

Dynamics of the smectic-*C* to -*A* transition in freely suspended thin films

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We consider the critical dynamics of the smectic-*C* to -*A* transition in freely suspended thin films. Close to the transition the films can be considered literally two-dimensional, and at sufficiently long wavelengths, the system should be equivalent to a two-dimensional *XY* model. The dynamics of this system are very similar to those of the hexatic-to-isotropic melting previously studied by Zippelius, Halperin, and Nelson [Phys. Rev. B 22, 2514 (1980)]. However, the order parameter in the smectic films is considerably easier to probe experimentally. We discuss the experimental predictions of the present theory and suggest possible experiments.

Freely suspended thin liquid-crystal films have proven to be very valuable experimental systems in which two-dimensional phase transitions are studied. These films can be made as thin as two molecular layers, making them literally two dimensional, and as thick as hundreds of layers to allow the study of dimensionality crossover effects. Furthermore, the absence of an underlying substrate leads one to hope that the experimental systems will be described by the isotropic theories of two-dimensional phase transitions, including those of Kosterlitz and Thouless¹ and of Halperin, Nelson, and Young.^{2,3}

The films exhibit a variety of smectic phases and associated phase transitions. In this paper, we consider the dynamics of the smectic-*C* to -*A* transition. We have in mind the films made of *p*-(*n*-decyloxybenzylidene)-*p*'-amino-(2-methylbutylcinnamate (abbreviated as DOBAMBC, with the chemical formula C₃₁H₄₄NO₃), which have been studied by several groups.⁴⁻⁹ In the smectic-*C* phase, the rodlike molecules are tilted at an average tilt angle $\langle\theta\rangle$, with the tilt direction in the plane of the layers specified by a polar angle

ϕ . In the *A* phase $\langle\theta\rangle=0$, or, alternatively, $\langle\theta\rangle\neq 0$, but the polar angles ϕ are uncorrelated over long distances. The order parameter for this transition can be chosen as a two-dimensional vector \mathbf{c} lying in the plane of the layers with components

$$c_x = \sin\theta \cos\phi, \quad (1a)$$

$$c_y = \sin\theta \sin\phi. \quad (1b)$$

For a film of infinite extent in the *x-y* plane $\langle\mathbf{c}\rangle=0$, even in the *C* phase, because of the Mermin-Wagner-Hohenberg theorem.^{10,11} However, in the finite-size experimental samples, and in the presence of an external uniform electric field, $\langle\mathbf{c}\rangle\neq 0$ in the *C* phase.

As discussed by Pelcovits and Halperin,¹² fluctuations in the tilt angle can be neglected at long wavelengths in the *C* phase. Fluctuations in the orientational order are then described solely by ϕ . The remaining hydrodynamic variables are $\delta n(\mathbf{r})=n(\mathbf{r})-n_0$, the fluctuation of the molecular number density $n(\mathbf{r})$ about its equilibrium value n_0 , and the momentum density $\mathbf{g}(\mathbf{r})$. The free energy can be expanded in terms of the small fluctuations of these variables:

$$F = \frac{1}{2} \int d^2r \left[K_b(\theta) (\partial_x \phi)^2 + K_s(\theta) (\partial_y \phi)^2 + B \left(\frac{\delta n}{n_0} \right)^2 + \frac{\mathbf{g}^2}{mn_0} \right] + \frac{G}{2} \int d^2r \int d^2r' \frac{1}{|r-r'|} [\partial_x \phi(r)] [\partial_x \phi(r')]. \quad (2)$$

The first two terms are the elastic energies associated with bend and splay deformations, respectively. We have assumed that the local tilt is in the *x* direction, and have expanded the energies to second order in ϕ . The elastic constants K_b and K_s are both proportional to $\sin^2\theta_{MF}$, where θ_{MF} is the mean-field value of the tilt angle.¹² (Near T_{CA} , the *C-A* phase transition temperatures K_b and K_s acquire small additive terms which are not proportional to $\sin^2\theta_{MF}$ and are due to the presence of bound pairs of disclinations). The third and fourth terms in (2) describe the compressional and kinetic energies, respectively. The quantity m is the molecular mass. The last term in (2) represents the dipolar

interaction present in ferroelectric liquid crystals,^{6,12} which we have expanded to lowest order in ϕ . We have neglected the lowest-order coupling between ϕ and δn , first introduced in Ref. 13, since the hydrodynamic mode structure is unaffected by this term. Aside from the absence of this term and the presence of the dipolar interaction, (2) is identical to the nematic free energy of Ref. 13 and hexatic free energy of Ref. 14.

The equations of motion for the hydrodynamic variables appropriate for the free energy (2) can be readily adapted from Refs. 13 or 14 with the results

$$\partial_t(\delta n) = -\frac{1}{m} \nabla \cdot \mathbf{g}, \quad (3a)$$

$$\partial_t \mathbf{g} = -\frac{B}{n_0} \nabla(\delta n) - \frac{1}{2} (\mathbf{z} \times \nabla) \left[K_b \partial_x^2 \phi + K_s \partial_y^2 \phi - G \int d^2r' \left(\frac{\partial^2}{\partial x \partial x'} \frac{1}{|r-r'|} \right) \phi(r') \right] + \frac{\eta}{mn_0} \nabla^2 \mathbf{g} + \frac{\zeta}{mn_0} \nabla(\nabla \cdot \mathbf{g}), \quad (3b)$$

$$\partial_t \phi = -\frac{1}{2mn_0} \partial_y g_x + \frac{1}{2mn_0} \partial_x g_y + \Gamma \left[K_b \partial_x^2 \phi + K_s \partial_y^2 \phi - G \int d^2r' \left(\frac{\partial^2}{\partial x \partial x'} \frac{1}{|r-r'|} \right) \phi(r') \right], \quad (3c)$$

where η and ζ are shear and bulk viscosities, z is the normal to the film, and Γ is a relaxation rate for ϕ fluctuations. In writing (3) we have made several simplifying assumptions which will not affect the critical dynamics. We have set the molecular shape parameter λ (see Refs. 13 and 15) equal to zero, and we have used an isotropic dissipative stress tensor characterized by η and ζ . Given the uniaxial symmetry of the system, a more general dissipative stress tensor with four independent components is allowed.¹³

There are four modes associated with (3). (We have neglected local temperature fluctuations and the corresponding heat diffusion mode). Two modes are longitudinal (i.e., \mathbf{g} parallel to the wave vector \mathbf{q}) and correspond to ordinary sound waves with frequencies¹⁴

$$\omega_l^\pm(\mathbf{q}) = \pm c_l q - \frac{i}{2} D_l q^2, \quad (4)$$

where

$$c_l = \left(\frac{B}{mn_0} \right)^{1/2} \quad (5)$$

and

$$D_l = (\eta + \zeta)/mn_0. \quad (6)$$

Relaxation of our assumption of the isotropy of the dissipative stress tensor would introduce anisotropy into the damping constant D_l .¹³ The two transverse modes (\mathbf{g} perpendicular to \mathbf{q}) involve the transverse momentum and the field ϕ . These modes can be either diffusive or propagating. Experimentally,⁶ it appears that these modes are diffusive, and we display only that possibility.¹⁴

$$\omega_t^\pm = -i \frac{q^2}{2} \left[\frac{\eta}{mn_0} + \Gamma K(\mathbf{q}) \pm \sqrt{-\Delta} \right], \quad (7)$$

where,

$$K(\mathbf{q}) = K_b \left[\frac{q_x^2}{q^2} \right] + K_s \left[\frac{q_y^2}{q^2} \right] + G \frac{q_x^2}{q^3}, \quad (8)$$

and

$$\Delta = - \left[\Gamma K(\mathbf{q}) - \frac{\eta}{mn_0} \right]^2 + \frac{K(\mathbf{q})}{mn_0}. \quad (9)$$

In the A phase, (2) and (3) would be replaced by corresponding expressions with $K_s = K_b = G = 0$ (i.e., an isotropic liquid). The ordinary sound modes are the same as in the C phase (4). The two transverse modes (7) are replaced by a single diffusive shear mode

$$\omega_t = \frac{i\eta}{mn_0} q^2, \quad (10)$$

which can be obtained from (7) by setting $K(\mathbf{q}) = 0$.

We now discuss the critical dynamics in the vicinity of T_{CA} . Since the stiffness $K(\mathbf{q})$ is finite at T_{CA} ,¹⁶ the C phase modes (4) and (7) should be qualitatively correct even at T_{CA} . There are, however, a number of crossovers occurring as a function of \mathbf{q} . First, as $q \rightarrow 0$, $K_b(\theta) - K_s(\theta) \rightarrow 0$ at a wave-vector scale ξ_K^{-1} of magnitude,¹²

$$\xi_K^{-1} \approx a^{-1} \exp \left[\frac{-\pi [K_s(\theta) K_b(\theta)]^{1/2}}{k_B T} \right], \quad (11)$$

where a is a short-wavelength cutoff, e.g., the film thick-

ness. In the two-layer films made of DOBAMBC, $\xi_K \approx 500$ Å. For $q \ll \xi_K^{-1}$, the system is equivalent to a two-dimensional isotropic XY model with dipolar interactions. The dipolar interactions are irrelevant to the long-wavelength behavior until $q \approx \xi_G^{-1}$, where¹²

$$\xi_G^{-1} \sim a^{-1} G^{1/(1-\eta)}. \quad (12)$$

In (12), η is the critical exponent associated with the two-dimensional XY model, ranging from 0 at $T = 0$ to $\frac{1}{4}$ at T_{CA} . Thus, for $q \ll \xi_G^{-1}$, the stiffness parameter $K(\mathbf{q})$ defined in (8) can be replaced by K , the common value of K_s and K_b at long wavelengths. The dipolar forces, however, do ultimately control the critical behavior. There is another wave-vector scale $\xi^{-1}(T)$ associated with the disclinations in the system, which behaves as¹⁷

$$\xi^{-1}(T) \sim a^{-1} \exp \left[\frac{-\text{const}}{|T_{CA} - T|^{1/2}} \right]. \quad (13)$$

There will always exist a temperature T_x such that $\xi^{-1}(T_x) = \xi_G^{-1}$. For $T_x < T < T_{CA}$ the dipolar forces will dominate the critical behavior. However, estimates of the parameters appropriate to the films made of DOBAMBC suggest that this region is inaccessible to experimental probes due to the extremely small value of the molecular dipole moment.¹²

Thus, while the dipolar forces may be apparent in the mode structure (7) deep in the C phase, we will assume that ξ_G is sufficiently large, so that we may neglect G in our discussion of the critical dynamics. For $T < T_{CA}$, but not too much less than T_{CA} , we have the modes (7) with $K(\mathbf{q}) = K$. For $T > T_{CA}$, qualitatively similar modes will persist provided $q > \xi_+^{-1}(T)$, where $\xi_+(T)$ is the XY correlation length,¹

$$\xi_+(T) \sim a \exp \left[\frac{\text{const}}{|T - T_{CA}|^{1/2}} \right]. \quad (14)$$

For $q < \xi_+^{-1}(T)$, a finite density of free disclinations destroys the quasi-long-range C order and reduces the number of modes by one [i.e., the two modes in (7) are replaced by the single mode (10)]. This reduction can be studied by incorporating disclinations into the hydrodynamic equations. Instead of using ϕ as a hydrodynamic variable, it is convenient¹⁴ to introduce a "superfluid velocity" $\mathbf{V} = \nabla \phi$, which is a smooth function except at the sites of the disclinations. Aside from the difference in disclination strengths (multiples of $\frac{1}{2}$ in the hexatic case, and multiples of unity here), the analysis is identical to that of Sec. VI of Ref. 14. We will not reproduce the analysis; rather, we will simply quote the results and discuss their implications here.

With the introduction of \mathbf{V} , there are now five modes to consider. Two of the modes are ordinary sound and have the same form as in (4). They are unaffected by disclinations because of the linear form of the hydrodynamic equations. Mode coupling nonlinearities would presumably make some small differences. The equations for \mathbf{V} and the transverse part of \mathbf{g} [(6.9), (6.14), (6.29), and (6.30) of Ref. 14] can be solved with the following results:

(1) The transverse part of \mathbf{V} has a characteristic frequency

$$\omega_{V_T} = -i(Dq^2 + \gamma_0 \epsilon_c^{-1}). \quad (15)$$

(2) The longitudinal part of \mathbf{V} and the transverse part of

\mathbf{g} are coupled together. The eigenfrequencies are given by

$$\omega_{\pm} = -\frac{i}{2} \left[\frac{\eta q^2}{mn_0} + \gamma_0 \epsilon_c^{-1} + \lambda \epsilon_c^{-1} q^2 \right] \pm \frac{1}{2} \left\{ \left[-i\gamma_0 \epsilon_c^{-1} - iq^2 \epsilon_c^{-1} \left(\lambda - \epsilon_c \frac{\eta}{mn_0} \right) \right]^2 + \frac{K}{mn_0} \epsilon_c^{-1} q^4 \right\}^{1/2} \quad (16)$$

The parameters appearing in (15) and (16) are D , the disclination diffusion constant, γ_0 , which is proportional to the disclination mobility, ϵ_c , the bound disclination dielectric constant, and γ , which is ΓK . The diffusion constant γ_0 is proportional to the density of free disclinations and goes to zero at T_{CA} as $\xi_{\mp}^{-2}(T)$. The solutions (15) and (16) exhibit crossover behavior from A -like to C -like hydrodynamics as a function of $q\xi_{\pm}(T)$. For $q\xi_{\pm} \ll 1$ we obtain A behavior. Equation (15) yields $\omega_{VT} \approx -i\gamma_0 \epsilon_c^{-1} \approx -i\xi_{\pm}^{-2}$, and the transverse part of \mathbf{V} relaxes in a nonhydrodynamic fashion (i.e., ω does not vanish as $q \rightarrow 0$). In the same limit, (16) yields

$$\omega_{-} \approx -i \frac{\eta q^2}{mn_0}, \quad (17a)$$

$$\omega_{+} \approx -i\gamma_0 \epsilon_c^{-1} \approx -i\xi_{\mp}^{-2}. \quad (17b)$$

Equation (17a) represents the viscous shear mode of the A phase [compare with (10)], and we see that there is no anomaly in this mode as T_{CA} is approached from above. Equation (17b) represents a nonhydrodynamic mode associated with the longitudinal part of \mathbf{V} . Thus, (17a) and the ordinary sound modes give us the three expected *hydrodynamic* modes of the A phase.

In the opposite limit, $q\xi_{\pm} \gg 1$ we obtain C -like behavior, since we are probing small length scales where the presence of free disclinations is not apparent. Equation (15) is irrelevant since the transverse part of \mathbf{V} is zero when disclinations are absent. From (16) we obtain in this limit

$$\omega_{\pm} = -\frac{1}{2} q^2 \left\{ \lambda \epsilon_c^{-1} + \frac{\eta}{mn_0} \pm \left[\left(\lambda \epsilon_c^{-1} - \frac{\eta}{mn_0} \right)^2 - \frac{K \epsilon_c^{-1}}{mn_0} \right]^{1/2} \right\}. \quad (18)$$

If we identify $K \epsilon_c^{-1}$ as the renormalized stiffness and $\lambda \epsilon_c^{-1}$ as the renormalized quantity ΓK , then (18) is in agreement with (7).

We now discuss our results (15) and (16) for the mode structure above T_{CA} in terms of their experimental implications. While formally identical results were obtained previously for hexatics,¹⁴ experimental probing of the orientational fluctuations near T_{CA} are far simpler than corresponding probes of the bond angle fluctuations in hexatics. One probe of orientational order is inelastic light scattering. The intensity $I(q, \omega)$ of scattered light is given by⁷

$$I(q, \omega) = \langle |\delta\epsilon(q, \omega)|^2 \rangle, \quad (19)$$

where $\delta\epsilon(q, \omega)$ is the Fourier transform of

$$\delta\epsilon(r, t) = \sin^2\theta(r, t)\phi(r, t). \quad (20)$$

Equations (19) and (20) assume that the local C order is along the x axis, and that the light is polarized initially per-

pendicular to the film and finally in the y direction. The thermal average in (19) will factor into separate averages over the ϕ and θ degrees of freedom. As noted in (1), $\sin\theta$ is the magnitude of the XY order parameter \mathbf{c} . In the Kosterlitz-Thouless picture of the XY model this magnitude is assumed to be unity away from the core of a disclination, and zero at the core. Fluctuations about either extreme are assumed to be unimportant. Thus, within this approximation we can write

$$\sin^2\theta(r, t) = 1 - S^2(r, t), \quad (21)$$

where $S(r, t)$ is the free disclination field (assumed to take on the values $0, \pm 1$). At the disclination cores $S = 1$, and away from the cores $S = 0$. In neglecting values of $|S|$ greater than one, we are assuming that T is near T_{CA} . Since S satisfies

$$S(r, t) = \epsilon_c \nabla \times \mathbf{V}(r, t), \quad (22)$$

we can calculate thermal averages of $\sin\theta$ by evaluating thermal averages of the transverse part of \mathbf{V} . The Fourier space (22) becomes

$$S(q, \omega) = i\epsilon_c \mathbf{q} \times \mathbf{V}(q, \omega). \quad (23)$$

Similarly, for ϕ we have

$$\phi(q, \omega) = i \frac{\mathbf{q} \cdot \mathbf{V}(q, \omega)}{q^2} \quad (24)$$

The correlation functions of \mathbf{V} can be evaluated by adding a Langevin noise source to the equation of motion for \mathbf{V} [i.e., Eq. (6.30) of Ref. 14]. Solving that equation of motion and using (23) and (24), we find

$$\langle \phi(q, \omega)\phi(-q, -\omega) \rangle = \frac{2\Gamma k_B T}{\omega^2 + (\Gamma K q^2 + \xi_{\mp}^{-1})^2} \approx \begin{cases} \frac{2\Gamma k_B T}{\omega^2 + \xi_{\mp}^{-2}}, & q\xi_{\pm} \ll 1, \\ \frac{2\Gamma k_B T}{\omega^2 + (\Gamma K q^2)^2}, & q\xi_{\pm} \gg 1, \end{cases} \quad (25)$$

and

$$\langle S(q, \omega)S(-q, -\omega) \rangle = \frac{2\Gamma k_B T [\omega^2 + (Dq^2)^2]}{\omega^2 [\omega^2 + (Dq^2 + \xi_{\mp}^{-2})^2]} \approx \begin{cases} \frac{2\Gamma k_B T}{\omega^2 + \xi_{\mp}^{-2}}, & q\xi_{\pm} \ll 1, \\ \frac{2\Gamma k_B T}{\omega^2}, & q\xi_{\pm} \gg 1. \end{cases} \quad (26)$$

Using (20) and (21), we have

$$I(q, \omega) = \langle \phi(q, \omega)\phi(-q, -\omega) \rangle \times \left[1 - 2 \int \langle S(q')S(-q') \rangle d^2q' + 3 \left[\int \langle S(q')S(-q') \rangle d^2q' \right]^2 \right]. \quad (27)$$

Close to T_c we can write, using (26),

$$\int \langle S(q')S(-q') \rangle d^2q' \approx \frac{2\pi\Gamma k_B T a^{-2}}{\omega^2}, \quad (28)$$

and thus, our final result for the intensity is

$$I(q, \omega) = \langle \phi(q, \omega) \phi(-q, -\omega) \rangle \\ \times \left[1 - \frac{4\pi\Gamma k_B T a^{-2}}{\omega^2} + \frac{12\pi^2(\Gamma k_B T a^{-2})^2}{\omega^4} \right]. \quad (29)$$

For the films made of DOBAMBC, the crossover point $q\xi_+(T) \approx 1$, with $q = 1000 \text{ cm}^{-1}$, corresponds to $T - T_c \approx 0.02 \text{ K}$.

Another possible experiment to explore the mode structure of this system would involve shear waves. For $T > T_{CA}$, the dispersion relation for shear waves is given by (10). For $T < T_{CA}$, the coupling of the shear to orienta-

tional fluctuations yields an effective viscosity ν_{eff} , different from the bare viscosity $\nu = \eta/nm_0$, as first noted in Ref. 14 for the case of hexatics. From (6.44) of Ref. 14, we expect shear waves below T_{CA} to exhibit a viscosity given by

$$\nu_{\text{eff}} = \nu \left(1 + \frac{1}{4\Gamma\nu mn_0} \right). \quad (30)$$

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¹J. M. Kosterlitz and D. J. Thouless, *J. Phys. C* **6**, 1181 (1978); J. M. Kosterlitz, *ibid.* **7**, 1046 (1974).

²B. J. Halperin and D. R. Nelson, *Phys. Rev. Lett.* **41**, 121 (1978); **41**, 519(E) (1978); D. R. Nelson and B. J. Halperin, *Phys. Rev. B* **19**, 2457 (1979).

³A. P. Young, *Phys. Rev. B* **19**, 1855 (1979).

⁴C. Y. Young, R. Pindak, N. A. Clark, and R. B. Meyer, *Phys. Rev. Lett.* **40**, 773 (1978).

⁵C. Rosenblatt, R. Pindak, N. A. Clark, and R. B. Meyer, *Phys. Rev. Lett.* **42**, 1220 (1979).

⁶C. Rosenblatt, R. B. Meyer, R. Pindak, and N. A. Clark, *Phys. Rev. A* **21**, 140 (1980).

⁷C. Rosenblatt, Ph.D thesis, Harvard University, 1979 (unpublished).

⁸S. Heinkamp, R. A. Pelcovits, E. Fontes, E. Yi Chen, R. Pindak,

and R. B. Meyer, *Phys. Rev. Lett.* **52**, 1017 (1984).

⁹D. H. Van Winkle and N. A. Clark, *Phys. Rev. Lett.* **53**, 1157 (1984).

¹⁰N. D. Mermin and H. Wagner, *Phys. Rev. Lett.* **17**, 1133 (1966); N. D. Mermin, *J. Math. Phys.* **8**, 1061 (1967).

¹¹P. C. Hohenberg, *Phys. Rev.* **158**, 383 (1967).

¹²R. A. Pelcovits and B. I. Halperin, *Phys. Rev. B* **19**, 4614 (1979).

¹³S. Ostlund, J. Toner, and A. Zippelius, *Ann. Phys. (N.Y.)* **144**, 345 (1982).

¹⁴A. Zippelius, B. I. Halperin, and D. R. Nelson, *Phys. Rev. B* **22**, 2514 (1980).

¹⁵D. Forster, *Phys. Rev. Lett.* **32**, 1161 (1974).

¹⁶D. R. Nelson and J. M. Kosterlitz, *Phys. Rev. Lett.* **39**, 1201 (1977).

¹⁷See, e.g., V. Ambegaokar, B. I. Halperin, D. R. Nelson, and E. Siggia, *Phys. Rev. Lett.* **40**, 783 (1978); *Phys. Rev. B* **21**, 1806 (1980).