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Phase transition of molecular orientation at the liquid-air interface

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On the basis of the interaction of dipolar molecules with a liquid surface we calculate the thermodynamics of the molecular orientation and related mechanical and electric effects for a monolayer of molecules on an air-liquid interface. It is shown that compressing the molecular area should lead to a weak first order phase transition of the molecules from isotropic to polar orientation. Although the main source of the phase transition may not be the polar interactions, the polar nature of the molecules offers a nice way of monitoring the phase transition. The anomalous slope of the pressure-area isotherms is found to be related to the transition. It was shown theoretically that a Maxwell displacement current with a sharp pulse shape is generated at the onset of the transition.

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The thermodynamics of insoluble molecular monolayers at a gas-liquid or liquid-liquid interface is especially interesting at the meeting point of two- and three-dimensional systems [1]. In many respects the monolayer of an amphiphile may be considered as half of a membrane and is the simplest model system that can be discussed without looking into chemical details [2]. On the other hand the monolayer of a liquid crystal on a water-air interface can reveal the anchoring properties of the molecules at the surface, which play an important role in the working process of the display cells [3]. In the experimental study of these systems various techniques have been developed. Among these the measurement of pressure-area isotherms of a Langmuir monolayer is most often used [4]. Typical pressure-area isotherms can be written as a two-dimensional van der Waals equation of state analogous to the three-dimensional one [5],

$$(\Pi + a/A^2)(A-b) = kT , \tag{1}$$

where Π is the externally applied lateral pressure, A is the mean area occupied per molecule, k is Boltzmann's constant, T is the absolute temperature, and a and b are constants to account for the attractive intermolecular forces (van der Waals forces) and for the finite size of molecules, respectively. By analogy with real gases, Eq. (1) indicates a traverse from a gaseous state via a fluid to a solid state by compressing molecular area A. This is nearly but not exactly fulfilled in the experiments. In the traverse from a gaseous state via a fluid to a solid state of the monolayers, some sharp increases in Π are often observed in phospholipids and fatty acids [4,6,7] as well as in liquid crystals [3,8]. Judged from x-ray diffraction with polarization micrographs [9], electron diffraction [10], and optical second-harmonic generation [3], the sharp change in Π indicates some ordered phase transitions, especially the monolayer orientation (a liquid crystalline structure).

Surprisingly, most theoretical studies on the molecular orientation of monolayers have considered only the nematic ordering [11], which is represented as the order parameter $\langle (3\cos^2\theta - 1)/2 \rangle \equiv \langle P_2(\cos\theta) \rangle$; θ is the tilt angle of hydrocarbon chains away from the normal direction of the monolayer, $\langle\ \rangle$ denotes a thermodynamics average, and P_2 is the second Legendre polynomial. The consideration of $\langle P_2 \rangle$ as an orientational order parameter can take advantage of the results in liquid crystal theory, such as the Maier-Saupe theory and the Landau–de Gennes model [12]. However, it gives no detailed information on the polar orientational order, which is defined as

$$S = \langle P_1(\cos\theta) \rangle = \langle \cos\theta \rangle , \tag{2}$$

where P_1 is the first Legendre polynomial. In a physical meaning for molecules with dipoles, the polar ordering may be of major importance in Langmuir monolayers. Water-insoluble molecules are terminated by both the hydrophilic group and hydrophobic group (usually one or two long hydrocarbon chains). Due to the amphiphilic nature of the molecules, a polar alignment must be induced in the monolayer [13]. In the 1980s, Brochard, Joanny, and Andelman [14] made progress in the polar properties of monolayers by the surface contact potential using an order parameter in Landau-Ginzburg theory. The results can yield only the mean value of the permanent dipoles of the amphiphiles, but do not give details of the molecular orientation, namely for probing $\langle P_1 \rangle$, $\langle P_2 \rangle$, and so on. Even for very intuitive thinking one expects that the tilt angle θ can be reduced towards zero by the compression as observed in many experiments [15]. Up to now, however, no theory can take account of the phenomenon and the associated effects. Therefore, the following general questions may arise: How can one connect the orientation change of the molecules with their compression in area, and what kind of interaction force is responsible for the effect?

As a first step, in this paper we try to provide a primitive answer to these questions. Starting from the interaction model of an amphiphilic molecule with a medium surface, we calculate the effect of the molecular orientation and the associated mechanical and electric changes

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in the thermodynamics of the monolayer.

For simplicity, we now discuss a monolayer on an air-water interface. The polar interaction for one molecule on the surface monolayer can be obtained by an intuitive structure as illustrated in the inset of Fig. 1, where each molecule occupies a mean area A on the water surface. The critical area A_0 is defined as πl^2, in which l is the partial length of the molecules along their long axis above the liquid surface. We assume that the dipoles have terminal charges $\pm q$ a distance l apart, i.e., the dipole moment being $p=ql$, the orientational distribution of the molecules in the azimuthal plane is random (i.e., C_∞ symmetry), and the effect of the interaction between the dipolar molecules is considered by introducing a dielectric constant ϵ_m for the monolayer. Now the contribution of the tilt angle to the interaction is only that of the terminal charge q at a distance $d=l\cos\theta$ from the interface. However, it is well known that such a charge experiences a force as if there were an image charge of strength $-q(\epsilon_w-\epsilon_m)/(\epsilon_w+\epsilon_m)$ at the same distance d on the other side of the interface, i.e., the water, where ϵ_w is the dielectric constant of the water. This force corresponds to an interaction energy as

$$W(\theta)=-(p^2/16\pi\epsilon_0\epsilon_m l^3\cos\theta)[(\epsilon_w-\epsilon_m)/\epsilon_w+\epsilon_m]\ , \tag{3}$$

where ϵ_0 is the permittivity of free space. From Eq. (3) and $\epsilon_w>\epsilon_m$, it is clear that for the molecular area $A>A_0=\pi l^2$, the dipolar molecules should lie on the interface plane ($\theta=90°$). On the other hand, when the area is compressed to $A<\pi l^2$,the molecule can align in the range of $0\le\theta\le\theta(A)$, where $\theta(A)=\arcsin(\sqrt{A/A_0})$ with the orientational distribution function

$$f(\cos\theta)=\exp[-W(\theta)/kT]/Z\ , \tag{4}$$

where Z is the single-particle partition written as

$$Z=\int_0^{\theta(A)}\exp[-W(\theta)/kT]\sin\theta\,d\theta\ . \tag{5}$$

The expressions of Eqs. (3)–(5) are what we want to investigate; they reveal the character of the transformation from the isotropic phase to the polar one of the monolayer. For a complete treatment the dielectric constant ϵ_m has to be a function of area A. For the first approximation in the following, however, we assume it is a constant. A simple calculation of Eq. (4) gives the area dependence of the polar order parameter as follows:

$$\begin{aligned}S&=\int_0^{\theta(A)}\cos\theta\,f(\cos\theta)\sin\theta\,d\theta\\&=\frac{x}{2}+[e^x-\cos^2\theta(A)e^{x/\cos\theta(A)}]/2[e^x-\cos\theta(A)\\&\quad\times e^{x/\cos\theta(A)}+x\{\mathrm{Ei}(x/\cos\theta(A))-\mathrm{Ei}(x)\}]\ ,\end{aligned} \tag{6}$$

where $\mathrm{Ei}(x)\equiv\int(e^x/x)dx$ and induced parameter $x=(p^2/16\pi\epsilon_0\epsilon_m l^3)[(\epsilon_w-\epsilon_m)/\epsilon_w+\epsilon_m]/kT$ describes the relative strength of the polar interaction with respect to kT. The numerical results are depicted in Fig. 1. From this figure one finds that on compressing A to A_0 the value of S jumps just from zero to near $\frac{1}{2}$. The latter can be seen from the limit of S for $x\to 0$, i.e.,

$$S(x\to 0)=\tfrac{1}{2}[1+\cos\theta(A)]\ . \tag{7}$$

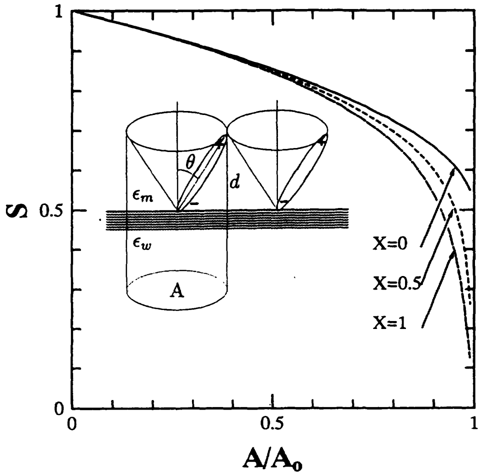

FIG. 1. Theoretical molecular area dependence of the polar order parameter $S=\langle\cos\theta\rangle$ for a monolayer of dipolar molecules at a liquid-air interface. The parameter x is the relative strength of the polar interaction between the molecule and liquid in comparison with kT. The inset is the geometry of the monolayer at the air-water interface.

Equation (7) represents the order parameter in the case of weak or nonpolar molecules, i.e., $x=0$. The value of S tends to unity at $A/A_0=0$ and represents the perfect polar phase, i.e., all molecules align with the direction normal to the monolayer surface. From Fig. 1, a remarkable property is that the changes of S with A are relatively independent of x; in other words, the isotropic-polar phase transition of the monolayer is somewhat universal.

In order to compare with the usual isotropic-nematic phase transition, we also calculate the nematic order parameter using Eq. (4), $\langle P_2\rangle=(3\langle\cos^2\theta\rangle-1)/2$, where

$$\langle\cos^2\theta\rangle=\frac{1}{3}\left\{Sx+\frac{(2S-x)[e^x-\cos^3\theta(A)e^{x/\cos\theta(A)}]}{e^x-\cos^2\theta(A)e^{x/\cos\theta(A)}}\right\}\ . \tag{8}$$

The calculation result is shown in Fig. 2. The most dramatic feature viewed from Figs. 1 and 2 is that, except for a narrow region near A_0, in which $\langle P_2\rangle$ is negative, the behavior of $\langle P_1\rangle$ and $\langle P_2\rangle$ via A is quite similar to that of $\langle P_2\rangle$ via T in nematic liquid crystals [12]. There seems to be a physical reason for this: If ignoring a and b in Eq. (1) fixing Π, one has to decrease T to compress A. In other words, the role of the area change is equivalent to temperature. In Fig. 2, the relative standard deviation of the polar order parameter S, $\delta S/S=\sqrt{\langle\cos^2\theta\rangle-S^2}/S$, is also demonstrated. The big value of $\delta S/S$ at $A=A_0$ shows the strong fluctuation near the transition area that is a common character for the weak first order phase transition and can be examined in the experiment (see below). As a general principle, the strong fluctuations are not expected for the rigorous first order phase transitions but only for the continuous phase transitions. Our present result reveals that the polar ordering (the case of $x\neq 0$) is the source of the weak first order phase transition of the monolayer (see Fig. 1).

To reveal the effects of the polar order phase transition in the expedient, we calculate the additional surface pressure by the thermodynamics function with Eqs. (3)–(5) as

$$\delta\Pi = kT(\partial/\partial A)\ln Z \ . \tag{9}$$

It then results in the following simple form:

$$A\delta\Pi/kT = \frac{(S-x/2)\tan^2\theta(A)\cos\theta(A)}{e^{x[1-1/\cos\theta(A)]}-\cos^2\theta(A)} \ . \tag{10}$$

Numerical results of $A\delta\Pi/kT$ for various A and several x are shown in Fig. 3. We can obtain a surprising feel for Fig. 3: A Dirac-function-like pulse should appear in the Π-A isotherms at $A = A_0$ if we think $\delta\Pi$ in addition to a normal one [i.e., given by Eq. (1)]. Because the width of the pulse is so narrow, the practical observation for the true shape of $\delta\Pi$ seems to be difficult. From the viscosity effect, however, the $\delta\Pi$ pulse may change to two cases: one dynamically extended into a broad and dull one, or one transferred to a sharp slope only. It seems that the experimental result in a smectic monolayer at the air-water interface [8] shows the present theoretical prediction of the former case. Of course the peaks appearing in Π-A isotherms (Fig. 1 in Ref. [8]) are caused by the layer-number transition, but should include the contribution of the orientation transition. For the latter case it may have more important significance. In most Π-A experiments, a long lasting problem as mentioned in the beginning is that both the isotherms and the isobars are with a sharp slope in the gas-fluid transition region [4,6,7]. This is in striking contrast to the behavior of the two-dimensional van der Waals equation. For example, in two very recent experiments of a 5CB (4-cyano-4'-5-alkyl-bipheneyl) [16] and 8CB (4-cyano-4'-8-alkyl-bipheneyl) [17] monolayer on an air-water interface, the experimental value of the slope $-d\Pi/dA$ is (4.7 dyn/cm)/[(47–40) Å^2]$=6.7\times10^{15}$ dyn/cm^3, which is three times that calculated from the van der Waals equation, i.e., $-d\Pi/dA = kT/A^2 = (4.1\times10^{-14}$ erg)/(44^2 Å^4)$=2.1\times10^{15}$ dyn/cm^3. In Fig. 3, the experimental data of Π vs A of Ref. [16] is inserted to show such an anomalous slope in Π-A isotherms of 8CB. For this, in the literature the most popular suggestion is to attribute this peculiarity to impurities or the electro-static interaction of the dipoles [18], but the additional surface pressure for the latter case is too small ($\delta\Pi \sim 10$ dyn/cm) as pointed out in Ref. [2]. The present theoretical prediction shown in Fig. 3 is obviously more evident and is the physical base for causing a slope higher by a factor of 3 than the normal one. The transition in an orientational order is also consistent with the x-ray and electron diffraction experiment in the monolayers [9,10]. In the above calculation the orientation dependence of the steric interactions [not included in parameter b in Eq. (1)] is taken into account. Therefore orientational ordering induced by the short range steric interactions is a source of the anomalous slope in the Π-A isotherm. This type of phase transition for monolayers has been previously studied in the nonpolar case [19,20]. From Eq. (10) and Fig. 3, indeed, the result for $x=0$ (nonpolar case) is qualitatively the same as that for $x\neq0$ (polar case). The most important point in the present model and in previous ones [19,20] is the inclusion of the cutoff $\theta(A)$ in Eq. (5). The cutoff reflects the existence of the short range repulsive forces between molecules and is the most important source of this orientational phase transition. This is also reflected in the calculation of $\langle P_2\rangle$. Our present result shown in Fig. 2 is qualitatively the same as the result shown in Fig. 2 of Ref. [20].

There is more direct evidence for attributing the anomalous behavior to the polar ordering transition. As shown in Figs. 1 and 2, after $A < A_0$ by the compression the more stable region for S is $S > \frac{1}{2}$. This means that the tilt angle θ should surely be in the region of $\theta \leq 60°$. This is observed in the experiments with many measurement methods. For example, for the fatty acid monolayer the tilt angle has been measured beginning with $\theta = 30°$ and reducing towards zero by compression [15]. With optical second-harmonic generation the tilt angle θ of sodium-dodecylnapthalene-sulfonate on a water-air interface is shown to vary from 37° to 30° with increasing surface pressure [3]. Furthermore, the strong fluctuation near the critical area as shown in Fig. 2, in fact, has been already found in the experiment of 8CB [17]. Near the anomalous slope of the Π-A diagram, in region I, as

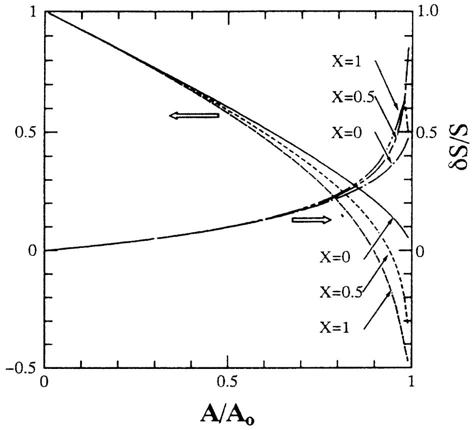

FIG. 2. Area dependencies of the relative strength of the fluctuation of the polar order parameter $\delta S/S$ and the "nematic" order parameter $\langle P_2\rangle$, where $\delta S = \sqrt{\langle\cos^2\theta\rangle - S^2}$ and $\langle P_2\rangle = \langle(3\cos^2\theta - 1)/2\rangle$.

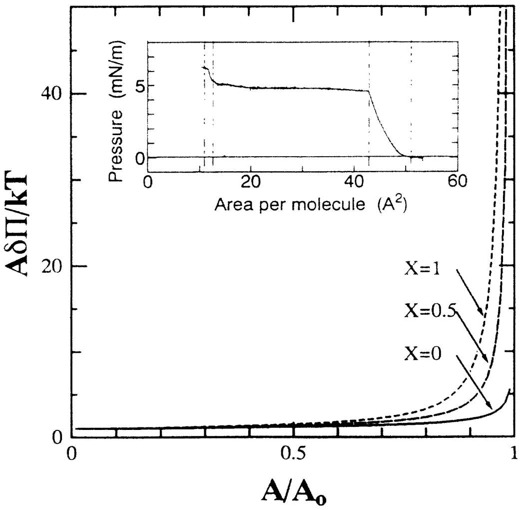

FIG. 3. The peak of an additional surface-pressure–area isotherm $\delta\Pi$-A appears at the critical molecular area A_0 of the polar orientational transition. The inset shows an anomalous slope of Π by compressing an 8CB monolayer [16].

termed by these authors, both the ellipsometry signal and the second-harmonic generation intensity measured for the 8CB monolayer on an air-water interface show the same strong fluctuating behavior, and change into a more steady state with the continuous compression. Such a feature is just the case of $\delta S/S$ shown in Fig. 2.

Our most promising attempt is to answer the question of how one can probe the true property of the polar order S at the transition region in an experiment. The mechanical method used in the usual cases using balance to measure Π-A isotherms is not suitable. In order to detect the fast change of S at critical area A_0, an electric measurement is essential. For the past few years, one of the present authors has been developing an electrical technique [21] in which the fast orientational change of polar molecules in monolayers on a water-air interface can be probed by measuring the Maxwell-displacement current generated from the change. In the inset of Fig. 4, we show the schematic experimental setup for this measurement. Two electrodes parallel to the monolayer are placed above and below the water surface, respectively. An ampere meter connected to the electrodes can measure the Maxwell-displacement current I with the compression of the monolayer as follows [21]:

$$I=(B\gamma_0/d_1)[(m/A)-(dm/dA)] , \tag{11}$$

where B is the working area of the electrode, $\gamma_0=-(1/A)(dA/dt)$ is the constant compression ratio, m is the average vertical component of the dipole moment of one molecule, and d_1 is the distance between the above electrode and the water surface. With polar ordering S defined in Eq. (2), $m=Sp$, Eq. (11) may be written as

$$I=(pB\gamma_0/d_1A)[S-A(dS/dA)] . \tag{12}$$

In Eq. (12) the term associated with $-AdS/dA$ represents the fast varying component of the current. From Eqs. (3)–(5), we have

$$-A\frac{dS}{dA}=\frac{\sin\theta(A)\tan\theta(A)[S-\cos\theta(A)](2S-x)}{2[e^{x[1-1/\cos\theta(A)]}-\cos^2\theta(A)]} . \tag{13}$$

Figure 4 shows the numerical result of Eq. (13), which displays a clear sharp peak appearing at $A=A_0$. Evidently the experiment in a 5CB monolayer [16] has measured such a current peak at $A=90$ Å^2. Assuming $A=A_0=\pi l^2$, one then obtains the estimation of $l=5.4$ Å, which is well located in the range of the Tanford inequality [22] $l\leq l_{\max}\approx(1.54+1.265n)$ Å≈7.9 Å for $n=5$. Here we assume that the molecular length above the water surface is the hydrophobic part C_5H_{11}. The Tanford estimation specifies for a saturated hydrocarbon chain with n carbon atoms and, of course, can be applied to C_5H_{11}.

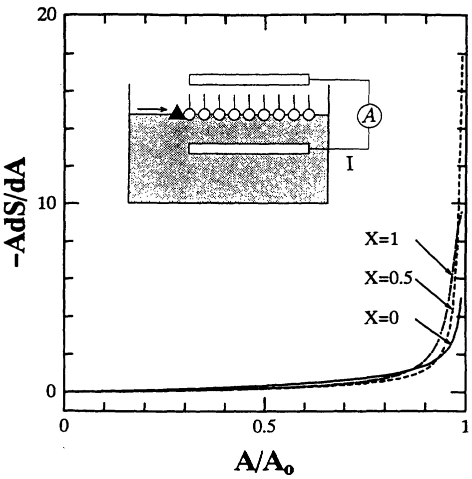

FIG. 4. Theoretical area dependence of the relative compression ratio of the polar order, $-AdS/dA$. The compression induces a sharp pulse of Maxwell-displacement current at $A=A_0$, which is proportional to the ratio. The inset shows the experimental setup.

In summary, we have shown theoretically how the polar interaction between a dipolar molecule and a medium, such as water, can be considered to investigate the phase transition of the orientation for a molecular monolayer at the medium-air interface. The isotropic-polar transition appears to be a weak first order phase transition and this reveals the common feature for this type of phase transition for the monolayer, the anomalous slope of Π-A isotherms, and a strong fluctuation of the order parameter. These predictions offer a better understanding of the process of the monolayer compression or expansion and the associated effects. The good agreement with previous and recent experiments confirms our theoretical proposal.

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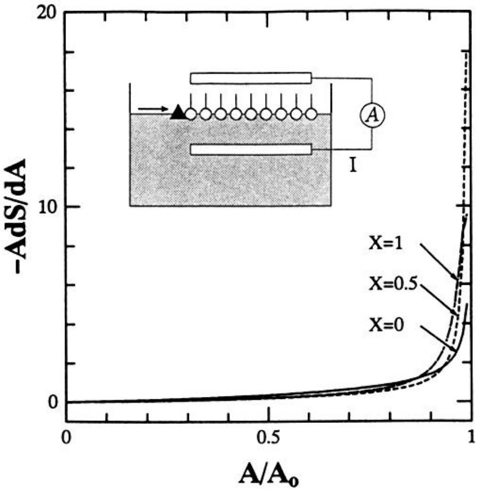
[1] N. Israelachvili, *Intermolecular and Surface Forces* (Academic, London, 1992).
[2] O. Albrecht *et al.*, J. Phys. (Paris) **39**, 301 (1978).
[3] Th. Rosing *et al.*, Phys. Rev. A **31**, 537 (1985).
[4] A. M. Bibo and I. R. Peterson, Adv. Matter. **2**, 309 (1990).
[5] I. Langmuir, J. Chem. Phys. **1**, 756 (1933).
[6] S. Ställberg-Stenhagen and E. Stenhagen, Nature **156**, 239 (1945).
[7] M. Lundquist, Chem. Scr. **1**, 5, 207 (1971).
[8] B. Rapp and H. Gruler, Phys. Rev. A **42**, 2215 (1990).
[9] I. R. Peterson, J. Mol. Electron. **2**, 95 (1986).
[10] C. Böhm *et al.*, Thin Solid Films **178**, 511 (1989).
[11] S. Marcelza, Biochem. Biophys. Acta **367**, 165 (1974).
[12] P. G. de Gennes, *The Physics of Liquid Crystals* (Clarendon, Oxford, 1975).
[13] G. L. Gaines, *Insoluble Monolayers at Liquid-Gas Interfaces* (Wiley, New York, 1966).
[14] F. Brochard *et al.*, in *Physics of Amphiphilic Layers*, edited by J. Meunier, D. Langevin, and N. Boccard (Springer, Berlin, 1987).
[15] See, for example, K. Kjaer *et al.*, J. Phys. Chem. **93**, 3200 (1989).
[16] M. Iwamoto, T. Kubota, and M. R. Muhamad (unpublished).
[17] J. Xue *et al.*, Phys. Rev. Lett. **69**, 474 (1992).
[18] H. L. Scott, B. B. A. (Biochim. Biophys. Acta) Libr. **406**, 329 (1975).
[19] A. Halperin *et al.*, J. Chem. Phys. **86**, 6550 (1987).
[20] Zhong-Ying Chen *et al.*, Phys. Rev. Lett. **61**, 1376 (1988).
[21] M. Iwamoto *et al.*, Nature **353**, 645 (1991).
[22] C. Tanford, *The Hydrophobic Effect* (Wiley, New York, 1973).



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