Boundary Effects in Chiral Polymer Hexatics

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(Received 1 April 1999)

Boundary effects in liquid-crystalline phases can be large due to long-ranged orientational correlations. We show that the chiral-hexatic phase can be locked into an apparent three-dimensional $N + 6$ phase via such effects. Simple numerical estimates suggest that the recently discovered "polymer hexatic" may actually be this locked phase.

PACS numbers: 64.70.Rh, 61.25.Hq, 87.16.Ka

Liquid crystals provide a tabletop laboratory to study broken symmetries and the resulting low-energy Nambu-Goldstone modes [1]. Viewing two-dimensional crystallization in this way led to the proposal of an intervening phase between the liquid and the solid: the hexatic [2], a two-dimensional phase with long-range orientational order but short-range positional order. In three dimensions, arguments based on Landau theory suggest that there is no similar orientationally ordered phase between the three-dimensional liquid and solid [3]. However, between a nematic phase and a crystal phase, the mesogens can have hexatic order in the plane perpendicular to the nematic director [4]. While this "$N + 6$" phase could, in principle, exist (it is not terribly different from a biaxial-nematic phase) it was not immediately discovered. Recently, however, Strey *et al.* [5] have examined a phase of DNA, having a structure consistent with $N + 6$ order, which they call the polymer hexatic. In this Letter, we will consider the effects of boundaries on an $N + 6$ phase consisting of chiral molecules, such as DNA. We will argue that while symmetry predicts that the hexatic bond order should twist [6] surface effects can "lock in" a preferred set of directions which can effectively unwind the twisting hexatic.

The phase sequence of a chiral mesogen usually starts with the cholesteric at the highest temperatures or lowest concentrations. As the temperature is lowered or the density increased, the mesogens can form any number of phases, including the (achiral) smectic-*A* phase, the smectic twist-grain-boundary phase [7], or the chiral hexatic [6]. In the last case, the free energy which governs the transition from cholesteric to chiral hexatic depends on both the nematic director $\mathbf{n}$ and the complex hexatic order parameter ψ_6:

$$F_{\text{bulk}} = \int d^3x \Big\{ |(\nabla - i\tilde{q}_0\mathbf{n})\psi_6|^2 + r|\psi_6|^2 + u|\psi_6|^4 + \frac{1}{2}K_1(\nabla\cdot\mathbf{n})^2 + \frac{1}{2}K_2(\mathbf{n}\cdot\nabla\times\mathbf{n} + q_0)^2 + \frac{1}{2}K_3[\mathbf{n}\times(\nabla\times\mathbf{n})]^2 \Big\}, \tag{1}$$

where r and u are Landau parameters and K_i are the Frank elastic constants. In the cholesteric phase, $\langle\psi_6\rangle = 0$ and (1) reduces to the free energy of a cholesteric with equilibrium pitch $P = 2\pi/q_0$. When hexatic order persists $\psi_6 = |\psi_6|e^{i6\theta_6}$ and, as in the Meissner phase of superconductors [7], the nematic director satisfies $\nabla\times\mathbf{n} = 0$. However, in this phase, it is straightforward to see that the hexatic bond order rotates about the average nematic direction: $\nabla\theta_6 = \tilde{q}_0\mathbf{n}_0$. Recalling the phenomenology of the superconductor or smectic-*A* liquid crystal [8] we emphasize that if the director unwinds then the hexatic bond order *must* twist. Further, we expect the cholesteric pitch to unwind continuously to infinity at the cholesteric-to-chiral-hexatic phase transition, as has, in fact, been observed [5]. Possible phase diagrams are shown in Fig. 1.

Deep in the chiral-hexatic phase the nematic order freezes [6] and we can rewrite (1) in the "London limit":

$$F_{\text{bulk}} = \int d^3x \Big\{ \frac{1}{2}K_A(\nabla\theta_6)^2 - K_A\tilde{q}_0\mathbf{n}_0\cdot\nabla\theta_6 \Big\}, \tag{2}$$

where $K_A = 72|\psi_6|^2$. In the following we take the average nematic axis to be $\mathbf{n}_0 = \mathbf{z}$. This free energy, however, applies only deep inside the sample. In general there will be surface terms which can bias the hexatic bond-order direction. For instance, if the boundary is a flat surface, then the mesogens will be either "surface loving" or "surface hating" and will try to maximize or minimize their contact with the surface, respectively. If the surface tension is large, the first few layers of molecules will be locked and then simple geometric arguments, akin to the classic Onsager treatment of nematics [9], show that there is an entropic penalty for the hexatic order to rotate away from the preferred direction, as shown in Fig. 2.

To model the effect of this surface interaction, we add to (2) the surface term

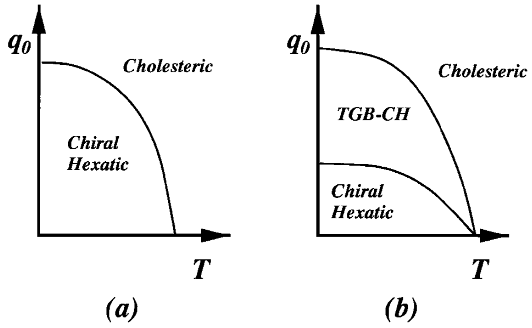

FIG. 1. Phase diagram of a chiral mesogen that can form an $N + 6$ phase. In the cholesteric phase there is no hexatic order ($\psi_6 = 0$) and $\nabla \times \mathbf{n} \neq 0$. In the chiral-hexatic phase $\nabla \times \mathbf{n} = 0$ but $\psi_6 \neq 0$ and $\nabla\theta_6 = \tilde{q}_0\mathbf{n}$. (a) Type-I behavior with no intervening defect phase. (b) Type-II behavior in which a twist-grain-boundary phase (akin to the Abrikosov flux phase in a superconductor) intervenes between the cholesteric and chiral-hexatic phase.

$$F_{\text{surface}} = \int_{\partial\Omega} ds dz\, h \cos(6\theta_6)\,, \tag{3}$$

where Ω is the volume of the sample and $\partial\Omega$ is the boundary in the xy plane. The sign of h is determined by the surface affinity of the mesogens, while the magnitude of h can be estimated through an excluded-volume, entropic analysis. Taking the mesogens to be polymers (so that in Fig. 2, the disks are the polymer cross sections in the xy plane), we consider a hexagonal crystallite of extent ξ (the translational correlation length) in the xy plane and length L_P along $\hat{\mathbf{z}}$, rotating away from its preferred direction. Presumably L_P is precisely the polymer persistence length, which is the typical correlation of the polymer positions along the nematic axis. In this case, the number of allowed states for a small rotation θ away from the preferred angle can be expanded in powers of $\cos(6\theta)$. The entropic contribution to the free energy is then

$$\Delta F = -k_B T \Delta S = -k_B T N \ln\left\{\frac{L_P \xi^2[1 - \gamma\cos(6\theta)]}{L_P \xi^2}\right\}$$
$$\approx k_B T N \gamma \cos(6\theta)\,, \tag{4}$$

where γ is a geometric factor of order unity, $N = V/(L_P\xi^2)$ is the number of polymer crystallites, and V is the volume of the system. Note that $\gamma < 1$ to ensure that the entropy is well defined. Converting (4) into an integral over the surface gives $|h| \approx k_B T/(L_P\xi)$. For the polymer hexatic phase studied in [5], $L_P \approx 500$ Å and $\xi \approx 400$ Å.

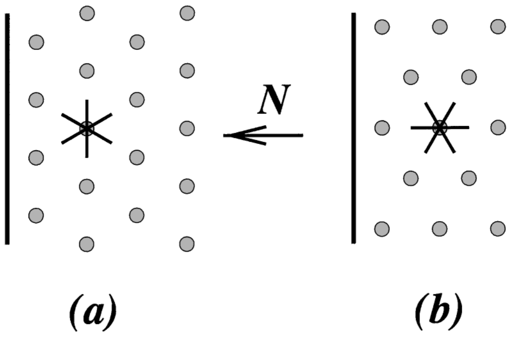

FIG. 2. Hexagonally close-packed disks near a wall with surface normal **N**. Each hexagonal crystallite defines a set of hexatic axes shown as six-pointed arrows. In (a) we show a favorable packing for surface loving disks, while in (b) we show a packing of surface hating disks. For either case, deviations away from this packing are disfavored entropically.

We propose that this surface anchoring can prevent the equilibrium twisting that a chiral-hexatic phase must exhibit whenever the nematic director is aligned. To pursue this, we consider configurations in which the hexatic bond order is uniform at any constant height z. This should be reasonable deep inside the hexatic phase where there is true long-range bond order. The free energy is

$$F_{\text{eff}} = \int dz \left\{\frac{K}{2}(\partial_z\theta_6)^2 - K\tilde{q}_0\partial_z\theta_6 + H\cos(6\theta_6)\right\}, \tag{5}$$

where $K \equiv K_A A$, $H \equiv hL$, A is the cross-sectional area of the sample, and L is the length of the sample along the wall which provides the anchoring. This effective free energy has frequently been studied before in the context of commensurate-incommensurate transitions. For small values of $\tilde{q}_0$ the $\cos(6\theta_6)$ term prevents *any twisting*, while for larger values the system admits soliton solutions which let θ_6 slip by $2\pi/6$. In equilibrium, it is straightforward [10] to show that a soliton is the lowest energy configuration when

$$|\tilde{q}_0| \geq \frac{4}{\pi}\sqrt{\frac{L}{A}\frac{h}{k_A}}\,. \tag{6}$$

In addition to the estimate for h, we can estimate K_A via dimensional analysis: $K_A \sim k_B T/\xi$, where ξ is the (finite) translational correlation length in the hexatic phase. How should we estimate $\tilde{q}_0$? In the cholesteric phase of DNA, the pitch is on the order of 1 μm. We can use this to estimate the rate at which a polymer bundle twists about the average nematic axis. To do so we consider a bundle of N polymers, with separation a. We let them twist about the center of the bundle so that the polymer that crosses $z = 0$ at (ρ, ϕ) has conformation [11]

$$\mathbf{R}(z;\rho,\phi) = [\rho\cos(\tilde{q}_0 z + \phi), \rho\sin(\tilde{q}_0 z + \phi), z]\,. \tag{7}$$

We calculate the energy for a twisted bundle of radius ρ_0 and length L_z. There are two contributions to the energy: the bending energy of the individual polymers and the Frank free energy of the liquid crystal deformation. The first energy is proportional to the bending modulus κ. If the polymers sit at radii ρ_i and have an average spacing a, then, for $\tilde{q}_0\rho \ll 1$ we have

$$\begin{aligned}F_{\rm bend} &= \sum_i \frac{\kappa}{2}\int dz \left|\frac{d^2\mathbf{R}}{dz^2}\right|^2 [1 + (\rho_i\tilde{q}_0)^2]^{-3/2} \\ &\approx \frac{\kappa\pi}{a^2}\int dz \int_0^{\rho_0} \rho\, d\rho\, \rho^2 \tilde{q}_0^4 \\ &\approx \frac{L_z\kappa\pi}{4a^2}\rho_0^4\tilde{q}_0^4 = \frac{L_z\kappa\pi N^2 a^2 \tilde{q}_0^4}{4}, \qquad (8)\end{aligned}$$

where N is the number of polymers in the bundle. The liquid crystal deformation has no splay and we have just accounted for the bend deformations. The remaining energetic contribution is from the twist:

$$\frac{F_{\rm twist}}{L_z} = \frac{NK_2\pi a^2}{2}(2\tilde{q}_0 + q_0)^2. \qquad (9)$$

Finally, minimizing the total free energy $F = F_{\rm bend} + F_{\rm twist}$ over $\tilde{q}_0$, we find

$$\left[1 + \frac{N\kappa\tilde{q}_0^2}{4K_2}\right]\tilde{q}_0 = -\frac{q_0}{2}. \qquad (10)$$

The bending modulus is $\kappa = k_B T L_P$, where L_P is the persistence length, while $K_2 = k_B T/d$, where d is the Odijk length, given by $d \sim (L_P a^2)^{1/3}$. Thus an estimate of the coefficient of $\tilde{q}_0^2$ is $N\pi^2 L_P^{4/3} a^{2/3}/P^2$, where P is the hexatic pitch. The experiment [5] finds a translational correlation length on the order of ten $a = 4$ nm intermolecular separations so presumably each twisting bundle is composed of $N \sim 100$ molecules. In this case, $N\kappa/K_2 \approx 10^{-2}\ \mu\text{m}^2$. If we take a typical range $1\ \mu\text{m} < 2\pi/q_0 < 10\ \mu\text{m}$ then (10) shows that $2\ \mu\text{m} < 2\pi/\tilde{q}_0 < 20\ \mu\text{m}$. This follows from the fact that though the persistence length is long for DNA, it is still 2 orders of magnitude smaller than the cholesteric pitch: twisting on this length scale is easy for the polymers.

Using (6), we find that twisting (through the introduction of solitons in the θ_6 field) becomes unfavorable for systems of linear dimension smaller than a certain critical length. For system sizes such that $L < 16/(L_P\pi^2\tilde{q}_0^2)$ the boundary terms dominate the free energy so the bond order is effectively pinned by these surface effects. From the above estimates of the equilibrium pitch of the hexatic bond order we find that the largest system which allows surface pinning is on the order of 300 μm when the pitch is 20 μm. The sample was on the order of 1 mm [12] so the outer boundaries of the sample are possibly too far away to cause lock-in. However, it is possible that sample preparation introduced interior walls. A wall spacing on the order of ~300 μm would imply internal regions of roughly 10^7 DNA molecules. If, on the other hand, we were to take the smallest reasonable pitch of 1 μm, we would find a wall spacing of 3 μm, which is *unreasonable*. Indeed, it is likely that in the hexatic phase, intermolecular correlations can modify the chiral interaction as argued in [5] and [13] and lead to a lengthening of the pitch. It is thus reasonable that in the hexatic phase the chiral strength can be reduced and we are somewhere between these two extremes.

The data, if taken to represent only the bulk physics, show that $2\pi/\tilde{q}_0 \sim 1$ mm since the hexatic order does not twist by $2\pi/6$ inside the illuminated region. However, with walls 1 mm away, the data are consistent with an equilibrium pitch of 44 μm, not that far from our naive estimate of the pitch. Thus, bearing in mind the Landau free energy of this system, one can conclude only that the hexatic pitch is longer than 44 μm, but not *infinite*. The absence of the observation of a finite hexatic pitch can be attributed to the surface pinning effects. If we take our estimate of the hexatic pitch and make the reasonable assumption of a few internal walls in the sample or if we imagine the hexatic pitch to be within a factor of 2 of typical pitches, it is clear that such a pinned state is expected. In either case the effects of surface pinning are required to interpret the data. As further evidence for our pinning hypothesis, it is known that the hexatic director tends to align with the long axis of the sample [12].

Since both sides of (6) are the same order of magnitude the condition to prevent solitons is, at best, marginally satisfied. What happens if we have solitons? We shall see that even close to the transition a state with solitons will still have an achiral hexatic signature. When (6) is an equality, it becomes energetically favorable for the system to introduce one soliton into the bond-order field, $\theta_6(z)$. Such a field configuration, in which the hexatic bond order jumps by $2\pi/6$ near $z = 0$, is shown by the dotted line in Fig. 3. At low densities two solitons interact via a weak exponential repulsion with a range set by the distance over which $\theta_6(z)$ changes rapidly with z.

This weak interaction of two solitons leads to the rapid proliferation of such twists in the system upon tuning the system parameters, L and $\tilde{q}_0$. Once these parameters are tuned so that the chemical potential of a soliton becomes negative, numerous solitons are spontaneously created until their weak mutual repulsion returns the soliton chemical potential to zero. In this case the bond-order field takes the form [14]

$$\theta_6(z) = \frac{\pi}{6}\left[1 + \frac{2}{\pi}\,\mathrm{am}\!\left(\frac{6z}{k}\sqrt{\frac{H}{K_A}}, k\right)\right], \qquad (11)$$

where $\mathrm{am}(x, m)$ is the inverse of the incomplete elliptic integral of the second kind and the parameter k is related to the energy via $E(k^2) = k\pi\tilde{q}_0\sqrt{L_P L}/4$, where $E(x)$ is the complete elliptic integral of the second kind. The solution to (11) describes a regular array of solitons with a density controlled by the value of the parameter k.

As shown in Fig. 3 the parameter k controls the equilibrium density of solitons in the system. When $k = 1$, there is precisely one soliton in the infinite system and, as k decreases from unity, the soliton density grows monotonically. When $k = 0.95$ this soliton density reaches a point where mutually overlapping solitons join to form an almost uniform gradient in the bond order. The system

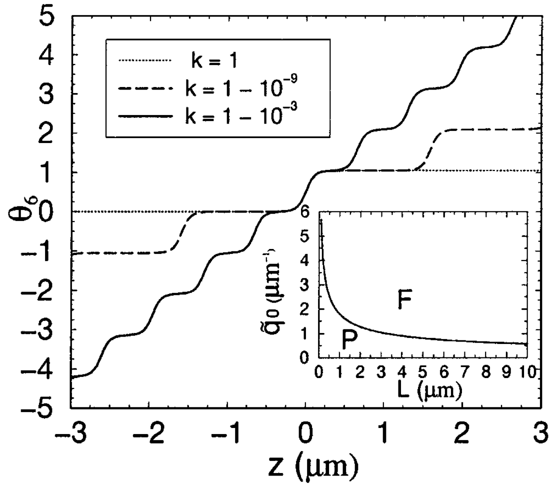

FIG. 3. Three solutions for the bond-order field as a function of height. We show the one soliton ($k = 1$, the dotted line) solution, as well as multisoliton solutions for $k < 1$. The parameter k is determined by the sample dimension L and the equilibrium pitch $\tilde{q}_0$ allowing the construction of the phase diagram shown in the inset. In the "pinned" phase (P) the bond-order field θ_6 is prevented from twisting by the surface pinning while in the "free" (F) phase the bond order can twist. Upon approaching the phase boundary (solid line) from below, the bond order begins to twist by the creation of solitons. The actual phase boundary line is chosen by arbitrarily assigning a maximum (nonzero) soliton density as described in the text.

returns to its "free" behavior with $\theta_6(z) \propto z$. On the other hand, if k is larger than unity, there are no solitons in the system in equilibrium. The bond-order field is completely pinned by the edges of the sample so that $\theta_6(z)$ is constant.

The experimental signature of the pinned phase is a sixfold modulation of the in-plane scattering intensity. It can, in fact, persist into regions of the phase diagram which allow modest densities of solitons. The sixfold modulation of the scattering intensity should remain evident as long as the density of solitons is small enough so that distinguishable plateaus in the θ_6 shown in Fig. 3 exist. We take a somewhat arbitrary but nevertheless conservative estimate of the transition to be the point at which the plateaus are twice as long as the intervening regions where the θ_6 field changes rapidly [15]. By this criterion the solid curve in Fig. 3 represents a free phase configuration of θ_6. The division of the parameter space between the pinned and freely twisting bond order selects a critical value of $k = k^\star$. Solving for $k^\star$ leads to a phase boundary between pinned and free states of the form $\tilde{q}_0 L^{1/2} = \text{const.}$ This curve (with the constant set by $k^\star$) is shown in the inset in Fig. 3. Additionally, the soliton lattice could, in principle, be observed via scattering due to its periodic structure along $\hat{z}$.

Finally, we comment on the role of the thermal effects. Fluctuation effects become important near the boundary of the pinned and free phases since there the system exhibits a delicate balance of the bulk elastic and surface energies. The qualitative effect of thermally produced solitons is to move the phase boundary down and to the left in the inset in Fig. 3. To assess the magnitude of this shift, we compare the surface free energy cost to $k_B T$. In a system with a size as small as $L \sim 10\ \mu\text{m}$ the surface energy is on the order of $10^3 k_B T$. The transition is controlled then by the balance of energies 3 orders of magnitude greater than the thermal energy, so we conclude that thermal effects are negligible except in the narrow region along the phase boundary where the surface and bulk energies are balanced to within 0.1%. Additionally, at higher temperatures the long-range hexatic order will melt, leaving a surface hexatic along with a bulk cholesteric. The details of this transition could be confirmed through experiments along the lines of [5].

It is a pleasure to acknowledge stimulating conversations with T. C. Lubensky, V. A. Parsegian, R. Podgornik, and H. Strey. R. D. K. was supported by NSF CAREER Grant No. DMR97-32963, by Research Corporation, and by L. J. Bernstein. A. J. L. was supported in part by the Donors of The Petroleum Research Fund, administered by the American Chemical Society.

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