# Polar orientational phase transition in smectic monolayers induced by monolayer compression

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Taking into consideration the mean electric field produced by a molecular configuration, a self-consistent-field state equation is derived to describe the behavior of polar smectic phase for monolayers. A general equation of orientational phase transition between a normal-director phase and a tilted-director phase induced by monolayer compression for monolayers is obtained. It was revealed that smectic monolayers show a possible second-order orientational phase transition under a necessary condition $4-16/g_y < g_z < g_y/4$. Here $g_y$ and $g_z$ are two parameters proportional to the internal electric fields in the directions parallel and perpendicular to the monolayer surface, respectively. The two-dimensional orientational phase transition theory developed here may reveal such a transition in smectic monolayers by some techniques, for example, the Maxwell-displacement-current measuring technique. [S1063-651X(98)03605-8]

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Investigations of smectic-$C$ liquid crystals (LCs) can be traced back to the 1970s and most of them are based on the elastic theory [1]. An elastic theory for smectic-$C$ liquid crystalline systems has already been given by de Gennes *et al.* [2–4]. However, many difficulties were encountered in developing a theory for the orientational smectic-$C$–smectic-$A$ phase transition. Apart from the reports by Gießelmann and co-workers [5,6], scientific papers concerning the polar orientational smectic-$A$–smectic-$C$ phase transition for liquid crystals are very rare in the literature. At the same time, some excellent experimental observations of the orientational phase transition between smectic-$A$ and smectic-$C$ LCs in monolayers on a water surface have been achieved by monolayer compression [7]. For ferroelectric LCs, the electromagnetic interactions appear to be inevitably associated with this kind of transition. This is more obvious for polar monolayers, as for them the dipole-dipole interaction is very important in this case [8,9]. Although some of the theoretical results for liquid crystals are applicable to the analysis of monolayers, an alternative theory for single monolayers is expected due to the dimensional difference between them (two dimensions for monolayers rather than three dimensions for liquid crystals) and due to the change in molecular states as a result of external stimulation, for example, monolayer compression. Moreover, the molecular configuration in the monolayer plane plays an important part in many physical phenomena concerning Langmüir-Blodgett films [9–11]. In monolayers of polar molecules on a water surface, there are at least two order parameters: one is the molecular configuration, i.e., the positional distribution pattern of the heads of the molecules on a water surface [10–12], and the other is the orientational distribution of the molecular tails [8]. The aim of this paper is to provide a physical sound picture of polar orientational phase transition for smectic monolayers that are structurally different from bulk LCs to describe the behavior of the polar orientational phase transition in smectic monolayers on a water surface under monolayer compression.

Considering a tilted-director smectic phase with a tilt angle $\theta_c$ as shown in Fig. 1, we choose the coordinate system in such a way that the smectic monolayer planes are parallel to the $xy$ plane and the monolayer normal falls along the positive $z$ axis. Constituent molecules of monolayers are assumed to be rodlike and have a permanent dipole moment $\mu$ in the direction parallel to the molecular long axis. The angle that the dipole moment at the origin makes with the layer normal is denoted by $\theta$. As the monolayer concerned is amphiphilic, the hydrophilic parts, the head groups of the dipoles in the monolayer, are pinned onto the water surface due to the strong hydrophobic interaction, while the tails of these dipoles are free to rotate in the air. Thus, in the case of monolayers, the dipoles prefer to line up in the same direction above the water surface rather than take an antiferroelectric state in LCs, due to the surface component of the interaction. The dipole at the origin discussed is assumed to be restricted within the angular range $[0, \theta_A]$ with $\sin^2\theta_A = A/\pi l^2$ ($A$ is the molecular area and $l$ is the length of long molecular axis) [8] due to the hard-core interaction among molecules in monolayer films. A strong steric repulsion takes places if $\theta$ approaches $\theta_A$. The molecular area decreases as the monolayer films are compressed. The electric field produced by the tilted dipole array is decomposed into two directions: one produces the dipole component array standing perpendicular on the water surface and the other produced by the projection of the tilted dipole array onto the smectic
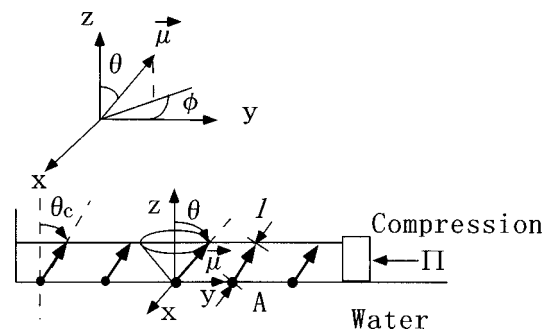


FIG. 1. Basic geometry of the molecular-orientational model used in the present paper.

monolayer plane. For convenience, we assume that the in-plane projection dipole array on the monolayer surface orients in the positive $y$ direction, so that the internal electric field can be written as $\mathbf{E}=(0,E_y,E_z)$. The electric field at the origin is the sum of the fields created by the dipole array (excluding the dipole at the origin) and it is given by [13]

$$E_y=\mu(\sin\theta_C)\frac{2\epsilon_m}{\epsilon_m+1}\sum_{dipoles}\frac{3(\mathbf{e}_y\cdot\mathbf{r}_i)\mathbf{r}_i-r_i^2\mathbf{e}_y}{4\pi\epsilon_0 r_i^5}\cdot\mathbf{e}_y,$$

$$E_z=-\mu(\cos\theta_C)\frac{2\epsilon_m}{\epsilon_m+1}\sum_{dipoles}\frac{1}{4\pi\epsilon_0 r_i^3}, \quad (1)$$

where $\mu$ is the permanent dipole moment of molecules, $\epsilon_0$ is the dielectric permittivity of a vacuum, $\mathbf{r}_i$ is the spatial vector of the molecules in the monolayer plane, $\epsilon_m$ is the relative dielectric constant of the material surface, for example, the water surface, and $\mathbf{e}_y$ and $\mathbf{e}_z$ are the unit vectors along the $y$ axis and the $z$ axis, respectively. The summation in Eq. (1) should exclude the dipole at the origin. For further treatment, it is convenient to introduce Euler angles for the dipole at the origin $\boldsymbol{\mu}/\mu=(\sin\theta\sin\phi,\sin\theta\cos\phi,\cos\theta)$. Here $\phi$ is the azimuthal angle of the dipole discussed. With the definition and the introduction above, we can write down the mean-field potential

$$W=\boldsymbol{\mu}\cdot\mathbf{E}=-(g_y\sin\theta_c\sin\theta\cos\phi-g_z\cos\theta_c\cos\theta)a^{-3/2}kT \quad (2)$$

for each dipole. Here $a$ is the normalized molecular area defined as $a=A/\pi l^2=\sin^2\theta_A$ and

$$g_y=\frac{\mu^2 a^{3/2}}{kT}\frac{2\epsilon_m}{\epsilon_m+1}\sum_{dipoles}\frac{3(\mathbf{e}_y\cdot\mathbf{r}_i)\mathbf{r}_i-r_i^2\mathbf{e}_y}{4\pi\epsilon_0 r_i^5}\cdot\mathbf{e}_y,$$

$$g_z=\frac{\mu^2 a^{3/2}}{kT}\frac{2\epsilon_m}{\epsilon_m+1}\sum_{dipoles}\frac{1}{4\pi\epsilon_0 r_i^3}. \quad (3)$$

Here $k$ is the Boltzmann constant and $T$ is the temperature. $g_y$ and $g_z$ are two normalized parameters reflecting the molecular configuration of monolayers. They are independent of the tilt angle $\theta_c$ of the monolayer director and the molecular area $A$ as long as the molecular configuration does not change in the monolayer compression process. Molecular interactions of some other phases with all possible molecular configurations are also included in Eq. (3) and can be calculated by considering the configuration of polar molecules (for example, smectic $H$ if it is hexatic molecular configuration). For some of the artificial two-dimensional arrangement of dipoles, $g_y$ and $g_z$ have already been calculated [12]. Using Boltzmann statistics, the $y$ axis orientational order parameter, the average projection of molecular orientation onto the $y$ axis, reads

$$\langle\sin\theta\cos\phi\rangle$$

$$=\frac{1}{Z}\int_0^{2\pi}\int_0^{\theta_A}(\sin\theta)$$

$$\times(\cos\phi)e^{(g_y\sin\theta_c\sin\theta\cos\phi-g_z\cos\theta_c\cos\theta)a^{-3/2}}$$

$$\times\sin\theta\,d\theta\,d\phi, \quad (4)$$

where $Z$ is the single-partition function given by

$$Z=\int_0^{2\pi}\int_0^{\theta_A}e^{(g_y\sin\theta_c\sin\theta\cos\phi-g_z\cos\theta_c\cos\theta)a^{-3/2}}$$

$$\times\sin\theta\,d\theta\,d\phi.$$

In order to express the integration of Eq. (4), we introduce the Bessel function $I_\nu(z)$, which satisfies [14]

$$\frac{d}{dz}[z^\nu I_\nu(z)]=z^\nu I_{\nu-1}(z),\quad \frac{2\nu}{z}I_\nu=I_{\nu-1}-I_{\nu+1}. \quad (5)$$

Special cases when $\nu=0$, 1, and 2 are

$$I_0(z)=\frac{1}{\pi}\int_0^\pi e^{z\cos\phi}d\phi,$$

$$I_1(z)=\frac{1}{\pi}\int_0^\pi e^{z\cos\phi}\cos\phi\,d\phi,$$

$$I_2(z)=\frac{1}{\pi}\int_0^\pi e^{z\cos\phi}d\phi-\frac{2}{\pi z}\int_0^\pi e^{z\cos\phi}\cos\phi\,d\phi. \quad (6)$$

Set $p=g_y\sin\theta_c a^{-3/2}$ and $q=g_z\cos\theta_c a^{-3/2}$ and with the small tilt angle assumption ($\sin\theta=\theta$), the $y$ axis orientational order parameter (4) becomes

$$\langle\sin\theta\cos\phi\rangle=\frac{2\pi e^{-q}}{Z}\int_0^{\theta_A}\theta^2\left(1+\frac{q\theta^2}{2}\right)I_1(p\theta)d\theta, \quad (7)$$

under the assumption that $|q\theta^2|\ll 1$. Here the single-partition function $Z$ turns out to be

$$Z=2\pi e^{-q}\int_0^{\theta_A}\theta\left(1+\frac{q\theta^2}{2}\right)I_0(p\theta)d\theta. \quad (8)$$

With the relations in Eq. (5), Eq. (7) can be further calculated as

$$\langle\sin\theta\cos\phi\rangle=\frac{\int_0^{\theta_A}\theta^2\left(1+\frac{q\theta^2}{2}\right)I_1(p\theta)d\theta}{\int_0^{\theta_A}\theta\left(1+\frac{q\theta^2}{2}\right)I_0(p\theta)d\theta}=\theta_A\frac{I_2(p\theta_A)}{I_1(p\theta_A)}$$

$$\times\left[1-\int_0^{\theta_A}\frac{q\theta^3}{2}I_0(p\theta)d\theta\bigg/\frac{1}{p}\theta_A I_1(p\theta_A)\right]$$

$$=\theta_A\frac{I_2(p\theta_A)}{I_1(p\theta_A)}\left[1-\frac{q}{2}\theta_A^2+\frac{q\theta_A}{p}\frac{I_2(p\theta_A)}{I_1(p\theta_A)}\right]$$

$$\equiv f(\theta_c). \quad (9)$$

The self-consistent field requires that the $y$ axis orientational order parameter as written above should be equal to $\sin\theta_c$. If we define a function $\sigma(z)$ $[=I_2(z)/I_1(z)]$ and set $\langle\sin\theta\cos\phi\rangle=\sin\theta_c\approx\theta_c$, we get a self-consistent equation describing a polar smectic phase in monolayers with consideration of the configuration of molecules,

$$\theta_c = a^{1/2}\sigma\left(\frac{g_y\theta_c}{a}\right)\left\{1-g_z a^{-1/2}\left[\frac{1}{2}-\frac{a}{g_y\theta_c}\sigma\left(\frac{g_y\theta_c}{a}\right)\right]\right\}$$
$$\equiv f(\theta_c). \qquad (10)$$

The function $\sigma(z)$ can be expanded as a Taylor series in the vicinity of $z=0$,

$$\sigma(z)=\frac{1}{4}z-\frac{1}{96}z^3-\frac{5}{1536}z^5+\cdots. \qquad (11)$$

Substituting the above relation into Eq. (10), it is possible for one to obtain the polynomial expansion of $f(\theta_c)$,

$$f(\theta_c)=\frac{1}{4}\frac{g_y}{a^{1/2}}\left[1-\frac{1}{4}\frac{g_z}{a^{1/2}}\right]\theta_c-\frac{a^{1/2}}{96}\left(\frac{g_y}{a}\right)^3\theta_c^3$$
$$-\frac{5a^{1/2}}{1536}\left(\frac{g_y}{a}\right)^5\theta_c^5+\cdots. \qquad (12)$$

As the second and third coefficients of the expansion (12) have the same sign, we draw a conclusion that the polar orientational transition between a normal-director phase and a tilted-director phase in smectic monolayers cannot be a first-order transition. In other words, a second-order transition is the most possible. The critical condition of such a second-order transition, induced by monolayer compression, is given by

$$\frac{1}{4}\frac{g_y}{a_c^{1/2}}\left[1-\frac{1}{4}\frac{g_z}{a_c^{1/2}}\right]=1, \qquad (13)$$

that is,

$$a_c=\frac{g_y^2}{64}(1+\sqrt{1-4g_z/g_y})^2. \qquad (14)$$

Equation (14) gives the relation between the critical molecular area and the molecular configuration at the point of the orientational phase transition between a normal-director phase and a tilted-director phase. A variety of orientational phase transitions, for example, polar smectic-$A$–smectic-$C$, polar smectic-$B$–smectic-$H$, etc., can be described by such a relation by only changing the $g$ parameters ($g_y$ and $g_z$). Figure 2 shows the numerical calculation of the present argument. The molecular configuration is assumed to be unchanged in the monolayer compression process, that is, $g_y$ and $g_z$ are independent of the molecular area $A$. As an example, we set $g_y=3$ and $g_z=0.4$ in Figs. 2 and 3. The values of $g_y$ and $g_z$ were chosen on the basis of our previous Maxwell-displacement-current (MDC) measurement on 4-cyano-4′-5-alkyl-biphenyl [15]. It can be seen from Fig. 2 that when the slope $k$ of $y=f(\theta_c)$ at the origin becomes 1, a second-order phase orientational transition occurs. If $g_y$
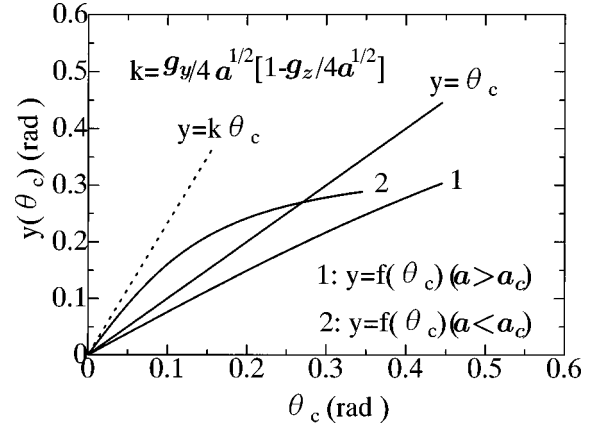


FIG. 2. Numerical calculation of the self-consistent equation $\theta_c=f(\theta_c)$ of a tilted-director phase for smectic monolayers. $k=1$ corresponds to the second-order orientational transition between a normal-director phase and a tilted-director phase induced by the monolayer compression.

$\geqslant 4g_z$ one gets a critical area, which is simply expressed as $a_c=g_y^2/16$. With the fundamental condition for $a$, $0<\sqrt{a}<1$, in Eq. (13), we get a necessary condition on the molecular configuration for possible orientational transition,

$$4-\frac{16}{g_y}<g_z<\frac{g_y}{4}. \qquad (15)$$

Equation (15) implies that for monolayer films under monolayer compression, some kinds of molecular configurations may not exist at the orientational transition between a normal-director phase and a tilted-director phase.

For a full understanding of the orientational phase transition process discussed above, it is crucially important to find an experimental way to determine the orientational phase transition point. As discussed in our previous paper [8], the orientational order parameter $S$, which is the first term of
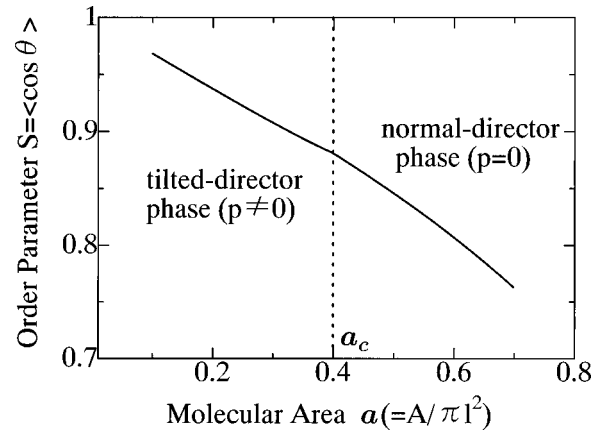


FIG. 3. Orientational order parameter $S$ of smectic monolayers with respect to the molecular area $a$. The orientational transition between the normal-director phase and the tilted-director phase induced by the monolayer compression is a second-order one. It is predicted that the MDC will experience a sudden change at the transition point, as the MDC is proportional to the differentiation of the orientational order parameter $S$ with respect to the molecular area $a$.

Legendre polynomial and the main characteristic parameter for monolayers, can also be introduced for smectic monolayers in a tilted-director phase as

$$S = \langle \cos \theta \rangle$$

$$= \frac{1}{Z} \int_0^{2\pi} \int_0^{\theta_A} \cos \theta e^{-q\cos\theta} I_0(p\sin\theta) \sin\theta \, d\theta \, d\phi.$$

$$(16)$$

It can be found from Eq. (16) that in the case $p=0$ ($\theta_c = 0$), $I_0(p\sin\theta) = 1$, $S$ returns to the orientational order parameter of normal-director smectic monolayers. Figure 3 shows an example of the orientational order parameter $S$ for the normal-director phase and the tilted-director phase for smectic monolayers, respectively. The result reveals that the orientational transition between this two phases is a second-order one. The phase transition area $a_c$ can be measured by the MDC measuring technique, as its displacement current is proportional to the differentiation of the orienta-

tional order parameter $S$ with respect to molecular area $A$ [15]. From the change of the experimental MDC, it is possible to find the orientational phase transition point $a = a_c$.

In summary, we formulate a self-consistent equation for smectic monolayers and derive a general equation of the orientational phase transition between a normal-director phase and a tilted-director phase for smectic monolayers under monolayer compression taking into consideration the molecular configuration. It is found that the orientational phase transition induced by monolayer compression is a second-order one. A necessary condition between $g_y$ and $g_z$ reveals that only monolayer films with certain kinds of molecular configurations have such a phase transition. The orientational phase transition area $a_c$ might be measured by the MDC technique, as predicted from Fig. 3. The polar orientational transition theory presented in this paper draws together the polar orientational phase transition in smectic monolayers, the molecular configuration of monolayers, and the MDC technique.

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