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Surface-monolayer-induced bulk alignment of liquid crystals: From nematic to smectic-*A* phase

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The Landau–de Gennes theory of surface-induced bulk alignment of nematic liquid crystals is extended to the smectic-*A* case where both orientational ordering and positional ordering are present. Assuming strong surface anchoring, we find that in both nematic and smectic phases, the bulk pretilt angle is determined by the liquid crystalline order of the first liquid-crystal monolayer at surface through a biaxial surface-bulk transition layer. The smectic layer ordering tends to reduce the spatial variation of the director tilt in the transition layer, making the bulk pretilt angle somewhat closer to the director tilt angle at the surface. Experimental measurement shows results in semiquantitative agreement with theory. [S1063-651X(99)12902-7]

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I. INTRODUCTION

The study of surface-induced bulk alignment of liquid crystals (LCs) is not only interesting from the basic physics point of view, but also important for the design of LC display devices. With the accumulated experimental results, it has become well known that proper surface treatment can be used to control bulk alignment, especially the bulk pretilt angle [1]. To understand the mechanism of such control, various theoretical and experimental investigations have been carried out for decades. Two distinct models have been proposed, one based on the short-range molecule-molecule interaction [2] and the other on long-range elastic interaction due to surface undulation [3]. The former appears to be valid for polyimide or surfactant-coated substrates [4]. In several recent publications, it was found that the nematic LC bulk alignment is fully determined by the orientational ordering of the first LC monolayer adsorbed on the substrate [4,5]. Take the rubbed polyimide-coated substrate as an example. An approximate orientational distribution of the first LC monolayer on the substrate can be deduced from measurement of surface optical second-harmonic generation (SHG) [6]. The orientational ordering obtained has a strong biaxial character, reflecting the presence of a short-range LC-surface interaction. Then through LC molecule-molecule correlation, governed by the Landau–de Gennes (LdG) theory [7,8], the orientation and alignment of the surface LC monolayer yields the homogeneous bulk LC alignment and the pretilt angle. The latter has been found to agree with experiment [5].

With the understanding of surface-induced bulk LC alignment on rubbed polymer surfaces being satisfactory in the nematic case, it is natural to attempt extending our investigation to other mesophases, in particular to the various smectic phases. Due to the coexistence of orientational (nematic) and positional (smectic) ordering, the smectic bulk alignment is more complex than the nematic counterpart. A similar situation has already been encountered in the investigation of the surface-induced wetting behavior of LCs with a direct isotropic-smectic *A* (*I*-Sm*A*) transition [9].

Being the simplest of all smectic phases, Sm*A* constitutes the first object for our study. In this paper, we investigate surface-induced bulk alignment of 4′-*n*-octyl-4- cyanobiphenyl (8CB) on rubbed poly-*n*-alkyl-pyromellitic imide (P6)-coated substrates. 8CB has a nematic-smectic *A* (*N*-Sm*A*) transition [10]. We study how surface-induced bulk alignment varies as the temperature is varied across the transition, from the nematic to the Sm*A* phase. It is known that orientation of the surface monolayer at the substrate hardly depends on temperature [4]. The study then enables us to deduce the sole effect of smectic ordering on LC bulk alignment. In this case, the LC bulk is again aligned by the surface LC monolayer via molecule-molecule correlation through a surface-bulk transition region. The theoretical description we adopt here is an extension of the early approach used on nematics using the LdG formalism, which now incorporates both nematic and smectic ordering. The calculation shows that in changing from the nematic to the Sm*A* phase, the bulk pretilt angle experiences a small but clear increase that is expected from the elastic energy argument. This result is in good agreement with our measurement. The calculation also shows how the nematic and smectic order parameters vary spatially in the surface-bulk transition region. In this respect, we note that the biaxial character of orientational ordering of the surface LC monolayer and the surface-bulk transition region is of qualitative importance to the determination of the structure of the surface-bulk transition region, but was neglected in a recent publication by Skačej *et al.* [11].

II. THEORY

The theoretical description of surface-induced bulk alignment for a homogeneously aligned nematic film with strongly anchored boundary monolayers has been reported elsewhere [5]. Here we will extend it to the Sm*A* phase. For completeness, we will first review briefly the nematic case.

A. Nematic phase

Consider a semi-infinite LC sample in the half-space $z \geqslant 0$ having a C_{1v} symmetry with xz being the mirror plane. The local nematic ordering and alignment can be described by a traceless symmetric tensor $\overleftrightarrow{Q}(z)$ given by

$$\overleftrightarrow{Q}=\begin{bmatrix} \left(\frac{S}{4}-\frac{P}{4}\right)+\left(\frac{3S}{4}+\frac{P}{4}\right)\cos 2\alpha & & \left(\frac{3S}{4}+\frac{P}{4}\right)\sin 2\alpha \\ & -\frac{S}{2}+\frac{P}{2} & \\ \left(\frac{3S}{4}+\frac{P}{4}\right)\sin 2\alpha & & \left(\frac{S}{4}-\frac{P}{4}\right)-\left(\frac{3S}{4}+\frac{P}{4}\right)\cos 2\alpha \end{bmatrix}, \tag{1}$$

where S and P specify the nematic orientational order which is in general biaxial, and α is the tilt angle of the average orientational direction of the long molecular axis. The LdG free energy density associated with the nematic ordering takes the form [8]

$$\mathcal{F}_N=\frac{1}{2}(L_1 Q_{ij,k}^2+L_2 Q_{ij,j}Q_{ik,k})+\frac{2}{3}AQ_{ij}^2-\frac{4}{3}BQ_{ij}Q_{jk}Q_{ki}+\frac{4}{9}C(Q_{ij}^2)^2, \tag{2}$$

where $A=a(T-T^*)$, T^* is the supercooling temperature, a, L_1, L_2, B, and C are phenomenological constants, summation over terms with different i, j, and k subindices is implied, and a comma in the subscript means derivative with respect to the spatial coordinate that follows. In the present problem, $Q_{ij}=Q_{ij}(z)$. Substitution of Eq. (1) into Eq. (2) yields

$$\begin{aligned}\mathcal{F}_N=&\left[\frac{3}{4}L_1+\frac{1}{8}L_2(1+3\sin^2\alpha)\right](\partial_z S)^2\\ &+\left[\frac{1}{4}L_1+\frac{1}{8}L_2\cos^2\alpha\right](\partial_z P)^2+\frac{1}{4}L_2\cos^2\alpha\,\partial_z S\,\partial_z P\\ &+\left[\frac{1}{4}L_1+\frac{1}{8}L_2\right](3S+P)^2(\partial_z\alpha)^2\\ &+\left[\frac{1}{8}L_2(3S+P)\sin 2\alpha\right]\partial_z\alpha(\partial_z S-\partial_z P)\\ &+A\left(S^2+\frac{1}{3}P^2\right)-B(S^3-SP^2)+C\left(S^2+\frac{1}{3}P^2\right)^2.\end{aligned} \tag{3}$$

The local order parameter $\overleftrightarrow{Q}(z)$ can be determined from minimization of the total free energy $\int dz\mathcal{F}_N$ given the boundary values $\overleftrightarrow{Q}(0)$, i.e., $S_0\equiv S(0)$, $P_0\equiv P(0)$, and $\alpha_0\equiv\alpha(0)$, and knowing that at $z\rightarrow\infty$, $\overleftrightarrow{Q}(z)$ approaches the bulk value with $S=S_b,P_b=0$. The bulk pretilt angle α_b also comes out from the calculation. In our studies, $\overleftrightarrow{Q}(0)$ can be obtained from the definition

$$\overleftrightarrow{Q}=\int\frac{1}{2}(3\boldsymbol{\zeta}\boldsymbol{\zeta}-\mathbf{I})f(\theta,\phi)\sin\theta\,d\theta\,d\phi, \tag{4}$$

where $\boldsymbol{\zeta}$ is the unit vector along the long LC molecular axis and $f(\theta,\phi)$ is the orientational distribution function of the surface LC monolayer deduced from the surface SHG measurement with θ and ϕ denoting the polar and azimuthal angles of $\boldsymbol{\zeta}$, respectively. The nematic ordering changes from the surface values S_0, P_0, and α_0 to the bulk values $S_b,P_b=0$, and α_b as z increases from 0 across the surface-bulk transition layer, which has a thickness of the order of the LC correlation length. In the free energy expression Eq. (3), the fifth term on the right-hand side describes coupling of $\partial_z\alpha$ with $\partial_z S$ and $\partial_z P$ originating from the L_2 elastic term in Eq. (2). It can be said that the variation of α in the surface-bulk transition region is induced by the variations of S and P in the same region. Assuming (i) S_b-S_0 and P_b-P_0 are much smaller than unity, (ii) S and P spatially vary from the surface into the bulk with the same characteristic length, i.e., $S(z)=S_0+(S_b-S_0)(1-e^{-z/\xi_N})$ and $P(z)=P_0+(P_b-P_0)(1-e^{-z/\xi_N})$, and (iii) α_0 is very small ($<4°$ as measured) [5], we find that α_b deep in the nematic phase has an approximate analytical expression

$$\alpha_b=\alpha_0\left[1-\frac{L_2}{3(2L_1+L_2)S_b}(S_b-S_0+P_0)\right]. \tag{5}$$

Both theory and experiment have found that α_b is very close to α_0 (they often differ by less than 1°). While the theory can predict how α varies in the surface-bulk transition layer, experimentally this is difficult to verify. It is, however, possible to measure how α_b varies with temperature (with α_0 fixed), especially as the LC bulk changes from nematic to Sm*A*. The results enable us to provide a further check on the theory.

B. Smectic-*A* phase

Below the *N*-Sm*A* transition temperature, positional ordering of molecules corresponding to a layer structure is present in the bulk. However, it is not clear how the layer structure would appear at the surface. In one extreme, the adsorption energy of the LC molecules on polymer is very large so that molecules are not likely to desorb. Since the LC molecules should adsorb on the surface more or less randomly in position, the positional ordering vanishes at the surface and changes from zero to the bulk value across the surface-bulk transition layer. In the other extreme, the bulk layer may imprint the bulk positional ordering at the surface via desorption and adsorption of LC molecules on the polymer surface. Then the positional ordering is at the bulk value throughout the LC film. We shall consider both cases in the following discussion. The real situation is probably somewhere between the two cases. The finite positional order in the transition layer has an appreciable effect on the surface-induced bulk pretilt angle, which can be qualitatively understood as follows. The elastic distortion associated with a spatially varying $\alpha(z)$ is of the splay-bend character. The presence of positional ordering must hinder the spatial variation of α since the elastic distortion is inevitably accompanied by the compression of the smectic layers and/or the layer normal deviating from the director [12,13]. The former is associated with change of the layer periodicity while the latter describes smectic *C* ordering, each corresponding to a kind of elastic distortion from the equilibrium Sm*A* ordering that costs energy. Consequently, the deviation of α_b from α_0 must be reduced. One may expect that since $\alpha_b-\alpha_0$ is induced by the spatially varying *S* and *P*, it could also be affected by the slightly enhanced value of S_b in the Sm*A* phase. This is, however, relatively weak and less important.

First introduced by de Gennes [12], the complex order parameter describing the smectic layer ordering is

$$\psi(\mathbf{r})=\tau(\mathbf{r})\exp[-iq_0u(\mathbf{r})].$$

Here τ is the first harmonic in the density modulation: $\rho(\mathbf{r})=\rho_0+\psi(\mathbf{r})\exp(iq_0\mathbf{N}\cdot\mathbf{r})+\text{c.c.}$, $2\pi/q_0$ is the periodic layer thickness of the undistorted bulk Sm*A* structure with the unit vector $\mathbf{N}$ denoting its layer normal, and $u(\mathbf{r})$ describes the local deviation from the undistorted bulk layer structure. With $u(\mathbf{r})\neq 0$, the local layer normal is along the direction of $\mathbf{N}-\boldsymbol{\nabla}u(\mathbf{r})$. In the first-order approximation, $-\boldsymbol{\nabla}_{\perp\mathbf{N}}u(\mathbf{r})$ denotes a change of the layer normal direction and $-\boldsymbol{\nabla}_{\parallel\mathbf{N}}u(\mathbf{r})$ is associated with a change in the layer thickness. It is known that spatial variation of layer thickness is energetically highly unfavorable [13]. We shall therefore neglect it in our calculation. Now the layer normal can be denoted by a unit vector $\mathbf{N}_L=(\cos\beta,0,\sin\beta)$, where β is the tilt angle of $\mathbf{N}_L$ away from the *xy* plane. Since the spatial variation of β along the *z* axis inevitably leads to $\boldsymbol{\nabla}\times\mathbf{N}_L\neq\mathbf{0}$, indicating a spatial variation of layer periodicity, which is forbidden in our treatment, $\beta(z)$ has to be equal to β_b, the bulk tilt angle of the layer normal. In other words, there is no bending of the layers throughout the sample.

The free energy density can be written as

$$\mathcal{F}=\mathcal{F}_N+\mathcal{F}_S+\mathcal{F}_{\rm coup}. \tag{6}$$

Here $\mathcal{F}_N$, still given by Eq. (3), is the contribution from orientational ordering, $\mathcal{F}_S$ is the contribution from layer ordering, involving the order parameter τ only, and $\mathcal{F}_{\rm coup}$ describes the coupling between orientational and positional ordering. $\mathcal{F}_S$ is of the form

$$\mathcal{F}_S=\frac{1}{2}C_\tau(\partial_z\tau)^2+\frac{1}{2}v\tau^2+\frac{1}{4}w\tau^4, \tag{7}$$

where $v=v_0(T-T_{NS}^*)$, and C_τ, v_0, and w are positive phenomenological constants. For the nematic-smectic coupling, since the smectic layer ordering is described by the order parameter τ together with the unit vector $\mathbf{N}_L$ denoting the layer normal, the leading term in $\mathcal{F}_{\rm coup}$ can be phenomenologically expressed as $-G\tau^2N_{Li}Q_{ij}N_{Lj}$, with G being a positive coupling constant. The term is proportional to τ^2 as expected because $\mathcal{F}$ should be even in τ. It is interesting to note that the effect of layer structure on orientational ordering can be viewed as that of an effective aligning field $\tau\mathbf{N}_L$. Accordingly, $\mathcal{F}_{\rm coup}$ can be, to the lowest order, written as

$$\mathcal{F}_{\rm coup}=-\frac{1}{2}C_S\tau^2(S-P)+\frac{1}{2}C_\beta\tau^2\left(S+\frac{1}{3}P\right)(\beta-\alpha)^2, \tag{8}$$

where C_S and C_β are two positive coupling constants determined by *G*. In the uniaxial limit $(P=0)$, the $-C_S\tau^2S$ term represents interaction that mutually enhances *S* and τ and contributes significantly to the character of the *N*-Sm*A* transition [14]. The C_β term represents the incremental free energy density resulting from angular deviation of the director from the local layer normal (i.e., local smectic *C* ordering) [15]. For the experimental case discussed in the paper, we find that $S+\frac{1}{3}P$ is nearly a constant $(\sim S_b)$ throughout the transition layer. We therefore let the $S+\frac{1}{3}P$ factor be absorbed into C_β. We can also include higher-order terms such as $\tau^2N_{Li}Q_{ij}Q_{jk}N_{Lk}$ and $\tau^2(N_{Li}Q_{ij}N_{Lj})^2$. They can be put in the form of the following groups of terms: (i) angular-independent coupling terms between *S*, *P*, and τ order parameters; (ii) angular-dependent coupling terms proportional to $(\beta-\alpha)^2$; and (iii) angular-dependent coupling terms proportional to $(\beta-\alpha)^n$ with even *n* larger than 2. The effect of (i) and the C_S term in Eq. (8) on the LC bulk alignment at temperatures far away from the transition point is negligible. In a more rigorous treatment, we can drop the angular-independent coupling terms in $\mathcal{F}_{\rm coup}$ by replacing v in Eq. (7) by a renormalized $v=v_0(T-T_{NS})$, with T_{NS} denoting the nematic-Sm*A* transition temperature. The angular-dependent coupling terms (ii) can be incorporated into the C_β term in Eq. (8). We can still express the term in the form of $C_\beta\tau^2(\beta-\alpha)^2$ but C_β is now a function of *S*, *P*, and τ. In the approximation, we will let C_β be a constant. The higher-order angular coupling terms (iii) can be neglected due to the small value of $|\beta-\alpha|$ $(\leqslant 0.01\text{ rad})$. The simplified expression for the free energy density in Eq. (6) is now given by

$$\mathcal{F}=\mathcal{F}_N+\frac{1}{2}C_\tau(\partial_z\tau)^2+\frac{1}{2}v\tau^2+\frac{1}{4}w\tau^4+\frac{1}{2}C_\beta\tau^2(\beta-\alpha)^2. \tag{9}$$

III. NUMERICAL CALCULATION AND DISCUSSION

As in the nematic case, we can minimize the total free energy $\int dz\mathcal{F}$ to find the spatial variations of *S*, *P*, α, and τ, given the surface boundary values S_0, P_0, α_0, and τ_0, and the known bulk values S_b, $P_b=0$, and $\tau_b=\sqrt{-v/w}$. Note that in the bulk $\beta=\alpha_b$, which is to be calculated.

The solutions for $S(z)$, $P(z)$, $\alpha(z)$, and $\tau(z)$ from minimization of total free energy can be obtained numerically. For convenience in calculation, we transform the free energy and free energy density into dimensionless form,

$$\bar{F}\equiv\frac{\int dz(\mathcal{F}_N+\mathcal{F}_{SN})}{\Delta B^4/C^3}=\int d\zeta(\bar{\mathcal{F}}_N+\bar{\mathcal{F}}_{SN}), \tag{10}$$

with $\bar{\mathcal{F}}_N$ and $\bar{\mathcal{F}}_{SN}$ expressed as

TABLE I. Measured parameters characterizing the orientational distribution of the first LC monolayer. For case 1 (unrubbed substrate), $\sigma=7.0°$ is assumed.

Rubbing strength	θ_0	σ	d_1	d_2	d_3
1	80°	7.0°	0.0	0.0	0.0
2	80°	7.0°	0.08	0.29	0.04
3	80°	7.0°	0.19	0.75	0.07
4	80°	7.0°	0.26	0.78	0.14
5	80°	7.0°	0.39	0.81	0.21

$$\overline{\mathcal{F}}_N=\left[\frac{3}{4}\overline{L}_1+\frac{1}{8}\overline{L}_2(1+3\sin^2\alpha)\right](\partial\overline{S})^2+\left[\frac{1}{4}\overline{L}_1+\frac{1}{8}\overline{L}_2\cos^2\alpha\right](\partial\overline{P})^2+\frac{1}{4}\overline{L}_2\cos^2\alpha\,\partial\overline{S}\,\partial\overline{P}+\left[\frac{1}{4}\overline{L}_1+\frac{1}{8}\overline{L}_2\right](3\overline{S}+\overline{P})^2(\partial\alpha)^2+\left[\frac{1}{8}\overline{L}_2(3\overline{S}+\overline{P})\sin 2\alpha\right]\partial\alpha(\partial\overline{S}-\partial\overline{P})+\left(t+\frac{1}{4}\right)\left(\overline{S}^2+\frac{1}{3}\overline{P}^2\right)-(\overline{S}^3-\overline{S}\overline{P}^2)+\left(\overline{S}^2+\frac{1}{3}\overline{P}^2\right)^2 \tag{11}$$

and

$$\overline{\mathcal{F}}_{SN}=\frac{1}{2}\overline{C}_\tau(\partial\overline{\tau})^2+\frac{1}{2}\overline{v}\,\overline{\tau}^2+\frac{1}{4}\overline{w}\,\overline{\tau}^4+\frac{1}{2}\overline{C}_\beta\overline{\tau}^2(\beta-\alpha)^2, \tag{12}$$

where $\Delta=\sqrt{L_1C/B^2}$ is a length unit, $\zeta=z/\Delta$, $\partial\equiv\partial_\zeta$, $\overline{L}_1=1$, $\overline{L}_2=L_2/L_1$, $\overline{S}=(C/B)\,S$, $\overline{P}=(C/B)\,P$, $\overline{\tau}=(C/B)\,\tau$, $t=(T-T_{IN})/4(T_{IN}-T^*)$ with $T_{IN}=T^*+B^2/4aC$ being the isotropic-nematic transition temperature, $\overline{C}_\tau=C_\tau/L_1$, $\overline{v}=v_0(T-T_{NS})/4a(T_{IN}-T^*)$, $\overline{w}=w/C$, and $\overline{C}_\beta=C_\beta/4a(T_{IN}-T^*)$. Through a finite-difference scheme, the dimensionless free energy $\overline{F}$ can be cast into the form of a multivariable function to which a numerical minimization program can be applied. In our calculation, we consider the case of 8CB on rubbed polyimide. The material constants are chosen as follows: (i) $T_{IN}=40.5$ K, $T_{NS}=33.5$ K, $a=0.055$ J/cm, $B=0.5$ J/cm^3, and $C=1.0$ J/cm^3, yielding $T_{IN}-T^*=1.14$ K (values approximately suitable for 8CB) [16]; (ii) $L_1=1.6\times10^{-7}$dyn and $L_2=3.7\times10^{-7}$dyn [17] with $\Delta\simeq2.5$ nm; (iii) $\overline{v}=-1$ (at $t=-1.8$ to be used for the smectic case) and $\overline{w}=1$ based on $v_0\simeq4a$ and $w\simeq C$ [18]. Accordingly, $\tau_b=B/C\sqrt{|\overline{v}|/\overline{w}}=0.5$ at $t=-1.5$; (iv) $C_\tau\simeq L_1/4$ and $\overline{C}_\beta\simeq150$ [18]. As a dimensionless parameter, $\overline{C}_\beta$ may look large, but it is estimated from two correlation lengths, ξ_N and ξ_S. The former, ξ_N, is associated with the nematic order parameter and is usually derived from Eq. (3) or Eq. (11) to be [19]

TABLE II. S_0, P_0, and α_0 calculated from the measured parameters d_1, d_2 (in Table I), γ, and δ.

Rubbing strength	S_0	P_0	α_0	γ	δ
3	0.48	0.38	1.6°	0.72	0.090
4	0.50	0.37	2.2°	0.72	0.090
5	0.51	0.36	3.2°	0.72	0.091

$$\xi_N=\Delta\sqrt{\frac{\frac{3}{4}\overline{L}_1+\frac{1}{8}\overline{L}_2}{\frac{1}{8}(1-32t)+\frac{3}{8}\sqrt{1-32t}}}.$$

The latter, ξ_S, is associated with the surface-induced smectic C ordering in the surface-bulk transition region. It is also known as the penetration depth of the director bending distortion, defined in Ref. [13]. The usual derivation gives

$$\xi_S=\sqrt{\frac{9(2L_1+L_2)S_b^2}{4C_\beta\tau_b^2}}.$$

We now have $\overline{C}_\beta$ related to ξ_N and ξ_S as

$$\overline{C}_\beta=\frac{\xi_N^2}{\xi_S^2}\,\frac{(1-32t)+3\sqrt{1-32t}}{6L_1+L_2}\,\frac{9(2L_1+L_2)S_b^2}{4\tau_b^2}. \tag{13}$$

Assuming $\xi_S\sim\xi_N$ [20], we find $\overline{C}_\beta\sim150$ for $t=-1.8$.

As an example, we present the spatial variations of order parameters S, P, τ, and director tilt α calculated using the above theory with the boundary conditions $S_0=0.51$, $P_0=0.36$, $\alpha_0=3.2°$, which correspond to the experimental case of 8CB on a rubbed P6-coated substrate with the rubbing strength 5 listed in Tables I and II. Two different boundary conditions for τ, i.e., $\tau_0=0$ and $\tau_0=\tau_b$, have been considered. Figure 1 depicts the spatial variations of S and P in a nematic case at $t=-1.5$ (with $S_b=0.63$ and $\overline{C}_\beta=0$), and those of S, P, and τ in a SmA case at $t=-1.8$ (with $S_b=0.67$ [21], $\overline{C}_\beta=150$, and $\tau_0=0$). As expected, the order parameters vary monotonically from their surface values to the bulk values across the surface-bulk transition region. In

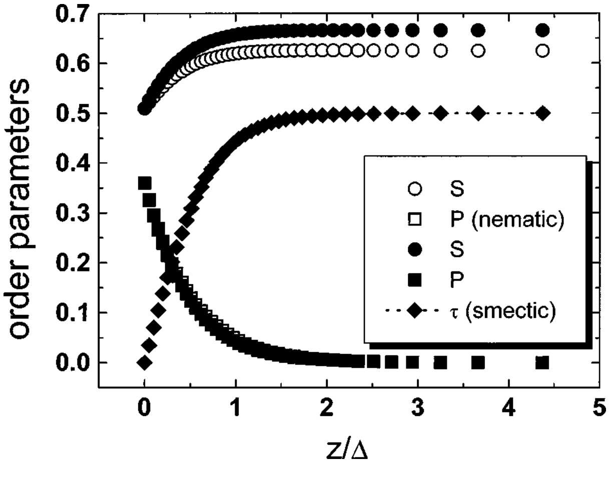

FIG. 1. Spatial variations of S and P in the nematic phase and of S, P, and τ in the smectic phase with $\tau_0=0$. The material constants used in the calculation are given in the text.

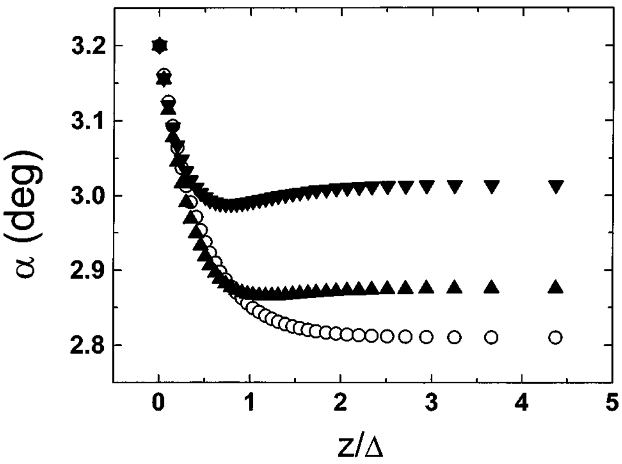

FIG. 2. Spatial variations of tilt angle α in the nematic (circles) and smectic (up triangles for $\tau_0=0$ and down triangles for $\tau_0=\tau_b$) phases.

particular, we find that the effect of smectic ordering or τ on the spatial variations of S and P is rather weak. It is seen from Fig. 1 that for $\tau_0=0$, $P(z)$ obtained for the two phases are nearly identical and so is $S(z)$ if it is normalized against S_b. Numerical calculation also shows that $S(z)$ and $P(z)$ undergo very little change as τ_0 varies from 0 to τ_b. Figure 2 depicts the spatial variation of α. While in the nematic case α also changes monotonically from α_0 to α_b, in each smectic case it exhibits a shallow dip in the variation. This is due to the competition between the nematic $\partial_z\alpha\partial_z(S-P)$ and the smectic $(\beta-\alpha)^2$ terms which drive and hinder the variation of α, respectively. It is noted that $|\alpha_b-\alpha_0|$ obtained for $\tau_0=0$ is larger than that for $\tau_0=\tau_b$. This is because a zero τ_0 imposes less layering influence on α in the transition region and therefore makes α_b closer to its nematic value.

We can understand qualitatively how α_b differs from α_0 in response to the spatial variations of the order parameters in the surface-bulk transition region. The approximate analytical expression of Eq. (5) shows $\alpha_b-\alpha_0\propto\alpha_0(S_b-S_0+P_0)$. This is because the spatial variation $\partial_z\alpha$ is induced by $\partial_z(S-P)$ through the coupling term between $\partial_z\alpha$ and $\partial_z(S-P)$ in the free energy density in Eq. (3) and the coupling strength is proportional to $\sin 2\alpha\sim 2\alpha$. Note that $\int\partial_z(S-P)dz=S_b-S_0+P_0$ and $\alpha-\alpha_0$ is small. The sign of $\alpha_b-\alpha_0$ must be negative, opposite to that of $S_b-S_0+P_0$, since the $\partial_z\alpha\partial_z(S-P)$ term, in competition with the $(\partial_z\alpha)^2$ term in the free energy, should always be negative in order to lower the free energy. The magnitude of $|\alpha_b-\alpha_0|/\alpha_0$ estimated from Eq. (5) is on the order of 0.1, in agreement with the numerical calculation. It is important to recognize that the biaxial order parameter P is crucial in determining the magnitude of $\alpha_b-\alpha_0$. As seen from Table II, $P_0\simeq 0.3$ as compared with $S_b-S_0\sim 0.1$, and hence the boundary layer biaxiality must be of qualitative importance. This conclusion is supported by the experimental results for a number of different rubbed polyimide-coated substrates [5]. In a recent report on the theoretical calculation of surface-induced nematic bulk alignment, the importance of biaxiality in orientational ordering in the surface-bulk transition region was, however, neglected [11].

In the Sm*A* case with the presence of the positional order, α_b^S is determined by the competition of the $\partial_z\alpha\partial_z(S-P)$ term with the $(\partial_z\alpha)^2$ term in $\mathcal{F}_N$ as well as the $(\alpha_b-\alpha)^2$ term in $\mathcal{F}_{SN}$. The elastic energy due to the short-range smectic C ordering with $\tau\neq 0$ and $\alpha\neq\beta$ is proportional to C_β, and being positive, such an energy tends to reduce the variation of the director tilt in the transition layer. Therefore, the ratio of ξ_S/ξ_N, and hence the value of $\overline{C}_\beta$, governs the magnitude of $r_{NS}\equiv(\alpha_b^S-\alpha_0)/(\alpha_b^N-\alpha_0)$, where α_b^N and α_b^S denote the bulk tilt angles deep in the nematic and Sm*A* phases, respectively. For $\xi_S/\xi_N\ll 1$ $(C_\beta\to\infty)$, $r_{NS}\to 0$, while for $\xi_S/\xi_N\gg 1$ $(C_\beta\to 0)$, $r_{NS}\to 1$. The usual situation is that $\xi_N/\xi_S\sim 1$. So, more than one length scale, i.e., ξ_N,ξ_S, and the smectic correlation length ξ_τ associated with the variation of τ, are involved in determining r_{NS}. Under the same assumptions used in deriving Eq. (5) together with $\tau_b-\tau_0\ll\tau_b$, we find that α_b^S has an approximate analytical expression

$$\alpha_b=\alpha_0\left[1-\frac{\xi_S}{\xi_N+\xi_S}\frac{L_2}{3(2L_1+L_2)S_b}(S_b-S_0+P_0)\right], \tag{14}$$

which simply gives $r_{NS}=\xi_S/(\xi_N+\xi_S)$.

IV. EXPERIMENTAL VERIFICATION

Experimentally, there is not yet any effective method one can use to measure spatial variation of molecular ordering and alignment in the surface-bulk transition region. It is, however, possible to deduce an approximate orientational distribution for a surface LC monolayer adsorbed on a rubbed polyimide-coated substrate from SHG measurement. From the orientational distribution, S_0, P_0, and α_0 can be calculated. The LdG theory described in the preceding two sections can be used to find $S(z)$, $P(z)$, $\alpha(z)$, and $\tau(z)$. In particular, the bulk pretilt angle $\alpha_b\equiv\alpha(z\to\infty)$ can be obtained and compared with the experimental value measured by ellipsometry.

The SHG technique for LC surface monolayer studies has been described in detail elsewhere [6]. Basically, the measurement yields the six independent, nonvanishing elements of the second-order nonlinear susceptibility tensor for the LC monolayer. They allow the determination of five coefficients in an orientational distribution function of the form [5]

$$f(\theta,\phi)\propto N_f\exp\left[-\frac{(\theta-\theta_0)^2}{\sigma^2}\right](1+d_1\cos\phi+d_2\cos\phi+d_1\cos\phi_3). \tag{15}$$

From Eqs. (1) and (4), we obtain

$$S_0=\gamma-\frac{1}{2}+\frac{1}{2}\gamma d_2, \tag{16a}$$

$$P_0=3\gamma-\frac{3}{2}-\frac{1}{2}\gamma d_2, \tag{16b}$$

$$\alpha_0=\frac{\delta d_1}{2\gamma-1+\gamma d_2/3}, \tag{16c}$$

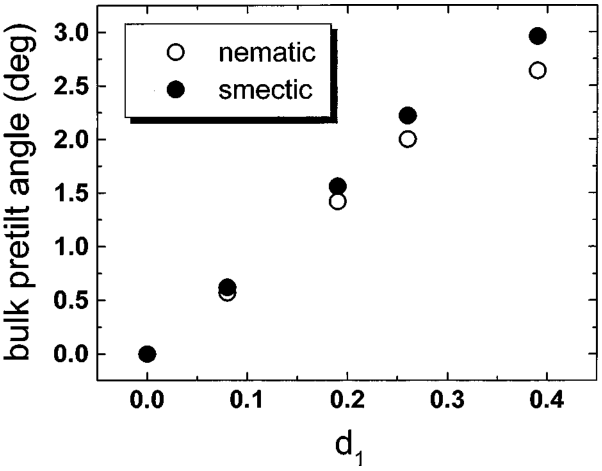

FIG. 3. Correlation between the orientational distributions of the 8CB surface monolayer and the bulk pretilt angles of a smectic LC film on P6-coated substrates rubbed with five different rubbing strengths.

with $\gamma=\frac{3}{4}\langle\sin^2\theta\rangle$ and $\delta=\frac{1}{4}\langle\sin 2\theta\rangle$, and their values can be calculated from the distribution function in Eq. (15). We have studied 8CB on rubbed P6-coated substrates with different rubbing strengths. The absolute value of the rubbing strength is not a well-defined quantity (see Ref. [4c]). However, its effect on the orientational distribution of 8CB monolayers can be quantified by the parameters in distribution function Eq. (15). The results are listed in Table I for $\{\theta_0,\sigma,d_1,d_2,d_3\}$ and Table II for S_0, P_0, τ_0 (for rubbing strengths 3, 4, and 5). According to Eq. (16c), the surface tilt angle α_0 is proportional to d_1, the parameter characterizing the forward-backward azimuthal asymmetry along the rubbing direction. Meanwhile, its dependence on d_2 is rather weak with δ and γ being almost constant for different rubbing strengths. As $\alpha_b-\alpha_0$ is approximately proportional to α_0, a nearly linear relation between α_b and d_1 is expected. This was verified by measuring both α_b^N and α_b^S (Fig. 3).

The ellipsometry technique we used was adopted from Ref. [22]. LC cells of 70μm thickness were prepared by sandwiching an 8CB film between two equally but oppositely rubbed P6-coated substrates. (The same substrates were used in the SHG measurement.) The optical uniaxis of the bulk film is along the LC director, which is tilted from the surface and the rubbing direction by the angle α_b. By measuring the optical phase retardation of a laser beam traversing the film as a function of the incidence angle, the optical axis of the film and hence α_b can be determined. The accuracy of the α_b measurement is better than 0.1°. We have measured α_b of the 8CB cells in both nematic and smectic phases, with emphasis of α_b as a function of temperature around the *N*-Sm*A* transition (Fig. 4) to see the effect of positional ordering on α_b. We notice in Fig. 4 that for each rubbing case, α_b exhibits a drop across the Sm*A*-to-nematic transition. The difference between α_b^N and α_b^S is clearly measurable. The experimental data in Fig. 4 together with the values of α_0 (having uncertainty on the order of 0.1°) obtained from SHG measurement show that $\alpha_b^N<\alpha_b^S<\alpha_0$ with the difference being small, and the smectic ordering effect on α_b only sets in for $T<T_{NS}$. They are in agreement with our theoretical understanding.

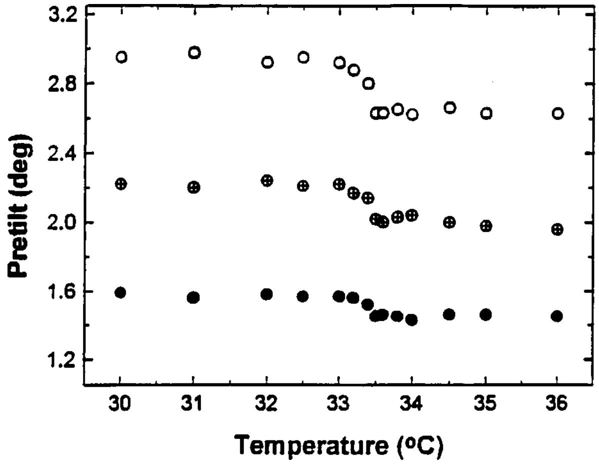

FIG. 4. Measured bulk pretilt angles of 8CB films on rubbed P6-coated substrates versus temperature. *N*-Sm*A* transition occurs at 33.5°. Solid, cross-centered, and open circles correspond to rubbing strengths 3, 4, and 5 in Tables I and II.

Quantitative comparison between theory and experiment is always more difficult because of uncertainty in the values of the material parameters. We find that variation of α in the surface-bulk transition region does not have a critical dependence on the values of material parameters as long as they are within the appropriate range. The material parameters we used in the numerical calculation were somewhat arbitrarily chosen. We focus on the two quantities, x and y, defined as $(\alpha_0-\alpha_b^N)/\alpha_0$ and $(\alpha_b^S-\alpha_b^N)/\alpha_b^N$, respectively, reflecting α's variation in the nematic phase and its change after entering the Sm*A* phase. The predicted values of x for rubbing strengths 3, 4, and 5 are 15%, 14%, and 14% as calculated from Eq. (5), or 14%, 13%, and 12% as obtained numerically. The experimental values of x for rubbing strengths 3, 4, and 5 are 10%, 9%, and 17%. Considering the relatively large uncertainties in the values of α_0 obtained from SHG measurement (~0.1°) and in the values of α_b^N and α_b^S (~0.1°), we deem that the agreement between theory and experiment is fairly satisfactory. The predicted values of y for rubbing strengths 3, 4, and 5 are 3%, 2%, and 2% as numerically obtained with $\tau_0=0$ and $\overline{C_\beta}=150$, while the experimental values of y as obtained from Fig. 3 are 10%, 11%, and 12%. It is therefore clear that the influence of layer ordering governed by a vanishing τ_0 and a smectic correlation length $\xi_\tau\sim\xi_N$ is too weak to reproduce the experimental values of y. Using $\tau_0\simeq\tau_b$ can yield better quantitative agreement. The predicted values of y for rubbing strengths 3, 4, and 5 are 10%, 9%, and 9% as calculated from Eq. (14) with $\xi_S/\xi_N=0.8$, or 9%, 8%, and 7% as numerically obtained with $\overline{C_\beta}=150$. Therefore, with the numerical agreement being semiquantitative, not only is the sign of y correct, that y is almost independent of α_0 is also reproduced. The better agreement with $\tau_0\simeq\tau_b$ indicates that the smectic layer structure probably persists all the way from the bulk to the surface [23]. This agrees with most of the established results on surface smectic ordering [23]. The deviation of the predicted y from the measured one certainly can be reduced by adjusting the material parameters within the appropriate range. Of course, there are also approximations in the model that could render quantitative calculations not so meaningful. First, the LdG theory with truncated series expansion in order parameters may not be a good approximation since the order parameters are fairly large. Second, biaxiality has been neglected in the coupling between orientational and positional ordering. A more rigorous model would be helpful in obtaining a better understanding of surface-induced bulk alignment, particularly for the various smectic phases.

V. CONCLUDING REMARKS

We have shown that the bulk LC alignment in nematic and Sm*A* phases can be predicted from the liquid crystalline order of the surface monolayer. The prediction is based on an extended Landau–de Gennes theory which incorporates an appropriate coupling between the positional and the orientational ordering. Satisfactory agreement between the predicted and the measured bulk pretilt angle variation across the nematic-smectic transition has been obtained, suggesting that our understanding of the mechanism responsible for surface-induced bulk alignment is semiquantitatively correct. According to this mechanism, the boundary layer is characterized by spatially varying unaxial/biaxial order parameters and in the Sm*A* phase by a short-range smectic *C* ordering with the layer normal deviating from the average molecular orientation in addition. This may only be directly verified by x-ray reflection [24].

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