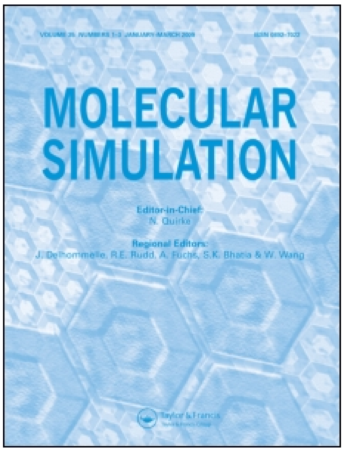

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MOLECULAR DYNAMICS OF LANGMUIR-BLODGETT FILMS: II. BILAYERS

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We have simulated Langmuir Blodgett bilayers of stearic acid at 25°C for two head-group areas using the molecular dynamics method. At $A_m = 21.2$ Å^2 the molecules are tilted at 18° to the surface normal with a next-nearest-neighbour azimuthal orientation. The head-group dipoles are parallel to the plane of the surface and antiparallel to each other. The precise ordering of the dipoles depends on the density of the bilayer. There is a strong correlation between the translational and orientational ordering of the molecules in the two layers due to strong inter-layer electrostatic coupling between the head-groups. The head-groups exhibit a strong crystalline structure in the plane of the bilayer at both densities. Increasing the density to 20.6 Å^2 does not significantly alter the tilt angle, this contrast to the energy minimisation results and the molecular dynamics results for the monolayer at the same temperature and head-group area. It produces a distortion of the translational ordering of the molecular centres from the initial triangular arrangement towards a rectangular structure which is evocative of the crystal B structure.

KEY WORDS: Langmuir-Blodgett films, bilayer, stearic acid.

1 INTRODUCTION

Monolayer and multilayer Langmuir-Blodgett films have been the object of considerable interest since they were first made over fifty years ago [1, 2]. The study of supported films of monolayer thickness offers insights into the physics of phase transitions in systems with dimensions between two and three and is relevant to biological membranes as well as active surface layers in, for example, corrosion studies. The ability provided by Langmuir-Blodgett technology, to manipulate materials at the molecular level, opens up significant opportunities for engineering applications [3]. Although no large scale commercial use for LB films have been found, the area remains promising with research efforts directed at applications including second-order non-linear optics (materials characterisation, thick film and waveguide structures), sensors (gas, ion, bio and molecular recognition), membranes and electronic devices [4].

Despite this level of research activity our understanding of the relationship between molecular structure, surface structure and LB layer structure remains incomplete. The degree to which reliable information can be obtained from experiments on LB films intended to characterise their structure and dynamics (e.g. X-ray

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diffraction, electron diffraction and atomic force microscopy) is determined by the reliability of the theoretical models used in the interpretation of the data. Unfortunately such models are often quite crude.

Molecular simulation has a key rôle to play in helping to improve models of film behaviour due to its unique ability to provide thermodynamic, structural and dynamical information for model hamilitonians. By adjusting the hamilitonian so that the simulation fits the observed experimental results, the microstructure and dynamics of the film can be predicted. However, at present, simulation studies are directed at the less ambitious task of elucidating the features of the model hamilitonian which control film behaviour.

For example there is now strong evidence from both energy minimisation (EM) [5, 6] and from molecular dynamics simulation (MD) [7] that stearic hindrance between the hydrogen on the hydrocarbon backbones of neighbouring amphiphilic molecules determines the surface areas at which monolayer tilting occurs as well as the average molecular orientation. Therefore simplified models of amphiphilic molecules with single Lennard-Jones (LJ) sites representing the methylene groups are unlikely to be reliable. The representation of the hydrophilic head-groups of the model amphiphile has received less attention as have the details of its interaction with the supporting surface (for recent work see references [5, 7, 8, 9].

In the preceding paper, referred to as (I), the rôle of the head-group in determining the monolayer structure and dynamics of stearic acid films was examined in some detail using an atom representation of the carboxylic group including the dipole-dipole term modelled using partial charges. Torsional potential were use to control the relative orientation of the plane of the backbone and the plane of the head-group. The hydrophilic interaction between the head-group and the surface was represented using an integrated repulsion-dispersion interaction and an image charge interaction between the dipole and the underlying dielectric medium. The addition of a realistic interaction has no significant effect on the minimum energy structure, in which the torsional angles are fixed. However, the detailed structure of the monolayer at 300 K was quite different to that predicted by our previous single site effective head-group model [6]. The all-atom model predicted significant conformational disorder at the torsion connecting the carboxylic acid head-group to the alkyl chain of the molecule. This effect is found experimentally in the structure of the B-form of the stearic acid crystal. The molecular tilt of the layer at a density of 21.2 Å^2 was 18.8°, double the value of 9° found for the simple head-group model [6] and closer to the tilt angle obtained by energy minimisation as well as the value inferred from electron diffraction measurements [10]. The head-group dipoles were found to be aligned parallel to the surface and in the tilted phase to formed a two sub-lattice structure in the surface plane.

This short paper extends our study of LB films, using the same realistic model of the stearic acid monolayer, to bilayers. We report the effect of hydrogen bonding between subsequent layers of the bilayer structure and compare these results with those for the monolayer at similar head-group areas. Section (2) describes the modifications to the potential model required to handle the 128 molecules which make up the bilayer. Section (3) considers the results of the energy minimisation and compares the situation for monolayers and bilayers. The molecular dynamics results are reported in section (4) and section (5) contains our conclusions.

2 POTENTIAL MODEL

In our previous work three types of potential model for stearic acid have been considered: a united-atom model (UA) in which the head-group, tail group and back-bone methylene units were modelled as Lennard-Jones force sites [6]; an explicit-hydrogen model (EH) where the hydrogen atoms in the methylene groups were modelled as additional Lennard-Jones atoms [6]; an all-atom model (AA) where the flexible head-group is represented by four atoms and where partial charges are used to represent the molecular dipole [7]. For monolayers at densities typical of a Langmuir Blodgett film the explicit representation of the back-bone hydrogens was necessary to produce the correct intermolecular packing. The AA head-group introduces a larger effective head-group diameter as well as a new competition between electrostatic and the repulsion-dispersion force. As discussed in I, this shifts the 0 K global energy minimum to a lower density and increases the molecular tilt. The AA model has been described in detail in I.

In simulating the AA model [7], a system of 64 molecules required 80 hours of cpu time on 1 processor of a CRAY/XMP-48 to simulate 90000 timesteps. Since the time required for the present simulation scales approximately as N^2 where N is the number of atoms, the simulation of a bilayer in the Y-configuration (see Fig. 1) containing 128 molecules would be prohibitively expensive.

To complete a bilayer simulation of a stearic acid system which preserves the key elements of the explicit hydrogen and all-atom head-group models, we have formulated a hybrid model. In this model an amphiphile interacts with its six nearest-neighbours using the full all-atom model. The atoms in the hydrocarbon chain interact with the next-nearest-neighbours and all further chains through a united-atom interaction in which the methylene groups of the hydrocarbon chain are represented as single Lennard-Jones site. The Lennard-Jones parameters of this interaction are $\sigma_{ua} = 4.3$ Å and $\epsilon_{ua}/k_B = 52$ K. These parameters are chosen so that full model and hybrid model exhibit the same tilting transition as a function of coverage when studied at 0 K using the energy minimization techniques discussed in section 3. Figure 2 shows the tilt angle at the minimum energy as a function of coverage for the full AA model and the hybrid model. This transition is particularly sensitive to the value of σ_{UA} and is less strongly effected by the choice of ϵ_{UA} (80% of the total energy in the hybrid bilayer comes from the unaltered nearest-neighbour interaction). At the densities studied in this paper, the bilayers exhibits a solid-like translational structure and the nearest-neighbours of a particular amphiphile do not change with time. The overall potential is time-independent and the total energy is conserved in the molecular dynamics simulation of this model. The interaction between charges in different head-groups are always handled within the all-atom representation.

3 ENERGY MINIMIZATION

Before reporting the results of the molecular dynamics simulation, it is instructive to consider the behaviour of the monolayer and bilayer at 0 K. Energy minimisation calculations are considerably faster than molecular dynamics for Langmuir-Blodgett films and permit a wide range of densities and potential models to be studied.

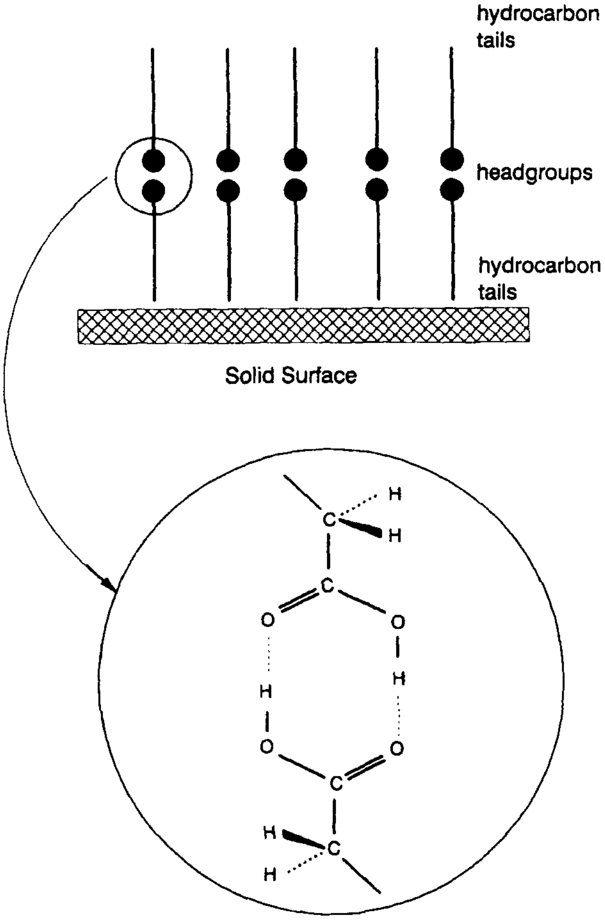

Figure 1 A schematic representation of the arrangements of the molecules in the bilayer with a Y-type structure.

Further, many of the structural features present at OK are preserved in the room temperature simulations.

Energy minimisation of monolayers of monolayers with the EH and AA potential models have already been reported in I. We recall that in these cases there is a sharp structural transition between a tilted and non-tilted solid in which the head-groups form a triangular lattice. This transition occurs at head-group areas per molecule, A_m of 20.8 Å^{-2} (AA model) and 20.7 Å^{-2} (EH model). The energy minimisation studies of the monolayers show that, for the AA model, the minimum energy monolayer occurs at $A_m = 21.5$ Å^{-2}. This structure has a triangular unit cell, the long-axis of the inertia tensor of the molecule is tilted at an angle of 36° to the surface normal in the direction of next-nearest-neighbour molecules in the lattice and the short axes of the inertia tensor form a two-sublattice orientational structure. Figure 3(a) and (b) show the minimum energy as a function of A_m for

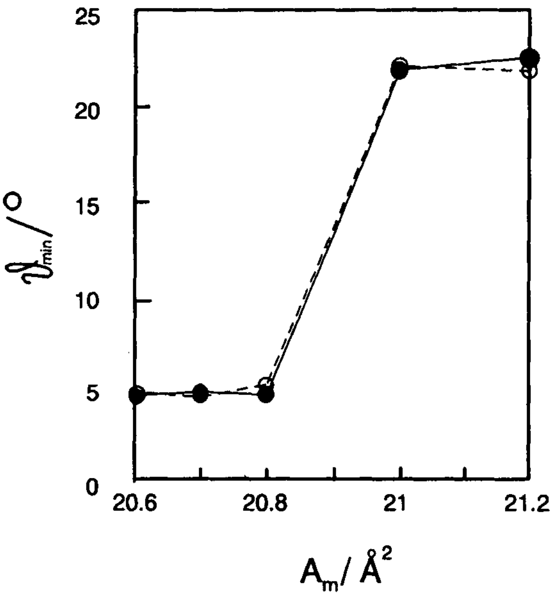

Figure 2 The molecular tilt, θ_{min}, for both layers as a function of the headgroup area per molecule: all atom model, —; hybrid model: ---.

the EH and AA models of the monolayer with the head-groups in a triangular lattice.

In contrast the E_{min} as a function of A_m for the bilayer is shown in Figure 3(c). There is no sharp peak in the energy at the tilting transition and the energy of the bilayer falls smoothly by 2 kJ mol^{-1} for A_m between 21.2 Å^2 and 20.3 Å^2. However, Figure 2 shows that there is a clear change in the tilt angle of the bilayer from 21° to 5° at $A_m \approx 20.9$ Å^2. The tilt in both layer for $A_m > 20.9$ Å^2 is approximately 21°; this is 15° less than the tilt found in the monolayer [7] and indicates the importance of the inter-layer H-bonding in controlling the properties of the bilayer. Interestingly, as the density is increased the tilt of both layers tends to a value of approximately 3° at $A_m = 20$ Å^2. This contrasts with the monolayer where the molecules are effectively upright at densities at 20.5 Å^2.

4 THE LANGMUIR-BLODGETT BILAYER

In this section the structural and dynamic properties of the bilayer at room temperature are considered. Molecular dynamics calculations were performed using the hybrid representation of the stearic acid molecule on a hydrophobic surface at room temperature and at head-group areas of 20.6 Å^2 and 21.2 Å^2 per molecule. The orientational structure, translational structure and conformational structure of the bilayer are reported. The details of the simulations are summarized in Table 1. A typical configuration from the low density simulation is shown in Figure 4. The picture shows that the layers are strongly translationally ordered

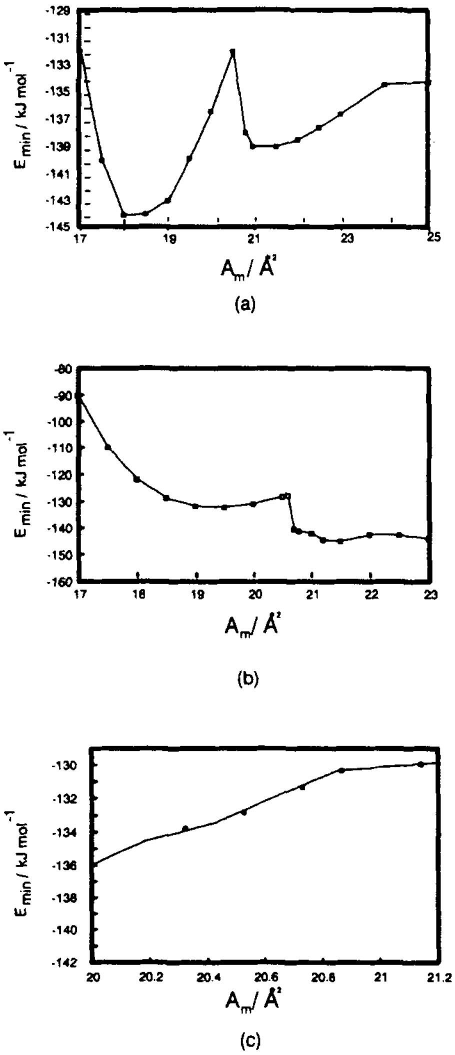

Figure 3 E_{min} as a function of A_m for the triangular lattice of head-groups: (a) the monolayer EH model; (b) the monolayer AA model and (c) the bilayer AA model.

and that there is a significant collective molecular tilt along one of the lattice directions.

The average tilt in the low-density simulation is 17.6 Å in the upper layer and the same in the lower layer. Increasing the temperature from 0 K to room temperature increases the in-plane vibration of the head-groups in the lattice structure and the average molecular tilt of the layer decreases by approximately 4°.

The high density bilayer also exhibits a tilt of 17.6 Å. This is in sharp contrast with the 0 K result for the bilayer at the same head-group area (5°) and the monolayer (2.4°). Presumably, entropic effects shift the tilting transition to lower

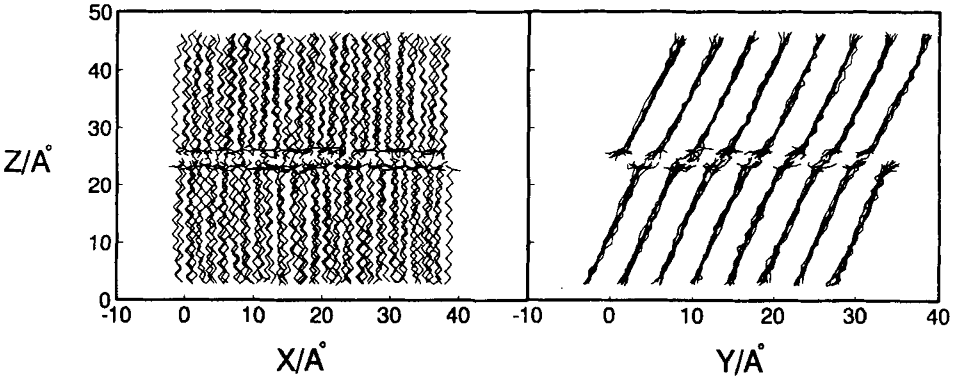

Figure 4 A snapshot of the structure of the stearic acid bilayer at a head-group area of A_m = 21.2 Å^2.

Table 1 Details of the molecular dynamics simulations

A_m	20.6 Å^2	21.2 Å^2
Number of equilibration steps	50000 (100 ps)	55000 (100 ps)
Number of production steps	39000 (78 ps)	46000 (92 ps)
T/K	293	297
Tilt/° (upper layer)	17.6	17.4
Tilt/° (lower layer)	17.6	18.7
Azimuth/°	−87 (nnn)	90 (nnn)
Dipole orientation	parallel in layers, antiparallel between layers	antiparallel

temperatures. The bilayer tilting at room temperature is closer to that in the B-form of the stearic acid crystal; this has a head-group area of 20.7 Å^2 and a collective tilt of 27°. At both densities the tilts of the amphiphiles in both layers are strongly correlated.

In both systems the azimuthal angles in both layers are approximately 90° indicating tilting in the next-nearest-neighbour direction, in agreement with the energy minimisation calculations.

Most of the dipoles in the bilayers at both densities are oriented almost parallel to the surface. There are a smaller number of dipoles in the lower layer oriented at 20° to the surface normal matched by a number in the upper layer oriented at 160°. These are due to conformational disordering around the C1—C2 bond (see Figure 1 of I). Figure 5 shows the distribution of azimuthal angles ϕ_u of dipoles in the bilayers. The in-plane dipolar orientations between the lower and upper layers are anti-parallel at both densities. The dipoles at A_m = 20.6 Å^2 exhibit a structure with one dipole per unit cell in each layer. The dipoles in the bilayer with A_m = 21.2 Å^2 exhibit a two-dipole per unit cell with structure with anti-parallel orientations in each layer. The small peaks around ϕ_μ = −90° in the lower layer and ϕ_μ = 100° in the upper layer are due to the "gauche" defects characteristic of the conformational disordering around the C1—C2 bond. (In an alkane chain a gauche defect is often defined as a bond which has a dihedral angle (ϕ) such that $60° < \phi < 180°$ and $-60° < \phi < -180°$. This is the definition of a gauche

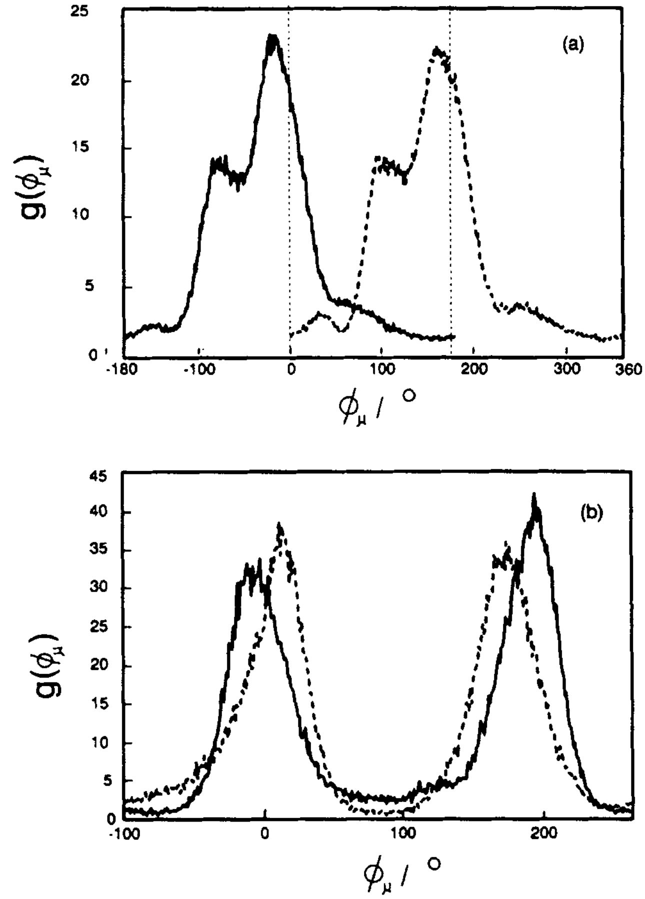

Figure 5 The distribution of dipolar azimuthal angles of the lower layer (solid line) and the upper layer (dashed line) of the bilayer: (a) A_m = 20.6 Å^2; (b) A_m = 21. Å^2.

bond used throughout this paper). The idealized structures for the dipoles in the bilayers at both densities are sketched in Figure 6.

The radial distribution function, $g(r)$, of the molecular centres of mass in the lower and upper layers of both bilayers are shown in Figure 7. Both the distributions are solid-like, but surprisingly, for the bilayer at A_m = 20.6 Å^2, the first peak around 5 Å is split into three peaks. These peaks were not resolved in the simulation of the monolayer at the same density. Note, that the translational correlation is much stronger than that found in the monolayer. An hexagonal order parameter

$$\mathrm{OP}_{hex} = \left\langle \frac{1}{6} \sum_{i=1}^{6} \exp(i6\theta_i) \right\rangle$$

was calculated for each configuration during the production phase of both simulations. The angles θ_i are between imaginary bonds from the centre of mass of a

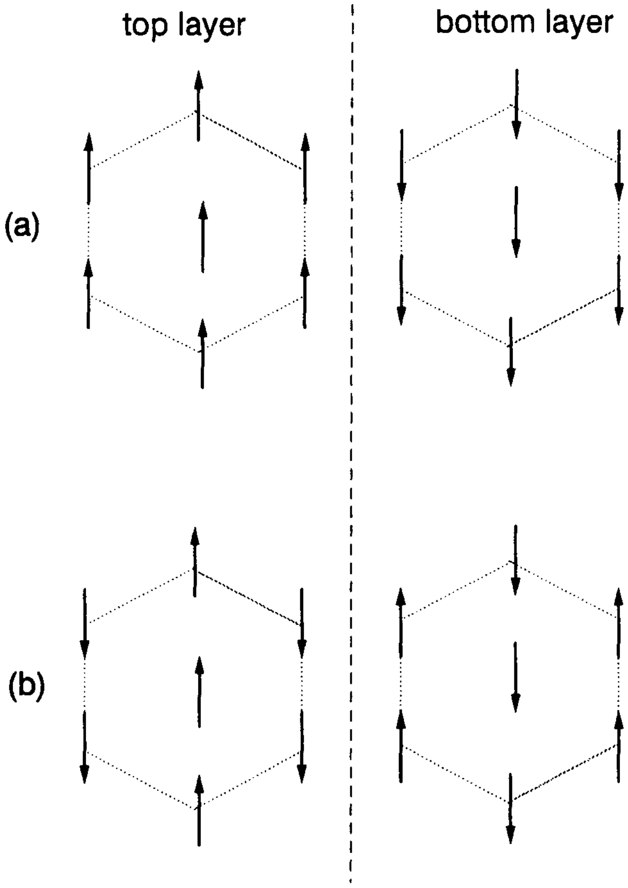

Figure 6 A sketch of the dipolar orientations in the bilayer: (a) $A_m = 20.6$ Å^2; (b) $A_m = 21.$ Å^2.

molecule to the centre of mass of its six nearest neighbour molecules. The average is over all the molecules in the simulation cell. OP_{hex} at 21.2 Å^2 is shown in Figure 8. The figure shows an almost perfect correlation between structural fluctuations in the top and bottom layers of the film. The hexagonal order parameters of the lower and upper layers, averaged over the entire production phase, with $A_m =$ 21.2 Å^2 are 0.745 ± 0.1 and 0.753 ± 0.1 respectively. These are not much lower than the average hexagonal order parameter of the monolayer at the same density (0.8 ± 0.02). However, the averaged OP_{hex} for the bilayer with $A_m = 20.6$ Å^2 are 0.62 ± 0.05 and 0.63 ± 0.05 for the lower and upper layer respectively. These values are significantly lower than the value for the monolayer at this density (0.8 ± 0.02, and taken with the sharply peaked $g(r)$, they indicate that there is a distortion of the in-plane structure of the bilayer. These average positions of the centre of mass in the simulation at 20.6 Å^2 are sketched in Figure 9. This distortion of the triangular lattice can be produced within the periodic conditions of the simulation and leads to the observed splitting of the first peak in $g(r)$.

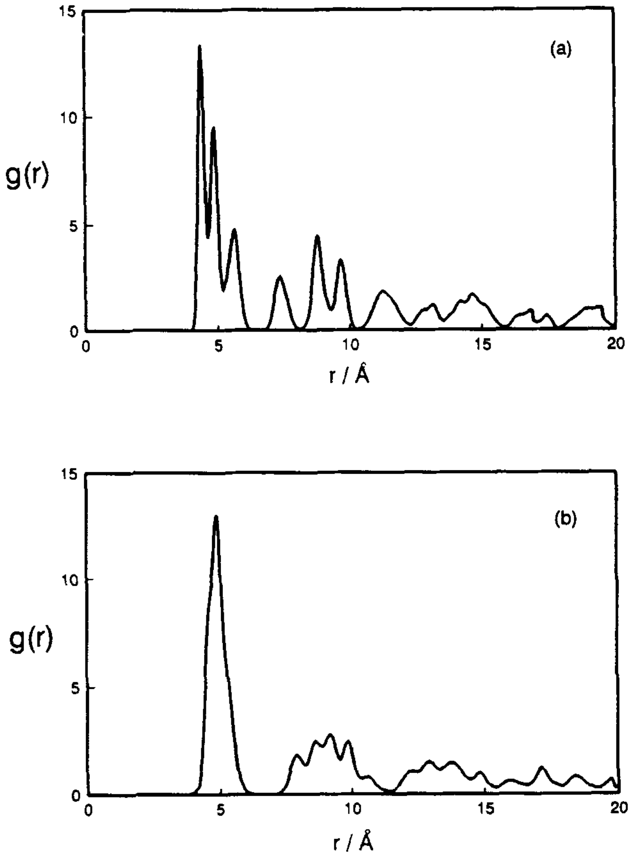

Figure 7 The radial distribution functions $g(r)$: (a) A_m = 20.6 Å^2; (b) 21.2 Å^2. The radial distribution functions of molecules in the upper and lower layers are indistinguishable on this scale.

The distribution of atoms and gauche conformations along the direction normal to the surface are shown in Figure 10. The distribution of atoms in both layers is quite solid-like and similar to those of the monolayer discussed in I. There is no significant interpenetration of the lower and upper layers. Gauche defects in the chain are located at both ends of the molecules especially in the C1—C2 bond close to the head-group. Figure 11 shows the distribution of dihedral angles around the C1—C2 bond in the upper and lower layers in both bilayers. The dihedral rotation in the lower and upper layers are strongly correlated. In the bilayer with A_m = 20.6 Å^2, the gauche minus defects centred at −80° in the lower layer correspond to gauche plus defects at approximately 80° in the upper layer. In monolayer at A_m = 20.6 Å^2, the distribution of the C1—C2 dihedral angles is symmetric around $\gamma = 0$, but the distribution in the bilayer is highly asymmetric. This asymmetry results from the high barrier to reorient the dipole at this density. This reflects the different strengths of the charge-dielectric image charge inter-action in the monolayer and the intermolecular charge-charge interaction between amphilphiles in the bilayer.

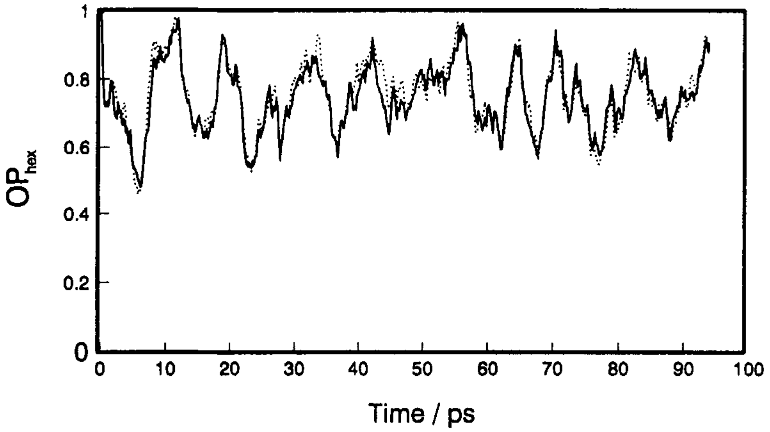

Figure 8 The hexagonal order parameter OP$_{hex}$ for the lower layer (solid line) and the upper layer (dashed line) at $A_m = 21.2$ Å^2 as a function of time during the production phase of the simulation.

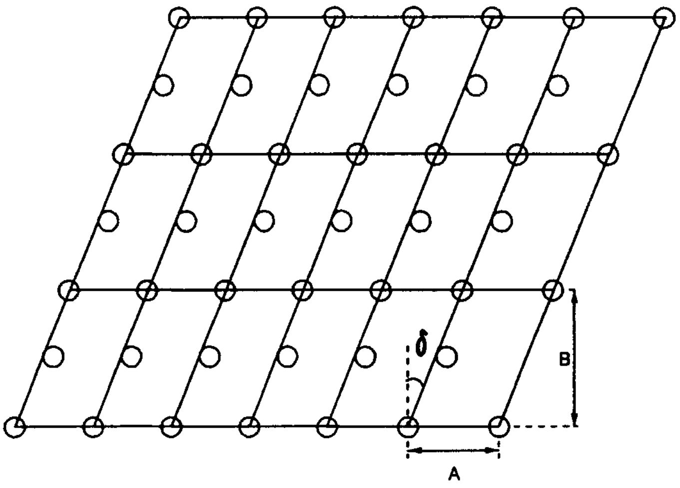

Figure 9 A sketch of the average positions of the centres of mass of the molecules in the simulation with $A_m = 20.6$ Å^2. $A = 4.8772$ Å, $B = 8.4475$ Å and $\delta = 20°$.

5 CONCLUSIONS

Using a novel form of hybrid potential, we have simulated a Langmuir-Blodgett bilayer of stearic acid at 25°C for two head-group areas. At $A_m = 21.2$ Å^2 the molecules are tilted at 18° to the surface normal with a next-nearest-neighbour azimuthal orientation. The head-group dipoles are parallel to the plane of the surface and antiparallel to each other. The precise ordering of the dipoles depends on the density of the bilayer. There is a strong correlation between the translational and orientational ordering of the molecules in the two layers due to strong

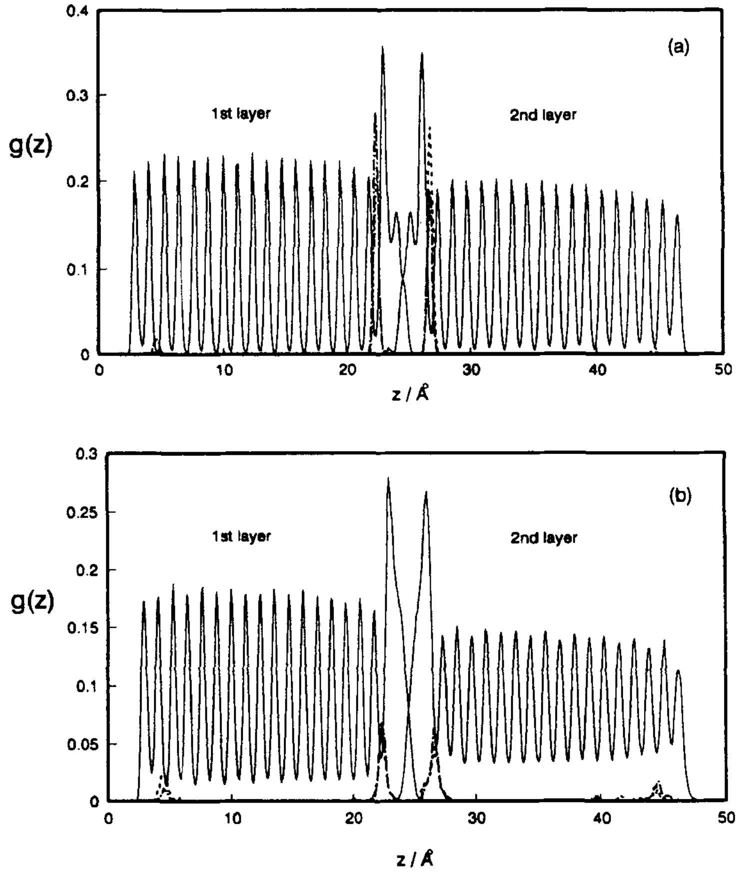

Figure 10 The distribution of atoms (solid line) and gauche defects (g^+ (dash-dot) and g^- (dashed)) along the surface normal for the bilayer with (a) A_m = 20.6 Å^2 and (b) A_m = 21.2 Å^2. The distribution for gauche defect is multipied by 5.

inter-layer electrostatic coupling between the head-groups. Clearly a realistic representation of the head-group is an essential prerequisite to the accurate modelling of multilayer Langmuir Blodgett films. Indeed recent results on multilayers of chain molecules without specific electrostatic interactions between the head-groups and which used the united-atom model for the hydrocarbon chain show very little correlation of azimuthal ordering [11]. The head-groups exhibit a well-developed crystalline structure in the plane of the bilayer at both densities. In contrast the tail groups at the vacuum interface exhibit radial distribution functions which are more liquid-like, raising the question of whether it is possible to image air-film interface using invasive techniques such as the atomic force microscope.

Surprisingly, decreasing the head-group area to 20.6 Å^2 does not significantly alter the tilt angle, in contrast to both the energy minimisation results and the molecular dynamics results for the monolayer at the same temperature and head-

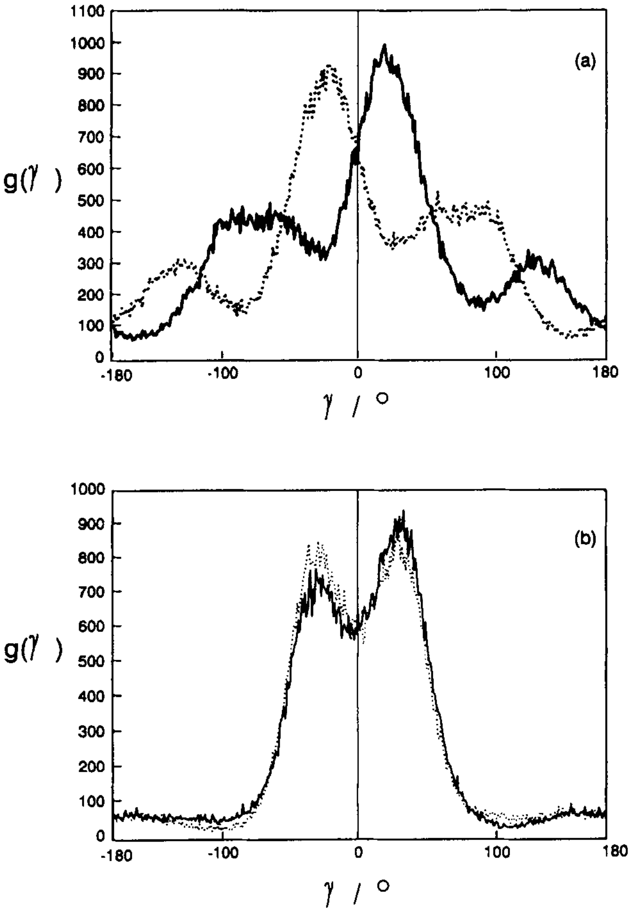

Figure 11 The distributions of the dihedral angle of the bond C1—C2 of the lower layer (solid line) and upper layer (dashed line) in the bilayer with (a) A_m = 20.6 Å^2 and (b) A_m = 21.2 Å^2.

group area. It does however produce a rectangular distortion of the molecular centres of mass away from the initial triangular arrangement towards a rectangular structure which is evocative of the crystal B structure. The simulations suggest that for the head-group area studied, the tilting transition in the monolayer may be replaced by a structural rearrangement from a triangular to a rectangular lattice. In view of the difficulties of simulating at constant spreading pressure (or surface tension), simulations of large patches may be the only way to test these ideas on rectangular distortion of the lattice.

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