Smectic-C^* to Smectic-A Transition in Variable-Thickness Liquid-Crystal Films: Order-Parameter Measurements and Theory

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This paper presents the results of experimental measurements and a mean-field-theory analysis of the behavior of the average tilt angle near the smectic-C^* to smectic-A transition in thin films of two through ten molecular layers. These films provide one of the few physical realizations of systems where the surface layers remain ordered to a higher temperature than the bulk. The mean-field theory provides excellent quantitative fits to the critical-temperature spectrum and good qualitative fits to the order-parameter behavior.

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Free-standing liquid-crystal films which can be varied in thickness from two to hundreds of molecular layers provide a viable experimental system to study the evolution from surface- to bulk-dominated behavior. In this Letter we present measurements on the temperature dependence of the average smectic-C^* tilt angle as it continuously approaches zero at the smectic-C^* to smectic-A transition. Films from two to ten molecular layers were studied and a mean-field theory developed to understand the results. In this theory, the N-layer smectic-C^* film is modeled as a stack of two identical exterior surface layers characterized by surface critical parameters and $N-2$ interior layers with bulklike parameters. These films provide one of the few physical examples of systems where experimentally[1] it is found that the surface layers remain ordered to a higher temperature than the bulk (binary liquid mixtures are possibly the only other realization known at this time[2]). Hence, for a range of temperatures above the bulk transition temperature an N-layer film appears as illustrated in Fig. 1(a). $|\psi_i|$ is the magnitude of the tilt angle of the ith layer and h_i its thickness. First, we will discuss the technique used to measure the average tilt angle, $|\bar{\psi}|$, which for an N-layer film is defined as $(1/N)\sum_{i=1}^{N}|\psi_i|$; then we will discuss the measured temperature and film-thickness dependence of $|\bar{\psi}|$ in the context of the mean-field theory.

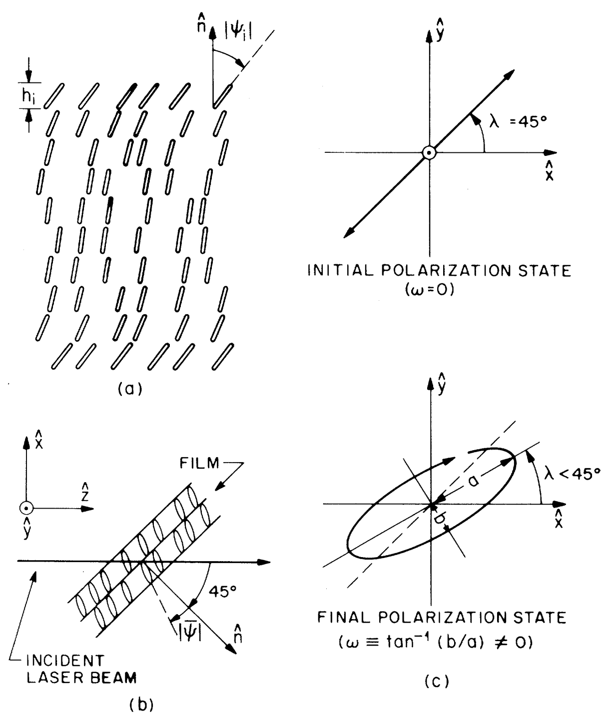

FIG. 1. (a) Variation of the molecular tilt angle through a ten-layer free-standing film at a temperature above the bulk transition temperature but below the ten-layer film transition temperature. (b) Schematic of the experimental geometry. (c) Polarization states of the incident and transmitted light.

Free-standing films were prepared across a $3\times 10\text{-mm}^2$ rectangular hole in a glass microscope cover slip as described elsewhere.[3] The liquid-crystal compound studied was chiral 2-methylbutyl 4-(4′-*n*-decyloxybenzylideneamino) cinnamate (DOBAMBC). The chirality of the compound was important since this resulted in a spontaneous polarization in the smectic-C^* phase perpendicular to the plane of the molecular tilt.[4] This polarization could be oriented by a small external electric field to establish a uniform tilt direction across the sample. The films were contained in a two-stage oven regulated to better than 0.01 °C and maintained in a dry nitrogen atmosphere. The transition temperatures were found to decrease at a rate of approximately 10 mdeg/h. Each set of data for an N-layer film was preceded and followed by a measurement of the transition temperature of a three-layer film to correct for this drift. The average tilt angle, $|\bar{\psi}|$, for each smectic-C^* film was measured by observing the change in the polarization state of laser light transmitted through the film. The experimental geometry used will be described here, but the complete details of the experimental apparatus and data reduction will appear in a separate publication.[5]

As illustrated in Fig. 1(b), laser light (2 μW at 6328 Å) propagating in the z direction was incident on the free-standing films. The films were oriented so that the normal to smectic layers, $\hat{n}$, was in the xz plane at 45° to the z axis. The molecules were aligned to tilt in the xz plane by an electric field applied in the y direction, $\vec{E}_+ = E_0\hat{y}$ with $E_0 = 6$ V/cm. Reversing the direction of the field, $\vec{E}_- = -E_0\hat{y}$, caused the molecules to rotate 180° around the n axis and tilt in the opposite direction. The polarization state of the incident and transmitted light can be described by the two angles λ and ω defined in Fig. 1(c). The incident light was linearly polarized in the xy plane at an angle of 45° to the x axis ($\lambda = 45°$, $\omega = 0$). The polarization state of the transmitted light was measured for both directions of the applied field E_+ and E_- resulting in the ellipticity angles (λ_+, ω_-) and (λ_-, ω_-), respectively. The experimental geometry used yields $\lambda_+ = \lambda_- \equiv \lambda_\pm$.[5] These angles were measured to an accuracy of 0.004° with a computer-controlled, rotating-analyzer ellipsometer.[6] To determine an average tilt angle from the measured ellipticity angles, the film was modeled as a uniform, uniaxial dielectric of thickness $h = \sum_{i=1}^{N} h_i$ with its extraordinary axis tilted at the same angle $|\bar{\psi}|$ as the average molecular tilt angle. With use of the bulk refractive indices for DOBAMBC[7] and the relation $h_i = h_0 \cos(|\psi_i|/R)$ established by x-ray measurements on other compounds,[8] a set of curves of the ellipticity angles $(\lambda_\pm, \omega_+, \omega_-)$ as a function of $|\bar{\psi}|$ was generated for each film thickness. The curves were found to fit the complete experimental data set for $R = 1.1$ and $h_0(T) = 33.3\ \text{Å} - (0.035\ \text{Å/deg})(T - T_B)$ where T_B is the bulk transition temperature. The resultant curves could be approximated in several limiting cases; namely, for $|\bar{\psi}| \leq 10°$, $\Delta\omega \equiv \omega_+ - \omega_- \simeq 0.052N|\bar{\psi}|$, and for $|\bar{\psi}| = 0°$ and $N < 8$, $\Delta\lambda \equiv 45° - \lambda_\pm \simeq (0.010°)N^2$.

The second relationship was useful for determining the number of layers in each new film as it was drawn at a temperature in the smectic-A range. In Fig. 2 the measured temperature dependence of $|\bar{\psi}|$ is shown for films of two, three, four, five, seven, and ten molecular layers. Also shown are measurements of $|\bar{\psi}|$ on a bulk sample of DOBAMBC taken from Ostrovskii *et al.*[9] The temperature scale for the bulk data was shifted so that the transition temperature coincided with the bulk transition temperature measured in our sample.

Our mean-field model is based on the following free energy:

$$F = F_S + F_B + F_C, \tag{1}$$

where

$$F_S = A'[|\psi_1|^2 + |\psi_N|^2] + B'[|\psi_1|^4 + |\psi_N|^4] + D'[|\psi_1|^6 + |\psi_N|^6], \tag{2a}$$

$$F_B = \sum_{i=2}^{N-1} [A|\psi_i|^2 + B|\psi_i|^4 + D|\psi_i|^6], \tag{2b}$$

$$F_C = \sum_{i=1}^{N-1} C(|\psi_{i+1}| - |\psi_i|)^2. \tag{2c}$$

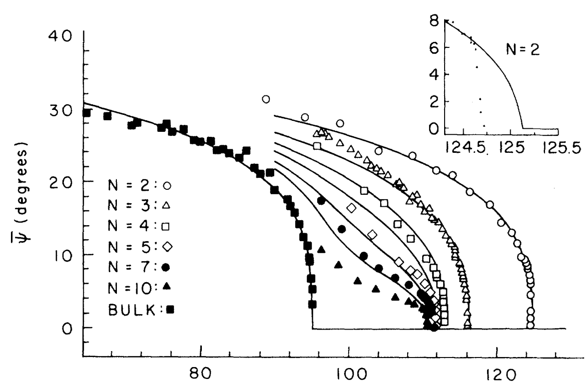

FIG. 2. Average tilt angle vs temperature as a function of film thickness. The solid curves are the discrete mean-field theory fit, with use of the parameters $T_S = 125.11$, $T_B = 95.15$, $\alpha = 0.0503$, $\alpha' = 0.0408$, $B = 0.1438$, $B' = 0.7063$, $D = 5.85$, and $D' = 5.25$. Inset: the $N = 2$ data within 0.5° of T_S where deviations from mean-field behavior are apparent.

Fluctuations in the phase of the tilt order parameter have been neglected.[10] Equations (2a) and (2b) are the free energies of the exterior (surface) and interior layers, respectively, while F_C describes the interlayer coupling. We assume that the film is symmetric about a plane passing through its center and parallel to the layers so that $|\psi_i| = |\psi_{N+1-i}|$. We choose $A = \alpha(T - T_B)$ and $A' = \alpha'(T - T_S)$ where T_B and T_S are the bulk and two-layer (surface) critical temperatures, respectively. We require that α, α', B, B', D, and D' all be positive and choose $C = 1$ for convenience. Mean-field theory has been found to describe the bulk smectic-C to smectic-A transition[8]; however, sixth-order terms in $|\psi|$ need to be included to describe correctly the temperature dependence of the order parameter and heat capacity.[11,12]

For $N = 2$ we have simply $F = F_S$ and F is minimized with the choice[11,12]

$$|\psi_1| = |\psi_2| = \left(\frac{B'}{3D'}\right)^{1/2}\left[\left(1 + \frac{3t}{t_0}\right)^{1/2} - 1\right]^{1/2}, \qquad (3)$$

where $t = T - T_S$ and $t_0 = -B'^2/\alpha' D'$. This expression exhibits the crossover between ordinary critical and tricritical behavior depending on the value of t relative to t_0. Equation (3) provides an excellent fit to the $N = 2$ data (see Fig. 2) excluding the range within 1° of T_S where the data drop precipitously. This precipitous drop may be the result of two-dimensional fluctuations and is currently under further investigation.[5] From the fit using (3) we obtained values for T_S and two of the three surface parameters α', B', and D'. Similarly, the bulk data shown in Fig. 2 can be fitted by an expression of the form (3) with primed parameters replaced by the unprimed bulk parameters. Values for T_B and two of the three bulk parameters α, B, and D were thus obtained.

For general N, we minimized Eq. (1) numerically. We fitted the critical temperature of the three-layer film and remained with one adjustable parameter. Figure 3 indicates that this parameter can be chosen to give excellent agreement between theory and experiment for the critical temperatures T_N of the N-layer films $N = 4$, 5, 7, and 10. The same choice for this parameter yields the tilt angle curves shown in Fig. 2. For $N \leq 4$ the agreement with the experimental data is quantitatively quite good. For larger N the agreement is more qualitative in nature though the bulk-to-surface crossover (evidenced by the bend in the curves) occurs at roughly the correct temperature.

Further insight into the physics of this system can be gained from an analytical study of the continuum

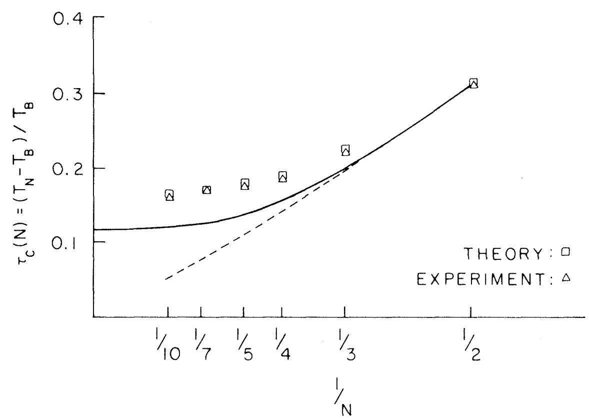

FIG. 3. Critical temperature shift vs the inverse of the film thickness. The solid curve is given implicitly by Eq. (4) which is derived from the continuum mean-field theory. The theory points (squares) correspond to the discrete mean-field theory based on Eq. (1). The dashed line is an extrapolation of the solid curve from the "thin" film regime and would intersect the origin.

version of (1). A similar model has already been considered by several authors.[13,14] Adapting the calculation of Ref. 13 to our model[15] we have analytically calculated the critical temperature T_N as a function of N, and it is given implicitly by

$$\tanh\{\tfrac{1}{2}(N-2)[\alpha(T_N - T_B)]^{1/2}\} = \alpha'(T_S - T_N)/[\alpha(T_N - T_B)]^{1/2}. \qquad (4)$$

The value of $\tau_c(N) \equiv (T_N - T_B)/T_B$ as a function of N given by (4) is plotted as the solid line in Fig. 3, with use of our previously determined values of α, α', T_S, and T_B. From Eq. (4) we determine the following limiting behavior for $\tau_c(N)$:

$$\tau_c(N) \approx 1/N, \quad N \ll 2\xi_B(T_N), \qquad (5a)$$

$$\tau_c(N) \approx \text{nonzero constant}, \quad N \gg 2\xi_B(T_N), \qquad (5b)$$

where $\xi_B(T_N) = [\alpha T_B \tau_c(N)]^{-1/2}$ is the bulk mean-field correlation length evaluated at T_N and measured in units of the interlayer spacing. As first noted by Kaganov and Omelyanchuk,[13] T_N does not approach T_B as $N \to \infty$ because of the surface order present when $T_S > T_B$. Equation (5) indicates that the departure from linearity in the curve shown in Fig. 3 when $N \approx 4$ occurs when $2\xi_B(T_N)$ approximately equals the thickness of the film. We can thus distinguish "thin" versus "thick" films. In "thin" films [i.e., $N \ll 2\xi_B T_N$)] the tilt angle is nonzero throughout the film for all $T < T_N$ (i.e., the entire film exhibits smectic-C^* order). On the other hand in "thick" films the tilt angle is nonzero throughout the film only for temperatures less than a crossover temperature T^* defined by $2\xi_B(T^*) \sim N$ (T^* corresponds approximately to the upward bend in the curves and data points for $N=5$, 7, and 10 in Fig. 2). For $N=10$ we find using our model parameters that $T^* \approx T_B + 0.25\,°\mathrm{C}$. For temperatures T such that $T^* \leq T \leq T_N$ the interior of the film is disordered; nonzero tilt occurs only near the surfaces of the film penetrating exponentially into the interior to a depth given by $\xi_B(T)$.

In conclusion, we have presented measurements of the temperature dependence of the order parameter in a physical system where the surface transition temperature is higher than that of the bulk. A discrete mean-field model was proposed to describe the results. In addition to providing a good physical understanding of the behavior of the order parameter, the model also indicates how mean-field theory, which describes the bulk transition even in the vicinity of T_B, can be extended to thin films, although as indicated in Fig. 2, two-dimensional fluctuations cannot be neglected near T_N.

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