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# Biaxiality ordering of molecular orientation in a monolayer at the liquid-air interface

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The biaxiality ordering of molecular orientation of a monolayer at the liquid-air interface is theoretically analyzed assuming that the molecular dipole of the constituent rodlike molecules is not parallel to the molecular long axis. Two independent order parameters, biaxiality parameter $\xi$ and the orientational order parameter $S_{zz}$ $[=\langle P_2(\cos\theta)\rangle]$, exhibit a smooth change from zero at a critical molecular area $A_0$ by monolayer compression. $\xi$ is found to be not so weak in monolayers on a water surface, due to the dipole-medium interaction. This prediction may be confirmed by nuclear magnetic resonance and nonlinear optical techniques. [S1063-651X(96)04112-8]

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The equilibrium physico-chemical properties of insoluble monolayers at the air-water interface, Langmüir monolayers, have been studied intensively for over a half century. Only recently, a variety of experimental methods including scattering, spectroscopic, and electrical techniques have been developed to study the molecular order and orientation of monolayers on a water surface [1–3]. On the theoretical side, however, most studies on the molecular orientation of monolayers have considered only the uniaxial nematical ordering [4], which is represented by the Saupe ordering matrix [5]:

$$\mathbf{S}=\begin{pmatrix} S_\perp & 0 & 0 \\ 0 & S_\perp & 0 \\ 0 & 0 & S_\parallel \end{pmatrix}, \tag{1}$$

with $S_\parallel - S_\perp = \Delta S_0 \langle P_2(\cos\theta)\rangle = \Delta S_0 S$. Here $\theta$ is the tilt angle of hydrocarbon chains away from the normal direction of the monolayer surface. That is, $\theta$ is the tilt angle of the long axis of the rodlike molecule in the monolayer or the director $\vec{n}$ of the nematic layer. $\langle\ \rangle$ denotes the thermodynamics average and $P_2$ is the parameter represented as the second-order Legendre polynomial. Unfortunately, in these studies, the polar alignment of monolayers has not been discussed although it is of great importance for a profound understanding of Langmüir monolayers [6].

Recently, we have investigated the polar orientational ordering of the molecular orientation in a monolayer at the water-air interface, using the interaction model by taking into account the interaction working between an amphiphilic molecule and a medium surface [7]. The model starts from a uniaxial molecular structure, assuming that the molecular dipole of the constituent rodlike molecule is parallel to the molecular long axis, i.e., a molecular structure having cylindrical symmetry. Generally, this is inconsistent in the practical structure of the molecules because there is an angle between the molecular dipole and long axis.

In this paper we extend our previous study of the molecular orientation in the monolayer to the general case, and discuss the biaxiality ordering of molecular orientation of the monolayer, assuming that the molecular dipole is not parallel to the molecular long axis. We show that even if the molecules of the monolayer at the liquid-air interface constituting the phase have macroscopically cylindrical symmetry, we still require two independent order parameters to represent the monolayer phase, corresponding to the biaxiality of the phase [8]. The obtained relationship between the biaxiality ordering and the molecular structures may have practical significance in the experiment with nuclear magnetic resonance (NMR) and nonlinear optical techniques [9].

The basic geometry used in the present model is the same as that used in our previous work [7], except that the dipole direction and position are different, as illustrated in Fig. 1. Each molecule occupies a mean molecular area $A$ on the water surface. The critical area $A_0$ is defined as $\pi l^2$, where $l$ is the partial length of the molecules along their long axis above the liquid surface, e.g., the length of the hydrophobic group (usually one or two long hydrocarbon chains). The molecular dipole with a moment $P$ is assumed in the long molecular axis at a distance $\sigma l$ $(0<\sigma<1)$ from the terminal point at the water surface and with an angle $\theta_D$ from the long axis, as shown in Fig. 1. The distribution of the tilted angle $\theta$, the angle between the molecular long axis and the normal direction to the water surface, i.e., the $z$ direction of the laboratory frame, is governed by the interaction of the dipole with water. It is well known that such a dipole at a distance $d=\sigma l\cos\theta$ from the water surface experiences an electrostatic Coulomb force as if there were an image dipole with a moment $-P(\epsilon_w-\epsilon_m)/(\epsilon_w+\epsilon_m)$ at the same distance on the other side of the interface, i.e., the water surface, where $\epsilon_m$ and $\epsilon_w$ are the dielectric constant of the monolayer and the water, respectively. This force corresponds to an interaction energy given by [10]

$$W(\theta,\theta_L)=-P^2\left(\frac{\epsilon_w-\epsilon_m}{\epsilon_w+\epsilon_m}\right)\frac{1+\cos^2\theta_L}{32\pi\epsilon_0(\sigma l\ \cos\theta)^3}, \tag{2}$$

where $\epsilon_0$ is the permittivity of free space and $\theta_L$ is the angle of the dipole direction from the $z$ direction. Obviously, from Eq. (2), we have the same conclusion as that described in our previous paper [7]. That is, because of $\epsilon_w>\epsilon_m$, the dipole always experiences an attractive force to the water surface, therefore the molecules must lie on the water surface ($\theta=\pi/2$) when the molecular area $A>A_0$. In contrast, in the case of the molecular area $A<A_0$ by monolayer compression, the molecular orientation is confined in the range of $0\leqslant\theta\leqslant\theta(A)=\arcsin\sqrt{A/A_0}$), due to the effect of hard-core-intermolecular repulsive forces. The major progress in the present model is the interaction energy written by Eq. (2), which has included the effect of the biaxial molecules [11] by using the angle $\theta_L$.

In order to reveal the effect of $\theta_L$, let us consider a frame $(x_\mu,y_\mu,z_\mu)$ fixed in the discussed molecule where $z_\mu$ direction is parallel to the molecular long axis, with Euler angles $(\alpha,\beta,\gamma)$ defined as the convention in Ref. [12]. We have the following relationship between the molecular frame and the laboratory one $(x,y,z)$ as

$$\begin{pmatrix} x\\ y\\ z\end{pmatrix}=\begin{pmatrix} \cos\alpha\ \cos\gamma-\sin\alpha\ \cos\beta\ \sin\gamma, & -\cos\alpha\ \sin\gamma-\sin\alpha\ \cos\beta\ \cos\gamma, & \sin\alpha\ \sin\beta\\ \sin\alpha\ \cos\gamma+\cos\alpha\ \cos\beta\ \sin\gamma, & -\sin\alpha\ \sin\gamma+\cos\alpha\ \cos\beta\ \cos\gamma, & -\cos\alpha\ \sin\beta\\ \sin\beta\ \sin\gamma, & -\sin\beta\ \cos\gamma, & \cos\beta \end{pmatrix}\begin{pmatrix} x_\mu\\ y_\mu\\ z_\mu\end{pmatrix}. \tag{3}$$

From Eq. (3) it is clear that $\beta$ is just the tilt angle $\theta$. Without loss of generality, we can here assume that the dipole is in the plane of $y_\mu=0$; i.e., $\vec{P}/P=(\sin\theta_D,0,\cos\theta_D)$ in the molecular frame, then we have

$$\cos\theta_L=(\vec{z}/z)\cdot(\vec{P}/P)=\sin\beta\ \sin\gamma\ \sin\theta_D+\cos\beta\ \cos\theta_D. \tag{4}$$

By substituting the equation above into Eq. (2) and replacing $\beta$ with $\theta$, we obtain the orientation distribution function:

$$f(\theta,\gamma)=\frac{e^{-W(\theta,\gamma)/kT}}{Z}, \tag{5}$$

where $Z$ is the single-particle partition written as

$$Z=\int_0^{2\pi}d\gamma\int_0^{\theta(A)}e^{-W(\theta,\gamma)/kT}\sin\theta\ d\theta. \tag{6}$$

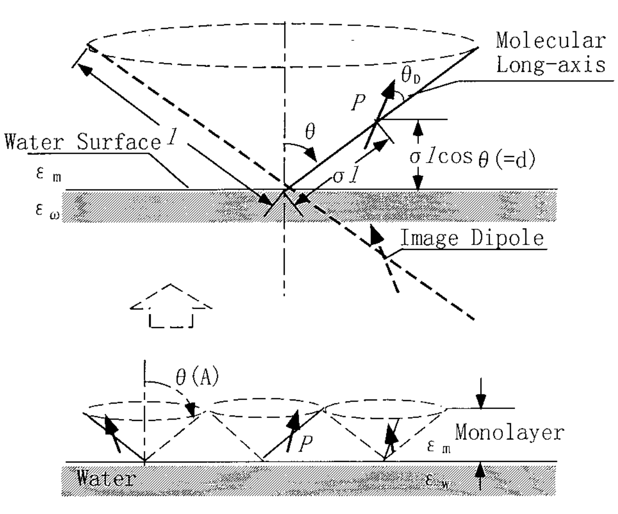

FIG. 1. Sketch of rodlike molecular model for Langmüir film at the air-water interface.

Here $k$ is Boltzmann constant and $T$ is the absolute temperature.

So far, all the attempts to extend the Maier-Saupe theory, which is a uniaxial-molecule model [5], to a biaxial molecule still make some special assumptions about the molecular symmetry and the potential form [8,11], which are still not close to the real physical interaction as presently proposed in Eq. (2) for the monolayer. Moreover, the challenging problem here is to prove that the real interaction between molecular dipole and medium is able to induce the biaxiality ordering. For the purpose, one should calculate the Saupe ordering matrix [8]:

$$S_{\alpha\beta}=\frac{3\overline{l_\alpha l_\beta}-\delta_{\alpha\beta}}{2}, \tag{7}$$

where $l_\alpha$ $(\alpha=x,y,z)$ is the direction cosine of the director $\vec{n}$ with respect to the molecule fixed frame [13]. In the present case, the director is just the normal of the surface, i.e., $\vec{z}$ direction. Hence we have from Eq. (3) the direction $l_x=(\vec{z}/z)\cdot(\vec{x}_\mu/x_\mu)=\sin\theta\ \sin\gamma$, $l_y=(\vec{z}/z)\cdot(\vec{y}_\mu/y_\mu)=\sin\theta\ \cos\gamma$, and $l_z=(\vec{z}/z)\cdot(\vec{z}_\mu/z_\mu)=\cos\theta$. Substituting these into Eqs. (5), (6), and (7), one now can obtain the detailed form of $S_{\alpha\beta}$. Unfortunately, because of the complexity of the $f(\theta,\gamma)$ defined in Eq. (5), one only can calculate them with numerical method and we cannot gain a clear picture of the detailed form of $S_{\alpha\beta}$. To search for an analytical solution we follow the treatment in the hard rod model of the nematic-isotropic phase transition by Onsager [14] by expanding the function of $\exp[-W(\theta,\gamma)/kT]$ and neglecting higher-order terms as in the following approximation:

$$e^{-W(\theta,\gamma)/kT}=1-W(\theta,\gamma)/kT. \tag{8}$$

Given these, we then have from Eq. (6) the approximate partition function:

$$Z=2\pi[1-\cos\theta(A)]+\frac{\pi}{2}\,\eta\{(3-\cos^2\theta_D)\times[\cos^{-2}\theta(A)-1]+(2-6\cos^2\theta_D)\ln\cos\theta(A)\},\qquad(9)$$

where $\theta(A)$ has been defined above and dimensionless parameter $\eta=P^2[(\epsilon_w-\epsilon_m)/(\epsilon_w+\epsilon_m)]/32\pi\epsilon_0(\sigma l)^3kT$ describes the relative strength of the dipolar-medium interaction energy with respect to $kT$. With this first-order approximation, we have obtained the following results:

$$\overline{l_zl_z}=\overline{\cos^2\theta}=\int_0^{2\pi}d\gamma\int_0^{\theta(A)}\cos^2\theta f(\theta,\gamma)\sin\theta\,d\theta\qquad(10)$$

$$=\frac{2\pi}{Z}\left(\frac{1}{3}[1-\cos^3\theta(A)]+\frac{1}{4}\,\eta(3\cos^2\theta_D-1)[1-\cos^2\theta(A)]+\frac{1}{2}\,\eta(\cos^2\theta_D-3)\ln\cos\,\theta(A)\right),\qquad(11)$$

$$\overline{l_xl_x}=\overline{\sin^2\theta\,\sin^2\gamma}=\int_0^{2\pi}d\gamma\int_0^{\theta(A)}\sin^2\theta\,\sin^2\gamma f(\theta,\gamma)\sin\theta\,d\theta$$

$$=\frac{2\pi}{Z}\left(\frac{1}{6}[2-3\cos\theta(A)+3\cos^3\theta(A)]+\frac{1}{16}\,\eta(3-7\cos^2\theta_D)[1-\cos^2\theta(A)]+\frac{5}{4}\,\eta(1-\cos^2\theta_D)\ln\cos\theta(A)+\frac{1}{16}\,\eta(7-3\cos^2\,\theta_D)[\cos^{-2}\theta(A)-1]\right),\qquad(12)$$

$$\overline{l_yl_y}=\overline{\sin^2\theta\,\cos^2\gamma}=\int_0^{2\pi}d\gamma\int_0^{\theta(A)}\sin^2\theta\,\cos^2\gamma f(\theta,\gamma)\sin\theta\,d\theta=\frac{2\pi}{Z}\left(\frac{1}{6}[2-3\cos\theta(A)+\cos^3\theta(A)]+\frac{1}{16}\,\eta(1-5\cos^2\theta_D)[1-\cos^2\theta(A)]+\frac{3}{4}\,\eta(1-\cos^2\theta_D)\ln\cos\theta(A)+\frac{1}{16}\,\eta(5-\cos^2\theta_D)[\cos^{-2}\theta(A)-1]\right),\qquad(13)$$

and

$$\overline{l_xl_y}=\overline{l_xl_z}=\overline{l_yl_z}=0.\qquad(14)$$

Now, from Eqs. (7)–(13) it is shown that the Saupe ordering matrix is a diagonalized matrix but biaxial order parameter $S_{xx}-S_{yy}$ does not vanish if $\eta\neq0$. In other words, we have achieved the conclusion that the dipole-medium interaction must induce the biaxiality of the monolayer. In fact, with Eqs. (7)–(13) we can write the obtained ordering matrix as [8]

$$\mathbf{S}=\begin{pmatrix}-\frac{1}{2}S_{zz}+\xi & 0 & 0\\ 0 & -\frac{1}{2}S_{zz}-\xi & 0\\ 0 & 0 & S_{zz}\end{pmatrix},\qquad(15)$$

where $\xi$ is the biaxiality parameter expressed as

$$\xi=-\frac{3\pi}{16Z}\,\eta\,\sin^2\theta_D[\cos^{-2}\theta(A)-\cos^2\theta(A)+4\ln\cos\theta(A)].\qquad(16)$$

This clearly reveals the origin of the biaxiality, which is induced by the symmetry breaking from cylindrical symmetry of the molecules (i.e., $\theta_D\neq0$). If the molecules have the cylindrical symmetry (i.e., $\theta_D=0$), biaxiality parameter $\xi$ vanishes and only $S_{zz}$ is left. This is exactly equivalent to $\langle P_2(\cos\theta)\rangle$, which represents the uniaxial nematic ordering.

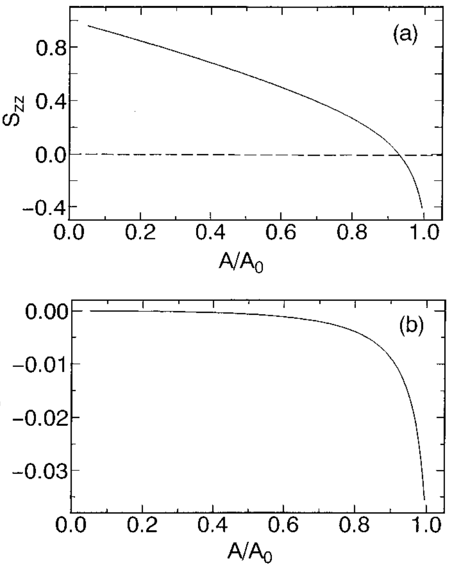

FIG. 2. Two order parameters as a function of molecular area $A/A_0$. (a) The biaxial order parameter $S_{zz}$. (b) The biaxiality parameter $\xi$.

The analytical results of Eqs. (9)–(11) also reveal that on compressing molecular area $A$ to $A_0$, both order parameters $S_{zz}$ and $\xi$ smoothly change from zero as long as $\eta \neq 0$. So we called the orientation phase transition a weak first-order phase transition induced by compressing the molecular area [7]. These can be seen from the numerical calculation shown in Fig. 2, in which we chose $l = 0.56$ nm, $P = 0.8$ D on the basis of our experimental data on 4-cyano-4′-*n*-pentyl-bi-phenyl(5CB) monolayers [15]. Further, for simplicity, we assumed $\epsilon_w = 80$, $\epsilon_m = 1$, $\sigma = 0.5$, $\theta_D = \pi/6$, and $T = 300$ K in the calculation. From Fig. 2 we found that the biaxiality parameter $\xi$ is on the order of $10^{-2}$ for the monolayer. For a long time the biaxial order parameter has been very difficult to determine, although the parameter has been measured for certain mesogens by measuring the dipolar splitting of the NMR spectrum, and it was found to be nonzero [16]. Applying a HD decoupling experiment to a deuterated 5CB in the nematic phase, one measured $S_{zz} = 0.66$ and $\xi = 0.012$ [16]. The remarkable difference in the magnitude between $S_{zz}$ and $\xi$ is of two orders, which confirms our present theoretical prediction: If $\xi$ is seen as a perturbation quantity then the biaxial order parameter is a higher-order perturbation comparing with $S_{zz}$ as shown in Refs. [10,14]. But for the strongly polar molecules this situation may change and should be confirmed in future experiments. In fact, the previous measurements, such as those reported in Ref. [16], are performed in the bulk phase. It is expected from our present theory that the biaxiality order parameter may be found to be not so weak in the monolayer at the liquid-air interface. This may open the field to a study of the connection between the theory relating to monolayer's and experimental technique, such as the NMR spectrum, nonlinear optics, and other techniques.

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