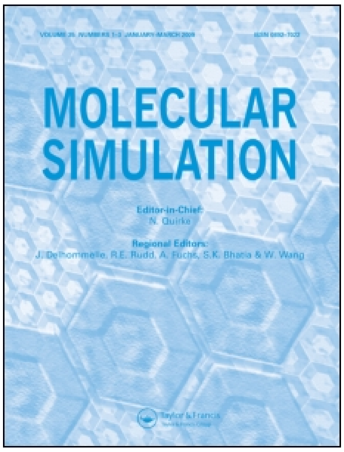

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A Molecular Dynamics Investigation of Compressed Aqueous Alkanoate Monolayers

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Molecular dynamics are conducted on a dodecanoic acid monolayer/aqueous surface. Surface pressure is controlled by imposing constant-volume conditions for series of lengths of the square slab constituting the MD cell. The response of the alkanoate chains to the pressure is followed by examining various computed quantities that monitor their conformational order. These include atom-pair radial distribution functions, chain torsional angles, energies, atomic densities perpendicular to the interface, diffusivities and atomic plots. These quantities lead to chain separations which in the range 4–5 Å implying order when the alkanoate chains have a mean area of 0.18 nm^2.

Keywords: Monolayer; Alkanoate chains; Amphiphiles; Molecular dynamics; Conformational order; Surface pressure

INTRODUCTION

The first self-assembled systems to be investigated were monolayers of amphiphile molecules on a water surface. The hydrophilic ends of these chains consist of carboxylic acid groups which associate with the aqueous medium, while the hydrophobic (lipophilic) chains orient in almost fully extended conformations often perpendicular to the surface. The structural response of such a surface array of chains to the restriction of their total surface area is well known and may be investigated experimentally [l,2] by compressing the portion of the surface containing the amphiphile molecules and using the surface geometry to gain information on the conformations of the alkyl chains directed away from the aqueous surface [2]. In addition, diffraction [3,4], electron microscopic [5,6] and spectroscopic methods [2] have been used to elucidate the molecular structures of the films. The present work reports a molecular dynamics (MD) simulation of amphiphile molecules represented by dodecanoic acid, $C_{12}H_{25}COOH$ on a water surface. The investigation includes a study of the changes in the structures, dynamics and energetics of the chains that accompany their surface compression.

STRUCTURAL MODEL

As an initial structure on which to perform the MD the aqueous medium was modeled at time zero as a body-centred square-packed, ten-layer slab of water molecules, the side of each square being $a = 4.150$ Å and the interlayer distance 3.5275 Å. These spacings produced a system of molecules which prior to the MD runs has the correct density for bulk water. In order to facilitate the attainment of equilibrium some orientational features of the water molecules alternated between successive layers.

The upper surface of the water layer (in the *ab* plane) is referred to as the *interface* and is defined as a plane with zero **c** axis coordinate. As shown in Fig. 1 (a) an amphiphile molecule was inserted at the centre of each cell of the interface. The atoms of the carboxylic groups were "immersed" in the water layer by defining their **c**-axis coordinates with negative values and the atoms of the alkyl "tails" were appropriate to fully extended chain conformations along the **c** axis as shown in Fig. 1 (b). The **c** axis atomic coordinates of each chain's hydrophobic alkyl moiety were all positive, the terminal hydrogen atom of the methyl group being 15.7 Å from the interface. The repeat unit consisting of a square cell of alkanoate chains in contact with a body-centered

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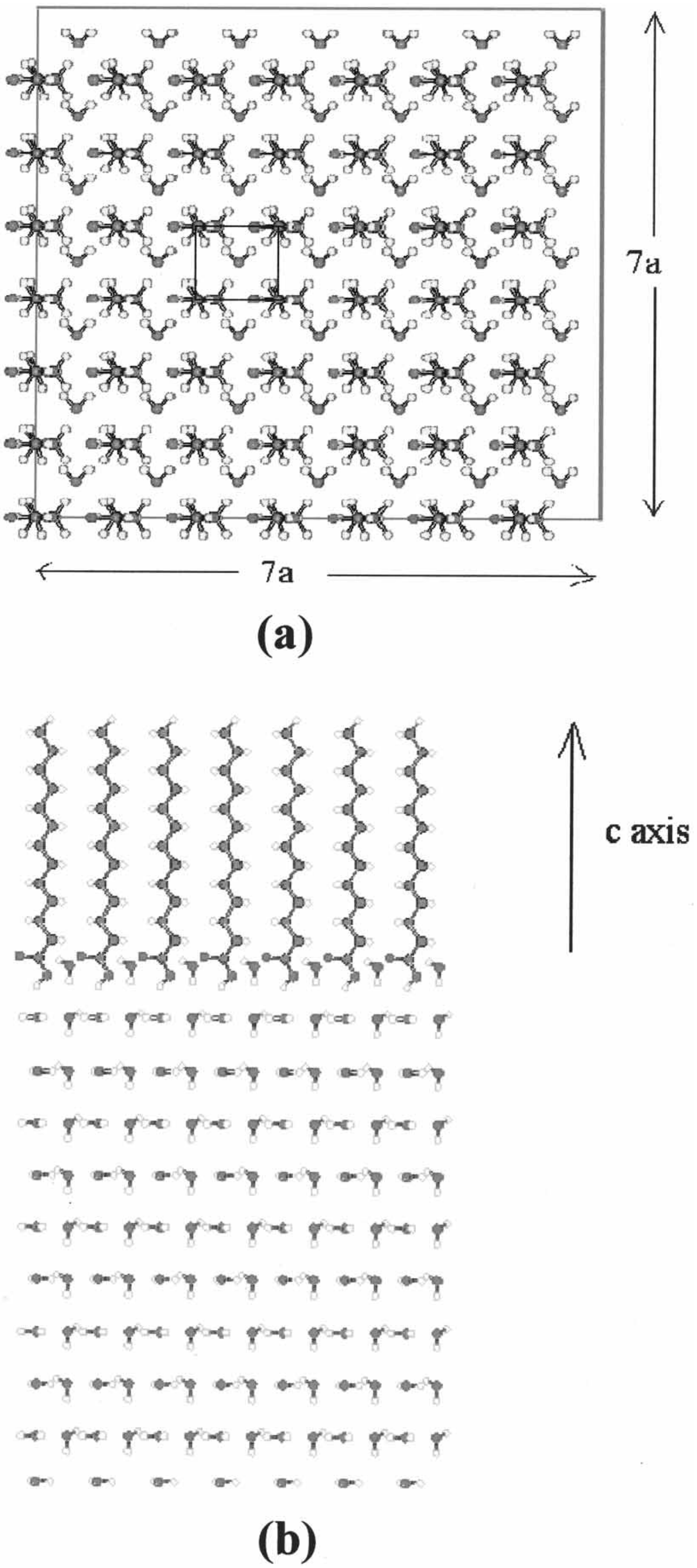


FIGURE 1 The monolayer system prior to MD. (a) is the the *ab* plane (view perpendicular to the liquid interface) and (b) is the *ac* plane (view parallel to the interface).

square cell of water molecules constituted a "basic" cell from which a 7 × 7 MD supercell, or 49-cell simulation box, was formed. The simulation cell then contained 2009 amphiphile atoms and 2940 liquid atoms. In order to create the required space to accommodate the COOH groups in the surface layers of the water slab while conserving the total number of particles, some water molecules were eliminated from the surface and displaced to the "bottom" of the water slab, i.e. to the face of the liquid layer furthest from the interface. The whole surface was finally simulated by imposing two-dimensional periodic boundary conditions on this supercell.

The surface pressure in the *ab* plane was controlled via the separation of the alkanoate chains by altering the lengths of the cell axes. But because of the commensurability between the periodicities of the water and amphiphile systems required by the periodic boundary conditions, changing the lengths of the cell simultaneously also alters the initial in-layer separation of the water molecules in the *ab* plane prior to the MD. However the subsequent equilibration of the 7 × 7 simulation cell by the MD runs was found to lead to satisfactory separations of both the water and alkanoate subsystems.

The molecular geometry selected to model the hydrophobic moieties of the dodecanoate chains was taken from Kitaigorodskii's description of long alkane chains [7] and used in several of our earlier work on systems involving alkyl chains [8–13]. The bond lengths and angles in the aliphatic chain were $r(\mathrm{C{-}C}) = 1.535\,\text{Å}$, $r(\mathrm{C{-}H}) = 1.1\,\text{Å}$, $\theta(\mathrm{C{-}C{-}C}) =$, $\theta(\mathrm{C{-}C{-}H}) = 112.2°$, $\theta(\mathrm{H-C-H}) = 106.3°$, while those in the carboxyl group were $r(\mathrm{C} - 0) = 1.27\text{Å}$, $r(\mathrm{O{-}H}) = 1.0\,\text{Å}$, $\theta(\mathrm{O{-}C{-}O}) = 122.0°$. The length of the $\mathrm{C(sp^3){-}C(sp^2)}$ bond between the two moieties was taken as 1.52 Å.

The total force field used for the MD simulation included bond-length and bond-angle deformation potentials and non-bonded atom-pair potentials. For the hydrocarbon moiety of the amphiphiles the potentials were again those used in our work on molecules containing alkyl chains [8–10], the additional ones, those for the C, H and O atoms in the carboxylic acid group, being described by Dreiding potential functions [l4]. The force field set [11–13] included torsional potentials for the polythiophene main chain but not for the alkyl side chains.

The liquid water layer was simulated *via* the SPC/E model [15] in which charges of −0.8476 and +0.4238 are placed on the O and H atoms, respectively, which are "frozen" at a O—H bond length of 1.0000 Å and at a bond angle 109.47°. The non-bonded interactions are defined by one intermolecular function—solely that between the O atoms. In producing the SPC/E model the authors had tuned the parameters so as to reproduce selected properties of liquid water: density, diffusivity and dipole moment. The resulting SPC/E potential (energy in eV, distance r inÅ) is

$$V(r) = \frac{27291.58}{r^{12}} - \frac{27.12}{r^{6}}$$

THE CALCULATIONS

The MD calculations were performed at a series of constant volume and temperature conditions (NVT thermostat) using the program code DL_POLY [16] with the two-dimensional boundary conditions required to describe an infinite slab structure. The atomistic model was generated using purpose-written code which allowed the user to specify parameters characterising the monolayer such as alkyl chain length and repeat distance of the alkanoate chains. The alkanoate atoms filled the simulation cell in the *ab* plane, where the periodic boundary conditions generated a monolayer that was uniformly extended into an infinite sheet. The monolayer/water slab was created near the centre of the cell in the **c** direction so as to leave free space below the slab into which some water molecules could "flow" when compression was applied in the *ab* plane. The initial configuration of the alkanoate chains and the water molecules is shown in Fig. 1.

The simulations were conducted with a potential cutoff of 11.5 Å, an Evans NVT thermostat at $T = 300\,\mathrm{K}$ and a timestep of 0.001 ps. The structure, which had energetically equilibrated by 1000 timesteps, showed no significant structural changes after 10,000 timesteps. The MD runs were routinely performed for 10^5 timesteps except when the conditions produced some new structural feature, whose stability was tested by continuing the runs for a further 2×10^5 timesteps.

RESULTS

This section describes the response of the chains of the alkanoate monolayer to the application of a "surface pressure" that constricts them to occupying a reduced total area of the surface, changes in the structure will be shown by the use of various means to monitor the effects of the compression at various stages: (a) molecular "snapshots" (i.e. plots of the atomic positions defining the molecular structure after the MD run), (b) atom-pair radial distribution functions (rdf, a statistically-computed quantity revealing data relating to the environment of the chain atoms, providing information about chain conformation), (c) energy changes, (d) diffusion coefficients, (e) atomic densities along the direction normal to the interface and (f) mean torsional angles in the alkanoate chains.

Atomic Plots

When the in-plane separation of the alkanoate chains (the length of the basic cell square a) are in the range $4.0 < a < 4.8$ Å the atomic plots in Fig. 2 show the chains directed, with a rather high degree of *trans* conformational order, fairly perpendicular to the liquid surface. The plots in Fig. 3 demonstrate that, as the separation a increases, the chains exhibit progressively greater disorder; the chains entangle and the resulting loss of their fully-extended conformations reduces the thickness of the monolayer. Also, as the separation *decreases* from 4.1 Å the thickness of the monolayer remains about the same as most of the chains keep their all-*trans* conformations. But the only way in which the monolayer can minimize its steadily increasing potential energy and retain some measure of conformational integrity in a progressively more pressurised condition is to expel some of its amphiphile chains. This expulsion, which is described by practical investigators as a stage in the pressure-induced collapse of a monolayer [17], is shown by the snapshots for small separations in Fig. 3, where some chains have been uprooted from the water

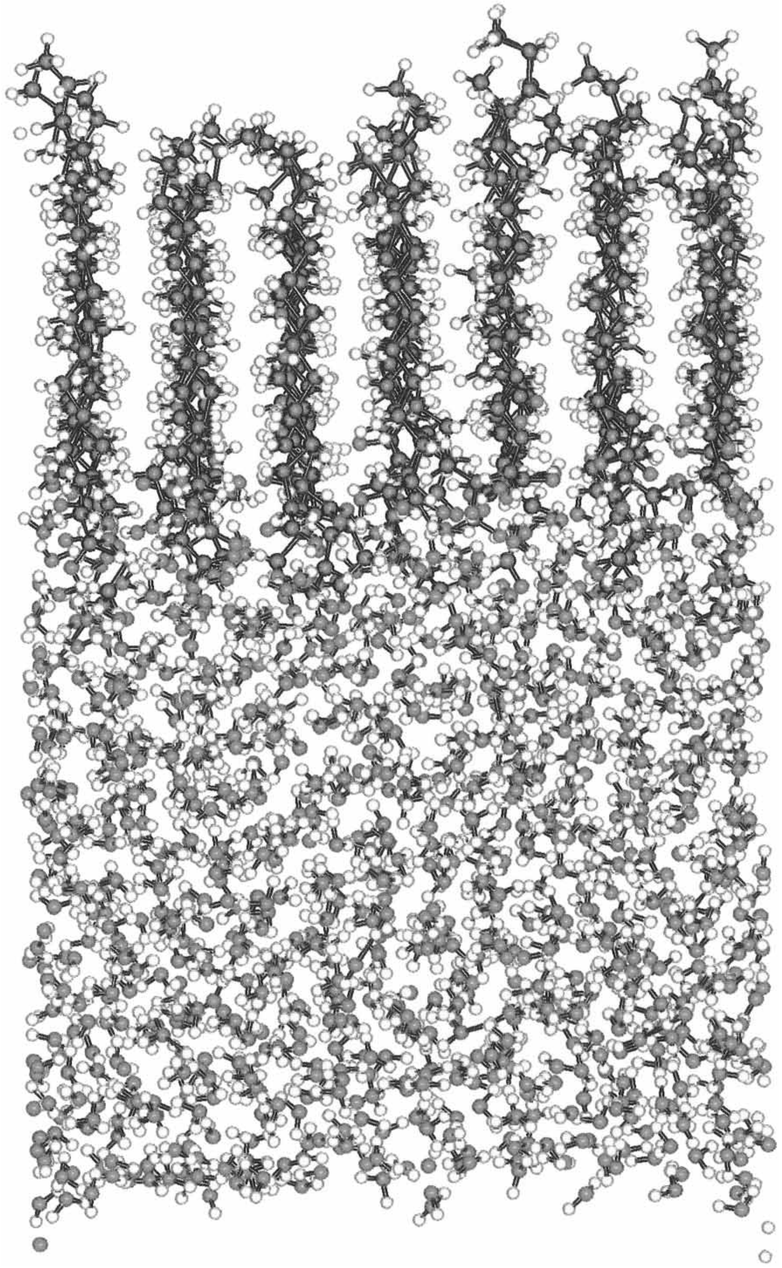
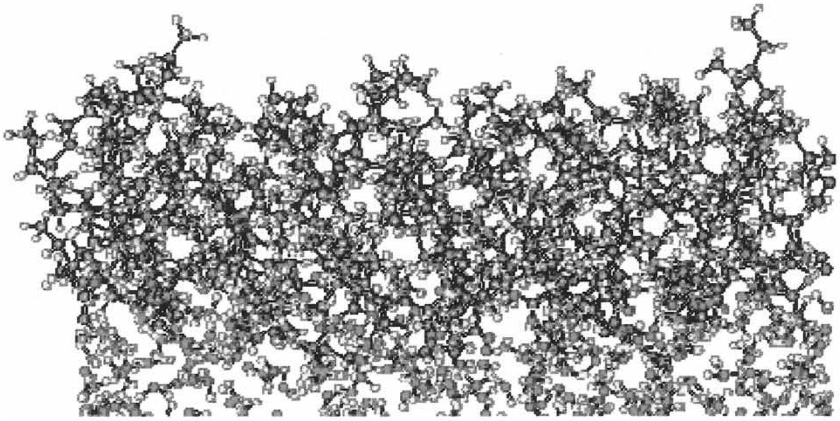
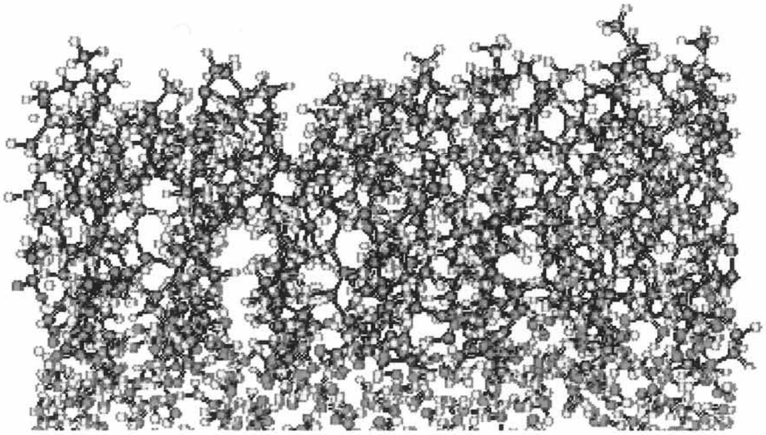


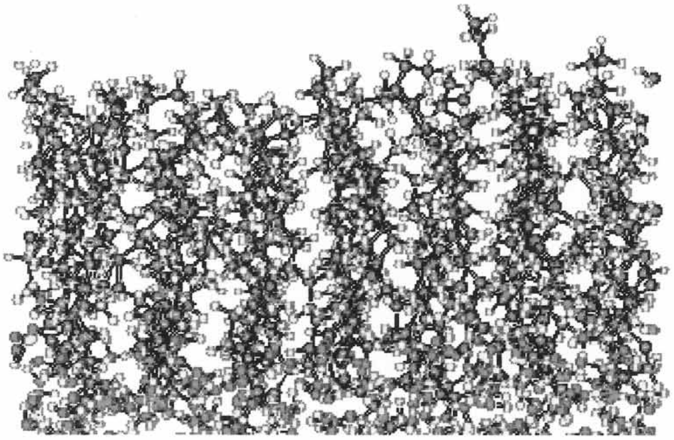
FIGURE 2 An atomic "snapshot" of the monolayer structure after 10^5 MD timesteps. This is in the optimum configurational order régime, for which the alkanoate separation in the interface is given by $a = 4.3$ Å.



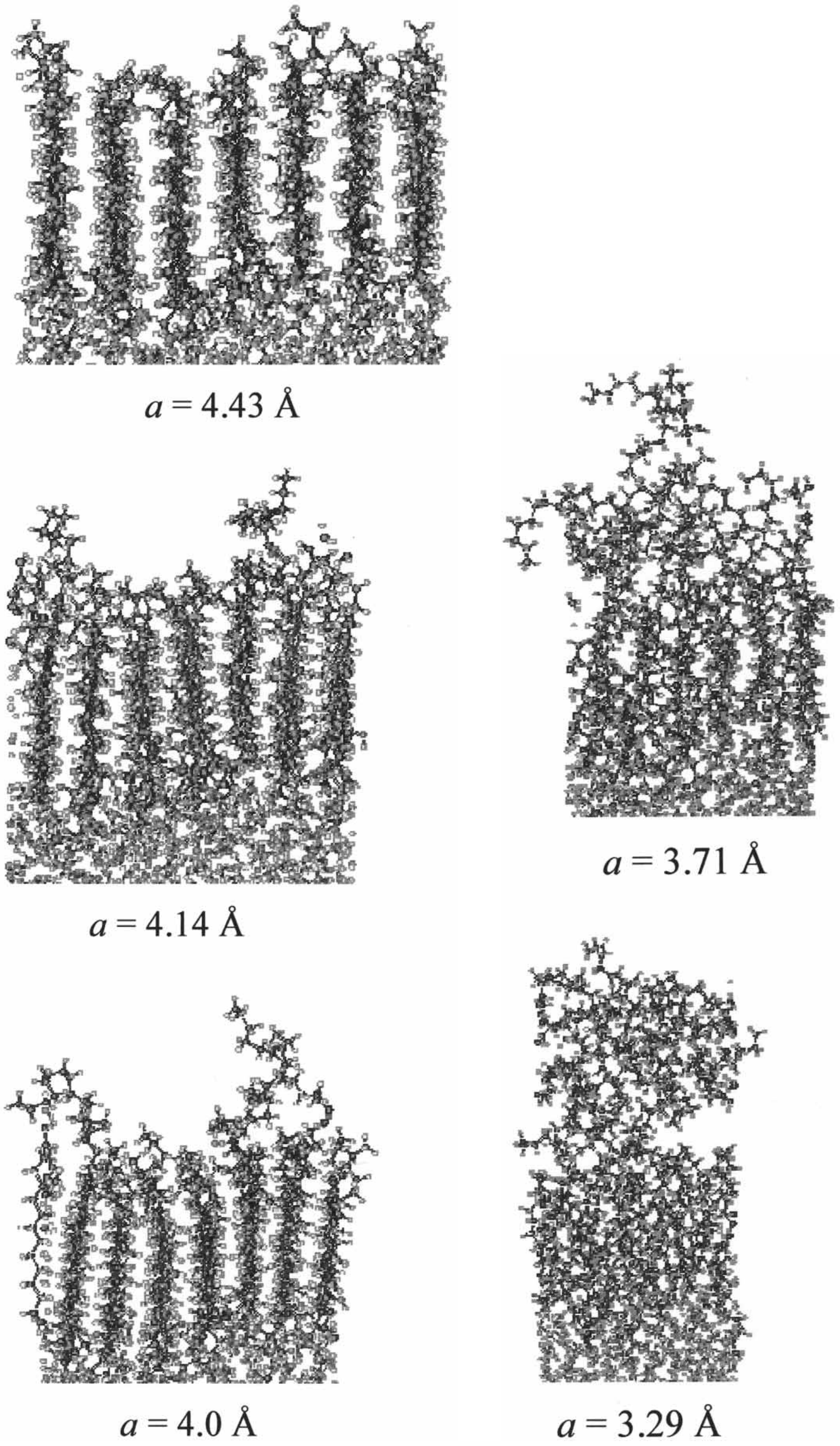
$a = 6.0$ Å



$a = 5.43$ Å



$a = 5.0$ Å



$a = 4.43$ Å

$a = 3.71$ Å

$a = 4.14$ Å

$a = 4.0$ Å

$a = 3.29$ Å

FIGURE 3 Snapshots showing the effect of surface pressure (monitored by the alkanoate chain separation *a*) on the conformations of the chains.

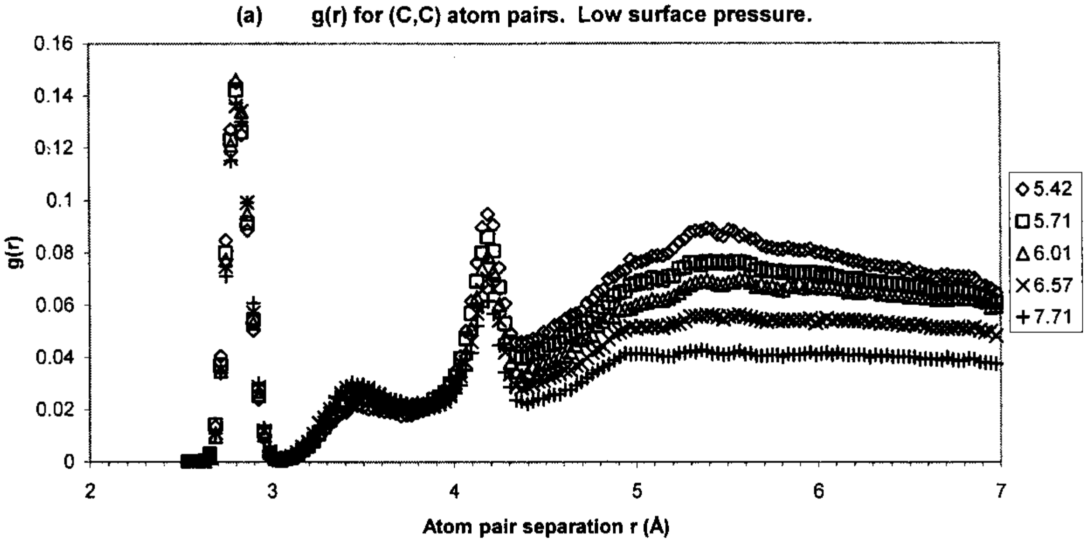
surface and displaced to the outer surface of the monolayer.

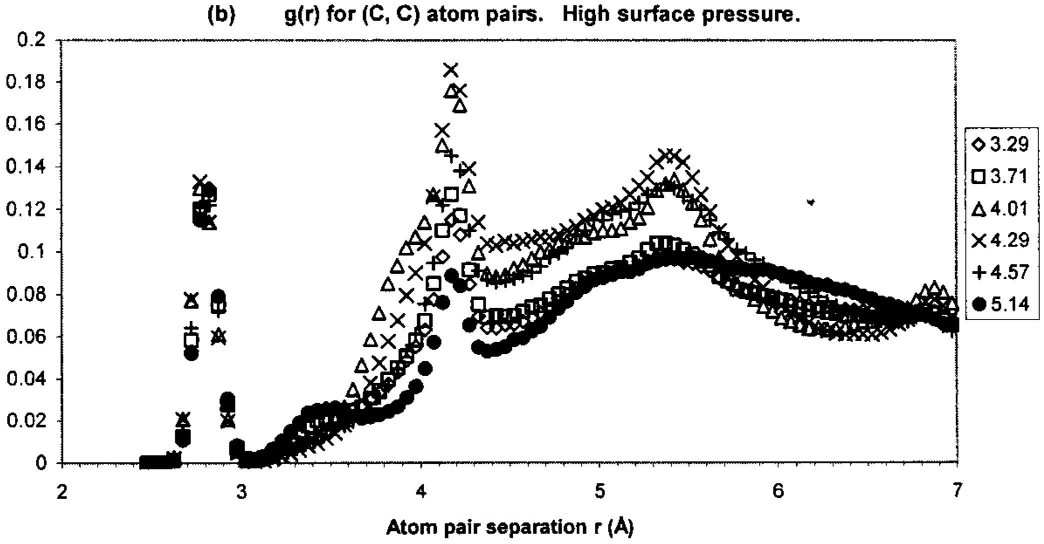
Radial Distribution Functions

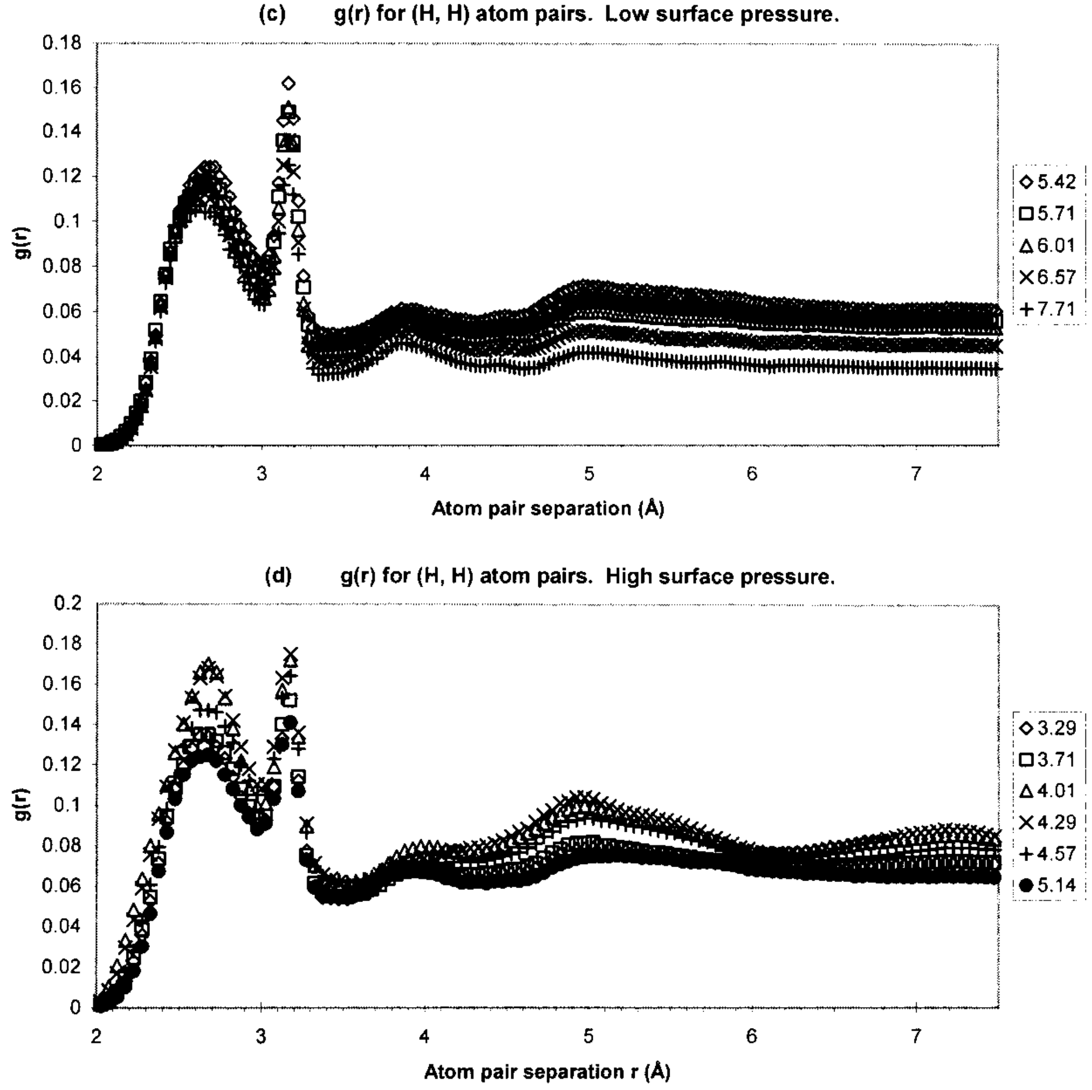
Figure 4 shows the rdf for atom pairs (C,C) and (H,H) for different compressions of the monolayer. These will be called $g_{CC}(r)$ and $g_{HH}(r)$. For clarity, separate Fig. 4(a) and (b), are used to display $g_{CC}(r)$ for two compression ranges. Similarly Fig. 4(c) and (d) show $g_{HH}(r)$ for the same ranges. The prominent (C,C) peak at 2.8 Å, arises from chain carbon atoms in (1,3) (i.e. next nearest neighbour) positions and that at 4.2 Å comes from the (1,4) pairs. The $g_{CC}(2.8)$ peak is independent of conformational changes and therefore remains narrow throughout the compression range, while the broadening of $g_{CC}(4.2)$ is due to the sensitivity of the (1,4) distance to changes in the chain conforational angles, which must, therefore, change over the range of chain separations.

The first two peaks in the (H,H) rdfs *both* arise from CH_2 (methylene) H atoms on (1,2) and on (1,3) carbons. In each of these methylene pairs there are H···H separations of 2.5 and 3.1 Å. They are sensitive to (1–2)- and (2–3)- link torsional angles, and so their varying amplitudes imply chain conformational changes.

As the monolayer is expanded from its ordered condition the onset of chain disorder noted in the atomic plots of Fig. 3 is reflected in the reduction of the $g(r)$ peak amplitudes as the precise atom pair separations associated with a lattice are replaced by separation *ranges* which broaden the peaks. As the chain separations are decreased the peaks initially gain amplitude as the chains become more ordered. The sharpest peaks occur at an imposed chain separation $a = 4.29$ Å, which lies in the 4.0–4.8 Å range selected from the Fig. 3 plots in the previous subsection to describe chain order. As the compression increases with decreasing cell size,






(c) g(r) for (H, H) atom pairs. Low surface pressure.

(d) g(r) for (H, H) atom pairs. High surface pressure.

FIGURE 4 The radial distribution function (a) and (b) for (C,C) and (c) and (d) for (H,H) showing their response to the chain separations *a* shown in the legends.

returning the chains to disordered configurations most of the peaks diminish. The only g_{CC} peak which sharpens as we proceed from $a = 4.29$ Å is $g_{\mathrm{CC}}(3.5)$, which appears when the chain separation departs from the 4.0 to 4.8 Å range. At small *a* a peak would be expected as the separation of atoms in *adjacent* chains then fall into this range. At large chain separations, where we have already noted that conformational disorder is expected, a torsion of about 90° around the 2–3 link in a $C^{(1)}C^{(2)}C^{(3)}C^{(4)}$ section of the chain would bring atoms $C^{(1)}$ and $C^{(4)}$ to a separation of 3.5 Å.

Energy

Figure 5(a) shows the non-bonded, or van der Waals energy of the dynamics system as a function *a* of the separation of the alkanoate chains in the *ab* plane. As the separation *a* is reduced from the range resulting in disordered chains, the energy shows a small variation and then passes through a minimum at $a = 5.8$ Å. As the surface contracts further the energy increases smoothly as the chain separation decreases from 5.8 to 3.8 Å, suggesting a gradually increasing pressure of an ordered system. This range contains the $4.0 < a < 4.8$ Å range which was identified by a visual examination of the atomic plots of Fig. 2 in "Atomic plots" section as a region of conformational order. The abrupt change at $a = 3.6$ Å could be due to the relief of strain resulting from the onset of monolayer collapse. In this process alkanoate chains are expelled from the monolayer, as noted in section 4.1.

Our original intention to monitor the total configurational energy including the Coulombic

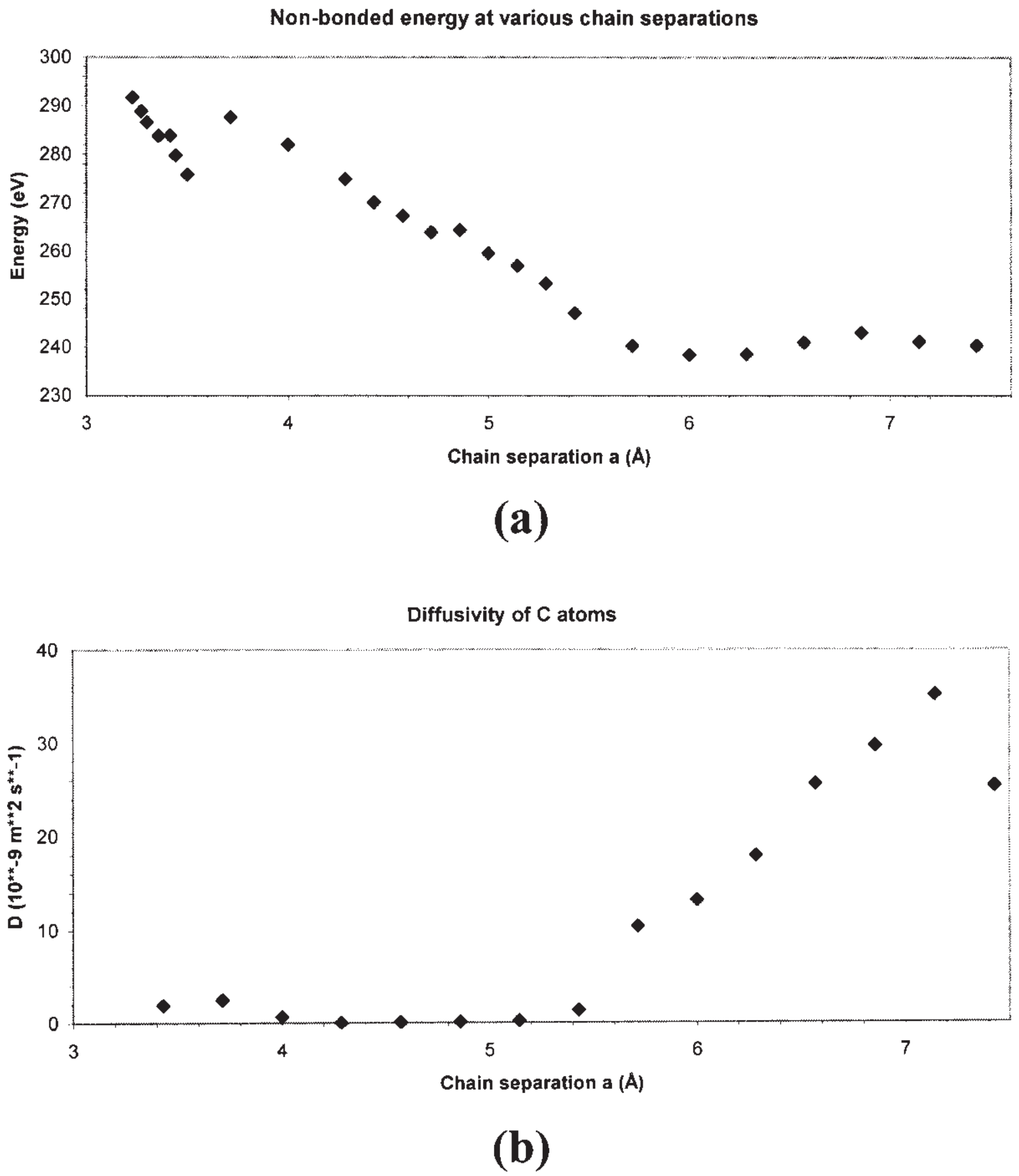


FIGURE 5 The response of (a) non-bonded energy and (b) diffusion coefficient to alkanoate chain separation *a*.

contribution did not succeed. This is because of the uncertainty the latter component from the approximate nature of the charges placed on the atoms of the carboxyl group. Not only is the charge distribution imperfectly known, but so also is the manner in which it changes when the alkanoate chains approach close proximity. Indeed it was at short chain separations that the problem was manifested when the plotted points in this region were found to be considerably scattered. Investigation showed the Coulombic energy to be highly sensitive to the separations and relative orientations of the 49 carboxyl groups in the simulation cell. Presumably the scattered total-energy would be eliminated by the creation of a drastically larger simulation cell than the present one containing 2009 alkanoate atoms.

Diffusion Coefficients

The approximate diffusion coefficients of the carbon atoms plotted in Fig. 5(b) as a function of *a* show uniformly low values for $a < 5.2$ Å above which the migration of the chains on the more sparsely populated surface is easier. When the surface is highly compressed to small $a(<4.0$ Å$)$ the origin of the slightly greater diffusion may again be the mobility of the alkanoate chains which are expelled from the surface at the collapse point. Over the remaining *a* range which is close to the 4.0–4.8 Å range from the atomic plots in "Atomic plots" section, and contained in the 3.6–5.8 Å range from the non-bonded energy in "Energy"section the mobility is quite low on the plotting scale of Fig. 5(b).

Atomic Densities

In order to gain further structural details on the monolayer as it reponds to the changing surface pressure the mean densities of the atoms constituting the monolayer were profiled for various positions along the c direction, i.e. perpendicular to the interface. Figure 6(a) shows the density profile for a monolayer in which the chain separation *a* is 5.14 Å which is in the chain-order 3.6–5.8 Å range defined by the energies ("Energy" section). The regular chain conformations are apparent from the shape of the profile, whose plateau top extends for about 12 Å and becomes zero at 16 Å. These numbers should be compared with the 15 Å length of the amphiphile's hydrophibic moiety when it is in its strictly fully-extended conformation.

Part (b) of the Figure shows the effect of departing from the ordered régime as a result of decreasing and increasing the surface pressure. At low surface pressures (cell length in the range 5.7 < *a* < 8.0 Å) the alkanoate chains, whose conformations the previous subsections showed to be disordered,

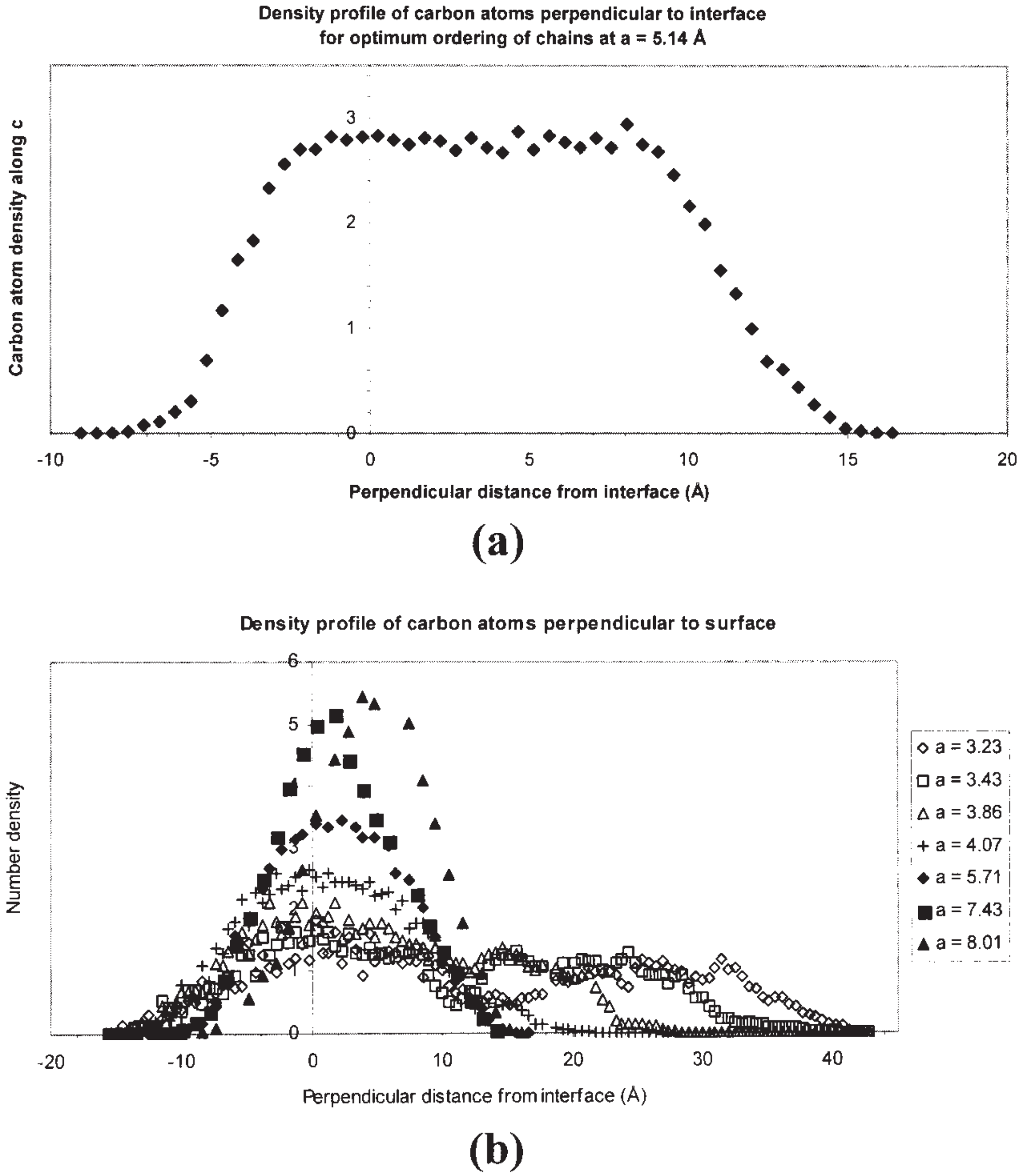


FIGURE 6 C atom density along the direction perpendicular to the water surface: (a) ordered chain régime, (b) response to chain separation *a*.

produce a monolayer whose atomic densities are peaked close to the interface and decay to zero at about 15 Å. The increasing surface pressure results in a greater degree of "fully-extended" chain conformations and at $a = 4.28$–5.71 Å the density profiles show increasing uniformity over the centr′al region. At still higher surface pressures ($a <$ 3.86 Å) the profile rapidly becomes broad and irregular as "uprooted" amphiphile chains are expelled to the surface of the monolayer.

The density traces in the figure are derived from the carbon atoms, but as essentially equivalent profiles were obtained for the hydrogen atoms they are not presented.

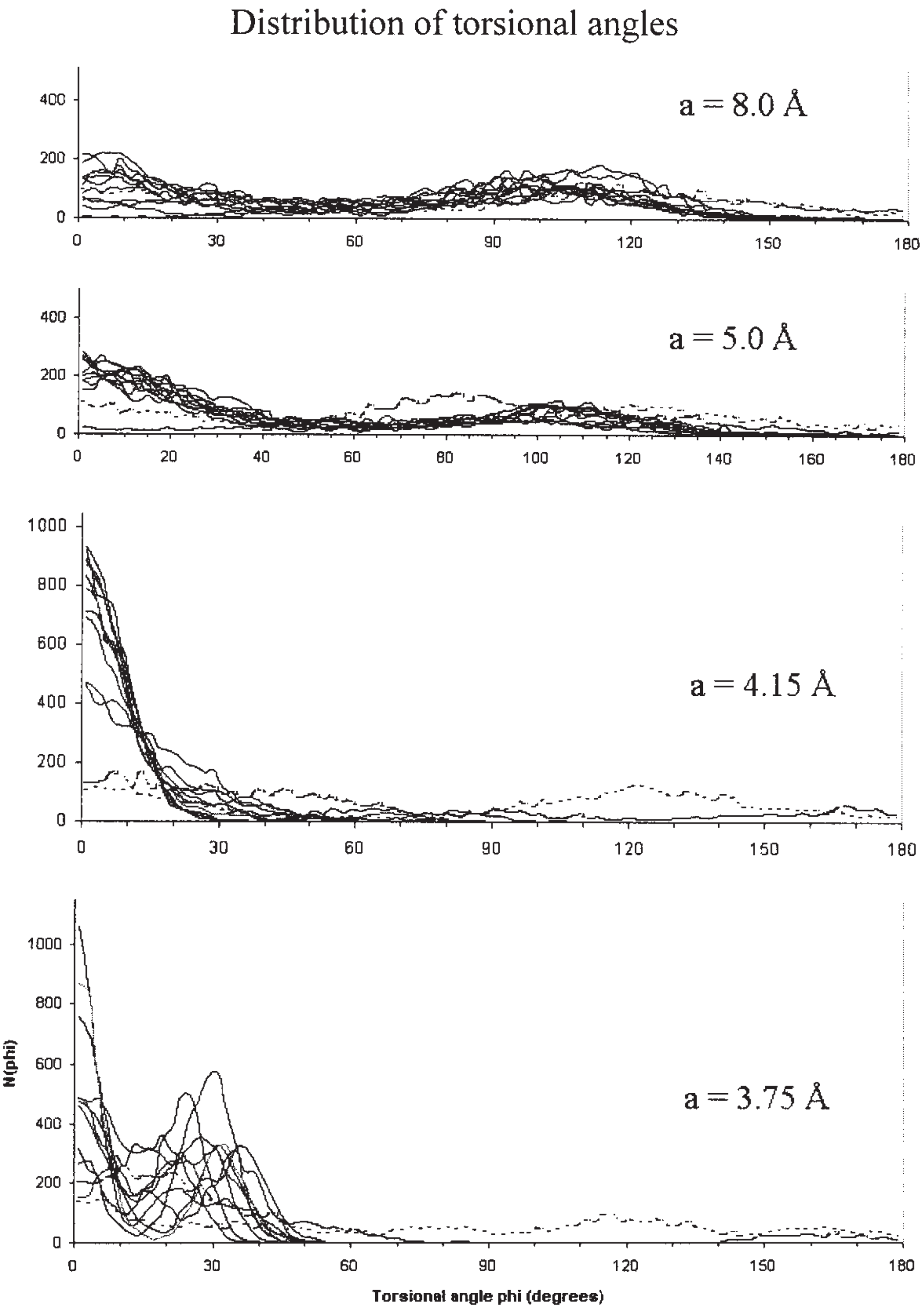


FIGURE 7 The effect of alkanoate separation a identified in the legend on the torsional angles in the twelve C—C bonds in the chain. The dotted trace relates to the terminal CH_2—CH_3 link.

Chain Torsional Angles

The surface pressure imposes a conformational order on the amphiphile chains by favouring the establishment of *trans* links on the C—C bonds. If ϕ is the torsional angle of a C—C bond measured from the *trans* conformation (i.e. $\phi = 0$ for the "fully extended" link), we define $N(\phi)$ as the number of links with torsional angles from ϕ to $\phi + 2°$. The results in Fig. 7 record traces of $N(\phi)$ for each of the twelve C—C links in all the alkanoate chains in the simulation cell, that for the methyl group at the end of the chain being shown dotted. The traces show that at low surface pressures, although the conformational angles of the disordered chains have wide variations, they are mainly *trans*($\phi \sim 0$) and *gauche*($\phi \sim 120°$) in roughly equal proportions. The imposition of surface pressure (monitored by decreasing the chain separation a) has a powerful effect on the torsional angles when a is less than 5.0 Å, by eliminating the *gauche* linkages and conferring fully extended conformations on the chains. The descriptions of the conformations of course are not valid for the methyl group whose torsions (dotted trace) are rather evenly distributed as expected. The results at surface pressures corresponding to $a < 4.0$ Å show a high degree of all-*trans* conformations even in those chains that are expelled from the interface although some links show tendencies to adopt small torsional angles around 30°. The chain separation range indicating an ordered monolayer with distributions like that for $a = 4.15$ Å, in Fig. 7 is $3.8 < a < 4.5$Å

CONCLUSIONS

The MD simulations of the alkanoate monolayer on a water surface have established conditions in which the amphiphiles' carboxylic groups —COOH are embedded in the aqueous layer while the aliphatic chains are perpendicular to the surface, leading to structurally stable configurations. The conditions pertain to the separations a of the alkanoate chain molecules in the monolayer where a is also the length of the square micro-cell defining the surface. Various methods of interpreting the results of the MD provide ranges of a that give ordered monolayers. Although the ranges derived by these different approaches do not entirely coincide, they are all similar.

1. Visual examination of molecular plots: 4.0–4.8 Å;
2. Radial distribution functions: sharpest at 4.29 Å;
3. Non-bonded energy: 3.8–5.8 Å;
4. Diffusion coefficients 4.0–5.2 Å;
5. Atomic density perpendicular to the surface 4.28–5.71 Å;
6. Torsional angles in the alkyl chains: 3.8–4.5 Å.

An inter-chain distance $a = 4.2$ Å which is in all the above ranges and is suggested by (2) to describe maximum order of the chains implies an area of 0.18 nm^2 $\mathrm{molecule}^{-1}$ which is close to the 0.2 value for the final stage of the ordered phase measured for various alkanoate chain monolayers [2].

In order to compare our results with surface pressure measurements we would need to monitor the total potential energy (or series of forces) of the system as a function of a. However it was found that the Coulomb interactions between the partial atomic charges at small interatomic separations were strongly dependent on the relative orientations of the hydrophilic —COOH groups. And as the abundance of these atoms is considerably less than those in the hydrophobic tails and in the solvent, the statistics were too weak to average out the Coulomb contributions efficiently; the total energy plot was consequently too scattered to monitor the compression and to evaluate quantities relating to surface pressure. But neglect of the forces acting in the direction of the compression (the coulombic effects act to *stabilise* the compressed monolayer) result in surface pressures that are too large.

An obvious extension of this investigation is to attempt to use the powerful computing power becoming available to increase the size of the MD cell considerably to include sufficient alkanoate chains to extract semi-bulk virial quantities such as total energy and surface pressures. However preliminary investigations in this direction show that the cell's required size for this purpose is still excessive for current resources. Other results which we have obtained showing that changing the polarity and certain other features of the liquid medium have an effect on the degree of chain-ordering in the monolayer will form the subject of a forthcoming paper.

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