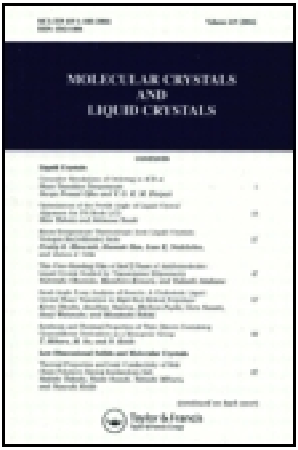

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MOLECULAR DYNAMICS SIMULATIONS OF SMECTIC C PHASE APPEARING IN LANGMUIR MONOLAYERS

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MOLECULAR DYNAMICS SIMULATIONS OF SMECTIC C PHASE APPEARING IN LANGMUIR MONOLAYERS

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We perform molecular dynamics simulations using a simple model system of liquid crystal substance on air-water interface. A system of soft spherocylinders, which do not show smectic C phase in bulk, exhibits a tilted smectic phase when interacting with a model water plane. We observe not only macroscopic properties such as the pressure-surface area curve, but also correlation functions and diffusions as well.

Keywords: Langmuir monolayers; molecular dynamics simulation; smectic C; tilted liquid phase

I. INTRODUCTION

Liquid crystalline substance without hydrophilic head groups can form stable Langmuir layers on water spontaneously [1]. Recent experimental findings have revealed that many materials with terminal di-alkyl chains form smectic C phase (soft tilted phase) which make optical observations possible [2]. Starting from a monolayer, the number of such layers can be increased by compression. This is a reversible process.

The object of this work is to clarify to what extent can a simple model reproduce the basic features observed in these new experiments. Liquid crystalline molecules are expressed as soft spherocylinders which are affected by a model force representing the interaction between the water surface. We show that such simple model systems can exhibit a tilted smectic phase due to the broken symmetry by the water surface. This means that the simulation predicts that a symmetrical substance without

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a SmC phase in its bulk phase sequence can also form a tilted smectic phase when expanded on water. As a matter of fact, we have found such substance and also give experimental results. Microscopic structure and dynamics of the tilted smectic phase are also investigated by molecular dynamics simulations.

II. MODEL AND SIMULATION METHOD

As a model of the liquid crytal substance, we use soft spherocylinders of anisotropy $L/D = 3$ and 4. The model of soft spherocylinders interact through the vector of minimum distance $\mathbf{R}_{ij}$ between the hard lines representing the long axis core of the spherocylinders i and j [3]. The soft core is purely repulsive and expressed by the following pair potential energy between particles i and j;

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

where $r_0 = 2^{1/6}D$. The force $\mathbf{f}_{ij} = -\partial\Phi_{ij}/\partial\mathbf{R}_{ij}$ acts at each end of $\mathbf{R}_{ij}$ which is divided in rotation and translation forces correctly reflecting the geometry of the particles. Thus, the kinetic energy is interchanged freely among translational and rotational degrees of freedom. The system of these soft spherocylinders is known to give the phase sequence of crystal- smectic LC – nematic LC -isotropic liquids under constant pressure [3]. The interaction with the water surface is expressed as a force F_ω applied on one end of the hard line representing the spherocylinder core. Three different models were investigated;

(a) $\mathbf{F}_\omega = -C_\omega \mathbf{h}_z^3/|\mathbf{h}_z|$: non-linear model [4]

(b) $\mathbf{F}_\omega = -C_\omega \mathbf{h}_z$: linear model [5]

(c) $\mathbf{F}_\omega = -C_\omega \mathbf{h}_z/|\mathbf{h}_z|$: constant model

where $\mathbf{h}_z$ is the normal vector from the xy-surface to the spherocylinder core. The constant C_ω is a parameter which define the strength of the force between the molecule and water against the intermolecular forces. Reduced simulation units, where $D = 1$, $\varepsilon = 1$, and mass of particle $m = 1$, are used throughout this work. Systems of size $N = 504$ and 2016 were simulated.

Here we report the simulation results obtained from model (c) which give a tilted smectic phase. In Table 1, the parameters which simulations

TABLE 1 Simulated Parameters of Model (c)

	L = 4	L = 3
T^*	C_w	C_w
100	3000, 6000, 8000, 10000, 12000	2000, 3000, 8000
120	3000, 6000, 8000, 12000	2000, 3000
140	3000, 6000, 8000	3000
160	6000, 8000	3000

were conducted are given. Only several selected systems in Table 1 are simulated for $N = 2016$ particles.

III. RESULTS

First of all, we show the lateral pressure P_{xy} versus area per molecule in Figure 1. Due to the limited calculation time, the compression speed is not slow enough to retain equilibrium in some cases ($T^* = 100$ and 140). In such case, the pressure does not increase monotonically. However as an overall tendency, the pressure curve shows a smooth increase upon compression.

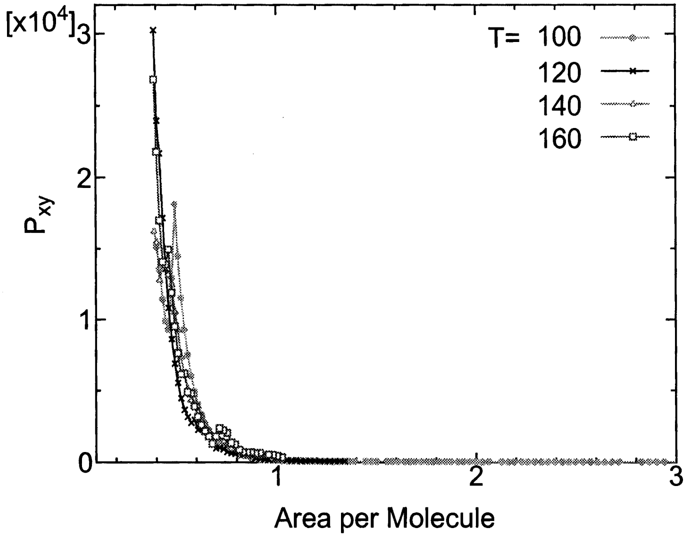


FIGURE 1 Lateral pressure versus area per molecule of model (c) of various temperature ($C_w = 6000, N = 504$).

When the surface area per molecule is around 0.79 or larger, the average molecular orientation shows some tilt. We show the tilt angle of average molecular orientation versus time in Figure 2. The average molecular orientation is defined by the vector sum of direction of the long axis of all particles and the tilt is the angle between this average molecular orientation and the normal direction of the model water plane (xy-plane). Although the tilt angle is not large, it does not diminish even for the larger system with $N = 2016$ molecules at surface area A = 1.34. In comparison, we also plot the tilt of the average molecular orientation for smaller surface area A = 0.75 for a short time. Note that the time scale of the fluctuation is two orders larger than that of the orientational order parameter. The azimuth angle of the average molecular orientation is also fluctuating in the same slow time scale as the tilt. The orientation of molecules is somewhat distributed and in some cases a domain structure with different tilt in neighboring domains appears.

We show in Figure 3 the orientational pair correlation function versus the distance projected on the xy-surface. The orientational correlation does not diminish through-out the system size which is characteristic to liquid crystals.

Imitating the macroscopic optical intensities in experiments [6], we observe optical intensity pair correlation functions I_L and I_C defined as a function of relative distance r_{ij} between two molecules. To see the

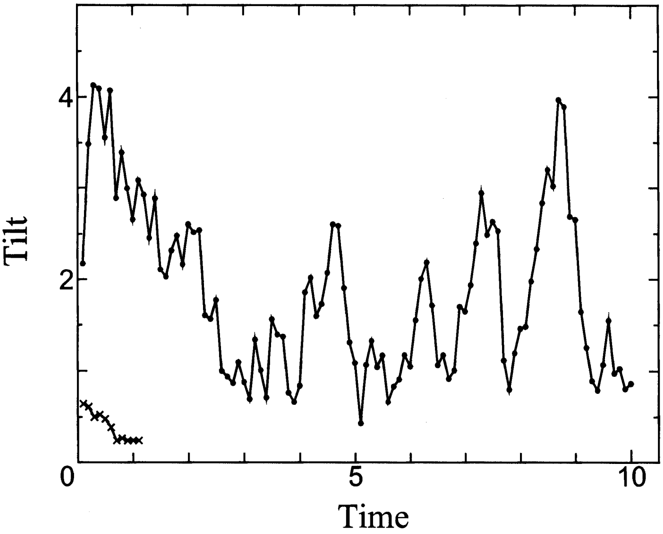


FIGURE 2 Time evolution of tilt angle of the average molecular orientation. ($C_w = 6000$, $T = 100$, $N = 2016$, ○: $A = 1.34$, ×: $A = 0.75$).

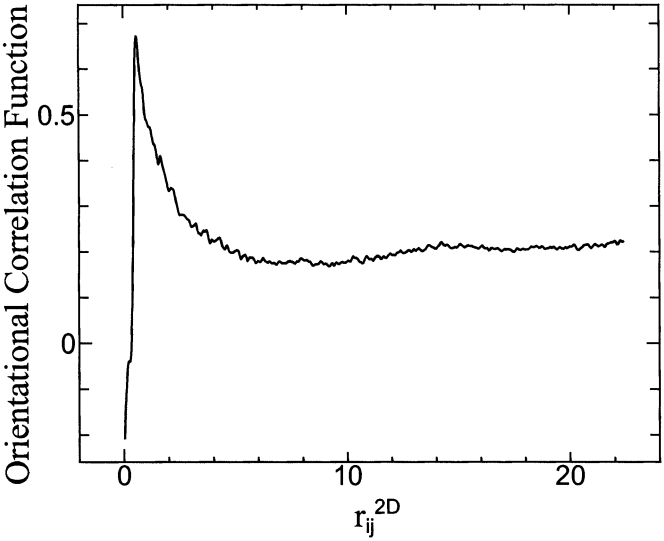


FIGURE 3 Orientational pair correlation function vs. distance between the centers of mass projected on the xy-plane. ($A = 1.34$, $C_w = 6000$, $T^* = 100$, $N = 2016$).

correlation, we define a distance dependent director $\mathbf{u}_{ij}(r_{ij})$ as a sum of vectors $\mathbf{u}_i$ and $\mathbf{u}_j$ which are the orientations of molecules i and j: $\mathbf{u}_{ij}(r_{ij}) = \mathbf{u}_i + \mathbf{u}_j$. We use the tilt angle (β) and the azimuthal angle (α) of $\mathbf{u}_{ij}$ in the following definition of I_L and L_C.

$$I_L(r_{ij}) = \sum_{j \neq i} \cos\alpha \sin^2 \alpha \sin^2 \beta, \tag{2}$$

$$I_C(r_{ij}) = \sum_{j \neq i} \sin^4 \beta. \tag{3}$$

The summation is taken over all pairs of molecules in the system. Figure 4 shows I_L and I_C against the distance between two particles projected on the xy-plane. The intensities do not hardly change for $r_{ij}^{2D} \geq 12$ which show that correlation remains throughout the system size.

In Figure 5, mean square displacements in directions perpendicular and parallel to the average molecular orientation are shown. There is a constant diffusion in direction perpendicular to the molecular orientation which indicates that the phase is liquid like.

We conclude that the phase, which appears in spherocylinder systems with interaction (c) with a plane, is a tilted smectic phase. Simulations for a wide variety of parameters are conducted and from the results we conclude the followings; when expanded on a plane, even if the substance

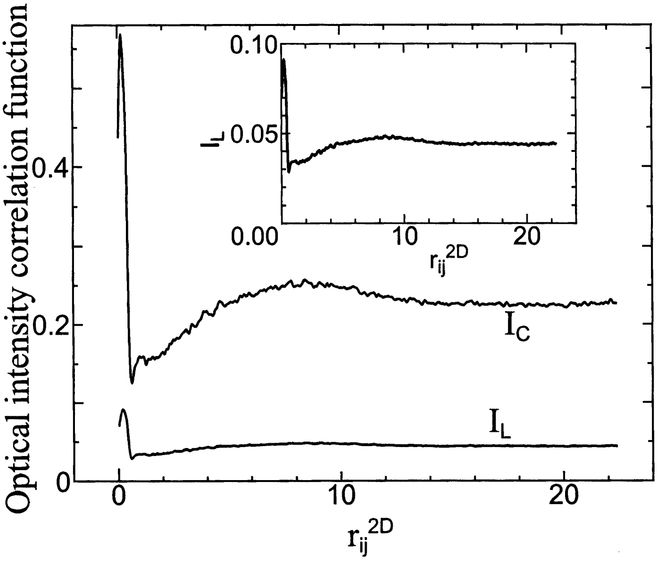


FIGURE 4 Optical intensity pair correlation functions vs. distance between the centers of mass projected on the xy-plane. ($A = 1.34$, $C_w = 6000$, $T = 100$, $N = 2016$).

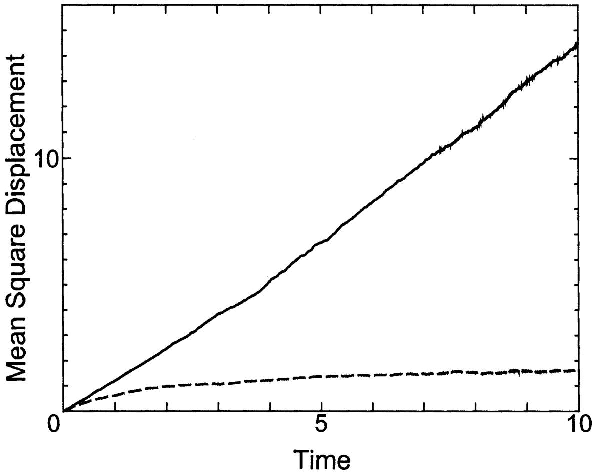
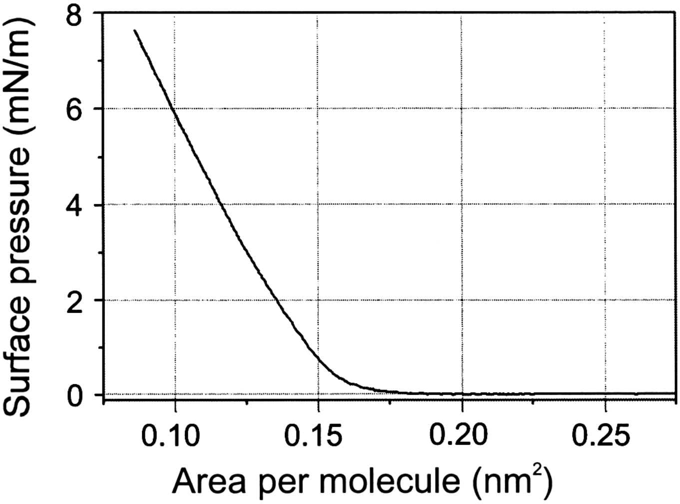
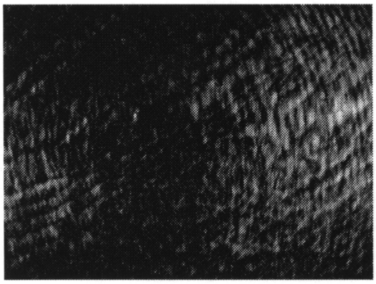
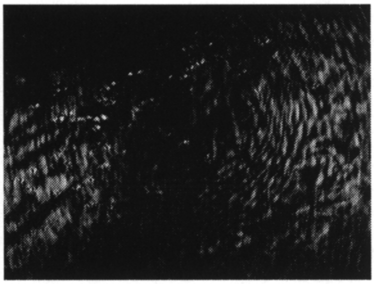


FIGURE 5 Mean square displacements vs. simulation time. Solid and broken curves respectively denote the diffusions in directions perpendicular and parallel to the average molecular orientation. ($A = 1.34$, $C_w = 6000$, $T = 100$, $N = 2016$).

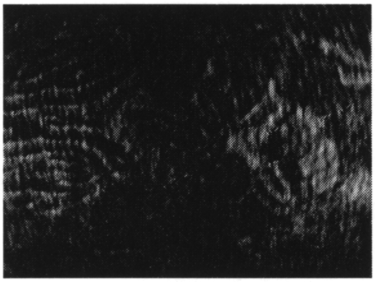




A=0.18 nm^2



A=0.08 nm^2



A=0.12 nm^2

10AB10 monolayer at 50°C
(K 42 SmB 44 SmA 53 I)

FIGURE 6 Surface pressure vs. area per molecule and optical images of 4,4′-Di-n-decylazobenzene obtained from experiments.

does not show SmC phase in the bulk phase sequence, it can exhibit a tilted smectic phase. This is true not only in the temperature range where Sm phass appear in bulk, but also in the temperature range where nematic phase appear. Actually, we have found a symmetrical non-polar substance (4,4′-Di-n-decylazobenzene) which shows a tilted smectic phase when expanded on water surface. Figure 6 shows the surface pressure curve as well as the optical images.

We also observe a sign of layer by layer growth when the model system is highly compressed. Even in such highly compressed state, there exists constant diffusion of the molecules in direction perpendicular to the average molecular orientation.

IV. CONCLUDING REMARKS

We have conducted molecular dynamics simulations of a simple model system of Langmuir monolayers. As a result, the simulation predicts that even a symmetrical non-polar substance, which does not show the SmC phase in its bulk sequence, can exhibit a tilted smectic phase when expanded on air-water interface. Such a substance will exhibit the tilted smectic phase not only in the temperature range of untilted smectics but also of the nematic phase.

REFERENCES

[1] Dörfler Von, H.-D., Kerscher, W., & Sackmann, H. (1972). Oberflächenfilme von Azoxy-α-methylzimtsäureetern auf wäßrigem Substrat. *Z. Phys. Chemie, Lipzig*, *251*, 314–320.

[2] Tabe, Y., Nishiyama, I., & Yokoyama, H. (2000). Langmuir monolayer studies of chiral smectic C phase. In *Proc. 7th Int. Display Workshops.*, Kobe; 1143–1144. Tabe, Y., Nishiyama, I., Aoki, K. M., Yoneya, M., & Yokoyama, H. (2001). Anomalous spreading and layer growth of hydrophobic liquid-crystalline oils on water. In *The 2nd Anglo-Japanese seminar on liquid crystals*, York. Tabe, Y., Yamamoto, T., Nishiyama, I., Aoki, K. M., Yoneya, M., & Yokoyama, H. (2002). Can Hydrophobic Oils Spread on Water as Condensed Langmuir Monolayers? *J. Phys. Chem.*, *106*, 12089–12092.

[3] Aoki, K. M. & Akiyama, T. (1995). Investigation of liquid crystalline phases by means of constant-pressure molecular-dynamics simulation. *Mol. Cryst. Liq. Cryst.*, *262*, 543–553. (1996). Investigations of nematic-isotropic transition by means of constant pressure molecular dynamics simulations. *Mol. Sim.*, *16*, 99–105. (1997). Molecular dynamics simulations of liquid crystal phase transitions. *Mol. Cryst. Liq. Cryst.*, *229*, 45–50. Aoki, K. M. & Yokoyama, H. (2001). Simulation studies of Crystal-Smectic transition. *Mol. Cryst. Liq. Cryst.*, *366*, 117–124. Aoki, K. M., Yoneya, M. & Yokoyama, H. (2002). Constant pressure molecular dynamics method for anisotropic liquids. *Proceedings of ILCC.*

[4] Aoki, K. M., Tabe, Y., & Yokoyama, H. (2001). Simulation studies of Langmuir monolayers. *Mol. Cryst. Liq. Cryst.*, *367*, 191–198.

[5] Aoki, K. K., Tabe, Y., Yoneya, M., & Yokoyama, H. (2001). *Unpublished.*

[6] Tabe, Y., Shen, N., & Mazur, E. (1992). Simulationeous Observation of Molecular Tilt and Azimuthal Angle Distributions in Spontaneously Modulated Liquid-Crystalline Langmuir Monolayers. *Phys. Rev. Lett.*, *82*, 759–762. Tabe Y. & Yokoyama, H. (1995). Fresnel Formula for Optically Anisotropic Langmuir Monolayers: An application to Brewster Angle Microscopy. *Langmuir*, *11*, 699–704.