

## Liquid-Crystal Fréedericksz Transition and Surface-Induced Smectic Ordering

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An anomalous increase is observed in the Fréedericksz critical field in a very thin, homeotropically aligned liquid-crystal cell near the second-order nematic-smectic-*A* phase transition. The anomaly is analyzed in terms of smectic layering induced at the two surfaces of the cell, decreasing the effective thickness of the nematic region and thereby increasing the effective critical field.

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When a sufficiently intense magnetic field is applied perpendicular to the director of an aligned nematic liquid crystal sandwiched between two parallel substrates, the director reorients in what is commonly known as a Fréedericksz transition.<sup>1</sup> This transition, which involves a tradeoff between magnetic and elastic forces, occurs at a critical field  $H^*$  given by

$$H^* = (\pi/l)(K_i/\chi_a)^{1/2}, \quad (1)$$

where  $l$  is the sample thickness,  $K_i$  the relevant elastic constant, and  $\chi_a$  the volume-susceptibility anisotropy. This form for the critical field, however, is based upon two assumptions: that the director remain rigidly anchored at the two surfaces (i.e., perpendicular for the case of the bend elastic constant  $K_3$ ) and that the physical properties of the liquid crystal are uniform over the entire sample. For wide samples (typically  $l > 50 \mu\text{m}$ ), anchoring plays only a minor role and the second assumption is generally valid; for narrow samples, however, the effects of surfaces need to be examined more closely. When anchoring is nonrigid Fréedericksz deformations of wave vector  $q < \pi/l$  can occur,<sup>2</sup> resulting in a fractional reduction of the expected critical field equal to  $2K_3/lB$ , where  $B$  is the anchoring strength coefficient. Only when  $B \rightarrow \infty$  does the rigid-anchoring case hold. Naemura, in fact, determined  $B$  by measuring  $H^*$  in narrow cells and using known values of  $K_3$  obtained from wide-cell measurements.<sup>3,4</sup> More recently, I used this technique<sup>5</sup> in conjunction with an ultranarrow cell ( $l < 2.5 \mu\text{m}$ ) to obtain the temperature dependence of  $B$  in the nematic phase.

In addition to nonrigid anchoring, spatial inhomogeneities of various physical parameters (including, but not limited to, the nematic order parameter  $S$ ) need to be considered. It is well established that surfaces can induce a small incremental increase in  $S^{6-8}$ ; nevertheless, such effects are limited to distances of order  $\xi_N$ , the nematic correlation length.

Since  $\xi_N$  is typically less than  $0.015 \mu\text{m}$ , the effects on  $H^*$  due to inhomogeneities in  $S$  are negligible, even in cells of thickness 2 to  $3 \mu\text{m}$ .

In two recent publications Als-Nielsen, Christensen, and Pershan<sup>9</sup> and Pershan and Als-Nielsen<sup>10</sup> reported the results of an elegant x-ray experiment at the free surface of a nematic liquid crystal near the onset of a smectic-*A* phase transition. From their scattering data they inferred a surface structure composed of two parts: a surface-induced smectic density wave decaying exponentially into the liquidlike nematic bulk, as well as an additional nonexponential term. In fact, Rosenblatt and Ronis predicted<sup>11</sup> smectic order induced at a free surface in the context of a lattice model solved in the mean-field approximation. Since the nematic-smectic-*A* (NA) transition can be second order *with diverging correlation lengths*, one also needs to consider the effects on  $H^*$  of surface-induced smectic-order-parameter inhomogeneities in the nematic phase. Thus, in light of the free-surface results, I have performed a Fréedericksz measurement in an ultranarrow, bend-configured sample and analyzed the data in terms of substrate-induced smectic-ordering. My central result is that an anomalous increase in the critical field was observed near  $T_{\text{NA}}$ , the nematic-smectic-*A* second-order transition temperature. This behavior is ascribed to smectic layering near the rigid substrates, resulting in a decrease in the effective sample thickness. This is the first report of smectic ordering induced at a wall, an effect otherwise inaccessible to nonperturbative probes such as x rays and neutrons.

In the smectic-*A* phase, the molecules prefer to remain parallel to the density wave vector  $\vec{Q}_0$ , i.e., perpendicular to the smectic "layers." (In fact, just above  $T_{\text{NA}}$  short-range smectic ordering contributes a diverging term to the bend and twist elastic constants.<sup>1</sup>) Thus, if smectic order were induced by a surface in a perpendicularly aligned nematic liquid crystal, a transverse magnetic field  $\vec{H}$  would be un-

able to deform the induced smectic region. For a Fréedericksz experiment in a  $K_3$  configuration, the effective thickness of the nematic cell would therefore be reduced by order  $2\xi$ , where  $\xi$  is the smectic correlation length parallel to  $\bar{Q}_0$ . In a wide cell,  $l - 2\xi \approx l$  (except *very* close to  $T_{NA}$ ) and the critical field  $H^*$  is given approximately by Eq. (1). In narrow samples, however,  $2\xi$  can be significant relative to  $l$  (especially near the second-order NA transition, where  $\xi$  is diverging and is typically of order  $0.1 \mu\text{m}$  within  $100 \text{ mK}$  of  $T_{NA}$ ) and thus surface-induced smectic ordering could substantially increase  $H^*$ .

The experiment was performed in two steps: measurement of  $H_W^*$  vs  $T$  in a wide cell of thickness  $l_W$  [for which surface effects are negligible and Eq. (1) holds] and measurement of  $H_N^*$  vs  $T$  in a narrow cell of thickness  $l_N$ . Samples of octylcyanobiphenyl (8CB) were obtained from BDH Chemicals and used without further purification. The cells consisted of two  $\lambda/20$  fused-silica windows separated by Mylar spacers and adjusted for optimum parallelism. The windows were treated with the surfactant dodecyltrimethylammonium chloride to achieve perpendicular molecular alignment. Cell thickness was measured by an interferometric scheme<sup>5</sup> and found to be  $l_N = 2.627 \pm 0.015 \mu\text{m}$  for the narrow cell and  $l_W = 76.2 \pm 0.3 \mu\text{m}$  for the wide cell. The oven and temperature controller are described elsewhere.<sup>5</sup>

Two birefringence schemes were used to obtain the critical fields. For the wide cell, where the optical phase shift (integrated birefringence)  $\alpha \geq 30\pi$ , light from a Spectra Physics model 120B He-Ne laser (attenuated to  $0.8 \text{ mW}$ ) passed consecutively through a polarizer, perpendicularly through the sample, an analyzer, and into a photodiode detector. The polarizer and analyzer were oriented at  $45^\circ$  with respect to the field  $\bar{H}$ . For  $H < H_W^*$ , the intensity at the detector was zero. Above  $H_W^*$ , the intensity was nonzero and passed through several minima and maxima as the field was swept upward at approximately  $60 \text{ G/min}$ .  $\alpha$  vs  $H$  was obtained from the intensity extrema and  $H_W^*$  obtained with an accuracy of  $\pm 1\%$  by extrapolation to  $\alpha = 0$ . For the narrow sample, where  $\alpha < \pi$ , the birefringence was measured using an automatically compensating modulated Pockels cell, described in detail elsewhere.<sup>5</sup> Again,  $H_N^*$  was obtained to better than  $1\%$  by extrapolation of  $\alpha$  vs  $H$  to  $\alpha = 0$ . Near the critical field,  $H$  was typically swept at about  $4000 \text{ G/min}$  to obtain values of  $H_N^*$  ranging between  $30$  and  $100 \text{ kG}$ .

Critical fields versus  $T$  for the two samples were compared at their respective reduced temperatures

$T - T_{NA}$ , where  $T_{NA}$  was obtained for each sample to  $\pm 15 \text{ mK}$  by extracting the divergent part of  $K_3$  [cf. Eq. (1)] and fitting  $K_3^{-1/\nu}$  vs  $T$ .<sup>12</sup>  $\nu$ , the critical exponent for  $\xi$ , was taken to be  $0.67$ .<sup>13</sup>

In the absence of surface-induced ordering,  $H^*$  is a function of temperature only, independent of  $l$  [cf. Eq. (1)]. Nevertheless, from the critical-field data one can define a quantity  $\Phi$  such that

$$\Phi = l_N H_N^* / l_W H_W^* - 1, \quad (2)$$

where  $\Phi$  represents the fractional increase in  $H^*$  above the expected critical field as a result of surface order. Far above  $T_{NA}$  where  $\xi$  is small,  $\Phi$  was found to be zero to within the experimental error. Although in this region  $\Phi$  is expected to be dominated by possible nonrigid-anchoring effects,<sup>2-5</sup> the data clearly indicate very rigid boundary conditions. This is consistent with other cyanobiphenyl compounds I have studied<sup>14</sup> and considerably larger than values for methoxybenzylidene butylamine.<sup>4,5</sup> It is thus possible to neglect nonrigid anchoring effects from further consideration. For  $T_{NA} + 0.1 \text{ K} \leq T \leq T_{NA} + 0.8 \text{ K}$  an anomalous increase in  $H_N^*$  was noted;  $\Phi$  is plotted versus temperature in Fig. 1. The small error bar in  $T$  represents both temperature drift during the

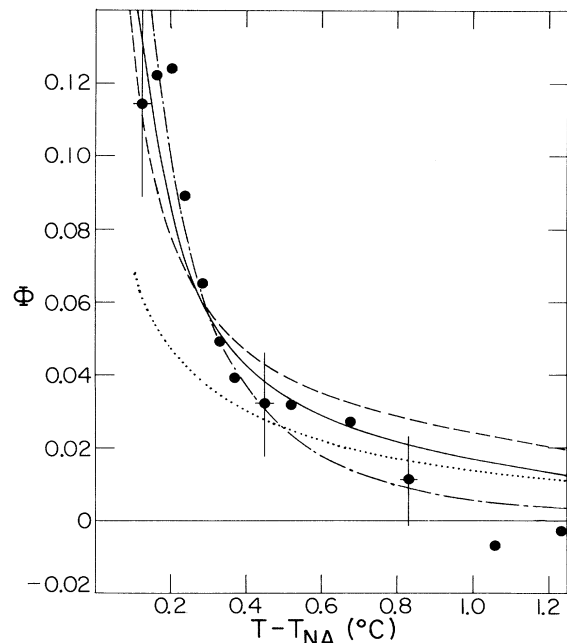


FIG. 1. The fractional increase  $\Phi$  [cf. Eq. (2)] in the critical field  $H^*$  for the narrow sample ( $l_N = 2.63 \pm 0.015 \mu\text{m}$ ) vs temperature. Typical error bars are shown. Equation (8) is plotted for three different forms for  $D_0$ ; see text for details. Dotted line is a plot of  $2\xi/l_N$ .

measurements and a possible small systematic error in precisely locating  $T_{NA}$ . The larger error bar in  $\Phi$  arises from the uncertainty in measuring  $H^*$  as well as the error  $\Delta T$  in  $T - T_{NA}$  in one sample relative to the other. The former error is small, whereas the latter, which is partially systematic in nature, can be large (especially near  $T_{NA}$ ) and is of order  $(\Delta T/H_w^*)dH_w^*/dT$ . Values of  $\Phi$  are not sufficiently reliable for  $T_{NA} \leq T \leq T_{NA} + 0.1$  K because of temperature control effects and effects arising from uncertainty in  $T_{NA}$ .

Since the data in Fig. 1 indicate that  $H^*$  does not scale as  $1/l$ , the effects of surface-induced smectic ordering need to be examined. The free energy of deformation is given by

$$F = \frac{1}{2} \int_0^l [K_3 \dot{\theta}^2 - \chi_a H^2 \theta^2 + D(z) \theta^2] dz, \quad (3)$$

where  $\chi_a$  and  $K_3$  are assumed to be spatially uniform, the term  $D(z) \theta^2$  is the energy required to tilt the director by an angle  $\theta$  relative to the layer normal in a smectic- $A$  phase,<sup>13</sup> and the derivative is taken with respect to  $z$ . In a de Gennes model<sup>15</sup>  $D \propto |\psi|^2$ , where  $\psi$  is the smectic order parameter; thus, for surface-induced smectic order decaying into the bulk,  $D(z) = D_0 \{\exp(-2z/\xi) + \exp[-2(l-z)/\xi]\}$ , where both  $D_0$  and  $\xi$  are temperature dependent. (This model does not account for the small nonexponential component of surface ordering by Pershan and Als-Nielsen.<sup>10</sup>)

The Euler-Lagrange equation resulting from minimizing Eq. (3) is

$$-K_3 \ddot{\theta} - \chi_a H^2 \theta + D_0 (e^{-2z/\xi} + e^{-2(l-z)/\xi}) \theta = 0. \quad (4)$$

Near the two walls the  $D_0$  term dominates; on the other hand, the  $\chi_a H^2$  term dominates in the middle region as long as  $\xi < l$ . Thus Eq. (4) is solved in three separate regions and the solutions are asymptotically matched. Near  $z=0$

$$\theta = C_1 \left[ \frac{-K_0(\lambda)}{I_0(\lambda)} I_0(\lambda e^{-z/\xi}) + K_0(\lambda e^{-z/\xi}) \right], \quad (5)$$

where  $C_1$  is a constant,  $\lambda \equiv (\xi^2 D_0 / K_3)^{1/2}$ ,  $I_0$  and  $K_0$  are modified Bessel functions, and a boundary condition of  $\theta(z=0) = 0$  is assumed. A similar solution is obtained near  $z=l$ . As a result of symmetry about  $z=l/2$ , the solution in the center is

$$\theta = C_2 \cos[(\chi_a H^2 / K_3)^{1/2} (z - l/2)]. \quad (6)$$

With the imposed symmetries,  $C_1$  can be written in terms of  $C_2$  and the critical field  $H^*$  can be obtained

by asymptotically matching the two solutions, Eqs. (5) and (6). Thus,  $C_1 = C_2 \xi (\chi_a H^{*2} / K_3)^{1/2} \sin[l \times (\chi_a H^{*2} / K_3)^{1/2} / 2]$  and

$$\cot[(\chi_a H^{*2} / K_3)^{1/2} l / 2] = -\xi (\chi_a H^{*2} / K_3)^{1/2} \Lambda, \quad (7)$$

where  $\Lambda \equiv [K_0(\lambda) / I_0(\lambda) + \ln \lambda + \gamma - \ln 2]$  and Euler's constant  $\gamma \approx 0.5772$ . For  $l(\chi_a H^{*2} / K_3)^{1/2} \approx \pi$  (i.e., for small surface-induced smectic perturbations), the critical field  $H^*$  can be found by performing a perturbation expansion on Eq. (7); to first order this gives  $H^* \approx \pi (K_3 / \chi_a)^{1/2} / l (1 + 2\xi \Lambda / l)$ . For  $l = l_w$ ,  $2\xi / l_w \ll 1$  and  $\pi (K_3 / \chi_a)^{1/2} / l_w$  can be associated with  $H_w^*$ . Thus, we finally find that

$$\Phi \approx \frac{2\xi}{l_w} \left[ \frac{K_0(\lambda)}{I_0(\lambda)} + \ln \lambda + \gamma - \ln 2 \right]. \quad (8)$$

The fractional increase in the narrow-cell critical field is just the fraction of the cell over which smectic ordering is important.

As a result of the slowly varying terms involving  $\lambda$  [not to mention the approximations needed to arrive at Eq. (8)], the divergence of  $\Phi$  is not a precise power law. In Fig. 1, Eq. (8) is fitted using three different forms for  $D_0$ , where  $\xi$  was obtained from Ref. 13 and  $K_3$  from the wide-cell measurements. The solid trace is a least-squares fit assuming  $D_0$  is constant;  $D_0$  is found to be  $(2 \pm 1) \times 10^6$  erg/cm<sup>3</sup>, a value typically found well into the smectic- $A$  phase.<sup>13</sup> The origin of the large uncertainty is the logarithmic dependence of Eq. (8) on  $D_0$ , coupled with the scatterer in the data. The dashed curve, which is consistent with the free-surface results of Pershan and Als-Nielsen,<sup>10</sup> takes  $D_0 = d_0 (T / T_{NA} - 1)^{2-2\nu}$ , where  $d_0 = (2 \pm 1) \times 10^8$  ergs/cm<sup>3</sup>. (To obtain this form for  $D_0$ , I assume that  $D_0 = \text{const} \times |\psi_0|^2$ , where  $\psi_0$  is the smectic order parameter at the wall. It is implicitly assumed that the exponent  $\eta_{||} = 0$ , which is an excellent approximation.<sup>15</sup>) At a temperature  $T - T_{NA} = 0.2$  K, for example,  $D_0$  would be equal to  $1.6 \times 10^6$  ergs/cm<sup>3</sup> in this model. Finally, the dash-dotted line assumes that  $D_0 = d_0 (T / T_{NA} - 1)^{-2\nu}$ , where  $d_0$  is found to be  $(2 \pm 1) \times 10^2$  ergs/cm<sup>3</sup>; unlike Ref. 10, this case involves a constant coefficient in the smectic-surface coupling term in the free energy. At  $T - T_{NA} = 0.2$  K,  $D_0$  would be about  $3.5 \times 10^6$  ergs/cm<sup>3</sup> in this model. Within error bars all three models provide reasonable agreement with experimental results, with the dash-dotted line being perhaps the best. Nevertheless, because of the weak dependence of Eq. (8) on  $D_0$ , the results can-

not distinguish among the three models.

The origin of substrate-induced smectic order is similar to that at a vapor interface, although with a few subtle differences. At a rigid wall, excluded-volume and other orientation-dependent surface interactions potentially play a more significant role in the free energy than in the free-surface case. The effects, however, may enter with opposite signs; for example, the presence of a surfactant, especially one with a partially flexible tail, mitigates the influence of the substrate. Unlike the free-surface case, then, the value of  $|\psi_0|$  (and thus  $D_0$ ) at the wall depends upon the surfactant used, as well as its coverage. Fortunately,  $\Phi$  is only a weak function  $D_0$  [cf. Eq. (8)] and is effectively given by  $2\xi/l_N$  times some constant (of order 1) which depends weakly on the surface treatment.

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