Surface-Monolayer-Induced Bulk Alignment of Liquid Crystals

Xiaowei Zhuang, Lorenzo Marrucci, and Y. R. Shen
Department of Physics, University of California, Berkeley, California 94720-7300

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Bulk liquid crystal alignment can be completely determined by the orientational distribution of the surface monolayer. The bulk pretilt angles predicted from the measured monolayer orientational distribution using the Landau–de Gennes formalism agree very well with the observed values. Surface anchoring energies can also be estimated.

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The design of liquid crystal (LC) display devices relies heavily on preferred bulk molecular alignment, which is often effected by surface treatment. Accordingly, surface-induced bulk alignment is of great importance to LC display technology, and has been extensively investigated by many researchers in recent years [1]. Despite the concerted efforts, however, a clearly understood picture has not yet emerged. Recent experiments indicate that, if the surface is flat and smooth, the orientation of the first LC monolayer at the surface can effectively determine the bulk alignment [2,3]. To obtain a homogeneous bulk alignment (LC molecules aligned more or less parallel to the surface), rubbed polymer-coated substrates are commonly used. Rubbing stretches the polymer chains along a certain direction on the surface [3,4]; the ordered polymer chains in turn induce a preferred molecular alignment in the adsorbed LC monolayer. The strong LC molecular correlation then leads to the desired bulk homogeneous alignment. Yet this bulk alignment is not completely parallel to the surface, but tilted at a small angle known as the pretilt angle. This angle is an important design parameter for LC displays. For example, the quality of a supertwisted nematic display cell can be greatly improved if the pretilt angle is $\gtrsim 15°$ [5]. While it is known that the surface treatment and the alignment of the surface LC monolayer can affect the bulk pretilt angle [6], the relation between them is still not understood.

In this paper, we show conclusively that indeed the orientational distribution of the surface LC monolayer completely determines the nematic bulk alignment and its pretilt angle. We used optical second harmonic generation (SHG) to measure the orientational distribution of LC monolayers on rubbed polyimide-coated subtrates. With the help of the Landau–de Gennes formalism, we then predicted the bulk pretilt angle from the measured monolayer orientational distribution. The prediction was compared with the pretilt angle measured by ellipsometry and excellent agreement was found. As a by-product, surface anchoring energies of LC on rubbed polyimide surfaces were also deduced. This work is the first success in our search for a quantitative understanding of the phenomenon of surface-induced bulk alignment.

Let us first describe briefly the underlying theory [2]. In our model, the surface is considered as a smooth plane. The direct LC/surface interaction is of short range and does not extend beyond the first monolayer. We also assume the only difference of importance between LC at the surface and in the bulk is in their nematic order parameters. For an LC film on a rubbed polyimide surface, we choose a coordinate system with x along the rubbing direction, and z along the surface normal, pointing into the LC bulk. The nematic order parameter follows the usual definition of [7]

$$Q_{ij} = \langle (3\zeta_i\zeta_j - \delta_{ij})/2 \rangle, \tag{1}$$

where ζ is a unit vector along the long molecular axis and δ_{ij} is the unit matrix. With the presence of an xz mirror plane, Q_{ij} may be diagonalized by a rotation of angle α around the y axis. In the rotated system $x'yz'$, we can define the two "scalar" order parameters $S = Q_{x'x'}$ and $P = Q_{yy} - Q_{z'z'}$ describing in general the biaxial ordering. In the proximity of the surface, Q_{ij} or equivalently S, P, α are all functions of z. In the bulk limit, $z \to \infty$, $\vec{Q}$ becomes uniaxial, with $P = 0$, and S and α approaching the bulk order parameter S_b and the bulk pretilt angle α_b, respectively. In the opposite limit of $z = 0$, Q_{ij} can be determined from Eq. (1) if the orientational distribution function $f(\zeta)$ of the surface LC monolayer is known. We assume that f can be expressed in the form

$$f(\vartheta, \varphi) = \frac{f_1(\vartheta)}{2\pi}(1 + d_1\cos\varphi + d_2\cos 2\varphi + d_3\cos 3\varphi), \tag{2}$$

where ϑ and φ are the polar and azimuthal angles of ζ with respect to the xyz axes. The precise expression for f_1 does not need to be specified at this moment. Using Eq. (2) to perform the average in Eq. (1) at $z = 0$, we obtain

$$\begin{aligned} S_s &= S(0) = \gamma - \tfrac{1}{2} + \tfrac{1}{2}\gamma d_2, \\ P_s &= P(0) = 3\gamma - \tfrac{3}{2} - \tfrac{1}{2}\gamma d_2, \\ \alpha_s &= \alpha(0) = \frac{\delta d_1}{S_s + P_s/3}, \end{aligned} \tag{3}$$

with

$$\gamma = \tfrac{3}{4}\langle \sin^2 \vartheta \rangle_{f_1} \text{ and } \delta = \tfrac{1}{2}\langle \sin \vartheta \cos \vartheta \rangle_{f_1}. \tag{4}$$

In Eqs. (3), we neglect for simplicity terms quadratic or higher in δd_1 which is anticipated to be much less than 1. Note that S_s, P_s, and α_s are independent of d_3.

To describe the transition region which connects the first monolayer to the bulk, we adopt the Landau–de Gennes formalism [7]. The free energy density of a nematic film subject to a variation of Q_{ij} along z can be approximated by

$$F = \tfrac{1}{2}A_s(S - S_b)^2 + \tfrac{1}{2}A_p P^2 + \tfrac{1}{2}L_1 Q'_{ij}Q'_{ij} + \tfrac{1}{2}L_2 Q'_{iz}Q'_{iz},$$

where the prime indicates the derivative with respect to z, and A_s, A_p, S_b, L_1, and L_2 are material constants which are functions of temperature. We have also considered the contribution of the order-electricity effect to F [8], but found that it is negligible for the cases in study. From F, using the standard Euler-Lagrange procedure, we obtain a set of coupled nonlinear equations for $S(z)$, $P(z)$, and $\alpha(z)$. Since α is usually small and $S(z)$ and $P(z)$ do not deviate much from their bulk value, we can limit ourselves to a linearized theory in α, $S(z) - S_b$, and $P(z)$. In that case, the solution to the equation for $\alpha(z)$, with the boundary conditions $\alpha(0) = \alpha_s$ and $\alpha'(\infty) = 0$, is found to be

$$\alpha(z) = \alpha_s \left\{ 1 - \frac{L_2[S(z) - S_s - P(z) + P_s]}{3(2L_1 + L_2)S_b} \right\}.$$

The bulk pretilt angle $\alpha_b = \alpha(\infty)$ is then given by

$$\alpha_b = \frac{\delta d_1}{2\gamma - 1 + \gamma d_2/3} \times \left[1 - \frac{L_2(S_b + 2\gamma - 1 - \gamma d_2)}{3(2L_1 + L_2)S_b} \right]. \tag{5}$$

Equation (5) allows us to predict α_b from the four surface parameters d_1, d_2, γ, and δ that characterize the orientational distribution of the surface monolayer, assuming the material constants L_1, L_2, and S_b are known.

We can now assess the relative importance of the surface parameters in determining the pretilt angle. The average polar angle ϑ_0 of the LC molecular alignment is related to δ and γ by Eqs. (4). With ϑ_0 close to 90°, we have $\delta \approx (90° - \vartheta_0)/2$ and $\gamma \approx 3/4$. In this limit, α is simply proportional to $90° - \vartheta_0$, i.e., the average angle of inclination the adsorbed LC molecules make with the surface. The pretilt angle is also proportional to the parameter d_1, describing the surface forward-backward azimuthal asymmetry along the rubbing direction. The dependence on the xy anisotropy d_2 is more complex, but is rather weak.

The anchoring energy $\mathcal{F}_s$, defined as the surface-excess free energy in the presence of a bulk deformation [9], can also be found. The surface monolayer is assumed to be fixed and the bulk undergoing a splay-bend deformation with a constant $(d\alpha/dz)_{z\to\infty}$ and a twist deformation around z with a constant rate of angular change $(d\beta/dz)_{z\to\infty}$. We can then calculate the total free energy due to such deformation. Subtracting from it the free energy obtained by replacing the surface-bulk transition region with the continuation of the bulk yields $\mathcal{F}_s$. For small deformations, $\mathcal{F}_s$ is commonly written as $\mathcal{F}_s = W_p(\alpha_0 - \alpha_b)^2/2 + W_a\beta_0^2/2$, where α_0 and β_0 are defined from the bulk limits $\alpha(z) \sim \alpha'(\infty)z + \alpha_0$ and $\beta(z) \sim \beta'(\infty)z + \beta_0$, and W_p and W_a are known as the polar and azimuthal anchoring coefficients, respectively. We find

$$W_a = \frac{K_2}{\xi\left(\frac{3S_b}{2\gamma d_2} - 1 + \ln \frac{3S_b}{2\gamma d_2}\right)}, \tag{6}$$

$$W_p = \frac{K_1}{2\xi\left(\frac{2K_1+K_2}{3K_1} - \frac{4K_1-K_2}{3K_1}\frac{2\gamma-1}{S_b} - \frac{K_2}{3K_1}\frac{\gamma d_2}{S_b}\right)}, \tag{7}$$

where K_1 and K_2 are the bulk splay-bend and twist elastic constants, respectively, and ξ is the nematic-order correlation length. Note that W_p is only approximated to first order in $S(z) - S_b$ and $P(z)$. Contrary to the pretilt, both W_p and W_a depend strongly on d_2 but not on d_1.

Experimentally, using SHG in reflection we measured the orientational distributions of LC monolayers on polyimide-coated substrates at various rubbing strengths [3]. The LC used was the 4′-*n*-octyl-4-cyanobiphenyl (8CB) and the polyimide was the poly-*n*-hexyl-pyromellitic imide (P6). The measurement technique has been described in detail in Ref. [3]. The 8CB molecules preferentially adsorb with their CN group hinged on the substrate. SHG is then generated mainly from this polar-oriented monolayer. The surface nonlinear susceptibility tensor can be written as $\overleftrightarrow{\chi}^{(2)} = N\langle \overleftrightarrow{\alpha}^{(2)} \rangle_f$, where N is the surface density of molecules, $\overleftrightarrow{\alpha}^{(2)}$ is the molecular hyperpolarizability dominated by a single element $\alpha^{(2)}_{\zeta\zeta\zeta}$ [10], and f denotes the monolayer orientational distribution. The xz mirror symmetry reduces the number of nonvanishing independent elements of $\overleftrightarrow{\chi}^{(2)}$ to 6. They can be determined (apart from a common factor) from a best fit of the SHG data versus the azimuthal angle of rotation of the sample with different input/output polarizations. With the further specification of a normalized $f_1 \propto \exp[-(\vartheta - \vartheta_0)^2/\sigma^2]$ in Eq. (2), the three azimuthal orientation parameters d_1, d_2, d_3 and the two polar orientation parameters ϑ_0, σ, or equivalently γ, δ, can be deduced. The polyimide substrate produces a not completely negligible background SHG, which can, however, be subtracted from the total signal. The input laser wavelength was 532 nm. The incidence angle of 67° was chosen to optimize the accuracy in the determination of ϑ_0.

The orientational distributions of 8CB monolayers on rubbed polyimide surfaces deduced from the SHG measurements are shown in Fig. 1. It is seen that the polar distribution f_1 is hardly affected by the rubbing strength, i.e., ϑ_0 and σ remain nearly unchanged at 80° and 7°, respectively. The azimuthal distribution, however, changes appreciably with rubbing; d_1 and d_2 increase from 0 to their saturation values of 0.4 and 0.8, respectively, upon increase of rubbing strength. From the deduced values of ϑ_0, σ, d_1, and d_2, together with the bulk constant of $S_b = 0.6, L_1 = 1.6 \times 10^{-7}$ dyn, and $L_2 = 3.7 \times 10^{-7}$ dyn [11], we can calculate from Eq. (5) the pretilt angles expected if the same rubbed polyimide-coated substrates are used to align the bulk 8CB film, knowing that the adjacent LC bulk hardly affects the monolayer alignment [3]. The calculated results are presented in Fig. 2. In this figure, for the sake of clarity, the full surface-parameter space is projected onto the axis of d_1, which is the dominant parameter affected by rubbing. The straight line in the figure is obtained from Eq. (5) assuming $d_2 = 0$. The weak dependence of the pretilt angle α_b on d_2 is readily seen. The prediction here shows that α_b increases with the rubbing strength from 0 to a saturation value of 2.7°.

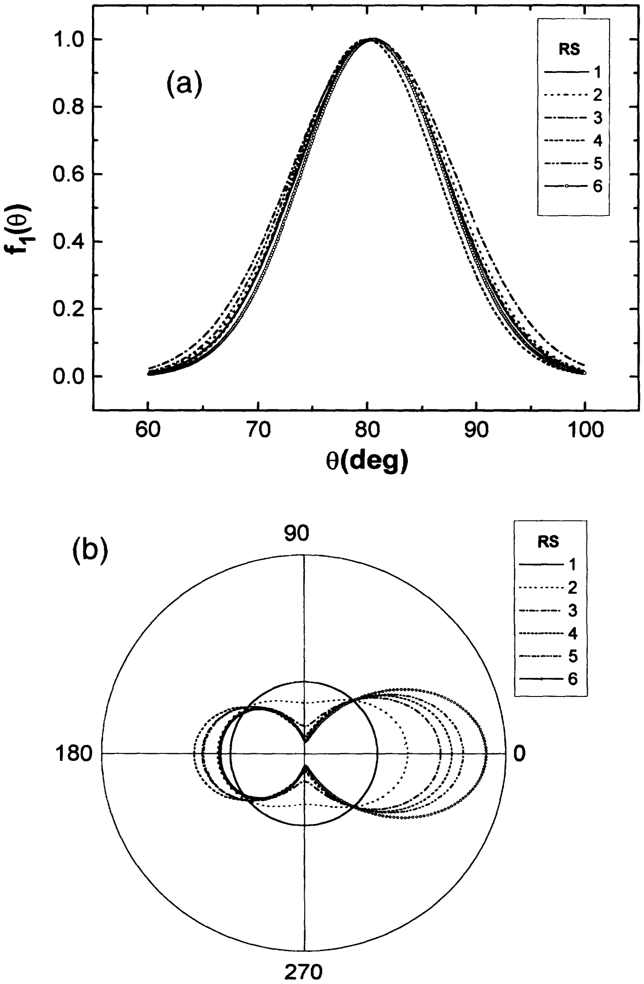

FIG. 1. Polar (a) and azimuthal (b) components of orientational distributions of surface 8CB monolayers on rubbed P6. Rubbing strength (RS) increases from 1 (unrubbed substrate) to 6 (saturation rubbing).

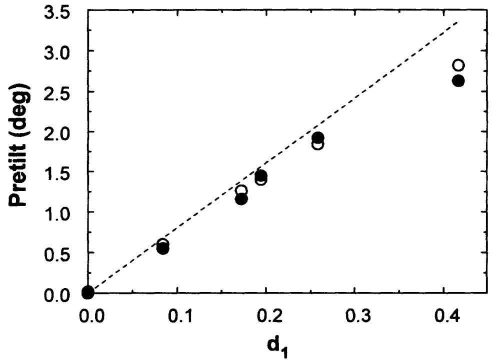

FIG. 2. Correlation between orientational distribution of surface LC monolayers and bulk pretilt angles at different rubbing strengths on the same polyimide (P6). Solid circles are bulk pretilt angles measured by ellipsometry and open circles are predictions from Eq. (5). Data points from left to right correspond respectively to rubbing strength 1 to 6, and measured values $d_2 =$ 0, 0.29, 0.62, 0.75, 0.77, 0.81; ϑ_0 (deg) = 80, 80.5, 80.5, 79.9, 80.2, 80.5; σ (deg) = 7.0, 7.0, 7.5, 6.5, 7.0, 6.5. The dashed line is calculated from Eq. (5) with $d_2 = 0, \vartheta_0 = 80°$, and $\sigma = 7°$.

To check the theoretical predictions, we measured separately the bulk pretilt angles of the corresponding 8CB cells using a simple ellipsometric method known as the crystal-rotation method [12]. The LC cells of 70 μm were constructed by incorporating an 8CB film between two equally treated but oppositely rubbed polyimide-coated substrates. The same substrates were used previously in the SHG measurement. In the weak rubbing limit, a strong magnetic field along the rubbing direction was employed to help the initial bulk alignment. The effect of the magnetic field on the pretilt angle was checked to be negligible. The measured pretilt angles for cells with substrates rubbed with different strengths are also presented in Fig. 2. The accuracy of the measurements is within 0.1°. As seen in Fig. 2, the predicted and the measured pretilt angles do not differ by more than 8% in all cases. Considering that there is no adjustable parameter in the calculation, this agreement between theory and experiment is certainly most satisfying.

As a further test, we studied the case where the substrates were rubbed back and forth in opposite directions. We would expect d_2 to increase with rubbing and d_1 remain small, leading to a small pretilt angle. As an example, we obtain, in one case, $d_1 = 0.03$ and $d_2 = 0.8$ from the SHG measurement, yielding a predicted pretilt angle of 0.25°. The measured pretilt angle was 0.23°. We have also tested our predictions using the experimental results reported in Ref. [6]. In that experiment, the rubbing strength was kept fixed, but different polyimides were used. The LC material involved was 5CB, the material constant of which were listed in Ref. [11]. Again, we can predict the pretilt angles from their data on monolayer orientational distributions using Eq. (5) and compare the results with their measured values. As shown in Fig. 3, the agreement is remarkably good.

For an estimate of the anchoring coefficients W_a and W_p, we have studied the monolayer of 8CB on three different polyimides: P6, P3 (poly-*n*-propyl-pyromelliticimide), and JIB-1 (synthesized by Japanese Rubber Synthetic Co.). With increasing rubbing strength, d_2 varied from 0 to 0.8, 0.3, and 0.08 for P6, P3, and JIB-1, respectively, while γ remained nearly unchanged at around 0.7. Using $K_2 = 2 \times 10^{-7}$ dyn, $K_1 = 4 \times 10^{-7}$ dyn [11], and $\xi = 50$ Å [13], we calculated from Eqs. (6) and (7) that W_a should change from 0 to 0.4, 0.08, and 0.02 erg/cm^2, for P6, P3, and JIB-1, respectively, while W_p should vary from 2.2 to 20 ergs/cm^2 for P6, from 2.2 to 3.3 ergs/cm^2 for P3, and from 2.2 to 2.5 ergs/cm^2 for JIB-1. We can compare these values with the measured anchoring energies of rubbed polyimide surfaces reported in Ref. [14], where W_a ranges from 0.005 to 0.014 ergs/cm^2 for weak to strong rubbing, while W_p is constant and slightly higher than 1 erg/cm^2. These results are close to our predictions for JIB-1. Notice that if the predicted W_p and W_a are larger than the interaction energy between the surface LC monolayer and the substrate, then the effect of the induced reorientation in the LC surface monolayer by the bulk alignment may not be negligible. In that case, our predictions would overestimate the anchoring energy.

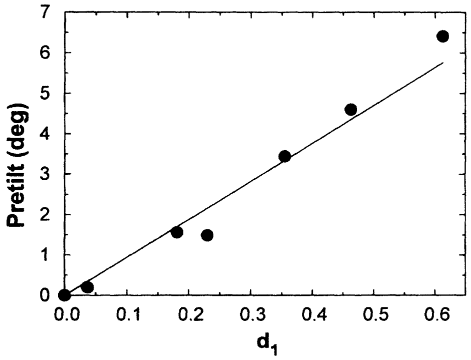

FIG. 3. Correlation between orientational distributions of surface LC monolayer and bulk pretilt angles, for different polyimides, at the same RS. The circles are the measured pretilt angles and the line is calculated from Eq. (5), with $d_2 = 0.88, \vartheta_0 = 77°$, and $\sigma = 4°$. The data are taken from Ref. [6].

In summary, we show that it is possible to predict the LC bulk homogeneous alignment including the bulk pre tilt angle from the measured orientational distribution of the surface LC monolayers. The predictions, based on a Landau–de Gennes model to describe the long range molecular correlation in LC, agree surprisingly well with experiment. Surface anchoring energies can also be estimated. This work then provides a quantitative understanding of the phenomenon of surface-induced bulk alignment in LC. The same physics certainly applies to other types of bulk alignment induced by specially treated flat surfaces.

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