

Orientational phase transition in molecular monolayer on an air–water interface

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A theoretical model is presented to study the phase transition of molecular orientation in a Langmuir monolayer on air–water interface. The polar molecules are treated as rodlike dipoles with three types of interactions; short-range steric repulsive interaction among the molecules, polar interaction between the molecules and water surface, and dipolar interaction among the molecules. The orientational order parameters, $\langle \cos \theta \rangle$ and $\langle (3 \cos^2 \theta - 1)/2 \rangle$, are calculated as functions of the molecular density and temperature. It is shown that compressing the molecular area will lead to a continuous phase transition of the molecular orientation. © 1997 American Institute of Physics. [S0021-9606(97)51214-1]

I. INTRODUCTION

Insoluble molecular monolayers at gas–liquid interfaces are interesting, not only because of their broad range of application and their relevance to biology, but also because they are rather ideal for studies of the rich world of two-dimensional phase transitions. The successive phase transitions observed in Langmuir monolayers, e.g., surfactants, fatty acids or lipids on water, comprise one of the classic problems in physical chemistry.¹

In monolayers of polar molecules there are usually two types of order parameters. One is the molecular configuration, i.e., the position distribution of hydrophylic polar heads of the molecules on the air–water interface. It is closely related to two-dimensional liquid–gas and liquid–solid transitions. Another order parameter is the orientation of the molecular tails.^{2–8} The liquid expanded–liquid condensed transition is associated with an orientation phase transition. By using a Maxwell displacement current measuring technique,⁹ Iwamoto *et al.*⁸ found a phase transition from isotropic gaseous phase to a phase accompanying the polar ordering in Langmuir films of liquid-crystal 4-cyano-4'-5-alkyl-biphenyl (5CB), 7CB, 8CB, and 10CB.

Both order parameters mentioned above are determined by the density of the polar molecules as well as the temperature. Analogous to three-dimensional systems, the applied lateral pressure, the mean area occupied per molecule, and the temperature of a Langmuir monolayer satisfy a two-dimensional van der Waals equation, which can describe a transition from a gaseous state to a liquid state by compressing molecular area (or increasing molecular density). At the same time, compressing the molecular area may lead to a

change in the orientation order parameter and an orientation phase transition. Thus, it becomes an interesting task to explore the relation between orientation order parameters and the molecular density.

At very low surface pressure the surface density of molecules is low and the monolayer is in a gaseous state. In this state, the interaction between the molecules is very small, and the dominant force comes from an attractive interaction between the polar molecule and its image below the air–water interface.⁵ Such an image force makes the molecules lie on the azimuthal plane. The average area A occupied by one molecule decreases with the surface pressure. As A decreases to a critical value A_0 , the molecules start to align on the water surface due to a strong steric repulsion between them. As a result, an orientation phase transition will occur at $A = A_0$. A theoretical approach to this phase transition has been made by Sugimura, Iwamoto, and Ou-Yang.⁵

In this paper, we apply the statistical mechanism approach to the orientation phase transition of a Langmuir monolayer by considering three types of interactions; short-range steric repulsive interaction among the molecules, polar interaction between the molecules and water surface, and dipolar interaction among the molecules. In Ref. 5 the electrostatic attractive energy between a molecule and the water surface, $W(\theta)$, is assumed to vary inversely with $\cos \theta$, where θ is the tilt angle of the dipolar molecule away from the normal direction of the monolayer. Under this assumption $W(\theta = \pi/2) = -\infty$ so that the molecules always lie on the water surface for $A > A_0$, regardless of the temperature as well as finite interactions between the molecules. In the present model the dipoles are assumed to locate at the free space

above the air–water interface and so $W(\theta)$ is always finite.¹¹ The resulting order parameters of orientation are temperature dependent. Besides, the dipolar interaction among the molecules is included in the present model. This interaction will be important for a higher molecular density ($A < A_0$). Two types of orientation order parameters, $\langle \cos \theta \rangle$ and $\langle (3 \cos^2 \theta - 1)/2 \rangle$ are calculated, where $\langle \dots \rangle$ stands for a thermodynamic average. The calculated results show that the orientation phase transition occurring at $A = A_0$ is second order. At the phase transition point the order parameter is found to vary continuously, but there is a jump in its differential quotient.

II. MODEL

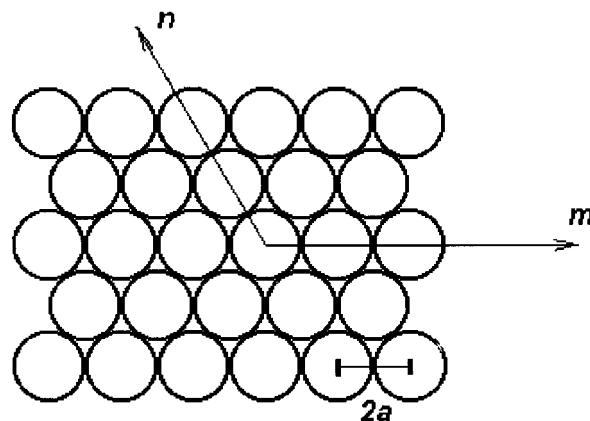
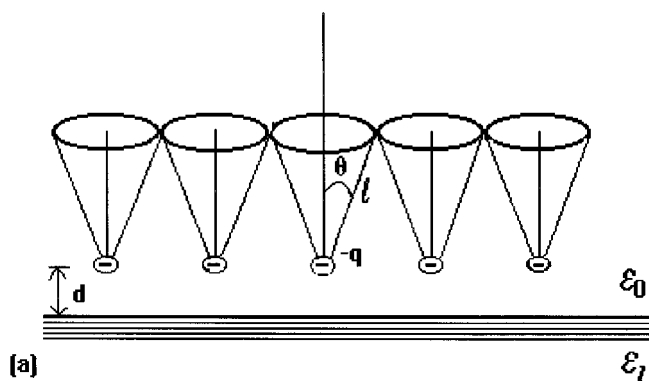
Consider a monolayer on an air–water interface as a plane infinite array of identical rodlike dipoles. The dipoles are assumed to have terminal charges $\pm q$ with a distance l apart so that the permanent dipole moment along the axis of the rodlike molecule is given by $p = ql$. In a three-layer-capacitor model¹⁰ the monolayer at the air–water interface can be divided into three regions; hydrophobic tail, hydrophilic head group, and underlying water subphase. Following Taylor and Bayes,¹¹ both the permittivities of the first two regions are taken to be ϵ_0 , the permittivity of free space, and the relative permittivity of the water subphase is taken to be ϵ_1 . As a result, the monolayer under consideration is modeled as dipoles located in free space at a height d above a subspace of the relative permittivity ϵ_1 , as shown in Fig. 1(a). First, we consider the steric repulsive interaction among the molecules. Define $2a$ as the average distance between two nearest-neighbor molecular head-group and then the area per molecule is given by $A = 2\sqrt{3}a^2$ in the model of hexagonal packing. The steric repulsion is assumed to be infinite for $A < A_0 \sin^2 \theta$ with $A_0 = 2\sqrt{3}l^2$ and zero in the opposite case. As a result, such a repulsive interaction is short-range, always vanishing when $A > A_0$.

Second, the polar interaction energy $W_I(\theta)$ working between a molecule and the water surface is the electric potential energy between the two terminal charges of the dipole molecule and their images in the water, which is given by

$$W_I(\theta) = -\frac{p^2(\epsilon_1 - 1)}{16\pi\epsilon_0(\epsilon_1 + 1)l^3} \times \left(\frac{1}{u + \cos \theta} - \frac{2}{\sqrt{\frac{1}{4} + u \cos \theta + u^2}} \right) \quad (1)$$

with $u = d/l$.

Third, the dipolar interaction among the molecules is taken into account by a mean field approximation. For a real monolayer system under consideration, both space distribution of the molecular heads and orientation distribution of the molecular tails are random due to temperature effect. The mean field approximation is to assume that the molecular heads are uniformly and hexagonally arranged¹¹ at a separation distance $2a$, as shown in Fig. 1(b), and the molecular tails are vertically oriented with an effective dipole moment pS with $S = \langle \cos \theta \rangle$. The former assumption is relatively



(b)

FIG. 1. Schematic description of the model of a monolayer on the air–water interface. (a) Geometry of the dipolar molecules. (b) Hexagonal arrangement of the molecular head groups.

more reasonable in the range of molecular area $A \leq A_0$, but appears simplistic for $A > A_0$. Fortunately, it is found¹² that when $A > A_0$ $W_I(\theta)$ makes a dominant contribution and the dipolar interaction among the molecules has little effect so that the present approach is rough-and-ready. Under the mean-field approximation, an effective interaction experienced by a dipole with tilt angle θ is given by¹¹

$$W_D(\theta) = \frac{p^2 S \cos \theta}{32\pi\epsilon_0 a^3} \left(1 + \frac{\epsilon_1 - 1}{\epsilon_1 + 1} \right) \times \sum_{m=-\infty}^{+\infty} \sum_{n=-\infty}^{+\infty} \frac{1}{(m^2 + n^2 - mn)^{3/2}}, \quad (2)$$

where m and n are integers not simultaneously zero. The double summation is readily evaluated as 11.0342.¹³ Here the term including the factor $(\epsilon_1 - 1)/(\epsilon_1 + 1)$ is the mean-field contribution of the image dipole array.

By taking into account the three types of interactions mentioned above, the single-particle partition function is given by

$$Z = \int_0^{\theta_A} \exp[-W(\theta)/k_B T] \sin \theta d\theta. \quad (3)$$

Here $W(\theta)$ is the sum of $W_I(\theta)$ and $W_D(\theta)$, which can be written as

$$W(\theta) = -k_B T_I \left(\frac{1}{u + \cos \theta} - \frac{2}{\sqrt{\frac{1}{4} + u \cos \theta + u^2}} \right) + k_B T_D \cos \theta, \quad (4)$$

with

$$k_B T_I = \frac{p^2(\epsilon_l - 1)}{16\pi\epsilon_0(\epsilon_l + 1)l^3}, \quad (5)$$

$$T_D = 5.5171ST_I \left(\frac{l}{a} \right)^3 \left(1 + \frac{\epsilon_l + 1}{\epsilon_l - 1} \right). \quad (6)$$

The short-range repulsive interaction between the molecules is embodied in the upper limit of the integral in Eq. (3); $\theta_A = \sin^{-1}(\sqrt{A/A_0})$ for $A < A_0$ and $\pi/2$ for $A > A_0$. The orientation distribution function is given by

$$f(\theta) = \frac{1}{Z} \exp \left[-\frac{W(\theta)}{k_B T} \right]. \quad (7)$$

With the aid of $f(\theta)$ two types of order parameter for describing the molecular orientation of the monolayer are readily calculated. The nematic order parameter is given by a statistical average of the second Legendre polynomial

$$\langle P_2 \rangle = \int_0^{\theta_A} \frac{3 \cos^2 \theta - 1}{2} f(\theta) \sin \theta d\theta. \quad (8)$$

The consideration of $\langle P_2 \rangle$ as an orientation order parameter can take advantage of the results in liquid crystal theory, such as the Maier–Saupe theory and the Landau–de Gennes model.¹⁴ The polar order parameter defined as $S = \langle \cos \theta \rangle$ can give detailed information on the polar orientation order and is evaluated by

$$S = \int_0^{\theta_A} \cos \theta f(\theta) \sin \theta d\theta. \quad (9)$$

For monolayers of polar molecules, this order parameter is of major importance because it corresponds to the vertical component of dipole moment, which can be measured by the so-called surface potential.

III. ORIENTATIONAL PHASE TRANSITION

From Eqs. (3)–(7), it is easy to see that the integrand on the right-hand side of Eq. (9) is a function of S . It follows that Eq. (9) is a self-consistent integral equation of S and needs to be numerically solved. Substitution of the solution for S into Eqs. (3)–(8) will yield $\langle P_2 \rangle$. By taking $T = T_I$, the calculated results of the polar order parameter S as a function of A/A_0 for several values of u are shown in Fig. 2. It is found that, the order parameter S has a continuous change at $A = A_0$, but there is a jump in its first derivative, exhibiting typical behavior of a continuous phase transition. This is also

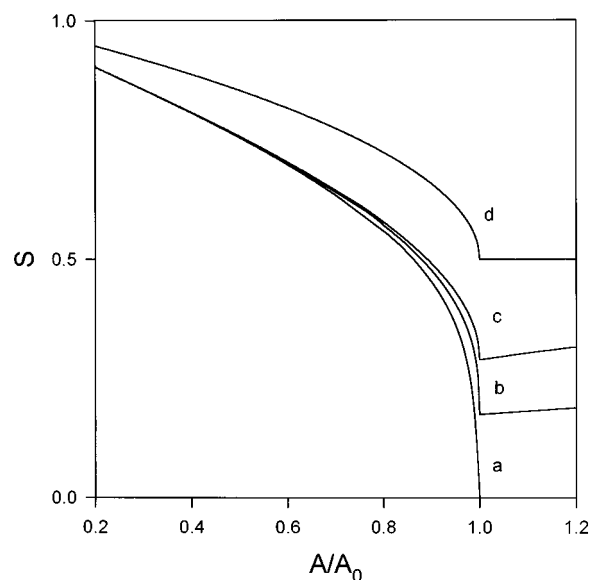


FIG. 2. The polar order parameter $S = \langle \cos \theta \rangle$ as a function of the molecular area for several values of u . (a) $u=0$, (b) $u=0.15$, (c) $u=0.5$, and (d) nonpolar case of $p=0$.

illustrated in Fig. 3 by the relative standard deviation of the order parameter S , calculated by $\delta S / (S - S_C) = \sqrt{\langle \cos^2 \theta \rangle - S^2} / (S - S_C)$, where S_C is the value of order parameter S at $A = A_0$. The big value of the $\delta S / (S - S_C)$ at $A = A_0$ indicates a strong fluctuation near the transition area, exhibiting common character of the continuous phase transition.

For $A > A_0$, the magnitude of S for polar molecules depends on the magnitude of u as well as the temperature. In Ref. 5 it was assumed that $u=0$ and $W_I(\theta=\pi/2) = -\infty$ so that S is always zero for $A > A_0$. In the present model, u takes nonzero values and so $W_I(\theta=\pi/2)$ is finite, leading to non-

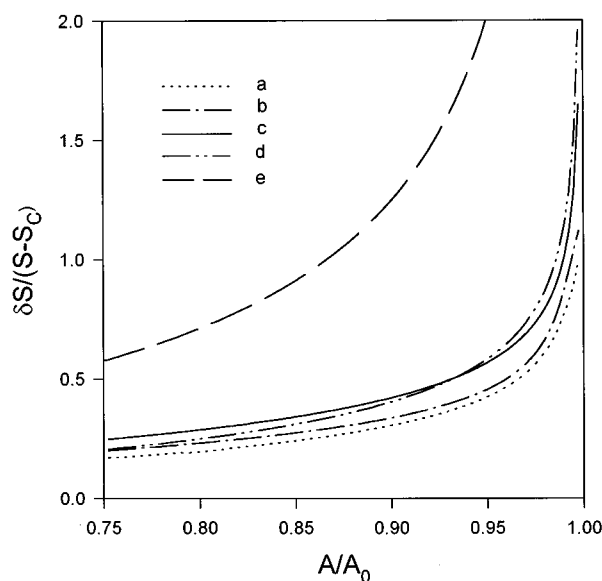


FIG. 3. Area dependence of the relative strength of the fluctuation $\delta S / (S - S_C)$. (a) $u=0$, (b) $u=0$, no dipolar interaction, (c) $u=0.1$, (d) $u=0.1$, no dipolar interaction, (e) nonpolar case.

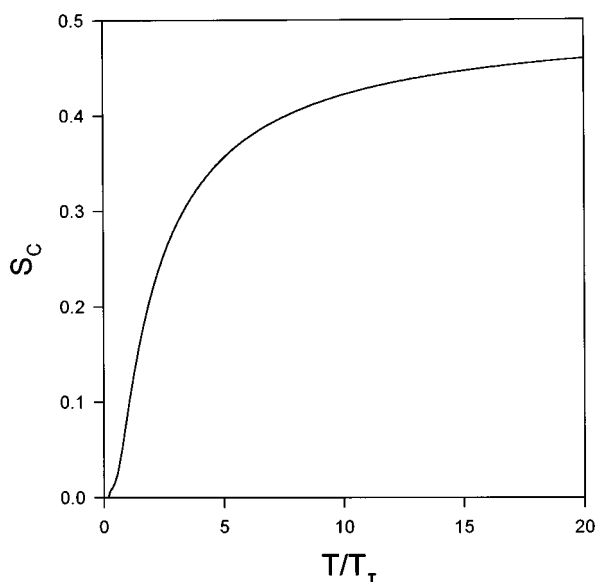


FIG. 4. Temperature dependence of the polar order parameter S at $A=A_0$ for $u=0.15$.

zero values of S for $A>A_0$ due to a competition between W_I and the temperature. The attractive interaction between the polar molecules and the water is the weaker, the greater the value of u . It results in S_C increasing with u . On the other hand, the temperature is the origin of disorder and always leads to a deviation of S from zero except in the case of $u=0$. A monotonous increase of S_C with temperature is shown in Fig. 4. For $A>A_0$, a slight increase of S with A shown in Fig. 2 arises from a decrease in the dipolar interaction $W_D(\theta)$. Such an interaction is unfavorable to the alignment of the polar molecules. It follows from Eq. (6) that with increasing A , this interaction becomes weak and so S tends to increase. Since this interaction is relatively weaker compared with the polar interaction for $A>A_0$, the increase of S with A is very slow. For nonpolar molecules ($p=0$), there is no interaction as $A>A_0$ and the temperature effects give a complete disorder of molecular orientation, i.e., $S=1/2$.

For $A<A_0$, the strong steric repulsion between the molecules gives rise to rapid increase of S as displayed also in Fig. 2 by curve *d* for the nonpolar case. Because no other interactions exist in this case, every molecule can fluctuate freely between $\theta=0$ and θ_A , restricted only by the steric repulsions. Including the polar interaction between the molecules and the water surface but with $u=0$ produces a deep potential well near $\theta=\pi/2$, and so essentially removes the fluctuations of the molecules. Accordingly, the increase of S also arises mainly from the steric repulsions near $\theta=\pi/2$. In these two opposite limits, S changes continuously with A and one can define a critical-point exponent of the order parameter as $S(A)\propto(A_0-A)^\beta$ for $A\leq A_0$; a simple calculation yields $\beta=0.5$. Away from A_0 , the polar interaction, though becomes weak, still reduces the fluctuations and hence S from the nonpolar case, as is evident from Fig. 2. This same effect can start from A_0 for nonzero u when the polar interaction becomes finite and so is comparable to thermal fluctuations.

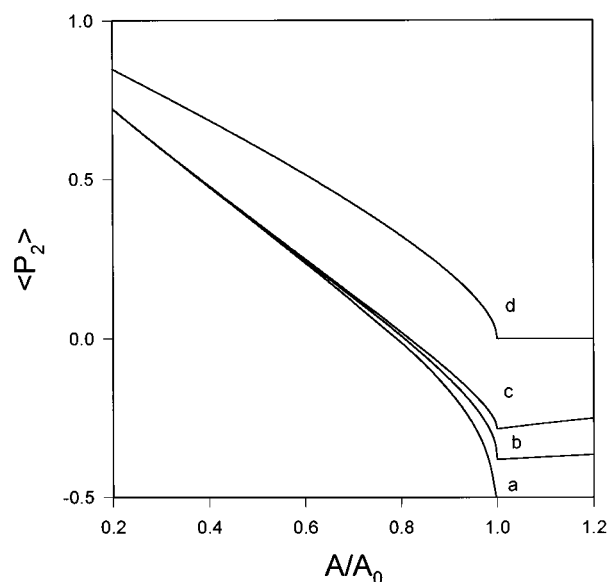


FIG. 5. The nematic order parameter $\langle P_2 \rangle$ as a function of the molecular area for several values of u . (a) $u=0$, (b) $u=0.15$, (c) $u=0.5$, (d) nonpolar case.

This is clearly illustrated in Fig. 3; the relative standard deviations get larger from $u=0$ to $u\neq 0$ to $p=0$. Demonstrated in Fig. 3 are also curves with the dipolar interaction. Owing to its long-range nature, the fluctuations become smaller. It can be seen, however, that the dipolar interaction is rather weak near A_0 , as has also been shown in Ref. 12.

All the cases discussed above lead to a conclusion that a continuous phase transition occurs at A_0 . A mean-field approximation, however, has been used for the dipolar interaction. One might then worry about whether or not strong fluctuations near the transition point would destroy the result of a continuous transition. Here the mean-field approximation has two meanings; one assumes that each molecule aligns a mean tilt angle, another assumes that each molecule is uniformly and hexagonally arranged. As has been shown from Fig. 3, the dipolar interaction among the molecules tends to reduce the fluctuations of the angles. On the other hand, the effect of the fluctuations from the uniform and hexagonal arrangement should be negligible. Since the dipolar interaction falls off as $1/R^3$, the dominant contribution must arise from the close-packed configuration. Any deviation from this arrangement can only alleviate the effect of the dipolar interaction, which, as has been pointed out, just makes a minor contribution to the phase transition. Accordingly, it is unlikely that the scenario of fluctuation-driven first-order phase transition could apply here, and the orientational phase transition is thus continuous. This is also in agreement with the existing experiments, in which a smooth increase of the displacement current was detected on compression, indicating a continuous phase transition of orientation.⁸

Figure 5 shows the calculated results of the nematic order parameter $\langle P_2 \rangle$. $\langle P_2 \rangle$ vs A/A_0 behavior is found to be quite similar to that of S vs A/A_0 except that $\langle P_2 \rangle$ for the

polar molecules is negative in a small region near A_0 . For the nonpolar molecules, since $\langle P_2 \rangle = 0$ and $S = 1/2$ for $A \geq A_0$, it is better to choose $\langle P_2 \rangle$ as their order parameter.

IV. CONCLUSION

We have studied the phase transition of molecular orientation in a monolayer on the air–water interface. The polar molecules are modeled as rodlike dipoles with short-range steric repulsive interaction and dipolar interaction among the molecules, and polar interaction between the molecules and water surface. The dipoles are assumed to locate in free space at a height d above the water surface so that the polar interaction between the dipoles and the water surface is a function of d . The dipolar interaction among the molecules is considered in the mean-field approximation. If one neglects the dipolar interaction among the molecules and consider the special case of $d=0$, the present model is reduced to that of Ref. 5. Two types of order parameters, $\langle \cos \theta \rangle$ and $\langle (3 \cos^2 \theta - 1)/2 \rangle$, as well as the orientational fluctuation $\delta S / (S - S_c)$ have been calculated. It is shown that with increasing the molecular density a continuous phase transition of molecular orientation occurs at $A = A_0$ due to competition between interactions under consideration. This agrees qualitatively with the existing experiments.

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