Bend expulsion from the smectic-A phase: Analogy to type-I superconductor

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Abstract

Using an atomic force microscope to nanopattern a substrate for liquid crystal alignment, a bend distortion is imposed on a liquid crystal. In regions of large bend the smectic-A phase melts into the nematic phase, and the width of the melted region is measured as a function of temperature. The results are consistent with type-I superconducting (nematic – smectic-A) behavior, wherein a large magnetic field (bend or twist distortion) induces an order to disorder transition. A model that accounts for non mean-field behavior is presented.

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DeGennes first recognized the similarity between the smectic-A (Sm-A) liquid crystalline and the superconducting phases [1]. The smectic-A phase is characterized by long-range orientational order described by the unit vector $\hat{n}$, also called the “director.” The molecules are arranged in two-dimensional liquid-like layers perpendicular to $\hat{n}$; the layers are stacked, producing a quasi-long range one-dimensional periodicity. Using a two-dimensional (amplitude and phase) Sm-A order parameter, DeGennes showed that the free energy has a form similar to the Landau-Ginzburg superconductor free energy. As the superconductor free energy is gauge invariant, the Sm-A free energy is invariant under simultaneous rotation of the smectic layers and the director. Moreover, smectic fluctuations over a correlated fluctuation volume $\xi_||^2\xi_\perp^2$ in the higher temperature nematic phase exclude bend and twist director distortions (which involve $\nabla \times \hat{n}$), which is analogous to fluctuation diamagnetism in superconductors (which involves $\nabla \times \vec{A}$). Here $\xi_||$ and $\xi_\perp$ are the smectic correlation lengths parallel and perpendicular to $\hat{n}$, and $\vec{A}$ is the vector potential. One well known consequence of bend/twist expulsion in the presence of smectic order — in this case smectic fluctuations in the nematic phase — is the divergence of the associated elastic constants $K_{33}$ and $K_{22}$ on approaching the nematic – Sm-A transition temperature $T_{NA}$ [2]. Another well known consequence is the “twist grain boundary” phase [3,4]: The propensity of chiral liquid crystals to undergo a twist distortion can cause the chiral Sm-A phase to break into domains with a well defined rotation of the layer normal from one domain to the next. Yet another consequence of bend/twist expulsion is the “melted grain boundary” phase for a bent Sm-A liquid crystal, discovered by Dozov and Durand [5]. For a region of Ginzburg parameter space $\kappa \equiv \lambda/\xi_|| > 1/\sqrt{2}$, where $\lambda$ is the penetration length, the melted grain boundary is characterized by a series of quantized Sm-A domains. It can be stable over a wide region of $\kappa$ space, and exists in $\kappa$ space between type-I and type-II smectic analogs of superconductors.

Despite the rich physics associated with this problem, there have been few other experimental reports involving bend deformations in the Sm-A phase. The reason for this absence has been the inability to control the local orientation of the director on length scales
sufficiently small that pretransitional effects near \( T_{NA} \) could be observed. But this situation has changed, as new nanomanipulation methods have been developed and applied to liquid crystals. In particular, the technique of scribing a polyimide-coated substrate using the stylus of an atomic force microscope (AFM) facilitates patterned “easy axes” on nanoscopic length scales that control the local director orientation [6,7]. In this paper we describe an experiment in which herringbone easy axis patterns are scribed into a polyimide substrate, thereby enforcing a bend-type distortion very close to the pixel interfaces. On filling the cell with a type-I (\( \kappa < 1/\sqrt{2} \)) liquid crystal, for \( T < T_{NA} \) we find regions of temperature-dependent width \( L(T) \) at the pixel interfaces that have melted into the nematic phase. This bend-induced melting is equivalent to the magnetic field induced superconducting to normal transition. The behavior of \( L(T) \) is found to be consistent with that predicted by the Landau-Ginzburg-DeGennes free energy for a type-I material in the temperature region (close to \( T_{NA} \)) for which smectic fluctuations are important.

The cell was composed of two microscope slides. One slide was spin-coated with the polyamic acid PI-2555 (Dupont) and baked at 275° C for 120 min. This slide then was rubbed using the stylus (Nanodevices Tap300) of an Topometrix Explorer atomic force microscope with three herringbone patterns, each 100 × 100 \( \mu \text{m} \) in size, each occupying one quadrant in the \( xy \)-plane, with one corner of each located at the origin. Two of the patterns, as well as the coordinates \( x, y, \) and \( z \), are shown schematically in Fig. 1a. The vertical force of the AFM stylus was 3.4 \( \mu \text{N} \), the writing speed was 15 \( \mu \text{m s}^{-1} \), and the spacing between the lines was \( h \cos \gamma \), where \( h = 196 \text{ nm} \). The half angle, \( \gamma \), of the herringbone is equal to 20°, 15°, and 10° for the three patterns. In the fourth quadrant a spiral easy axis pattern was scribed; this forces a large-scale bend distortion on the liquid crystal, which makes it easier to determine the actual transition temperature \( T_{NA} \) during the course of the experiment. The opposing substrate was spin coated with polymethyl methacrylate (PMMA; \( M_w = 101000; \ M_n = 39500 \)) dissolved in a mixture of propylglycolmethyl ether acetate and \( \gamma \)-butyrolactone. PMMA serves as a planar degenerate alignment agent [8,9], such that the director is planar at the surface and the azimuthal orientation is controlled.
by the opposing (scribed) substrate. The two substrates were clipped together. Using interferometry, the thickness of the cell at the patterned region was found to be \( t = (1.4 \pm 0.2) \mu m \). The cell was placed into a temperature controlled oven, heated to a temperature of 76\(^\circ\) C, and filled with the liquid crystal octyloxycyanobiphenyl (8OCB; Merck) in its nematic phase. 8OCB was chosen in part because of the large body of temperature-dependent physical parameter data (e.g., elastic constants, smectic correlation lengths) available in the literature. These data allowed us to determine that 8OCB has a type-I Sm-A phase over a large temperature region below \( T_{NA} \), which will be discussed below. The sample was placed onto the stage of a model Olympus BX51 microscope with crossed polarizers, such that the pixel interfaces were oriented at an angle of \( \frac{\pi}{8} \), i.e., 22.5\(^\circ\), with respect to the polarizer direction (Fig. 1b). This angle was chosen to give an approximately linear change of intensity with director orientation angle \( \beta \), where \(-\gamma \leq \beta \leq \gamma\). The sample then was slowly cooled through the transition temperature \( T_{NA} = 67^\circ\) C into the Sm-A phase. A calibration image was recorded at \( T = T_{NA} - 450\) mK using a CCD camera having resolution \( 2048 \times 2048 \) pixels, where each pixel corresponds to 0.145 \( \times \) 0.145 \( \mu m \) in the sample (Fig. 1b). Later we will see that the width \( L \) of the region over which the director varies at \( T = T_{NA} - 450\) mK is less than 0.2 \( \mu m \), and thus for all intents and purposes we can treat the director angle \( \beta \) as undergoing a discontinuous change of 2\( \gamma \) across the pixel interface. The temperature then was ramped upward at a rate of 0.67 mK s\(^{-1}\). An image was recorded once every two seconds, corresponding to temperature increments of 1.33 mK.

The resulting images were converted into a movie, which was examined to determine \( T_{NA} \); the uncertainty in \( T_{NA} \) is \( \pm 3\) mK. The calibration image (using the \( \gamma = 20^\circ \) scribed square) and images at representative temperatures closer to \( T_{NA} \) were analyzed, whereby the intensity \( I(y) \) across the interface (Fig. 1c) was determined in one region across the central interface in each of the three (\( \gamma = 20^\circ, 15^\circ, \) and \( 10^\circ \)) scribed squares. To mitigate detector noise, \( I(y) \) was taken as the average of five consecutive pixels along the \( x \)-axis. Owing to diffraction and pixel averaging, \( I(y) \) for the calibration image was found not to be a step function, but rather varied smoothly with \( y \). We chose an ad hoc function — a Lorentzian
with full width \( w \) at half maximum — as the “instrument function” and convoluted this function with a step function, i.e., the calibration profile for \( I(y) \) as if no diffraction were present. For \( w = 1.28 \) \( \mu \)m, we found that the resulting convolution excellently mimicked the actual intensity profile for the calibration image, and ascertained that the cell’s thickness contributed only \(~ 0.1 \) \( \mu \)m to \( w \). Then, for all other images, this instrument function was convoluted with an \textit{ad hoc} form — the error function \( \text{erf}(y/u) \), where \( u \) is a function of temperature — to simulate the measured \( I(y) \). For each image, \( u \), and thus the width of the error function, was adjusted to give the best approximation to the measured intensity profile; figure 2 shows one example. In all cases the fits were excellent, although it should be noted that the fits were rather insensitive to the steepness of the error function far below \( T_{NA} \). Thus, we are confident in data only for \( T \gtrsim T_{NA} - 200 \) mK. Since \( I \propto \sin^2 \left( \frac{\pi}{4} + 2\beta \right) \), the \( \text{erf}(y/u) \) curves then were transformed into \( \beta(y) \). The width \( L \) over which the director orientation varies was taken arbitrarily as the “10/90 points” of the full variation of \( \beta(y) \), i.e., for \( \beta = \pm 0.8\gamma \). Figure 3 shows \( L \) vs. \( \Delta T \equiv T - T_{NA} \) for \( \gamma = 20^\circ \) and \( 15^\circ \); data are not shown for \( \gamma = 10^\circ \) because of the tendency for each pixel to break into subpixels.

Let us return to the issue of type-I vs. type-II. Litster, et al. measured the ratio \( D(T)/K_{33}^0 \) [10], where \( D(T) \) is the elastic constant associated with director tilt relative to the layer normal and \( K_{33}^0 \) is the background elastic constant, which excludes the component due to smectic fluctuations. Taking \( K_{33}^0 = 7 \times 10^{-7} \)dy [10], applying their data for \( K_{33}(T) \) in the nematic phase to the corresponding reduced temperature in the Sm-A phase, we extract the bend penetration length \( \lambda(T) = \sqrt{K_{33}(T)/D(T)} \). Finally, using their data for \( \xi_{||}(T) \) above \( T_{NA} \) and applying it to the corresponding temperature below \( T_{NA} \), we find that the Ginzburg parameter \( \kappa = \lambda/\xi_{||} \) decreases smoothly from 0.33 at reduced temperature \( |\tau| \equiv \Delta T/T_{NA} \sim 10^{-2} \) to \( \kappa = 0.27 \) at \( |\tau| \sim 10^{-3} \) to \( \kappa = 0.16 \) at \( |\tau| \sim 10^{-4} \). This is clearly type-I in the experimentally relevant region \( |\tau| < 10^{-3} \). Moreover, relative to \( L \), the small values of \( \lambda (= 4.9, 20, \) and \( 62 \) nm at these temperatures), indicate that the director varies in orientation only in a \textit{very} narrow slice of the unmelted Sm-A region, and that most of the variation occurs in the melted (nematic) region centered on the pixel interfaces.
We now turn to theory. The free energy has three primary contributions, viz., $F_{Sm-A}$ associated with the melting energy into the nematic phase, $F_{Nem}$ due to curvature energy in the melted region, and $F_{Surf}$ due to the energy cost associated with director deviations from the easy axes at the surface. DeGennes’ mean field approach [1] is not expected to be accurate near $T_{NA}$, where smectic fluctuations significantly modify both the free energy and effective elastic constants. The contribution of critical fluctuations and ordering to the free energy $F$ (per unit volume) has been studied extensively [11,12], and can be written as

$$F = k_B T_{c} X_{\pm} R^{-1} \xi^{-d} \left| \tau \right|^{-2},$$

where $k_B$ is Boltzmann’s constant, $T_{c}$ is the critical temperature (here equal to $T_{NA}$), $d$ is the dimensionality, $R \equiv \alpha(1 - \alpha)(2 - \alpha)$, $\alpha$ is the specific heat critical exponent, and $X_{\pm}$ are universal constants that depend upon whether the phase is ordered (-) or disordered (+). This form for $F$ is based upon the divergent part of the specific heat having a form $k_B X_{\pm} \xi^{-d} \alpha^{-1} |\tau|^{-2}$ [12]. In the Sm-A phase there are two correlation lengths $\xi_{||}$ and $\xi_{\perp}$, which, as for $K_{33}$ above, we evaluate at the corresponding temperature $> T_{NA}$; there they are known experimentally and are expected to differ only by a universal constant, yielding $F_{Sm-A} = k_B T_{NA} X_{\pm} R^{-1} \xi_{||}^{-1} \xi_{\perp}^{-2}$, with $X_{\pm} \approx 0.031$ [12,13] and $\alpha = 0.18$ for 8OCB [13].

Below $T_{NA}$, regions of large bend distortion melt into the nematic phase, giving rise to an elastic-like energy cost. As the effects of smectic fluctuations in this melted nematic region have not been addressed theoretically, we approach this problem with a simple DeGennes-like scaling argument [1]. We consider only the free energy functional quadratic in the complex smectic order parameter $\psi(\vec{r}) = |\psi| \exp(i\phi)$, where $\phi$ is related to the position of the layers. For bend only, we take the nematic director to be $\hat{n}(\vec{r}) = \hat{y} + \delta \hat{n} \approx \hat{y} + 2\hat{x} y \gamma / L = \hat{y} + \hat{x} \beta(y)$, where the second term is small and $2\gamma$ is the total angular bend over the distance $L$ [1]. The free energy density is given by

$$\frac{1}{2} \left[ C_{||} \left| \frac{\partial \psi}{\partial z} \right|^2 + C_{\perp} \left| (\nabla_{\perp} + 2i q_0 \hat{x} y \gamma / L) \psi \right|^2 - |a| \left| \psi \right|^2 \right],$$

where $C_{||}$ and $C_{\perp}$ are parameters proportional to the smectic layer compression elasticity $B$ and to $D$, respectively [2], where $q_0 = 2\pi / \ell$, and $\ell$ is the smectic layer thickness. We will include the effect of non-quadratic terms in the free energy only by choosing appropriate
values for these parameters, specifically \( a = -C_\parallel \xi_\parallel^{-2} \), so as to obtain the correct correlation length at an equal temperature above the transition. This free energy functional clearly is identical to the Hamiltonian of a charged particle in a magnetic field in the Landau gauge [14]. We therefore can diagonalize it using techniques applied to the Landau level problem, and find that the eigenvalues are Landau levels with energies \([(m + 1/2) \omega - |a| + C_\perp k_\parallel^2] \), where \( \omega = (C_\parallel C_\perp)^{1/2} q_0 \gamma / L \), \( m \) is a non-negative integer, the second term is the offset due to the zero of energy being shifted by \( a \), and the last term is the kinetic energy in the direction parallel to the “magnetic field,” where \( k_\parallel \) is the wavevector along the \( z \)-axis. A detailed calculation of the implied free energy is beyond the scope of this paper. Here we simply note that above the critical temperature we have eigenvalues (for plane waves) of \( C_\parallel k_\parallel^2 + C_\perp (k_\parallel^2 + k_\parallel^2) + a_n \), and that the free energy per unit volume is \( F_{\text{Nem}} = k_B T_{NA} X_+ R^{-1} \xi_\parallel^{-1} \xi_\perp^{-2} \), where \( X_+ \approx 0.032 [12,13] \). As is known for the magnetic problem, the discrete sum over \( m \) approximates the continuous integrals over \( k_\parallel, k_\perp \). In consequence it is reasonable to use a similar formula for the free energy, although replacing the correlation lengths with the values they would have when \( a_n = b \omega - |a| \), where \( b \) is a factor of order unity that we take to be \( 1/2 \). The result is \( F_{\text{Nem}} \sim k_B T_{NA} X_+ R^{-1} \xi_\parallel^{1/2} \xi_\perp^{-1/2} \left( q_0 \gamma / L - \xi_\parallel^{-1} \xi_\perp^{-1} \right)^{3/2} \). Note that this \( F_{\text{Nem}} \) implies a non-Hookean elasticity, and includes only the divergent part due to Sm-A fluctuations.

The surface anchoring contribution to the energy (per unit volume) in the Rapini-Papoular approximation is \( \frac{1}{2} W_\phi \left[ \gamma(y) - \beta(y) \right]^2 \) [15], where \( W_\phi \) is the azimuthal anchoring strength coefficient and is not expected to have important pretransitional behavior [16]. For simplicity, we assume that \( \beta(y) \) varies linearly with \( y \). The overall free energy \( f \) can be obtained by integrating \( F_{\text{Sm-A}} + F_{\text{Nem}} + F_{\text{Surf}} \) over one period \( P \) along the \( y \)-axis, where we assume that a region of width \( L \) has melted into the nematic phase. This results in

\[
f = -k_B T_{NA} X_+ R^{-1} \xi_\parallel^{-1} \xi_\perp^{-2} (P - L) + k_B T_{NA} X_+ R^{-1} \xi_\parallel^{1/2} \xi_\perp^{-1/2} \left( q_0 \gamma / L - \xi_\parallel^{-1} \xi_\perp^{-1} \right)^{3/2} L + W_\phi \gamma^2 L / 6 \tau.
\]

We then minimize \( f \) with respect to \( L \) — notice that \( P \) drops out — yielding an implicit equation for \( L \) in which all parameters except for \( W_\phi \) are known. Figure 3 shows calculated
curves for $L$ vs. $\Delta T$ for several different values of $W_\varphi$. The consistency of the theoretical result with the experimental data is extremely satisfying, despite the fact that our model is a highly simplified scaling theory, does not include the background nematic elasticity $K_{33}^0$, nor does it include a self-consistent determination of $\beta(y)$. Instead, $d\beta/dy$ is treated as a constant, consistent with the spirit of this model. In reality, the presence of nonzero $W_\varphi$ would tend to concentrate the bend distortion very close to the pixel interfaces, thereby modifying $F_{Surf}$, although relaxation of bend distortion by means of twist along the $z$-axis results in our assumed profile for $\beta$ closer to the PMMA surface. (Keep in mind that $\beta$ still must vary from $-\gamma$ to $+\gamma$ over the entire cell thickness due to the boundary conditions imposed by the Sm-A regions). The “fitted” values for $W_\varphi$, of order a few tenths of an erg cm$^{-2}$, may at first appear to be larger than expected. However, previous measurements for anchoring strength coefficients using a somewhat weaker AFM rubbing force, more widely separated rub lines, and a shorter mesogen (pentylcyanobiphenyl) resulted in a value of $W_\varphi$ about an order of magnitude smaller than obtained here [17], and thus we believe these values (representing much stronger rubbing) to be quite reasonable. Although one also might expect that $W_\varphi$ for the two different herringbone angles $\gamma$ should be the same, their relatively small difference may be due to the asymmetric shape of the stylus, asymmetry of the forces on the cantilever, or our simplified theoretical and experimental modeling.

To summarize, we have presented quantitative experimental evidence of type-I bend-induced melting in a smectic liquid crystal. We also have presented a simple scaling model that accounts for the most important physics associated with the phenomenon, and which is in reasonable agreement with the experimental results. Although it’s beyond the scope of the present paper, a more detailed theory will be presented in the future.

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REFERENCES


FIGURES

FIG. 1. a) Schematic representation of rubbing pattern for $\gamma = 10^\circ$ (top) and $\gamma = 15^\circ$ (bottom). Period $P = 50 \mu m$. Rub line spacing projected onto the $x$-axis is $h = 196$ nm. b) Polarized micrograph of sample, showing three herringbone patterns and the spiral (upper right). The tiny square in the $\gamma = 20^\circ$ pattern is enlarged in panel c), which shows the intensity variation across the pixel interface.

FIG. 2. Measured intensity $I(y)$ vs. pixel number at $\Delta T = -24$ mK. (1 pixel = 0.145 $\mu m$). Solid line shows the fit using the error function.

FIG. 3. Fitted widths $L$ vs. $T - T_{NA}$ for $\gamma = 15^\circ$ (top) and $\gamma = 20^\circ$ (bottom). Theoretical curves are shown for various values of $W_\phi$ (in erg cm$^{-2}$). Typical error bars in $L$ are shown. Uncertainty in $T - T_{NA} = \pm 3$ mK.
\[ P = 50 \, \mu m \]

\[ \gamma = 10^\circ \]

\[ \gamma = 15^\circ \]

\[ \gamma = 20^\circ \]
\( \gamma = 15^\circ \)

\( \gamma = 20^\circ \)