The Structure of TGB\(_C\) Phases

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(Dated: March 22, 2022)

We study the transition from the cholesteric phase to two TGB\(_C\) phases near the upper critical twist \(k_{c2}\): the Renn-Lubensky TGB\(_C\) phase, with layer normal rotating in a plane perpendicular to the pitch axis, and the Bordeaux TGB\(_C\) phase, with the layer normal rotating on a cone parallel to the pitch axis. We calculate properties, including order-parameter profiles, of both phases.

Smectic liquid crystalline phases\([1]\) are layered structures: they are fluid-like in two-dimensions and solid-like in the third. Twist-grain-boundary or TGB phases\([2, 3, 4]\) are phases of smectic liquid crystals induced by molecular chirality. They consist of periodically spaced grain boundaries, each composed of an array of parallel dislocations, separating smectic slabs as depicted in Figs. 1 and 2. The layer normals \(N\) of the slabs rotate in discrete jumps across the grain boundaries. These remarkable phases are the analog in liquid crystals\([5]\) of the Abrikosov flux lattice in superconductors\([6]\) with the complex smectic mass-density-wave amplitude \(\psi\) the analog of the superconducting order parameter, dislocations in the grain boundary the analog of vortices, and the chiral coupling constant \(h\) induced by molecular chirality the analog of the external magnetic field \(H\).

The simplest TGB phase is the TGB\(_A\) phase in which the smectic slabs between grain boundaries have the character of a bulk smectic-\(A\) phase in which the layer normal \(N\) and the director \(n\), specifying the direction of average molecular alignment, are parallel to each other in a plane perpendicular to the pitch axis along \(p\). In TGB\(_C\) phases, the smectic slabs have the character of a bulk smectic-\(C\) with \(n\) tilted relative to \(N\). Two distinct structures for the TGB\(_C\) phase immediately come to mind. In the first\([7, 8]\), both \(N\) and \(n\) rotate in the plane perpendicular to \(p\), but with a finite angle between them as shown in Fig. 1. We will refer to this as the Renn-Lubensky or RL TGB\(_C\) phase. In the second TGB\(_C\) phase, first discovered\([9]\) and subsequently studied in detail by the Bordeaux group and collaborators\([10]\), \(n\) rotates in the plane perpendicular to \(p\), but \(N\) rotates on a cone with a component parallel to \(p\) so that \(p\) does not lie parallel to the smectic layers as shown in Fig. 2. We will refer to this as the Bordeaux or B TGB\(_C\) phase. No pure form of the RL phase has been reported, though phases with two-dimensional modulation of the local RL TGB\(_C\) structure have been observed\([11]\). Though the RL TGB\(_C\) structure may be unstable with respect to these modulations, we assume here that it can be stable. We will not discuss the TGB\(_C^*\) phase\([5]\) with smectic-\(C^*\) slabs in which the director rotates in a cone from layer to layer.

Our goal is to study the structure of both the RL and B phases near the upper critical field \(h_{c2}\) where the TGB\(_C\) phase becomes unstable with respect to the cholesteric phase in which the smectic order parameter is zero and the director twists in a helical fashion about \(p\) with a pitch \(P\). We follow closely the procedure developed by Abrikosov\([6]\) in his analysis of the superconducting flux phase near the upper critical field \(H_{c2}\) and applied successfully to the TGB\(_A\) phase near \(h_{c2}\). Our analysis of the transition to the bordeaux TGB phase is essen-
FIG. 3: The square amplitude $|\psi(x,0,0)|^2$ smectic order parameter as a function of $x$ in (a) the Bordeaux and (b) the RL TGB$_C$ phases. These figures show the squared slab wavefunctions $|\phi(x-x_0)|^2$ with $n=+1$ centered at $-l_b$ (short dash, short space) with $n=1$ centered at $l_b$ (long dash, short space) and with $n=0$ (short and long dashes) and $|\psi(x,0,0)|^2$ (full line). Though $|\phi(x)|$ dies off fairly rapidly, $|\psi(x,0,0)|^2$ has a robust value at grain-boundary positions $x/l_b=\pm 0.5$. Note the asymmetry about $x=0$ in the RL case.

TABLE I: $H_\alpha$ and proportionality of $l_b$, $l_a$, and $\xi$ to powers of $P$ and $d$ in TGB phases.

| Phase   | $H_\alpha$ | $l_b$ | $l_a$ | $\xi$ |
|---------|-------------|-------|-------|-------|
| TGB$_A$ | $-d^2/du^2 + u^2$ | $p^{1/2}d^{1/2}$ | $p^{1/2}d^{1/2}$ | $p^{1/2}d^{1/2}$ |
| Bordeaux| $-d^2/du^2 + u^2$ | $p^{2/3}d^{1/3}$ | $p^{1/3}d^{2/3}$ | $p^{2/3}d^{1/3}$ |
| RL      | $d^2/du^2 + u^2$  | $p^{1/3}d^{2/3}$ | $p^{2/3}d^{1/3}$ | $p^{2/3}d^{1/3}$ |

and nematic-to-smectic-$C$ transitions. In this model, the smectic molecular number density is expressed as $\rho = \psi + \psi^*$, where $\psi$ is the complex mass-density-wave amplitude with wavenumbers with magnitude peaked near $q_0 = 2\pi/d$. The free energy, $F_\psi = F_A + F_{NL}$ is the sum of a nonlinear part, $F_{NL} = \frac{1}{2} g \int d^3x |\psi|^4$, and a part harmonic in $\psi$,

$$F_H = \int d^3x [\hat{P} |\psi|^2 + D_\parallel |\nabla^2(x) + q_0^2|\psi|^2$$

$$+ D_\perp |\nabla^2(x) + q_0^2|\psi|^2$$

$$+ D_{\parallel \perp} |\nabla^2(x) + q_0^2|\psi|^2 + (q_0^2 + \psi^*) |\nabla^2(x) + q_0^2|\psi + c.c.]$$

where $\nabla^2(x) \equiv (n(x) \cdot \nabla)^2$ and $\nabla^2(x) = \nabla^2 - \nabla^2(x)$. With the identification $q_0^2 = -C_{\parallel 2}/2D_\perp$ and $\tilde{r} = r - C_{\parallel 2}^2/(4D_\perp)$, this model is simply a alternative representation of the CL model except for the term proportional to $D_{\parallel \perp}$, which, as we shall see, is needed to stabilize the RL phase. When $q_0^2 < 0$, this model has a phase transition from the nematic to the smectic-A phase with $\psi = \psi_A e^{i\omega_\psi}$, where $\psi_A = (4\pi \tilde{r}^2)^{1/2}$. When $q_0^2 > 0$, it has transition to the SmC phase with $\psi = \psi_C e^{i\omega_\psi x}$, with $\psi_C = r(4\pi \tilde{r}^2)^{1/2}$, with $q_{C} = (q_{0,\perp} \cos \gamma, q_{0,\perp} \sin \gamma, q_0)$ for any angle $\gamma$.

To complete the description of our system, we add the Frank free energy, $F_n$, for the director including the contribution from molecular chirality:

$$F_n = \frac{1}{2} \int d^3x [K_1 (\nabla \cdot n)^2 + K_2 |n \cdot (\nabla \times n)|^2$$

$$+ K_3 |n \times (\nabla \times n)|^2 + h n \cdot (\nabla \times n)]$$. (2)

When $\psi = 0$, the equilibrium state is the cholesteric phase determined by $F_n$ alone with director

$$n_0(x) = (0, -\sin k_0 x, \cos k_0 x)$$

where $k_0 = h/K_2 \equiv 2\pi/P$.

There are several dimensionless quantities in $F = F_\psi + F_n$ that play a role in our analysis. One is the ratio $k_0/q_0 = d/P$, which is of order $10^{-2}$ or less. Our primary concern will be the limit in which $k_0/q_0$ approaches zero, and we will consider only leading terms in this ratio. Other parameters are the ratios,

$$\eta_\perp = D_\perp/D_\parallel, \quad \eta_{||} = D_{||}/D_\parallel, \quad \omega = q_{\perp 0}^2/q_0^2$$

and the twist Ginzburg parameter, $\kappa_2 = (gK_2)^{1/2}/(4D_\parallel q_0^2)$. In at least one material, $\eta_{||} \approx 0$ and $\eta_\perp \ll 1$, but there is no a priori reason why either of these conditions should not be violated. $\omega = \tan^2 \alpha$ is a measure of the equilibrium tilt angle $\alpha$ between $n$ and $N$. It is more convenient to use the twist $k_0 = h/K_2$ rather than $h$ as a measure of chirality. The critical twist at which the cholesteric phase becomes unstable to the TGB phases is $k_\perp = h/K_2$.

To determine when the cholesteric phase first becomes unstable with respect to the development of smectic-$A$ order and to find our variational wave functions for the
TGB phases, we calculate the momentum eigenvalues and associated eigenfunctions of the harmonic kernel obtained from $F_H$ with $\mathbf{n}(x)$ replaced by $\mathbf{n}_u(x)$. This kernel $K$ is a periodic function of $x$ with period $P/2$. Its eigenfunctions are, therefore, plane waves in the $yz$ plane that can be expressed as $\psi(x) = \Phi_{q \hat{p}}(x)e^{iq \cdot x}$ where $q_{\hat{p}} = (q_0, q_x, q_y)$ and where, as indicated, the form of the function $\Phi_{q \hat{p}}(x)$ can depend on $q_{\hat{p}}$. When $k_0 = 0$, the eigenfunctions associated with the lowest eigenvalue of $K$ are $\psi(x) = e^{i\hat{p} \cdot x}$ in which $q_{\hat{p}}$ can have a nonvanishing $x$-component. We allow explicitly for this component of $\psi$ that varies periodically with $x$ by setting $\Phi_{q \hat{p}}(x) = \phi_{q \hat{p}}(x)e^{-i\hat{p} \cdot x}$ and $\psi(x) = \phi_{q \hat{p}}(x)e^{iq \cdot x}$ where $q = (q_x, q_p)$. With this form for $\psi$, $F_H$ becomes

$$F_H = A \int dx \phi_{q \hat{p}}(x) H(x, \hat{p}, q) \phi_{q \hat{p}}(x) \quad (4)$$

where $\hat{p} = i^{-1}d/dx$ is the momentum operator and

$$H(x, \hat{p}, q) = \hat{p} + D_s^2 \mathbf{q}(x, \hat{p}, q) + D_s \mathbf{q}(x, \hat{p}, q)$$

$$+ D_s \mathbf{q}(x, \hat{p}, q) Q_s \mathbf{q}(x, \hat{p}, q), \quad \mathbf{q} = (q_x, q_p)$$

(5)

where $Q_s(x, \hat{p}, q) = q_x^2(x) - q_0^2$, with $q_x^2(x) = (q \cdot \mathbf{n}(x))^2$, and $Q_s(x, \hat{p}, q) = \hat{p}^2 + 2q_0 \hat{p} + q_0^2(x) - q_0^2$, where $q_0^2(x) = q_x^2 - q_0^2(x)$. $H(x, \hat{p}, q)$ is a periodic function of $x$ with a band spectrum and Bloch eigenfunctions. To lowest order in $k_0/q_0$, however, eigenfunctions are localized at spatial minima in $\hat{p}(x, q)$, which can be approximated by the lowest-order terms in a Taylor expansion about these minima. For any given $q$, $\hat{p}(x, q)$ will have a minimum at some $x = x_m(q)$. Since $\hat{p}(x, q)$ depends on $x$ only in the combination $x_m(q) \cdot q$, $x_m(U(\theta)q) = x_m(q) + \theta/k_0$, where $U(\theta)$ is the operator that rotates $q_m$ through an angle $\theta$ about $p$, it is always possible to find a $q = \mathbf{q}_m$ such that $x_m(q_m) = 0$. If $\phi(x)$ is an eigenfunction of $\mathcal{H}(x, \hat{p}, q_m)$ with energy $\epsilon$, then $\psi(x) = \phi(x - \theta/k_0)e^{i\epsilon q \cdot x}$, where $q_m(\theta) = U(\theta)q_m$, is an eigenfunction of the harmonic kernel of $F_H$ with energy $\epsilon$ for all $\theta$.

Our approach, therefore, is to find those $q$’s that minimize $\hat{p}(0, q)$ or, equivalently, those $q$’s for which $Q_s(x, \hat{p}, q) = 0$. Since $q_0^2(0) = q_0^2$, and $q_0^2(0) = q_0^2 + q_0^2$, it follows that $\hat{p}(0, q)$ is at its minimum equal to $\hat{p}$ for $q = q_0$ and $(q_x, q_y) = q_0(\cos \gamma, \sin \gamma)$ for any $\gamma$. The Borode phase corresponds to $\gamma = 0$ and the RL phase to $\gamma = \pi/2$. Having found $q_m$, we can expand $Q_s$ and $Q_r$ in powers of $x$ and $\pi$:

$$Q_s = -2k_0q_0q_0 \sin \gamma x + (q_0^2 - q_0^2 \sin^2 \gamma) + ...$$

$$Q_r = \hat{p}^2 + 2q_0 \cos \gamma \hat{p} - Q_s \quad (6)$$

These expressions simplify in the Borode and RL cases to

$$Q_s^B = q_0^2q_0^2, \quad Q_r^B = 2q_0 \hat{p} - 2q_0^2 \hat{p}^2$$

$$Q_s^{RL} = -2k_0q_0q_0 \sin x, \quad Q_r^{RL} = \hat{p}^2 - 2k_0q_0q_0 \sin x$$

(7)

plus terms, which we show shortly, that yield corrections to the lowest order terms in $(k_0/q_0)$. If it is clear from these expressions that the B and RL phases enjoy a sort of duality obtained by interchanging $x$ and $\pi$. The Hamiltonian for the B phase will have terms proportional to $x^2\hat{p}^2$ and $\pi^2\pi^2 + \hat{p}^2\hat{p}^2$, whereas that for the RL phase will have terms proportional to $\pi^2\pi^2$, $x^2\pi^2$, and $\pi^2\pi^2 + \pi^2\hat{p}^2$. In the B case, the $x^2\pi^2 + \hat{p}^2\hat{p}^2$ term can be removed by transforming the wave function via $\phi_B(x) = \exp(i\mu_B x^3)\hat{p}_B(x)$ for an appropriate choice of $\mu_B$ while the $\pi^2\pi^2 + \pi^2\hat{p}^2$ term in the RL case can be removed by transforming the Fourier transform $\phi_{RL}(k) = \int dx e^{-i\varepsilon x} \phi_{RL}(x)$ to an appropriate change of $\mu_{RL}$ (k). In both cases, the eigenfunction $\phi_B(x)$ and $\phi_{RL}(x)$ are localized near $x = 0$ over some characteristic length $l$, and it is convenient to express them as functions of the unitless variable $u = x/l$. This leads to the Hamiltonians for the RL and B phases expressed to lowest order in $u$ and $\pi = u^{-1}d/dx$:

$$\mathcal{H}_{RL} = 2d_s^2q_0^2s_2\omega_{E_0}^2 \left[ u^2 + (k_0/q_0)^2 \right]$$

$$\mathcal{H}_B = 2d_s^2q_0^2s_2\omega_{E_0}^2 \left[ u^2 + (k_0/q_0)^2 \right]$$

(9)

With these choices, $\mathcal{H}_{RL} = \hat{p} + E_0(\eta_2)/(k_0/q_0)^2 + (u^2 + \hat{p}_0^2)$ and $\mathcal{H}_B = \hat{p} + E_0(\eta_2)/(k_0/q_0)^2 + (u^2 + \hat{p}_0^2)$. In the B case, the $\hat{p}^2$ term in the RL scale as $D_0^2(q_0^2s_1^2)$, which is dual to each other with $u^2 + \hat{p}_0^2$ and $u^2 + \hat{p}_0^2$ having the same lowest eigenvalue $\epsilon_0$.

The eigenvalues of both $\mathcal{H}_{RL} - \hat{p} - \hat{p}^2$ scale as $D_0^2(q_0^2s_1^2)$, higher order terms in $k_0x$ and $\pi$ neglected in Eq. (C) yield corrections to the dominant $(k_0/q_0)^2$ behavior of both $\mathcal{H}_B - \hat{p} - \hat{p}^2$ and $\mathcal{H}_{RL} - \hat{p} - \hat{p}^2$ of order $(k_0/q_0)^2$ or higher. In addition $\mathcal{H}_B - \hat{p}^2$ scales as $k_0(q_0^2s_1^2)$ when $\gamma = 0$, $\pi/2$, and corrections to $\mathcal{H}_{RL} - \hat{p}^2$ scale, respectively, as $\gamma^2(k_0/q_0)^2$ and $(\pi/2 - \gamma)^2(k_0/q_0)^2$. Thus the B and RL phases always have lower energy than phases with intermediate values of $\gamma$.

The cholesteric phase becomes unstable at $k_0 = k_{c2}$ when the smallest eigenvalue of $\mathcal{H}_{c2}$ becomes zero. Thus

$$k_{c2}^{RL} = \frac{q_0}{\eta_2{s_1^{1/4}} \left( \frac{|\pi|}{\epsilon_0 E_0} \right)^{3/4}}$$

$$k_{c2}^{B} = \frac{q_0}{\eta_2{s_1^{1/2}} \left( \frac{|\pi|}{\epsilon_0 E_0} \right)^{3/4}}$$

and near $|\pi| = 0$, both $k_{c2}(RL)$ and $k_{c2}(B)$ scale as $|\pi|^{3/4}$. Their ratio is $k_{c2}^B/k_{c2}^{RL} = (s_2s_1)^{1/4}$. Thus, $k_{c2}^B > k_{c2}^{RL}$ and the cholesteric phase becomes unstable to the B phase before the RL phase when $s_2 = 1 + \eta_2 - 2\eta_1 > \eta_1$, i.e., when $|\pi| < 1/2$, and it becomes unstable to the RL phase before the B phase when $|\eta| > 1/2$. This means that the RL phase is not stable in the original CL model.
in which $D_{\parallel \perp} = 0$. Stability of the nematic phase in the absence of chirality requires $D_{\parallel \perp}^2 - D_{\parallel \parallel}^2 = D_{\parallel \perp} s_1 > 0$ or $\eta_0 < \eta_\parallel$. It is clearly possible to satisfy both this condition and $\eta_0 > 1/2$, so that there is a range of parameters for which the RL phase is stable.

The B eigenfunctions are of the form $\phi(u) = e^{i u^3} \tilde{\phi}_B(u)$ where $(u^4 + u^2) \tilde{\phi}_B(u) = \epsilon_0 \tilde{\phi}_B(u)$. The RL eigenfunctions are of the form $\phi_{RL}(u) = \int (dk/2\pi) e^{-i u^3 k^2} \tilde{\phi}_B(k)$, where $\phi_B(u)$ and $\tilde{\phi}_B(k)$ are identical functions of different arguments. $\tilde{\phi}_B(u)$ can be obtained numerically using the shooting method, and it, along with $\phi_{RL}(u)$, is plotted in Fig. 4. The resulting eigenvalue is $\epsilon_0 = 1.060357$. An excellent approximation to $\phi_B(u)$ over the entire range of $u$ is $\tilde{\phi}(u) = \exp[-\frac{1}{2} \frac{A u^2}{\sqrt{1 + \frac{3}{8}(u/A)^2}}]$ where $A = 1.035$. This function satisfies the requirement that $\tilde{\phi}(u) \to \exp(-\frac{1}{3} |u^3|)$ as $|u| \to \infty$.

To determine the structure of the TGB$_C$ phases, we construct variational smectic order parameters from the degenerate set of lowest eigenfunctions of $H(x, \pi, q)$:

$$\psi(x) = C \sum_s \phi((x - nl_b)/l) e^{i q_m(\theta) \cdot x},$$  

(11)

where $q_m(\theta) = U(\theta) q_m$ and, as discussed in the paragraph preceding Eq. (2), $q_m$ has different forms in the Bordeaux and RL phases. Following the treatment of the cholesteric-to-TGB$_A$ transition, we can write the total free energy after minimizing over director fluctuations as

$$F \overset{K_2g_b^2}{\rightarrow} \frac{1}{2} - \frac{A}{4\beta(l_b/l)} \left( \frac{k_0 - k_{c2}}{k_0} \right)^2,$$  

(12)

where $\beta(l_b/l)$ depends on the separation $l_b$ between grain boundaries, and $A$ depends on $k_0$ and $l$ but not on $l_b$. Thus, the equilibrium value of $l_b$ is that which minimizes $\beta(l_b/l)$, which can be expressed as $([\psi^4]_{av} - \kappa_2^2 (k_0/q_0)^{2/3} [f]_{av}) / [\psi^2]_{av}^2$, where $f$ is a complicated function of order $\psi^4$ and $[g]_{av} = V^{-1} \int d^3x g$ is the spatial average of $g$. Carrying out this minimization procedure using the analytic approximation for $\phi_B(u)$, we find $l_b/l \approx 2.15$ for the Bordeaux and $l_b/l \approx 3.0$ for the RL TGB$_C$ phases, respectively. To find the spacing between dislocations in a grain boundary, we use the geometric relation $l_d = d / (\sin \alpha_0 l_d l_4)$, where $\pi/2 - \alpha_0$ is the angle between $\mathbf{N}$ and $\mathbf{p}$. Our results for $l_b/l$, $l_d/l \sim \rho d/l$ and $\xi \sim (D_0^2/\rho l)^{1/2} \sim d^{1/3} \rho^{2/3}$ are summarized in table I.

The wave function $\psi$ for our calculated values of $l_b$ for both TGB$_C$ phases are shown in Fig. 3.

We have presented an overview of the properties of the the Bordeaux and RL TGB$_C$ phases and the transition to them from the cholesteric phase obtained from an Abrikosov-like analysis near the upper critical twist $k_{c2}$ at which the cholesteric phase becomes unstable. In a future publication, we will present more details of our calculations, including a discussion of the transition from type I to type II behavior. We will also discuss the relation between our work and that of Dozov [12].

We thank Randall Kamien for a careful reading of this manuscript. This work was supported in part by the National Science Foundation under Grant DMR 00-96531.

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