Molecular Dynamics Simulations of Large Systems

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MOLECULAR DYNAMICS
SIMULATIONS OF LARGE SYSTEMS

By Patrick B. Kohl
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Date 5/30/2001
Chiral Symmetry Breaking in Interfacial Fluids of Achiral Molecules

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Abstract: Chiral symmetry breaking in a fluid of achiral molecules at a liquid-solid interface was studied using atomistic molecular dynamics simulation. The molecules were achiral in three dimensions, but left- and right-handed forms could be distinguished in the reduced symmetry environment of an interfacial fluid. The system consisted of a thick fluid film in contact with a crystalline monolayer adsorbed to a solid surface. When molecules in the crystalline monolayer were arranged in uniformly chiral configurations, a homochiral enantiomeric excess developed in the adjacent interfacial fluid. Fluid properties were characterized through measurements of chiral, nematic, and ferroelectric order parameters, and diffusion coefficients, as a function of distance from the interface. The emergence of chirality is attributed to fluid layering near the solid surface, suggesting that interfacial chirality is commonplace in fluids composed of molecules with certain symmetry characteristics.

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Introduction

Fluid properties near an interface often differ substantially from those in the bulk. For example, simulations\textsuperscript{1} and experimental measurements\textsuperscript{2} of interfacial fluids commonly show density oscillations in the first few atomic or molecular fluid layers, which arise as a consequence of constraints on molecular packing imposed by the presence of a solid wall. Fluids of non-spherical molecules often display orientational anisotropy, with molecules showing preferential polar or azimuthal orientation.\textsuperscript{3} Fluids adsorbed to corrugated surfaces can develop in-plane translational order, or epitaxy in the first one to two fluid layers.\textsuperscript{4} Solutions may also undergo partial demixing driven by selective segregation of one component to the surface. These and related phenomena occur when some anisotropic property of the (lower symmetry) solid is partially communicated to the (higher symmetry) fluid. This paper examines communication of another property — *chirality* — from a solid surface to an interfacial fluid.

In certain cases, reduced dimensionality at a flat surface can lead to a breaking of chiral symmetry, causing individual achiral molecules to become chiral, or to form a chiral supramolecular pattern, or both. Chiral symmetry breaking has been studied in crystalline molecular films adsorbed on solid surfaces,\textsuperscript{4} in Langmuir-Blodgett monolayers at air-water interfaces,\textsuperscript{6} and more recently in the context of smectic liquid crystals (LC), which are layered fluids.\textsuperscript{7} In many respects, interfacial fluids are nearly two-dimensional systems, with dimensionality increasing gradually to three-dimensions over a distance of a few molecular layers from the interface. Chiral symmetry breaking may occur in this transitional region as well, and if it does, fluid "chirality" would be expected to gradually diminish moving away from the surface. Here we examine this postulate through computer simulation of interfacial molecular fluids whose local chirality was characterized by a non-integer chiral order parameter.

Two-dimensional chirality is important in a number of different systems. For example, chiral surfaces formed by terminating a chiral crystal or by adsorbing a chiral film on the surface of an achiral crystal have been predicted to exhibit exceptional non-linear optical properties,\textsuperscript{8} and have been known for nearly 70 years to display catalytic stereospecificity.\textsuperscript{9} Recently discovered chiral smectic LC phases comprised of achiral...
molecules may show useful properties in optical switching and display applications, and are interesting systems from a fundamental perspective. Interfacial chirality is also of paramount importance in chiral chromatography and related technologies, and in heterogeneous enantioselective catalysis.

What are the origins of chiral symmetry breaking in two-dimensions? In three-dimensions, all chiral molecules lack both an inversion center and a mirror plane, and hence the symmetry operations of reflection ($\sigma$), inversion ($i$), and improper rotation ($S_n$). Thus all chiral molecules belong to one of the point groups: $C_1$ (asymmetric), $C_n$, $D_n$, $T$, $O$, or $I$, of which the last three rotational cubic groups are as a practical matter unlikely to be encountered.

If a molecule is confined to two-dimensions, certain symmetry operations become disallowed. By the phrase "confined to two-dimensions" we mean that motion along one direction – call it the $z$-axis – is forbidden. A molecule confined to two-dimensions may still rotate about the $z$-axis, and it may undergo translations in the $x$- and $y$-directions, but it may not undergo any motion (rotation or translation) that displaces some atoms in the $z$-direction. Following this definition, a non-planar molecule freely diffusing across a flat surface, but able to rotate only about the surface normal, would be considered confined to two-dimensions.

The symmetry operations disallowed by two-dimensional confinement include all operations whose symmetry element(s) (point, line, or plane) lies wholly in the confinement plane, as symmetry operations involving these elements necessarily transfer some part of the molecule out of the plane or across the plane. Consequently the emergence of chirality in two dimensions may depend on a molecule's orientation with respect to the confinement plane, as well as its symmetry point group: only if the orientation is such that the elements $\sigma$, $i$, and $S_n$ all lie in the confinement plane (or if they are absent to begin with) will the molecule be chiral in two dimensions.

Using this principle, we can identify the point groups that may be chiral in two-dimensions. They include those listed above for three-dimensions, plus three more: $C_{nh}$, $C_s$, and $C_i$. Molecules in the $C_i$ point group are chiral in two-dimensions regardless of their orientation, since the only requirement is that the inversion center, $i$, lie in the
confinement plane. Molecules belonging to the \( C_{nh} \) and \( C_2 \) point groups are chiral in two-dimensions only when oriented with their horizontal mirror plane in the confinement plane.\(^{13}\)

We simulated films of \( C_2 \) symmetry molecules, which lacked a stereocenter and hence were achiral in three dimensions. However when properly oriented in a two-dimensional environment, the molecules display chirality, because one can distinguish between two configurations nonsuperimposable on their mirror images. This is illustrated in Fig. 1a, which shows the molecule we simulated and its mirror image confined to the plane of the page. The two molecules are nonsuperimposable unless some part is rotated out of the plane. Therefore although they lack a stereocenter in three-dimensions, they are chiral when confined as shown to two-dimensions.

Although chiral symmetry breaking has been observed in two-dimensional molecular monolayers, it remains unknown whether a similar phenomenon can occur in an interfacial fluid. To investigate this question, we performed a computer simulation study of chiral symmetry breaking among fluid molecules whose ground state conformation belonged to the \( C_2 \) symmetry point group. This shape was chosen to roughly mimic 4'-octyl-4-cyanobiphenyl (8CB), an achiral molecule which has been shown in STM studies to form a single chiral monolayer on graphite.\(^{14}\) When deposited onto graphite as a neat liquid, the chiral monolayer coexists with its own melt at room temperature. 8CB is probably the most widely studied molecule forming this type of solid-liquid interface.\(^{15}\)

The simulations revealed the emergence of chirality in an interfacial fluid, with chiral order extending several molecular diameters into the bulk. Along with chirality, enantiomeric excess and several structural parameters of the fluid were measured in order to identify the origins of fluid chirality.

**Simulation Methods**

The system consisted of a fluid film 6 – 7 nm thick bounded below by a graphite surface, and above by vacuum. Molecules in the monolayer adsorbed to graphite were held frozen in one of two configurations, described below. All other molecules were
treated as fully dynamic. Periodic boundaries were applied parallel to the graphite
surface resulting in simulation cells measuring 4.57 x 5.38 nm and 5.78 x 3.46 nm for the
ferroelectric and antiferroelectric monolayers, respectively.

As stated above, molecular shape, internal mass distribution, and conformational
flexibility were chosen to resemble the molecule 8CB, possesses a rigid cyanobiphenyl
head group and conformationally flexible alkyl tail. At room temperature 8CB is a bulk
smectic-A LC; however as discussed below, our model was a conventional liquid in the
bulk, with a nematic order parameter less than 0.1. The rigid head group was constructed
from five atoms arranged in a line and spaced 0.144 nm apart. The intramolecular
geometry of head group atoms was held fixed using a combination of bond angle and
distance constraints implemented using the SHAKE algorithm.\(^{21}\) The mass of each head
group atom was 35.6 amu, giving a total head group mass equal to that of a
cyanobiphenyl moiety. The tail group was modeled as a five atom alkane-like chain
using the Ryckaert-Bellemans\(^ {16}\) potential function for alkane fluids. The mass of each tail
atom was 14.53 amu, and the bond length for tail atoms was 0.153 nm. The equilibrium
bond angle between the tail and head group was 109.47°, resulting in a bent conformation
with a fully-extended tail forming an angle of ~ 147° with respect to the head group.
Interactions between atoms in different molecules, and atoms within the same molecule if
separated by more than 3 skeletal bonds were calculated using the Lennard-Jones
potential. Potential energy functions and parameters are listed in Table 1.

Two different monolayer structures were investigated: a “ferroelectric”
arrangement in which each adsorbed molecule was oriented in nearly the same direction
(Fig. 2a), and an “antiferroelectric” arrangement in which molecular orientation in
adjacent rows alternated by 180° (Fig. 2b).\(^ {17}\) The two monolayers were constructed with
33 and 28 molecules, respectively. Similar domain structures have been reported in STM
observations of crystalline monolayers of alkylcyanobiphenyl molecules on graphite.\(^ {18}\)
The graphite surface was modeled using the series expansion potential introduced by
Steele.\(^ {19}\) The temperature of both systems was held constant at 375 K using a Berendsen
thermostat,\(^ {20}\) which was slightly above the freezing point of the fluid (~350 K).
Molecular monolayers were prepared by performing ~5000 steps of energy minimization of a single monolayer on graphite under conditions of constant cell size. The positions and conformations of molecules did not change appreciably during minimization, but no effort was made to find a configuration that resulted in global minimization of the energy. After minimization the monolayer was frozen and the remaining molecules introduced within the simulation cell.

Introduction of the remaining molecules was done in two steps. First, the bulk fluid was placed in a cubic simulation cell with fully periodic boundaries and equilibrated for 100 psec at 375 K. The resulting disordered liquid was then placed atop the frozen monolayer and the entire system was equilibrated for a further 1,000 psec with periodic boundaries in the x- and y-directions only. Equilibration was followed by 5,000 psec of simulation during which structural and dynamical parameters were tabulated and averaged. A snapshot of the fully equilibrated antiferroelectric monolayer system is shown in Fig. 2c. The systems contained a total of 396 and 401 molecules for the ferroelectric and antiferroelectric monolayers. Simulations were performed using a modified version of the parallel molecular dynamics package DL_POLY with a timestep of 0.001 psec.\textsuperscript{21}

Analysis Methods

We employed a simple geometric measure of the chirality of fluid molecules that accounted for both molecular conformation and orientation with respect to the graphite substrate (the confinement plane). The chirality of a fluid molecule was defined as

$$\chi = \pm \left( \frac{A}{A_0} \right),$$

where $A$ is the area of the triangle whose vertices are obtained by projecting onto the surface plane both ends of the rigid head group and the last atom in the tail, as shown in Fig. 1b. $A_0$ was the average area so obtained for molecules in the frozen monolayer. $\chi$ was assigned a positive value if the molecule's chirality was the same as those in the monolayer (homochiral), and a negative value if it was opposite (heterochiral). The range of $\chi$ for fluid molecules was nearly -2 to +2. Projected molecular area provides a suitable measure of chirality because: 1) it is a continuously
varying quantity, 2) it provides an unbiased way to distinguish between molecules with similar conformations, but opposite chirality, and 3) it accounts for the impact of molecular conformation and orientation on chirality, including out-of-plane orientation. Note that this chirality measure is only meaningful in an interfacial system or layered material with two-dimensional character.

The chirality parameter, $\chi$, was close to zero for molecules with crumpled tails, and those with nearly linear conformations, since their projected areas were small. Molecules whose long axis was oriented out of the surface plane also gave small projected areas, and hence a small chirality. Molecules with the largest chirality were oriented parallel to the surface and had fully extended tails. Because molecules in the frozen surface layer were both parallel to the surface and fully extended, $\chi$ may also be viewed as an approximate measure of the combined conformational and orientational similarity between fluid and surface molecules, where differences in orientation about the $z$-axis are disregarded.

The root-mean-squared average of molecular chirality, $<\chi^2>^{1/2}$, is a measure of the overall chirality of a set of molecules, and the mean value, $<\chi>$, provides a measure of enantiomeric excess. In the bulk fluid, where molecule orientations were completely random, the enantiomeric excess $<\chi> = 0$. However, $<\chi^2>^{1/2}$ does not vanish in the bulk, but rather levels off at some constant, positive value (in our system this constant was $\approx 0.7$). This does not mean that the bulk fluid is chiral. It results instead from the fact that the projected area $A$ associated with a randomly oriented molecule is usually different from zero, so $<\chi^2>^{1/2} = <(\pm A / A_o)^2>^{1/2}$ is greater than zero. This is easily confirmed by projecting a set of randomly shaped, randomly oriented triangles onto a fixed plane. In presenting data for overall fluid chirality, we therefore subtracted the constant $<\chi^2>^{1/2}$ measured for bulk fluid.

The chirality of molecules as a function of their height above the graphite surface was measured by dividing the system into thin slices and computing over the simulation interval the time averaged chirality of all molecules whose center of mass occupied each slice. This procedure produced a set of histograms showing subpopulations of
homochiral and heterochiral molecules at each height range. These histograms were then normalized by dividing by the bulk fluid distribution, giving the relative probability of observing a molecule with a certain chirality at a certain height.

Translational and orientational order in the fluid were assessed by measuring the height dependence of the fluid density and nematic order parameter. The scalar nematic order parameter, \( s \) at a height \( z \) above the substrate was defined as the largest eigenvalue of the \( Q \)-tensor

\[
Q_{\alpha\beta}(z) = \frac{1}{N(z)} \sum_{i=1}^{N(z)} \left( \frac{3}{2} u_{i\alpha} u_{i\beta} - \frac{1}{2} \delta_{\alpha\beta} \right)
\]

where \( N(z) \) is the number of molecules in a slice 0.1 nm thick centered at \( z \), \( u_{i\alpha} \) and \( u_{i\beta} \) are components of the unit vector defining the orientation of the rigid head group of molecule \( i \), and \( \delta_{\alpha\beta} \) is the Kronecker delta function.\(^{22}\) The nematic order parameter, \( s \) is a measure of the extent to which molecules in the fluid orient parallel to one another. It has a value between 0 and +1, with 0 representing an isotropic fluid, and +1 representing a fluid with perfect uniaxial order.

For the ferroelectric monolayer system, we measured an additional order parameter, calculated as the dot product of the unit vector defining the orientation of the head group of a molecule in the monolayer with the unit vector for the head group of each fluid molecule. These values were between -1 and 1. This "ferroelectric order parameter", \( F \), is a measure the extent to which a particular molecule in the fluid is aligned parallel \((F = +1)\), antiparallel \((F = -1)\), or perpendicular \((F = 0)\) to molecules in the monolayer. \( F \) was measured for every fluid molecule, then tabulated into a set of histograms for each height range.

Dynamic properties of the fluid were quantified through diffusion coefficients, calculated using the Einstein relation, measured as a function of height above the surface.\(^{21}\)

Results

Fluid Chirality

Overall fluid chirality, \( \left\langle \chi^2 \right\rangle^{1/2} - \left\langle \chi^2 \right\rangle_{\text{bulk}}^{1/2} \) in the first 45 Å above the surface is shown in Fig. 3. The abscissa origin is at the graphite surface, and the vacuum interface
is located at 60 - 70 Å. For comparison, fluid density is also shown as a dashed line, plotted with an arbitrary ordinate scale. The frozen monolayer is at a height of about 4 Å, and the first fluid layer is centered at about 7 Å. The chirality plots show a set of 3 - 4 oscillations, decaying in amplitude with increasing distance from the surface. These oscillations correspond to regions of non-zero chirality in the fluid. Note that the peak centers generally coincide with the positions of density maxima, indicating that molecules near the center of the fluid layers are most chiral. Chirality is low in the intralayer regions because molecules at those heights tended to orient with a large out-of-plane component. We observe that variations in fluid chirality closely resemble the density oscillations, both in the rate of decay and overall shape. This correspondence agrees with the expectation that regions of higher layer confinement - and hence larger and sharper density oscillations - will produce higher chirality. Also note that the plots for the two systems do not differ significantly within the level of statistical noise, indicating that overall chirality was insensitive to the structure of the frozen monolayer.

Further insight fluid chirality comes from examination of individual subpopulations of chiral molecules, shown in Fig. 4. The histograms in the upper half of the figure show the distribution of molecular chirality at regions within the first fluid layer, while those in the lower half show fluid chirality at more widely spaced intervals further into the bulk. The histograms for the first layer reveal two primary populations of molecules: one homochiral and one heterochiral. The achiral population (\( \chi \sim 0 \)) was suppressed by layer confinement, since rotation out of the surface plane is one of the principal ways molecules achieve low chirality. The homochiral population was larger than the heterochiral one in both systems, leading to an enantiomeric excess at the interface. This excess was most pronounced above the antiferroelectric monolayer (see below). Further from the surface, in the region between the first and second fluid layers, the homo- and heterochiral populations became equal, and a significant number of achiral molecules began to appear. In the second and third fluid layers, the distributions continued to evolve toward that of the bulk, and by the fourth or fifth fluid layer (not shown) the transition was complete.
Enantiomeric excess, \( < \chi > \) is plotted in Fig. 5, with fluid density again shown as a dashed line. A statistically significant excess of homochiral molecules was observed in the leading half of the fluid layer closest to graphite in both systems. The effect was more pronounced above the antiferroelectric monolayer, but in both systems it exceeded the level of statistical noise, judged from fluctuations in \( < \chi > \) measured far from the surface. The maximum value for \( < \chi > \) was 0.08 above the ferroelectric monolayer, and 0.29 above the antiferroelectric monolayer. The ferroelectric system also showed one data point closest to the frozen monolayer indicating heterochiral excess (i.e. a negative value for \( < \chi > \)). However, this point corresponds to a region with a density 1/700th of the bulk fluid (more than an order of magnitude smaller than any other measured point), and so we ascribe it to noise arising from undersampling.

**Fluid Density**

The dashed lines in Figs. 3 and 5 show variations in the density of the molecules' center of mass as a function of height. The oscillatory pattern is similar to that seen in other interfacial fluids.\(^1\) These effects and others are illustrated more clearly in Fig. 6, which plots separately the density of head and tail group atoms. Several features are noteworthy. Firstly, except in the first fluid layer, the density maxima for head and tail atoms do not coincide exactly, but are shifted relative to one another by 0.024 nm, or 6\% of the mean interlayer spacing. Peaks associated with head atoms are also sharper than those of the tail. Peak width is inversely proportional to the extent of positional disorder, which near the graphite wall was greater among tail atoms than among head atoms. This difference can be understood in terms of the relative conformational flexibility of head and tail groups: confinement of the flexible molecular tails to two dimensions incurs a greater loss of configurational entropy than confinement of the rigid head groups, and so the tails are less well positionally ordered. The fluid - vacuum interface was quite diffuse, extending over a region of \( \sim 1 \) nm. There was no layering at this interface, nor any discernible enrichment of head or tail group atoms. Comparison of the two systems shows that the structure of the frozen monolayer had little effect on fluid density.
Nematic Order

Figure 7 shows the height dependence of the nematic order parameter. In both systems, orientational order was highest near the frozen monolayer, decaying to a bulk value of \( s \sim 0.25 \) by the beginning of the third fluid layer. This value is higher than the average nematic order parameter measured in bulk simulations with fully periodic boundaries \( (s = 0.08) \). The discrepancy results from artificially dividing the system into thin slabs in order to calculate the height dependence of the order parameter, which leads to an overestimation of nematic order. Based on simulations using fully periodic boundaries in which the cell was not divided into thin slices, it was clear that this model does not form a bulk LC phase, despite the high nematic order parameter near the interface.

The ferroelectric monolayer system displayed marginally higher nematic order in the first and second fluid layers. It is notable however, that this did not coincide with increased fluid chirality, or with a larger enantiomeric excess of homochiral fluid molecules (viz. Figs. 3 and 5). Visual inspection of snapshots taken throughout the simulations also showed that the first fluid layer in both systems exhibited strong in-plane density oscillations parallel to the nematic director, with density maxima centered above molecules in the frozen monolayer. In other words, molecules in the first fluid layer were arranged similarly to those in the frozen monolayer, forming a nearly epitaxial fluid (see Fig. 9). Density oscillations parallel to the nematic director are a characteristic of smectic-A LCs. Thus over a distance of just four molecular layers, the structure evolves from crystalline \( \rightarrow \) smectic LC \( \rightarrow \) nematic LC \( \rightarrow \) isotropic. The sharp peak at the leading edge of the first fluid layers in both graphs is an artifact of the extremely low density at those data points.

Ferroelectric Order

The ferroelectric order parameter measured at various heights above the ferroelectric monolayer is shown in Fig. 8. It quantifies orientational similarity between fluid and surface molecules. In the first fluid layer (upper panel) molecules overwhelming oriented either parallel or antiparallel to those in the monolayer, witnessed
by large populations at extreme values of the ferroelectric order parameter. Other orientations were almost completely suppressed. In this region, very close to the surface, the parallel population was much more sharply peaked than the antiparallel population, and contained a greater number of molecules. This asymmetry in the histogram, combined with a high nematic order parameter, means the first fluid layer possessed unidirectional (polar) symmetry, similar to (but not as pronounced as) the frozen monolayer.

The ferroelectric order parameter between the first and second fluid layers was qualitatively different from within the layers, as shown by the dashed line in the upper panel of Fig. 8. The distribution tended toward lower overall ferroelectric order (peak centers shifted from ±1 to ±0.8), and became symmetric (biaxial fluid symmetry). The shift in peak centers occurred because intralayer molecules were frequently oriented out of the surface plane, spanning two or more layers. Fluid biaxiality persisted until about the fourth fluid layer, gradually becoming less pronounced with increasing distance from the interface. The bulk distribution was a flat line.

**Molecular Diffusion**

The diffusion data for the two systems (not shown) were very similar, and rather typical of interfacial fluids. The mean diffusion coefficient in the first fluid layer was $6.3 \times 10^6$ cm$^2$ s$^{-1}$, high enough to indicate a fluid phase. Diffusion increased sharply at the second fluid layer, and continued in a linear progression into the bulk. Diffusion near the liquid / solid interface was dominated by motion approximately parallel to the nematic director. Near the surface in-plane motion was 5 – 10 times greater than motion along the surface normal.

**Discussion**

These results demonstrate that the interfacial fluid is chiral, and that this chirality as measured by the parameter $< \chi^2 >^{1/2}$ decays into the bulk over a distance of 3 – 4 fluid layers. There exists moreover an enantiomeric excess of homochiral molecules in the first fluid layer, the extent depending on monolayer structure. Here we shall discuss the
relationship between this chirality and other elements of fluid and monolayer molecular order.

Based on arguments presented in the introduction, in-plane confinement of the molecule's \( C_s \) mirror plane should by itself be sufficient to produce chirality, and so a similar fluid film adsorbed to a perfectly smooth surface would also be expected to break chiral symmetry. Indeed, Fig. 3 shows that differences in the structure of the frozen monolayer had little or no impact on overall fluid chirality. Likewise, nematic order does not appear to be necessary for fluid chirality, as the data demonstrate in two ways: Firstly, \( s \) had decayed to its bulk value by the beginning of the third fluid layer, while chirality persisted into the third or fourth layers. Secondly, although nematic order was greatest above the ferroelectric monolayer system, r.m.s. chirality was essentially indistinguishable from the antiferroelectric system. Fluid chirality also showed little correlation to ferroelectric order. The ferroelectric order parameter data show that fluid layers with either polar or uniaxial symmetry can be chiral, and like \( s \), the ferroelectric order parameter had nearly decayed to its bulk distribution in fluid regions where chirality still persisted. We conclude that the emergence of chirality in this type of fluid can be singularly attributed to layer confinement (or density oscillations).

In the absence of a further reduction in symmetry, a film adsorbed to a smooth wall would be racemic. We have seen that the frozen chiral monolayer can break racemic symmetry, leading to a homochiral excess in the first fluid layer. This further symmetry breaking occurred above both monolayer structures, and was stronger in the antiferroelectric system (although it did not penetrate any farther into the fluid). Examination of snapshots showing molecules in the region of homochiral excess indicated that in order to approach close to the surface, fluid molecules had to adopt nearly the same conformation as molecules in the monolayer, and to "nestle" into one of the grooves between frozen molecules. Thus the molecules that contributed most to enantiomeric excess were those which were most nearly epitaxial to the frozen monolayer. Molecules in the first fluid layer that were slightly further from the surface were less constrained by epitaxy, and consequently showed less enantiomeric excess, despite possessing significant chirality.
To gain further insight into this issue, we labeled molecules in the first fluid layer as being either homochiral or heterochiral, and also as being oriented either substantially parallel or antiparallel to molecules in the frozen monolayer. The small number of molecules with ambiguous chirality or orientation were not included. The results are summarized in Table 2 using data from the ferroelectric system. They reflect the homochiral excess of the first fluid layer (56% homochiral vs. 44% heterochiral), as well as its uniaxial symmetry (56% parallel vs. 44% antiparallel). In addition they show a strong positive correlation between chirality and ferroelectric order; fluid molecules that oriented parallel to those in the frozen monolayer (positive ferroelectric order parameter) were overwhelmingly homochiral, and those that oriented antiparallel were overwhelmingly heterochiral. This correlation results from fluid epitaxy. In order for a fluid molecule to align in registry with the frozen monolayer, it must adopt either a parallel/homochiral configuration, or an antiparallel/heterochiral configuration, with the former being slightly preferred. Any other configuration forces part of the molecule out of the intermolecular grooves in the frozen monolayer. Several examples are shown in Fig. 9, which is a snapshot of the frozen monolayer and first fluid layer in the ferroelectric system. Arrows indicate representative molecules with different configurations. The molecule denoted “A” (parallel and homochiral), and the molecule denoted “B” (antiparallel and heterochiral) are able to conform more closely to the shapes of the grooves between molecules in the frozen monolayer than fluid molecules with other configurations, such as the one denoted “C” (antiparallel and homochiral). It is clear that occurrence of an enantiomeric excess is very sensitive to the structural details of the solid surface, and is therefore likely to differ significantly between systems.

Research on a number of subjects — from chiral crystal growth to the origins of homochirality in living systems — seeks to understand how chiral preferences are communicated between different components of a heterogeneous system, and how small chiral perturbations can lead to large-scale enantiomeric excess. In the simulations the size of these perturbations is readily calculated as a free energy difference, $\Delta E$ between homochiral and heterochiral molecules arising from the proximity of the solid wall. $\Delta E$ is computed from the relative numbers of homochiral and heterochiral molecules:
\[ \Delta E = -kT \ln \left( \frac{P_{\text{homo}}}{P_{\text{hetero}}} \right) \]

where \( P_{\text{homo}} \) and \( P_{\text{hetero}} \) are the probabilities of observing homochiral and heterochiral molecules at a particular height above the surface, and \( \Delta E = E_{\text{homo}} - E_{\text{hetero}} \) is the free energy difference of the two configurations. The probabilities are found by separately integrating the homochiral and heterochiral peak areas in Fig. 4. Performing the calculation for molecules in the region of strongest homochiral excess (\( z = 6.5 - 7.0 \) Å), gives \( \Delta E = -0.35 \ kT, \) or \( -7.6 \ \epsilon \) for the ferroelectric system, and \( \Delta E = -1.1 \ kT, \) or \( -24 \ \epsilon \) for the antiferroelectric system, where \( \epsilon \) is the Lennard-Jones well depth. Viewed in terms of free energy, the homochiral influence of the antiferroelectric monolayer was more than three times greater than the ferroelectric one.

The effects of changes in temperature and the molecular mechanics forcefield were not investigated in this work, but one can make some deductions about their likely importance based on the findings reported above. Chirality and enantiomeric excess are aspects of fluid structure, arising from layering and epitaxy, respectively. The gross structural features of interfacial fluids are dominated by entropic factors (not energetic factors), so the most important parameters are likely to be those that alter the contribution of entropy to the system free energy. Thus small changes in system parameters such as the van der Waals interaction strength, \( \epsilon, \) or atomic radii are unlikely to be very important. Indeed, even fluids composed of hard spheres (which have no attractive interactions) develop structure at an interface.\(^1\) Conversely, parameters such as temperature, or the number and position of flexible units in a molecule may be very important, as these directly affect entropy.

Conclusions

We have observed chiral symmetry breaking in a fluid of achiral molecules at two solid-liquid interfaces. This chirality extended \( \sim 20 \) Å or \( 3 - 4 \) liquid layers away from the surface. Examination of a variety of fluid structural parameters led to the conclusion that chiral symmetry breaking occurs as a result of layer confinement, and is largely independent from other aspects of molecular order. Since density oscillations appear to be a common feature of interfacial fluids, near-surface chirality may be widespread in
fluid systems with molecules of appropriate symmetry. A significant homochiral excess was also observed in the first fluid layer, which unlike overall chirality, appears to be strongly dependent on the structure of the surface monolayer.

Acknowledgments

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Table 1. Forcefield parameters and potential functions.

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<th>Potential Function</th>
<th>Parameter</th>
<th>Value</th>
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</thead>
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</tr>
<tr>
<td>Bond angle bending: ( U_{angle} = \frac{1}{2} k_\theta (\theta - \theta_0)^2 )</td>
<td>( k_\theta = 126 \text{ kJ/mol-deg}^2 )</td>
<td>( \theta_0 = 109.47, \text{deg} )</td>
</tr>
<tr>
<td>Bond stretching: ( U_{bond} = \frac{1}{2} k_r (r - r_0)^2 )</td>
<td>( k_r = 310 \text{ kJ/mol-Å}^2 )</td>
<td>( r_0 = 1.53, \text{Å} )</td>
</tr>
<tr>
<td>Non-bonded interactions: ( U_y = 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right] )</td>
<td>( \varepsilon = 0.143 \text{ kJ/mol} )</td>
<td>( \sigma = 3.923, \text{Å} )</td>
</tr>
</tbody>
</table>

Table 2. Molecular configuration statistics in the ferroelectric system.

<table>
<thead>
<tr>
<th>Orientation</th>
<th>Homochiral</th>
<th>Heterochiral</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parallel orientation</td>
<td>43%</td>
<td>13%</td>
</tr>
<tr>
<td>Antiparallel orientation</td>
<td>13%</td>
<td>31%</td>
</tr>
</tbody>
</table>
References


13) From this it also follows that a molecule which is chiral in $m$ dimensions will always be chiral in $n$ dimensions if $n \leq m$.


17) The terms ferroelectric and antiferroelectric are descriptive of the type of orientational order only – no electrostatic terms were used in the forcefield.


21) Forester, T. R.; Smith, W. Daresbury Laboratory, U.K.


Molecules belonging to the C₃ point group are achiral in three-dimensions, but become chiral if the mirror plane is confined to two-dimensions. The figure shows a C₃ symmetry molecule simulated in this study confined to the plane of the page. It is non-superimposable on its mirror image unless some part is rotated out of the plane, and hence it is chiral in two-dimensions. (b) The chirality parameter $\chi$ is computed from the area of the triangle formed by projecting the three atoms indicated onto the surface plane.

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Fig. 2. Two monolayer structures were used in the study, with molecules held frozen during the simulations. (a) the "ferroelectric" structure, and (b) the "antiferroelectric" structure. Part (c) shows the equilibrated antiferroelectric system with its fluid film. For clarity molecular tails in part (c) have been rendered as tubes, and the atoms drawn smaller than the van der Walls radius.
Fig 2c

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Fig. 3. The root-mean-squared chirality \( \left( \chi^2 \right)^{1/2} - \left( \chi^2 \right)^{1/2}_{\text{bulk}} \) for fluid molecules near the graphite surface shows an oscillatory pattern. Chirality is plotted as a solid line, with fluid density (dashed line) provided for reference (plotted with an arbitrary ordinate scale). Peaks correspond to regions of high fluid chirality. The graphite surface is located at \( h = 0 \), and the frozen monolayer is located at \( h = 4 \AA \).

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Fig. 4. The histograms show probability distributions for observing different values of molecular chirality at various heights above the surface. The upper panels represent regions within the first fluid layer, and the lower panels regions further from the surface. Results from the ferroelectric monolayer system is shown on the left and results from the antiferroelectric system on the right. Each curve was normalized by dividing by the bulk distribution.

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Fig. 5. A significant enantiomeric excess, $\langle \chi \rangle$ was observed in the leading edge of the first fluid layer in both systems. Positive values indicate a homochiral excess. Fluid density is shown for comparison, plotted with an arbitrary ordinate scale. The graphite surface is located at $h = 0$, and the frozen monolayer is located at $h = 4$ Å.

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Fig. 6. The density of molecular head group atoms (solid lines) and tail group atoms (dashed lines) displayed an oscillatory pattern near the graphite wall indicating strong fluid layering. Insets show details of these oscillations in the first 20 Å. Oscillations were followed by a region of bulk fluid 30 - 40 Å thick. The vacuum interface was located at $z = 60$ Å in the ferroelectric system, and $z = 70$ Å in the antiferroelectric system. The graphite surface is located at $h = 0$, and the frozen monolayer is located at $h = 4$ Å.

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Fig. 7. The fluid showed strong in-plane orientational order in the first two layers, but by the third layer the nematic order parameter had decayed to its bulk value. The method used to calculate \( s \) resulted in an overestimation (refer to text); simulations using fully periodic boundaries gave a bulk nematic order parameter \( s \approx 0.08 \), indicating a nearly isotropic fluid. The graphite surface is located at \( h = 0 \), and the frozen monolayer is located at \( h = 4 \) Å.

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Fig. 8. The ferroelectric order parameter is a measure of the extent to which fluid molecules oriented parallel (+1) or antiparallel (-1) to molecules in the monolayer. The data were measured above the ferroelectric monolayer. The upper panel shows regions close to the graphite surface and the lower panel shows regions further into the bulk liquid.

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Fig. 9. The figure shows a snapshot of the ferroelectric monolayer and first fluid layer. Three types of molecules are labeled with arrows: (A) parallel and homochiral, (B) antiparallel and heterochiral, (C) antiparallel and homochiral. Note that molecules possessing configurations similar to (A) or (B) conform more closely to the shapes of grooves between molecules in the frozen monolayer. Molecules tended to adopt one of these two configurations, with configuration (A) slightly favored over configuration (B).

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Molecular Dynamics Simulations of Chemical Force Microscopy

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Abstract: The chemical force microscope (CFM) measures tribological interaction forces between a sharp stylus coated with a self-assembled monolayer and a solid surface. The interpretation of measurements like CFM involving interactions between single asperities requires a detailed understanding of atomistic forces, dynamics, and microscopic mechanics at the point of contact. We performed large-scale molecular dynamics simulations to study these details in a model system comprising a 5 nm spherical stylus, covered with an alkylthiol self-assembled monolayer, brought into and out of contact with a smooth gold wall. We simulated continuous approach-retract sequences, along with quasi-static “force curves” with the stylus equilibrated at each height to mimic infinitely slow motion. The simulations provide information about the distribution of forces within the contact zone, contact area, hysteresis and energy dissipation, chain dynamics, and film structure. We make comparisons to experimental measurements and to continuum contact mechanics models such as Johnson-Kendall-Roberts theory.

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Introduction

Chemical force microscopy (CFM) is a useful form of scanning probe microscopy due to the well-defined chemical nature of the probe. The probe tip is covered with a self-assembled monolayer (SAM) of chainlike molecules with a chosen terminal group. The SAM is robust and will not desorb or collect contaminants under typical use. The drawback to CFM and related scanning probe microscopy techniques is that detailed interpretation of the data obtained can be hindered by a lack of an atomic-level understanding of the processes involved. Several contact mechanics models exist (JKR\(^1\), DMT\(^2\), Hertzian\(^3\), etc.) which allow, for example, relation of measured surface free energies and forces of adhesion to the dimensions of the probe tip. However, these are continuum models and may not be appropriate on microscopic scales. Our goal in this simulation was to perform an atomic-scale simulation of a CFM approach/retract sequence in order to collect information not accessible to direct experiment. The results of these simulations allow us to describe in detail the formation and rupture of contact between a SAM-coated gold CFM tip and a gold substrate. Also, most interactions between two real surfaces involve at a microscopic level interaction between asperities and flat surfaces, so the results of this work may be applied to the study of friction and adhesion in general.

The Model

Our system consists of a smooth planar gold wall (the substrate) and a smooth spherical gold wall of radius 50 Å (the probe tip). The gold tip is covered with 278 S(CH\(_2\))\(_{11}\)CH\(_3\) alkylthiol chains. The molecules are represented using the model of Hautman and Klein in their simulations of alkylthiols adsorbed on gold (their Model I\(^4\), in which the CH\(_2\) and CH\(_3\) groups are treated as single pseudoatoms.

The alkylthiol chain consisted of thirteen pseudoatoms (one sulfur, 11 CH\(_2\) groups, and one CH\(_3\) group). Chemical bonds were represented by a harmonic bond potential of the form:

\[ U_{\text{bond}} = \frac{1}{2} k (r - r_0)^2 \]

where \( r_0 \) is the equilibrium distance between two groups and \( k \) is a constant that depends on the pair of atoms involved. Valence angles were maintained using a harmonic potential of the same form. Dihedral interactions were represented using the cosine sum potential of Ryckaert and Bellemans\(^5\)
\[
U_{\text{dihedral}} = a_0 + a_1 \cos(\phi) + a_2 \cos^2(\phi) + a_3 \cos^3(\phi) + a_4 \cos^4(\phi) + a_5 \cos^5(\phi)
\]
where \( \phi \) is the dihedral angle, and \( \phi = 0 \) is a Trans conformation. Note that S-C-C-C and C-C-C-C dihedrals are treated with the same potential.

Interatomic interactions are governed by a standard Lennard-Jones potential,

\[
U_{\text{LJ}} = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right]
\]
where \( r \) is the distance between two interacting atoms, and \( \sigma \) and \( \epsilon \) are pair-dependent parameters. This potential applied to all pairs of atoms from different molecules, and all pairs of atoms within the same molecule separated by at least three atoms. The potential was truncated at 12.0 Angstroms.

The interaction between atoms and the planar wall is 12-3 in form,

\[
U_{\text{wall}} = \frac{C_{12}}{(z - z_0)^{12}} - \frac{C_3}{(z - z_0)^3}
\]
where \( z \) is the distance between the atom and the wall. The spherical wall uses the same 12-3 form and parameters for forces acting radially with respect to the sphere’s center, and also includes ‘tethering’ forces in the theta and phi directions, to prevent the adsorption sites of the molecules from migrating during approach and retraction of the tip. The tethering forces come from a simple harmonic potential, whose parameter is obtained by fitting a quadratic to the bottom of the 12-3 potential well for the gold wall. Note that the wall potentials do not have a cutoff distance.

**Simulation Setup**

All simulations were executed using the molecular dynamics package DL-POLY. Simulations were run at a temperature of 300K, using the Berendsen constant-temperature thermostat with a time constant of .1 ps. The timestep for the simulations was set at \( 10^{-15} \) seconds.

Approach and retraction of the tip was simulated by adjusting the height of the planar wall potential by small increments every timestep. Typical approach increments of \( 2 \times 10^{-4} \) Angstroms/timestep corresponded to real approach speeds of 2 m/s.
The system was prepared by covering the bottom of the spherical wall with 278 chains arranged in equal-spaced rings, with the chain backbones pointing radially outward (the backbone is defined as the line joining the 1st, 3rd, 5th,...,13th groups). The chain density was 21.57 Å² per chain, close to the 21.4 Å² observed for an alkylthiol SAM on a planar gold surface. The outer ring of 52 molecules was 'frozen' in place for the length of the simulations, in order to prevent molecules from splaying out towards the upper region of the spherical wall. With the chains in place, the effective radius of our probe tip (calculated as the average distance between a terminal group and the sphere center) was 65.3 Å.

After placing the molecules, we equilibrated the system at zero Kelvin for 50 ps, followed by 450 ps at 300K. The planar gold wall was not present in the system. During this equilibration period the tethering potential was not engaged, and the sulfur atom 'adsorption sites' were free to migrate about the tip. At the end of the 450 ps at 300K, the potential energy of the system was relatively constant in time. The tethers were then applied, effectively locking the sulfurs into place. This configuration was used as the starting point for all further simulations.

**Characterization of an Isolated Asperity**

To our knowledge there has been no study of the properties of this model molecule on a curved surface, so it was necessary to characterize the behavior of the system with the planar wall removed, thus giving the situation where the probe tip is very far from the substrate. The equilibrated configuration described above was simulated for an additional 200 ps, over which time structural and energetic data were collected.

**Visual Inspection**

In Figure 1 we present snapshots of the isolated asperity viewed from below and from the side. We can see that the chains have segregated themselves into three domains (lower left, upper left, right). In each domain the chains form an ordered structure, in which they all tilt in roughly the same direction. At the borders between domains we see more disordered chains, some of which have enough room to lie almost completely flat on the wall. It is also apparent that at the tip of sphere there is something of a 'bald spot', since it is at that point that the three domains meet and all molecules tilt away from each other.
Examining the sulfur atom distribution (not shown), we see that the molecules have migrated towards the frozen ring and ordered themselves into two or three additional rings. Beyond this point, the structure in the sulfur atoms breaks down and becomes random at the tip. Based on the observed ordering of the adsorption sites to match the frozen ring, and the fact that all three domains tilted towards the frozen ring, it is apparent that the ordered domains began to form at the ring and then built towards the center of the sphere.

Distribution of Gauche Defects

We monitored the distribution of gauche defects in the system as a function of theta location on the sphere and as a function of dihedral angle number, where angle 1 is the dihedral angle that includes the sulfur. Figure 2(a) shows the fraction of dihedrals that are gauche as a function of theta. We see the number of dihedrals increase sharply as we move away from the influence of the frozen ring. The gauche fraction then becomes fairly constant until we approach the bottom of the tip, where the gauche fraction increases again, representing the decreasing order in that region.

Figure 2(b) shows the gauche fraction versus the dihedral angle number. In the dihedral that includes the sulfur, we see a fraction of 0.078. The fraction then increases and decreases in an alternating pattern as the angle number increases. In the final four dihedral angles, we see a sharp increase in the number of gauche defects. Two conditions contribute to create this distribution. First, because of the curved geometry of the system, atoms that are farther from the spherical wall have more room, and thus defects are less energetically unfavorable in that region. The alternating up and down pattern in the distribution comes from the fact that consecutive gauche defects would cause a severe distortion in the shape of the molecule, which is prohibited in the tightly ordered domains. However, ‘kink’ defects which consist of a gauche of +60 degrees, followed by a trans bond and a gauche of −60 degrees, preserves the linearity of the molecule and are thus more permissible in an ordered system. The presence of a gauche defect in the dihedral angle closest to the sphere would be the most unfavorable (due to the tight packing of the atoms in that region), so we see the first spike in the alternating pattern occur in the second dihedral angle. The direct measurement of the average number of kink defects and consecutive gauche defects supports this interpretation of the data. Counting the average total number of gauche defects, we see that 108 out of 271 are a part of a kink, whereas only 25
participate in consecutive gauche defects. The described gauche distribution, with its concentration of defects in kinks and in bonds closer to the surface of the SAM, has been observed in previous studies of planar SAMs.

The Continuous and Equilibration Runs

Two varieties of simulation were performed, to be referred to as continuous and equilibrated runs. In the continuous simulations, the tip approached the surface continuously, starting from a tip-surface separation of 20.4Å, with the separation distance defined as the spacing between the flat gold wall and the surface of the gold sphere. The tip approached the wall until the separation reached 7.2Å, at which point the system was retracted to its original height. The approach speed was $2 \times 10^{-5}$ Å per timestep, leading to a simulation length of approximately 1.4 million timesteps (1.4 ns).

To complement the continuous approach, we saved the system configurations at 20 points along the continuous run, and equilibrated each of those systems until all energetic and structural parameters had become constant (~1 ns). We then collected data on the equilibrated systems for an additional 1 ns. This gave us a set of points which should match roughly the data that would be generated by a continuous run in which the tip moved at an infinitesimal rate, thus keeping the system in constant equilibrium.

Shown in Figure 3 is the force vs. distance curve for the continuous simulation. The force curve contains some of the most important information, both qualitative and quantitative. The location of contact rupture is resolvable as a discontinuity on the retraction curve, as is the point of initial contact. The Young’s modulus of the tip can be recovered from the slope of the linear retraction region, and the work done by the tip is equal to the integral of the difference between the curves. Two regions can be defined: the repulsive region, where the net force between the two surfaces is positive, and the attractive region.

Most notable is the great deal of hysteresis present when we compare the approach and retraction curves. This can be explained if we note that though our approach/retract speed is as slow as is practical on modern workstations, it is still about four orders of magnitude faster than the speeds in an actual CFM experiment. This means that our simulated system was not in equilibrium over the course of an approach/retract sequence, which can be seen in plots of the total potential energy vs. time (the energy did not return to its initial state by the end of the
simulation). This non-equilibrium situation appears to be responsible for the force curve hysteresis, as the hysteresis is not present in the equilibrium simulations to be described below.

In Figure 4 we see the force curve assembled from the equilibrium simulations. We can see that the approach and retract curves match each other closely, with some hysteresis remaining near the point of contact rupture. In addition, the force minima appear to occur at the same separation. These qualities are common to experimental CFM force curves. Further analysis with involve the data from these equilibrium simulations.

Data Analysis

Contact area and JKR analysis

The dominant model used to treat contacts between spheres and flats is the JKR model. This model has been well-tested on macroscopic, continuous systems, but may fail when applied to microscopic, discrete systems. Since the JKR model has been used by experimentalists to assist in the interpretation of CFM data, it is important to determine whether or not the model is indeed applicable. To this end, we make several comparisons between our experimental results and the JKR predictions.

We begin with a treatment of the contact area in our system. The idea of contact area on a atomic level is somewhat ambiguous. Instead of measuring the total area in contact, we have measured the time-averaged number of atoms in contact near the end of each equilibration run. The number of contacts increases with a decrease in tip separation, as expected. From the number of contacts, we were able to define an effective contact area by multiplying the number of contacts by the effective area of each contact (given by the van der Walls cross section of the pseudoatom in contact).

The JKR model predicts a contact area relation of the form

$$ a^3 = \frac{R}{K} \left[ F + 3\pi W R + \sqrt{6\pi W F + (3\pi W R)^2} \right] $$

where $a$ is the contact area radius, $F$ is the tip-contact force, $W$ is the work of adhesion, $K$ is the elastic modulus, and $R$ is the sphere radius. Assuming this to be valid, we graphed the force vs. area data and found best fits for the constants $K$ and $W$. The values thus obtained were reasonable,\(^7\)\(^8\) with $K=3.82\text{Gpa}$ and $W=195\text{mJ/m}^2$. Using these constants, we could then compare the area vs. force curve from our data to that predicted by the JKR model. In the
repulsive region of the force curve, the fit was nearly perfect (Figure 4b). However, the fit was extremely poor in the attractive region of the curve.

**Stress contour plots**

We also measured the time-averaged force per unit area on the planar wall for each of the equilibrium points. Figures 5 (a) and (b) depict this data for two of the equilibrium simulations, the first in the repulsive regime of the force curve, and the second in the attractive regime. Red and orange represent repulsive forces, while blues and greens indicate attractive forces. The dots indicate points of contact between the flat and the molecules on the sphere. The force is not continuously distributed, as we would expect in a continuum situation, and as JKR predicts. Rather, we see pockets of attractive and repulsive force, some of which are expected (e.g. repulsive domains occurring near the center), but others being quite counterintuitive (e.g. pockets of repulsive regions occurring in the middle of highly attractive regions). The magnitude of these random fluctuations increases as the tip separation decreases.

In Figures 6 (a) and (b), we see the stress distribution as a function of radial distance from the center of the tip, obtained by averaging the data in the plots from Figure 5. The force distribution is smooth on the outside of the asperity, but becomes very noisy as it approaches the center. These stress distributions are also predicted by the JKR model, and are given by

\[ \sigma(x) = \frac{3Ka}{2\pi R} \left(1 - x^2 \right) - \frac{3WK}{2\pi a} \left(\sqrt{1 - x^2} \right)^{-1} \]

In Figure 6 these predicted distributions are overlaid onto the plots obtained from the simulations. As was noted before, the JKR model fits tolerably well in the repulsive regime (Figure 6 (a)), but fails completely elsewhere.

**Diffusion coefficients**

We obtained diffusion coefficients by taking the average displacement of each pseudoatom from its initial position over an appropriate time interval. The diffusion coefficient is related to this displacement by

\[ 2D = \frac{(r_f - r_i)^2}{3} \]
where \( D \) is the diffusion coefficient. Plotting this diffusion coefficient as a function of tip-surface separation, we determined that the SAM changes from being approximately fluid at large separations, to solid under large compressions. This results in a variable value for the elastic modulus, \( K \). Since the JKR theory assumes a constant \( K \) value, this suggests that JKR may be inapplicable to this system. Indeed, we have seen so far that the JKR fit is good only in the repulsive region of the simulation, corresponding to the region where the SAM is solid and \( D \) is relatively constant.

Conclusions

We have shown that there are serious discrepancies between the predictions made by the JKR theory and the results obtained from our CFM simulations. This suggests that JKR theory must be used with great care, if at all, when analyzing experimental data. The failure of the model is at least partially due to the fact that an actual CFM tip appears to undergo a phase transition from a liquid to a solid over the course of an approach. This results in a variable elastic modulus, which greatly complicates the theoretical treatment and renders invalid the use of models that assume a constant \( K \). The situation is further complicated by the discrete, patchy nature of the CFM tip, which suggests that continuum models in general may be doomed to failure when applied to this microscopic system. In addition, our results suggest that many tribological processes, being based on microscopic interactions of this form, might not be easily described by continuum theory.
References


2) B. V. Derjaguin, V. M. Muller, Y. P. Toporov, J. Coll. Interface Sci. 1975, 314, 53


6) DLPOLY, T.R. Forester, Daresbury Laboratory, Warrington WA4 4AD


8) R. Henda, M. Grunze, A.J. Pertsin, Tribology Letters

9) M.P. Allen, D.J. Tildesley, “Computer Simulation of Liquids”
Kohl, Flanagan, and Patrick. Fig. 1.
Kohl, Flanagan, and Patrick  Fig. 2 a,b
Kohl, Flanagan, and Patrick Fig. 3
Kohl, Flanagan, and Patrick Fig. 4
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