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Bond-orientationally-ordered phases that scatter light strongly

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Bond-orientational order in materials that form three-dimensional uniaxial solids is investigated. New phases are found that scatter light strongly, like nematics, but with a quantitatively different anisotropy of scattering. X-ray scattering from these phases would also exhibit novel anisotropy. This type of order may occur at higher temperatures in materials that form "stacked hexatic" phases at lower temperatures, and will occur whenever a hexagonal crystal melts via dislocation unbinding.

I. INTRODUCTION

One of the most exciting recent developments in the study of liquid crystals has been the theoretical prediction[1-5] of new phases characterized by "bond-orientational order" (BOO), and the subsequent experimental discovery of a bulk example[6] of such a phase. In this paper I study the implications of BOO for three-dimensional systems of simple hexagonal symmetry. These are of interest because such phases would scatter light strongly, as do nematic liquid crystals,[7,8] due to large fluctuations of the bond angle fields which are the Goldstone modes for this system. (In contrast, the BOO phases of cubic[4] or icosahedral[5] symmetry do not scatter light strongly because their symmetry is too high.) This enhanced light scattering provides a much more experimentally accessible signature of the appearance of bond-orientational order than the anisotropy of the x-ray structure factor that is the chief operational manifestation of cubic or icosahedral BOO.

The type of order considered here is that of the stacked hexatic,[6] but without the smectic layering, and is sketched roughly in Fig. 1. A unique direction $\hat{n}$ is singled out by a clustering of the nearest-neighbor bonds either along or orthogonal to $\hat{n}$. (In the stacked hexatic $\hat{n}$ is just the normal to the layers.) In one of the most ordered phases the projections of the nearest neighbors of a given molecule onto the plane normal to $\hat{n}$ has (on average) hexagonal symmetry, with the orientation of the hexagonal pattern persisting throughout the sample. (A more precise characterization of the order is given in Sec. II.) In short, the symmetry of this phase is like the conventional uniaxal nematic,[7] but with the azimuthal isotropy about the uniaxial director broken down to sixfold order.

Phases in which the sixfold ordering has disappeared but the uniaxial ($\hat{n}$) order persists are also possible; these of course just have conventional nematic symmetry. I will hereafter refer to the nematic and sixfold phases as N and $N+6$, respectively.

In addition, there are phases in which the nearest-neighbor bonds are arranged icosahedrally (as discussed by Steinhardt *et al.*[5]), and a phase in which this perfect icosahedral pattern is uniaxially distorted. The latter phase will have the same light scattering properties as the $N+6$ phase, while the former would not scatter light any more than an isotropic fluid.

One or more of these phases could occur in any material that forms a hexagonal crystal as an intermediate phase between the crystal and liquid state,[9] *even if the constitutent molecules or atoms are spherical.* This last point must be emphasized: The order I am considering has nothing to do with the orientations of the constituents of the material, but rather, only concerns the bonds[10] between them; hence the molecules themselves need not even be ca-

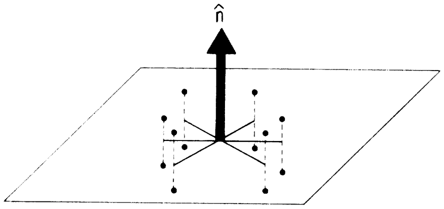

FIG. 1. Configuration of nearest neighbors in the $N+6$ phase. In this illustration the nearest neighbors lie predominantly near the plane whose normal is defined as $\hat{n}$; the projections onto the plane form a hexagonal pattern.

pable of singling out a direction at all. This is a completely novel feature of these phases and is precisely the property that characterizes the two-dimensional hexatic[1,2] and the three-dimensional cubatic[4] and icosahedral[5] phases as well.

Either the N or $N+6$ phases could be easily experimentally distinguished from an isotropic liquid by their milky appearance, which is a consequence of the enhanced light scattering. Such an observation in a system composed of spherical or nearly spherical molecules would be the most striking (and easily observable) manifestation yet seen of bond-orientational order, and would clearly display its independence of molecular-orientational order.

Of course, such a milky phase would hardly be a surprise in a material composed of nematogens; indeed, the N phase in such a system *is* just an ordinary nematic[7]; the uniaxial order of the bonds is induced by that in the molecular directors or vice versa.[11] The $N+6$ phase, however, would be quite novel even for nematogenic systems. The broken azimuthal rotational invariance would have two important experimental signatures: First, light scattering assumes a more complicated dependence on the direction of the scattering wave vector $\vec{q}$, and second, x-ray scattering shows a sixfold in-plane modulation. More specifically, taking the ($\perp$) z axis to be (orthogonal to) along the mean direction of $\hat{n}$, the spatially Fourier-transformed thermal fluctuations in $\hat{n}$ (to which light scattering at wave vector $\vec{q}$ is proportional) are given by

$$\frac{k_B T}{\langle n_L(\vec{q}) n_L(-\vec{q})\rangle} = K_1 q_\perp^2 + K_3 q_z^2 - \frac{K_4^2 q_\perp^2 q_z^2}{K_5 q_\perp^2 + K_7 q_z^2}\,, \tag{1.1a}$$

$$\frac{k_B T}{\langle n_T(\vec{q}) n_T(-\vec{q})\rangle} = K_2 q_\perp^2 + K_3 q_z^2\,, \tag{1.1b}$$

where

$$n_L(\vec{q}) \equiv \vec{q}_\perp \cdot \vec{n}(\vec{q})/q_\perp \tag{1.1c}$$

and

$$n_T(\vec{q}) \equiv (\hat{z} \times \vec{q}_\perp) \cdot \vec{n}(\vec{q})/q_\perp\,. \tag{1.1d}$$

Fluctuations in n_T [Eq. (1.1b)] are the same as in a nematic,[7,8] while those in n_L are modified by the $K_4^{2'}$ term. Note that despite the sixfold ordering these expressions are azimuthally symmetric; the in-plane symmetry is still too high to modulate light scattering in the plane.

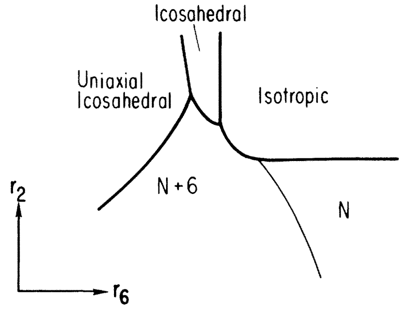

FIG. 2. Phase diagram for systems with a weak tendency towards sixfold ordering. Light and heavy lines denote continuous and first-order transitions, respectively.

Fairly detailed suggestions as to how the $N+6$ phase might be found in liquid-crystal systems can be made with the help of a knowledge of the phase diagram. In Sec. II a Landau theory is constructed for these phases and solved in mean-field theory. A variety of phase-diagram topologies are found, depending on the values chosen for the parameters in the Landau theory. Given the paucity of systems that exhibit hexatic B phases, it would seem reasonable to suppose that the interactions favoring sixfold ordering are quite weak; choosing values of the parameters consistent with this leads to the phase diagram of Fig. 2. Should this assumption of weak sixfold ordering prove incorrect, a number of different topologies (Fig. 3) are possible. The icosahedral regions are probably unphysical for nematogenic systems (a set of long rods would hardly seem prone to icosahedrally arranging their centers of mass); on the other hand, they may be fairly common in systems of spherical atoms.[5]

In the discussion that follows I will only consider nematogenic systems for which BOO is already known to exist. The result of interpolating the already known phases into the phase diagram of Fig. 2 is shown in Fig. 4. (The topology around the point $P1$ is not known.)

To find the $N+6$ phase in such a material an experimentalist must somehow "tune" the Landau parameters into the appropriate range. Operationally, this might be done as follows: Suppose one has a material which, under certain conditions (of pressure, composition, etc.), exhibits the sequence of phases Hex $B \rightarrow$ Sm $A \rightarrow N$ with increasing temperature. (Many such materials are known.[6,12]) This would correspond to tracing out path 1 in the phase

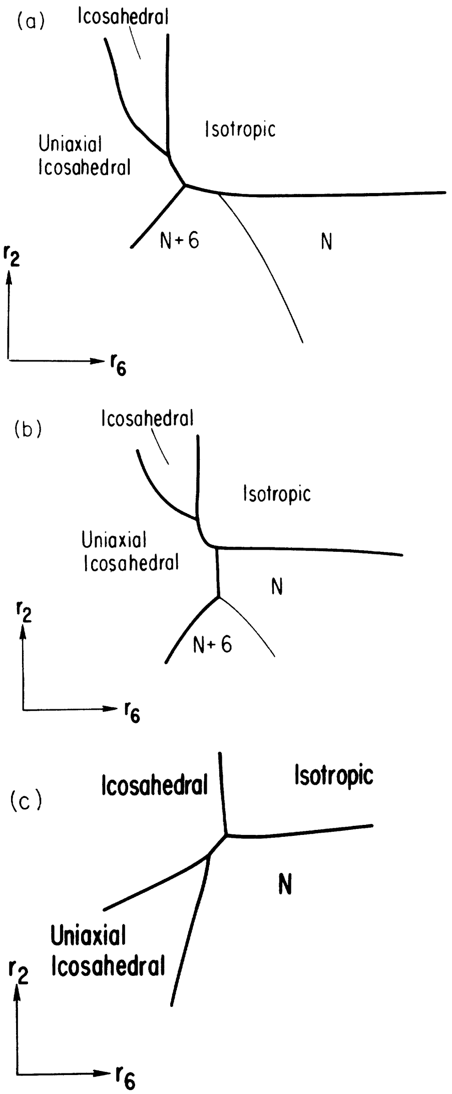

FIG. 3. Phase diagrams for progressively stronger sixfold tendencies. Light and heavy lines have the same significance as in Fig. 2.

diagram of Fig. 4. Now let us imagine that after changing one or more of these conditions the material has the same sequence of phases, but with T_{BA} and T_{AN} closer together than before (i.e., the smectic A exists over a narrower range). This would correspond to having moved to path 2 in Fig. 4., which passes *closer to the $N+6$ phase.*[13] Continued change of the external parameter in the same direction could thus eventually bring one to path 3 and the $N+6$ phase.

The above phase diagram was derived entirely within mean-field theory, and it is important to decide what features of it will persist in the presence of fluctuations. Using Ginsburg criterion arguments one can conclude fairly confidently that the *topology* of the phase diagram will only be altered at those points where, in mean-field theory, two *continuous* phase-transition lines cross. This only occurs at the point $P1$ in Fig. 4. In addition, the detailed geometry at $P2$ may be incorrect, although the topology is correct. Otherwise, the only effect of fluctuations is to change the critical properties of the continuous transitions—that is, the $N \rightarrow N+6$ transition. Because this transition involves the ordering of a single phase varible, it should be in the universality class of the three-dimensional X-Y model. One would therefore expect a λ-like specific-heat anomaly and a correlation length ξ which diverges like $|t|^{-\nu_s}$, where $\nu_s \approx \frac{2}{3}$ is the superfluid correlation-length exponent.

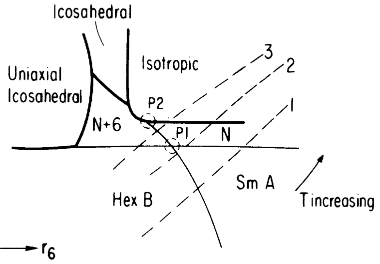

FIG. 4. Interpolation of Fig. 2 onto the already known liquid-crystal phases. Path 1 corresponds to the locus of r_2 and r_6 traced out with increasing temperature in the systems reported to date; note that this does not pass through the $N+6$ phase. By varying external parameters one might be able to move this locus to 2; continued change of the parameters in the same direction might lead to 3 and the $N+6$ phase. Again, heavy and light lines denote first-order and continuous transitions, respectively.

While this length might be difficult to measure experimentally, it can be probed indirectly through the Franck-type constants K_4, K_5, and K_7 of Eq. (1.1a) which can be measured by light scattering. These are analogous to the superfluid density in He^4 and should vanish like[14,15] ξ^{-1} as the transition is approached from below.

There is a complication of the nematogenic systems, however. In studies of the Hex-$B \rightarrow$Sm-A transition the specific heat has been found to depart appreciably from the helium analogy, diverging in fact with an exponent $\alpha \sim \frac{1}{2}$.[12] Bruinsma and Appeli[16] have interpreted this anomaly as evidence that the system is near a tricritical point induced by herringbone packing of the nematogenic molecules. This interpretation is supported by recent measurements[17] which show a small latent heat at the transition corresponding to a fluctuation-induced first-order transition. If their theory is correct, then these effects should modify the $N+6 \rightarrow N$ transition as well, giving rise to the same specific-heat behavior ($\alpha = \frac{1}{2}$, small latent heat) as is observed at the Hex-$B \rightarrow$Sm-A transition. Furthermore, the correlation-length exponent ν would then take on its $d=3$ tricritical value of $\frac{1}{2}$, and K_4, K_5, and K_7 would vanish as $|t|^{1/2}$. Crossover between this behavior and a λ transition might also be observed. If, on the other hand, the anomalous features of the Hex-$B \rightarrow$Sm-A transition are due in some way to the layering of the Hex-B phase, then the $N+6 \rightarrow N$ transition (for which neither phase is layered) should be heliumlike over the full critical regime.

In Sec. II of this paper the Landau free energy is constructed and the phase diagram and critical properties are discussed, and in Sec. III the light and x-ray scattering intensities are calculated.

II. PHASE DIAGRAM AND CRITICAL PROPERTIES

As shown in Ref. 4 any three-dimensional bond-orientationally-ordered phase can be described by a set of order parameters Q_{lm} defined as follows: Associated with each molecule a set of nearest neighbors (by, for example, a Voronoi construction). With the αth such neighbor we can associate a set of polar angles $(\theta_\alpha, \phi_\alpha)$ giving the direction to that neighbor from the central one. We then define

$$Q_{lm} = \left\langle \sum_\alpha Y_{lm}(\theta_\alpha, \phi_\alpha) \right\rangle , \tag{2.1}$$

where the Y_{lm} are spherical harmonics and the angle brackets denote thermal averaging. In an isotropic liquid the angles are distributed uniformly over the sphere and hence all the Q_{lm} are zero except Q_{00} (which is just the average number of nearest neighbors). Thus a nonzero Q_{lm} with $l \neq 0$ is the signature of a phase with orientational order beyond that of a liquid, and so these quantities make useful orientational order parameters.

This paper focuses on phases with the Q_{2m}'s and Q_{6m}'s as the important ordering fields. To motivate this let us evaluate all the Q_{lm}'s for a *simple,* perfect hexagonal lattice. Performing the sums in Eq. (2.1) gives

$$Q_{2n,0} = \frac{[2+6(-1)^n](2n-1)!!}{[2^n(4n+1)/4\pi]^{1/2}} , \tag{2.2a}$$

$$Q_{6n,6m} = 6 \left[\frac{[6(n-|m|)]!(12n+1)}{4\pi[6(n+|m|)]!} \right]^{1/2} , \tag{2.2b}$$

where n and m are integers ($m < n$) and all other Q_{lm}'s vanish. The only essential feature of this result is that all the nonzero Q_{lm}'s are harmonics of just two, Q_{20} and $Q_{6\pm 6}$, which characterize the uniaxial and sixfold order, respectively. Thus in constructing a Landau free energy of phases with this type of orientational order it should be sufficient to consider only the Q_{2m}'s and Q_{6m}'s explicitly,[18] treating the others are tied to these.

This free energy must, of course, be invariant under rotations of the reference coordinate system. By construction, the Q_{lm} transform like quantum-mechanical angular momentum eigenstates under rotations; thus the problem of writing a rotationally invariant free energy is equivalent to the familiar one of constructing a zero angular momentum state out of higher ones.

The sole quadratic invariants are simply

$$I_{2,2} \equiv \sum_{m=-2}^{2} |Q_{2m}|^2 \tag{2.3a}$$

and

$$I_{2,6} \equiv \sum_{m=-6}^{6} |Q_{6m}|^2 , \tag{2.3b}$$

while the cubic invariants can be constructed with the 3-j symbols

$$\begin{bmatrix} l_1 & l_2 & l_3 \\ m_1 & m_2 & -m_1-m_2 \end{bmatrix}$$

as follows:

$$I_{222} = \sum_{m_1 m_2} \begin{bmatrix} 2 & 2 & 2 \\ m_1 & m_2 & -m_1-m_2 \end{bmatrix} \times Q_{2m_1} Q_{2m_2} Q_{2-m_1-m_2} , \tag{2.4a}$$

$$I_{666} = \sum_{m_1 m_2} \begin{bmatrix} 6 & 6 & 6 \\ m_1 & m_2 & -m_1-m_2 \end{bmatrix} \times Q_{6m_1} Q_{6m_2} Q_{6-m_1-m_2} , \tag{2.4b}$$

$$I_{266} = \sum_{m_1 m_2} \begin{bmatrix} 6 & 6 & 2 \\ m_1 & m_2 & -m_1-m_2 \end{bmatrix} \times Q_{6m_1} Q_{6m_2} Q_{2-m_1-m_2} . \tag{2.4c}$$

I will keep only two of the plethora of fourth-order invariants (namely, $I_{2,2}^2$ and $I_{2,6}^2$) since all the essential symmetry features are already contained in the three cubic invariants. The free energy is then

$$F=r_2I_{2,2}+w_2I_{222}+u_2I_{2,2}^2+r_6I_{2,6}$$
$$+w_6I_{666}+u_6I_{2,6}+gI_{266}\;. \tag{2.5}$$

The mean-field phase diagram is now found by minimizing this free energy, treating r_2 and r_6 as variables and all other parameters as fixed. There are four types of minima possible: (i) Isotropic, which are all $Q_{lm}=0$; (ii) N, which are $Q_{20}\neq 0$, $Q_{60}\neq 0$, and all others $=0$; (iii) $N+6$, which are Q_{20}, Q_{60}, $Q_{6\pm 6}\neq 0$, and all others$=0$; (iv) Icosahedral, which are Q_{60}, $Q_{6\pm 5}\neq 0$, $|Q_{65}/Q_{60}|^2=\frac{7}{11}$, and all others$=0$; where in all cases I have assumed that the orientation of the coordinate axes has been chosen so that as many Q_{lm}'s vanish as possible. Minimum (iv) was previously considered in Ref. 5. The topology of the phase diagram depends upon the dimensionless ratio $\alpha\equiv|W_6u_2/gw_2|$ and upon the sign of the product gw_2. For nematogenic materials, which have a strong proclivity to uniaxial (Q_{2m}) ordering, I expect w_2 to be quite large compared to w_6 and hence, all other things (i.e., u_2 and g) being roughly equal, α should be quite small. The phase diagram in this case is Fig. 2. With decreasing values of α one obtains the sequence of phase diagrams shown in Figs. 3(a) and 3(b), while when $gw_2<0$ one obtains Fig. 3(c). This last possibility is certainly not realized in materials that exhibit stacked hexatic phases, since such phases cannot be continuously interpolated into Fig. 3(c). The effect of fluctuations on these mean-field results was discussed in the Introduction.

III. LIGHT AND X-RAY SCATTERING

The most experimentally strking consequence of the type of order discussed here is the existence of large orientational fluctuations, which manifest themselves in tremendously enhanced light scattering. One can visualize these fluctuations by imagining that, at different points in the material, the local arrangement of nearest neighbors has the same shape[19] but varies in orientation. We can obtain any such local arrangement from some reference arrangement by rotating the reference configuration through some angle about some axis. Following Ref. 4 I will parametrize this rotation (at each point $\vec{r}$) by a vector field $\vec{\theta}(\vec{r})$ which points along the rotation axis and whose magnitude is the rotation angle.

If we define the z axis to point along the average uniaxial direction, then for small $|\vec{\theta}|$, $\theta_{x(y)}(\vec{r})=n_{x(y)}(\vec{r})$ [where $\hat{n}(\vec{r})$ is the local uniaxial direction] and $\theta_z(\vec{r})$ gives the angle of rotation of the in-plane sixfold pattern about that direction. In the N phases, which are azimuthally isotropic, θ_z does not exist, and $\theta_{x(y)}$ or, equivalently, $\hat{n}$ are the only important variables. The long-wavelength static and dynamic properties of these phases are therefore just the standard nematic ones.[7,8]

Even in the $N+6$ or uniaxial icosahedral phases only fluctuations of θ_x and θ_y are detected in light scattering. This is because light scattering measures only fluctuations in the dielectric tensor, which depends only on θ_x and θ_y:

$$\epsilon_{ij}=\epsilon_0+\Delta\epsilon n_in_j \tag{3.1}$$

(recall that $\theta_{x,y}=n_{x,y}$).

Nonetheless, the existence of θ_z in these systems has important consequences for light scattering because it couples to $\theta_{x,y}$ and thereby modifies their fluctuations. These modifications provide an indirect way of determining the elastic constants for θ_z, which cannot be measured by direct observation of the sixfold order through, say, x-ray scattering.

To calculate fluctuations in $\vec{\theta}$ in the $N+6$ or uniaxial icosahedral phases we need the elastic free energy for $\theta(\vec{r})$ for uniaxial systems, which by elementary symmetry considerations must, at the harmonic level, have the following form[4,20]:

$$F=\tfrac{1}{2}\int d^3r[K_1'(\vec{\nabla}_\perp\cdot\vec{\theta}_\perp)^2+K_2\,|\,\vec{\nabla}_\perp\vec{\theta}_\perp\,|^2+K_3(\partial_z\vec{\theta}_\perp)^2$$
$$+K_4'\partial_z\theta_z(\vec{\nabla}_\perp\cdot\vec{\theta}_\perp)+K_5(\vec{\nabla}_\perp\theta_z)^2+K_6'(\vec{\nabla}_\perp\theta_z)\cdot(\partial_z\vec{\theta}_\perp)+K_7\,|\,\partial_z\theta_z\,|^2]\;, \tag{3.2}$$

where $\perp$ denotes that part of a vector orthogonal to $\hat{z}$. The harmonic approximation to the Fourier-transformed θ-θ correlation function can now readily be computed. For wave vectors $\vec{q}$ in the x-z plane the results are

$$\frac{k_BT}{\langle\theta_x(\vec{q})\theta_x(-\vec{q})\rangle}=K_1q_x^2+K_3q_z^2$$
$$-\frac{K_4^2q_x^2q_z^2}{4(K_5q_x^2+K_7q_z^2)}\;, \tag{3.3a}$$

$$\frac{k_B T}{\langle \theta_y(\vec{q})\theta_y(-\vec{q})\rangle}=K_2 q_x^2+K_3 q_z^2\;, \tag{3.3b}$$

$$\langle \theta_x(\vec{q})\theta_y(-\vec{q})\rangle=0\;, \tag{3.3c}$$

where $K_1 \equiv K_1' + K_2$ and $K_4 \equiv K_4' + K_6'$.

Note that the first two terms in (3.3a) are all that one would have in a nematic; the last term is the correction due to sixfold ordering in the plane, and vanishes when either q_x or $q_z=0$. The *y-y* and *x-y* correlations are exactly the same as those of a nematic.

Operationally, one can determine K_1, K_2, and K_3 by looking only at scattering with either q_x or $q_z=0$; the ratios K_4^2/K_5 and K_4^2/K_7 can then be determined by fitting the *deviation* of $\langle \theta_x(\vec{q})\theta_x(-\vec{q})\rangle^{-1}$ from the nematic prediction obtained from the *known* K_1 and K_3.[21]

The orientational order can also be probed by x-ray scattering. Here one would measure the Fourier-transformed density-density correlation function

$$S(\vec{q})\equiv\langle\, |\rho(q)|^2\rangle\;. \tag{3.4}$$

In an isotropic liquid $S(\vec{q})$ should be independent of the direction of $\vec{q}$; but this will not be the case when BOO is present. Then one should expect that in the expansion of $S(\vec{q})$ in spherical harmonics

$$S(\vec{q})=\sum_{l,m} A_{lm}(\vec{q})Y_{lm}(\vec{q})\;. \tag{3.5}$$

The A_{lm}'s will be nonzero for all values of l and m such that $Q_{lm}\neq 0$, i.e., $A_{2m,0}$ and $A_{6n,\pm p}$ for the $N+6$, and $A_{2m,0}$ and $A_{6n,\pm 5p}$ for the uniaxial icosahedral phase, for the m, n, and p integers, should be nonzero. This implies that

$$S(\vec{q})=F(\,|\vec{q}\,|,2\alpha_{\vec{q}},6\phi_{\vec{q}}) \tag{3.6}$$

in the $N+6$ phase, and

$$S(\vec{q})=F(\,|\vec{q}\,|,2\alpha_{\vec{q}},5\phi_{\vec{q}}) \tag{3.7}$$

in the uniaxial icosahedral phase, where $(\alpha_{\vec{q}},\phi_{\vec{q}})$ are the polar angles of $\vec{q}$ with respect to the uniaxial direction, and F is periodic (with period 2π) in its last two arguments.

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[7] P. G. de Gennes, *The Physics of Liquid Crystals* (Oxford University Press, London, 1974).

[8] D. Forster, *Hydrodynamic Fluctuations, Broken Symmetry and Correlation Functions* (Benjamin, Reading, Mass., 1975).

[9] It will occur if the melting is dislocation mediated; see Ref. 4.

[10] By bonds I mean merely lines between nearest neighbors; no chemical bonding is implied.

[11] A general free energy that allowed for independent fluctuations of $\hat{n}$ and the molecular director (call it $\hat{m}$) would contain a term $\alpha(\hat{n}\cdot\hat{m})^2$ (squared because the sign of $\hat{n}$ and $\hat{m}$ is arbitrary) which caused $\hat{n}$ to induce order in $\hat{m}$ and vice versa. Thus the nematic director need never be explicitly introduced as an independent variable.

[12] C. C. Huang, J. M. Viner, R. Pindak, and J. W. Goodby, Phys. Rev. Lett. 46, 1284 (1981).

[13] Actually, one could accidentally move *away* from the $N+6$ phase if either the experimental paths or the phase boundaries in Fig. 2 were sufficiently "wiggly"; however, this seems rather unlikely.

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[17] J. M. Viner, C. C. Huang, R. Pindak, and J. W. Goodby, Bull. Am. Phys. Soc. 27, 327 (1982).

[18] This is analogous to Landau's theory of melting in which in principle one must consider an infinite set of order paramters $\rho_{\vec{G}}$ (one for each reciprocal lattice vector) but in practice keeps only the lowest few $\vec{G}$'s.

[19] Fluctuations in the shape will also occur, of course, but these are not Goldstone modes of the system. Fluctuations of this latter type amount to changes in the *amplitudes* of the Q_{lm}'s, while orientational fluctuations are changes in the *phases* of the Q_{lm}'s, and cost vanishingly small energies at long wavelength due to rotational invariance.

[20] The expression for this free energy given in Ref. 4 is incorrect unless (in the notation used there) $K_3=0$.

[21] In particular, a plot of

$$\left[K_1 q_x^2 + K_3 q_z^2 - \frac{k_B T}{\langle \theta_x(\vec{q})\theta_x(-\vec{q})\rangle}\right]^{-1} \frac{q_x^2 q_z^2}{q^2}$$

vs $\sin^2\phi_{\vec{q}}$, where $\phi_{\vec{q}}$ is the angle $\vec{q}$ made with the z axis, should yield a straight line with slope $(K_5-K_7)/K_4^2$ and intercept K_7/K_4^2.