Relieving Cholesteric Frustration: The Blue Phase in a Curved Space

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The problem of minimizing the full cholesteric free energy in flat space is difficult since the bending and bulk energies favor different forms of the order parameter. It is shown, however, that the problem can be solved exactly on the surface of a sphere in four-space, where the curvature relieves the strains induced by the "double twist." The conventional Landau bulk free energy leads to a rigorously uniaxial structure. The model is also of interest as a simple and explicit example of the ideas underlying recent theories of glasses.

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Equilibrium theories of cholesteric liquid crystals[1-3] are based on the minimization of a simple mean-field free energy, yet they display a bewildering variety of "blue phases," as do the materials themselves.[4] This complexity is the manifestation of an incompatibility in the free energy: Structures that favor bulk terms in the free energy do not take full advantage of the possibilities for minimizing the gradient energy, and vice versa. We have found that this difficulty disappears on the surface of a sphere in four dimensions with circumference given by the cholesteric pitch p: There is a unique unfrustrated texture which minimizes the free energy, providing an exact solution to a problem which has proved extremely difficult to treat in flat space. A recent proposal for a model of the blue phase as a "doubly twisted" structure threaded by a network of disclination lines is seen from this perspective to be nothing but the result of flattening out our exact curved-space solution. The cholesteric thus emerges as an extremely simple, explicit, and, in the curved space, analytically manageable continuum model of the general kinds of ideas that people have been formulating to account for the structure of glasses.[5,6]

The order parameter in nematic or cholesteric liquid crystals is a real traceless symmetric tensor Q_{ij} that characterizes the deviation from isotropy of some appropriate local tensor property of the system[7] such as the dielectric constant. To second order in spatial gradients and to leading nonvanishing order in Q there are just three independent terms in the bending free-energy density:

$$f_{\text{grad}} = \tfrac{1}{2}K_1(\nabla_k Q_{ij})^2 + \tfrac{1}{2}K_2(\nabla_k Q_{kj})^2 + \tfrac{1}{2}K_3\epsilon_{kis}(\nabla_k Q_{ij})Q_{js}\ , \tag{1}$$

where sums on indicies are implied. The K_3 term is allowed only in cholesterics, which are distinguished from nematics by the absence of microscopic inversion symmetry. The simplest model for the bulk free-energy density requires terms through fourth order in Q. Since the only independent invariants of a traceless three-tensor are $\mathrm{Tr}Q^2$ and $\mathrm{Tr}Q^3$, this has the general form

$$f_{\text{bulk}} = \alpha\,\mathrm{Tr}Q^2 - \beta\mathrm{Tr}Q^3 + \gamma(\mathrm{Tr}Q^2)^2 \tag{2}$$

The solution to the simple mean-field problem of minimizing $f_{\text{grad}} + f_{\text{bulk}}$ is unknown. The problem is that f_{bulk}, which determines the amplitude and shape of the local order parameter, favors a uniaxial form[8] for Q,

$$Q_{ij} \propto n_i n_j - \tfrac{1}{3}\delta_{ij}\ , \tag{3}$$

since $\mathrm{Tr}Q^3$ is extremized by a uniaxial form for given $\mathrm{Tr}Q^2$. However, minimization of the bending energy (1) for given $\int d^3x\,\mathrm{Tr}Q^2$ leads to the linear condition

$$\nabla \times Q = -2q_0 Q \tag{4}$$

which is satisfied by the biaxial form

$$Q_{ij}{}^0 = (\hat{x}_i\hat{x}_j - \hat{y}_i\hat{y}_j)\cos 2q_0 z + (\hat{x}_i\hat{y}_j + \hat{y}_i\hat{x}_j)\sin 2q_0 z\ , \tag{5}$$

where

$$q_0 = K_3/4K_1 = 2\pi/p\ , \tag{6}$$

with p the cholesteric pitch. Thus f_{grad} is uniquely minimized by a biaxial texture formed from linear combinations of Q^0 and its rotations, which fails to take full advantage of the cubic terms in f_{bulk}. This incompatibility of f_{grad} can impose on Q some rather intricate compromise structures near the

transition temperature. These are the blue phases. (Well below the transition from the disordered "isotropic" phase, theory and experiment[9] agree that the equilibrium structure is essentially a uniaxial phase with

$$\hat{n} = \hat{z}\cos q_0 x - \hat{y}\sin q_0 x , \tag{7}$$

with a slight biaxiality induced by the anisotropy in the twisting of $\hat{n}$.)

In discussing the blue phase, Meiboom *et al.*[3] consider a uniaxial order parameter, as favored by the bulk terms, and attempt to build structures reducing f_{grad} as much as possible. They find that locally the "double-twist" structure

$$\hat{n} = \hat{z}\cos q_0 r - \hat{\varphi}\sin q_0 r \tag{8}$$

lowers the gradient energy near the line $r=0$ well below that of the low-temperature spiral structure (7). The term "double twist" refers to the fact that in the vicinity of $r=0$ the director $\hat{n}$ twists away from $\hat{z}$ in all radial directions, in contrast to the spiral form (7), which twists only in the x direction. The coordinate-independent condition for double twist is given by the differential relation

$$\nabla_i \hat{n}_j = -q_0 \epsilon_{ijk}\hat{n}_k , \tag{9}$$

which (8) evidently satisfies at $r=0$.

Note that perfect double twist cannot be achieved throughout an extended region, since (9) implies $\nabla_i\nabla_j\hat{n} \neq \nabla_j\nabla_i\hat{n}$. Meiboom *et al.*[3] propose a structure in which $(\nabla_i \hat{n}_j + q_0\epsilon_{ijk}\hat{n}_k)^2$ is made small throughout a network of cylindrical tubes.[10] They show that this attempt to spread double twist through the system necessarily introduces defects threading the intercylinder regions and propose that near the transition to the disordered "isotropic" phase, the energy gain of the local ordering outweighs the cost of the defects and stabilizes the structure.

The impossibility of extending the double-twist ordering throughout the system can be viewed as a form of frustration. Nelson[11] has remarked that this frustration is completely relieved on the surface $S^3(q_0)$ of a sphere of radius $1/q_0$ in four dimensions, so that double twist can exist at every point. We show here that this doubly twisted uniaxial form uniquely provides the exact minimum of the full free energy.

Consider first a nematic liquid crystal ($K_3=0$). The gradient energy is minimized[12] by *any* constant Q_{ij}. The bulk terms (2) then require Q to be uniaxial.[13] This solves the problem.

A similar argument can be made for the cholesteric on $S^3(q_0)$. Notice first that the term in (1) linear in gradients, which is responsible for the complexities of the cholesteric, can be combined with the other gradient terms, if we redefine f_{grad} to be given by

$$f_{\text{grad}} = \tfrac{1}{2}K_1(\nabla_k Q_{ij} - q_0\epsilon_{iks}Q_{sj} - q_0\epsilon_{jks}Q_{is})^2 + \tfrac{1}{2}K_2(\nabla_k Q_{kj})^2 . \tag{10}$$

[This differs from the form (1) by a term proportional to $\mathrm{Tr}Q^2$, which can be subtracted by a corresponding redefinition of f_{bulk}.]

We now introduce a set of orthonormal basis vectors in four-space. Let (x_0,x_1,x_2,x_3) be a point on $S^3(q_0)$, and let $\hat{e}^{(0)}=q_0(x_0,x_1,x_2,x_3)$ be the unit radius vector and $\hat{e}^{(1)},\hat{e}^{(2)},\hat{e}^{(3)}$ be a local orthonormal basis for the tangent three-space. Take Q_{ij} to be the components of Q in this basis ($i,j=1,2,3$): $Q = Q_{ij}\hat{e}^{(i)}\hat{e}^{(j)}$. The derivative of Q on the sphere is given by projecting the usual four-dimensional gradient into the tangent three-space[14]:

$$Q_{ij;k} = \hat{e}^{(i)}\hat{e}^{(j)}(\hat{e}^{(k)}\cdot\nabla)Q = \hat{e}^{(i)}\hat{e}^{(j)}\nabla_k Q = \nabla_k Q_{ij} + Q_{sj}(\hat{e}^{(i)}\nabla_k\hat{e}^{(s)}) + Q_{is}(\hat{e}^{(j)}\nabla_k\hat{e}^{(s)}) . \tag{11}$$

Equation (11) includes the contribution from any spatial variations of the basis vectors. The generalization of the gradient energy (10) to the curved space $S^3(q_0)$ is simply

$$f_{\text{grad}} = \tfrac{1}{2}K_1(Q_{ij;k} - q_0\epsilon_{iks}Q_{sj} - q_0\epsilon_{jks}Q_{is})^2 + \tfrac{1}{2}K_2(Q_{kj;k})^2 . \tag{12}$$

Consider now the basis[15]

$$\begin{aligned}\hat{e}^{(1)} &= q_0(-x_1,x_0,x_3,-x_2) ,\\ \hat{e}^{(2)} &= q_0(-x_2,-x_3,x_0,x_1) ,\\ \hat{e}^{(3)} &= q_0(-x_3,x_2,-x_1,x_0) .\end{aligned} \tag{13}$$

One easily verifies that

$$\hat{e}^{(i)}\nabla_k\hat{e}^{(s)} = q_0\epsilon_{iks} . \tag{14}$$

Equation (12) then simplifies to

$$f_{\text{grad}} = \tfrac{1}{2}K_1(\nabla_k Q_{ij})^2 + \tfrac{1}{2}K_2(\nabla_k Q_{kj})^2 . \tag{15}$$

As in the case of a flat-space nematic, any constant Q_{ij} in the basis (13) minimizes the gradient energy (for $K_1,K_2>0$).[16] The bulk energy (2) requires Q to be uniaxial, and Q therefore has the form (3), where the components of $\hat{n}$ are constant

in the basis (13).[17]

Of course, our structure on $S^3(q_0)$ does not resolve the computational problem of optimizing blue-phase structures in real space. It does, however, vividly bring home several important points. First, the importance of double twist is clear. The components $\hat{n}_j$ of the major axis of Q (which are constant in the basis $\{\hat{e}^{(i)}\}$) satisfy the double-twist condition at all points [c.f. (9)]:

$$\hat{n}_{j;i} = \nabla_i \hat{n}_j + \hat{n}_k \hat{e}^{(j)} \nabla_i \hat{e}^{(k)} = -q_0 \epsilon_{ijk} \hat{n}_k . \qquad (16)$$

Second, the relationship of the uniaxial and biaxial models is clarified. When the cubic term β in (2) is not equal to zero, the unfrustrated texture is rigorously uniaxial,[18] and biaxiality will occur only to relax imposed strains. This lends support to the assertion[19] that biaxiality in the order parameter is not an essential feature of the blue phase except in the cores of disclination lines.[20] Third, in contrast to analogous theories of glasses, the radius of curvature of the "natural" space $S^3(q_0)$ for the cholesteric is very large compared with atomic dimensions, and there is therefore no ambiguity about whether or not a given flattened configuration should or should not be viewed as containing defects. Fourth, the essence of the complexity of the blue phases lies in frustration: In a space curved so as to relieve this frustration the minimization problem has a simple, exact solution.

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[4]See, for example, W. Elser, J. L. W. Pohlman, and P. R. Boyd, Mol. Cryst. Liq. Cryst. 20, 77 (1973); K. Bergmann and H. Stegemeyer, Z. Naturforsch. 34a, 251 (1979); M. Marcus, J. Phys. (Paris) 42, 61 (1981); A. J. Nicastro and P. H. Keyes, Phys. Rev. A 27, 431 (1982).

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[8]A uniaxial tensor has a pair of degenerate eigenvalues and therefore an axis of symmetry $\hat{n}$ (rodlike symmetry). This is the basis for the conventional description of cholesterics in terms of a director. A biaxial tensor has unequal eigenvalues (bricklike symmetry).

[9]Z. Yaniv, N. A. P. Vaz, G. Chidichimo, and J. W. Doane, Phys. Rev. Lett. 47, 46 (1981).

[10]See also R. M. Hornreich, M. Kugler, and S. Shtrikman, Phys. Rev. Lett. 48, 1404 (1982).

[11]D. R. Nelson, private communication, who learned of this possibility from D. Eardley.

[12]When $K_1, K_2 > 0$ this is evident. In flat space it remains true throughout the region of stability of f_{grad} ($K_1 > 0$, $K_2 > -\frac{3}{2}K_1$).

[13]Since f_{grad} is minimized by any constant tensor, the form of Q is determined by minimizing f_{bulk}. Should f_{bulk} have the more general form $F(\mathrm{Tr}Q^2, \mathrm{Tr}Q^3)$ with F minimum at a nonextremal value of $\mathrm{Tr}Q^3$ [$|\mathrm{Tr}Q^3| < (\mathrm{Tr}Q^2)^{3/2}/\sqrt{6}$] then the bulk free energy would favor a biaxial structure. Biaxial nematics are rare [L. J. Yu and A. Saupe, Phys. Rev. Lett. 45, 1000 (1980); R. Bartolino, T. Chiaranza, M. Meuti, and R. Compagnoni, Phys. Rev. A 26, 1116 (1982)], but even should f_{bulk} have this unusual form, the cholesteric structure would still admit a locally biaxial solution on the three-sphere analogous to the locally uniaxial solution required when f_{bulk} has the form (2).

[14]For any four-tensor A, by $\hat{e}^{(i)}\hat{e}^{(j)}A$ we mean $\hat{e}_\mu{}^{(i)} \times \hat{e}_\nu{}^{(j)} A_{\mu\nu}$. (Greek indices are summed from 0 to 3, and Latin from 1 to 3.) See also C. W. Misner, K. S. Thorne, and J. A. Wheeler, *Gravitation* (Freeman, San Francisco, 1973), p. 259.

[15]To understand the symmetries of the $\{\hat{e}^{(i)}\}$ and to simplify computations, it is useful to note that $\hat{e}^{(i)}$ can be compactly defined in terms of two-dimensional unitary unimodular matrices by $\hat{e}_\nu{}^{(\mu)} \tau^{(\nu)} = \tau^{(\mu)} q_0 (x_\nu \tau^{(\nu)})$, where $\tau^{(0)} = 1$, $\tau^{(i)} = i\sigma^{(i)}$, and the $\sigma^{(i)}$ are the Pauli matrices.

[16]We suspect that this remains true throughout the region of stability of f_{grad} (cf. Ref. 12) but have not constructed a proof.

[17]Note that we can define a "cholesteric covariant derivative" D_c (see Ref. 6) by adding a torsion $T^i{}_{jk} = q_0 \epsilon_{ijk}$ to the ordinary connection coefficients $\Gamma^i{}_{jk} = \hat{e}^{(i)} \nabla_k \hat{e}^{(j)}$. The double-twist equations (9) and (16) and the gradient free energy (10) are naturally expressed in terms of D^c. In flat space, parallel transport around closed loops under D^c does not close, reflecting the negative curvature $R_{\beta\alpha\beta}{}^\alpha = -6q_0{}^2$ induced by the torsion. The basis $\{\hat{e}^{(i)}\}$ satisfies $(D^c)_i \hat{e}^{(j)} = 0$ on $S^3(q_0)$, so that the net curvature vanishes and parallel transport is unfrustrated. This makes our texture possible.

[18]One might note that SO(4) modulo the symmetry group of the uniaxial texture is topologically equivalent to RP^2, the space of directors.

[19]S. Meiboom, M. Sammon, and W. F. Brinkman, Phys. Rev. A 27, 438 (1983).

[20]As the cubic term goes to zero the bulk free energy becomes a function only of $\mathrm{Tr}Q^2$ and the uniaxial minimum becomes a member of a four-parameter family of biaxial minima. Thus for small β (nearly second-order phase transitions) small strains will lead to large biaxiality. Indeed, for zero β the ground state in flat space is a maximally biaxial spiral phase (5).