Smectic Phases with Cubic Symmetry: The Splay Analog of the Blue Phase

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We report on a construction for smectic blue phases, which have quasi-long-range smectic translational order as well as long-range cubic or hexagonal order. Our proposed structures fill space with a combination of minimal surface patches and cylindrical tubes. We find that for the right range of material parameters, the favorable saddle-splay energy of these structures can stabilize them against uniform layered structures.

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Liquid crystalline blue phases exhibit true three-dimensional, periodic orientational order. Two of these phases possess cubic symmetry ($BP1$ and $BP2$) while the third ($BP3$) is thought to be an isotropic melt of double-twist cylinders [1,2]. Recently, new phases of matter have been identified that possess the quasi-long-range translational order of smectics [3] and, at the same time, three-dimensional orientational order. These three distinct smectic blue phases have been observed near the isotropic transition of these compounds: $BP_{smA}1$ has cubic symmetry, $BP_{sm}2$ has orthorhombic symmetry, and $BP_{sm}3$ is isotropic [4]. The precise physical properties of these materials have been the study of intense investigation in recent years [4–7]. However, there is no obvious way to incorporate smectic ordering into the traditional double-twist tube blue phase ordering put forward by Meiboom *et al.* [8] for nematic blue phases. In general, since smectic ordering is incompatible with cubic symmetry, it is expected that any blue phase structure must include smectic defects as well as orientational defects. Though a model for double-twist cylinders with smectic order has been proposed [9], the simplest variant of that model is incompatible with experimental details [6]. In this Letter, we propose a new scheme for constructing an achiral smectic blue phase that fills space with continuous concentric layers possessing cubic symmetry. This new phase suffers elastic energy costs arising from nonuniform layer spacing and layer bending as well as condensation energy costs arising from melted regions. However, we show that when the saddle-splay constant, K_{24}, is negative enough, these energy costs can be compensated by the gain in Gaussian curvature energy in the surfaces. Note that screw dislocations are also favored when $K_{24} < 0$ [9], suggesting that twist grain boundary (TGB) phases are more likely to occur in such systems. Since our new phase does not require chirality, it could be realized in a thermotropic liquid crystal near a compensation point [10], especially in the vicinity of a TGB phase.

The key ingredient in our construction is the observation that saddle splay and the Gaussian curvature are identical [11] for layered systems with uniform spacing. The saddle-splay energy of a director field $\mathbf{N}$ is [8]

$$F_{SS} = K_{24} \int d^3x \boldsymbol{\nabla} \cdot [(\mathbf{N} \cdot \boldsymbol{\nabla})\mathbf{N} - \mathbf{N}(\boldsymbol{\nabla} \cdot \mathbf{N})], \quad (1)$$

where K_{24} is a Frank constant. Because this term is a total derivative it is often a neglected boundary term. However, defects introduce boundaries, and it is precisely the saddle-splay energy that stabilizes the standard nematic blue phase. Since that phase is riddled with defects, the saddle-splay boundary energy grows linearly with volume.

If space can be filled with surfaces normal to $\mathbf{N}$, then F_{SS} has a different interpretation—if we replace the z integration in (1) with an integration over a Lagrangian coordinate n, which labels the surfaces, then

$$\begin{aligned} F_{SS} &= -2K_{24} \int dn \int dxdy \frac{dz}{dn} K_n(x, y) \\ &= -2K_{24} \int dn \int dxdy \sqrt{g_n(x, y)} a_n(x, y) K_n(x, y), \end{aligned} \quad (2)$$

where $a_n(x, y)$ is spacing between layer n and $n + 1$ at (x, y), K_n is the Gaussian curvature of the nth surface, g_n is the determinant of the two-dimensional surface metric, and $\sqrt{g_n} a_n = dz/dn$ follows from conservation of volume. Since the Gauss-Bonnet theorem [11] implies that for a surface of genus g the integrated Gaussian curvature is $4\pi(1 - g)$, we expect that higher-genus surfaces are favored by the saddle-splay term. Note that since $a_n(x, y)$ is not necessarily constant, the integral (2) is not simply topological. Nonetheless this identification will aid us in our choice of smectic structures. We note that in our model, the saddle splay is a measure of the layer normals, not the nematic director. When the nematic director follows the layer normal these are, of course, equivalent. However, in type-II smectics it is possible for the saddle splay of the director field to differ in its precise numerical value from the saddle splay in the layers.

We must choose our structures in the context of the standard bulk free energy of a smectic liquid crystal:

$$F_{Sm} = \int d^3x \left\{ \frac{B}{4} [(\boldsymbol{\nabla}\Phi)^2 - 1]^2 + 2K_1 H^2 \right\}, \quad (3)$$

where the smectic density is $\rho \propto \cos(2\pi\Phi/a)$, $\Phi(x, y, z)$ is a phase field, a is the layer spacing, B is the compression modulus, K_1 is the bend modulus, and $H = \frac{1}{2}\boldsymbol{\nabla}\cdot\mathbf{N}$ is the mean curvature of the layers. Though we could capture the same physics by replacing H with $\frac{1}{2}\nabla^2\Phi$, we choose the former for computational convenience.

We note that there is an intrinsic frustration between the two terms in (3). Consider a family of layers $\mathbf{x}_n(\sigma, \tau)$ which are solutions to $\Phi[\mathbf{x}_n(\sigma, \tau)] = na$. If $\mathbf{N} = \boldsymbol{\nabla}\Phi/|\boldsymbol{\nabla}\Phi|$ is the normal to $\mathbf{x}_0$, then $\mathbf{x}_n = \mathbf{x}_0 + na\mathbf{N}$ is a solution with vanishing compression energy: $\mathbf{N}\cdot\boldsymbol{\nabla}\Phi(\mathbf{x}_n) = \frac{d}{d(an)}\Phi(\mathbf{x}_0 + na\mathbf{N}) = 1$ and so $|\boldsymbol{\nabla}\Phi| = 1$. However, if $\kappa_{i,0}$ are the principal curvatures of $\mathbf{x}_0$, then, since these surfaces are uniformly spaced, $\kappa_{i,n} = \kappa_{i,0}/(1 + na\kappa_{i,0})$ are the principal curvatures of $\mathbf{x}_n$. Thus, if the mean curvature $H = \frac{1}{2}(\kappa_1 + \kappa_2)$ vanishes for some value of n, it will not vanish for any other value of n unless $\kappa_{i,n} = 0$. Conversely, if H vanishes everywhere and $\kappa_{i,n}$ does not, then it is impossible to have equally spaced layers. Therefore it is impossible to have both the bending and the compression terms vanish unless all the layers are flat. Thus any ground state must necessarily be a compromise between nonuniform spacing and bending.

Though we may choose any number of initial space-filling surfaces of constant Φ, we illustrate our approach with a cubic structure. The Schwartz P surface, or plumber's nightmare, is a triply periodic minimal surface which has the topology we seek. Because it is minimal, $H = 0$ and $K \leq 0$ everywhere on this surface. Moreover, because of the mathematical interest in minimal surfaces, the P surface has a simple parametric representation which proves useful in computation. This surface will be the template within which we fill with "concentric" surfaces. We refer to the section of the P surface in the unit cell as the P cell and fill it in with concentric, rescaled P cells. The smaller P cells will no longer intersect the walls of the unit cell. We attach cylinders to the open ends of the P cells to fill in the gaps. The advantage of this construction is that we can easily calculate the compression energy for the cylinders and the bending energy for the P cells. Because the inside and the outside of the P surface are identical, our construction self-consistently fills the entire unit cell and we need focus only on the interior of the P cell—the remainder of the unit cell is filled with eight separate octants of the P cell. Our approach solves the frustration between compression and bending by building the smectic phase out of pieces that have no curvature (the P cells) and pieces which can have uniform spacing (the cylinders) as shown in Fig. 1.

The energetics of this structure has four components: the bending energy, the core energy, the saddle-splay energy, and the compression energy. By our construction there is no bending energy on the P cells since they are minimal. Thus the curvature energy is nonvanishing only on the cylindrical sections of the unit cell. If ρ_o is the radius of the largest cylinder, then geometry requires $\rho_o = L/4$, where L is the size of the unit cell. By construction the length of the cylindrical region of radius r is $2\rho_o - 2r$ and $H = 1/(2r)$ so the bending energy is

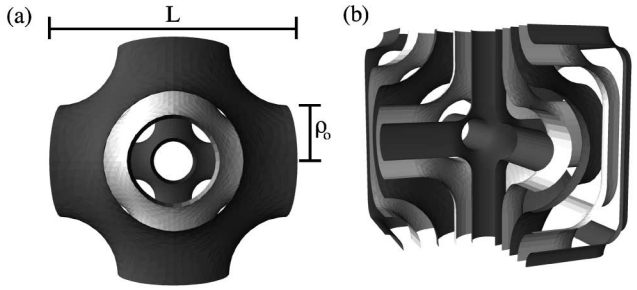

FIG. 1. Proposed P surface smectic. In (a) we show the P cell and the interior structure composed of concentric P cells and cylinders. In (b) we fill in the entire (cubic) unit cell with eight-eighths of the central structure. We have cut away one-quarter of the volume to show interior smectic layers.

$$F_B = 24\pi\rho_o K_1\left[\log\left(\frac{\rho_o}{\rho_C}\right) + \left(\frac{\rho_C}{\rho_o} - 1\right)\right], \tag{4}$$

where ρ_C is the short-distance cutoff. Inside this cutoff region the smectic order vanishes and there is an energy penalty proportional to the disordered region. If the cutoff is comparable to the molecular scale then, in addition, there is a $+1$ nematic disclination line down the cylindrical core which contributes to the core energy as well [12]. Including the energy of the core region at the intersection of these lines, we have

$$F_{\text{core}} = 24(\rho_o - \rho_C)\varepsilon + \frac{64}{\pi}\rho_C\varepsilon, \tag{5}$$

where ε is a line tension. The saddle-splay energy offsets these positive energy contributions. As in the traditional chiral blue phases, the saddle splay can easily be calculated as a boundary term along the $+1$ disclination lines. Converting the volume integral (1) into a surface integral we see that the cylindrical cores of the P cells contribute -2π per unit length, and each unit cell has a length $24(\rho_o - \rho_C)$ of such tubes (including the contribution from the other P cell in the unit cell). Because the integral over the P cell in the center vanishes, $F_{SS} = -48\pi a|K_{24}|N$, where $N = (\rho_o - \rho_C)/a$ is the number of layers (recall that K_{24} must be negative).

The final energetic contribution to the smectic free energy arises from the nonuniform spacing of the P cells. By our construction, the part of the smectic which consists of concentric pieces of P surface cannot have uniform spacing across the layers. However, there is an energetically preferred difference in average radius between consecutive layers which we can vary to minimize the compression energy. To perform the spatial integral we divide our proposed structure into those parts which have cylindrical symmetry and those which are pieces of

the P surface. In each region we define our coordinates such that surfaces of constant phase are constants of one variable. In the cylindrical region we use polar coordinates. For the region filled with rescaled P cells, we may define a new variable ζ through

$$r = \zeta r_o(\theta, \phi), \tag{6}$$

where r, θ, and ϕ are the usual spherical coordinates and $r = r_o(\theta, \phi)$ is the equation of the P cell. Thus inside the P cell ζ runs from zero to 1 and labels layers of constant Φ.

For the phase field to capture the concentric layers, we must have $\Phi[\zeta r_o(\theta, \phi), \theta, \phi]$ independent of θ and ϕ for fixed ζ. It follows that $\Phi[\zeta r_o(\theta, \phi), \theta, \phi]$ can depend only on ζ. As we now show, the angular dependence of $|\nabla\Phi|$ (which appears in the free energy) is completely separable from the ζ dependence as well.

Since $|\nabla\Phi|$ is related to the layer normal through $\mathbf{N} = \nabla\Phi/|\nabla\Phi|$, we have $r\partial_r\Phi = \mathbf{r}\cdot\nabla\Phi = (\mathbf{r}\cdot\mathbf{N})|\nabla\Phi|$. But since $\Phi = \Phi(\zeta) = \Phi(r/r_o)$, we also have $r\partial_r\Phi = (r/r_o)\partial_\zeta\Phi = \zeta\partial_\zeta\Phi(\zeta)$ and so $(\mathbf{r}\cdot\mathbf{N})|\nabla\Phi| = \zeta\partial_\zeta\Phi(\zeta)$ and is thus constant on any surface of fixed ζ. Choosing an arbitrary reference direction (θ_o, ϕ_o) we can write $(\nabla\Phi)^2 = p(\theta, \phi)\Delta(\zeta)$, with

$$p(\theta, \phi) = \left[\frac{\mathbf{r}(\theta_o, \phi_o)\cdot\mathbf{N}(\theta_o, \phi_o)}{\mathbf{r}(\theta, \phi)\cdot\mathbf{N}(\theta, \phi)}\right]^2, \tag{7}$$

$$\Delta(\zeta) = [\nabla\Phi]^2|_{\zeta,\theta_o,\phi_o}, \tag{8}$$

where $p(\theta, \phi)$ is evaluated on a shell of constant Φ. Note that $p(\theta, \phi)$ is scale independent and may be evaluated on any of the concentric P cells. By choosing the reference direction, (θ_o, ϕ_o), to be a point on the interface between the P-cell region and the cylindrical region we can define $\zeta = \rho/\rho_o$ inside each of the six cylindrical regions, where ρ is the radius in cylindrical coordinates. This choice allows us to naturally continue $\Delta(\zeta)$ into the cylindrical regions. The angular and ζ integrations decouple in these coordinates and the compression energy is quadratic in $\Delta(\zeta)$:

$$F_C = \frac{B}{2}\rho_o^3\int d\zeta[\zeta^2[I_{P1} - I_{P2}\Delta(\zeta) + I_{P3}\Delta^2(\zeta)] + 24\pi\zeta(1-\zeta)[1-\Delta(\zeta)]^2], \tag{9}$$

where the three numerical constants $I_{P1} \approx 72.42$, $I_{P2} \approx 65.74$, and $I_{P3} \approx 17.10$ are moments of $p(\theta, \phi)$ which capture the geometry of the P cell and were calculated with the aid of the Surface Evolver software package [13]. Since the other contributions to the total free energy do not depend on $\Delta(\zeta)$, we minimize F_C by varying the integrand in (9) with respect to $\Delta(\zeta)$ and find that the resulting total compression energy in the layered P surface structure is $F_C \approx 2.77B\rho_o^3$, with a very weak dependence on the core size ρ_C for $\rho_C \ll \rho_o$.

For our proposed smectic structure to be stable against the uniform flat phase, the positive energy contributions from F_C, F_B, and F_{core} must be compensated by a large negative saddle-splay energy. Choosing the cutoff ρ_C to be the molecular scale a, we minimize the free energy density $\mathcal{F} = (4\rho_o)^{-3}[F_C + F_B + F_{\text{core}} + F_{SS}]$ with respect to ρ_o and find a stable minimum when

$$\begin{aligned} &|K_{24}| \gtrsim \varepsilon/\pi, \qquad |K_{24}| \gg K_1 N\ln N, \\ &|K_{24}| \gg B\rho_o^2 N. \end{aligned} \tag{10}$$

The preferred cell size is on the order of

$$N = \frac{\rho_o}{a} \approx \frac{3\pi|K_{24}| + [4/\pi - 3/2]\varepsilon}{2\pi|K_{24}| - \varepsilon}. \tag{11}$$

It is worth commenting on the limits in (10). At the smectic to nematic transition, neither K_1 nor K_{24} suffer from anomalous divergences. Thus this phase is stable only when $|K_{24}|$ is exceptionally large. Numerically minimizing to give a concrete example, we find that when $K_{24} = -20K_1$ and $\varepsilon = 0.88(2\pi|K_{24}|)$ that $N \approx 15$ (thus $L \approx 60a$, consistent with experimental results for $BP_{smA}1$ [4]). For this structure to be stable against the flat phase, $B\rho_o^2$ must be smaller than $\sim 20K_1$. Since $B = K_1/\lambda^2$, where λ is the penetration length, this requires that $\lambda > 4a$; i.e., the system must be an extreme type-II smectic. Were we to relax the constraint that $H = 0$ in the central region, the compression and curvature could compete and we would expect that $F_C \sim \sqrt{BK_1}\rho_o^2 \sim B\lambda\rho_o^2$. In this case λ could be significantly smaller, though it would still scale as N.

The resulting nematic texture of the cubic smectic is the splay analog of the traditional chiral blue phase. However, this splay version of the blue phase arises through a completely different mechanism than the traditional cholesteric blue phase: in the traditional blue phase the defects are kept apart by the pitch of the cholesteric; here the defects are kept apart by the large energy cost of the line defects which connect them. Additionally, though the traditional blue phase is stabilized by a large positive value of K_{24} our blue phase requires a large negative value of K_{24} [8]. The smectic order, however, is essential to prevent the unwinding of the $+1$ disclinations which are responsible for the saddle-splay energy. Note that if this smectic phase is energetically stable, then the equivalent nematic phase with $B = 0$ would also be stable. Because there is no condensation energy associated with the absence of smectic order, in the nematic phase ε will be smaller than in the corresponding smectic phase. As ε shrinks, the number of layers approaches a limiting value of 1.5 and the lattice constant is comparable to the core size. It is likely that such a configuration would melt due to fluctuations, though this warrants further investigation. The remarkable aspect of both the smectic and nematic phases presented here is that they exist without any chirality of the molecules. Since the stability of this phase

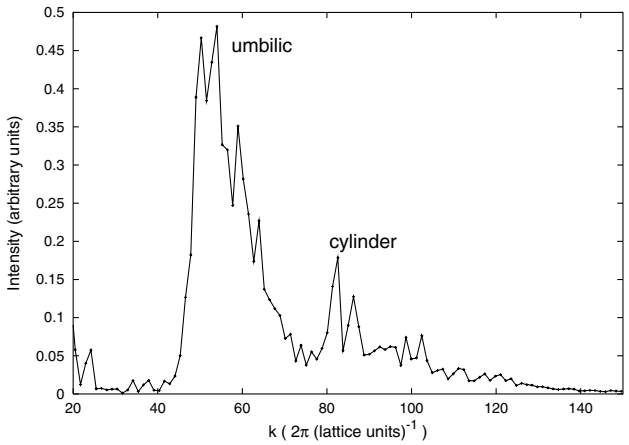

FIG. 2. Rotationally averaged form factor for the unit cell with $N = 15$. The umbilic peak corresponds to the layering along the diagonal of the unit cube. The cylinder peak arises from the concentric cylinder regions.

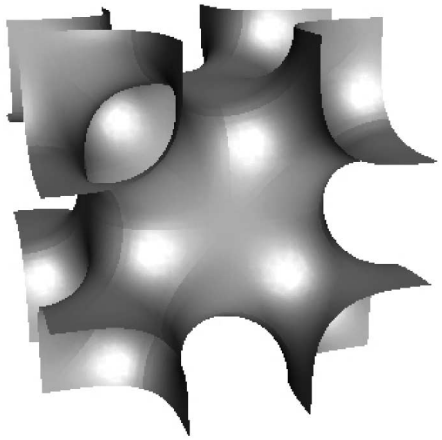

FIG. 3. Repeat unit of Schoen's *I-WP* surface. This surface has genus $g = 7$ so $\int KdS = -24\pi$.

requires a careful tuning of the core energy density ε and K_{24}, it can occur only over a small range of temperature.

To determine the degree of ordering in our structure, we calculated the powder-averaged form factor of the unit cell for $N = 15$. Since every line passing through the center of the unit cell intersects precisely 60 layers, we can infer the degree of ordering along any direction simply from the location of the peak. Our results are shown in Fig. 2. Not surprisingly, we found a large peak in the directions normal to the eight points at which the *P* surface is perfectly flat (the umbilics of the *P* surface). The corresponding direction relative to the unit cell is $(\pm 1, \pm 1, \pm 1)$. We also found weaker peaks along the $(\pm 1, 0, 0)$, $(0, \pm 1, 0)$, and $(0, 0, \pm 1)$ directions. These arise from the concentric cylinder regions. We note that the eight peaks along the cell diagonal do not correspond to the observed symmetry of the smectic blue phases, though this can be changed with a different choice for our unit cell. However, we have demonstrated a "proof of principle" that the construction of splay blue phases is possible. A better candidate for $BP_{smA}1$ is Schoen's *I-WP* surface, pictured in Fig. 3. This surface is also triply periodic, though it is flat along the $(\pm 1, 0, 0)$, $(0, \pm 1, 0)$, and $(0, 0, \pm 1)$ directions and so in x ray we would expect the primary peaks along these directions. Since the *I-WP* surface has genus $g = 7$, the integrated surface Gaussian curvature is -24π and we expect that the saddle-splay energy would be even more negative than for the *P* cell. Calculation of the total energy of an *I-WP* smectic is more difficult than for the *P* smectic because the region of the cubic cell outside the *I-WP* surface is not identical to the region inside. Based on the results here we expect that the compression energy will be unimportant for sufficiently large λ/a.

We have outlined a model for smectic blue phases and the splay analog of the traditional blue phase. The favorable saddle-splay energy of our structure is sufficient to stabilize it against the flat smectic phase for a realistic range of material parameters which may be encountered near the isotropic transition. Our model presents an entirely new and promising organizational principle for smectic systems.

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