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Effect of Perturbing Strata on Chain Conformations and Ordering in Closely Packed Layered Structures of Chain Molecules

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Received January 8, 1993

Two-dimensional assemblies of packed alkyl chains can be viewed as stacks of microlayers or *strata*, where each stratum is comprised of closely packed atomic groups with intrachain bonding constraints between the strata. A perturbing stratum can be introduced by imposing spacing, symmetry, and size constraints in one of the strata that are incommensurate with close-packing requirements of the other strata. Using molecular mechanics and dynamics simulations, we study two concrete examples: a chemisorption potential incompatible with planar close-packing and a mid-chain bulky group. We find a progressive rearrangement from the packing at the perturbing stratum toward a lower energy-packing, at the expense of progressive distortions of the chains that increase their total bond angle energy. The experimental implications of such rearrangements are discussed briefly.

Introduction

Understanding the relationships between the molecular structure of chainlike molecules and how they are organized in aggregates is a fundamental problem. Such understanding is indispensable for achieving the capability of engineering assemblies with predicted architectures and material properties, starting from known molecular properties. Layered aggregates such as Langmuir monolayers at the air-water interface, Langmuir-Blodgett (LB) films, self-assembled monolayers (SAMs),¹ lipid membranes,² liquid crystals,³ and certain molecular crystals,⁴ in addition to being important in their own right, may be thought of as simpler prototypes for the general phenomena of aggregation. The common feature to all these layered systems is the presence of varying degrees of translational and orientational order in two dimensions. Within these layers, the ordering is thought to be dominated by intermolecular interactions.⁵⁻⁸ In the case of simple hydrocarbon chains, for example, this leads to the relationship between interchain spacing and chain tilt.⁹⁻¹¹ Hopefully, principles governing packing and ordering in simple assemblies will carry over to more complicated systems.

The idea that three-dimensional molecular crystals can be viewed and analyzed as an assembly of commensurate two-dimensional *molecular* layers has been developed in recent years by Scaringe.¹² Starting from the structure of

the molecule, and taking advantage of the fact that molecular assemblies can be described as close-packed, a technique for the prediction of molecular layer structures was developed. While testing the technique primarily on rigid aromatic molecules, a general suggestion has been made that "... If the molecule has several stable conformations then each one can be treated as a separate molecule ..."¹² It was also noted that "... with the exception of rotations around single bonds, the field produced by the surrounding molecules in the condensed phases produces only minor deformations of the gas-phase molecular structure ...".^{12,13} However, flexible molecules may have a large number of possible conformers; therefore, it may be difficult to use each of them separately in the calculations suggested above. Moreover, a brief search in the Cambridge Structural Database reveals that a large number of molecules that contain alkyl chains with $n > 6$ show dramatic deformations from the gas-phase structure due to packing. We shall get back to both points later.

Ulman and Scaringe took the idea of molecular commensurability one step further, developed the broader concept of commensurability of intraassembly planes, and discussed its importance in the formation of stable two-dimensional molecular assemblies.¹⁴ They suggested that it is not enough to examine the matching of cross-sectional areas (S_m) of different molecular parts. Thus, while matching of S_m is necessary, it is not sufficient at the next level of complexity. Hence, it is also important to consider the crystallographic commensurability of the different molecular parts within the assembly. Finally, they argued that even with S_m match and a given epitaxy, one still has the bond between these molecular parts, i.e., the valence geometry, to worry about. Nevertheless, incommensurability of molecular parts does not mean that a two-dimensional assembly cannot be formed. It is evident that the stability of a layered assembly can be augmented by chemisorption or physisorption to a solid surface, or by applying pressure, as is the case at the air-water interface in a Langmuir trough. However, while two-dimensional assemblies with perfect intraassembly match of atomic planes exhibit close-packing like a normal molecular crystal, increasing intraassembly mismatch decreases the

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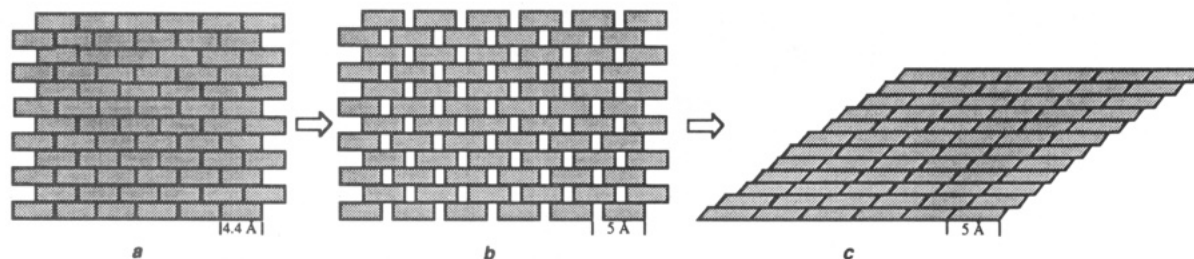


Figure 1. Perturbation of brick strata from close-packing. Note that free volume can be eliminated by changing the shape of the bricks, while keeping their volume constant.

cohesive energy and should lead to enhanced defect density, ultimately decreasing the layered structure stability.

Alkyl chains may be viewed as a segment of a one-dimensional crystal, simply because of the constant distance (2.52 Å) found between second-nearest-neighbor carbon atoms. Likewise, two-dimensional assemblies of packed alkyl chains, where chemisorption enforces coplanarity and thus a lamellar structure, might be viewed alternatively as stacks of microlayers or *strata*, where each stratum is comprised of closely packed atomic groups, i.e., methylene (CH_2) units (Figure 1). In fact, if one looked at the distribution of atomic positions—neglecting chemical bonding between these groups—these neatly ordered, tightly packed strata would be the most striking feature of such systems. Hence, we might ask what forces govern the ordering within these strata. Posing the problem in such a way, we note a striking similarity to many molecular crystals that have highly anisotropic, stratified packing. There, the forces *within* layers are strong, while the forces *between* a layer and its neighboring layers are relatively weak. The actual packing realized by any chain assembly will result from a competition between energetically favorable interchain packing and energetically costly minor distortions of the intrachain bonds, as well as entropic effects. Understanding chain-chain packing may be facilitated, in many cases, by analysis in terms of the packing of these stacked strata.

To further elaborate on this notion, let us consider an ideal monolayer system composed of straight chain alkanes with their tails attached to an *atomically flat* substrate with a spacing of 4.4 Å between attachment points (Figure 1a). In this assembly, the intrastratum packing energy is minimized without putting any strain on the individual molecules. Now, if the system is perturbed by the introduction of a single stratum with packing or spacing different from the others, free volume will be introduced into the system (Figure 1b). For example, one could create a perturbed system by moving the attachment points from ~4.45 Å—as is the case for alkanethiolates chemisorbed on Ag(111)—to 4.97 Å—as is the case for alkanethiolates chemisorbed on a Au(111) surface.¹⁵ As a result, close-packing can no longer be present for undistorted vertical alkyl chains. In the perturbed system, the packing requirements of the perturbing stratum (bottom in this case) and those of the other strata conflict. How will such a system accommodate the conflicting demands? In this case the system responds by tilting the chains over in such a way as to reestablish optimum van der Waals (vdW) contacts within and between the strata.¹⁰ The rearranged strata occupy the same volume, although they are different in shape and one favorable $\text{CH}_2\cdots\text{CH}_2$ interaction is lost.

It is the purpose of this paper to develop the concept of a perturbing stratum and study its consequences for two concrete examples, a chemisorption potential incom-

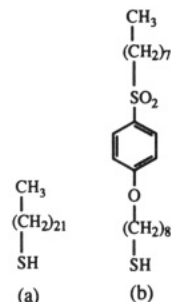


Figure 2. Docosanethiol (a) and octyl 4-(8-mercaptooctyloxy)-phenyl sulfone (b).

patible with planar close-packing and a mid-chain bulky group. These examples correspond to specific self-assembled monolayer systems (thiolates on gold) that were investigated experimentally in great detail.^{15,16}

Thiol derivatives (R-SH) adsorb spontaneously onto clean gold surfaces (Au/Si) to form ordered monolayers.^{17–21} These two-dimensional assemblies are excellent model systems for the study of packing and ordering of molecules with increasing complexity. While the chemisorption mechanism is not understood fully, it is now widely accepted that the adsorbing species is the thiolate (RS^-). This has been shown by X-ray photoelectron spectroscopy (XPS),^{22,23} FTIR spectroscopy,²³ Fourier transform mass spectrometry,²⁴ electrochemistry,²⁵ and Raman spectroscopy.²⁶ The bonding of the thiolate group to the gold surface is very strong (homolytic bond strength is ~44 kcal/mol²⁷).

Electron diffraction studies (both high^{15,28} and low energy²⁹) of monolayers of simple alkanethiolates (docosanethiol, Figure 2) on Au(111) surface show that the symmetry of sulfur atoms is hexagonal with an $\text{S}\cdots\text{S}$ spacing of ~5 Å, and calculated area per molecule of 21.4 Å².

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Helium diffraction,³⁰ and atomic force microscopy (AFM)³¹ studies confirmed that the structure formed by docosanethiol on Au(111) is commensurate with the underlying gold lattice and is a simple ($\sqrt{3} \times \sqrt{3}$)R30° overlayer. Hence, the S...S spacing corresponds to the second-nearest-neighbor distance on Au(111). Recent ab initio geometry optimization of HS⁻ and CH₃S⁻ on cluster models of Au(111) surfaces support this chemisorption picture.³² These calculations reveal that the thiolate group is chemisorbed at the hollow sites on the Au(111) surface. IR spectra,¹⁷ electron diffraction,^{15,28,29} and helium scattering studies³⁰ indicate a high degree of translational ordering, corresponding to hexagonal close-packing of parallel all-trans chains, tilted at ~35°, reminiscent of a two-dimensional crystal. Recent molecular mechanics and dynamics simulations of simple alkanethiolates on Au(111) provide a detailed picture of packing and ordering within the monolayer.^{10,33} The structure emerging from these simulations is a periodic, closely packed arrangement of tilted chains, predominantly in the all-trans conformation, with minimal elastic energy associated with the intrachain degrees of freedom, and with a relatively small number of gauche defects, concentrated at the chain termini. The uniform chain tilt arises because it optimizes the vdW interactions between atoms on separate chains, under the constraint of fixed separation between thiolate groups, imposed by the chemisorption potential of the Au(111) surface. Note, in particular, that the thiolate, methylene, and methyl groups are arranged in two-dimensional hexagonal close-packed strata. These strata are, in turn, stacked in such a manner as to minimize the total vdW energy within the constraint of fixed chain conformation.

On the other hand, the symmetry of sulfur atoms in a monolayer of docosanethiolate on Au(100) is a simple square lattice with an S...S spacing of 4.54 Å.¹⁵ Both the square lattice symmetry and S...S spacing are not commensurate with the intralayer close-packing arrangement of methylene groups favored by their vdW interactions.¹⁰ Therefore, this is an excellent example of the concept of perturbing stratum.³⁴

Recently, we published a detailed experimental work on SAMs containing bulky aromatic groups (an example is depicted in Figure 2).¹⁶ We found that the position of the bulky moiety within the chain significantly affects the intermolecular fitting together of both the alkyl chains and the rigid aromatic part. Thus, the introduction of a bulky group into an alkyl chain will serve as a second example of a perturbing stratum to be considered here.

We note that our ability to understand the relationship between the structures of an individual molecule and its assembly is a function of the analytical tools we use. In the case of monolayers, different analytical techniques provide information on different aspects of the assembly. For example, electron diffraction studies provide information mainly on the chemisorbed thiolate groups,^{15,28,29} helium scattering studies probe only the chain termini,³⁰ and other analytical tools can give only average structures.

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Typically, it is not clear a priori how to combine and interrelate those isolated pieces of information so as to construct a comprehensive microscopic picture of the assembly. This becomes even more complicated when complex molecules, such as one of the examples in this paper, are of interest. Thus, realistic molecular mechanics (MM) and dynamics (MD) simulations provide a natural complement to such experiments and should enable one to gain a detailed, comprehensive understanding of the balance of forces determining conformation and packing at the molecular level.

In this paper we develop the concept of *perturbing strata* in a closely packed layered hydrocarbon structure and consider its effects on intramolecular conformation and intermolecular organization. The particular examples presented in this paper are models of specific self-assembled monolayer systems of thiolates on gold, which have been previously studied experimentally. We present MD simulations of docosanethiolate on Au(100) and of octyl 4-(8-mercaptooctyloxy)phenyl sulfone (Figure 2) on Au(111) as specific examples and discuss the molecular structure in these monolayers within the framework of this concept. We find in both cases that the disruption of intrastratum close-packing is greatest in the strata adjacent to the perturbing stratum. The disruption lessens progressively through several strata before optimal intrastratum close-packing is restored. This gradual healing is achieved at the cost of many small intrachain distortions.

Simulation Methods

Force Fields. To speed up the computation, most MD simulations coarse-grain the atomic representation to united atoms. However, for a tightly packed system such as LB and SAMs, the use of united atoms representation for the alkyl CH₂ and CH₃ groups does not allow a full expression of molecular stereochemistry. Thus, as in-depth understanding of packing and ordering in the two model systems presented here requires an explicit representation of all atoms, including hydrogens, in the atomic force-field model. This sets a fundamental limitation on the length of the time step used in the MD simulations, which cannot exceed 1 fs, if the vibrations of the C-H bonds are explicitly accounted for. In the present simulations we have used the MM2 force field,^{35,36} with augmentations elaborated below for each system. The original MM2 force field represents the vdW interactions by an exp-6 potential, which is computationally costly. Therefore, we have replaced it by a 12-6 Lennard-Jones potential.

Energy Minimization and Molecular Dynamics. Energy minimization provides solutions for local minima of the potential energy function of the molecular assembly, with or without periodic boundary conditions. Sorting out the global minimum among them is rather complicated.³⁷ A local minimum is needed also as an input for MD simulations. The energy of the system in the present studies was minimized using a variant of the constant stress minimization method³⁸ as implemented in the POLY-

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(37) For an example of a systematic search method for global minima of packing energies for two-dimensional assemblies of rigid organic molecules, see ref 9.

(38) The value chosen for the constant stress constraint was an external pressure of 1 atm in the x- and y-directions. This external pressure was kept during energy minimization but was set to zero during MD simulations to allow the simulation cell to adjust its size and shape.

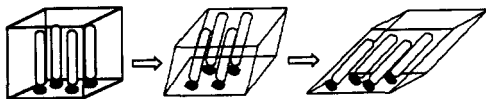


Figure 3. Deformation of cell shape and variation of its volume allowed through constant stress minimization and dynamics.

GRAPH software.³⁹ This allows for variation of the unit cell volume and shape (Figure 3), as well as of the intra- and intermolecular degrees of freedom within the cell. The use of constant stress MD at a finite temperature explores a whole region of the phase space around the starting minimum, yielding an ensemble of conformations fluctuating in time from which an *average* conformation can be calculated.

In many cases the problem of getting stuck in a rarely visited local minimum—which is not representative of the ensemble—can be avoided by using simulated annealing energy minimization methods,⁴⁰ in which MD steps are employed to get the system out of a local minimum. MD methods have been applied lately with increasing success to systems such as amphiphilic monolayers,^{41–44} lipid bilayers,^{45–49} paraffin crystals,^{50,51} and self-assembled monolayers of simple alkanethiolates on gold³³ and are a powerful tool to address the issue of packing and ordering in molecular organizes of complex molecules. We used a variant of the constant stress (Parrinello-Rahman) MD method as implemented in the POLYGRAPH software.³⁹ The time step for the MD was chosen to be 1 fs. We note that in both energy minimization and MD simulations we used 8 Å as a finite cutoff for the nonbond interactions.

Representation of Chemisorbed Monolayers. It is clear that chemisorption potential plays an important role in the delicate balance of forces determining the conformation and packing of SAMs. Thus, accurate MM and MD simulations require the implementation of chemisorption parameters of the specific system, expressed through classical force field terms.⁵² We note, however, that the primary purpose of this paper is to investigate the *perturbing stratum concept* and its effects. Therefore, a simple representation of chemisorption, using a force field that neglects many aspects of the chemisorption phenomena, is suitable.

Thus, we constrained the thiolate groups to the chemisorption plane by means of harmonic torsion and inversion

constraints, the details of which are discussed below for each specific example. Isolated monolayer conditions were effected by constraining the vertical edge of the periodic simulation cell to a distance large enough so that the separation between atoms in vertically adjacent cells was kept beyond the cutoff of the nonbonded interactions.

Results and Discussion

Docosanethiolate Monolayer on Au(100). The monolayer on Au(100) was simulated by a periodically replicated simulation cell subjected to constant stress and containing four molecules (all-*trans*-CH₃(CH₂)₂₁SH). The molecules were originally arranged in a square,¹⁵ with the sulfurs coplanar and the molecular axes normal to the sulfur plane. The square symmetry was maintained throughout the simulation by the imposition of harmonic inversion, torsion, angle bend, and distance (4.54 Å)¹⁵ constraints.⁵⁶ The energy of the system was minimized using the constant stress minimization method. Subsequently, a 100-ps constant-stress, constant-temperature (50 K) MD trajectory was generated. The alkyl chains in the resulting monolayer are tightly packed and exhibit very little thermal disorder.

The time evolution of selected components of the system energy over a period of 100 ps is shown in Figure 4. We see that it takes slightly over 50 ps to achieve equilibration. Interestingly enough, the onset of equilibration coincides with an abrupt decrease in both the total potential and the total van der Waals energies. The increase in total angle bend energy and torsional energy is more gradual. This can be interpreted as locking of the CH₂ units into an optimal close-packed arrangement within and between the strata at the expense of increased chain distortion. The nature of these distortions can be seen in Figure 5, where two side views of a 6 × 6 assembly (three simulation cells by three simulation cells) of a typical low energy snapshot from the equilibrated portion of the MD trajectory are shown. In Figure 5a we observe both a concerted lean (~30°) of the chains and a mild bending distortion of the chains. We define the tilt as an angle from the normal within the plane that bisects the methylene groups, and the *lean* as the angle from the normal in a plane perpendicular to it. Figure 5b, a view parallel to the other face of the simulation cell, shows that alternating rows of chains acquire a staggered tilt (~5°) from the surface normal. Notice that while in alkanethiolate monolayers on Au(111) there is a *tilt* of ~30° and a *lean* of ~22°,¹¹ in monolayers on Au(100) there is a *lean* of ~30° and a *tilt* of ~5°. We suggest that the tilt and lean result from the relationship between molecular spacing and the dimensions of the methylene group, the latter being oval in shape with a ratio of ~1.13 between the two axes (Figure 6). Outka et al.⁹ and later Ulman et al.¹⁰ noted that tilt of alkyl chains should obey the formula $\phi = nR/D$, where ϕ is the tilt angle from the normal, $R = 2.52$ Å, D is the minimum van der Waals separation between the chains (4.24 Å from MM simulations, ~4.45 Å from crystallographic data⁵⁷), and $n = 0, 1$, or 2. While not carrying out detailed calculations, we believe that a corresponding formula should exist for the lean. Thus, the choice of molecular orientation within the assembly might be determined by the best combination of tilt and lean. Notice that in the lean the vdW interactions are

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(54) Spohr, E. *J. Phys. Chem.* 1989, 93, 6171. Spohr, E. *J. Chem. Phys.* 1990, 141, 87.

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(57) Seto, T.; Hara, T.; Tanaka, K. *Jpn. J. Appl. Phys.* 1968, 7, 31.

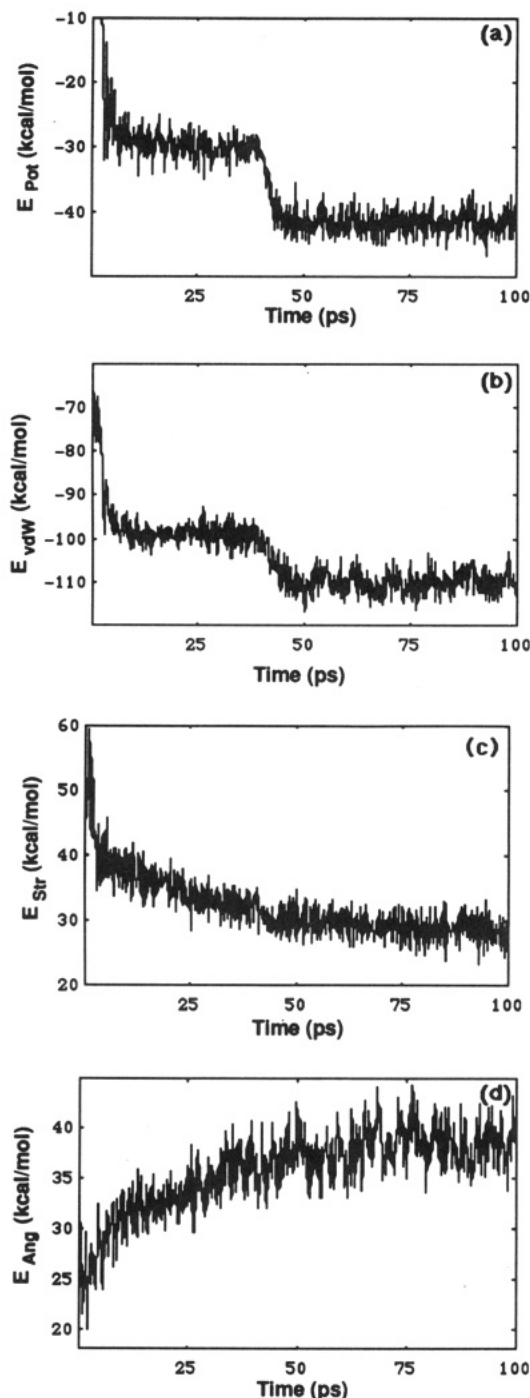


Figure 4. Time evolution of various contribution to total energy in the MD trajectory of the docosanethiol system on Au(100). The total potential energy, total van der Waals energy, total angle bend energy, and total bond stretch energy are represented by a, b, c, and d, respectively.

mainly H...H, while in the tilt there is a significant contribution from C...C interactions. Thus, it can be assumed that the larger contribution to the vdW energy comes from the tilt, and hence it should be the dominating factor in determining molecular orientation. In the present case, the S...S distance is 4.54 Å, which leaves very little if any free volume in the tilt direction. In the other direction, where the dimension of the methylene group is smaller, the difference between the distance and the group dimension is the same as the distance between rows of chains on Au(111). Both there and in this case we found, using the same MM calculations, a lean of $\sim 22^\circ$, provided that the chains are undistorted and adopt on all-trans

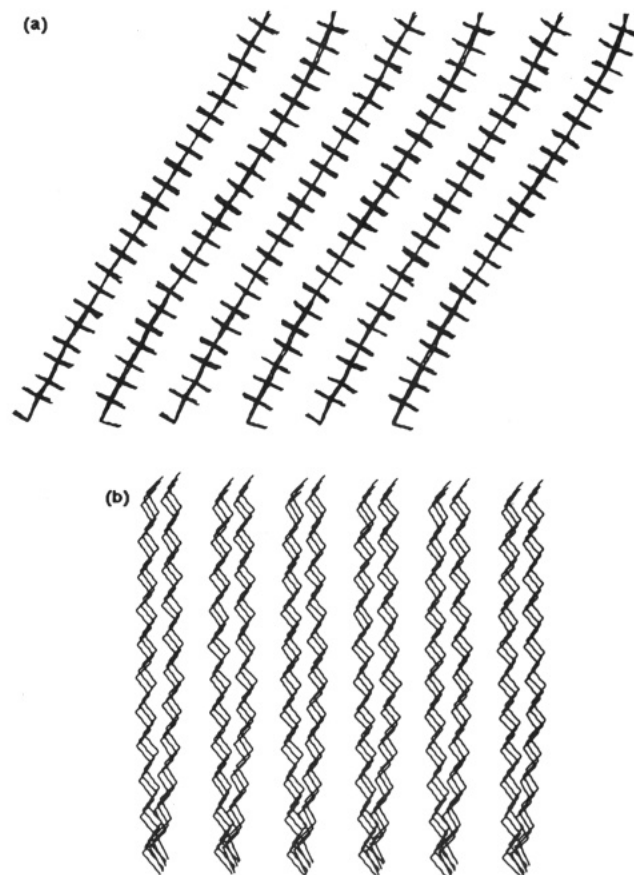


Figure 5. Two side views of a typical low energy snapshot from the equilibrated portion of the MD trajectory ($t = 83.7$ ps).

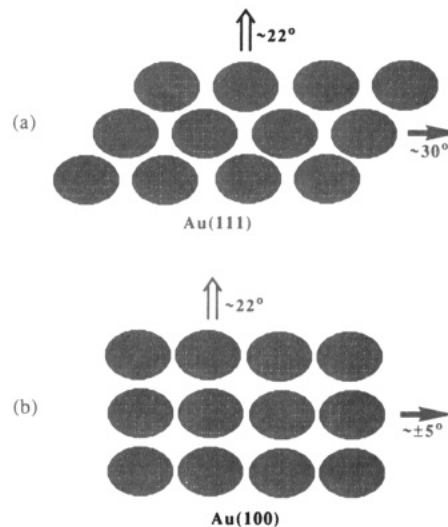


Figure 6. Tilt (black arrow) and lean (hollow arrow) directions and magnitudes for alkanethiolate monolayers on Au(111) (a) and Au(100) (b).

conformation.⁵⁸ We believe that the chain distortion evident in Figure 5a permits the increased tilt. It is conceivable that such differences can be detected using spectroscopic techniques, such as FTIR; however, caution should be called for in using calculations that assume an "ideal" chain conformation for systems such as thiolates on Au(100).

A clearer picture of the variation of the intralayer close-packing emerges from a stratum-by-stratum examination.

(58) Eilers, J. E. Unpublished results.

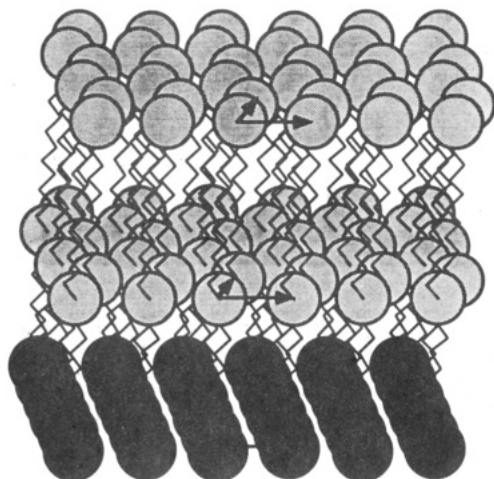


Figure 7. Packing of atomic layers within the monolayer of Figure 4. Shown as spheres are the sulfur atoms within the bottom layer, the carbon atoms within the tenth methylene layer from the thiols, and the carbon atoms within the top methyl layer.

Figure 7 presents a *typical* low-energy snapshot from the equilibrated portion of the MD run. Note the perfect square symmetry of the bottom thiolate stratum, the nearly hexagonal-close-packing obtained in one of the middle strata, and the greater distortion from hexagonal-close-packing in the top methyl stratum.

Figure 8 presents the distribution of angles defined in Figure 7 during the last 50 ps of the 100-ps MD run for the docosanethiolate monolayer on Au(100). For completion, we included in Figure 8 the distribution of the C...C...C angle in the first CH₂ stratum (Figure 8b). Notice that the atomic nuclei are not coplanar, except for the S-layer. However, the deviation of the C-atoms from the nuclear least-squares (NLS) plane of their respective layers should not have any significant effect on the issues discussed here. The narrow distribution of the S...S...S angles around 90° is evident.⁵⁶ On the other hand, a significant distortion of the C...C...C angles from the square lattice geometry already is present in the first CH₂ stratum (linked to the sulfur). The C...C...C angles in the tenth CH₂ stratum fluctuate around 72°, while that of the terminal CH₃ stratum exhibit a wide range of fluctuation around 77°. Notice that the MD simulations were carried out at 50 K, which is the temperature of the helium diffraction experiments;⁵⁹ therefore, helium diffraction from such a surface, which does not have a unique symmetry, may result in a quite complicated scattering data.⁵⁹

A minimized structure was obtained from the conformation depicted in Figure 6 and analyzed. Figure 9 shows (a) the nonbonded interactions and (b) the angle bend energy within the various methylene strata in the minimized structure. Notice the jump in energy between the first and second methylene strata. This can be connected to the considerable deviation from 90° of the C...C...C angle, as discussed above.

A stratum of methylenes packed in a square lattice can be deformed toward a trigonal hcp arrangement by the sliding of alternate rows of methylenes (Figure 10). Of course, sliding in opposite directions gives structures that have the same energy and should give the same diffraction data. The tilting of alternate rows seen in Figure 6b effects this kind of deformation in the individual strata. It is clear from Figure 7, however, that the minimum energy is a distorted hexagonal close-packed structure. The

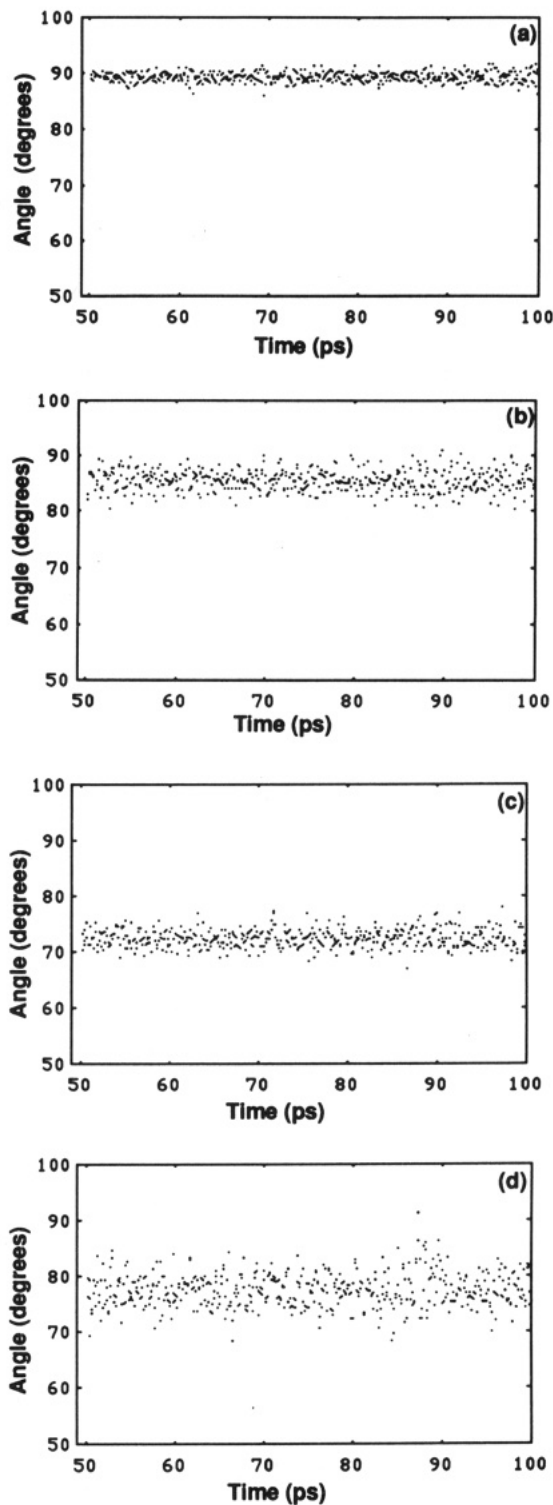


Figure 8. Distribution of angles defined in Figure 7 during the last 50 ps of the 100-ps MD run for the monolayer in Figure 4. For completion, we included the distribution of the C...C...C angle in the first CH₂ group. Notice that Figure 7 presents a minimum energy snapshot, which is represented here by one point.

chemisorption and intramolecular bonding constraints restrict the magnitude of sliding. The salient features that emerge from this discussion are as follows: (a) progressive rearrangement from [100] packing at the bottom chemisorbed thiolate stratum to a more closely packed, distorted hexagonal arrangement toward the tenth methylene stratum; accompanied by (b) a distortion of the bond angles along the chains, which increases the total bond angle energy of the chains, which are still in an all-trans conformation.

(59) Liu, G., Ph.D. Thesis, Princeton University, 1992.

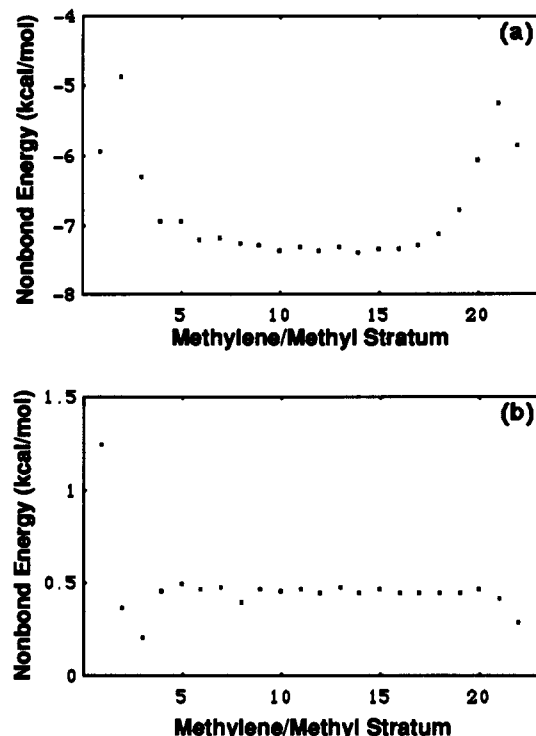


Figure 9. (a) Nonbonded interactions and (b) the angle bend energy within the various methylene strata in the minimized structure. Strata number is counted from the thiolate group.

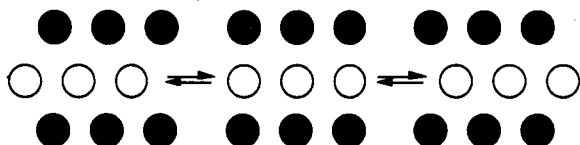


Figure 10. Deformation of a square lattice of methylene groups toward a trigonal hcp lattice by sliding alternate rows of methylene groups.

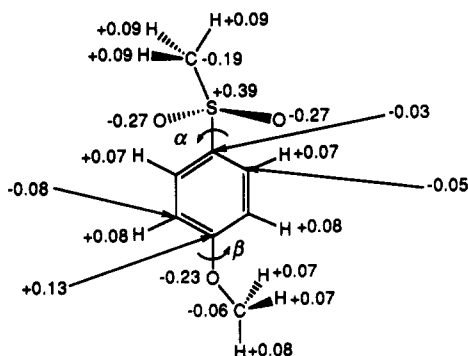


Figure 11. 4-Methoxyphenyl methyl sulfone used for calculation of α and β . Partial charges are also shown.⁴⁹

Octyl 4-(8-Mercaptooctyloxy)phenyl Sulfone monolayer on Au(111). *Calculation of Missing Parameters in the MM2 Force Field.* We chose to adhere as closely as possible to the published MM2 force field. However, terms for the torsional contributions to the strain energy of rotation around the dihedral angles α and β (Figure 11) are not part of the published parameter set or of the MACROMODEL extensions. We derived the constants for these contributions from semiempirical quantum mechanics using the MOPAC program⁶⁰ with the PM3 method. Taking 4-methoxyphenyl methyl sulfone (Figure 11) as the model molecule, we obtained a plot of the

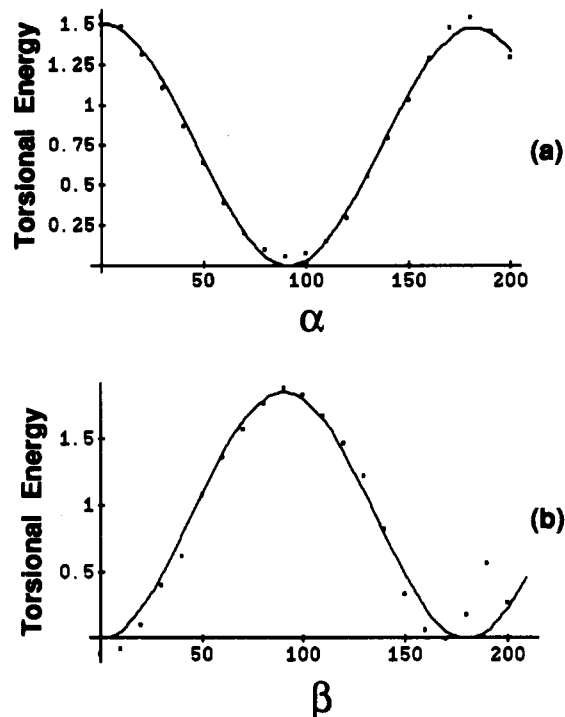


Figure 12. Derived torsional energy function for MM2. α - (a) and β -bond (b) indicated in Figure 11.

molecule's energy as a function of the dihedral angle in question. (The angle was stepped in 10° increments and all other geometry variables were fully optimized at each step.) Similarly, we obtained the dependence on this dihedral angle of the other contributions to the molecular mechanics energy.⁶¹ (The torsional energy of the dihedral angle being investigated was set to zero!) After putting the quantum mechanics and MM curves on a common energy scale (minimum = 0.0), their difference could be ascribed as the missing torsional energy function. The difference curves for α and β (Figure 12) were then fit with the MM2 torsional energy expression. No attempt was made to develop any cross terms.

Constant Stress Energy Minimizations. A single isolated molecule with partial atomic charges was minimized (using the conjugate-gradients method, with dielectric constant $\epsilon = 1$), resulting in the all-trans molecular conformation shown in Figure 13. Four such molecules were placed in a square arrangement in an orthogonal unit cell with dimensions significantly larger than the contact dimensions (6 Å), and periodic boundary conditions were invoked. This assembly was minimized under constant stress conditions, using harmonic constraints that restricted the sulfur atoms to a plane.⁶⁴ The result of this

(61) Partial charges (Figure 10) were taken from a Mulliken population analysis of an ab initio 3-21g* calculation.^{62,63}

(62) Mulliken, R. S. *J. Chem. Phys.* 1955, 23, 1833, 1841.

(63) Hayes, D. M.; Kolleman, P. A. *J. Am. Chem. Soc.* 1976, 98, 3335.

(64) Minimization started from this initial configuration (Figure 15), with the electrostatics turned on, traps the system in a nonphysical local minimum that is a loosely packed assembly. However, minimization with the electrostatics turned off gave initially a close-packed assembly with the two alkyl chains in a syn configuration. Rotating the upper chains 180° (resulting in an anti configuration), followed by minimization, gave a second close-packed structure with the same energy. Thus, two close local minima exist, corresponding to very different closely packed structures. A subsequent minimization with the electrostatics turned on (with $\epsilon = 1$) leads to large energy separation between these two structures, with a minimum significantly lower than the one corresponding to the loosely packed system mentioned in the text. Hence, while the vdW interactions are the major contribution to the close-packing of the assembly, in a case where two close local minima exist, introduction of electrostatics was found to pick only one of them.

(60) Stewart, J. J. P., Quantum Chemistry Program Exchange (QCPE) No. 455.

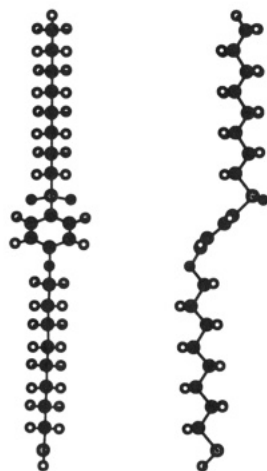


Figure 13. Two side views of octyl 4-(8-mercaptooctyloxy)phenyl sulfone molecule minimized in isolation.

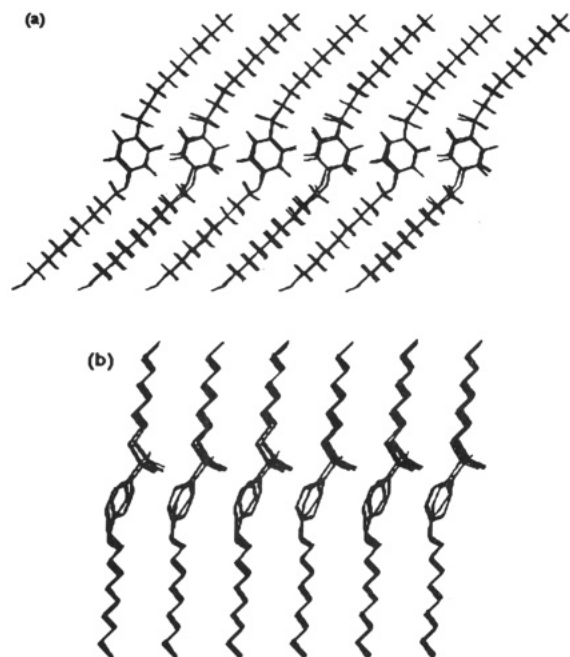


Figure 14. Two side views of 6×6 assembly of octyl 4-(8-mercaptooctyloxy)phenyl sulfone molecules (three simulation cells by three simulation cells), after constant stress minimization under monolayer constraints.

minimization is shown in Figure 14. Notice that this minimization process gives a local minimum. Within the minimized assembly, the chains are nearly all-trans with an overall lean of $\approx 30^\circ$ from the surface normal. This lean is in a plane that is about parallel to that of the phenyl ring. A very small tilt, in a plane that is about perpendicular to that of the phenyl ring, is observed, mainly in the upper chain. This is in agreement with the rectangular shape of the phenyl projection, with its different dimensions. Thus, since the phenyl-phenyl interactions determine the short chain-spacing, a small rotation of the alkyl chain with respect to the aromatic moiety will bring the spacing to that required for an effective tilt. On the other hand, the larger spacing in the perpendicular direction explains the lean angle of $\approx 30^\circ$. Noticeable chain distortions can be seen near the sulfone groups in Figure 14a. The packings of the sulfonyl groups within individual layers of the assembly are shown in Figure 15.

Constant Stress Molecular Dynamics. The minimized assembly described above served as the starting configuration for a 200-ps constant stress MD run at 300 K. The

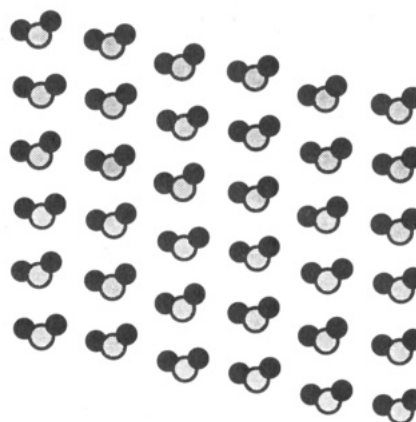


Figure 15. Packing of the SO_2 group layer within the monolayer of Figure 14. Note the two-dimensional ordering of the dipoles.

time evolution of various contributions to the total energy of the monolayer is shown in Figure 16. Notice that it takes on the order of 100 ps for the system to equilibrate. It seems that the electrostatic energy is the dominant contribution to the total potential energy, and equilibration follows soon after a sharp drop in the electrostatic energy, which can be attributed to the lock-in ordering of the molecular dipoles into states that lower the energy of the system. This is apparent from the ordering of the SO_2 groups, as depicted in Figure 15. Interestingly enough, this is accompanied by an increase in angle bend energy giving rise to chain distortions. The final snapshot from the MD trajectory is shown in Figure 17. Due to thermal motions, the assembly looks much more disordered than the minimized structure. Moreover, the lower chains are more disordered than their upper counterparts. Detailed examination reveals that most of this disorder is "chain-to-chain" rather than within the chains and is due to rotations about the ether bond. This can be seen by viewing of the animated trajectory or by following the time evolution of the dihedral angles. The time evolution of selected angles in one of the chains after "equilibration" is shown in Figure 18. For the upper chain we see the terminal methyl "twirl" (i), the occasional gauche defects for (h), and essentially constant values for (g) and (f) and the other interior C-C bonds. In contrast, the lower chain shows many more variations.

Conclusions and Arguments

Organization of complex, semiflexible organic molecules within quasi two-dimensional assemblies is the result of a delicate interplay between substrate-adsorbate interactions, nonbond interactions between adsorbates—electrostatic and vdW forces—and intramolecular interactions such as bond stretches, angle bends, and torsions. As a first level of approximation, packing of alkyl chains can be considered as packing of rigid bodies, similar to the description suggested by Kitaigorodski, Scaringe, and others for molecular crystals. On this level, chemisorption constraints lead to the loss of three translational degrees of freedom per monolayer chain.

Packing competition between vdW interactions and planar constraints in assemblies of chain molecules was addressed before on this level of approximation.⁶⁵⁻⁶⁸

(65) Larsson, K. *Chem. Phys. Lipids* 1977, 20, 225.

(66) Pearce, P. A.; Scott, H. L. *J. Chem. Phys.* 1982, 77, 951.

(67) Safran, S. A.; Robbins, M. O.; Garoff, S. *Phys. Rev. A* 1986, 33, 2186.

(68) Carlson, J. M.; Sethna, J. P. *Phys. Rev. A* 1987, 36, 3359.

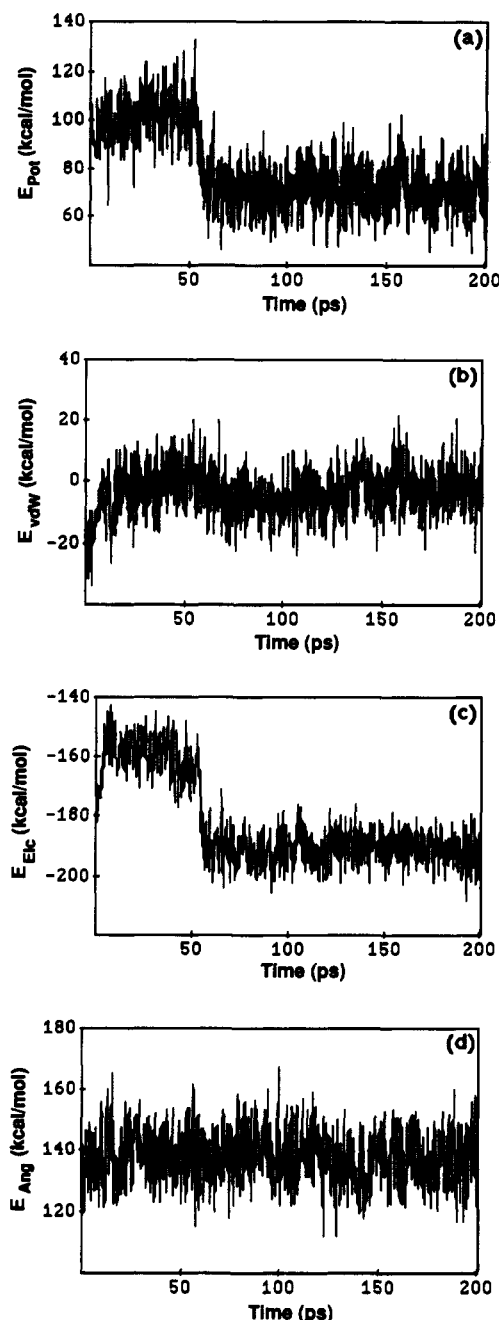


Figure 16. Time evolution of various contribution to total energy in the MD trajectory of the monolayer in Figure 14. The total potential energy, total van der Waals energy, total electrostatic energy, and total bond torsional energy are depicted by a, b, c, and d, respectively.

Safran et al.⁶⁹ considered the chains as rigid bodies that are confined to a common plane by headgroups, thus losing one translational degree of freedom. Carlson and Sethna⁶⁸ considered two-dimensional assemblies of chain molecules with vdW interactions and a planar distance constraint imposed by the headgroups. They studied a one-dimensional model where the chain molecules were approximated by *rigid rods*. The coupling between the headgroups and chains was described by an energy contribution associated with the tilt of the rods relative to the plane defined by the headgroups. Carlson and Sethna⁶⁸ derived a phase diagram for their model as a function of the ratio of lengths describing the fixed headgroup separation and the preferred vdW distance (head-chain size mismatch), and of the ratio of energy couplings associated with vdW attrac-

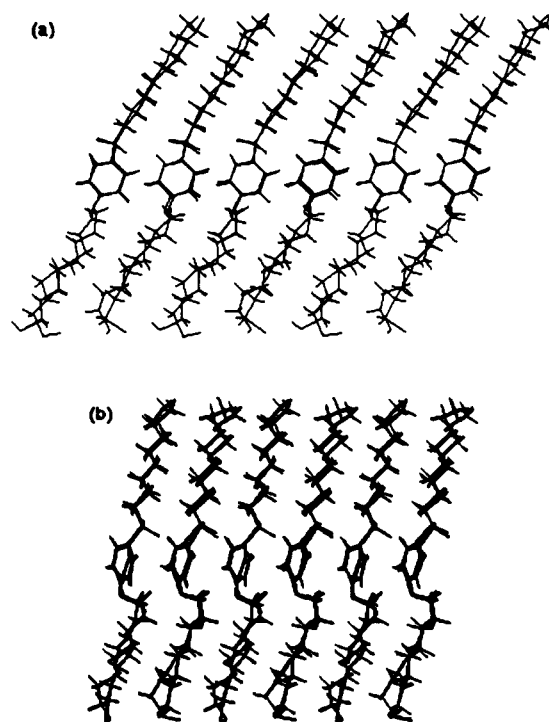


Figure 17. Two side views of a typical low energy snapshot from the equilibrated portion of the MD trajectory ($t = 200$ ps).

tion and molecular tilt. The plane of headgroups discussed in these works can be considered as a planar perturbation of the type discussed here.

In self-assembled monolayers, if the chemisorption sites form a nonclose-packed lattice (e.g., square lattice), the system cannot attain a voidless, optimal close-packing arrangement, given the remaining three rotational degrees of freedom per chain. Alkyl chains, however, are semiflexible, and thus should be able to fill some of the voids by different rearrangements of the *internal* degrees of freedom. Therefore, it is appropriate to use a less coarse-grained level of approximation to permit rearrangements toward a more closely packed structure. At this level, the arrangement of the assembly results from packing of the groups comprising the chain (e.g., methylene, methyl, sulfonyl, phenyl, etc.), each considered as a rigid body, under bonding and chemisorption constraints. Those constraints result in the formation of well-defined strata.

Representation of chainlike molecules by *rigid rods* results in the apparent loss of molecular details. Therefore, relaxation of the planar perturbation in the Carlson and Sethna⁶⁸ model could be realized only through *homogeneous* molecular tilt, or by an inhomogeneous phase of tilt defects propagating *parallel* to the plane of the perturbation. This is quite different from the relaxation mechanism suggested here, which is by means of chain distortions propagating *perpendicular* to the perturbing stratum. Nevertheless, for large enough mismatch between the imposed chain separation and the preferred vdW distance within the perturbing stratum, one cannot rule out appearance of defect relaxation *parallel* to as well as *perpendicular* to the stratum. This may lead to a complex picture, coupling the two types of defect relaxation. The use of full atomic representation for the molecules in our MM and MD simulations constrained our study to a small number of molecules in a periodic simulation cell. We note that using constant stress MD simulations can be problematic for systems exhibiting incommensurability between competing periodicities, such as implied in the phase diagram of Carlson and Sethna.⁶⁸

(69) Klein, M. L.; Hautman, J. Private communication.

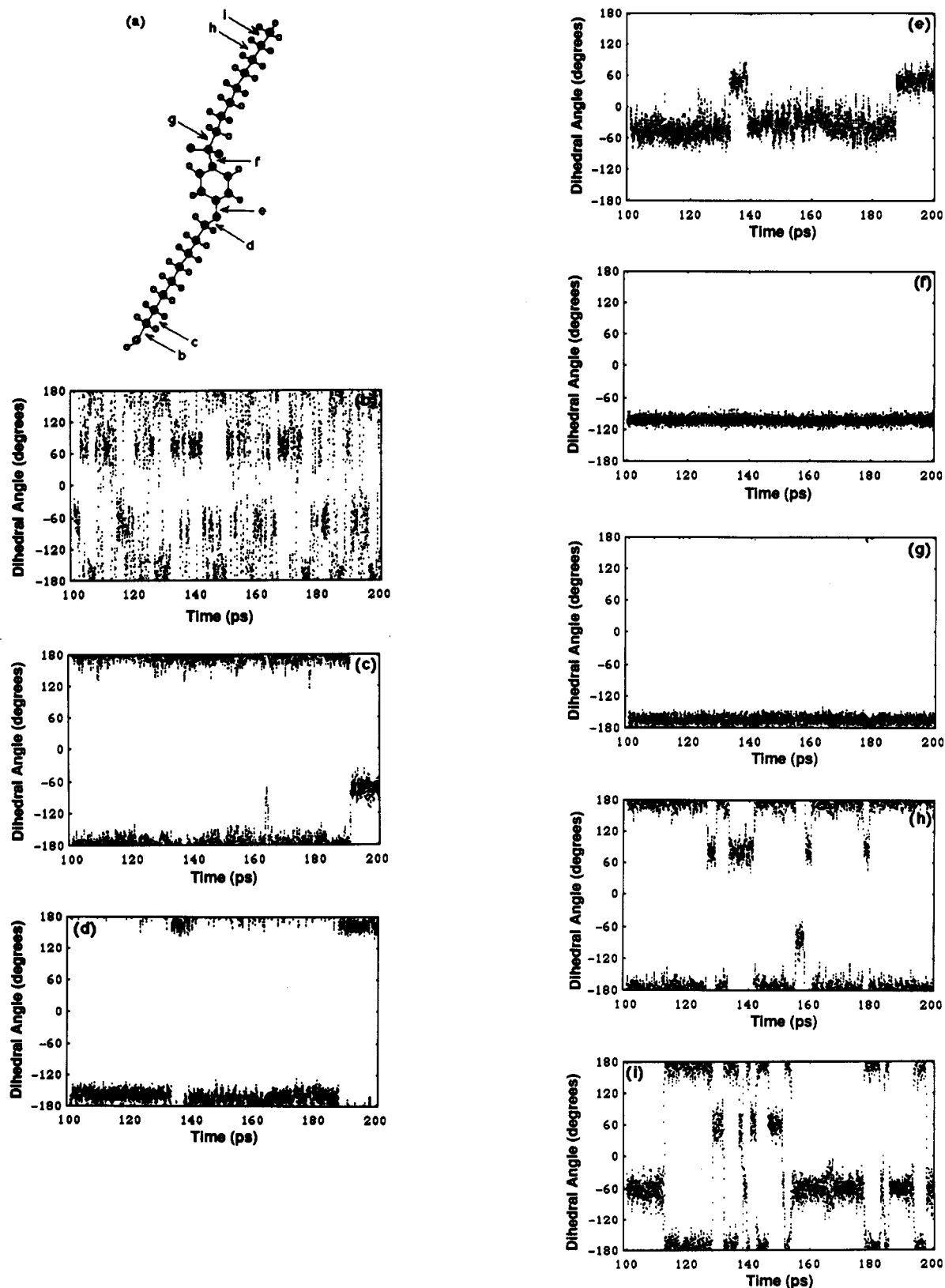


Figure 18. Distribution of torsional angles for various bonds along the chains in both sides of the aromatic moiety during last 100 ps of the 200-ps MD run for the monolayer in Figure 17 (b–i). The specific bonds are depicted in part a.

This prevented us from studying relaxation mechanisms *parallel* to the perturbation stratum. However, we stress that the systems simulated here were relatively close-packed where such relaxation mechanisms are not expected to play a major role. In any case, once the constraint of chain rigidity is relaxed, the existence of inhomogeneous phases of tilt defects at large areas per molecule is questionable. It has been demonstrated, both experi-

mentally and in molecular simulation, that increasing area per headgroup leads to coexistence of two-dimensional crystalline domains embedded in a continuous melted phase.³³

In assemblies of chain molecules composed of units identical or similar in size and chemical nature, the nonbonded interactions can be viewed as favoring stratum-by-stratum close-packing under bonding constraints.

When a stratum having different symmetry, spacing, or cross-sectional unit area is introduced into the close-packed assembly, it results in the increase of intrachain elastic energy, mainly through angle bend distortions in the vicinity of the perturbing stratum. These chain distortions tend to restore closer vdW contact between the chains, thus counteracting the intramolecular energy increase. The molecular conformation and the interchain packing in the assembly result from the competition between these free energy contributions.

In this paper we have studied two systems. In the first, chemisorption imposed a square symmetry, while in the second, the perturbing stratum was a bulky group introduced into the alkyl chain. Using MM and MD simulations, we were able to see in both cases the propagation of chain distortions and packing rearrangements from the stratum of defects. In the case of simple alkanethiolates on Au(100), this resulted in significant distortion of the planar packing from the simple square lattice arrangement of the S-atoms toward pseudo-hexagonal close-packing. Similar results were obtained by Hautman and Klein using the united atom approach, with a much larger number of molecules in the periodic simulation cell.⁶⁹ In the case of alkanethiolate chains containing a bulky aromatic chromophore, chain distortions and packing rearrangements were localized in relatively few strata of methylene groups in the vicinity of the aromatic moiety.

The significance and scope of the mechanism for packing rearrangements through chain distortions around a stratum of defects extend beyond the two specific examples discussed here. Similar mechanisms for propagation of planar perturbation about a plane of defects are expected in many other two- and three-dimensional assemblies of chainlike molecules, such as LB films, organic crystals and some closely packed liquid crystalline phases. In fact, the role of chain-bending around a dislocation plane in polymer and alkane crystals has been previously discussed.⁷⁰ However, there are significant differences between our examples and polymer crystals due to their high molecular weight and chain-folding effects.

The strategy of searching for low energy arrangements of two-dimensional assemblies of chainlike molecules by packing individual, rigid conformations,¹² is useful as a first level of approximation. Such a strategy ensures that a systematic mapping of packing energy minima takes place. Following this procedure, the lower energy packings can be further refined by relaxing internal chain degrees of freedom in MM and MD simulations. The present paper corresponds to such a refinement about a single local minimum. Our purpose here was to investigate the possible mechanisms for a progressive rearrangement for the packing at a perturbing stratum toward a low energy packing. We did not attempt a systematic search of all possible starting packings, and thus the two examples studied should be considered merely as illustrations. For quantitative predictions, a systematic search can be carried out using a combination of the methods alluded to above.

The experimental implications of a planar defect structure proposed here pose an interesting challenge. In the simple case of alkanethiolates on Au(100), one can suggest several tests for our simulation results. An obvious test for the assembly reorganization from the base-centered square lattice of the thiols to a pseudo-hexagonal close-

packing of the terminal methyl groups is by the comparison of electron diffraction results^{15,28,29} that probe mainly the chemisorbed S-atoms and helium scattering that should probe only the outmost methyl layer.^{30,59} One could also suggest a systematic deuteration of parts of the alkyl chain, thus separating contributions of different methylene layers to the vibrational spectra. Moreover, the chain distortion found in our MD simulation should be a function of chain length, to a certain limit. Thus, a systematic MD and experimental work using increasing chain length may provide an additional support to our model.

Before closing, we would like to raise the following observation. Traditionally, the symmetry of monolayers has been characterized by using one of the 80 crystallographic layer groups. The packing strategies mentioned above use a restricted subset of these groups. However, in systems such as those studied here, it might be appropriate to use a distinct *planar* group to characterize the symmetry of each of the individual strata and define a transformation to describe the transition from one stratum to another, while conserving the area per chain group, and satisfying commensurability requirements. This can be illustrated by returning to Figure 10. There, we observe that the loose square lattice packing can be transformed to an hcp arrangement—with the same area per CH₂ unit—by displacing alternating rows of molecules by ~ 0.5 of a lattice spacing. Obviously, probing strata exhibiting these two different packing symmetries will give rise to very different scattering patterns. Thus, if the displacement parameter of alternating rows, d , is the characteristic transformation between strata, then $d = 0$ will correspond to the chemisorbed thiolate groups at the Au(100) surface, $d = 1$ will correspond to an hcp arrangement, and each stratum will be characterized by a specific d value ($0 \leq d \leq 1$). Thus, it may be possible that while the entire monolayer belongs to a low symmetry layer group, the individual strata belong to a planar group with higher symmetry. The experimental methods mentioned above typically probe a limited number of strata in the assembly. The suggested description in terms of planar symmetries of individual strata, and the relationships among them, may be useful in relating the experimental information obtained from probing different strata, as well as suggesting an alternative packing strategy.

Acknowledgment. During the long process of simulations, trying to understand the results, and writing this manuscript, we have had stimulating discussions with a number of people. We greatly appreciate their input, criticism, and suggestions. They are as follows: Professor Giacinto Scoles, Department of Chemistry, Princeton University; Professor Michael Klein, Department of Chemistry, University of Pennsylvania; Professor George Whitesides, Department of Chemistry, Harvard University. Special thanks to Dr. Raymond Scaringe, Eastman Kodak Company, for his insight, criticism, suggestions, and for many discussions.

Recently, we received the Ph.D. thesis of Dr. Gang-yu Liu, who carried out most interesting and detailed helium diffraction on alkanethiolate monolayers on the different faces of gold under the instructions of Professor Scoles at Princeton University. Dr. Gang-yu Liu's work has helped us in our efforts to understand the packing and ordering of alkanethiolates on Au(100) surfaces. We are grateful for the opportunity to read her thesis.

(70) Predecki, P.; Statton, W. O. *J. Appl. Phys.* 1967, 38, 4140. Bonart, von R. *Kolloid Z. Z. Polym.* 1967, 231, 438.