used in the IFM experiments [6], since the interactions of hydrocarbon groups with the two metals are similar in nature, and both the radius of curvature of the experimental tip (radius  $\approx 500$  nm) and the contact area diameter ( $\approx 10$  nm) are significantly larger than the length of the simulation cell ( $\approx 44$  Å). The system studied consisted of 90 molecules placed in a rectangular cell, periodically replicated in the plane of the surface and with a surface area per molecule of  $21.4$  Å<sup>2</sup>. The calculations were carried out in the *NVT* ensemble at a temperature of 300 K. A well equilibrated configuration from an earlier run was taken as the initial state and the initial tip-substrate separation,  $d_{\text{TS}}$ , was taken as 30 Å. A single MC trial move consisted of a translation, a whole-body rotation, or a conformational change [9], chosen at random with equal probabilities. The loading/unloading motion of the tip was modeled by displacements of  $0.0005$  Å after every MC cycle (90 trial moves). Results for the SAM under full load and at the end of the loading/unloading cycle were gathered over additional periods, of  $10^3$  MC cycles each. The microscopic forces calculated in the simulation, obtained from  $F = \Delta U / \Delta d_{\text{TS}}$ , where  $U$  is the potential energy per chain in temperature units, can be converted to the forces measured in the IFM experiment [6] through the rule that  $10^4$  K Å<sup>-1</sup> (MC)  $\sim 0.5$  μN (IFM), where it is assumed that the IFM tip interacts only via a contact area precisely 10 nm in diameter [6], i.e., with approximately 370 admolecules. Since the estimated contact area is subject to considerable uncertainty, the quoted conversion factor provides only a rough guide to the re-

lation between the two forces.

The variations in  $U$ ,  $F$ , the mean molecular tilt  $\theta_m$  (measured with respect to the surface normal), and the fraction of *gauche* defects,  $f(g)$ , as functions of  $d_{TS}$  are shown in Fig. 1. The loading/unloading cycle can be divided into five regions. First, prior to tip-sample contact ( $d_{TS} > 26 \text{ \AA}$ ), there is no evidence of any structural changes in the monolayer and the measured attractive forces are smaller in magnitude than  $\sim 100 \text{ K \AA}^{-1}$ . The second region ( $26 \text{ \AA} > d_{TS} > 23 \text{ \AA}$ ) involves a "jump to contact," though not in the usual sense of that term [2], since the simulated tip cannot itself jump. Jump to contact occurs instead through an abrupt decrease of about  $5^\circ$  in  $\theta_m$ . At this stage, an appreciable attractive force ( $\sim -500 \text{ K \AA}^{-1}$ ) is observed. Third ( $d_{TS} < 23 \text{ \AA}$ ), a repulsive regime is entered, characterized by an initial soft repulsion which progressively stiffens as the tip moves

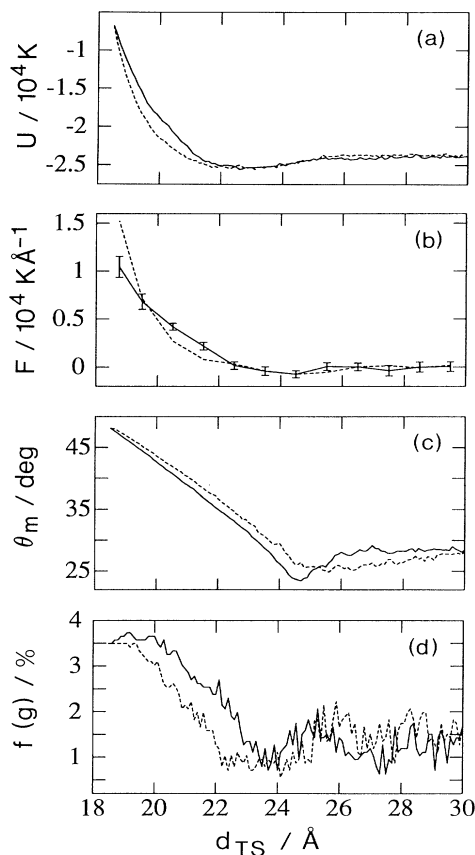


FIG. 1. Relaxation of the SAM during loading (solid lines) and unloading (dashed lines);  $d_{TS}$  is the tip-surface separation. (a) Instantaneous potential energy per chain. (b) Instantaneous force (averaged over  $1.0 \text{ \AA}$  intervals). Error bars are shown for the inward motion; similar errors apply to the outward motion. (c) Instantaneous molecular tilt angle. (d) Instantaneous fraction of *gauche* defects expressed as a percentage of all dihedral angles.

closer to the surface. The molecular tilt now increases almost linearly with decreasing  $d_{TS}$ , but an initial linear increase in  $f(g)$  is followed by a plateau region in which the number of defects stabilizes at a value about twice as large as in the uncompressed monolayer.

The loading cycle was halted at  $d_{TS} = 18.5 \text{ \AA}$  because the compression was becoming unphysically large. At this separation,  $U$  had increased by  $1.6 \times 10^4 \text{ K}$ , i.e.,  $130 \text{ kJ mol}^{-1}$ , which is 20% larger than the estimated chemisorption energy [10]. Roughly 90% of the increase comes from the interactions between chains, which are now strongly repulsive. Thus, in the experimental situation, it is highly likely that use of larger tip-surface forces would lead to expansion of the monolayer or to desorption of molecules. In our method of simulation, neither of these effects can be accommodated.

The behavior in the initial stage of withdrawal of the tip ( $18.5 \text{ \AA} < d_{TS} < 23 \text{ \AA}$ ) is similar to that of the third (repulsive) phase. Little or no hysteresis is seen in  $F$ , but there is some weak hysteresis evident in other properties. Note that the forces plotted in Fig. 1(b) have been averaged over intervals of  $1 \text{ \AA}$ ; this accounts for the apparent discontinuity in force at the turning point of the cycle. For a given value of  $d_{TS}$ ,  $U$ , and  $f(g)$  are always lower during the unloading part of the cycle, while  $\theta_m$  is larger and shows no pronounced minimum of the type seen at jump to contact. The fifth and final phase is characterized by smaller values of  $\theta_m$  than in the first region: adhesive forces cause the monolayer to "stick" slightly to the tip and the chains become correspondingly more erect. In principle, some molecules could detach themselves from the substrate and chemisorb on the tip, but in practice the probability of such an event occurring is negligible because the potential barrier involved is very high ( $\approx 14000 \text{ K}$ ).

Our results provide some guide to the microscopic processes that are likely to occur at low to moderate force levels in the IFM experiment of Joyce *et al.* [6]. There is evidence of a kink in the experimental force profile at  $F \approx 0.45 \text{ \mu N}$  and at a tip displacement from contact of less than  $8 \text{ \AA}$ , which in our calculations corresponds to the range  $24 \text{ \AA} > d_{TS} > 16 \text{ \AA}$  and therefore contains the region in which the simulated monolayer can be reversibly compressed. The slope of the experimental force curve for  $F \leq 0.45 \text{ \mu N}$  is between  $0.05$  and  $0.08 \text{ \mu N \AA}^{-1}$ ; this is in line with the results of Fig. 1, given the uncertainty mentioned earlier. Thereafter the experimental force profile acquires a significantly steeper slope. Experimentally, compression was continued up to  $F \approx 2.5 \text{ \mu N}$ , at which point the measured indentation was about  $20 \text{ \AA}$ . A large hysteresis was found during withdrawal of the tip, which the authors of [6] suggest could arise from entanglement of the chains under high compression. However, integration of the experimental force profile yields an energy loss per chain of approximately  $4 \times 10^5 \text{ K}$ , which is about 20 times larger in magnitude than the potential energy of the monolayer (see Fig. 1 and [10]). This

TABLE I. Selected results for the SAM without tip ( $d_{TS} = \infty$  [8]), under maximum load ( $d_{TS} = 18.5 \text{ \AA}$ ), and at the end of the loading/unloading cycle ( $d_{TS} = 30 \text{ \AA}$ ).  $U_i$  is the intermolecular contribution to  $U$ ; for the definition of  $S_{CC}$ , see [7].

	$d_{TS} = \infty$	$d_{TS} = 18.5 \text{ \AA}$	$d_{TS} = 30 \text{ \AA}$
$\langle U \rangle / 10^4 \text{ K}$	-2.37	-0.82	-2.37
$\langle U_i \rangle / 10^4 \text{ K}$	-1.22	+0.23	-1.22
$\langle z_{\text{head}} \rangle / \text{\AA}$	2.41	2.35	2.41
$\langle z_{\text{tail}} \rangle / \text{\AA}$	20.1	15.4	20.2
$\langle \theta_m \rangle / \text{deg}$	28.4	48.3	27.7
$S_{CC}$	0.34	-0.03	0.32
$f_T(g) / \%$	1.7	3.5	1.4
$f_T(k) / \%$	67	18	57
$f_M(g_0) / \%$	86	56	86
$f_M(g_1) / \%$	7	40	8

result, together with the high level of indentation that was observed, implies that very substantial structural rearrangement must have occurred within the monolayer, and this could well have had the effect of destroying it. It would clearly be of great interest to repeat the IFM experiment for a range of smaller values of the maximum load, in particular with a view to determining the load at which hysteresis first appears.

Table I contains a comparison of results for the SAM without tip, under maximum load, and at the end of the loading/unloading cycle. From this (and Fig. 1) it is clear that the SAM has gone through the cycle without suffering any permanent damage. Compression leads to only a small change in the mean distance between the sulfur atom and the substrate,  $\langle z_{\text{head}} \rangle$ , whereas the thickness of the monolayer, measured by the mean distance  $\langle z_{\text{tail}} \rangle$  between the terminal methyl groups and the substrate, decreases by almost 5  $\text{\AA}$ . Density profiles for the direction ( $z$ ) normal to the substrate for the uncompressed and fully compressed layers are shown in Fig. 2. As discussed elsewhere [7], the alternating sequence of amplitudes is caused by the twisting motion of the chains, and the splitting of the odd-numbered peaks close to the substrate reflects the preference for particular twist angles. A notable feature of the present results is the overlap under compression of the profiles corresponding to the two groups at the chain end adjacent to the tip. Linked to this structural change is an orientational disordering of the terminal C-C bonds, as measured by the order parameter  $S_{CC}$  defined by Hautman and Klein [7]. Inspection of the distribution of *gauche* defects along the chains shows that during compression the number of defects in the interior of the monolayer is greatly reduced, leading to a marked decrease, shown in the table, in the percentage of defects that form part of a kink,  $f_T(k)$ . The overall rise in the number of defects (see Fig. 1) comes about because there is a dramatic increase—from 6% to 38%—in the percentage of molecules having end-

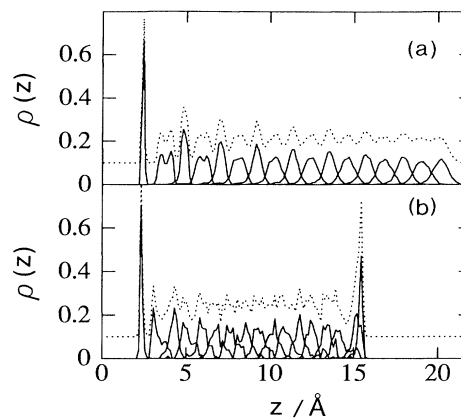


FIG. 2. Density profiles normal to the substrate plane for the individual pseudoatoms (solid lines) and the sum of all groups (dotted line, shifted upwards by 0.1). (a) Uncompressed SAM [8]. (b) SAM under full load.

*gauche* defects. This leads, in turn, as the table shows, to substantial changes in the numbers of molecules that are in all-*trans* conformations,  $f_M(g_0)$ , or contain only one defect,  $f_M(g_1)$ .

In summary, we find that the simulated SAM responds nearly elastically to microindentation caused by forces of the order of  $10^4 \text{ K \AA}^{-1}$ . Under these conditions, the monolayer is compressed to approximately 75% of its initial thickness; use of larger forces is likely to result in damage to the monolayer. Compression also leads to major changes in the mean molecular tilt and in the distribution of conformational defects along the chains, but the original structure is recovered as the load is removed, though there is some hysteresis. It is possible that the already weak level of hysteresis that we observe would be reduced if the loading/unloading cycle were carried out much more slowly. On the other hand, the jump to contact and the sticking of molecules to the tip in the final phase of unloading are features of the relaxation process that have well-defined physical origins. Significant differences in behavior on the two halves of the cycle must therefore be expected.

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