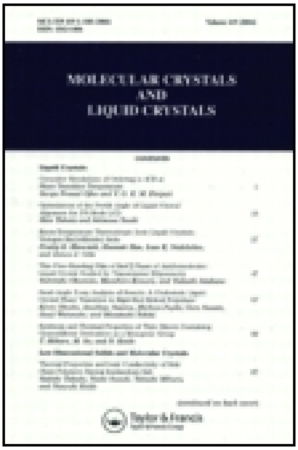

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Simulation Studies of Langmuir Monolayers

K. M. Aoki [a], Y. Tabe [a b] & H. Yokoyama [a b]

[a] JST ERATO Yokoyama Nano-structured Liquid Crystal Project, TRC 5-9-9 Tokodai, Tsukuba, 300-2635, Japan

[b] Electotechnical Laboratory, 1-1-4 Umezono, Tsukuba, 305-8565, Japan

Version of record first published: 24 Sep 2006

To cite this article: K. M. Aoki, Y. Tabe & H. Yokoyama (2001): Simulation Studies of Langmuir Monolayers, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 367:1, 191-198

To link to this article: http://dx.doi.org/10.1080/10587250108028638

Mol. Cryst. and Liq. Cryst., 2001, Vol. 367, pp. 191-198
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under the
Gordon and Breach Science Publishers imprint,
a member of the Taylor & Francis Group,
Printed in the USA

Simulation Studies of Langmuir Monolayers

K.M. AOKI[a], Y. TABE[ab] and H. YOKOYAMA[ab]

[a]*JST ERATO Yokoyama Nano-structured Liquid Crystal Project, TRC 5-9-9 Tokodai, Tsukuba 300-2635 Japan and* [b]*Electotechnical Laboratory, 1-1-4 Umezono, Tsukuba 305-8565 Japan*

It has been shown experimentally that molecules, which exhibit liquid crystal phases in bulk, also show interesting phenomena when they are formed in monolayers at air-water interface. The purpose of this work is to clarify to what extent can a simple model explain the complicated behavior of such Langmuir monolayers. Molecular dynamic simulation is conducted to observe the phase and dynamics of Langmuir monolayers.

Keywords: Langmuir Monolayers; Molecular Dynamic Simulation; Rigid Molecules

INTRODUCTION

Langmuir films are monolayers of molecules with hydrophilic head group dispersed on water surface. Some thermotropic liquid crystal(LC) materials in the form of Langmuir films are studied experimentally[1-6]. They show quite different properties compared to those consistent of flexible surfactants and polymer. A rigid core with shape anisotropy is the common character of thermotropic LC's which distinguish them from other materials. Here we model LC molecules as a rigid soft spherocylinder with both translational and orientational order and conduct molecular dynamics(MD) simulations. Our interest is to clarify to what extent can a simple model explain the complicated behavior of such Langmuir monolayers.

MODEL AND METHODS

As a model, we use soft spherocylinders with one end pulled from a base plane which is a model water surface. The force is proportional to the square of the height of that end from a base plane. Soft spherocylinders are expressed in terms of a Kihara type potential[7], which interact through the minimum distance of the two bodies in interaction. The model consists of a hard line of length L as a core of the spherocylinder which is embedded inside a purely repulsive soft core. The hard line of length L corresponds to the long axis of the molecule. The soft core is expressed by the following pair potential;

$$\Phi_{ij} = \begin{cases} \varepsilon\left[\left(\frac{D}{\mathbf{r}_{ij}}\right)^{12} - \left(\frac{D}{\mathbf{r}_{ij}}\right)^{6} + \frac{1}{4}\right] & \text{if } |\mathbf{r}_{ij}| < r_0 \\ 0 & \text{otherwise} \end{cases} \tag{1}$$

where $|\mathbf{r}_{ij}|$ is the minimum distance between the long axes of particles i and j, and $r_0 = 2^{1/6}D$. The interaction between particles occurs at the nearest points (the ends of the vector giving the minimum distance $\mathbf{r}_{ij}$) between two long axes, which determine how the force exerted on the spherocylinder will be divided between rotational and translational forces. Reduced simulation units, where $D = 1$, $\varepsilon = 1$, and mass of particle $m = 1$, are used throughout this work. The effective core diameter in bulk is defined for the present model as $\Phi(d_{eff}) = T^*$ where T^* is the reduced temperature.

At one end of the hard line of the core of the spherocylinder, a force **f** which tries to pull back the spherocylinder to the base plane works:

$$\mathbf{f} = -k\frac{(\Delta h)^3}{|\Delta h|}\mathbf{z} \qquad (2)$$

where Δh is the height of one end of the hard line from the base plane, k is a constant which determine the strength of this force and **z** is a unit vector in z-direction which is normal to the base plane. Note that this force acts only in the z-direction and is not a constraint to the position on the xy plane.

Constant volume MD simulation of $N = 504$ molecules are conducted. Periodic boundary condition in x, y direction are applied.

Throughout this work, we focus on dense areas of Langumir monolayer where the dominant contribution is supposed to be the steric interaction between the cores of liquid crystals since the model treat only the repulsive force between the molecules.

RESULTS

In Fig.1, we show a pressure-surface area diagram (P-A diagram) obtained from the simulations for $T^* = 30$ and $k = 5.0 \times 10^3$. The pressure P_{xy} is the average in the x-y direction calculated by the average of the diagonal elements of x and y direction in the stress tensor. The surface area per molecule (A) is presented in units of the square of effective core diameter in bulk of the spherocylinders. At each surface area the system is equilibrated for $1.0 \times 10^6 \sim 7.0 \times 10^6$ time steps where the time step is $dt = 1.0 \times 10^{-6}$. Relatively long time is necessary for unstable regions, such as in the plateau, to reach equilibrium.

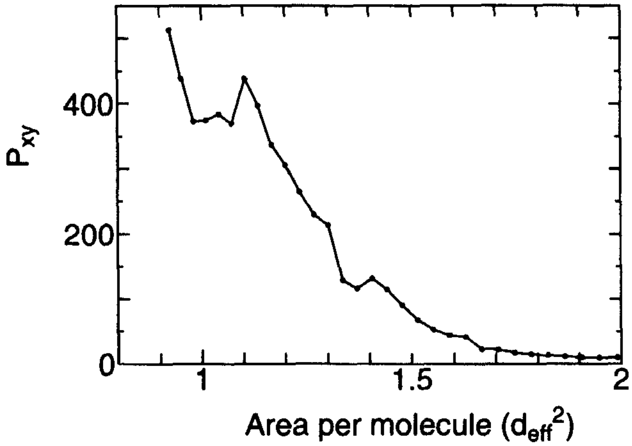

FIGURE 1 Pressure versus surface area diagram obtained from MD simulations.

Note that in the crystal region near the melting transition in bulk, the same model will yield layer area of 0.92 (d_{eff}^2) at $T^* = 100$ and $P^* = 1.0 \times 10^4$.

Fig.2 show order parameters S_2 and σ versus surface area in the same series of simulations as Fig.1. The orientational order parameter slightly increases as A decreases at the first plateau of the P-A diagram, and drastically decrease at A where the pressure starts to increase. When the area of the film gets quite small, the order parameter S_2 smoothly increase again.

Fig.3 show the orientational pair distribution function for different values of surface area. At A=1.91 which is at the first plateau of P-A diagram, the orientation pair distribution function show higher values than others. However, as shown in Fig.4(b), the snapshots show that there coexists well ordered domains and rather disordered domains at A=1.91. In the disordered domain, vortex like structure can be discerned. At smaller surface areas, the disordered domain become dominant however small domains with high order can still be seen (Fig.4 (a)).

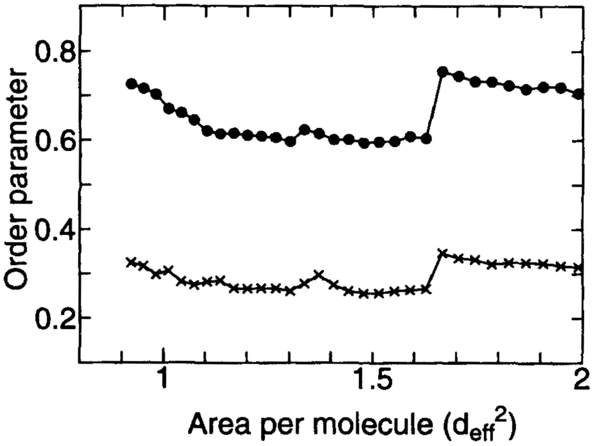

FIGURE 2 Order parameters versus surface area obtained from same simulation runs as Fig.1: o denote orientational order parameter $S_2 = \langle (3\cos^2\theta - 1)/2 \rangle$, × denote McMillan's order parameter $\sigma = \langle \cos(2\pi z_{ij}/d)(3\cos^2\theta - 1)/2 \rangle$.

DISCUSSION AND CONCLUDING REMARKS

The behavior of Langmuir films formed by cyano-biphenyls are reported in [1,6]. Iwamoto *et. al.* obtain polar orientational orders through measurements of the Maxwell displacement current[6]. According to this work, as the surface area of the film is reduced, dipole moment m_z (*i.e.* the polar orientational order) show increase at the beginning until a peak is reached. After the peak in m_z is reached, it decreases beyond further compression. This is in contrast to experimental results for flexible molecules which do not show such decrease in the dipole moment. They have interpreted that this behavior of cyano-biphenyls (as also suggested in [1]) as suggesting a formation of a three-layer film; an interdigitated bilayer on top of a monolayer.

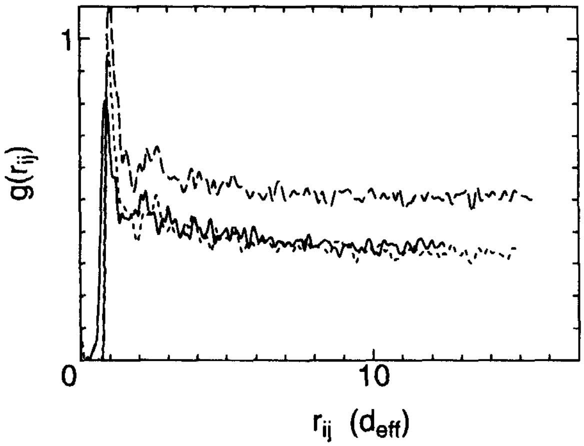

FIGURE 3 Orientational pair distribution function at various surface areas. $g_{\perp} = \langle P_2(\mathbf{1}(\mathbf{r}_1)\cdot\mathbf{1}(\mathbf{r}_2))\rangle$ where $\mathbf{1}(\mathbf{r})$ is orientation (unit vector) at $\mathbf{r}$. Solid line : A=1.23, dotted line : A=1.48, broken line : A=1.91.

Our simulation results suggests that such decrease in dipole moment can be interpreted as the actual result of the decrease in order parameter(which is probably due to the rigid core), and not necessary due to the formation of multi-layer structure.

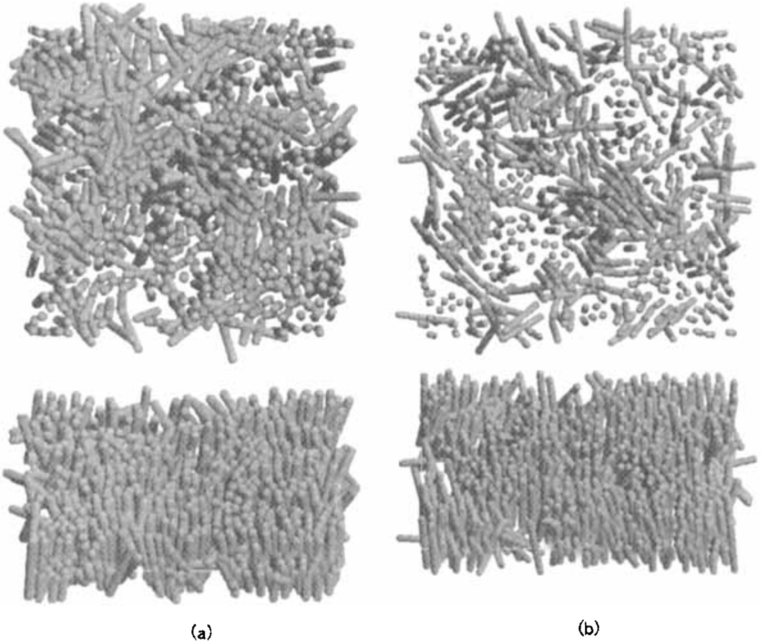

FIGURE 4 Snapshots of simulation at different surface areas; birds view (top) and perspective (bottom), for surface areas (a) A=1.23 and (b) A=1.91.

In this paper we only reported the results of simulation of molecules with $L = 4$. Dependence on the molecular length L should also be investigated in the near future.

Acknowledgment

The authors would like to thank Drs. M. Yoneya and J. Fukuda for useful discussion.

References

[1] J. Xue, C.S. Jung and M. Won Kim, *Phys. Rev. Lett.* **69**, 474 (1992).
[2] Y. Tabe and H. Yokoyama, *J. Phys. Soc. Jpn.* **63**, 2472 (1994).
[3] Y. Tabe and H. Yokoyama, *Langmuir* **11**, 4609 (1995).
[4] A. Feder, Y. Tabe and E. Mazur, *Phys. Rev. Lett.* **79**, 1682 (1997).
[5] Y. Tabe, N. Shen, E. Mazur and H. Yokoyama, *Phys. Rev. Lett.* **82**, 759 (1999).
[6] M. Iwamoto, T. Kubota, M.R. Muhamad, *J. Chem. Phys.* **102**, 9368 (1995).
[7] T. Kihara, *Rev. Mod. Phys*, **25**, 831 (1953).
[8] M. Iwamoto, T. Kubota, O-Y. Zhong-can, *J. Chem. Phys.* **104**, 736 (1996).