Surface-Surface Interaction in Smectic Liquid Crystal Films

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Null transmission ellipsometry was employed to study the field induced transition of the surface arrangements in freestanding films of smectic liquid crystals. The interlayer interaction between the two surfaces obtained from the threshold voltage for the transition is found to be antiferroelectric and is quasilong ranged. The possible microscopic origins of the measured interaction and its relevance to the interlayer interaction in antiferroelectric liquid crystal materials are discussed.

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Antiferroelectric liquid crystals (AFLC) are interesting materials that show a rich variety of different smectic phases in relatively narrow temperature windows [1–3]. Those phases all appear below the smectic-A (SmA, in which molecules align parallel to the layer normal) phase; thus, they are referred to as the smectic-C^* (SmC^*, in which molecules are tilted away from the layer normal) variant phases, and are distinguished by their different arrangements of tilt directions along the layer normal direction ($\hat{z}$). Although now we have a good understanding of the structures and properties of those phases, very little is known about the interlayer interactions that produce these many different phases [1–4].

Surface enhanced orders are commonly observed in liquid crystals [5]. For freestanding films of AFLC materials, it produces a surface tilt transition (T_S) several degrees higher than the corresponding bulk tilt transition (T_C) [6–8]. Since spontaneous polarization can be established in tilted chiral molecules [9], for $T_C < T < T_S$, we have tilted ferroelectric [(FE), or antiferroelectric (AFE), depends on the compound] surface layers while the interior layers are nontilted and paraelectric. This unique situation allows the possibility of a direct experimental study of the interaction between the two surfaces.

In this Letter we report our experimental study of the interlayer interaction between the two surfaces of the freestanding film through the field induced transitions of one AFLC compound. Since measuring the intermolecular interaction is a very challenging task (if possible at all), very few such studies have been carried out on smectic liquid crystals [10,11]. To the best of our knowledge, these types of studies have never been reported for AFLC materials. The lack of experimental knowledge also hindered theoretical advances, having no criteria to determine the applicability and validity of various theoretical models and assumptions. At this moment, the only available test for the theoretical models is whether or not they can produce all the observed SmC^* variant phases in the right sequences. Thus, our study will provide important insights into the understanding on the nature of the interlayer interactions in AFLC materials.

The AFLC used for this study is MHPBC [12]. Both the optically pure compound (R) and the near racemic mixture (49.5% R mixed with 50.5% S) of MHPBC were studied [13]. In the following text, they will be referred to as R and racemic MHPBC. Compared with other AFLC compounds, MHPBC has several unique properties that make it an ideal candidate for this study. First, it has a T_S sufficiently higher (about 20 K) than T_C, but still lower than the isotropic transition temperature. This makes T_S accessible for studies on freestanding films. Second, previous results demonstrated that above T_C the molecular tilt angle in freestanding films of MHPBC are mostly localized in the two outermost layers (the air-liquid crystal interface layer on each side, which will be referred to as surface layers in the following text). Third, the molecular tilts in the two surface layers (θ_S, from the $\hat{z}$ axis) are either parallel or antiparallel, making data interpretation relatively straightforward [6,14].

Freestanding films of R and racemic MHPBC were prepared and studied in our null transmission ellipsometry [15]. A weak in-plane dc electric field was created by applying a set of voltages on the electrodes around the film hole. The strength of the electric field was determined by the value of the applied voltage and the diameter of the film hole (4 mm). Ellipsometric parameter Δ_+ (Δ_-) was recorded as a function of temperature (T) and the applied voltage (V), with the direction of the field set to $\alpha = 270°$ ($90°$) from the projection of the laser's $\mathbf{k}$ vector. A schematic illustration of the experimental geometry is shown in Fig. 1. For smectic films, when the molecular tilts are in the same direction, $\Delta_+ - \Delta_-$ measures the average tilt of the film [16]. Thus for the temperature window we are interested in ($T_C < T < T_S$), it is proportional to the value of θ_S.

Shown in Fig. 2 is a sample V scan from an 11-layer film of R MHPBC at 1.25 K below T_S, all the voltage scans were performed with a rate of 0.1 V/min. At this temperature, the two surface layers are already tilted (ordered),

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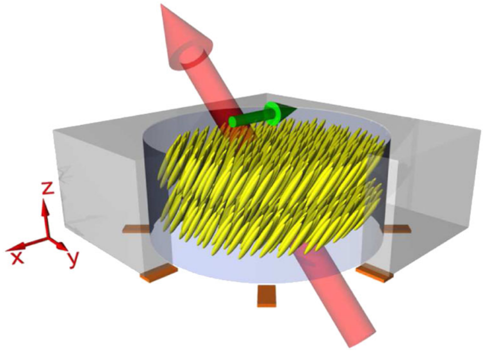

FIG. 1 (color online). Schematic illustration of the experimental geometry for $V > V_C$. In the figure the surface layers, laser beam, and the electrodes attached to the film plate are shown. The short green arrow shows the direction of the electric field for $\alpha = 90°$. A section of the film plate is not shown for better viewing.

while the interior layers are still nontilted (disordered). From the data, two field induced transitions can be identified, one at $V > 0$ ($\alpha = 270°$) and another at $V < 0$ ($\alpha = 90°$). Above the threshold voltage there is a finite difference between Δ_+ and Δ_-, indicating a parallel arrangement of the two surfaces. The difference between Δ_+ and Δ_- above the threshold voltage is proportional to θ_S [17]. While below the threshold voltage Δ has the same value for $V > 0$ and $V < 0$, indicating an antiparallel ground state arrangement of the two surfaces. Because of the first-order nature of this transition, a hysteresis exists in the scan, giving two values of the threshold voltage: the upper and the lower threshold voltage. Since the data are symmetric for $V > 0$ and $V < 0$, most scans are performed for $V < 0$ only.

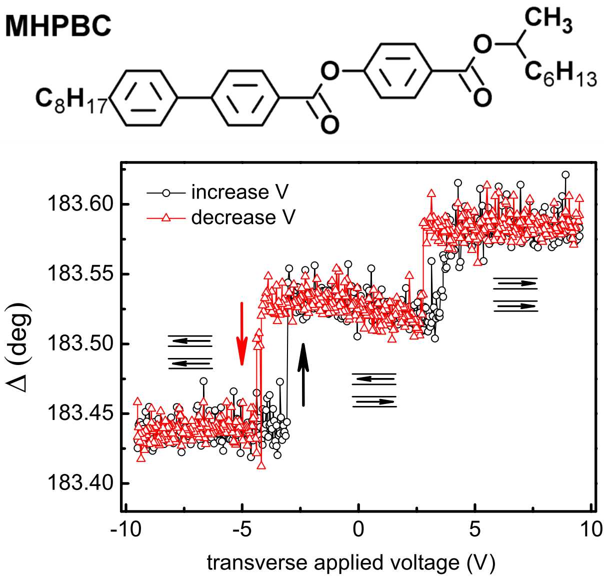

FIG. 2 (color online). Sample voltage scan data of an 11-layer *R*-MHPBC film at 1.25 K below T_S, together with the cartoon illustrations of the relative tilt directions of the two surface layers. On the top is the chemical structure of MHPBC.

The data presented in Fig. 2 show an intriguing resemblance to the magnetization verse field curve of two ferromagnetic (FM) layers coupled via antiferromagnetic (AFM) interaction across a nonmagnetic metal spacer layer [18]. Thus, the field induced transitions of the surface arrangement observed in MHPBC films can be viewed as a liquid crystal counterpart of the well-known phenomenon, interlayer exchange coupling in magnetism. Study on both systems reveals an interaction between two ordered surface layers (FM/FE) across a disordered spacer layer. Although the analogy between the two situations does not go beyond the phenomenological level, it provides us with a framework to calculate the strength of the interlayer interaction between the two surface layers from the threshold voltages.

The observed field induced transition of the surface arrangement is quite informative. Its mere existence demonstrates there is indeed an interaction between the two surface layers regarding their relative orientations. Otherwise we will not see such a transition at all. Second, the ground state surface arrangement being antiparallel indicates that the interlayer interaction between the two surface layers is of the AFE type. Third, the value of the threshold voltage measures the strength of this interlayer interaction. Additionally, the range of the film thickness over which we do observe the field induced transition will give the effective range of this interaction. Thus a complete understanding of the nature of this interaction can be achieved by studying the field induced transitions as a function of T and film thickness N.

To study the temperature dependence of the interlayer interaction between the surfaces, we performed voltage scans at different temperatures on the 11-layer *R*-MHPBC film in the $T_C < T < T_S$ region. The resulting threshold voltage V_C and the magnitude of θ_S ($\propto \Delta_+ - \Delta_-$) are shown in Fig. 3 as a function of $T - T_S$. The values of θ_S were obtained with a voltage value above V_C to ensure a parallel arrangement of the two surface layers, and measured immediately after each voltage scan.

From Fig. 3, we find that V_C increases sharply, and the hysteresis decreases upon approaching T_S. The hysteresis disappears above about 0.5 K below T_S (marked by a black dashed arrow). However, the data still show steplike transition behaviors. The surface tilt transition data in Fig. 3 can be described with a power law $\Delta_+ - \Delta_- \propto (T_S - T)^{\beta_S}$, with $\beta_S \approx 0.27$ being its critical exponent [6].

To explore the distance dependence of the interlayer interaction between the surfaces, we studied films with different thickness N for both R and racemic MHPBC. Since θ_S is mostly restricted to the outermost layer, by studying films with different N, we effectively change the distance between the two surfaces. This allows us to probe the distance dependence of this interaction.

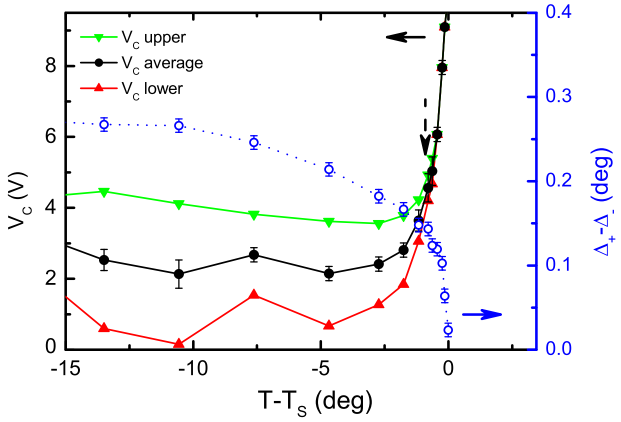

FIG. 3 (color online). The temperature dependence of the threshold voltage of the field induced transitions (solid lines and symbols) and the surface tilt angle measured in $\Delta_+ - \Delta_-$ (dotted line and open symbol) from the 11-layer film of *R* MHPBC. The upper and lower threshold voltage as well as their average value are shown. Black dashed arrow marks the temperature above which the hysteresis disappears.

Shown in Fig. 4 are the averaged threshold voltage V_C from *R*- and racemic-MHPBC films with different thickness. All films show an increase of V_C upon approaching T_S, which indicates increased interaction strength. On the other hand, for the same temperature V_C decreases with increasing N, which is expected, as in thicker films a larger distance is found between the two surfaces. For films thinner than 10 layers or very close to T_S where V_C is high, our experiments are limited by the maximum output voltage on the electrodes (10 V). Also, for films thicker than about 25 layers, V_C is too low to be measured accurately [19]. Thus our experiments are focused on the thickness region around 15 layers.

Since we measured V_C and $\Delta_+ - \Delta_-$ (measured with a voltage above V_C) together, we can also study their relation. In Fig. 5, we plotted in log-log scale the measured V_C as a function of $\Delta_+ - \Delta_-$ for the temperature window between about 0.5 and 5 K below T_S. In this temperature window, a power-law-like relation exists between the two quantities, as shown from the parallel and linear behavior of the data in log-log scale. A fitting to power law gives $V_C \propto \theta_S^{-2.1\pm0.3}$ for all the 7 films studied. This result demonstrates that V_C indeed increases a lot faster than θ_S^{-1}, indicating the interlayer interaction between surfaces also increases sharply upon approaching T_S [20]. However, outside this temperature window, data deviate from the observed power law behavior.

To study the distance dependence of this interlayer interaction, in Fig. 6 we plotted $V_C(d)$ with $\Delta_+ - \Delta_-$ equal to 0.1, 0.12, 0.14, and 0.16 for *R*-MHPBC films and $\Delta_+ - \Delta_-$ equal to 0.12, 0.14, and 0.16 for racemic-MHPBC films in log-log scale as a function of the distance d between the center of the two surfaces. Since for MHPBC films θ_S is restricted to the single outermost layer, $d = N - 1$. From the figure, we find that all values of V_C decrease with increasing d. A comparison with a power law behavior (straight lines) suggests that V_C decreases faster than power law. A closer look at the data finds the interaction decays a lot faster in racemic films than in *R*-MHPBC films [21].

Since $V_C(d)$ decays faster than power law, the interlayer interaction between the surface layers is not of the genuine long-range nature. However, the thickness of the films in which this interaction exists is much larger than nearest neighbors. Thus this interlayer interaction is quasilong ranged with a cutoff distance of about 35 layers for *R* MHPBC and about 24 layers for racemic MHPBC.

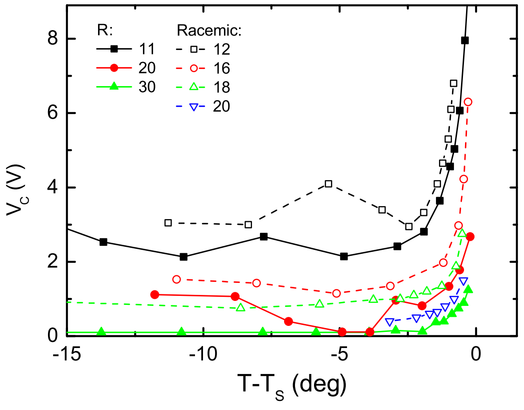

FIG. 4 (color online). The averaged threshold voltage V_C from *R*- (solid lines and symbols) and racemic- (dashed lines and open symbols) MHPBC films with different thickness N plotted verses $T - T_S$. The 3 (2) anomaly data points in the 20-layer *R*-MHPBC (12-layer racemic-MHPBC) film around 5 K below T_S are probably caused by domain walls.

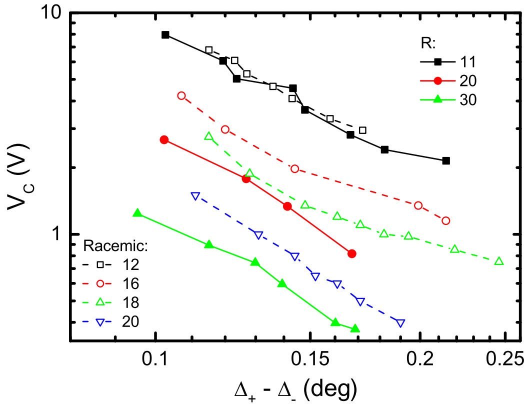

FIG. 5 (color online). Log-log plot of V_C as a function of $\Delta_+ - \Delta_-$ (which measures θ_S) for *R*- (solid lines and symbols) and racemic- (dashed lines and open symbols) MHPBC films. Only data within $0.5 < T_S - T < 5$ K are shown. Outside this temperature window, data show clear deviation from the power law behavior discussed in the text.

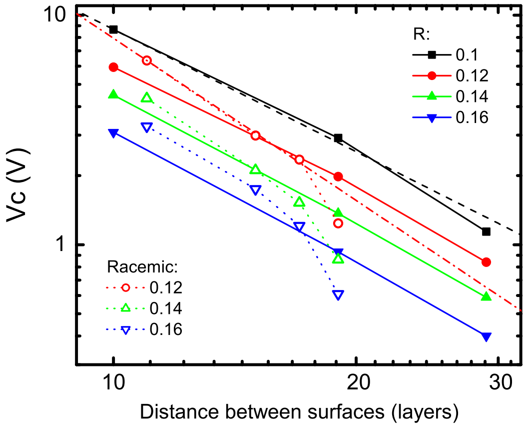

FIG. 6 (color online). Log-log plot of the threshold voltage V_C as a function of the distance between the two surfaces for *R*- (solid lines and symbols) and racemic- (dotted lines and open symbols) MHPBC films with different $\Delta_+ - \Delta_-$ values. The dashed (dash-dotted) line shows a power law behavior with a distance dependence $d^{-1.8}$ ($d^{-2.3}$).

Also worth noting is the fact that racemic films show a V_C comparable to *R*-MHPBC films. Given the fact that macroscopic polarization density is expected to be nearly zero in racemic mixtures, this result suggests that the mechanism of the observed interlayer interaction between two surfaces is more complicated than the simple dipole interaction. Otherwise, V_C from racemic films would be much lower than from *R*-MHPBC films. Similar studies on materials with different levels of chiralities and surface properties would yield more insights into this question.

In Fig. 6, we also find that near $d = 15$, $V_C(d)$ for *R*- (racemic-) MHPBC films follows the line $d^{-1.8\pm0.2}$ ($d^{-2.3\pm0.3}$) pretty well [22]. If we extrapolate the dashed line back to $d = 1$, we get a V_C value on the order of 1000 V, which corresponds to a field strength of about 1 V/μm. It has the same order of magnitude of the field induced AFE to FE transition in bulk AFLC materials. This leads us to an important question, is the interaction studied in this Letter representative of the interlayer interaction in AFLC materials? If so, what can we learn about the nature and microscopic origin of the interlayer interaction from the current study?

To answer these questions, we need to know if the surface layers brought in any unique attributes that are not found in bulk materials. Here we point out that the interaction studied is not due to the fluctuation induced surface-surface interaction, which would indeed be different from the interlayer interaction in bulk materials [23]. The fluctuation induced interaction is attractive or repulsive along the layer normal direction, which is clearly not the situation reported here [24]. Thus we argue that the interlayer interaction between the surfaces studied in this Letter should at least be able to yield qualitative information about the general behavior of the interlayer interaction in AFLC materials, which should show a quasilong ranged AFE behavior.

To conclude, we reported a direct experimental study of the interlayer interaction between the surface layers in freestanding films of AFLC. Results show this is a quasilong ranged AFE interaction. Our study provides new direction for the understanding of the SmC^* variant phases. The competition between nearest neighbor interlayer interaction (FE or AFE) and quasilong ranged AFE interlayer interaction might be the reason for the formation of those phases. Studies on a 1D FM Ising chain frustrated by long range AFM interaction revealed the existence of modulated phases in the phase diagram [25]. Thus our results call for detailed computation study with the proper model for AFLC (1D *XY* chain).

More importantly, our results provide a much needed testing ground for the various theoretical models on AFLC materials and SmC^* variant phases. For any theory with a realistic model of the interlayer interaction in AFLC materials should be able to explain the behavior of the interaction reported in this Letter.

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[19] For much thicker films, the two surfaces are effectively decoupled.

[20] The free energy of the field induced transition includes a $J_s \xi_1 \cdot \xi_2$ term that describes the interlayer interaction between the surfaces, with ξ being a unit vector describing the tilt direction of the surface layer, and a $\mathbf{E} \cdot (\mathbf{P}_1 + \mathbf{P}_2)$ term describing the dipole-field interaction as well as an anisotropy term that favors the planar arrangement: $(\xi_1 \times \xi_2)^2$. At the transition, the free energy of the two arrangements are equal; thus, we have $J_S \propto PE_C \propto PV_C$. Putting in $P \propto \theta_S$ and $V_C \propto \theta_S^{-2.1}$ from the power law fitting, we have $J_S \propto \theta_S^{-1.1}$.

[21] For larger distances, V_C decays faster. Also, V_C decays faster in racemic films, as is evident from the more negative power obtained from the fitting.

[22] Assuming the center of θ_S locates further away from the air-liquid crystal interface, the effective distance d will be smaller, which results in a less negative power in the fitting. However, for a given size of θ_S distribution, power from racemic films is always more negative. Similar distance dependence was observed in C. Y. Chao *et al.*, Phys. Rev. Lett. **86**, 4048 (2001).

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