

Surface and Bulk Uniaxial to Biaxial Smectic-A Transition in a Bent Core Liquid Crystal

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A null transmission ellipsometer was employed to study the uniaxial to biaxial smectic-A phase transition of a bent core liquid crystal material. Free-standing films of thicknesses ranging from 5 molecular layers to more than 300 were prepared and studied. Critical exponents for both the surface and interior biaxiality were obtained. The results were discussed in the general framework of phase transition in lower dimensions.

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Since the discovery of polar switching behavior in an achiral bent core liquid crystal [1], a considerable amount of research interest has been attracted to this type of material. Because of the bent shape of the molecules, mirror symmetry is intrinsically broken. Thus, polar order can be established even though the constituting molecules are achiral. During recent years, several new liquid crystal phases were discovered in the bent core materials [2,3]. Since those bent core phases usually exhibit high spontaneous polarization density, they are potentially good candidates for fast responding electro-optical devices.

Although the study of bent core liquid crystals has been a heated area of discussion, most researches were focused on elucidating the structures of the various bent core phases. Relatively few works have studied the phase transition behavior between those phases [4,5], which is a very important and interesting question in its own right.

Liquid crystals are also known to exhibit enhanced degrees of ordering [6] and increased interaction [7] at surfaces and interfaces, especially in smectic free-standing films. Theory suggests for systems with enhanced surface order, especially when a separate and elevated surface phase transition is observed (*surface transition*), the surface critical behavior exhibits lower dimensional characteristics compared with the bulk transition [8]. Although the theory about surface transition was first published more than 30 years ago, the predications are still to be confirmed in systems with enhanced surface interactions. In particular, no experiments have reported the comparison of critical exponents from surface and bulk system for the same transition.

In this Letter we report our experimental results on the uniaxial (SmA_u) to biaxial smectic-A (SmA_b) transition of a bent core liquid crystal. Critical behavior of the surface as well as the interior biaxiality of free-standing films were studied. Corresponding critical exponents were obtained for both the surface transition and the bulk transition. To our knowledge no previous work has reported this type of study on bent core materials. Thus our results should

provide new insights to better understand the nature of bent core liquid crystals, as well as, more generally, phase transitions in lower dimensions, e.g., surface phase transitions.

The liquid crystal material chosen for this study is bent core compound UD180 (compound 1g in Refs. [9,10]). Its phase sequence is isotropic-(146 °C)- SmA_u -(98 °C)- SmA_b -(88 °C)- B_2 . The SmA_b phase is found to be antiferroelectric [9,10]. Figures 1(a) and 1(b) illustrate the structure of the SmA_u and antiferroelectric SmA_b phases. The B_2 phase is a tilted antiferroelectric phase.

Optical parameter Δ is acquired from our null transmission ellipsometer as a function of temperature (T) and applied electric field orientation (α). Parameter Δ mea-

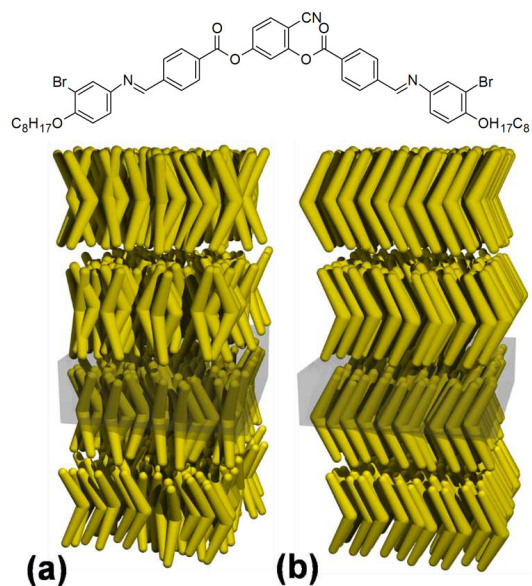


FIG. 1 (color online). Schematic illustration of the structure of (a) the SmA_u phase and (b) the antiferroelectric SmA_b phase with bent core molecules. Light gray boxes enclosing half layer for both phases will be discussed later in the text. On the top is the chemical structure of UD180.

asures the phase difference between the p and s component of the incident light necessary to produce linearly polarized transmitted light. The light source is a He-Ne laser with wavelength $\lambda = 632.8$ nm. The liquid crystal free-standing films are prepared over a cover glass slide with a 4-mm diameter hole in a temperature controlled oven with stability better than ± 15 mK. Argon is used as the exchange gas to minimize chemical degradation of the sample. A proper set of voltages applied to eight evenly spaced electrodes around the film hole creates a uniform weak rotatable in-plane dc electric field over the film. For films with nonzero in-plane polarization, the whole structure can be aligned with the electric field (\mathbf{E}). Variable α denotes the angle between \mathbf{E} and the projection of \mathbf{k} (wave vector of the laser beam) onto the film plane. The aligning field was set to be 2.5 V/mm, which is just sufficient to align the film without distorting the internal structure or inducing electroclinic effect.

As discussed, mirror symmetry is intrinsically broken in bent core molecules. Shown in Fig. 2(a) is a schematic of a bent core molecule in its molecular frame. The mirror symmetry along the x' axis, as observed in achiral rodlike or discotic molecules, is broken due to the bend of the two arms (the degree of the bend is defined with the green cones in the figure). Thus, although the molecule itself is achiral, it is biaxial and polar, even when the molecules are not tilted. The polarization is parallel to the bend direction (x' axis). The ellipsoid of index of refraction for a group of bent core molecules is illustrated in Fig. 2(b). Three principal axes are along the x' , y' , and z' directions. Because we are concerned with the transition between two nontilted

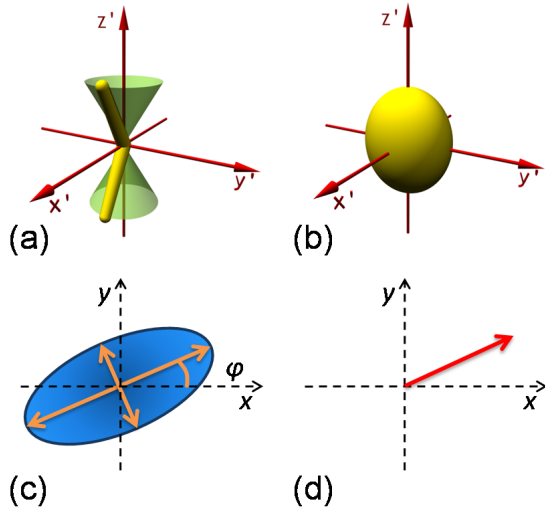


FIG. 2 (color online). Schematic illustration of (a) a bent core molecule in its molecular frame (the green cones define the bend angle), (b) the local index of refraction ellipsoid, (c) the in-plane index of refraction ellipse in the laboratory frame (orange arrows represent the principal axes and φ is the angle between one of the principal axes of the ellipse and the x axis), and (d) the local polarization density in the laboratory frame (red arrow represents the polarization vector).

phases, the z' axis of the molecular frame is parallel to the z axis of the laboratory frame.

The SmA_u - SmA_b transition is a process in which, with lowering temperature, the molecules develop a preferred average direction for the molecular orientation in the layer plane. Thus it is a uniaxial-to-biaxial transition as well as a nonpolar-to-polar transition. Since this transition is a process mainly in plane, we need to take a close look in the layer plane in order to identify the order parameter of this transition.

Shown in Fig. 2(c) is a local index of refraction ellipse in the layer plane of the laboratory frame. The direction of the x axis is defined by the direction of the applied aligning field \mathbf{E} , which defines the preferred average direction of the molecular polarization as well as the molecular bend. The local molecular frame $x'y'$ is an angle φ away from the laboratory frame xy . Thus, the local polarization and in-plane principal axes of index of refraction (\hat{n}) are also φ away from the x axis. Since the molecules are intrinsically polar and biaxial, we can write ($\hat{n}_{x'y'}$) as

$$(\hat{n}_{x'y'}) = \begin{pmatrix} n_{o1} & 0 \\ 0 & n_{o2} \end{pmatrix} \quad (1)$$

due to the molecular biaxiality. In order to obtain the total biaxiality $\langle n_x - n_y \rangle$ of the sample, we need to average over the whole film (here $\langle \rangle$ indicates thermal averaging). So we have

$$(\hat{n}_{xy}) = \hat{R}^T(\varphi)(\hat{n}_{x'y'})\hat{R}(\varphi), \quad (2)$$

where $\hat{R}(\varphi)$ is the rotation matrix in two dimensions. From the algebra, we have $\langle n_x - n_y \rangle = (n_{o1} - n_{o2})\langle \cos(2\varphi) \rangle$, while $\langle P_x \rangle = P_0 \langle \cos\varphi \rangle$, where P_0 stands for the local polarization density. Thus, for the SmA_u - SmA_b transition of bent core molecules, spontaneous polarization density $\langle P \rangle$ is the primary order parameter, while the biaxiality measured in $\langle n_x - n_y \rangle$ is the secondary order parameter (since UD180 is antiferroelectric in the SmA_b phase, $\langle P \rangle$ stands for the sublattice polarization).

As discussed in Ref. [4], when setting the aligning field \mathbf{E} to $\alpha = 0^\circ$ or 90° direction in the SmA_b phase, the film will have its principal axes of in-plane index of refraction parallel or perpendicular to the projection of the laser beam. The difference of ellipsometric parameter Δ obtained under these two situations will be a measure of the total biaxiality of the film; i.e., we will have,

$$\Delta_0 - \Delta_{90} \propto \langle n_x - n_y \rangle. \quad (3)$$

Thus by studying the temperature dependence of $\Delta_0 - \Delta_{90}$ for free-standing films of UD180 through the SmA_u - SmA_b transition, we will be able to obtain the critical behavior of the biaxiality of the sample, which is a secondary order parameter of this transition.

Various films with different thicknesses were prepared in the ellipsometer in the SmA_u phase. Following the same procedure as described in Ref. [11], we used a 4×4 matrix method to obtain values of the principal indices of refraction.

tion and layer spacing in the SmA_u phase to be $n_o = 1.549 \pm 0.006$, $n_e = 1.73 \pm 0.01$, and $d = 4.2 \pm 0.1$ nm. Those values are later used in the fitting to determine the thicknesses of the films studied.

Free-standing films of UD180 with thicknesses ranging from 5 to more than 300 molecular layers were studied. Biaxiality as a function of temperature is obtained by subtracting Δ acquired in two successive cooling runs with $\alpha = 0^\circ$ and 90° , respectively. The cooling rate was set to 60 mK/min. Data from a 9-layer film and a 65-layer film are shown in Fig. 3.

In free-standing films of UD180, surfaces establish polar biaxial order at a higher temperature (T_S) than the temperature at which the whole film goes into the new phase (T_C). For this material, the large temperature window of the SmA_u phase allows us to reach T_S experimentally. As shown in Fig. 3, at T_S , both films develop a small biaxiality which evolves with temperature rapidly. This marks the onset of a continuous surface biaxial transition. The surface biaxiality data were fitted to a power law $A'(T_S - T)^{\tilde{\beta}'}$; A' , T_S and $\tilde{\beta}'$ are all treated as fitting parameters. Only data within about 7°C of T_S were used in the fitting.

Contribution from the interior biaxial transition below T_C was obtained by subtracting the surface fitting equation extrapolated over the whole range from the total biaxiality of the film. As shown in Fig. 3, the sudden increase of biaxiality at about 12°C below T_S marks the interior biaxial transition. The interior biaxiality was also fitted to a power law $A(T_C - T)^{\tilde{\beta}}$, with A , T_C and $\tilde{\beta}$ being fitting parameters. The fitting results for the 9-layer and the 65-layer film are shown in Fig. 3 as solid lines. Log scale

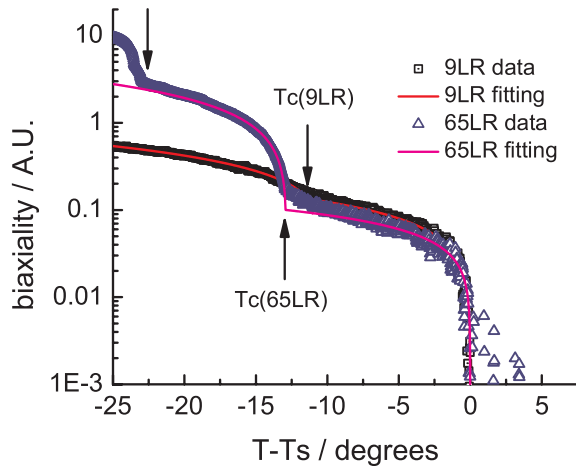


FIG. 3 (color online). Biaxiality measured in Δ_0 - Δ_{90} for a 9-layer film (black square) and a 65-layer film (blue triangle) is plotted in the reduced temperature scale of the surface transition. Lines are the fitting results discussed in detail in the text. Vertical axis is shown in log scale in order to present data clearly for both the surface and the interior transition. T_C is at $11.5 \pm 0.1^\circ\text{C}$ and $12.93 \pm 0.01^\circ\text{C}$ below T_S for the 9- and 65-layer film, respectively. Black arrow around 23°C below the T_S of the 65-layer film marks the transition into the B_2 phase.

is used for the vertical axis so that data from the surface transition can be visible. Note that just above T_C , there are obvious deviations from the power law behavior of the surface biaxial transition—these are probably due to the pretransitional behavior of the interior transition, or due to the effective field created by the biaxial polar surface layers. At 23°C below T_S , a sudden change of slope was observed in the biaxiality from the 65-layer film, which marks the onset of the B_2 phase. In the 9-layer film and a 5-layer film we studied, the B_2 phase was suppressed.

Similar to the studies on the surface effects in the SmA - SmC^* transition [12] and the SmA - HexB transition [13], we can define a characteristic length scale for the surface region ξ_S , which is related to the bulk correlation length in the temperature window studied; for films with thickness $N \leq 2\xi_S$, only the surface transition will be observed [14].

A least square fitting process, similar to the one described in Ref. [15], was used. The resolution of the biaxiality measured from the null transmission ellipsometer was found to be $\pm 0.008^\circ$. The resulting parameters $\tilde{\beta}'$ and $\tilde{\beta}$, for the surface and interior biaxial transition, are plotted in Fig. 4 as a function of film thickness [14].

The averaged value for the bulk exponent $\tilde{\beta}$ is 0.70 ± 0.03 , while the surface exponent $\tilde{\beta}'$ (excluding the 141 layer film result) is 0.58 ± 0.05 . Theory suggests that for $d < 4$, we have $\tilde{\beta} > 2\beta$, with β ($\tilde{\beta}$) being the critical exponent for the primary (secondary) order parameter [16]. Although the order parameter suggests this transition is of the XY type, with the measured $\tilde{\beta}$ value as well as the ones reported in some previous experiments [5], it is unlikely that this transition is of the 3D XY class (in Ref. [5], $\langle n_x - n_y \rangle$ was mistakenly treated as the primary order parameter). Because of the shape of bent core molecules, intralayer interaction is expected to be much stronger than

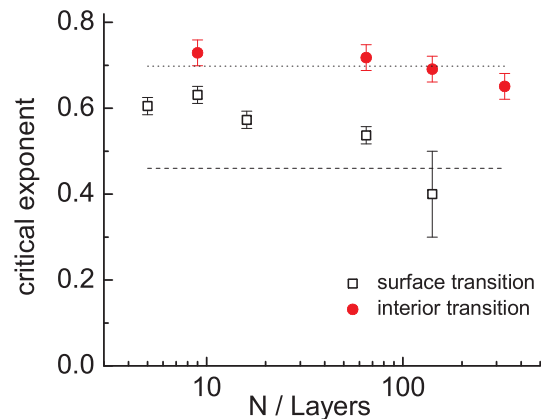


FIG. 4 (color online). Critical exponents of the biaxiality for the surface transition (black squares) and the interior transition (red circles) as a function of film thickness N . Results from $N = 5, 9, 16, 65, 141,$ and 330 layers are presented. Dashed and dotted lines mark twice the value of exponent β for 2D XY (finite sized systems) [22] and 3D XY models.

interlayer ones, thus making the system more toward 2D instead of 3D XY .

On the other hand, the surface exponent $\tilde{\beta}'$ is always smaller than $\tilde{\beta}$. This can be understood in the framework of surface transition [17]. In this situation, theory suggests the enhanced surface interaction will make the surfaces show lower dimensionality than the bulk. A direct comparison of β and β' of the primary order parameter would be preferable; however, it is not always achievable in experiments and remains to be obtained. Although there are no numerical results available for comparison for the exponents of the secondary order parameter, a smaller exponent value of the surface transition ($\tilde{\beta}'$) does suggest lower dimensional behavior.

Now let us look at this phase transition with its primary order parameter P ; the corresponding conjugate field is E . In this picture, the SmA_u - SmA_b transition of bent core materials is essentially a paraelectric-(anti)ferroelectric transition. (For the case of antiferroelectric SmA_b phase, the conjugate field is the stagger field.) Thus we can expect a phase diagram similar to a magnetic transition. As expected, below T_C first order field induced transitions are observed [9], while above T_C , field induced biaxial polar order has been reported for uniaxial nonpolar smectic phase with nontilted molecules [18].

Before we conclude this Letter, we would like to discuss the importance of studying the SmA_u - SmA_b transition from another perspective. In recent years, de Vries-type SmA materials have attracted a lot of attention [19,20]. However, there is still no direct experimental evidence for the *diffuse cone model*. Without a model physical system, theoretical advances of de Vries-type SmA - SmC transition have been limited.

In the diffuse cone model, the rodlike molecules are tilted in the SmA phase with uniform azimuthal distribution. At the transition to the SmC phase, a preferred azimuthal orientation develops with almost no change in the molecular tilt angle, thus producing minimal layer contraction. However, this is exactly what happens at the SmA_u - SmA_b transition of a bent core material, if we view one single layer of bent core SmA material as two layers of tilted rodlike molecules (see the part enclosed in the light gray box in Fig. 1). The *tilt angle* is thus defined by the *bend* of the two arms [the green cones in Fig. 2(a)]. As shown for UD180 [9,10], at the SmA_u - SmA_b transition, there is no layer spacing variation. Recent studies of a de Vries-type SmA material even showed qualitatively similar behavior under applied field as a nontilted smectic bent core material [18,21]. The above discussion suggests that bent core materials with a SmA_u - SmA_b transition can be used as a model system to study the de Vries-type SmA - SmC transition and will probably bring new insights into this field.

In summary, we studied the SmA_u - SmA_b transition of free-standing films of bent core material UD180. Biaxiality is identified as the secondary order parameter of this transition. Both surface and bulk exponents of the biaxiality were obtained. The significances of the results are discussed in the following aspects: (i) the nature of the SmA_u - SmA_b transition of bent core material; (ii) the experimental realization of surface transition and comparison of surface vs bulk exponent; (iii) the potential of using this type of material as a model system for studying the de Vries-type SmA phase.

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