

Bend-Induced Melting of the Smectic-A Phase: Analogy to a Type-I Superconductor

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(Received 9 June 2006; published 17 October 2006)

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.

DOI: 10.1103/PhysRevLett.97.167802

PACS numbers: 61.30.-v, 64.70.Md, 74.25.-q

The similarity between the smectic-A (Sm-A) liquid crystalline and the superconducting phases was first recognized by de Gennes [1]. 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 \hat{n} . Moreover, smectic fluctuations over a correlated fluctuation volume $\xi_{\parallel}\xi_{\perp}^2$ 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 ξ_{\parallel} and ξ_{\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 or twist expulsion in the presence of smectic order—in this case smectic fluctuations in the nematic phase—is the divergence of the elastic constants K_{33} and K_{22} on approaching the bulk nematic–Sm-A transition temperature T_{NA} [2]. Another consequence is the “twist grain boundary” phase [3,4], in which a *chiral* Sm-A phase breaks into domains with a well-defined rotation of the layer normal from one domain to the next. Yet another consequence of bend or twist expulsion is the “melted grain boundary” phase for a bent Sm-A liquid crystal [5]. For a region of Ginzburg parameter space $\kappa \equiv \lambda/\xi_{\parallel} \geq 1/\sqrt{2}$, where λ 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 κ space between the smectic analogs of type-I and type-II superconductors.

Owing to the inability to control \hat{n} on sufficiently small length scales, there have been few other experimental reports involving bend deformations in the Sm-A phase. But this situation has changed, as new nanomanipulation methods have been developed for 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” for control of \hat{n} on nanoscopic length scales [6,7]. In this Letter we describe an experiment in which herringbone 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 ($\kappa < \sim 1/\sqrt{2}$) liquid crystal [8], 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 $L(T)$ provides strong evidence that this system is type I, as predicted by the Landau-Ginzburg-de Gennes free energy, 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 polyamic acid PI-2555 (Dupont) and baked at 275 °C for 120 min. This slide then was rubbed using the stylus (Nanodevices Tap300) of a Topometrix Explorer AFM with three herringbone patterns, each $100 \times 100 \mu\text{m}$ in size, each occupying one quadrant in the xy plane, with one corner of each located near the origin. Two of the patterns, as well as the coordinates x , y , and z , are shown schematically in Fig. 1(a). 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

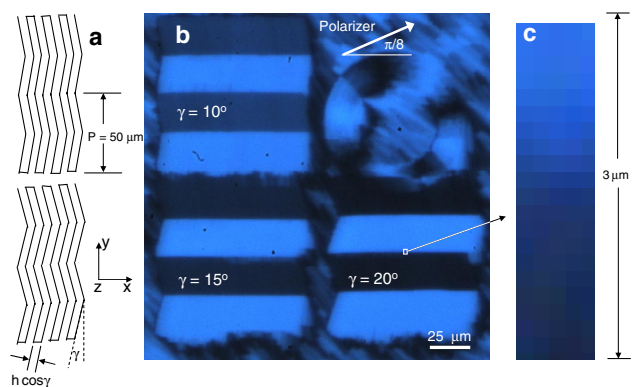


FIG. 1 (color online). (a) Schematic representation of rubbing pattern for $\gamma = 10^\circ$ (top) and $\gamma = 15^\circ$ (bottom). Period $P = 50 \mu\text{m}$. Rub line spacing projected onto the x axis is $h = 196 \text{ nm}$. (b) Polarized micrograph of sample, showing three herringbone patterns 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.

the lines was $h \cos \gamma$, where $h = 196$ nm. The half angle, γ , of the herringbone is equal to 20° , 15° , and 10° for the three patterns. (We note that the scribing conditions are not precisely identical for the three patterns due to the non-conical shape of the stylus, wear of the stylus, and asymmetry of the forces on the cantilever.) In the fourth quadrant a spiral easy axis pattern was scribed; this forces a weak bend distortion on the liquid crystal, which makes it easier to determine the bulk transition temperature T_{NA} during the course of the experiment. The opposing substrate was spin coated with polymethyl methacrylate (PMMA; $M_w = 101\,000$; $M_n = 39\,500$), which serves as a planar degenerate alignment agent [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 $t = (1.4 \pm 0.2)$ μm . The cell was placed into an oven, heated to a temperature of 76°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 an Olympus BX51 microscope with crossed polarizers, such that the pixel interfaces were oriented at an angle of $\pi/8$, i.e., 22.5° , with respect to the polarizer direction [Fig. 1(b)]. As the birefringence is approximately constant with temperature near T_{NA} , this angle was chosen to give an approximately linear change of intensity with director orientation angle β , where $-\gamma \leq \beta \leq \gamma$. The sample then was slowly cooled below $T_{NA} = 67^\circ\text{C}$ into the Sm-A phase. A calibration image was recorded at $T = T_{NA} - 450$ mK using a CCD camera having resolution 2048×2048 pixels, where each pixel corresponds to 0.145×0.145 μm in the sample [Fig. 1(b)]. Later we will see that the width L of the region over which \hat{n} varies at $T = T_{NA} - 450$ mK is less than 0.2 μm , and thus for all intents and purposes we can treat the director angle β as undergoing a discontinuous change of 2γ across the pixel interface at that temperature. T then was ramped upward at a rate of 0.67 mK s^{-1} . An image was recorded at 2 s intervals, corresponding to temperature increments of 1.33 mK.

The resulting images were examined to determine the bulk T_{NA} (with an uncertainty of ± 3 mK). The calibration image (using the $\gamma = 20^\circ$ scribed square) and images at temperatures closer to T_{NA} were analyzed, whereby the intensity $I(y)$ across the interface [Fig. 1(c)] was determined in one region across the central interface in each of the three ($\gamma = 20^\circ$, 15° , and 10°) scribed squares. To mitigate detector noise, $I(y)$ was taken as the average of five consecutive pixels along the x axis. Owing to diffrac-

tion 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 a Lorentzian with full width w at half maximum—this proved to be better than a Gaussian—as the “instrument function” and convoluted the Lorentzian with a step function, i.e., the calibration profile for $I(y)$ as if *no diffraction were present*. For $w = 1.28$ μm , 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 μm to w . Then, for all other images, this instrument function was convoluted with an *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 was adjusted to give the best approximation to the measured intensity profile; Fig. 2 shows one example. All 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} (as also would be the case if some other function, such as \tanh , were used). Thus, we are confident in data only for $T \geq T_{NA} - 200$ mK. Since $I \propto \sin^2(\frac{\pi}{4} + 2\beta)$, 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° ; data are not shown for $\gamma = 10^\circ$ because of the tendency to form domains—sometimes small—that are misaligned with the local easy axes below T_{NA} .

This experimentally observed variation L clearly is consistent with type-I behavior. Type-II behavior probably would result in a nonequilibrium “freeze-out” of a relatively wide spatial region in which bend is effected through disclinations. Let us now further consider the issue of type-I vs type-II behavior. Although the value of κ that results in a transition between type I and type II is not known accurately when thermal fluctuations are important [8]—this condition applies to our system—we note that Litster *et al.* measured the ratio $D(T)/K_{33}^0$ [10]. Here $D(T)$ is the

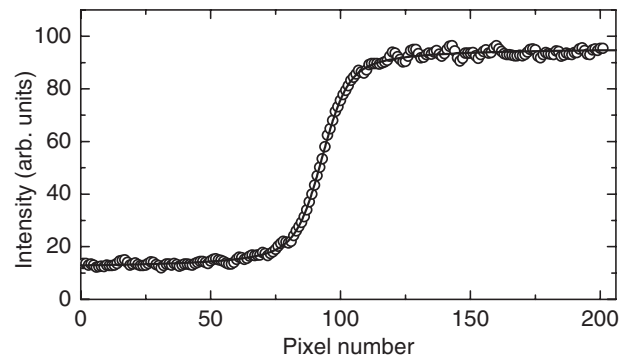


FIG. 2. Measured intensity $I(y)$ vs pixel number at $\Delta T = -24$ mK. (1 pixel = 0.145 μm). Solid line shows the fit using the error function.

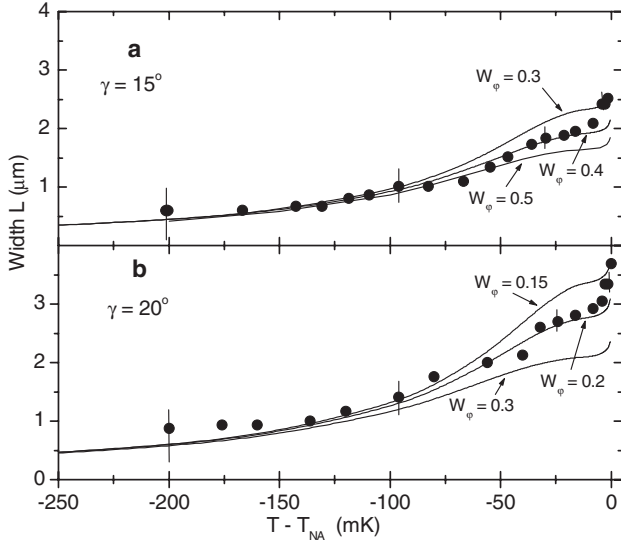


FIG. 3. Fitted widths L vs $T - T_{NA}$ for $\gamma = 15^\circ$ (top) and $\gamma = 20^\circ$ (bottom). Theoretical curves are shown for various values of W_ϕ (in erg cm^{-2}). Typical error bars in L are shown. Uncertainty in $T - T_{NA} = \pm 3$ mK.

elastic constant associated with director tilt relative to the layer normal and K_{33}^0 is the background nematic elastic constant far from T_{NA} . We take $K_{33}^0 = 7 \times 10^{-7}$ dyn [10]. Moreover, since $K_{33}(T)$ scales approximately as $\xi_{\parallel}(T)$ near T_{NA} and the ratio of bare correlation lengths below (ξ_0^-) and above (ξ_0^+) T_{NA} for a 3D-XY system is $\xi_0^-/\xi_0^+ = 3$ [11], we can use Litster's data for $K_{33}^N(T)$ in the nematic phase to obtain $K_{33}^{\text{Sm-A}}(T) [\approx 3K_{33}^N(T)]$ at the corresponding reduced temperature $|\tau| \equiv \Delta T/T_{NA}$ in the Sm-A phase.

Thus the bend penetration length $\lambda(T) \approx \sqrt{3K_{33}^N(T)/D(T)}$. Finally, using correlation length data above T_{NA} [10], applying the ratio $\xi_0^-/\xi_0^+ = 3$ at the corresponding value $|\tau|$ below T_{NA} , we find that the Ginzburg parameter $\kappa = \lambda/\xi_{\parallel}^- = \lambda/3\xi_{\parallel}^+$ decreases smoothly from 0.19 at $|\tau| \sim 10^{-2}$ to $\kappa = 0.09$ at $|\tau| \sim 10^{-4}$. These small values are consistent with type-I behavior in the experimentally relevant region $|\tau| < 10^{-3}$. Moreover, the small values of λ (8.5 and 107 nm at $|\tau| \sim 10^{-2}$ and 10^{-4}) relative to L indicate that \hat{n} varies in orientation only in a *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., $F_{\text{Sm-A}}$ 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. The de Gennes 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 [12,13] and can be written as $F = k_B T_c X_{\pm} R^{-1} \xi^{-d}$, where k_B is Boltzmann's constant; T_c is the critical temperature (here equal to T_{NA}), ξ is the correlation length above T_c , i.e., $\xi^+(\tau)$, d is the dimensionality, $R \equiv \alpha(1-\alpha)(2-\alpha)$, α is the specific heat critical exponent, and X_{\pm} are constants for a given universality class 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 $k_B X_{\pm} \xi^{-d} \alpha^{-1} |\tau|^{-2}$ [13]. Owing to the anisotropy of the nematic and Sm-A phases, there are two correlation lengths ξ_{\parallel} and ξ_{\perp} above T_{NA} (which are known experimentally [10]), yielding $F_{\text{Sm-A}} = k_B T_{NA} X_- R^{-1} \xi_{\parallel}^{-1} \xi_{\perp}^{-2}$, with $X_- \approx 0.031$ [14] and $\alpha = 0.18$ for 8OCB [14,15].

Below T_{NA} , regions of large bend distortion melt into the nematic phase and have an elasticlike energy cost. Small bend distortions have been treated theoretically [16], although nonperturbative bend has not. Here we approach this problem with a simple de Gennes-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 ϕ 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 2γ is the total angular bend over the distance L [1]. The free energy density is given by $\frac{1}{2} \times [C_{\parallel} |\partial\psi/\partial y|^2 + C_{\perp} |(\nabla_{\perp} + 2iq_0\hat{x}y\gamma/L)\psi|^2 - |a||\psi|^2]$ [2], where C_{\parallel} 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 ℓ is the smectic layer thickness. We include the effect of nonquadratic 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 is identical to the Hamiltonian of a charged particle in a magnetic field in the Landau gauge [17]. We therefore can diagonalize it using techniques applied to the Landau level problem, and find that the eigenvalues are Landau levels with energies $[(m + 1/2)\omega - |a| + C_{\perp}k_z^2]$, where $\omega = (C_{\parallel}C_{\perp})^{1/2}4q_0\gamma/L$, 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_z is the wave vector along the z axis. A detailed calculation of the implied free energy is beyond the scope of this Letter. Here we simply note that above the critical temperature we have eigenvalues (for plane waves) of $C_{\parallel}k_y^2 + C_{\perp}(k_z^2 + k_x^2) + a_n$, 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 $X_+ \approx 0.032$ [14]. As is known for the magnetic problem, the discrete sum over m approximates the continuous integrals over k_x, k_y . 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 $\frac{1}{4}$. The result is $F_{\text{Nem}} \sim k_B T_{NA} X_+ R^{-1} \xi_{\parallel}^{1/2} \xi_{\perp}^{-1/2} (q_0 \gamma / L - \xi_{\parallel}^{-1} \xi_{\perp}^{-1})^{3/2}$. Note that the elasticity is non-Hookean and includes only the divergent part due to Sm-A fluctuations.

The surface anchoring contribution F_{surf} to the energy (per unit volume) to lowest order is $\frac{1}{2l} W_{\varphi} [\gamma(y) - \beta(y)]^2$ [18], where W_{φ} is the azimuthal anchoring strength coefficient and is not expected to have important pretransitional behavior [19]. 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

$$f = -k_B T_{NA} X_- R^{-1} \xi_{\parallel}^{-1} \xi_{\perp}^{-2} (P - L) \\ + k_B T_{NA} X_+ R^{-1} \xi_{\parallel}^{1/2} \xi_{\perp}^{-1/2} (q_0 \gamma / L - \xi_{\parallel}^{-1} \xi_{\perp}^{-1})^{3/2} L \\ + W_{\varphi} \gamma^2 L / 6l.$$

We then minimize f with respect to L , yielding an implicit equation for L in which all parameters except for W_{φ} are known. Figure 3 shows calculated curves for L vs ΔT for several different values of W_{φ} . 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_{φ} 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 β closer to the PMMA surface. (Keep in mind that β 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_{φ} , of order a few tenths of an erg cm^{-2} , at first may appear to be large. However, previous measurements for W_{φ} using a weaker AFM rubbing force, more widely separated rub lines, and a shorter mesogen (pentylcyanobiphenyl) resulted in a value of W_{φ} about an order of magnitude smaller than obtained here [20]. Thus we believe these values (for much stronger rubbing) are quite reasonable. Although one also might expect that W_{φ} for the two different angles γ should be the same, that $W_{\varphi}(\gamma = 15^\circ) > W_{\varphi}(\gamma = 20^\circ)$ may be due to the not-quite-equivalent scribing conditions described earlier. Finally, domains may appear for small γ because, despite a possible increase in W_{φ} , F_{surf} is small for small herringbone angles. Therefore nucleation and/or small temperature gradients may result in such domains.

To summarize, we have presented semiquantitative experimental evidence of type-I bend-induced melting in a smectic liquid crystal that is in reasonable agreement with our simple scaling model.

We thank Professor Patrick Mather, Qiongyu Guo, Dr. Ronald Pindak, and Professor Carl W. Garland for useful discussions. This work was supported by the NSF under Grant No. DMR-0345109, by the U.S. Department of Energy under Grant No. DE-FG02-01ER45934, and by the DOE Nanoscale Science, Engineering, and Technology program at Brookhaven National Laboratory under Contract No. DE-AC02-98CH10886.

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