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# Dynamics Simulation of Langmuir-Blodgett Films

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# Dynamics Simulation of Langmuir-Blodgett Films

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## INTRODUCTION

Langmuir-Blodgett monolayers are formed when amphiphilic molecules dissolved in volatile solvent are deposited on water surface followed by compression. During the compression, the randomly oriented molecules reorient themselves with the hydrophilic head groups on the water surface and the hydrophobic tail standing away from the water surface. The monolayer can then be transferred onto a solid substrate. LB-film multilayer can be made when monolayers are repeat transferred onto the same solid substrate. By altering the amphiphilic molecule's chemical structure and the number and type of monolayers in an LB-film multilayer, we can tailor the thickness, physical and chemical properties of the films. It is also possible to initialize polymerization on certain function group in a monolayer to enhance the mechanical properties or create other unique electro-optical properties. These organic ultra-thin films with highly ordered layer structure, have shown a wide range of potential applications in biochemistry, microelectronics, integrated optics, microlithography, and many other fields.[1]

It is important to get a better understanding of the relationship between the properties of the films and the micro-structure, for example, the molecular conformation, packing, orientation and motion in the films. For this purpose, within the past few years, different computer simulation methods were applied on LB film monolayers, including Monte Carlo methods[2,3] and molecular dynamics simulations.[4–6]

In this paper, we present the results of a molecular dynamics simulation of a fatty acid ($CH_3(CH_2)_{27}COOH$) monolayer on a water surface. In the present research we use a pseudoatom to represent each methyl or methylene group in a manner used by earlier researchers.[4–6] In order to obtain a better simulation of the interaction amongst the acid groups and between the acid groups and the water

layer, each atom of the COOH group has been separately represented. The length of the hydrocarbon chain is also much longer and is closer to that of the molecule used in our laboratory, our next simulation object: $CH_3(CH_2)_{15}C \equiv C - C \equiv C(CH_2)_8COOH$.



## METHODOLOGY

QUANTA 2.0 (CHARMm 21), a comprehensive, integrated molecular modelling package developed by Polygen Corporation is used in the present simulation. In this calculation, the Steepest Descents method[7] is employed for energy minimization and the Verlet algorithm is employed for the dynamics simulation. The hardware employed is a GS1000 Graphics Supercomputer from Stellar Computer Inc.

The simulation starts with 169 molecules, in a 13 × 13 matrix, parallel to each other standing vertically on a layer of water. During the dynamics simulation, the position of the water molecules are frozen. A 15 × 15 molecule matrix (225 molecules) without water is also studied.

To relax the conformation and remove bad contacts (inter- and intra-molecular interaction with high energy), the system undergoes energy minimization at zero K. The potential energy terms concerned are:

$$E_p = E_{\text{bond length}} + E_{\text{bond angle}} + E_{\text{dihedral angle}} + E_{\text{improper torsion}} + E_{\text{electrostatic}} + E_{\text{van der waals}}$$

The energy for hydrogen bonding is included in electrostatic and van der waals terms.

The optimized system is then heated to the desired temperature, i.e. 300K, by gradually assigning random velocities to each atom. The relationship between the atom velocity, the kinetic energy and temperature of the system is:

$$E_{\text{kinetic}} = \frac{1}{2}\sum_{i=1}^{N} m_i \left\langle v_i^2 \right\rangle = \frac{3}{2} N k_B T$$

where N is the total number of atoms and $m_i$ and $v_i$ are the ith atom's mass and velocity, respectively; $k_B$ is Boltzmann's constant.

When the system is heated to 300K, it undergoes a equilibration period to stabilize average temperature and structure. After the system is equilibrated, the final molecular dynamics simulation starts. The coordinates of the molecules are recorded periodically. The simulation times range from 30 to 60 pico-seconds (ps) with time step 0.001ps. The sets of coordinates recorded during the dynamics simulation are then analyzed to extract information about molecular packing, orientation and motion.

## RESULTS AND DISCUSSION

Without water, both end-groups of the molecules have similar mobility, as represented by the large position fluctuations in the first two columns of Table I. Starting with a very crowded and a loosely arranged matrix, final molecular packing are obtained that are close to the packing experimentally observed. The molecules in the closely packed system with area per molecule of 21Å$^2$ have less room to move, therefore less mobility in X and Y directions than those in the loosely packed system with area per molecule of 25Å$^2$. To achieve low packing energy, the molecules in the closely packed system have to move more in Z direction which result in more mobility in that direction. This is seen by comparing the first column of Table I vs the second column.

Figure 1a shows the motion of the two end groups for the center molecule during the simulation without water. The cooperative motion of the two end-groups suggests that the molecule as a whole moves up or down and can move as much as 5Å. Figure 2a shows the time-averaged position of the molecules. The fluctuation of the head group the tail group and the center of mass of the molecule are respectively centered around 5Å, 40Å, and 20Å. The large fluctuations of the end-groups seen in these simulations indicates that the monolayer has very rough surfaces.

When water is introduced into the system, the mobility of the polar head groups decreases by as much as 50–75%; the mobility of the nonpolar tail groups however increases as listed in Table I (columns 3 and 4). A possible explanation for the high mobility of the tail groups is as follows. As water limits the motion of the polar groups, the molecules can still move about the free nonpolar tails to reach the low energy state. Large fluctuations in the nonpolar tails occur to accommodate the localization of the polar tails in order to achieve low packing energy for the total system. The motion of the end-groups of the center molecule, about 2Å as

TABLE I

The change of molecular area [Å$^2$/molecule] and the position fluctuation [Å] of the end-groups in the dynamics simulations with and without water.

| | Simulation without water | | Simulation with water | |
|---|---|---|---|---|
| | Molecular Area [Å$^2$/molecule] | | | |
| Start | 16 | 36 | 25 | 36 |
| End | 21 | 25 | 22 | 27 |
| | Fluctuation In Height (Z) [Å] | | | |
| Head Group | 1.98 | 1.63 | 0.51 | 0.50 |
| Tail Group | 2.15 | 1.84 | 1.59 | 2.17 |
| | Fluctuation In X Direction [Å] | | | |
| Head Group | 1.44 | 1.63 | 0.57 | 0.65 |
| Tail Group | 1.65 | 2.05 | 2.29 | 3.23 |
| | Fluctuation In Y Direction [Å] | | | |
| Head Group | 1.53 | 1.75 | 0.63 | 0.67 |
| Tail Group | 1.79 | 2.07 | 2.38 | 3.02 |

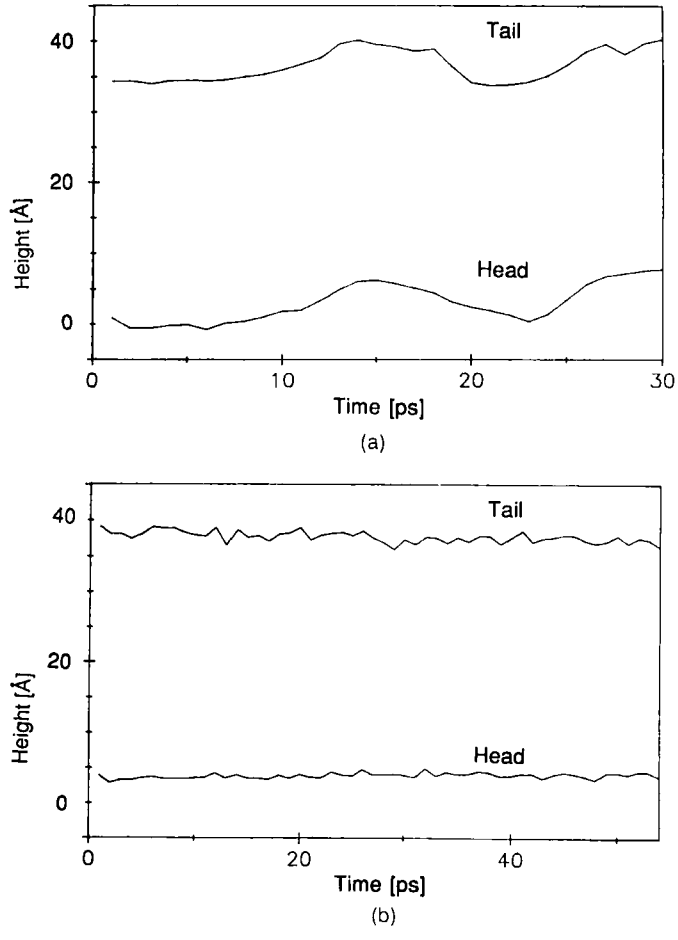


FIGURE 1 The height [Å] of the end-groups of the center molecule as a function of simulation time. (a) Without water (21 Å²/molecule). (b) With water (22 Å²/molecule).

shown in Figure 1b, is consistent with this. Due to the hydrophilic interactions, the average height of the head groups, or the surface formed by these groups (the lower curve in Figure 2b) is significantly smoother compared to the surface formed by the hydrophobic tails or the surfaces in the simulations without water molecules.

During the simulation the molecules tend to adjust the intermolecular distance to reach the minimum potential energy. For closely packed systems (i.e. with smaller area per molecule), the final molecular areas of 21–22Å² (see Table I) are consistent with that for 'close-packed heads' phase of fatty acids monolayers.[8] For the closely packed system, there is a pseudohexagonal packing with defects (Figure 3a). In the core areas of the molecule matrix we see defects such as line defects and domain boundaries that are typical in monolayer packing as observed in microscopy studies. Defects at the edge of the molecule matrix may however, simply result from edge effects. These defects can only be properly discussed when periodic

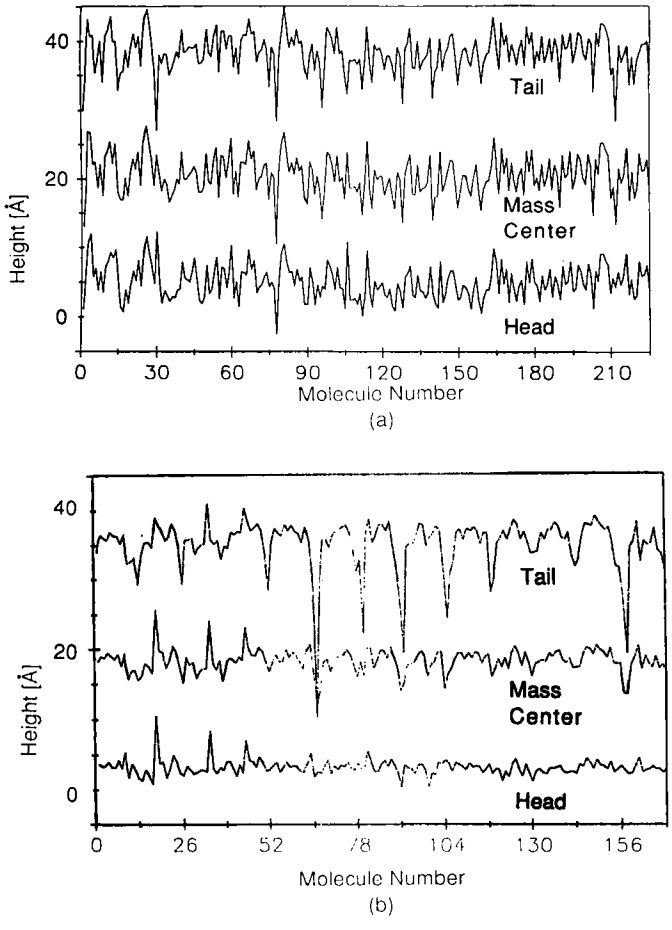


FIGURE 2 The time averaged height [Å] of the mass center and the two end-groups of the molecules. (a) Without water (21 Å²/molecule). (b) With water (22 Å²/molecule).

boundary conditions are included in the simulations. Relatively loosely packed systems have significantly less packing order. In the loosely packed matrix in Figure 3b no lattice pattern is apparent.

## CONCLUSION

Simulations of the LB films without periodic boundaries show clearly the effect of water and packing condition on the behavior of molecules in the monolayer. It is instructive to see appearance of domain boundaries and lattice defects in the simulation process as result already seen experimentally but whose origin in the monolayer formation process is not well understood.

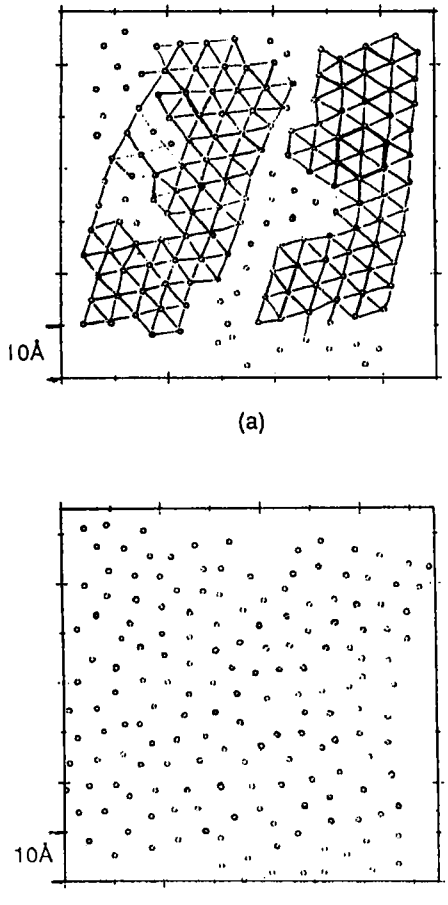


FIGURE 3 The projection of average mass centers of the molecules (30ps) on a water surface (open circle). (a) Molecular area 22Å²/molecule (starting from 25 Å²). (b) Molecular area 27Å²/molecule (starting from 36 Å²).

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