Extended Isotropic-to-Anisotropic Crossover above the Nematic–Smectic-A Phase Transition

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We perform a one-loop, self-consistent calculation of the density-wave and director fluctuations above the nematic–smectic-A phase transition, find the renormalization of the perpendicular and parallel correlation lengths, and for the first time calculate values of the anisotropic critical-point exponents $\nu_\parallel$ and $\nu_\perp$. As the transition is approached several distinct regions of scaling behavior are found with increasingly anisotropic critical behavior. A plot of effective exponents from experiment versus the anisotropy ratio $\nu_\parallel/\nu_\perp$ reveals a systematic correlation that agrees with our calculation.

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In the field of critical phenomena one of the most puzzling phase transitions has been the liquid-crystal transition from the nematic (N) phase to the smectic-A (A) phase. Theoretical studies of the NA transition based on the standard form of the free energy [1] have found different universality classes [2–4], some with isotropic values for the physical critical exponents and some with strongly anisotropic critical exponents. However, experimental studies, e.g., x-ray scattering [5], show weakly anisotropic behavior, with coherence-length critical-exponent anisotropy ratios of 1.1 to 1.5, much below the value of 2 predicted by the anisotropic fixed point. Because the scattering data are fitted well over three decades in reduced temperature with a single critical exponent, the weak experimental anisotropy cannot be a result of a simple crossover from high-temperature isotropic behavior to low-temperature strong anisotropy.

In this Letter we present the results of a simple model that, for the first time, exhibits a broad, weakly anisotropic region above the NA transition between the high-temperature, isotropic and the low-temperature, strongly anisotropic regions. This model, which is analogous to the large-N limit of an N-component order-parameter theory, incorporates couplings between the two fields in the free energy in a fully self-consistent, one-loop approximation. The large range of nonasymptotic exponents we find results from a manifest spatial asymmetry in the coupling of the two fields, which leads to qualitatively different renormalizations of the correlation lengths in different directions.

The nematic phase of liquid crystals is characterized by the director $\mathbf{n}$, which is a unit vector in the direction of average alignment of the rodlike liquid-crystal molecules. The Frank free energy describes the elastic deformations of the director [6]:

$$\mathcal{F}_{el}=\frac{1}{2}\int\frac{d^3k}{(2\pi)^3}[(K_1k_\perp^2+K_3k_\parallel^2)\delta n_s^2+(K_2k_\perp^2+K_3k_\parallel^2)\delta n_t^2]\,, \tag{1}$$

where K_1, K_2, and K_3 are the splay, twist, and bend elastic constants, and δn_s and δn_t are the splay and twist fluctuations of the director perpendicular to $\mathbf{n}_0$, parallel and perpendicular to $\mathbf{k}_\perp$, respectively. de Gennes [1] introduced a Landau-Ginzburg free energy for the order parameter ψ characterizing the smectic density wave near the NA transition:

$$\mathcal{F}_\psi=\int d^3r[a_0|\psi|^2+\tfrac{1}{2}b|\psi|^4+(\nabla+iq_0\mathbf{n})_i\psi^*\Gamma_{ij}(\nabla-iq_0\mathbf{n})_j\psi]\,, \tag{2}$$

where $a_0\propto t$, b is constant, q_0 is the wave vector of the density wave, and Γ_{ij} is the (diagonal) inverse mass tensor. The elements Γ_{ii} are $\xi_{\perp0}^2$, $\xi_{\perp0}^2$, and $\xi_{\parallel0}^2$, where $\xi_{\perp0}$ and $\xi_{\parallel0}$ are the bare (unrenormalized) correlation lengths perpendicular and parallel to $\mathbf{n}$, respectively. As the NA transition is approached, the physical correlation lengths diverge with critical exponents $\nu_\perp$ and $\nu_\parallel$: $\xi_\perp\propto t^{-\nu_\perp}$ and $\xi_\parallel\propto t^{-\nu_\parallel}$, where $t=T/T_{NA}-1$ is the reduced temperature. It is important to note that even if the mass tensor were isotropic, the coupling between the smectic wave and director fluctuations would still be anisotropic (unlike, for example, the superconductor), since, to lowest order, fluctuations in $\mathbf{n}=\mathbf{n}_0+\delta\mathbf{n}$ are perpendicular to the average value of $\mathbf{n}_0$. The anisotropic coupling is the origin of the unusual anisotropic behavior of this system and the extended crossover to the asymptotic critical region.

The correlation lengths are obtained from the smectic-order-parameter correlation function, $G(\mathbf{r})=\langle\psi^*(\mathbf{r})\psi(0)\rangle$, taking into account its coupling to the director-director correlation functions, $D_{s,t}(\mathbf{r})=\langle\delta\mathbf{n}_{s,t}(\mathbf{r})\delta\mathbf{n}_{s,t}(0)\rangle$. We identify the physical (renormalized) correlation lengths $\xi_\perp$ and $\xi_\parallel$ and elastic constants K_1,K_2,K_3 from the small-$\mathbf{k}$ expansions of the

Fourier transforms of these correlation functions:

$$G^{-1}(\mathbf{k}) = G_0^{-1}(\mathbf{k}) - \Sigma(\mathbf{k}) = a[1 + \xi_\perp^2 k_\perp^2 + \xi_\parallel^2 (k_\parallel - q_0)^2 + c\xi_\perp^4 k_\perp^4] \tag{3}$$

and

$$D_{s,t}^{-1}(\mathbf{k}) = D_{0s,t}^{-1}(\mathbf{k}) - \Pi_{s,t}(\mathbf{k}) = [K_{1,2} k_\perp^2 + K_3 k_\parallel^2], \tag{4}$$

where $a = a_0 - \Sigma(0) \propto t^\gamma$ and the $k_\perp^4$ term in Eq. (3) is included since $\xi_\perp^2$ may become anomalously small compared to $\xi_\parallel^2$.

The self-energies $\Sigma(\mathbf{k})$ and $\Pi(\mathbf{k})$ are calculated explicitly in the fully renormalized one-loop approximation, including vertex renormalization [7]. Ward identities arising from rotational invariance that relate the renormalized director-density wave interaction to the renormalized propagator are an essential feature of the self-consistency of the calculation. To fourth order in $\mathbf{k}_\perp$ and to second order in $k_\parallel$, we find

$$\Sigma(\mathbf{k}) = \Sigma(0) + \frac{a k_B T q_0^2 \xi_\perp^2}{\pi K_1 \xi_\parallel} [f_\perp \xi_\perp^2 k_\perp^2 - f_\parallel \xi_\parallel^2 (k_\parallel - q_0)^2 - g_\perp \xi_\perp^4 k_\perp^4], \tag{5}$$

where $f_\perp$, $f_\parallel$, and $g_\perp$ (all > 0) are functions of the dimensionless ratios $(K_3/\xi_\parallel^2)/(K_{1,2}/\xi_\perp^2)$, which approach constants as $t \to 0$. The sign of the $k_\perp^2$ term indicates fluctuations reduce the rate of growth of $\xi_\perp^2$. Combining Eqs. (3) and (5) yields $\xi_\perp$ and $\xi_\parallel$:

$$\xi_\perp^2 = \frac{\xi_{\perp 0}^2}{a} - \frac{k_B T q_0^2 \xi_\perp^4}{\pi K_1 \xi_\parallel} f_\perp, \tag{6a}$$

$$\xi_\parallel^2 = \frac{\xi_{\parallel 0}^2}{a} + \frac{k_B T q_0^2 \xi_\perp^2 \xi_\parallel}{\pi K_1} f_\parallel. \tag{6b}$$

Using Eqs. (5) and (6a) we find the coefficient c in Eq. (3) to be weakly temperature dependent [7]. Similarly, our calculation of $\Pi(\mathbf{k})$ yields elastic-constant corrections, δK_2 and δK_3, that have the Jähnig and Brochard [8] form but with correlation lengths given by Eqs. (6):

$$\delta K_2 = q_0^2 k_B T \xi_\perp^2 / 24\pi\xi_\parallel, \tag{7a}$$

$$\delta K_3 = q_0^2 k_B T \xi_\parallel / 24\pi. \tag{7b}$$

Thus there is only one set of exponents, $\nu_\parallel$ and $\nu_\perp$, which characterize both density-wave correlations as well as the elastic-constant divergences, unlike calculations which transform from the liquid-crystal to the superconductor free energy [2].

Because the correlation lengths are highly anisotropic, Eqs. (7) indicate the correction to the bend elastic constant is much larger than the corresponding correction to the twist elastic constant. Thus K_3 is renormalized at a higher temperature than K_2. We define crossover temperatures at which the corrections to the elastic constants become comparable to their bare values [9]:

$$a_2 = (k_B T q_0^2 \xi_{\perp 0}^2 / 24\pi K_{20} \xi_{\parallel 0})^2, \tag{8a}$$

$$a_3 = (k_B T q_0^2 \xi_{\parallel 0} / 24\pi K_{30})^2. \tag{8b}$$

Similarly, crossover temperatures for renormalization of the perpendicular and parallel correlation lengths are

$$a_{\perp,\parallel} = \left(\frac{k_B T q_0^2 \xi_{\perp 0}^2}{\pi K_1 \xi_{\parallel 0}} f_{\perp,\parallel} \right)^2 \sim t_{\perp,\parallel}^\gamma. \tag{9}$$

Because the fluctuations in $\mathbf{n}$ are to leading order perpendicular to $\mathbf{n}$, as discussed above, the ψ-$\delta\mathbf{n}$ coupling is a function of $\mathbf{k}_\perp$ but not of $k_\parallel$; this quasiorthogonality makes $f_\perp \gg f_\parallel$. Therefore $a_\parallel$ is typically 5 orders of magnitude smaller than $a_\perp$. Thus, as the transition is approached renormalization of $\xi_\perp$ due to the interaction with director fluctuations occurs before a similar renormalization of $\xi_\parallel$. Typical values of the elastic constants and correlation lengths result in a_3 comparable to $a_\perp$ and a_2 comparable to $a_\parallel$.

Above all four crossover temperatures the temperature dependence of the correlation lengths is $\xi_{\perp,\parallel} \propto t^{-\gamma/2}$. However, in the intermediate temperature range $t_{\parallel,2} < t < t_{\perp,3}$, where the correction to $\xi_{\parallel 0}$ in Eq. (6b) is unimportant, Eqs. (6) have the solutions $\xi_\perp \propto t^{-3\gamma/8}$ and $\xi_\parallel \propto t^{-\gamma/2}$, yielding a weak anisotropy with $\nu_\parallel/\nu_\perp = 4/3$. Depending on the values of the bare elastic constants and correlation lengths other intermediate temperature regimes are possible. In all regions $\nu_\parallel/\nu_\perp$ lies between 1 and 2, but is not necessarily equal to 4/3. Below all four crossover temperatures our explicit solution of Eqs. (6) and (7) yields an ultimate strongly anisotropic fixed point with $\nu_\parallel = \gamma$ and $\nu_\perp = \gamma/2$. The gradual crossover to increasing anisotropy indicates that the Landau-Peierls [10] nature of the smectic-A phase (i.e., a mode with energy proportional to $k_\perp^4 + k_\parallel^2$) develops continuously as the smectic transition is approached from the nematic side. While $\xi_\perp$ ultimately diverges near the transition with the same exponent that it would have were the transition isotropic, the effective prefactor has been reduced because of the weaker divergence that occurred in the temperature regime between $t_\perp$ and $t_\parallel$. On the other hand, $\xi_\parallel$ diverges twice as fast: $\xi_\parallel \propto \xi_\perp^2$. Thus, in the $t \to 0$ limit our results above the transition agree with the strong anisotropic scaling predicted by the dislocation theory of Nelson and Toner [3] approaching the transition from below. Our anisotropic results do not depend on using the x-ray scattering function [$\propto G(\mathbf{k})$] to define the correlation lengths, but apply also if the two lengths are defined from the renormalization of the elastic con-

stants: $(\xi_{\|}/\xi_{\perp})^2=\delta K_3/\delta K_2$. Thus the anisotropy in our solution is inherent in the thermodynamic phase transition and is not just a property of the smectic order-parameter correlation function [2,4].

ϵ- and $1/n$-expansion calculations [2] that rely on transforming the liquid-crystal free energy to that of a superconductor [11] predict isotropy for the physical (thermodynamic) critical exponents as $t\rightarrow 0$. However, large fluctuations for small K_1 inherent in the "gauge transformation" from superconductor to liquid-crystal system produce a ratio of the x-ray exponents $\nu_{\|}^{x}/\nu_{\perp}^{x}$ of 2 [2]. The following argument [7] indicates that the isotropy in the physical exponents can result from a relaxation of the constraint present in the liquid-crystal free energy, that the length of the director $\mathbf{n}$ is unity. When the length of $\mathbf{n}$ is fixed the fluctuations in $\mathbf{n}$ are restricted to the plane perpendicular to $\mathbf{n}$, resulting in anisotropic renormalization of the correlation lengths ($\nu_{\|}=2\nu_{\perp}$). If fluctuations in $\mathbf{n}$ are allowed in all directions relative to $\mathbf{n}$ (i.e., if the length of $\mathbf{n}$ changes) then the renormalization of the correlation lengths is isotropic, as in the superconductor ($\nu_{\|}=\nu_{\perp}$). This effect may be elucidated by adding a term to the free energy that controls the constraint:

$$\mathcal{F}_{\text{constraint}}=\tfrac{1}{8}K_4[\mathbf{n}\cdot\mathbf{n}-1]^2. \tag{10}$$

Equation (10) adds a mass K_4 to the fluctuations of the length of $\mathbf{n}$, δn_z, but not to δn_x and δn_y. For the isotropic liquid crystal (i.e., $\xi_{\|0}=\xi_{\perp 0}=\xi_0$ and $K_{10}=K_{20}=K_{30}=K_0$), it may be shown in each order of perturbation theory that as $K_4\rightarrow\infty$ one recovers de Gennes' liquid-crystal theory with $|\mathbf{n}|=1$ (for which we find $\nu_{\|}=2\nu_{\perp}$), while for $K_4=0$ the theory becomes manifestly isotropic (requiring $\nu_{\|}=\nu_{\perp}$). For finite K_4 the $K_4\rightarrow\infty$ limit controls the ultimate fixed point, with crossover determined by

$$(\xi_0^2/a)K_4/K_0\approx 1\,, \tag{11}$$

so that as $a\rightarrow 0$ the constraint dominates, yielding the anisotropic case. This indicates that the constraint on the director, $|\mathbf{n}|=1$, appears to be the crucial factor in determining the isotropy or anisotropy of the transition, rather than the value of the constant K_1 [2].

The presence of a weakly anisotropic intermediate temperature regime with $\nu_{\|}/\nu_{\perp}=4/3$ is consistent with experimental observations. Light scattering measurements [12] show that $10^{-5}<t_2<3\times 10^{-4}$ in the few systems that have been studied. Since $t_{\|}$ is somewhat smaller than t_2, the x-ray measurements on these systems (for $10^{-5}<t<10^{-2}$) have not yet probed the strong-scaling ($\nu_{\|}=2\nu_{\perp}$) temperature range, though they are approaching it. Indeed most of the experimental values for $\nu_{\|}/\nu_{\perp}$ lie between 1.1 and 1.33 [5], which our theory would predict if the temperature range over which the data were taken straddled the $t_{\perp}$ crossover temperature. However, there is a seeming lack of universality in the experimental exponents arising from the dependence of the crossover temperature [Eq. (9)] on differing system parameters. Therefore, in the absence of detailed crossover studies we use a simple linear interpolation between the high-temperature, isotropic region with $\nu_{\|}/\nu_{\perp}=1$ and the weak anisotropic region with $\nu_{\|}/\nu_{\perp}=4/3$. The theoretical predictions for effective exponents $\nu_{\|}/\gamma$ and $\nu_{\perp}/\gamma$ vs $\nu_{\|}/\nu_{\perp}$ are shown in Fig. 1 along with extensive x-ray scattering data [5]. The data clearly indicate that $\nu_{\perp}/\gamma$ drops as the ratio $\nu_{\|}/\nu_{\perp}$ increases, as our theory predicts. Finally, since the crossover into the weakly anisotropic region is gradual and extended, as indicated by numerical solutions of Eqs. (5) and (6) [7], it may be difficult to resolve the regions with different exponents.

A curious dependence of the critical behavior above the NA transition on the size of the temperature range of the nematic region has been seen [4,13]. In this connection our model predicts that the $t_{\perp}$ crossover temperature will be higher for narrow-range nematic systems with a larger values of T_{NA}/T_{NI} (the ratio of the NA and isotropic-nematic transition temperatures) because K_1, which grows as the square of the nematic order parameter, will be smaller for these systems, and $t_{\perp}$ depends inversely on K_1. Thus experimental measurements made on the narrow-range nematic systems should be deeper into the weak anisotropic regime predicted by our model, and could possibly begin to cross over into the strong anisotropic regime, unlike the broader-nematic-range materials which straddle the isotropic and weak anisotropic regimes. Therefore, our model predicts the following for systems with larger T_{NA}/T_{NI}: (1) $\nu_{\|}/\nu_{\perp}$ should be larger; (2) α, the specific-heat exponent, should be larger, since $\nu_{\|}$ and $\nu_{\perp}$ are thermodynamic exponents and obey the hyperscaling relation $\alpha=2-\nu_{\|}-2\nu_{\perp}$; and (3) ρ_2, the critical exponent for K_2, should be smaller. These predictions are all a result of the reduced value of $\nu_{\perp}$ in the weak anisotropic regime. Predictions (1) and (2) have

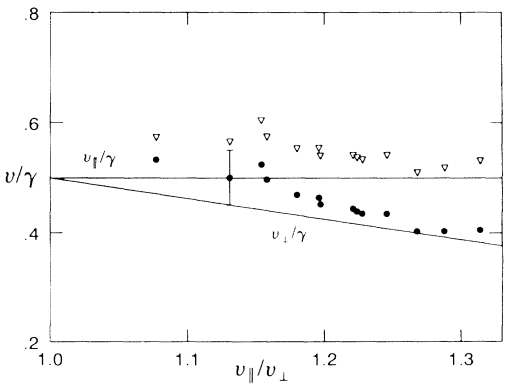

FIG. 1. Plot of the correlation-length exponents scaled with γ vs the anisotropy ratio $\nu_{\|}/\nu_{\perp}$. The lines are the theoretical predictions for the effective values of $\nu_{\|}/\gamma$ and $\nu_{\perp}/\gamma$. The triangles and circles are experimental values for $\nu_{\|}/\gamma$ and $\nu_{\perp}/\gamma$, respectively, taken from x-ray scattering experiments reported in Ref. [5]. A typical error bar is shown.

been seen experimentally; however, proximity to a possible tricritical point may complicate interpretation of the experiments. Studies of broad-nematic-range materials should help clarify the situation.

In conclusion, we have found a gradual crossover from isotropic to anisotropic behavior above the NA transition using a simple model which is based directly on de Gennes' free energy, without mapping onto the superconducting analog. The anisotropy in the critical behavior of the correlation lengths develops because of the anisotropic nature of the coupling of the density-wave and the director fluctuations in the free energy. This leads to a renormalization that is opposite in sign for the perpendicular and parallel directions and therefore yields, near T_{NA}, a perpendicular correlation length that is less than that for an isotropic system and a parallel correlation length that is much larger. Current experiments appear to be on the verge of entering the strong-coupling regime ($\nu_{\parallel}=2\nu_{\perp}$) for $t<10^{-5}$; observation of a sharp crossover to a larger exponent for $\xi_{\parallel}$ would be a clear confirmation of the theory presented here.

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