

# Theory of bent-core liquid-crystal phases and phase transitions

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We study phases and phase transitions that can take place in the recently discovered bow-shaped or bent-core liquid-crystal molecules. We show that to completely characterize phases exhibited by such bent-core molecules a third-rank tensor  $T^{ijk}$  order parameter is necessary in addition to the vector and the nematic (second-rank) tensor order parameters. We present an exhaustive list of possible liquid phases, characterizing them by their space-symmetry group and order parameters, and catalog the universality classes of the corresponding phase transitions that we expect to take place in such bent-core molecular liquid crystals. In addition to the conventional liquid-crystal phases such as the nematic phase, we predict the existence of other liquid phases, including the spontaneously chiral nematic  $(N_T+2)^*$  and chiral polar  $(V_T+2)^*$  phases, the orientationally ordered but optically isotropic tetrahedric  $T$  phase, and a nematic  $N_T$  phase with  $D_{2d}$  symmetry that is neither uniaxial nor biaxial. Interestingly, the isotropic-tetrahedric transition is *continuous* in mean-field theory, but is likely driven first order by thermal fluctuations. We conclude with a discussion of smectic analogs of these phases and their experimental signatures.

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## I. INTRODUCTION

Liquid crystals are extraordinary systems in that they continue to have a revolutionary technological impact and to consistently pose new theoretical challenges of fundamental interest. They exhibit a rich variety of phases with symmetries intermediate between those of the highest symmetry homogeneous isotropic liquid and the lowest-symmetry three-dimensional periodic crystal. In contrast to their magnetic and ferroelectric *solid state* analogs, whose ordering is driven by energy-entropy competition, liquid-crystal phase transitions are of predominantly entropic origin. Not unrelated to this is the fact that, with one exception of the chiral smectic- $C^*$  phase [1], commonly observed liquid-crystal phases are nonpolar. It is, therefore, not surprising that a recent experimental discovery by Niori *et al.* [2] of ferroelectricity in the liquid-crystal phase of *achiral* bent-core (banana-shaped) molecules has captured the attention of the liquid-crystal community. Subsequent light microscopy studies by Link *et al.* [3] elucidated the molecular organization of the newly discovered phase. They convincingly demonstrated that (what came to be known as) the  $B_2$  phase [4] is an antiferroelectric smectic- $C$  phase in which layers *spontaneously* break chiral symmetry (with chirality alternating from layer to layer) and exhibit polar order in achiral molecules. Eight distinct phases of bent-core molecules, tentatively labeled  $B_1$  to  $B_8$  have been identified [5,6], though most have not been fully characterized. Two of the most well studied,  $B_2$  and  $B_7$ , are smectic phases consisting of stacks of fluid layers with some internal tilt order, and are special because they can be switched with an electric field. A material composed of *achiral* nematogens having a ground state that is ferroelectric and *homogeneously* chiral has also recently been discovered [7]. This experimental discovery opens up a vast new class of achiral molecules that neverthe-

less exhibit ferroelectricity and are therefore of interest to the liquid-crystal display technology.

While the study of banana-shaped liquid crystals has seen substantial experimental strides [1–3,8], there has been relatively little basic theoretical work on this fascinating new class of materials. Brand *et al.* [9] presented an exhaustive, model-independent classification of the symmetry-allowed smectic phases, and Roy *et al.* [10] introduced a phenomenological Landau model that produces many of the banana-shaped smectic phases. There are also a number of numerical simulations [11–15] on systems of model bent-core molecules that produce nematic phases as well as some of the possible smectic phases. Because so far, experimental examples of orientationally ordered but spatially homogeneous phases *liquid* phases [16] are rare, most of the efforts have focused on the *smectic* phases of bent-core molecules. Here, we will instead focus on spatially homogeneous phases, which we will refer to as *liquid* phases, the understanding and classifying of whose phase behavior is in many ways a prerequisite to the study of more ordered (e.g., smectic) phases, which in addition break translational symmetry. We will take advantage of the formal developments and analysis presented in this paper for the liquid phases in our studies of smectic phases, which we defer to a future publication [17].

The first primary conclusion of our work, which forms the starting point of all further analysis presented here, is that a *third-rank* traceless symmetric tensor order parameter  $T^{ijk}$ , in addition to the usual nematic  $Q^{ij}$  and vector  $p^i$  order parameters, is necessary in order to capture the orientational order observed in experiments on banana-shaped molecules. Without introducing such an angular momentum  $L=3$  order parameter, only structures which have *at least*  $C_2$  and mirror symmetry, such as, e.g., the biaxial nematic can be captured, thereby precluding a first-principles order parameter descrip-

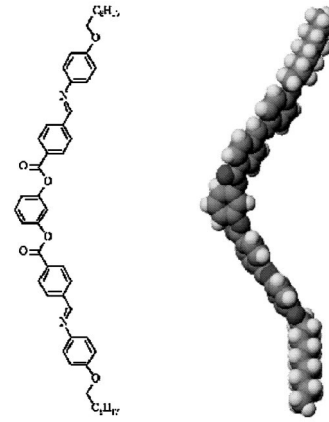
TABLE I. Anisotropic liquid phases of banana-shaped molecules, their symmetries in the Schoenflies notation, and their non-vanishing order parameters. The notation  $\vec{B}_{1,2}$ , etc., is explained in the text. Some of the phases, such as the  $N+V$  phase can be characterized by other sets of symmetry equivalent order parameters, involving, for example, linear combinations of  $p_1$  and  $p_2$  rather than  $p_1$  alone.

Phase	Symmetry	Order parameters
$V$	$C_{\infty v}$	$p_3, S, T_1$
$N$	$D_{\infty h}$	$S$
$N+2$	$D_{2h}$	$S, \vec{B}_{1,2}$
$N+3$	$D_{3h}$	$S, \vec{T}_{2,3}$
$T$	$T_d$	$\vec{T}_{6,7}$
$N_T$	$D_{2d}$	$S, \vec{T}_{6,7}$
$(N_T+2)^*$	$D_2$	$S, B_1, T_6, T_7$
$V+2$	$C_{2v}$	$p_3, S, B_1, T_1, T_6;$ or $p_1, S, B_1, T_2, T_4$
$V+3$	$C_{3v}$	$p_3, S, T_1, \vec{T}_{2,3}$
$(V_T+2)^*$	$C_2$	$p_3, S, B_1, T_1, T_6, T_7;$ or $p_1, S, B_1, T_2, T_4, T_5$
$N+V$	$C_{1h}$	$p_1, p_3, S, B_1, Q_3,$ $T_1, T_2, T_4, T_6$

tion of, for example, the most interesting spontaneously ordered *chiral* phases.

As we will demonstrate in great detail, once this higher-order order parameter  $T^{ijk}$  is introduced, a complex web (displayed in Fig. 7) of possible liquid phases emerges and, associated with them, a very rich phase behavior. Many of these phases exhibit exotic symmetries summarized in Table I, including  $D_{2d}$ ,  $D_2$ , and  $C_2$  symmetries [18], which have not to our knowledge been previously identified in spatially uniform (i.e., liquid) states. These anisotropic liquid phases are distinguished by the nature of their  $T^{ijk}$  ordering. The diversity in phase diagram topologies originates from a large number of symmetry-allowed transition sequences between many of the phases that exhibit some nontrivial combination of the  $p^i$ ,  $Q^{ij}$ , and/or  $T^{ijk}$  order parameters. Some of the orientationally ordered liquid states that we predict are the spontaneously chiral nematic  $(N_T+2)^*$  and chiral polar  $(V_T+2)^*$  phases, an optically isotropic tetrahedric  $T$  phase, and a nematic  $N_T$  phase, with  $D_{2d}$  symmetry, that is neither uniaxial nor biaxial, but rather exhibits a fourfold improper ( $S_4$ ) rotational symmetry about its nematic axis.

The paper is organized as follows. In Sec. II, we present a model of a banana-shaped liquid-crystal molecule. By considering mass moments of molecules with this shape, we are naturally led to introduce the three important order parameters,  $p^i$ ,  $Q^{ij}$ , and  $T^{ijk}$ , that are necessary to fully describe anisotropic liquid states into which such molecules can macroscopically order. In Sec. III we then catalog all thermodynamically distinct liquid phases characterizable by these three order parameters. We organize these phases according to symmetry groups under which they are invariant and present an exhaustive list of phase transition sequences allowed by symmetry. We construct a Landau theory of the



NOBOW: X – 152 °C – B4 – 155 °C – B2 – 173 °C – I

FIG. 1. Chemically accurate model of a bent-core (banana-shaped) NOBOW molecule studied in Refs. [2] and [3] that displays isotropic,  $B_2$ ,  $B_4$ , and crystal (X) phases. Instantaneously, a molecule can be found in a chiral nonplanar configuration (as shown on the right), but fluctuates equally between positive and negative chiralities, on average is planar and therefore achiral.

three order parameters in Sec. IV and analyze the nature of the complicated web of phase transitions that it predicts in Sec. V, finding full consistency with our general group-theoretic analysis. In Sec. VI, we briefly discuss possible smectic phases that could result when smectic ordering develops in the various liquid phases we identify. We conclude with Sec. VII by summarizing our results and discussing their relevance to future studies of smectic phases and to experiments.

## II. SIMPLE MODEL OF BANANA-SHAPED LIQUID CRYSTALS: ORDER PARAMETERS

As is clear from a chemically and geometrically accurate model of a bent-core molecule, shown in Fig. 1, the most notable characteristic of banana-shaped molecules is their “V” shape with bent, (on average) planar and therefore achiral cores. This shape earned such molecules a name “bow” shaped. The molecule is characterized by  $C_{2v}$  symmetry, defined by a nonpolar direction  $\mathbf{v}_3$  (the “string” of the bow), pointing from one endpoint of the “V” to the other and an orthogonal polar axis  $\mathbf{v}_1$  (the bow’s “arrow”), pointing to the vertex of the “V,” as illustrated in Fig. 2.

We can, therefore, expect the molecule to be characterized by both even- and odd-rank symmetric, traceless tensors with the preferred axis of odd-rank tensors along the molecular  $\mathbf{v}_1$  axis. We can capture these molecular features by a simple three-atom rigid bond model of the banana-shaped molecule illustrated in Fig. 2.

As just discussed, associated with each banana-shaped molecule  $\alpha$  is a body-fixed orthonormal coordinate system with unit vectors  $(\mathbf{v}_{\alpha,1}, \mathbf{v}_{\alpha,2}, \mathbf{v}_{\alpha,3})$ . Molecular  $C_{2v}$  symmetry implies invariance under the reflection operations  $\mathbf{v}_{\alpha,3} \rightarrow -\mathbf{v}_{\alpha,3}$  and  $\mathbf{v}_{\alpha,2} \rightarrow -\mathbf{v}_{\alpha,2}$  and the  $\pi$ -rotation (about  $\mathbf{v}_{\alpha,1}$ ) operation  $\mathbf{v}_{\alpha,2} \rightarrow -\mathbf{v}_{\alpha,2}$ ,  $\mathbf{v}_{\alpha,3} \rightarrow -\mathbf{v}_{\alpha,3}$ , but not under the reflection  $\mathbf{v}_{\alpha,1} \rightarrow -\mathbf{v}_{\alpha,1}$ . In this body-fixed frame, the

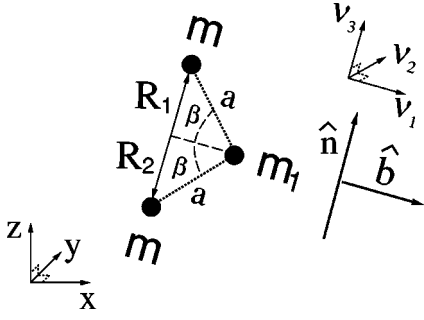


FIG. 2. A simple three-atom model of a banana-shaped molecule and a body-fixed orthonormal coordinate system, capturing the molecule's characteristic, achiral  $C_{2v}$  symmetry.

three atoms' coordinates are given by

$$\mathbf{R}_{\alpha,1} = (a \cos \beta) \mathbf{v}_{\alpha,1}, \quad (2.1a)$$

$$\mathbf{R}_{\alpha,2} = -(a \sin \beta) \mathbf{v}_{\alpha,3}, \quad (2.1b)$$

$$\mathbf{R}_{\alpha,3} = (a \sin \beta) \mathbf{v}_{\alpha,3}, \quad (2.1c)$$

where  $2\beta \approx 120^\circ$  is the opening angle of the "V" [15], as shown in Fig. 2, and with the origin located on the  $\mathbf{v}_{\alpha,3}$  axis, half way between  $m$  masses. As is the case for standard nematics where transitions are driven by entropic interactions, we expect that the dominant ordering mechanisms of banana-shaped liquid crystals will be associated with the shape of the molecule and not with electric dipoles. We, therefore, focus on the mass-moment tensors as the important order parameters for this problem. That is, throughout the paper we will assume that the liquid-crystal ordering is driven by steric interactions and, therefore, that it is the *mass-moment* tensors, rather than charge moments, that are the primary critical order parameters.

The lowest order mass moment is just the center of mass given, in terms of the body-fixed coordinate system, by

$$\mathbf{R}_{\text{cm}}^\alpha = \frac{1}{2m + m_1} \sum_{\mu=1}^3 m_\mu \mathbf{R}_{\alpha,\mu} \quad (2.2a)$$

$$= \left( \frac{m_1}{2m + m_1} a \cos \beta \right) \mathbf{v}_{\alpha,1}. \quad (2.2b)$$

It is natural to define mass moments relative to the center of mass coordinate  $\mathbf{R}_{\text{cm}}^\alpha$ . Positions of atom  $\mu$  relative to the center of mass are then  $\mathbf{r}_{\alpha,\mu} = \mathbf{R}_{\alpha,\mu} - \mathbf{R}_{\text{cm}}^\alpha$ . The second mass-moment tensor relative to the center of mass can be decomposed into a scalar (proportional to  $\delta^{ij}$ ) and a symmetric, traceless tensor

$$C_{2,\alpha}^{ij} = \sum_{\mu=1}^3 m_\mu \left( r_{\alpha,\mu}^i r_{\alpha,\mu}^j - \frac{1}{3} r_{\alpha,\mu}^2 \delta^{ij} \right). \quad (2.3)$$

The third mass-moment tensor can be decomposed into a vector part,

$$C_{1,\alpha}^i = \sum_{\mu=1}^3 m_\mu r_{\alpha,\mu}^2 r_{\alpha,\mu}^i \quad (2.4)$$

and a third-rank symmetric, traceless tensor

$$C_{3,\alpha}^{ijk} = \sum_{\mu=1}^3 m_\mu [r_{\alpha,\mu}^i r_{\alpha,\mu}^j r_{\alpha,\mu}^k - \frac{1}{5} r_{\alpha,\mu}^2 (\delta^{ij} r_{\alpha,\mu}^k + \delta^{jk} r_{\alpha,\mu}^i + \delta^{ki} r_{\alpha,\mu}^j)]. \quad (2.5)$$

These mass-moment tensors can be expanded in terms of complete sets of tensors of the appropriate rank formed from the vectors  $\mathbf{v}_{\alpha,1}$ ,  $\mathbf{v}_{\alpha,2}$ , and  $\mathbf{v}_{\alpha,3}$ ,

$$C_{1,\alpha}^i = c_1 v_{\alpha,1}^i, \quad (2.7a)$$

$$C_{2,\alpha}^{ij} = c_{23} Q_{\alpha,3}^{ij} + c_{22} (Q_{\alpha,1}^{ij} - Q_{\alpha,2}^{ij}), \quad (2.7b)$$

$$C_{3,\alpha}^{ijk} = c_{31} T_{\alpha,1}^{ijk} + c_{32} T_{\alpha,2}^{ijk}, \quad (2.7c)$$

where

$$Q_{\alpha,a}^{ij} = v_{\alpha,a}^i v_{\alpha,a}^j - \frac{1}{3} \delta^{ij}, \quad a = 1, 2, 3, \quad (2.8)$$

$$T_{\alpha,1}^{ijk} = v_{\alpha,1}^i v_{\alpha,1}^j v_{\alpha,1}^k - \frac{1}{5} (\delta^{ij} v_{\alpha,1}^k + \delta^{jk} v_{\alpha,1}^i + \delta^{ki} v_{\alpha,1}^j), \quad (2.9a)$$

$$T_{\alpha,2}^{ijk} = v_{\alpha,3}^i v_{\alpha,3}^j v_{\alpha,3}^k + v_{\alpha,3}^i v_{\alpha,1}^j v_{\alpha,3}^k + v_{\alpha,1}^i v_{\alpha,3}^j v_{\alpha,3}^k - \frac{1}{5} (\delta^{ij} v_{\alpha,1}^k + \delta^{jk} v_{\alpha,1}^i + \delta^{ki} v_{\alpha,1}^j), \quad (2.9b)$$

and

$$c_1 = \frac{2mm_1 a^3 \cos \beta (-m_1 + 2m \cos 2\beta)}{(2m + m_1)^2}, \quad (2.10a)$$

$$c_{23} = 2ma^2 \sin^2 \beta - \frac{mm_1}{2m + m_1} a^2 \cos^2 \beta, \quad (2.10b)$$

$$c_{22} = \frac{mm_1}{2m + m_1} a^2 \cos^2 \beta, \quad (2.10c)$$

$$c_{31} = \frac{2mm_1(m_1^2 + 4m^2)}{(2m + m_1)^3} a^3 \cos^3 \beta, \quad (2.10d)$$

$$c_{32} = \frac{4m^2 m_1}{2m + m_1} a^3 \sin^2 \beta \cos \beta. \quad (2.10e)$$

There are only two independent symmetric-traceless molecular parameters in the set  $Q_{\alpha,a}^{ij}$  because the completeness relation,

$$\sum_{a=1}^3 v_a^i v_a^j = \delta^{ij}, \quad (2.11)$$

implies the constraint

$$\sum_{a=1}^3 Q_{\alpha,a}^{ij} = 0. \quad (2.12)$$

For arbitrary orientation of the axes  $\nu_{\alpha,a}$ , a given molecule will in general exhibit five independent symmetric-traceless tensor mass moments. However, because we have chosen these axes to be symmetry axes of the molecule, there are only two independent tensors. Similarly, a given molecule will in general be characterized by seven independent third-rank mass-moment tensors. By utilizing three rotational degrees of freedom (e.g., Euler's angles) it is always possible to choose the axes  $\nu_{\alpha,a}$  so that there are only four independent such tensors. Our model of a bent-core molecule is sufficiently simple, that, with our convenient choice of basis vectors  $\nu_{\alpha,a}$ , each molecule is characterized by only two nonvanishing third-rank tensors.

The potential energy of interacting bent-core molecules can be expressed in terms of the generalized tensors  $\nu_{\alpha,1}^i$ ,  $Q_{\alpha,a}^{ij}$ , and  $T_{\alpha,a}^{ijk}$  and higher-rank tensors. In the phenomenological treatment we will pursue, it is convenient to introduce coarse-grained field versions of these tensors,

$$p^i(\mathbf{x}) = \frac{1}{\rho} \sum_{\alpha} \nu_{\alpha,1}^i \delta(\mathbf{x} - \mathbf{x}_{\alpha}), \quad (2.13a)$$

$$Q_a^{ij}(\mathbf{x}) = \frac{1}{\rho} \sum_{\alpha} Q_{\alpha,a}^{ij} \delta(\mathbf{x} - \mathbf{x}_{\alpha}), \quad (2.13b)$$

$$T_a^{ijk}(\mathbf{x}) = \frac{1}{\rho} \sum_{\alpha} T_{\alpha,a}^{ijk} \delta(\mathbf{x} - \mathbf{x}_{\alpha}), \quad (2.13c)$$

where  $\mathbf{x}_{\alpha}$  is the position in the lab frame of the center of mass of molecule  $\alpha$  and  $\rho$  is the molecular number density. Thus, a theory for our model bent-core molecules that includes all tensor order parameters up to those of third rank would include a single vector order parameter derived from the third-rank mass-moment tensor, two second-rank tensors, and two third-rank tensors. To simplify our discussion, we will consider phenomenological theories with only one second-rank tensor, which we denote  $Q^{ij}$ , and one third-rank tensor, which we denote  $T^{ijk}$ . This, however, is not a restriction on our model, because if the original theory had all four second- and third-rank tensors, we could, for example, integrate out  $Q_2^{ij}$  and  $T_1^{ijk}$  order parameters to obtain our model as an effective theory, depending only on  $p^i$ ,  $Q^{ij} \equiv Q_3^{ij}$ , and  $T^{ijk} \equiv T_2^{ijk}$  order parameters.

Each of these tensors can be expressed in terms of its components relative to a space-fixed orthonormal basis  $(\mathbf{n}_1, \mathbf{n}_2, \mathbf{n}_3) \equiv (\mathbf{m}, \mathbf{l}, \mathbf{n})$ , with  $\mathbf{m} \times \mathbf{l} = \mathbf{n}$ . To this end, we introduce second- and third-rank symmetric-traceless orthonormal basis tensors,  $J_{\mu}^{ij}$  and  $I_{\mu}^{ijk}$ , that transform, respectively, under  $L=2$  and  $L=3$  representations of the rotation group in three dimensions,

$$J_1^{ij} = \sqrt{3/2} \left( n^i n^j - \frac{1}{3} \delta^{ij} \right), \quad (2.14a)$$

$$J_2^{ij} = \sqrt{1/2} (m^i m^j - l^i l^j), \quad (2.14b)$$

$$J_3^{ij} = \sqrt{1/2} (n^i m^j + m^i n^j), \quad (2.14c)$$

$$J_4^{ij} = \sqrt{1/2} (n^i l^j + l^i n^j), \quad (2.14d)$$

$$J_5^{ij} = \sqrt{1/2} (m^i l^j + l^i m^j), \quad (2.14e)$$

and

$$I_1^{ijk} = \sqrt{5/2} \left[ n^i n^j n^k - \frac{1}{5} (\delta^{ij} n^k + \delta^{jk} n^i + \delta^{ki} n^j) \right], \quad (2.15a)$$

$$I_2^{ijk} = \frac{1}{2} (m^i m^j m^k - m^i l^j l^k - m^j l^k l^i - m^k l^i l^j), \quad (2.15b)$$

$$I_3^{ijk} = \frac{1}{2} (l^i l^j l^k - l^i m^j m^k - l^j m^k m^i - l^k m^i m^j), \quad (2.15c)$$

$$I_4^{ijk} = \sqrt{5/12} \left[ m^i n^j n^k + m^j n^k n^i + m^k n^i n^j - \frac{1}{5} (m^i \delta^{jk} + m^j \delta^{ik} + m^k \delta^{ij}) \right], \quad (2.15d)$$

$$I_5^{ijk} = \sqrt{5/12} \left[ l^i n^j n^k + l^j n^k n^i + l^k n^i n^j - \frac{1}{5} (l^i \delta^{jk} + l^j \delta^{ik} + l^k \delta^{ij}) \right], \quad (2.15e)$$

$$I_6^{ijk} = \frac{1}{\sqrt{6}} [n^i (m^j m^k - l^j l^k) + n^j (m^i m^k - l^i l^k) + n^k (m^i m^j - l^i l^j)], \quad (2.15f)$$

$$I_7^{ijk} = \frac{1}{\sqrt{6}} (n^i m^j l^k + n^i l^j m^k + m^i l^j n^k + m^i n^j l^k + l^i n^j m^k + l^i m^j n^k). \quad (2.15g)$$

These tensors are normalized so that

$$\sum_{ij} J_{\mu}^{ij} J_{\mu'}^{ij} = \delta_{\mu, \mu'}, \quad (2.16a)$$

$$\sum_{ijk} I_{\mu}^{ijk} I_{\mu'}^{ijk} = \delta_{\mu, \mu'}. \quad (2.16b)$$

We can now express our order parameters fields, Eq. (2.13), in terms of these bases

$$p^i = \sum_{\mu} p_{\mu} n_{\mu}^i, \quad (2.17a)$$

$$Q^{ij} = \sum_{\mu} Q_{\mu} J_{\mu}^{ij}, \quad (2.17b)$$

$$T^{ijk} = \sum_{\mu} T_{\mu} I_{\mu}^{ijk}. \quad (2.17c)$$

The space-fixed orthonormal basis  $(\mathbf{m}, \mathbf{l}, \mathbf{n})$  can be rotated to diagonalize the tensors  $p^i$ ,  $Q^{ij}$ , and  $T^{ijk}$ . In general, there is no reason why the rotated bases of these three order parameters should coincide. We should, therefore, in general introduce three bases  $(\mathbf{m}_A, \mathbf{l}_A, \mathbf{n}_A)$  where  $A \in \{p, Q, T\}$ . Any of these bases are fully specified by three angles, and we can choose them to eliminate up to three components of the tensors  $Q^{ij}$  and  $T^{ijk}$ . In particular, we can choose the two independent angles in  $\mathbf{n}_Q$  to eliminate  $Q_3$  and  $Q_4$ . This leads to

$$Q^{ij} = S \left( n_Q^i n_Q^j - \frac{1}{3} \delta^{ij} \right) + B_1 (m_Q^i m_Q^j - l_Q^i l_Q^j) + B_2 (m_Q^i l_Q^j + l_Q^i m_Q^j). \quad (2.18)$$

The independent angle defining the direction of the pair  $(\mathbf{m}_Q, \mathbf{l}_Q)$  can be used to eliminate either  $B_1$  or  $B_2$ . A similar line of arguments allows us to choose the basis  $(\mathbf{m}_T, \mathbf{l}_T, \mathbf{n}_T)$  so that  $T_3 = T_4 = T_5 = 0$ . We can parametrize the four remaining components of  $T^{ijk}$  in terms of an amplitude  $T$  and three angles,  $\theta_1$ ,  $\theta_2$ , and  $\theta_3$  and write

$$T^{ijk} = T (\cos \theta_1 I_1^{ijk} + \sin \theta_1 \cos \theta_2 I_2^{ijk} + \sin \theta_1 \sin \theta_2 \cos \theta_3 I_6^{ijk} + \sin \theta_1 \sin \theta_2 \sin \theta_3 I_7^{ijk}), \quad (2.19)$$

in the basis  $(\mathbf{m}_T, \mathbf{l}_T, \mathbf{n}_T)$ . There are other representations of the general tensor  $T^{ijk}$  involving other sets of four of the tensors  $I_{\mu}^{ijk}$  and a different set of three angles. The representation of Eq. (2.19) is the most useful for our purposes. Finally, we can choose the  $p$  basis so that

$$\mathbf{p} = p \mathbf{n}_p. \quad (2.20)$$

In what follows, we will, unless otherwise specified, express all quantities in the basis  $(\mathbf{m}_Q, \mathbf{l}_Q, \mathbf{n}_Q) \equiv (\mathbf{m}, \mathbf{l}, \mathbf{n})$  that diagonalizes  $Q^{ij}$  with  $B_2 = 0$ . We will then have to worry about the possibility of seven independent components of  $T^{ijk}$  and three independent components of  $p^i$  in this basis rather than the angles of the  $T$  and  $p$  bases relative to those of the  $Q$  basis. When  $Q^{ij}$  is zero, we can of course choose the  $p$  or the  $T$  basis.

### III. PHASES AND THEIR SYMMETRIES

We have just seen that phases of banana-shaped molecules can be characterized by vector and second- and third-rank tensor order parameters. Before developing a Landau field theory for these order parameters and analyzing it in mean-field theory, we summarize in this section the various phases and their symmetries that can arise from these order parameters, and we review possible phase sequences produced by the simplest version of the Landau theory.

Before cataloging the possible phases of our model and their symmetries, we observe that many of these phases can be successfully described in terms of effective theories that are functions of only one of the order parameters  $p^i$ ,  $Q^{ij}$ , or

$T^{ijk}$ . Some of the phases, however, particularly those of lower symmetry, require two or more of these order parameters for their full description. Furthermore, these order parameters are coupled by rotationally invariant contributions to the free energy like  $p^i p^j Q^{ij}$ ,  $Q^{ij} T^{ikl} T^{jkl}$ , or  $p^i Q^{jk} T^{ijk}$ , and the existence of one kind of order induces another. Thus, for example, a model based on  $T^{ijk}$  alone would miss the fact that the lower-rank tensor  $Q^{ij}$  is automatically induced by  $T_2$  order.

Table I lists the phases we consider, their symmetries, and the nonvanishing order parameters that characterize them. This list includes phases with all symmetries that can be constructed from the order parameters  $p^i$ ,  $Q^{ij}$ , and  $T^{ijk}$  except for the lowest-symmetry phase with  $C_1$  symmetry [33,34], which we do not consider. All other point-group symmetries including cubic, icosahedral, simple tetrahedral ( $T$ ), and even lower symmetries such as  $S_2$ ,  $C_3$ , and  $C_{2h}$  cannot be characterized without the introduction of fourth- or higher-rank tensor order parameters. As is customary, we denote the isotropic phase by  $I$  and the nematic phase by  $N$ . The  $N$  phase has  $D_{\infty h}$  symmetry, and it is completely characterized within the space of  $p^i$ ,  $Q^{ij}$ , and  $T^{ijk}$  by the single uniaxial order parameter  $S$ . In general, the  $N$  phase will also have nonvanishing components of all even rank tensors [explicitly induced through  $\text{Tr}(Q^n T_{2n})$  coupling], but we will ignore them, focusing on the nontrivial order parameters of rank 3 or less that actually drive the ordering transitions. There is a phase with vector or, equivalently,  $C_{\infty v}$  symmetry, which we denote by  $V$ . The predominant order parameter of this phase is the vector  $\mathbf{p}$ , which we take to be along  $\mathbf{n}$  (i.e., nonzero  $p_3$ ). Once  $p_3$  orders, it explicitly induces  $S$  and  $T_1$  order parameters, through the  $p^i p^j p^k T^{ijk}$  and  $p^i p^j Q^{ij}$  couplings, respectively.

There are a number of phases in which anisotropy develops in the plane perpendicular to  $\mathbf{n}$  or  $\mathbf{p}$ . As we will find in Sec. V, phases that break uniaxial symmetry (isotropy of the transverse plane), will exhibit  $O(2)$  invariance corresponding to internal rotation within pairs of order parameters. For convenience, we will collectively refer to these pairs as:  $\vec{p}_{1,2} \equiv (p_1, p_2)$ ,  $\vec{B}_{1,2} \equiv (B_1, B_2)$ ,  $\vec{T}_{2,3} \equiv (T_2, T_3)$ ,  $\vec{T}_{4,5} \equiv (T_4, T_5)$ ,  $\vec{T}_{6,7} \equiv (T_6, T_7)$ . Also, following Toner [19], we denote the phases with  $r$ -fold anisotropy (or equivalently  $r$ -atic order) in the plane perpendicular to  $\mathbf{n}$  by  $N+r$  and those with similar anisotropy perpendicular to the vector axis  $\mathbf{p}$  by  $V+r$ . There is the standard biaxial nematic or  $N+2$  phase with  $D_{2h}$  symmetry and  $S$  and  $\vec{B}_{1,2}$  order. There is an  $N+3$  phase with  $D_{3h}$  symmetry and nonvanishing  $S$  and  $\vec{T}_{2,3}$  order. The  $V+2$  (equivalent to the  $N+1$  phase) and  $V+3$  phases have  $C_{2v}$  and  $C_{3v}$  symmetry, respectively. The  $V+3$  phase develops from the  $N+3$  phase by developing vector order along the  $\mathbf{n}$  axis. It, therefore, has  $p_3$  and  $T_1$  order in addition to the  $S$  and  $\vec{T}_{2,3}$  order of the  $N+3$  phase. The  $V+2$  phase has one twofold axis and two perpendicular reflection planes. Which order parameters describe this phase depends on whether the vector order  $\mathbf{p}$  lies along  $\mathbf{n}$  (which diagonalizes  $Q^{ij}$ ) or perpendicular to  $\mathbf{n}$ , within the  $\mathbf{m}$ - $\mathbf{l}$  plane. If  $\mathbf{p}$  is parallel to  $\mathbf{n}$ , the  $V+2$  phase is characterized by

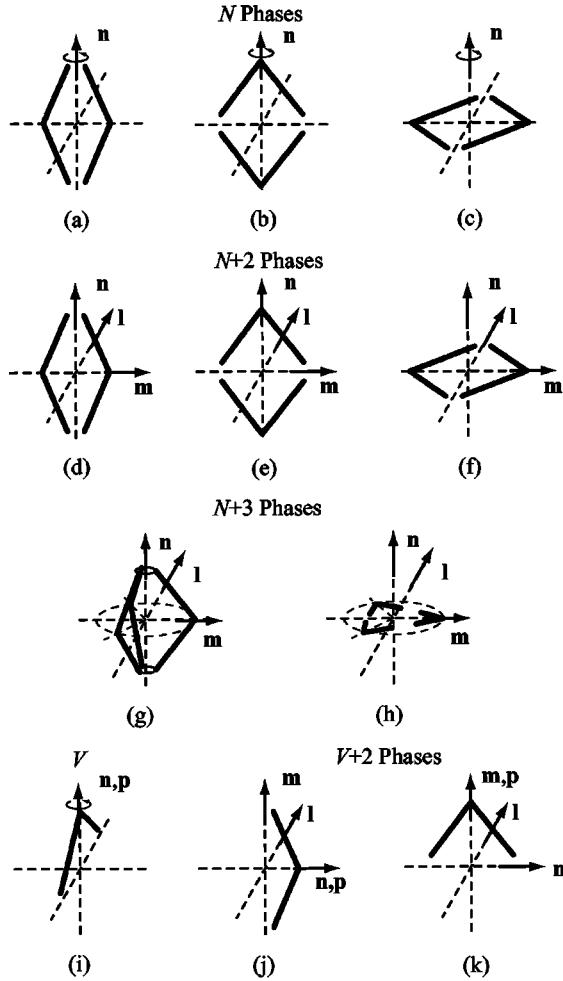


FIG. 3. Schematic representations of the  $N$ ,  $N+2$ ,  $N+3$ ,  $V$ , and  $V+2$  phases. Three versions, (a), (b), and (c), of the  $N$  phases are depicted with respective predominant alignment of  $\nu_3$ ,  $\nu_1$ , and  $\nu_2$  along  $\mathbf{n}$ , specifying the direction of the principal axis of  $Q^{ij}$  with the largest eigenvalue. The  $N+2$  phases, (d), (e), and (f), are obtained, respectively, from the  $N$  phases (a), (b), and (c) by restricting rotations in the plane perpendicular to  $\mathbf{n}$  to have twofold symmetry, whereas the  $N+3$  phases, (g) and (h), are obtained by restricting these rotations to have a threefold symmetry. In the uniaxial  $V$  phase (i), the molecular  $\nu_1$  aligns on average along  $\mathbf{p} \parallel \mathbf{n}$ , sampling equally all orientations about the  $\mathbf{p}$  axis. The  $V+2$  phase can be produced either by introducing biaxial order perpendicular to  $\mathbf{p}$  and  $\mathbf{n}$  into the  $V$  phase (j) or by introducing vector order into the  $N+2$  phase by aligning  $\mathbf{p}$  along  $\mathbf{m}$  (k).

nonvanishing  $p_3$ ,  $S$ ,  $B_1$ ,  $T_1$ , and  $T_6$  or by a symmetry equivalent set such as  $p_3$ ,  $S$ ,  $B_2$ ,  $T_1$ , and  $T_7$ , where it is understood here that  $T_7$  is zero if  $B_1$  is nonzero and  $T_6$  is zero if  $B_2$  is nonzero (otherwise spontaneous chirality develops, as discussed below); if  $\mathbf{p}$  is perpendicular to  $\mathbf{n}$ , then it is characterized by nonvanishing  $\tilde{p}_{1,2}$ ,  $S$ ,  $B_1$ ,  $T_2$ , and  $T_4$  or symmetry-equivalent order parameters.

Schematic representations of the  $N$ ,  $N+2$ ,  $N+3$ ,  $V$ , and  $V+2$  phases derived from bent-core molecules are shown in Fig. 3. The distribution of molecular angles in the  $V+3$  phase is difficult to depict in the format of Fig. 3. Because of the symmetry of the bent-core molecule under  $\nu_3 \rightarrow -\nu_3$ , it

is impossible to produce  $V+3$  symmetry if the molecular  $\nu_1$  axis is rigidly aligned along  $\mathbf{p}$ . To produce such threefold symmetry, it is necessary for the molecular  $\nu_1$  axis to be tilted away from the  $\mathbf{p}$  axis and for its projection onto the plane perpendicular to  $\mathbf{p}$  to have threefold symmetry.

A comment about how  $\tilde{T}_{2,3}$  order describes  $N+3$  (and  $V+3$ ) symmetry is useful.  $r$ -atic order is generally described by an order parameter of the form  $\langle e^{ir\phi} \rangle$ , where  $\phi$  is the angle between a molecular axis in the  $\mathbf{m}$ - $\mathbf{l}$  plane and the  $\mathbf{m}$  axis. To represent  $\tilde{T}_{2,3}$  order in this way, we introduce the circular basis vectors,

$$\mathbf{e}_{\pm} = \frac{1}{\sqrt{2}}(\mathbf{m} \pm i\mathbf{l}), \quad (3.1)$$

( $i = \sqrt{-1}$ ) satisfying

$$\mathbf{e}_+ \cdot \mathbf{e}_- = 1, \quad \mathbf{e}_+ \cdot \mathbf{e}_+ = 0, \quad \mathbf{e}_- \cdot \mathbf{e}_- = 0, \quad (3.2)$$

and reexpress  $I_2^{ijk}$  and  $I_3^{ijk}$  as

$$I_2^{ijk} = \frac{1}{\sqrt{2}}(I_+^{ijk} + I_-^{ijk}), \quad I_3^{ijk} = \frac{-i}{\sqrt{2}}(I_+^{ijk} - I_-^{ijk}). \quad (3.3)$$

Then  $T_2 I_2^{ijk} + T_3 I_3^{ijk} = T_+ I_+^{ijk} + T_- I_-^{ijk}$ , where

$$T_{\pm} = \frac{1}{\sqrt{2}}(T_2 \mp iT_3) = e_{\pm}^i e_{\pm}^j e_{\pm}^k T^{ijk}. \quad (3.4)$$

If  $\nu_3$  is aligned along  $\mathbf{n}$ , then  $T_{\pm} = \langle e^{\pm i3\phi} \rangle$ , where  $\phi$  is the angle between  $\nu_1$  and  $\mathbf{m}$ . When  $\nu_3$  is not aligned along  $\mathbf{n}$ , the situation is similar, though more complicated. Thus, nonzero  $\tilde{T}_{2,3}$  describes *triadic* order in the plane perpendicular to  $\mathbf{n}$ . We will also briefly encounter even lower symmetry phases, in which, in contrast to the  $N+r$  and  $V+r$  phases discussed above, the additional order develops in a plane that is *not* perpendicular to the established nematic or vector axis. One prominent example is a phase in which the nematic and polar orders are neither parallel nor perpendicular. We will refer to this  $C_{1h}$ -symmetry phase as  $N+V$ , emphasizing its distinction from the  $N+1$  ( $\equiv V+2$ ) phase, discussed above. Although  $N+V$  phase (and its  $N+r+V$  analogs) is quite unlikely to develop in the liquid state, such order can quite naturally appear in the smectic- $C$  environment, where the additional axis is defined by the smectic layer-normal  $\mathbf{N}$ .

There is only one phase in which  $T^{ijk}$  has a nonvanishing component and in which *both*  $p^i$  and  $Q^{ij}$  are zero. This phase, which we denote by  $T$  and call tetrahedric, has tetrahedral symmetry and is invariant under all 24 operations of the tetrahedral group  $T_d$  [18]. It is characterized by an arbitrary nonvanishing linear combination of  $T_6$  and  $T_7$ , i.e., by the  $\tilde{T}_{6,7}$  order parameter, and is illustrated in Figs. 4(a) and 5(a).

A uniaxial distortion along one of the three twofold tetrahedral axes reduces the  $T_d$  symmetry of the tetrahedric phase down to  $D_{2d}$  symmetry. We denote the resulting *nonpolar* phase with this symmetry by  $N_T$ . It is characterized by nonvanishing nematic  $S$  and  $\tilde{T}_{6,7}$  order parameters, but it is

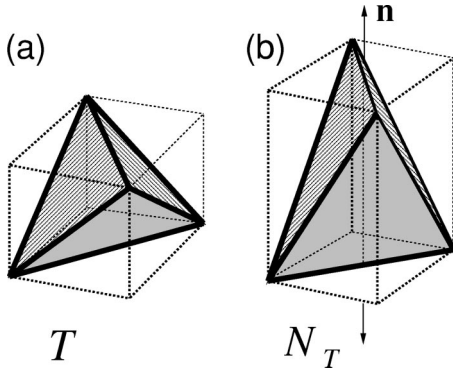


FIG. 4. (a) A tetrahedron that exhibits symmetry identical to that of the tetrahedral  $T$  phase, with all three axes of the cube,  $\mathbf{n}, \mathbf{m}, \mathbf{l}$  equivalent. The  $T$  phase can be visualized as being composed of banana-shaped molecule tetrahedral complexes on average decorating edges of randomly positioned but orientationally ordered tetrahedra as shown in Fig. 5(a). (b) A tetrahedron uniaxially distorted along the  $\mathbf{n}$  axis, exhibiting symmetry of the  $N_T$  phase, that is distinguished from the  $T$  phase by the nonzero nematic order parameter  $S$ . A depiction of this phase in terms of banana-shaped molecules is shown in Fig. 5(b)

neither a uniaxial nor a biaxial nematic, with  $\vec{T}_{6,7}$  breaking the isotropy of the plane transverse to  $\mathbf{n}$ , as illustrated in Figs. 4(b), 5(b), and 6(a).

The  $V+2$  phase with  $C_{2v}$  symmetry naturally emerges from the  $N_T$  phase through the development of longitudinal polar order  $\mathbf{p} = p_3 \mathbf{n}$  along the existing nematic axis. As we will see in Sec. V, once  $p_3$  develops in the presence of  $\vec{T}_{6,7}$ , a biaxial order  $\vec{B}_{1,2}$  with principal axes *parallel* to those of  $\vec{T}_{6,7}^{ijk} n^i$  is explicitly induced. Our final two phases, which we denote by  $(N_T+2)^*$  and  $(V_T+2)^*$ , respectively, have  $D_2$  and  $C_2$  symmetry. They are unique in that they are spontaneously *chiral* phases. The *nonpolar chiral*  $(N_T+2)^*$  phase depicted in Figs. 5(c) and 6(b) is formed from the nonpolar achiral  $N_T$  phase by the development of biaxial  $\vec{B}_{1,2}$  order (but in contrast to the polar achiral  $V+2$  phase) with principal axes *rotated exactly* by  $\pi/4$  relative to those of the  $\vec{T}_{6,7}^{ijk} n^i$  order parameter, which characterizes the  $N_T$  phase. More concretely, for the choice of the basis  $\mathbf{m}, \mathbf{l}$ , such that  $N_T$  is *exclusively* described by nonvanishing  $S$  and  $T_7$  order parameters, the polar achiral  $V+2$  and the nonpolar chiral  $(N_T+2)^*$  phases emerge when  $B_2$  and  $B_1$ , respectively, order; equivalently, if it is the nonzero  $S$  and  $T_6$  that are *exclusively* used to describe the  $N_T$  phase, then the roles of  $B_2$  and  $B_1$  are reversed and transitions to  $V+2$  and  $(N_T+2)^*$  take place when  $B_1$  and  $B_2$ , respectively, become nonzero. The polar chiral  $(V_T+2)^*$  phase emerges from the nonpolar chiral  $(N_T+2)^*$  phase via development of polar order  $p_3$  along the existing nematic  $\mathbf{n}$  axis.

Alternatively, a transition to it can also take place from the polar achiral  $V+2$  phase by spontaneously breaking chiral symmetry via development of biaxial  $\vec{B}_{1,2}$  order with principal axes *rotated exactly* by  $\pi/4$  from those of  $\vec{T}_{6,7}^{ijk} n^i$  order parameter. Not surprisingly, in all the polar phases the  $T_1$  order parameter is also explicitly induced. Since both the

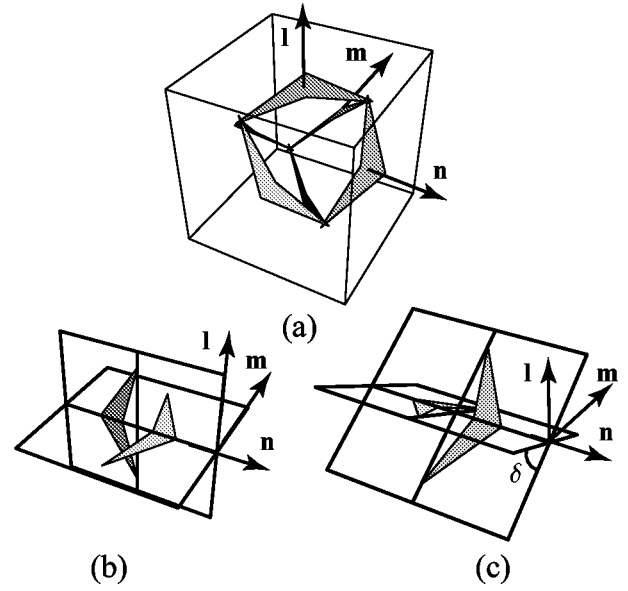


FIG. 5. Schematic representation in terms of banana-shaped molecules of (a) the  $T$  phase, (b) the  $N_T$  phase, and (c) the  $(N_T+2)^*$  phase. In the  $T$  phase, bent-core molecules align locally with their  $\nu_3$  axes aligned on average along the six edges of a tetrahedron and their  $\nu_1$  axes aligned parallel to the normals  $\pm \mathbf{m}$ ,  $\pm \mathbf{l}$ , and  $\pm \mathbf{n}$  to these edges. Opposite edges are (say with normals along  $\mathbf{n}$  and  $-\mathbf{n}$ ) orthogonal so that molecules aligned along opposite edges have perpendicular  $\nu_3$  axes. The  $N_T$  phase is obtained from the  $T$  phase by a uniaxial distortion along one of the cubic axes as shown in Fig. 4 to favor one pair of crossed bent-core molecules over the other two orthogonal pairs. Note the invariance of the  $N_T$  phase under the fourfold improper rotation  $S_4: \mathbf{m} \rightarrow \mathbf{l}, \mathbf{l} \rightarrow -\mathbf{m}, \mathbf{n} \rightarrow -\mathbf{n}$ . The chiral nonpolar  $(N_T+2)^*$  phase is obtained from the  $N_T$  phase by rotating the two molecular planes away from  $90^\circ$  to an angle  $0 < \delta < \pi/2$  to remove the  $S_4$  symmetry element, as also illustrated in Fig. 6.

$(N_T+2)^*$  and  $(V_T+2)^*$  phases are chiral, their ground-state configurations will exhibit spatial modulations like those of cholesteric and blue phases of chiral mesogens.

Given the *achirality* of the bent-core molecules, the transitions from  $N_T$  to  $(N_T+2)^*$  and  $V+2$  to  $(V_T+2)^*$  are ones in which chiral symmetry is broken *spontaneously*, and they are, therefore, relevant to the physics of chiral banana-shaped phases [3]. Figure 7 summarizes the phases we treat and the symmetry-lowering transitions among them that *can* take place, i.e., allowed by symmetry (as opposed to energetic) considerations. The fact that  $C_{2v}$  is a subgroup of  $C_{\infty v}$  ( $C_{2v} \subset C_{\infty v}$ ) implies that there can be a  $V \rightarrow V+2$  symmetry-lowering transition. The subgroup structure  $D_2 \subset D_{2d} \subset T_d \subset O(3)$  and  $C_{2v} \subset D_{3h} \subset O(3)$ , where  $O(3)$  is the full orthogonal group including inversions in three dimensions, imply, respectively, that the  $I \rightarrow T \rightarrow N_T \rightarrow (N_T+2)^*$  and  $I \rightarrow N+3 \rightarrow V+2$  phase sequences are possible. Other phase sequences shown in Fig. 7 follow from similar group-theoretic arguments, and are supported by the detailed analysis of the Landau mean-field theory given in Sec. V.

#### IV. CONSTRUCTION OF A LANDAU FIELD THEORY

Having identified the possible spatially homogeneous but anisotropic phases [20] of systems described by first-

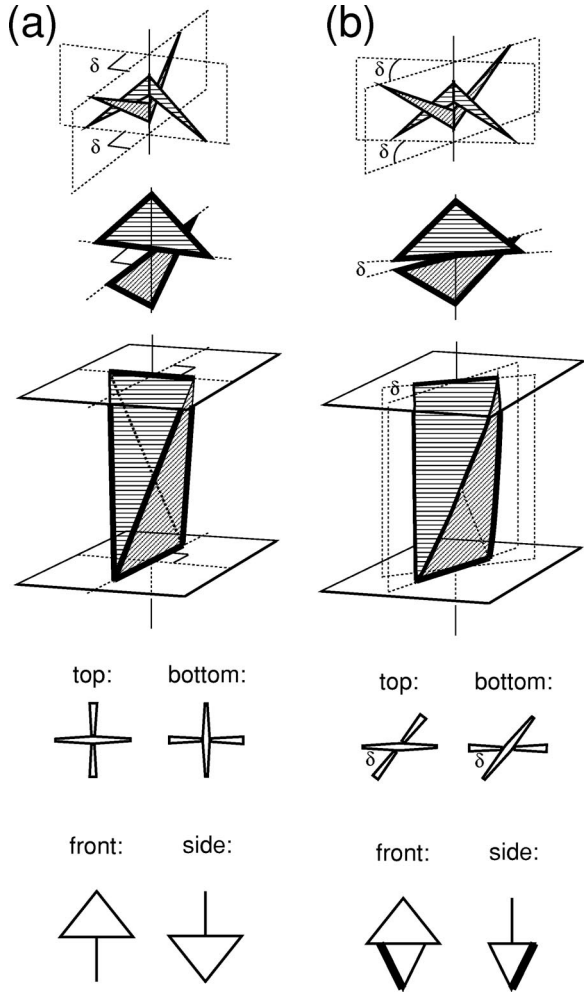


FIG. 6. Various representations of the achiral  $N_T$  (a) and the chiral  $(N_T+2)^*$  (b) phases. The two phases are distinguished by their opening angle  $\delta$ . In the achiral  $N_T$  phase,  $\delta = \pi/2$ , whereas in the chiral  $(N_T+2)^*$  phase,  $0 < \delta < \pi/2$ .

second-, and third-rank tensor order parameters, we now turn to the study of phase transitions among them. To this end we begin by constructing a Landau free energy that will describe transitions from the isotropic phase. The appropriate Landau free energy functional is a rotationally invariant power-series expansion in the order parameters  $p^i$ ,  $Q^{ij}$ , and  $T^{ijk}$ . The most general Landau free-energy density is produced by sums of scalars formed from the tensors  $p^i$ ,  $Q^{ij}$ , and  $T^{ijk}$ . It can be decomposed as

$$f = f_p + f_Q + f_T + f_{pQ} + f_{pT} + f_{QT} + f_{pQT} + f_{Q^2T^2}, \quad (4.1)$$

where  $f_p$ ,  $f_Q$ ,  $f_T$  are, respectively, the Landau energies for independent vector, second-rank, and third-rank tensor order parameters and the other energies are couplings between these order parameters. The vector energy  $f_p$  is given by the standard  $O(N=3)$  model,

$$f_p = \frac{1}{2} K_p (\partial_j p^i) (\partial_j p^i) + \frac{1}{2} r_p p^i p^i + u_p (p^i p^i)^2. \quad (4.2)$$

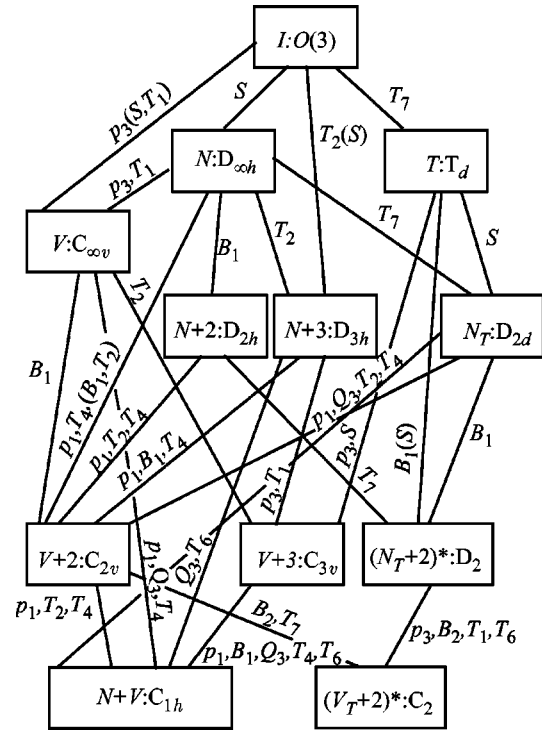


FIG. 7. A flowchart of phase transitions between liquid-crystal phases illustrated in Fig. 3. Order parameters, which become non-zero at each of the transitions and their symmetry groups are indicated. For transitions that we have studied in detail, we have also indicated the secondary (explicitly induced by nonlinear couplings) order parameters by placing them in parentheses.

The purely second-rank tensor part of  $f$  is the well-known Landau energy for isotropic-nematic transition [21,22], given by

$$f_Q = \frac{1}{2} K_Q (\partial_k Q^{ij} \partial_k Q^{ij}) + \frac{1}{2} r_Q Q^{ij} Q^{ij} - w_Q Q^{ij} Q^{jk} Q^{ki} + u_Q (Q^{ij} Q^{ij})^2, \quad (4.3)$$

and the purely third-rank-tensor part of  $f$  is given by

$$f_T = \frac{1}{2} K_T (\partial_i T^{ijk} \partial_i T^{ijk}) + \frac{1}{2} r_T T^{ijk} T^{ijk} + u_T (T^{ijk} T^{ijk})^2 + v_T T^{i_1 i_2 i_3} T^{i_1 i_4 i_5} T^{i_2 i_4 i_6} T^{i_3 i_5 i_6}. \quad (4.4)$$

In the above expressions we have suppressed the position dependence of order parameters, have used an Einstein convention for the repeated indices, and have left out the dipolarlike (“space-spin” coupling) gradient terms,  $\partial_i Q^{ik} \partial_j Q^{jk}$ , and  $\partial_{i_1} T^{i_1 j_2 k} \partial_{i_2} T^{i_2 j_3 k}$ , that couple internal indices of  $Q^{ij}$  and  $T^{ijk}$  to that of the spatial coordinate  $\mathbf{x}$ . Although this last simplification might modify the asymptotic nature of the phase transitions, it obviously will *not* affect our mean-field discussions, valid outside of a (typically) narrow critical region. The parameters  $r_p \sim T - T_p$ ,  $r_Q \sim T - T_Q$ , and  $r_T \sim T - T_T$  vanish at the temperatures  $T_p$ ,  $T_Q$ , and  $T_T$ , which are determined predominantly by the interaction potential between molecules, that characterize mean-field limits of meta-



stability. In writing down quartic nonlinearities in  $f_Q$  and  $f_T$ , we have used the nonobvious relations (valid in three dimensions)

$$\frac{1}{2}(Q^{ij}Q^{ji})^2 = Q^{ij}Q^{jk}Q^{kl}Q^{li}, \quad (4.5a)$$

$$\frac{1}{2}(T^{ijk}T^{ijk})^2 = T^{ij_1k_1}T^{lj_1k_1}T^{ij_2k_2}T^{lj_2k_2} + T^{i_1i_2i_3}T^{i_1i_4i_5}T^{i_2i_4i_6}T^{i_3i_5i_6}, \quad (4.5b)$$

to reduce the number of quartic couplings in  $f_Q$  from two to one and in  $f_T$  from three to two. The lowest-order contributions to the coupling energies are

$$f_{pQ} = -w_{pQ}p^iQ^{ij}, \quad (4.6a)$$

$$f_{pT} = -w_{pT}p^iQ^{ij}T^{ijk}, \quad (4.6b)$$

$$f_{QT} = -w_{QT}Q^{ij}T^{ijk}, \quad (4.6c)$$

$$f_{pQT} = -w_{pQT}p^iQ^{jk}T^{ijk}, \quad (4.6d)$$

$$f_{Q^2T^2}^{(1)} = -w_1Q^{i_1j_1}Q^{i_2j_2}T^{i_1j_1k}T^{i_2j_2k}, \quad (4.6e)$$

$$f_{Q^2T^2}^{(2)} = -w_2Q^{i_1j_1}Q^{i_2j_2}T^{i_1j_1k}T^{i_2j_2k}, \quad (4.6f)$$

$$f_{Q^2T^2}^{(3)} = -w_3Q^{i_1i_2}Q^{j_1j_2}T^{i_1j_1k}T^{i_2j_2k}, \quad (4.6g)$$

where we have decomposed  $f_{Q^2T^2}$  as  $\sum_{n=1}^3 f_{Q^2T^2}^{(n)}$ . The term  $p^iQ^{jk}T^{ijk}$  deserves special attention. If the product  $Q^{jk}T^{ijk}$  is nonzero this term will induce vector  $p^i$  order. Thus, it is possible to have a transition from the  $N$  phase that appears to be driven by  $T^{ijk}$  but which nonetheless develops vector order. In other words, a model expressed in terms of  $Q^{ij}$  and  $T^{ijk}$ , only, would miss the development of vector order, which by itself is unlikely to order in a realistic liquid crystal.

As usual, the average properties are computed by integrating over order parameter configurations with a Boltzmann weight with an effective Hamiltonian  $\mathcal{H} = \int d^3x f$ ,

$$\langle \mathcal{O} \rangle = \frac{1}{Z} \int \mathcal{D}p^i \mathcal{D}Q^{ij} \mathcal{D}T^{ijk} \mathcal{O}(p^i, Q^{ij}, T^{ijk}) e^{-\mathcal{H}/k_B T}, \quad (4.7)$$

where  $\mathcal{O}(p^i, Q^{ij}, T^{ijk})$  is a function of the order parameters  $p^i$ ,  $Q^{ij}$ , and  $T^{ijk}$  and  $Z$  is the partition function.

## V. PHASE TRANSITIONS

In the preceding two sections, we defined order parameters, identified possible rotationally anisotropic, but spatially homogeneous thermodynamic phases of bent-core molecules, and constructed a Landau theory to describe phase transitions among these phases. In this section, we will show how each of the phase transition sequences depicted in Fig. 7 arises in mean-field theory. We will organize our discussion by considering sequentially each symmetry-lowering transi-

tion from each of the phases in Fig. 7. Thus, we will first discuss transitions from the  $I$  phase to the  $V$ ,  $N$ ,  $N+3$ , and  $T$  phases. We will then study transitions from each of these phases, that is, from the  $V$ ,  $N$ ,  $N+3$ , and  $T$  phases into lower-symmetry phases and so on until the lowest-symmetry  $V+3$ ,  $(V_T+2)^*$ , and  $N+V$  phases are reached.

In our discussion of transitions out of various partially ordered phases, it will be useful to display explicitly the part of the free energy functional  $f$  that couples the order parameters  $p^i$ ,  $Q^{ij}$ , and  $T^{ijk}$ , which identify our phases. This coupling energy part, which we collectively call  $f_c$ , arises from the  $Q^3$  and  $Q^4$  parts of  $f_Q$ , from the  $T^4$  parts of  $f_T$ , and from  $f_{pQ}$ ,  $f_{pT}$ ,  $f_{QT}$ ,  $f_{pQT}$ ,  $f_{Q^2T^2}^{(1)}$ ,  $f_{Q^2T^2}^{(2)}$ , and  $f_{Q^2T^2}^{(3)}$ . It determines those order parameters that are coupled at harmonic order when long-range order has been established in a subset of order parameters, and it is, therefore, essential in establishing the nature of the phases and phase diagrams for our system.

### A. Transitions from the isotropic phase

The isotropic phase is the phase with the highest [ $O(3)$ ] symmetry. A symmetry-lowering transition to the  $V$  phase with vector symmetry takes place with the development of  $\mathbf{p}$  order and one to the  $N$  phase with the development of uniaxial  $Q^{ij}$  order. As Figs. 7 and 12 indicate, the development of  $T^{ijk}$  order in the isotropic phase  $I$ , can lead to two distinct phases: the tetrahedral phase  $T$  with  $\vec{T}_{6,7}$  order and the  $N+3$  phase with uniaxial  $Q^{ij}$  order in addition to  $\vec{T}_{2,3}$  order. At long length scales, small fluctuations within the isotropic phase are described by a harmonic free energy density

$$\tilde{f}^{(I)} = \frac{1}{2}(r_p p^i p^i + r_Q Q^{ij} Q^{ij} + r_T T^{ijk} T^{ijk}). \quad (5.1)$$

Thus, which of the fields  $p^i$ ,  $Q^{ij}$ , or  $T^{ijk}$  first becomes unstable is determined by which of the set of parameters  $S_I = \{r_p, r_Q, r_T\}$  first passes through zero. Some of the transitions from the  $I$  phase are, however, first order, and which of the possible transitions actually takes place depends on higher-order terms in the free energy. We will thus consider each transition separately.

#### 1. $I \rightarrow V$ transition

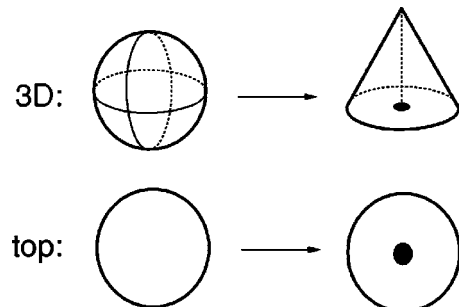


FIG. 8. A schematic representation of the  $I \rightarrow V$  transition.

The  $I \rightarrow V$  transition is driven by the development of  $\mathbf{p}$  order. Since  $\mathbf{p}$  is a vector, this transition is in the well-known  $O(3)$  universality class; it can be described in terms of an effective theory involving  $\mathbf{p}$  only (Fig. 8). Below this second-order transition, we can take  $\mathbf{p}$  to point along the 3 direction with

$$p_3 \sim |r_p - r_{pc}|^{\beta_{O(3)}}, \quad (5.2)$$

and  $\beta_{O(3)} \approx 0.366$ , where  $r_{pc}$  is the value of  $r_p$  at the critical point. Once  $\mathbf{p}$  develops, it drives both  $S$  and  $T_1$  order via the interactions

$$f_{pQ} = -\frac{2}{3} w_{pQ} p_3^2 S, \quad (5.3)$$

$$f_{pT} = -\sqrt{\frac{2}{5}} w_{pQT} p_3^3 T_1, \quad (5.4)$$

so that in mean-field theory [24]

$$S \sim |r_p - r_{pc}|^{2\beta_{O(3)}}, \quad (5.5a)$$

$$T_1 \sim |r_p - r_{pc}|^{3\beta_{O(3)}}, \quad (5.5b)$$

for  $r_p < r_{pc}$  in the  $V$  phase.

### 2. $I \rightarrow N$ transition

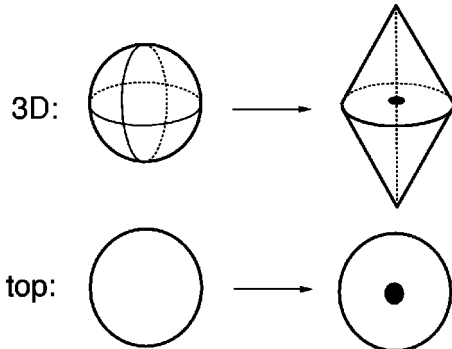


FIG. 9. A schematic representation of the  $I \rightarrow N$  transition.

The  $I \rightarrow N$  transition is driven by the development of  $Q^{ij}$  order from the isotropic phase. There are no couplings that explicitly drive either  $p^i$  or  $T^{ijk}$  order once  $Q^{ij}$  order develops (Fig. 9). Consequently, this well-studied transition [21,22], which is described completely by the  $f_Q$  part of the free energy density, is generically first order and in mean-field theory takes place at  $r_Q = w_Q^2/12u_Q$ . A direct transition from the isotropic to the biaxial nematic ( $N+2$ ) phase is also possible. Since it is fairly complicated and has been treated in detail [23], we will not consider it further here.

### 3. Transitions from $I$ driven by $T^{ijk}$

Transitions from the  $I$  phase involving the development of third-rank tensor [26,27] order are more complex than the other transitions from the  $I$  phase we have considered. The many degrees of freedom in the  $T^{ijk}$  tensor lead to the pos-

sibility of two distinct transitions, the  $I \rightarrow T$  and the  $I \rightarrow N+3$  transition [27]. Since it is fluctuations in  $T^{ijk}$  that drive these transitions, the noncritical degrees of freedom,  $p^i$  and  $Q^{ij}$  can safely be integrated out to produce an effective theory involving only  $T^{ijk}$  whose free energy is identical in form to Eq. (4.4). This is the energy that we will use to study transitions from the  $I$  phase involving  $T^{ijk}$  order. We will, however, have cause to return to the more general theory in our discussion of the  $I \rightarrow N+3$  transition. There are two important things to note about the free energy  $f_T$  in Eq. (4.4). First, in contrast to  $f_Q$ , this energy has no odd-order invariants because none can be formed with a third-rank tensor,  $T^{ijk}$ . Second, there are two fourth order invariants [27], which as we shall see, compete in the determination of the symmetry of the order parameter that develops from the isotropic phase. In the limit of vanishing  $v_T$  coupling,  $f_T$  is invariant under the operations of the group  $O(7)$ , as can be seen by reexpressing  $f_T$  with  $v_T = 0$  as

$$f_T^{O(7)} = \frac{1}{2} r_T |\vec{T}|^2 + u_T |\vec{T}|^4, \quad (5.6)$$

where  $\vec{T}$  is a seven-dimensional vector with components  $T_\mu$  defined by Eq. (2.17c). Because the underlying  $O(3)$  symmetry of our system is lower than  $O(7)$ , with  $T^{ijk}$  forming its seven-dimensional irreducible representation, it is not surprising that the full free energy is *not*  $O(7)$  invariant. The  $v_T$  quartic term, explicitly breaks the  $O(7)$  symmetry and determines which of the seven  $T_\mu$  irreducible components of  $T^{ijk}$  order at the transition from the isotropic phase.

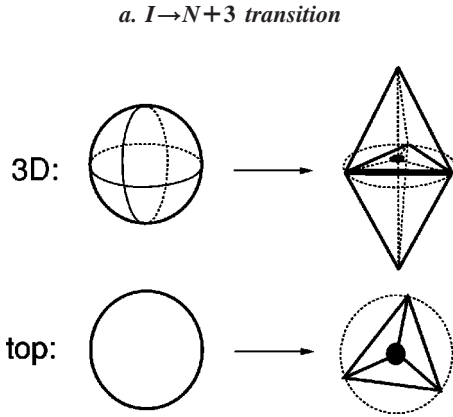
To determine which components order, it is convenient to use the alternative representation of  $T^{ijk}$  given by Eq. (2.19). In this representation we have

$$f_T = \frac{1}{2} r_T T^2 + u_T T^4 + f_{v_T}, \quad (5.7)$$

with

$$f_{v_T} = \frac{v_T T^4}{150} \left[ 9 \cos^4 \theta_1 + \frac{15}{2} \sin^2 2\theta_1 (1 + 2 \cos 2\theta_2) + 25 \sin^4 \theta_1 \sin^4 \theta_2 \right], \quad (5.8)$$

breaking the  $O(7)$  invariance of  $f_T$ .  $f_{v_T}$  (and thus  $f_T$ ) has an  $O(2)$  invariance, which, through our choice of parametrization of  $T^{ijk}$ , Eq. (2.19), is manifested by  $f_{v_T}$ 's being independent of  $\theta_3$ . Thus, finding the minimum-energy state requires the minimization of  $f_T(\theta_1, \theta_2)$  over two rather than three angles.

FIG. 10. A schematic representation of the  $I \rightarrow N+3$  transition.

Following standard analysis, for  $v_T > 0$  we find that the global minimum of  $f_{v_T}(\theta_1, \theta_2)$  at fixed  $T$  is given by

$$\theta_1^{\min} = \frac{\pi}{2}, \quad (5.9a)$$

$$\theta_2^{\min} = 0, \quad (5.9b)$$

which corresponds to a state with

$$T_{\min}^{ijk} = T_2 I_2^{ijk}, \quad (5.10)$$

i.e., a state with a planar triadic order [see Eqs. (3.1) to (3.4)], here chosen to lie in the  $\mathbf{m}-\mathbf{l}$  plane (Fig. 10). A rotation within this plane shows that for a more general choice [than that defined by the representation choice, Eq. (2.19)] of  $\mathbf{m}$  and  $\mathbf{l}$  axes relative to the molecular body axes, such triadic planar order is described by an arbitrary linear combination of the  $I_2^{ijk}$  and  $I_3^{ijk}$  tensors, corresponding to nonvanishing  $T_2$  and  $T_3$  order parameters, i.e., a nonvanishing  $\vec{T}_{2,3}$ .

Since this triadic order defines a plane that brings with it a normal invariant under reflection, it necessarily induces uniaxial nematic order,  $Q^{ij} = S(n^i n^j - \frac{1}{3} \delta^{ij})$  with  $\mathbf{n}$  along the normal. To lowest order, the development of  $S$  is brought about by the  $f_{QT}$  coupling of Eq. (4.6c),

$$f_{QT} = \frac{1}{3} w_{QT} T_2^2 S, \quad (5.11)$$

which leads to the expected uniaxial nematic order with

$$S = -\frac{T_2^2}{2r_Q}. \quad (5.12)$$

Hence the state for  $v_T > 0$  is the  $N+3$  phase in which the nematic and triadic order, transverse to the nematic axis, coexist. From the point of view of symmetry it is equivalent to a liquid of orientationally ordered equilateral triangles with aligned normals.

Another solution that minimizes the energy  $f_T(\theta_1, \theta_2)$  and that is degenerate with the state described by the solution in Eq. (5.9) is

$$\theta_1^{\min} = \arccos \sqrt{5/8}, \quad (5.13a)$$

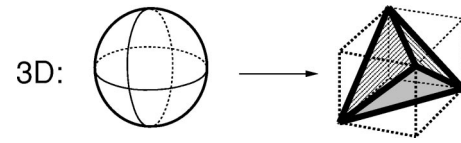
$$\theta_2^{\min} = \frac{\pi}{2}. \quad (5.13b)$$

It corresponds to a state

$$T^{ijk} = \frac{T}{\sqrt{8}} [\sqrt{5} I_1^{ijk} + \sqrt{3} I_6^{ijk}], \quad (5.14)$$

which is equivalent to  $T_{\min}^{ijk} = T I_2^{ijk}$ , Eq. (5.10) after  $\mathbf{n}$  and  $\mathbf{m}$  are interchanged. Clearly then this solution also represents the  $N+3$  phase, but with the nematic axis along  $\mathbf{m}$  rather than  $\mathbf{n}$ , and the triadic order in the  $\mathbf{n}-\mathbf{l}$  plane.

*b. I → T transition*

FIG. 11. A schematic representation of the  $I \rightarrow T$  transition.

When  $v_T < 0$  the global minimum of  $f_{v_T}(\theta_1, \theta_2)$  at fixed  $T$  is given by

$$\theta_1^{\min} = \frac{\pi}{2}, \quad (5.15a)$$

$$\theta_2^{\min} = \frac{\pi}{2}, \quad (5.15b)$$

which corresponds to the state with

$$T_{\min}^{ijk} = T_6 I_6^{ijk}, \quad (5.16)$$

which is invariant under the operations of the tetrahedral group  $T_d$ . As can be seen in Fig. 4, the group  $T_d$  has three  $C_2$  axes coinciding with the axes of the cube, four  $C_3$  axes coinciding with the body diagonals of the cube, six reflection planes passing through each edge and bisecting the opposite edge of the tetrahedron, and four  $S_4$  improper rotation axes corresponding to the axes bisecting (four) sets of two opposite edges of the tetrahedron. Because this state lacks  $\mathbf{n} \rightarrow -\mathbf{n}$  symmetry, no nematic or any other order is induced by the coupling free energy  $f_c$ , Eq. (4.6). Because of its tetrahedral symmetry and because only the  $T_6$  component of  $T^{ijk}$  is nonzero, we identify this state with the  $T$  phase illustrated schematically in Fig. 5(a). Since  $f_{v_T}$  is independent of  $\theta_3$ , an arbitrary linear combination of  $T_6$  and  $T_7$ , rather than  $T_6$  alone, will in general become nonzero at the  $I \rightarrow T$  transition (Fig. 11).

For  $v_T < 0$  we also find another solution that minimizes the energy  $f_T$  and is degenerate with the state in Eq. (5.15). It is given by

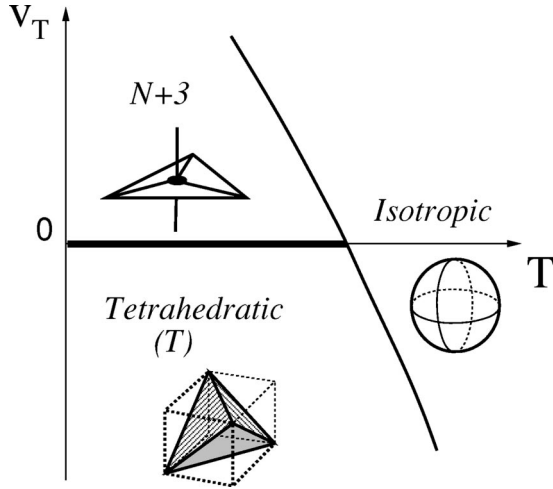


FIG. 12. A portion of a phase diagram for a banana-shaped liquid crystal, illustrating two possible transitions out of the isotropic phase. For  $v_T > 0$ , the transition is  $I \rightarrow N+3$ , and for  $v_T < 0$  it is the  $I \rightarrow T$  transition. Although in mean-field theory these transitions are continuous, we expect thermal fluctuations to drive them first order. Lowering temperature along a finely tuned  $v_T = 0$  curve, we expect a continuous transition in the  $O(7)$  universality class.

$$\theta_1^{\min} = \arccos \sqrt{5/9}, \quad (5.17a)$$

$$\theta_2^{\min} = 0, \quad (5.17b)$$

and corresponds to a state with

$$T^{ijk} = \frac{T_6}{3} [\sqrt{5}I_1^{ijk} + 2I_2^{ijk}]. \quad (5.18)$$

However, it can easily be shown that this solution is equivalent to  $T_{\min}^{ijk} = TI_6^{ijk}$ , after a rotation around the  $\mathbf{l}$  axis,

$$\mathbf{n} \rightarrow \sqrt{1/3}\mathbf{n} + \sqrt{2/3}\mathbf{m}, \quad (5.19a)$$

$$\mathbf{m} \rightarrow -\sqrt{2/3}\mathbf{n} + \sqrt{1/3}\mathbf{m}. \quad (5.19b)$$

It, thus, also corresponds to the  $T$  phase with pure  $T_6$  order in a rotated coordinate system. The corresponding phase diagram that graphically summarizes phase transitions outlined above is given in Fig. 12.

For  $v_T = 0$ , it is clear from Eqs. (5.7) and (5.8) that the transition from the  $I$  phase is in the  $O(7)$  universality class, and it is to a state that *spontaneously* breaks  $O(7)$  symmetry by picking out a particular direction in the  $O(7)$  symmetric space (a point on a seven-dimensional sphere) for the vector  $T_\mu$  to point in. Clearly, as we have seen above, the  $v_T$  coupling is relevant in the ordered phase and drives the resulting state toward  $N+3$  phase for  $v_T > 0$  and toward  $T$  for  $v_T < 0$  [28].

We have also investigated the stability of the  $O(7)$  symmetric *transition* (with  $v_T = 0$ ) to a finite value of the  $v_T$  symmetry breaking interaction [29]. In a renormalization group calculation, just below the upper-critical dimension  $d = 4$ , we find that in the presence of thermal fluctuations the  $v_T$  coupling always drives this transition first-order [30,31].

This is analogous to the similar phenomena known in magnetic systems in which cubic crystal fields drive the  $O(3)$  transition of hypothetical isotropic magnets first order [32,35].

### B. Transitions from the $N$ phase

As illustrated in the flowchart of Fig. 7, there are five symmetry-reducing transitions from the nematic phase. These are the  $N \rightarrow V$ ,  $N \rightarrow N+2$ ,  $N \rightarrow N+3$ ,  $N \rightarrow V+2$ , and  $N \rightarrow N_T$  transitions, all of which we will discuss in detail below. To determine which transitions will occur for a given set of phenomenological parameters, we focus on the part of the full free energy density,  $\tilde{f}^{(N)}$ , describing harmonic fluctuations about the nematic phase with nonvanishing  $S$ . This free energy,  $\tilde{f}^{(N)}$ , is determined by the harmonic parts of the energies  $f_p$ ,  $f_Q$ , and  $f_T$ , and by the coupling terms  $f_c$ . The most important contributions to  $f_c$  come from  $f_{pQ}$ , and  $f_{pQT}$ , which can be easily evaluated. The harmonic free energy  $\tilde{f}^{(N)}$  can be expressed as a sum of five independent parts,

$$\tilde{f}^{(N)} = \tilde{f}_{p_3, T_1}^{(N)} + \tilde{f}_{B_{1,2}}^{(N)} + \tilde{f}_{T_{2,3}}^{(N)} + \tilde{f}_{p_{1,2}, T_{4,5}}^{(N)} + \tilde{f}_{T_{6,7}}^{(N)}, \quad (5.20)$$

where

$$\tilde{f}_{p_3, T_1}^{(N)} = \frac{1}{2} \tilde{r}_{p_3}^{(N)} p_3^2 + \frac{1}{2} \tilde{r}_{T_1}^{(N)} T_1^2 + \tilde{\alpha}_{p_1, T_3}^{(N)} p_3 T_1, \quad (5.21a)$$

$$\tilde{f}_{B_{1,2}}^{(N)} = \frac{1}{2} \tilde{r}_{B_{1,2}}^{(N)} (B_1^2 + B_2^2), \quad (5.21b)$$

$$\tilde{f}_{T_{2,3}}^{(N)} = \frac{1}{2} \tilde{r}_{T_{2,3}}^{(N)} (T_2^2 + T_3^2), \quad (5.21c)$$

$$\begin{aligned} \tilde{f}_{p_{1,2}, T_{4,5}}^{(N)} &= \frac{1}{2} \tilde{r}_{p_{1,2}}^{(N)} (p_1^2 + p_2^2) + \frac{1}{2} \tilde{r}_{T_{4,5}}^{(N)} (T_4^2 + T_5^2) \\ &+ \tilde{\alpha}_{p_{1,2}, T_{4,5}}^{(N)} (p_1 T_4 + p_2 T_5), \end{aligned} \quad (5.21d)$$

$$\tilde{f}_{T_{6,7}}^{(N)} = \frac{1}{2} \tilde{r}_{T_{6,7}}^{(N)} (T_6^2 + T_7^2), \quad (5.21e)$$

with

$$\tilde{r}_{p_3}^{(N)} = r_p - \frac{4}{3} w_{pQ} S,$$

$$\tilde{r}_{T_1}^{(N)} = r_T - \frac{8}{15} w_{QT} S - \left( \frac{28}{45} w_1 + \frac{4}{3} w_2 + \frac{2}{9} w_3 \right) S^2,$$

$$\tilde{\alpha}_{p_3, T_1}^{(N)} = -\sqrt{\frac{2}{5}} w_{pQT} S,$$

$$\tilde{r}_{B_{1,2}}^{(N)} = 2r_Q + 4w_Q S + \frac{16}{3} u_Q S^2,$$

$$\tilde{r}_{T_{2,3}}^{(N)} = r_T + \frac{2}{3} w_{QT} S - \frac{2}{9} (w_1 + w_3) S^2,$$

$$\tilde{r}_{p_{1,2}}^{(N)} = r_p + \frac{2}{3} w_{pQ} S,$$

$$\tilde{r}_{T_{4,5}}^{(N)} = r_T - \frac{2}{5} w_{QT} S - \left( \frac{26}{45} w_1 + \frac{8}{15} w_2 + \frac{2}{45} w_3 \right) S^2,$$

$$\tilde{\alpha}_{p_{1,2},T_{4,5}}^{(N)} = -\frac{2}{\sqrt{15}}w_{pQT}S,$$

$$\tilde{r}_{T_{6,7}}^{(N)} = r_T - \frac{2}{9}(2w_1 - w_3)S^2, \quad (5.22)$$

Within mean-field theory, the  $N$  phase becomes unstable to the development of biaxial order (characterized by a linear combination of  $B_1$  and  $B_2$ ), of triaxial order (characterized by a linear combination of  $T_2$  and  $T_3$ ), and of  $N_T$  order (characterized by a linear combination of  $T_6$  and  $T_7$ ), when  $\tilde{r}_{B_{1,2}}^{(N)}$  [36],  $\tilde{r}_{T_{2,3}}^{(N)}$ , and  $\tilde{r}_{T_{6,7}}^{(N)}$ , respectively, pass through zero. The  $N$  phase becomes unstable to longitudinal vector order (characterized by coupled  $p_3$ - $T_1$  order parameters) and to transverse vector order (characterized by coupled  $p_1$ - $T_4$  order parameters), when the determinants,

$$\Delta_{p_3,T_1}^{(N)} = \tilde{r}_{p_3}^{(N)}\tilde{r}_{T_1}^{(N)} - (\tilde{\alpha}_{p_3,T_1}^{(N)})^2, \quad (5.23a)$$

$$\Delta_{p_{1,2},T_{4,5}}^{(N)} = \tilde{r}_{p_{1,2}}^{(N)}\tilde{r}_{T_{4,5}}^{(N)} - (\tilde{\alpha}_{p_{1,2},T_{4,5}}^{(N)})^2, \quad (5.23b)$$

respectively, pass through zero. The nature of transitions out of the  $N$  phase will be determined by which member of the set,  $\mathcal{S}_N = \{\Delta_{p_3,T_1}^{(N)}, \tilde{r}_{B_{1,2}}^{(N)}, \tilde{r}_{T_{2,3}}^{(N)}, \tilde{r}_{T_{6,7}}^{(N)}, \Delta_{p_{1,2},T_{4,5}}^{(N)}\}$ , first passes through zero on lowering the temperature.

### 1. $N \rightarrow V$ transition

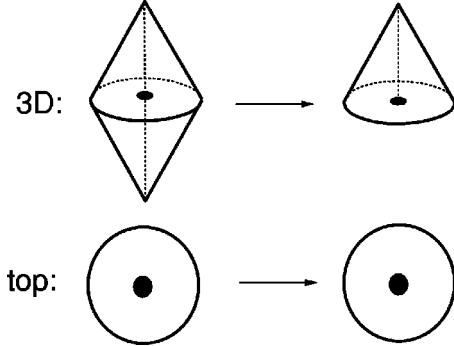


FIG. 13. A schematic representation of the  $N \rightarrow V$  transition.

The  $N \rightarrow V$  transition is signaled by the development of vector order along the unique direction  $\mathbf{n}$  of the  $N$  phase, i.e., by the development of  $p_3$  and  $T_1$  order. Thus, this transition occurs if  $\Delta_{p_3,T_1}^{(N)}$  is the first of the set  $\mathcal{S}_N$  to become zero. The relative sign of  $p_3$  and  $T_1$  is fixed by the eigenfunction associated with the smallest eigenvalue of the matrix defined by  $\tilde{f}_{p_3,T_1}^{(N)}$ . The overall sign is, however, arbitrary (Fig. 13). Since it is the associated  $\mathbb{Z}_2$  symmetry (with  $V$  pointing along or antiparallel to  $\mathbf{n}$ ) that is broken, the  $N \rightarrow V$  transition is in the well-studied Ising universality class with coupled order parameters

$$p_3 \sim |\Delta_{p_3,T_1}^{(N)} - \Delta_{p_3,T_1}^{(N)c}|^{\beta_{\text{Ising}}}, \quad (5.24a)$$

$$T_1 \sim |\Delta_{p_3,T_1}^{(N)} - \Delta_{p_3,T_1}^{(N)c}|^{\beta_{\text{Ising}}}, \quad (5.24b)$$

growing for  $\Delta_{p_3,T_1}^{(N)} < \Delta_{p_3,T_1}^{(N)c}$ . Once  $p_3$  and  $T_1$  become non-zero, they do *not* force the development of any other order, and the  $V$  phase is completely characterized by  $p_3$ ,  $S$ , and  $T_1$  order parameters, as illustrated in Figs. 3 and 7.

### 2. $N \rightarrow N+3$ transition

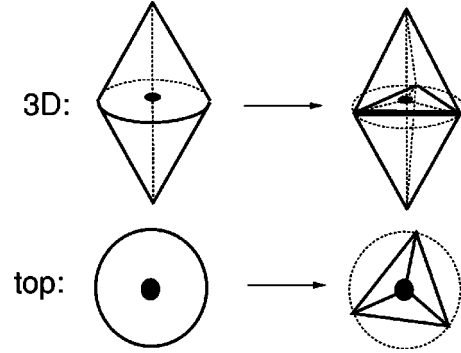


FIG. 14. A schematic representation of the  $N \rightarrow N+3$  transition.

The  $N+3$  phase develops out of the  $N$  phase with the appearance of a linear combination of  $T_2$  and  $T_3$  order (Fig. 14). As discussed in Eqs. (3.1) to (3.4),  $T_2$  and  $T_3$  define a two-dimensional representation of the group of rotations perpendicular to  $\mathbf{n}$  and describe triadic order in the plane perpendicular to  $\mathbf{n}$ . Since the  $N$  phase is invariant with respect to arbitrary rotations about  $\mathbf{n}$ , the free energy of the  $N$  phase is a function only of the rotationally invariant combinations  $T_2^2 + T_3^2 = |\vec{T}_{2,3}|^2$ . Thus, the  $N \rightarrow N+3$  transition is in the well-known  $XY$  universality class. Within mean-field theory, this transition occurs when  $\tilde{r}_{T_{2,3}}^{(N)}$  is the first in the set  $\mathcal{S}_N$  to pass through zero on cooling.  $\vec{T}_{2,3}$  order drives no other order, and the  $N+3$  phase is completely characterized by  $S$  and  $\vec{T}_{2,3}$  with

$$T_2 \propto T_3 \sim |\tilde{r}_{T_{2,3}}^{(N)} - \tilde{r}_{T_{2,3}}^{(N)c}|^{\beta_{XY}}, \quad (5.25)$$

for  $\tilde{r}_{T_{2,3}}^{(N)} < \tilde{r}_{T_{2,3}}^{(N)c}$ .

### 3. $N \rightarrow N+1$ ( $\equiv V+2$ ) transition

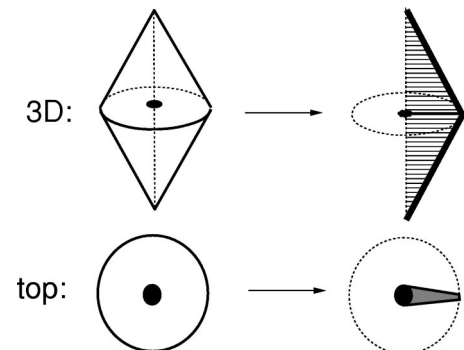


FIG. 15. A schematic representation of the  $N \rightarrow N+1$  transition.

The  $V+2$  phase is distinguished from the  $N$  phase by the existence of a vector order described by  $\mathbf{p}$  in the plane perpendicular to  $\mathbf{n}$ . We can arbitrarily choose  $\mathbf{p}$  to be along  $\mathbf{m}$  so that  $p_1$  is nonzero. Since there is already uniaxial order in the  $N$  phase,  $T_4$  order has the same symmetry in the  $N$  phase as does  $p_1$  order, and not surprisingly  $p_1$  and  $T_4$  (as are generically  $p_2$  and  $T_5$ ) are coupled in  $\tilde{f}^{(N)}$ , Eq. (5.21d). The invariance of the  $N$  phase with respect to arbitrary rotations about  $\mathbf{n}$  implies that the energy of the  $N$  phase must be a function of rotationally invariant combinations  $p_1^2 + p_2^2 = |\vec{p}_{1,2}|^2$ ,  $T_4^2 + T_5^2 = |\vec{T}_{4,5}|^2$ , and  $p_1 T_4 + p_2 T_5 = \vec{p}_{1,2} \cdot \vec{T}_{4,5}$  as is the harmonic free energy  $\tilde{f}_{p_1,2,T_4,5}^{(N)}$  in Eq. (5.21d). The  $N \rightarrow V+2$  transition is thus in the  $XY$  universality class. It occurs in mean-field theory when  $\Delta_{p_1,2,T_4,5}^{(N)}$  is the first of the set  $\mathcal{S}_N$  to pass through zero upon cooling. The order parameters  $p_1$  and  $T_4$  (and  $p_2$  and  $T_5$  related to them by a rotation in the  $\mathbf{m}-\mathbf{l}$  plane) will drive the  $N \rightarrow V+2$  transition, both growing continuously from zero as

$$p_1 \propto T_4 \sim |\Delta_{p_1,T_4}^{(N)} - \Delta_{p_1,T_4}^{(N)c}|^{\beta_{XY}}, \quad (5.26)$$

for  $\Delta_{p_1,T_4}^{(N)} < \Delta_{p_1,T_4}^{(N)c}$ . Once these order parameters become nonzero, however, they pick out a direction in the plane perpendicular to  $\mathbf{n}$  that drives the development of a nonvanishing biaxial order  $B_1$  via the  $f_{pQ}$  and  $f_{QT}$  coupling free energies, as is clear from Fig. 15. In mean-field theory,  $B_1 \sim p_1^2$  and  $T_2 \sim p_1^3$ . Below the critical dimension  $d_c = 4$ , however, potentials in the coupling energies are relevant, and [24,25]

$$B_1 \sim p_1^{\sigma_2} \quad T_2 \sim p_1^{\sigma_3}, \quad (5.27)$$

where  $\sigma_n = n + x_n n(n-1)$  with  $x_n$  only weakly dependent on  $n$ .

To emphasize the secondary role that  $B_1$  and  $T_2$  order parameters play at the  $N \rightarrow V+2$  transition, in Fig. 7,  $B_1$  and  $T_2$  are placed in parentheses along the  $N \rightarrow V+2$  line. Therefore, the  $V+2$  phase is reached from the  $N$  phase (characterized by a finite value of  $S$ ) via the well-studied, second-order  $XY$  transition upon the development of  $p_1$ ,  $B_1$ ,  $T_2$ , and  $T_4$  order parameters or a set that can be obtained from this one by an  $XY$  rotation.

#### 4. $N \rightarrow N+2$ transition

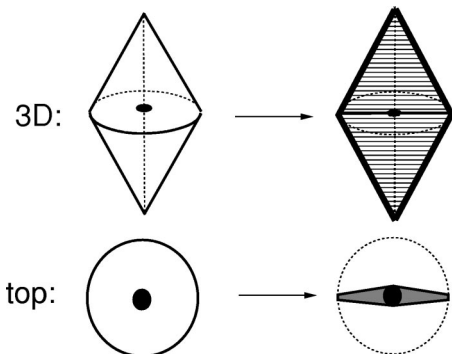


FIG. 16. A schematic representation of the  $N \rightarrow N+2$  transition.

The development of nonvanishing biaxial order parameter  $\vec{B}_{1,2} = (B_1, B_2)$  converts the uniaxial  $N$  phase to the  $N+2$  phase (Fig. 16). The biaxial order parameter is a rank-2 symmetric-traceless tensor, which, because of its confinement to the two-dimensional plane perpendicular to the uniaxial axis  $\mathbf{n}$ , is equivalent to a complex order parameter forming an irreducible  $L=2$  representation of the  $U(1)$  group. The  $N \rightarrow N+2$  transition is thus in the  $XY$  universality class. In mean-field theory, it takes place when  $\tilde{r}_{B_{1,2}}$  is the first of the set  $\mathcal{S}_N$  to pass through zero and more generically, in the presence of thermal fluctuations, we expect,

$$B_1 \propto B_2 \sim |\tilde{r}_{B_{1,2}}^{(N)} - \tilde{r}_{B_{1,2}c}^{(N)}|^{\beta_{XY}}, \quad (5.28)$$

for  $\tilde{r}_{B_{1,2}}^{(N)} < \tilde{r}_{B_{1,2}c}^{(N)}$ . Biaxial order forces no  $p^i$  or  $T^{ijk}$  order, so the  $N+2$  phase is fully characterized by nematic order parameter  $S$  and an arbitrary linear combination of  $B_1$  and  $B_2$  biaxial order parameters, i.e., by  $\vec{B}_{1,2}$ .

#### 5. $N \rightarrow N_T$ transition

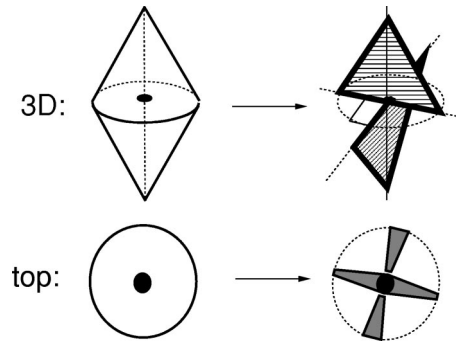


FIG. 17. A schematic representation of the  $N \rightarrow N_T$  transition.

Finally, the  $N_T$  phase is distinguished from the  $N$  phase by the development of an arbitrary linear combination of the  $T_6$  and  $T_7$ , i.e., of the  $\vec{T}_{6,7}$  order (Fig. 17). Since such an order parameter picks out a single direction within the isotropic plane perpendicular to  $\mathbf{n}$ , this transition, like the  $N \rightarrow N+2$ ,  $N \rightarrow N+3$ , and  $N \rightarrow V+2$  transitions, is in the  $XY$  universality class. In order for this transition to occur, in mean-field theory  $\tilde{r}_{T_{6,7}}$  must pass through zero before any of the other members of the set  $\mathcal{S}_N$ . If we restrict the interaction energies to  $f_{pQ}$ ,  $f_{QT}$  and  $f_{pQT}$ ,  $\tilde{r}_{T_{6,7}}^{(N)}$  will never be the smallest in the set. However, higher-order terms of the form  $f_{Q^2T^2}$  can favor the formation of  $T_6$ - $T_7$  order over the others and make this transition possible, with

$$T_6 \propto T_7 \sim |\tilde{r}_{T_{6,7}}^{(N)} - \tilde{r}_{T_{6,7}c}^{(N)}|^{\beta_{XY}}, \quad (5.29)$$

for  $\tilde{r}_{T_{6,7}}^{(N)} < \tilde{r}_{T_{6,7}c}^{(N)}$ . Because the  $T_6$ - $T_7$  order drives no other order, the  $N_T$  phase is characterized by nonvanishing  $S$ , and  $\vec{T}_{6,7}$  order.

### C. Transitions from the V phase

In the V phase, three order parameters,  $p_3$ ,  $S$ , and  $T_1$  are nonzero. Harmonic fluctuations of the other order parameters in this phase are described by the free energy density

$$\tilde{f}^{(V)} = \tilde{f}_{B_{1,2}, T_{6,7}}^{(V)} + \tilde{f}_{T_{2,3}}^{(V)} + \tilde{f}_{p_{1,2}, Q_{3,4}, T_{4,5}}^{(V)}, \quad (5.30)$$

where

$$\begin{aligned} \tilde{f}_{B_{1,2}, T_{6,7}}^{(V)} &= \frac{1}{2} \tilde{r}_{B_{1,2}}^{(V)} (B_1^2 + B_2^2) + \frac{1}{2} \tilde{r}_{T_{6,7}}^{(V)} (T_6^2 + T_7^2) \\ &\quad + \tilde{\alpha}_{B_1, T_6}^{(V)} (B_1 T_6 + B_2 T_7), \\ \tilde{f}_{T_{2,3}}^{(V)} &= \frac{1}{2} \tilde{r}_{T_{2,3}}^{(V)} (T_2^2 + T_3^2), \end{aligned} \quad (5.31)$$

$$\begin{aligned} \tilde{f}_{p_{1,2}, Q_{3,4}, T_{4,5}}^{(V)} &= \frac{1}{2} \tilde{r}_{p_{1,2}}^{(V)} (p_1^2 + p_2^2) + \frac{1}{2} \tilde{r}_{Q_{3,4}}^{(V)} (Q_3^2 + Q_4^2) \\ &\quad + \frac{1}{2} \tilde{r}_{T_{4,5}}^{(V)} (T_4^2 + T_5^2) + \tilde{\alpha}_{p_{1,2}, Q_{3,4}}^{(V)} (p_1 Q_3 + p_2 Q_4) \\ &\quad + \tilde{\alpha}_{p_{1,2}, T_{4,5}}^{(V)} (p_1 T_4 + p_2 T_5) \\ &\quad + \tilde{\alpha}_{Q_{3,4}, T_{4,5}}^{(V)} (Q_3 T_4 + Q_4 T_5), \end{aligned}$$

where

$$\begin{aligned} \tilde{r}_{B_{1,2}}^{(V)} &= \tilde{r}_{B_{1,2}}^{(N)} - \frac{2}{5} (2w_1 + w_3) T_1^2, \\ \tilde{r}_{T_{6,7}}^{(V)} &= \tilde{r}_{T_{6,7}}^{(N)} + (4u_T - \frac{2}{5} v_T) T_1^2, \\ \tilde{\alpha}_{B_{1,2}, T_{6,7}}^{(V)} &= \frac{4}{\sqrt{15}} w_{QT} T_1 - \sqrt{\frac{2}{3}} w_{pQT} p_3, \\ \tilde{r}_{T_{2,3}}^{(V)} &= \tilde{r}_{T_{2,3}}^{(N)} + (4u_T + \frac{6}{5} v_T) T_1^2, \\ \tilde{r}_{p_{1,2}}^{(V)} &= \tilde{r}_{p_{1,2}}^{(N)} + 4u_p p_3^2 + \frac{6}{\sqrt{10}} w_{pT} p_3 T_1, \\ \tilde{r}_{Q_{3,4}}^{(V)} &= r_Q - w_Q S + \frac{8}{3} u_Q S^2 - \frac{2}{10} (4w_1 + 2w_2 - w_3) T_1^2, \\ \tilde{r}_{T_{4,5}}^{(V)} &= \tilde{r}_{T_{4,5}}^{(N)} + (4u_T + \frac{6}{25} v_T) T_1^2, \\ \tilde{\alpha}_{p_{1,2}, Q_{3,4}}^{(V)} &= -\sqrt{2} w_{pQ} p_3 + \frac{1}{\sqrt{5}} w_{pQT} T_1, \\ \tilde{\alpha}_{p_{1,2}, T_{4,5}}^{(V)} &= \tilde{\alpha}_{p_{1,2}, T_{4,5}}^{(N)} - 2 \sqrt{\frac{3}{5}} w_{pT} p_3^2, \\ \tilde{\alpha}_{Q_{3,4}, T_{4,5}}^{(V)} &= -\frac{2}{5\sqrt{3}} w_{QT} T_1 - 2 \sqrt{\frac{2}{15}} p_3 \\ &\quad - \frac{2}{15\sqrt{3}} (w_1 + 6w_2 + 4w_3) S T_1. \end{aligned} \quad (5.32)$$

As Fig. 7 indicates, there are symmetry-lowering transitions from the V phase to the V+2, V+3, and N+V phases. Which one occurs is determined by which the set  $\mathcal{S}_V = \{\tilde{r}_{T_{2,3}}^{(V)}, \Delta_{B_{1,2}, T_{6,7}}^{(V)}, \Delta_{p_{1,2}, Q_{3,4}, T_{4,5}}^{(V)}\}$ , where

$$\Delta_{B_{1,2}, T_{6,7}}^{(V)} = \tilde{r}_{B_{1,2}}^{(V)} \tilde{r}_{T_{6,7}}^{(V)} - (\tilde{\alpha}_{B_{1,2}, T_{6,7}}^{(V)})^2 \quad (5.33)$$

(and  $\Delta_{p_{1,2}, Q_{3,4}, T_{4,5}}^{(V)}$  unenlightenly complicated) first reaches its critical value. The nature of the transition out of the V phase will be determined by which of these three mean-field reduced temperatures first reaches the respective critical temperature.

#### 1. V→V+3 transition

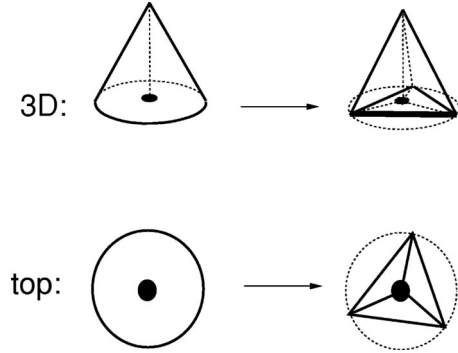


FIG. 18. A schematic representation of the V→V+3 transition.

This transition occurs if  $\tilde{r}_{T_{2,3}}^{(V)}$  reaches its critical value  $\tilde{r}_{T_{2,3}}^{(V)c}$  before  $\Delta_{B_{1,2}, T_{6,7}}^{(V)}$  and  $\Delta_{p_{1,2}, Q_{3,4}, T_{4,5}}^{(V)}$  reach their respective critical values, both zero in mean-field theory (Fig. 18). Since there is rotational invariance in the space defined by  $T_2$  and  $T_3$ , this transition is in the XY universality class and corresponds to development of triaxial order  $\tilde{T}_{2,3}$  in the plane perpendicular to the vector order axis  $p_3$ . Since no other order is driven by this development of the  $\tilde{T}_{2,3}$  order, this order parameter, together with  $p_3$ ,  $S$ , and  $T_1$  (already present in the V phase) completely characterizes the V+3 phase.

#### 2. V→V+2 transition

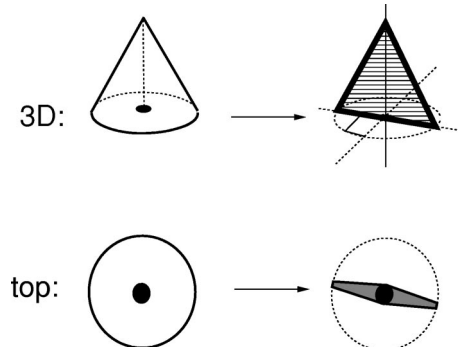


FIG. 19. A schematic representation of the V→V+2 transition.

If  $\Delta_{B_{1,2}, T_{6,7}}^{(V)}$  is the first in the set  $S_V$  to reach its critical value, there will be a transition from the  $V$  to the  $V+2$  phase signaled by the development of biaxial order in the plane perpendicular to  $\mathbf{n}$  characterized by a specific linear combination of  $\vec{B}_{1,2}$  and  $\vec{T}_{6,7}$  (Fig. 19). Rotational invariance in this plane implies that the transition will also be in the  $XY$  universality class in which an arbitrary linear combination of  $(B_1, T_6)$  and  $(B_2, T_7)$  will spontaneously order.

### 3. $V \rightarrow N+V$ transition

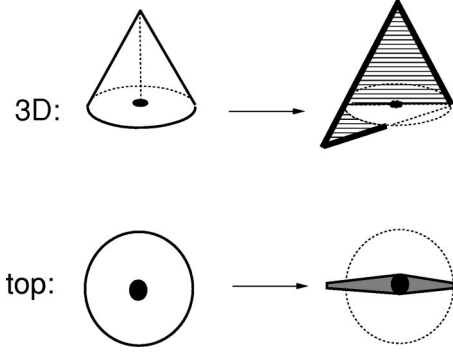


FIG. 20. A schematic representation of the  $V \rightarrow N+V$  transition.

If  $\Delta_{p_{1,2}, Q_{3,4}, T_{4,5}}^{(V)}$  is the first in the set  $S_V$  to reach its critical value, there will be a transition from the  $V$  phase to one in which vector  $(\vec{p}_{1,2})$  and third-rank tensor  $(\vec{T}_{4,5})$  order develop in the plane perpendicular to the already existing vector order,  $p_3$  (Fig. 20). Without loss of generality we represent this transverse vector ordering by nonzero  $p_1$  and  $T_4$ . This set of order parameters is invariant under only one non-trivial operation: reflection from  $y$  to  $-y$ . Thus the new phase has  $C_{1h}$  symmetry and is the  $N+V$  phase. Once these order parameters have been established, they will drive  $B_1$ ,  $T_2$ , and  $T_6$  nonzero via higher-order terms such as  $f_{pQ}$  and  $f_{pT}$ . Since the  $V \rightarrow N+V$  transition is controlled by the development of vector order in a plane, we expect it to be in the  $XY$  universality class.

### D. Transitions from the $N+2$ phase

The  $N+2$  phase is the standard biaxial nematic phase with nonvanishing  $S$  and an arbitrary linear combination of biaxial  $B_1$  and  $B_2$  order parameters; without loss of generality, for convenience, we choose our coordinate system  $(\mathbf{m}, \mathbf{l}, \mathbf{n})$  so that the biaxial order is described by  $B_1$ . As the flow chart of Fig. 7 indicates, the  $N+2$  phase can undergo symmetry-lowering transitions to the  $V+2$  and  $(N_T+2)^*$  phases. Harmonic fluctuations about the  $N+2$  phase, which determine the nature of transitions out of the  $N+2$  phase, are described by

$$\vec{f}^{(N+2)} = \vec{f}_{p_3, T_1, T_6}^{(N+2)} + \vec{f}_{p_1, T_2, T_4}^{(N+2)} + \vec{f}_{p_2, T_3, T_5}^{(N+2)} + \vec{f}_{T_7}^{(N+2)}, \quad (5.34)$$

where

$$\begin{aligned} \vec{f}_{p_3, T_1, T_6}^{(N+2)} &= \frac{1}{2} \vec{r}_{p_3}^{(N+2)} p_3^2 + \frac{1}{2} \vec{r}_{T_1}^{(N+2)} T_1^2 + \frac{1}{2} \vec{r}_{T_6}^{(N+2)} T_6^2 \\ &\quad + \tilde{\alpha}_{T_1, T_6}^{(N+2)} T_1 T_6 + \tilde{\alpha}_{p_3, T_1}^{(N+2)} p_3 T_1 + \tilde{\alpha}_{p_3, T_6}^{(N+2)} p_3 T_6, \end{aligned} \quad (5.35a)$$

$$\begin{aligned} \vec{f}_{p_1, T_2, T_4}^{(N+2)} &= \frac{1}{2} \vec{r}_{p_1}^{(N+2)} p_1^2 + \frac{1}{2} \vec{r}_{T_2}^{(N+2)} T_2^2 + \frac{1}{2} \vec{r}_{T_4}^{(N+2)} T_4^2 \\ &\quad + \tilde{\alpha}_{T_2, T_4}^{(N+2)} T_2 T_4 + \tilde{\alpha}_{p_1, T_2}^{(N+2)} p_1 T_2 + \tilde{\alpha}_{p_1, T_4}^{(N+2)} p_1 T_4, \end{aligned} \quad (5.35b)$$

$$\vec{f}_{T_7}^{(N+2)} = \frac{1}{2} \vec{r}_{T_7}^{(N+2)} T_7^2, \quad (5.35c)$$

where

$$\vec{r}_{p_3}^{(N+2)} = \vec{r}_{p_3}^{(N)},$$

$$\vec{r}_{T_1}^{(N+2)} = \vec{r}_{T_1}^{(N)} - \frac{2}{5} (2w_1 + w_3) B_1^2,$$

$$\vec{r}_{T_6}^{(N+2)} = \vec{r}_{T_6}^{(N)} - \frac{2}{3} (2w_1 + 2w_2 + w_3) B_1^2,$$

$$\tilde{\alpha}_{T_1, T_6}^{(N+2)} = \frac{4}{\sqrt{15}} w_{QT} B_1 - \frac{4}{3\sqrt{15}} (2w_1 + 3w_2 - w_3) S B_1,$$

$$\tilde{\alpha}_{p_3, T_1}^{(N+2)} = \tilde{\alpha}_{p_3, T_1}^{(N)},$$

$$\tilde{\alpha}_{p_3, T_6}^{(N+2)} = \sqrt{\frac{2}{3}} w_{pQT} B_1,$$

$$\vec{r}_{p_1}^{(N+2)} = \vec{r}_{p_{1,2}}^{(N)} - 2w_{pQ} B_1,$$

$$\vec{r}_{T_2}^{(N+2)} = \vec{r}_{T_{2,3}}^{(N)} - 2(w_1 + w_2) B_1^2,$$

$$\begin{aligned} \vec{r}_{T_4}^{(N+2)} &= \vec{r}_{T_{4,5}}^{(N)} - \frac{4}{3} w_{QT} B_1 + \frac{2}{15} [w_1(4S - 7B_1) + w_2(4S - B_1) \\ &\quad - 2w_3(2S + B_1)] B_1, \end{aligned}$$

$$\begin{aligned} \tilde{\alpha}_{T_2, T_4}^{(N+2)} &= \frac{2}{\sqrt{15}} w_{QT} B_1 - \frac{2}{3\sqrt{15}} [2w_1 S + 3w_2(2S - B_1) \\ &\quad + w_3(2S - 3B_1)] B_1, \end{aligned}$$

$$\tilde{\alpha}_{p_1, T_2}^{(N+2)} = -w_{pQT} B_1,$$

$$\tilde{\alpha}_{p_1, T_4}^{(N+2)} = \tilde{\alpha}_{p_{1,2}, T_{4,5}}^{(N)} + \frac{1}{\sqrt{15}} w_{pQT} B_1,$$

$$\vec{r}_{T_7}^{(N+2)} = \vec{r}_{T_{6,7}}^{(N)} - \frac{2}{3} (2w_1 - w_3) B_1^2, \quad (5.36)$$

and  $\vec{f}_{p_2, T_3, T_5}^{(N+2)}$  is obtained from  $\vec{f}_{p_1, T_2, T_4}^{(N+2)}$  by replacements:  $p_1 \rightarrow p_2$ ,  $T_2 \rightarrow T_3$ ,  $T_4 \rightarrow T_5$ ,  $B_1 \rightarrow -B_1$ .



Following our earlier analysis of other transitions, we introduce the determinants  $\Delta_{p_3, T_1, T_6}^{(N+2)}$ ,  $\Delta_{p_1, T_2, T_4}^{(N+2)}$ , and  $\Delta_{p_2, T_3, T_5}^{(N+2)}$  of the matrices, respectively, defined by the coefficients in the free energy densities  $\tilde{f}_{p_3, T_1, T_6}^{(N+2)}$ ,  $\tilde{f}_{p_1, T_2, T_4}^{(N+2)}$ , and  $\tilde{f}_{p_2, T_3, T_5}^{(N+2)}$ . Which transition from the  $N+2$  phase takes place is determined by the set

$$\mathcal{S}_{N+2} = \{\tilde{f}_{T_7}^{(N+2)}, \Delta_{p_3, T_1, T_6}^{(N+2)}, \Delta_{p_1, T_2, T_4}^{(N+2)}, \Delta_{p_2, T_3, T_5}^{(N+2)}\}.$$

### I. $N+2 \rightarrow V+2$ transition

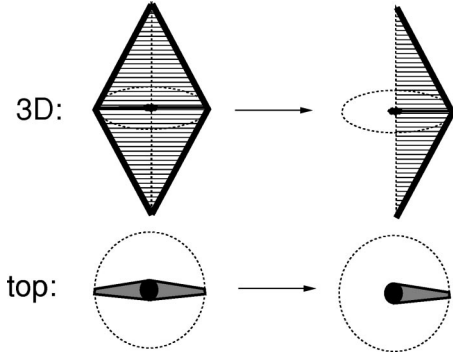


FIG. 21. A schematic representation of the  $N+2 \rightarrow V+2$  transition.

Interestingly, there are three routes from the  $N+2$  phase to a phase with  $V+2$  symmetry. In the first route, the nematic axis along  $\mathbf{n}$ , which in the  $N+2$  phase is invariant under  $\mathbf{n} \rightarrow -\mathbf{n}$ , is converted to a vector axis with the development of  $p_3$ ,  $T_1$ , and  $T_6$  order. The biaxial order of the  $N+2$  phase persists, resulting in the  $V+2$  phase with vector order along the twofold axis  $\mathbf{n}$ . In mean-field theory, this transition to  $V+2$  phase takes place when  $\Delta_{p_3, T_1, T_6}^{(N+2)}$  is the first in the set  $\mathcal{S}_{N+2}$  to pass through zero (Fig. 21).

In the second route, vector order develops along the direction  $\mathbf{m}$ , corresponding to the maximum eigenvalue of the nematic order parameter  $Q^{ij}$  in the plane perpendicular to  $\mathbf{n}$ . In this route, which, in mean-field theory occurs when  $\Delta_{p_1, T_2, T_4}^{(N+2)}$  is the first in  $\mathcal{S}_{N+2}$  to go through zero, the  $p_1$ ,  $T_2$ , and  $T_4$  order parameters become nonzero.

In the third route,  $\Delta_{p_2, T_3, T_5}^{(N+2)}$  is the first in  $\mathcal{S}_{N+2}$  to go through zero, and vector order develops along the  $\mathbf{l}$  axis perpendicular to  $\mathbf{m}$ , defined by the eigenvector of  $Q^{ij}$  with minimum eigenvalue in the plane perpendicular to  $\mathbf{n}$ . It is the  $p_2$ ,  $T_3$ , and  $T_5$  order parameters that become nonzero at the transition.

In all three versions of the  $N+2 \rightarrow V+2$  transition the vector  $\mathbf{p}$  order develops along one of the three twofold symmetry axes defined by the biaxial order of the  $N+2$  phase, the eigenvectors of  $Q^{ij}$ . In each case,  $\mathbf{p}$  can develop either a positive or negative value along an axis already chosen by the  $N+2$  phase. Consequently, these  $N+2 \rightarrow V+2$  transitions are in the Ising universality class, with well-known critical properties.

### 2. $N+2 \rightarrow (N_T+2)^*$ transition

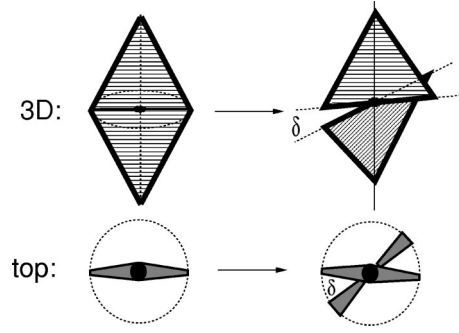


FIG. 22. A schematic representation of the  $N+2 \rightarrow (N_T+2)^*$  transition.

For our choice of the  $\mathbf{m}$ - $\mathbf{l}$  axes, for which the biaxial order of the  $N+2$  phase is characterized by  $B_1 \neq 0$  and  $B_2 = 0$ , another symmetry-reducing transition from the  $N+2$  phase is signaled by the appearance of the  $T_7$  order. It corresponds to the  $N+2 \rightarrow (N_T+2)^*$  and takes place when the reduced temperature  $\tilde{r}_{T_7}^{(N+2)}$  is the smallest in the set  $\mathcal{S}_{N+2}$ . For a different choice of axes, in which  $B_2 \neq 0$  and  $B_1 = 0$  characterize biaxial order, this transition would instead correspond to development of  $T_6$  order. And, more generally, in an  $N+2$  phase characterized by a particular linear combination of  $B_1$  and  $B_2$ , i.e., by  $\vec{B}_{1,2}$  a corresponding *orthogonal* linear combination of  $T_6$  and  $T_7$ , i.e., the  $\vec{T}_{6,7}$  order parameter, such that  $\vec{B}_{1,2} \cdot \vec{T}_{6,7} = 0$  develops at the  $N+2 \rightarrow (N_T+2)^*$  transition.

To understand the nature of this transition it is helpful to first visualize the  $N+2$  phase as a collection of orientationally ordered but positionally disordered *planar* diamond units, each consisting of two, leg-to-leg banana-shaped molecules, illustrated in Figs. 6(b), 5(c), and 22. One can choose the  $\{\mathbf{n}, \mathbf{m}, \mathbf{l}\}$  triad such that the diamonds lie in the  $\mathbf{n}$ - $\mathbf{m}$  plane and, therefore, that their biaxiality is characterized by nonvanishing  $S$  and  $B_1$  order parameters. Now the transition to the  $(N_T+2)^*$  phase corresponds to *counter*, out-of-plane twisting about the  $\mathbf{n}$  axis of the two diamond-forming banana-shaped molecules. It is signaled by the development of the  $T_7$  order parameter, with the twist angle  $\delta$  in the range  $0 \leq \delta \leq \pi/2$  given by

$$\tan \delta = T_7 / B_1. \quad (5.37)$$

We note that the lower limit of this range  $\delta = 0$  corresponds to the planar diamonds of the achiral  $N+2$  phase and the upper limit,  $\delta = \pi/2$  (reached only in the limit  $T_7 \rightarrow \infty$  or  $B_1 = 0$ ) corresponds to the  $N_T$  phase, which is also achiral, and lacks biaxial order. In contrast, all other values of the twist angle  $0 \leq \delta \leq \pi/2$ , corresponding to a nonzero value of  $T_7$  describe a *spontaneously* induced chirality of the  $(N_T+2)^*$  phase. Since the sign of the twist angle (and correspondingly the sign of  $T_7$ ) can be either positive (right handed) or negative (left handed), in mean-field theory the

$N+2 \rightarrow (N_T+2)^*$  transition is clearly in the well-known Ising universality class (but see below).

Finally, we observe that in a phase which spontaneously breaks chiral (mirror) symmetry, a tensor, totally antisymmetric in all its indices (akin to the well-known  $\epsilon_{ijk}$  tensor) must spontaneously emerge. It is easy to verify that in the chiral  $(N_T+2)^*$  phase, most generally characterized by finite  $S$ ,  $B_1$ ,  $B_2$ ,  $T_6$ , and  $T_7$  order parameters,  $\Xi_{ijk}$ , given by

$$\Xi_{ijk} = Q^{is} B^{jt} T^{stk} + Q^{js} B^{kt} T^{sti} + Q^{ks} B^{it} T^{stj} \quad (5.38a)$$

$$= \frac{1}{\sqrt{6}} S (B_1 T_7 - B_2 T_6) \epsilon_{ijk}, \quad (5.38b)$$

is indeed such a fully *antisymmetric* tensor, which develops spontaneously from our theory, that is based solely on fully *symmetric* tensors  $Q^{ij}$  and  $T^{ijk}$ .

The existence of a fully antisymmetric third-rank tensor allows for invariant couplings linear in spatial derivative. For example, a term of the form

$$\Xi_{ijk} Q^{il} \nabla_j Q^{kl} \sim T_7 \mathbf{n} \cdot \nabla \times \mathbf{n} \quad (5.39)$$

is permitted, where the right-hand side represents the dominant part near the transition where  $S$  and  $B_1$  are effectively constant,  $T_7$  is small, and  $\mathbf{n}$  is the Frank director. The elastic energy of the  $N+2$  phase includes the usual twist energy  $K_2[\mathbf{n} \cdot \nabla \times \mathbf{n}]^2$ . There are other terms in the elastic free energy arising from the biaxial order of the  $N+2$  phase, and they may influence the nature of the ground state of the  $(N_T+2)^*$  phase. The existence of terms such as that of Eq. (5.39) that are linear in spatial gradients implies that the ground state of the  $(N_T+2)^*$  phase will be spatially inhomogeneous. The simplest chiral inhomogeneous phase we can imagine is a cholesteric  $(N_T+2)^*$  phase in which  $\mathbf{n}$  rotates in a helical fashion as in the standard cholesteric with pitch  $P$  and pitch wave number  $q_0 = 2\pi/P$  which near the transition to the  $N+2$  phase at temperature  $T_c$  scales as

$$q_0 \sim T_7 / K_2 \sim |\Delta T|^{1/2} \quad (5.40)$$

in mean-field theory where  $\Delta T = T - T_c$ . In a true critical theory,  $q_0$  will also scale to zero as a power of  $|\Delta T|$  provided the transition remains second order. In the presence of fluctuations, the  $T_7 \mathbf{n} \cdot \nabla \times \mathbf{n}$  term is likely to modify the universality class of this transition to something other than the naively expected Ising universality class (possibly even driving the transition first order), but we have not, however, analyzed the critical theory in detail. If molecules themselves are chiral, or a chiral dopant is added, then the  $N+2$  phase will be a chiral  $(N+2)^*$  phase with a nonvanishing  $q_0$ . Chirality will act like an external ordering field (like the magnetic field

of an Ising model) for  $q_0$  with strength  $h$ , and if the  $N+2$ -to- $(N_T+2)^*$  transition is second order, one can expect  $q_0(T, h)$  to scale as

$$q_0(T, h) = |T - T_c|^{\beta_q} f(h/|T - T_c|^\Delta), \quad (5.41)$$

where  $T_c$  is the transition temperature,  $\Delta$  is the external-field gap exponent, and  $\beta_q$  is a critical exponent, which in mean-field theory is the order-parameter exponent  $\beta = 1/2$ .

### E. Transitions from the $N+3$ phase

As we indicate in Fig. 7, the  $N+3$  phase, described by coexistence of the uniaxial order parameter  $S$  and the transverse (to the nematic axis) triaxial order parameter  $\vec{T}_{2,3} \equiv (T_2, T_3)$ , can undergo symmetry-lowering transitions to the  $V+2$ ,  $V+3$ , and  $N+V$  phases.

These transitions are all signaled by the development of vector order  $\mathbf{p}$ . They are distinguished by whether this vector order is *along* [ $N+3 \rightarrow V+3$  transition], *transverse* to [ $N+3 \rightarrow V+2$  ( $\equiv N+1$ ) transition], or at an arbitrary polar angle  $0 \leq \delta \leq \pi/2$  to the uniaxial  $\mathbf{n}$  axis, singled out in the nematic phase. Although it is convenient to think of these transitions as driven by the vector order  $\mathbf{p}$ , more precisely they are driven by specific linear combinations of the vector and other order parameter, linearly coupled to  $\mathbf{p}$ .

It is convenient to choose the  $\mathbf{m}$ - $\mathbf{l}$  axes so that the triaxial order of the  $N+3$  phase, in the plane perpendicular to  $\mathbf{n}$  phase is described by  $T_2 \neq 0$  and  $T_3 = 0$ . For this choice, the harmonic fluctuations about the  $N+3$  phase are described by

$$\tilde{f}^{(N+3)} = \tilde{f}_{p_3, T_1}^{(N+3)} + \tilde{f}_{p_1, B_1, T_4}^{(N+3)} + \tilde{f}_{Q_{3,4}, T_{6,7}}^{(N+3)}, \quad (5.42)$$

where

$$\begin{aligned} \tilde{f}_{p_3, T_1}^{(N+3)} &= \frac{1}{2} \tilde{r}_{p_3}^{(N+3)} p_3^2 + \frac{1}{2} \tilde{r}_{T_1}^{(N+3)} T_1^2 + \tilde{\alpha}_{p_3, T_1}^{(N+3)} p_3 T_1, \\ \tilde{f}_{p_{1,2}, B_{1,2}, T_{4,5}}^{(N+3)} &= \frac{1}{2} \tilde{r}_{p_{1,2}}^{(N+3)} (p_1^2 + p_2^2) + \frac{1}{2} \tilde{r}_{B_{1,2}}^{(N+3)} (B_1^2 + B_2^2) \\ &\quad + \frac{1}{2} \tilde{r}_{T_{4,5}}^{(N+3)} (T_4^2 + T_5^2) + \tilde{\alpha}_{p_{1,2}, B_{1,2}}^{(N+3)} (p_1 B_1 - p_2 B_2) \\ &\quad + \tilde{\alpha}_{p_{1,2}, T_{4,5}}^{(N+3)} (p_1 T_4 + p_2 T_5) \\ &\quad + \tilde{\alpha}_{B_{1,2}, T_{4,5}}^{(N+3)} (B_1 T_4 - B_2 T_5), \end{aligned}$$

$$\begin{aligned} \tilde{f}_{Q_{3,4}, T_{6,7}}^{(N+3)} &= \frac{1}{2} \tilde{r}_{Q_{3,4}}^{(N+3)} (Q_3^2 + Q_4^2) + \frac{1}{2} \tilde{r}_{T_{6,7}}^{(N+3)} (T_6^2 + T_7^2) \\ &\quad + \tilde{\alpha}_{Q_{3,4}, T_{6,7}}^{(N+3)} (Q_3 T_6 - Q_4 T_7), \end{aligned} \quad (5.43)$$

with the coefficients

$$\tilde{r}_{p_3}^{(N+3)} = \tilde{r}_{p_3}^{(N)},$$

$$\tilde{r}_{T_1}^{(N+3)} = \tilde{r}_{T_1}^{(N)} + (4u_T + \frac{6}{5}v_T) T_2^2,$$

$$\tilde{\alpha}_{p_3, T_1}^{(N+3)} = \tilde{\alpha}_{p_3, T_1}^{(N)},$$

$$\tilde{r}_{p_{1,2}}^{(N+3)} = \tilde{r}_{p_{1,2}}^{(N)},$$

$$\tilde{r}_{B_{1,2}}^{(N+3)} = \tilde{r}_{B_{1,2}}^{(N)} - 2(w_1 + w_2)T_2^2,$$

$$\tilde{r}_{T_{4,5}}^{(N+3)} = \tilde{r}_{T_{4,5}}^{(N)} + (4u_T + \frac{4}{5}v_T)T_2^2,$$

$$\tilde{\alpha}_{p_{1,2}, B_{1,2}}^{(N+3)} = -w_{pQ}T_2,$$

$$\tilde{\alpha}_{p_{1,2}, T_{4,5}}^{(N+3)} = \tilde{\alpha}_{p_{1,2}, T_{4,5}}^{(N)},$$

$$\tilde{\alpha}_{B_{1,2}, T_{4,5}}^{(N+3)} = \frac{2}{\sqrt{15}}w_{QT}T_2 - \frac{4}{3\sqrt{15}}(w_1 + 3w_2 + w_3)ST_2,$$

$$\tilde{r}_{Q_{3,4}}^{(N+3)} = r_Q - w_Q S + \frac{8}{3}u_Q S^2 - \frac{1}{2}w_1 T_2^2,$$

$$\tilde{r}_{T_{6,7}}^{(N+3)} = \tilde{r}_{T_{6,7}}^{(N)} + 4u_T T_2^2,$$

$$\tilde{\alpha}_{Q_{3,4}, T_{6,7}}^{(N+3)} = -\frac{1}{\sqrt{3}}w_{QT}T_2 - \frac{2}{3\sqrt{3}}(6w_1 - w_3)ST_2. \quad (5.44)$$

Transitions out of the  $N+3$  phase are controlled by the set  $\mathcal{S}_{N+3} = \{\Delta_{p_3, T_1}^{(N+3)}, \Delta_{p_{1,2}, B_{1,2}, T_{4,5}}^{(N+3)}, \Delta_{Q_{3,4}, T_{6,7}}^{(N+3)}\}$  of determinants of the harmonic coefficients that can be read off from  $\tilde{f}^{(N+3)}$  above.

### 1. $N+3 \rightarrow V+3$ transition

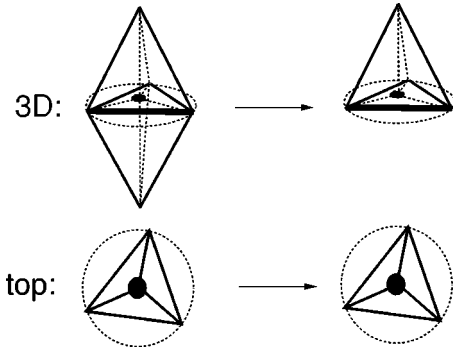


FIG. 23. A schematic representation of the  $N+3 \rightarrow V+3$  transition.

The  $N+3 \rightarrow V+3$  transition occurs when  $\Delta_{p_1, T_3}$  is smallest in the set  $\mathcal{S}_{N+3}$ . In this transition, vector order develops along the nematic  $\mathbf{n}$  axis to produce a linear combination of  $p_3$  and  $T_1$  order, with the latter explicitly induced as a third harmonic of the  $p_3$  order. The discrete,  $\mathcal{Z}_2$ ,  $\mathbf{n} \rightarrow -\mathbf{n}$  symmetry, characterizing the  $N+3$  phase is lost at this transition. Consequently, the  $N+3 \rightarrow V+3$  transition is in the familiar Ising universality class (Fig. 23).

### 2. $N+3 \rightarrow V+2$ ( $=N+1$ ) transition

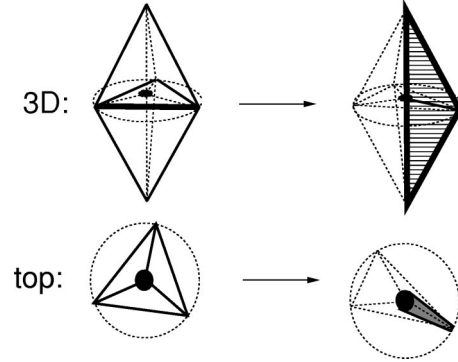


FIG. 24. A schematic representation of the  $N+3 \rightarrow N+1$  transition.

$V+2$  order develops from  $N+3$  order by spontaneously favoring one of the three equivalent directions in the plane perpendicular to  $\mathbf{n}$  and, thereby, converting transverse *triaxial* order of  $N+3$  into transverse *vector* order of  $N+1$ , equivalently described by  $V+2$  (Fig. 24). With  $\mathbf{p}$  chosen to be along  $\mathbf{m}$ , the transverse vector order is signaled by the development of finite  $p_1$  order parameter. As can be seen from  $\tilde{f}_{p_{1,2}, B_{1,2}, T_{4,5}}^{(N+3)}$ , Eq. (5.43), order parameters  $B_1$  and  $T_4$ , associated with  $p_1$  and linearly coupled to it, are also simultaneously induced at the  $N+3 \rightarrow V+2$  transition. For a more generic choice of the orientation of  $\mathbf{m}$ - $\mathbf{l}$  within the plane perpendicular to  $\mathbf{n}$ , the  $V+2$  phase is described by a specific linear combination of  $\vec{p}_{1,2} \equiv (p_1, p_2)$ ,  $\vec{B}_{1,2} \equiv (B_1, B_2)$ , and  $\vec{T}_{4,5} \equiv (T_4, T_5)$ , obtained from the basic set  $\{p_1, B_1, T_4\}$  by a planar rotation about the nematic axis  $\mathbf{n}$ .

The  $N+3 \rightarrow V+2$  transition is the exit of choice out of the  $N+3$  phase, when  $\Delta_{p_{1,2}, B_{1,2}, T_{4,5}}^{(N+3)}$  is the smallest in the  $\mathcal{S}_{N+3}$  set. Since the  $N+3$  phase is characterized by three equivalent directions (in the plane perpendicular to the nematic axis  $\mathbf{n}$ ) along which vector order  $\mathbf{p}$  can develop, we expect this transition to be in the universality class of the three-state Potts model, believed to be weakly first order in three dimensions and continuous in two.

These symmetry based expectations are born out by our detailed computations, which show that the rotational degeneracy in the  $\mathbf{m}$ - $\mathbf{l}$  plane, which is present in the harmonic free energy,  $\tilde{f}_{p_{1,2}, B_{1,2}, T_{4,5}}^{(N+3)}$ , Eq. (5.43) is lifted by energy contributions of the form

$$\delta \tilde{f}_{p_{1,2}, B_{1,2}, T_{4,5}}^{(N+3)} = -\alpha_p \cos 3\phi - \alpha_B \cos 6\phi, \quad (5.45)$$

where  $\phi$  is the angle between the developing transverse vector order parameters  $\vec{p}_{1,2}$  (as well as  $\vec{B}_{1,2}$  and  $\vec{T}_{4,5}$ ) and the  $\mathbf{m}$  axis defined by triaxial order of the  $N+3$  phase,

$$\alpha_p = \left( \frac{1}{2}w_p T p_{1,2}^3 - \frac{4}{5\sqrt{15}}v_T T_{4,5}^3 \right) T_2, \quad (5.46a)$$

$$\alpha_B = w_{Q^3 T^2} B_{1,2}^3 T_2^2, \quad (5.46b)$$

and  $\delta \tilde{f}_{p_{1,2}, B_{1,2}, T_{4,5}}^{(N+3)}$  arises from the following nonlinear couplings:

$$f_{pT} = -w_{pT} p^i p^j p^k T^{ijk}, \quad (5.47a)$$

$$f_{Q^3 T^2} = -w_{Q^3 T^2} Q^{i_1 j_1} Q^{i_2 j_2} Q^{i_3 j_3} T^{i_1 i_2 i_3} T^{j_1 j_2 j_3}, \quad (5.47b)$$

$$f_{T^4} = v_T T^{i_1 i_2 i_3} T^{i_1 i_4 i_5} T^{i_2 i_4 i_6} T^{i_3 i_5 i_6}. \quad (5.47c)$$

The three degenerate minima of the free energy  $\delta \tilde{f}_{p_{1,2}, B_{1,2}, T_{4,5}}^{(N+3)}$ , Eq. (5.45), for the vector order parameter to settle into, correspond precisely to the three equivalent states of the three-state Potts model, supporting our expectation that the  $N+3 \rightarrow V+2$  transition is in the three-state Potts model universality class.

### 3. $N+3 \rightarrow N+V$ transition

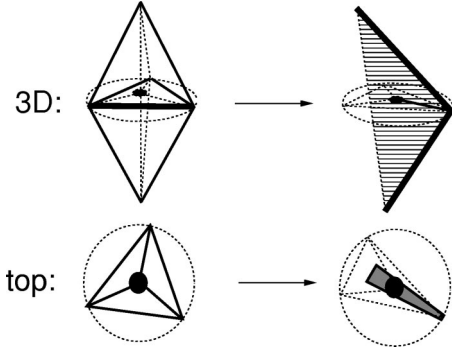


FIG. 25. A schematic representation of the  $N+3 \rightarrow N+V$  transition.

The transition that occurs when  $\tilde{\Delta}_{Q_{3,4}, T_{6,7}}^{(N+3)}$  is the smallest of the set  $\mathcal{S}_{N+3}$  is, as we shall see, to the  $N+V$  phase, but the development of all of the order parameters characterizing this phase is complicated. At the *harmonic* level in  $\tilde{T}_{6,7}$  and  $\tilde{Q}_{3,4}$ ,  $\tilde{f}^{(N+3)}$  possesses a rotational invariance in the plane perpendicular to the nematic axis  $\mathbf{n}$ . However, because the  $N+3$  phase is characterized by threefold order in the  $x$ - $y$  plane perpendicular to  $\mathbf{n}$  (aligned along the  $z$  axis), this continuous symmetry will be reduced to a discrete clock symmetry (Fig. 25).

It is convenient to focus on ordering of  $Q_3$  and  $T_6$ . The established  $N+3$  order can be viewed as an equilateral triangle that favors alignment of  $\mathbf{m}$  towards one of its vertices. Thus one might predict the symmetry of a three-state clock model. However, the apolar (nematic along  $z$  axis) nature of the  $N+3$  state ensures that the free energy  $\tilde{f}^{(N+3)}(Q_3, T_6)$  is invariant under  $\mathbf{n} \rightarrow -\mathbf{n}$ . This, combined with transformation properties of  $Q_3$  and  $T_6$  under  $\mathbf{n} \rightarrow -\mathbf{n}$ , with  $Q_3, T_6 \rightarrow -Q_3, -T_6$  guarantees an additional Ising symmetry of the free energy  $\tilde{f}^{(N+3)}(Q_3, T_6) = \tilde{f}^{(N+3)}(-Q_3, -T_6)$ . This then

leads to a total of six free-energetically degenerate states. Integrating out the  $\tilde{T}_{6,7}$  order parameter and focusing on  $\tilde{Q}_{3,4}$  alone, shows that the six states correspond to alignment of  $\mathbf{m}_Q$  along three vertices and three edge bisectors of the equilateral triangle defined by the  $N+3$  phase. Thus there is a six-state clock symmetry described by a coupling proportional to  $T_2^2 Q_3^6$ , and we expect the  $N+3 \rightarrow N+V$  transition to be in the universality class of the six-state clock model, which apart from irrelevant variables is in the universality class of the  $XY$  model. Once  $Q_3$  and  $T_6$  order is established,  $T_4$ ,  $p_1$ , and  $B_1$  order is driven by couplings of the form  $Q_3^3 B_1$  and others. Thus,  $p_1 \sim B_1 \sim T_4 \sim Q_3^2$ . Then in mean-field theory,  $B_1$  order will drive  $p_3$  and  $T_1$  order via couplings of the form  $B_1 T_6 p_3$ . Thus  $p_3 \sim T_1 \sim T_6^3 \sim Q_3^3$ .

### F. Transitions from the $T$ phase

The tetrahedral  $T$  phase with  $T_d$  symmetry is characterized by a nonvanishing arbitrary linear combination of  $T_6$  and  $T_7$ , which we collectively refer to as  $\tilde{T}_{6,7}$ . In this section, without loss of generality, we will choose the orientation of the  $\mathbf{m}$ - $\mathbf{l}$  axes so that  $T_7$  is the only nonvanishing order parameter in the  $T$  phase. The harmonic free energy density for fluctuations from the  $T$  phase can be expressed as

$$\tilde{f}^{(T)} = \tilde{f}_{Q_1}^{(T)} + \tilde{f}_{Q_2}^{(T)} + \tilde{f}_{p_{1,2,3} Q_{3,4,5}}^{(T)}, \quad (5.48)$$

where

$$\tilde{f}_{Q_1}^{(T)} = \frac{1}{2} \tilde{r}_{Q_1}^{(T)} Q_1^2,$$

$$\tilde{f}_{Q_2}^{(T)} = \frac{1}{2} \tilde{r}_{Q_2}^{(T)} Q_2^2, \quad (5.49)$$

$$\begin{aligned} \tilde{f}_{p_{1,2,3} Q_{3,4,5}}^{(T)} &= \frac{1}{2} \tilde{r}_{Q_{3,4,5}}^{(T)} (Q_3^2 + Q_4^2 + Q_5^2) + \frac{1}{2} r_p (p_1^2 + p_2^2 + p_3^2) \\ &\quad - \frac{1}{\sqrt{3}} w_{pQT} T_7 (p_1 Q_4 + p_2 Q_3 + p_3 Q_5) \end{aligned}$$

with the coefficients given by

$$\tilde{r}_{Q_1}^{(T)} = r_Q - \frac{1}{3} (2w_1 - w_3) T_7^2, \quad (5.50a)$$

$$\tilde{r}_{Q_2}^{(T)} = r_Q - \frac{1}{3} (2w_1 - w_3) T_7^2, \quad (5.50b)$$

$$\tilde{r}_{Q_{3,4,5}}^{(T)} = r_Q - \frac{1}{3} (2w_1 + 2w_2 + w_3) T_7^2. \quad (5.50c)$$

The structure of  $\tilde{f}^{(T)}$  implies that there are three symmetry-lowering transitions from the  $T$  phase, driven, respectively, by fluctuations in  $Q_1$ ,  $Q_2$ , and a linear combination of pairs  $p_1$  and  $Q_4$ ,  $p_2$  and  $Q_3$ , and  $p_3$  and  $Q_5$ . Which of these transitions occurs is determined by the set  $\mathcal{S}_T = \{\tilde{r}_{Q_1}^{(T)}, \tilde{r}_{Q_2}^{(T)}, \Delta_{p_{1,2,3} Q_{3,4,5}}^{(T)}\}$ .

In the presence of  $T_7$  order, all of the  $p_\mu^i$  and  $Q_\mu^{ij}$  order parameters exhibit third-order invariants. Since they play an important role in determining the nature of transitions from the  $T$  phase, we display them here,

$$f_{Q^3} = w_Q \left[ \sqrt{\frac{3}{2}} Q_1 (Q_2^2 + Q_3^2) - \frac{\sqrt{3}}{2\sqrt{2}} Q_1 (Q_3^2 + Q_4^2) - \frac{3}{2\sqrt{2}} Q_2 (Q_3^2 - Q_4^2) - \frac{1}{\sqrt{6}} Q_1^3 - \frac{3}{\sqrt{2}} Q_3 Q_4 Q_5 \right],$$

$$f_{p^3 T} = -\sqrt{6} w_{pT} T_7 p_1 p_2 p_3. \quad (5.51)$$

We note the appearance of the  $Q_3 Q_4 Q_5$  term in  $f_{Q^3}$ , which can be paired with the  $p_1 p_2 p_3$  product in  $f_{p^3 T}$ . There are of course also third-order terms in  $Q$ , whose coefficients are proportional to powers of  $T_7$ , which, for small  $T_7$ , are subdominant to  $w_Q$  term that we displayed above. Because these higher order terms do not qualitatively change our results, with their effects accounted for by an effective  $w_Q$  coupling, we will not consider them here.

### 1. $T \rightarrow N_T$ transition

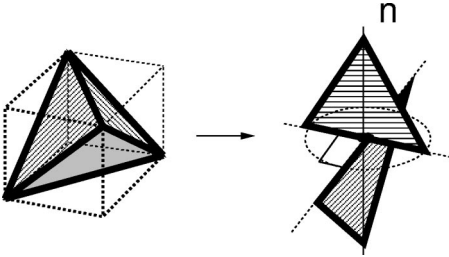


FIG. 26. A schematic representation of the  $T \rightarrow N_T$  transition.

As illustrated in Fig. 7, one of the three possible symmetry-reducing transitions out of the tetrahedral  $T$  phase is the  $T \rightarrow N_T$  phase transition. The  $N_T$  order develops by favoring one of the three twofold axes of the tetrahedron through the growth of uniaxial  $Q^{ij}$  order along that axis as shown in Figs. 4, 5, and 26. In our parametrization, we focus on the twofold axes defined by  $\pm \mathbf{n}$ . In this case, the  $T \rightarrow N_T$  transition is signaled by the development of  $Q_1$  (or equivalently  $S$ ) order. Because of the existence of the third-order  $Q_1^3$  invariant, Eq. (5.51), this transition is generically first order. It occurs in mean-field theory when  $\tilde{r}_{Q_1}^{(T)}(T_7) = \tilde{w}_Q^2(T_7)/12\tilde{u}_Q(T_7)$ , where the third- and fourth-order couplings  $\tilde{w}_Q(T_7)$  and  $\tilde{u}_Q(T_7)$  can in principle depend on strength of the  $T$  order, characterized by  $T_7$  order parameter. Because no other order parameter is explicitly induced at this transition, and with the convenient choice of the  $\mathbf{m}$ - $\mathbf{l}$  axes (that we have made here) the resulting  $N_T$  phase is fully characterized by the  $T_7$  and  $S$  order parameters.

### 2. $T \rightarrow (N_T+2)^*$ transition

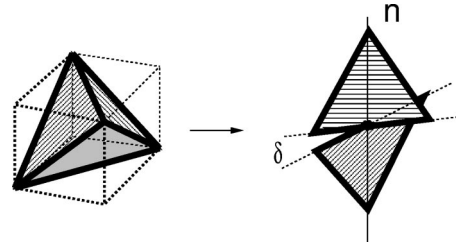


FIG. 27. A schematic representation of the  $T \rightarrow (N_T+2)^*$  transition.

If, for a  $T$  phase characterized by the  $T_7$  order parameter,  $Q_2$  (or equivalently  $B_1$ ) orders before  $Q_1$  or the  $p_1 - Q_3$  combination, the transition from the  $T$  phase is to the spontaneously chiral  $(N_T+2)^*$  phase (Fig. 27). If we focus on the  $\mathbf{m}$ - $\mathbf{l}$  plane,  $T_7$  order displays biaxiality ( $m^i l^j + m^j l^i$ ), with principal axes at  $\pi/4$  relative to the biaxiality of the  $B_1$  order characterized by ( $m^i m^j - l^i l^j$ ). Since  $T_7$  and  $B_1$  are different order parameters, a simple rotation to define a new biaxial axis is impossible, and the result is that the reflection invariance in the  $\mathbf{m}$ - $\mathbf{l}$  plane is spontaneously lost as  $B_1$  develops. The lack of reflection symmetry is the characteristic feature of the chiral  $(N_T+2)^*$  phase, discussed in Sec. V D 2. In analogy to the development of biaxial order from the isotropic phase, once  $B_1$  orders, the  $Q_1 Q_2^2$  coupling in  $f_{Q^3}$  drives the development of  $S$  (or  $Q_1$ ) order. Thus, the  $(N_T+2)^*$  phase has nonvanishing  $S$ ,  $B_1$ , and  $T_7$  (or equivalently  $S$ ,  $B_2$ , and  $T_6$ ) order. Although the  $T \rightarrow (N_T+2)^*$  transition is continuous within mean-field theory, based on the experience with the development of uniaxial and biaxial orders from the isotropic phase, we expect that here too, the  $T \rightarrow N_T$  transition will always preempt the  $T \rightarrow (N_T+2)^*$  transition.

Within second-order mean-field theory,  $B_1 \sim |\Delta T|^{1/2}$ ,  $S \sim B_1^2 \sim |\Delta T|$ , and  $\Xi_{ijk} \sim T_7 B_1 S \sim |\Delta T|^{3/2}$ . Since the  $T$  phase has elastic energies resisting spatial variations of the  $\mathbf{n}$ ,  $\mathbf{m}$ , and  $\mathbf{l}$  directions, the wave number of the cholesteric structure of the cholesteric  $(N_T+2)^*$  phase will scale as  $q_0 \sim |\Delta T|^{3/2}$  in mean-field theory.

### 3. $T \rightarrow V+3$ transition

The ordering of linear combinations of  $(p_1, Q_4)$ ,  $(p_2, Q_3)$ , and  $(p_3, Q_5)$ , which we will refer to as  $p$ - $Q$  ordering, leads to the  $V+3$  phase (Fig. 28). This can be seen by observing that the third order potential  $f_{p^3 T}$  in Eq. (5.51) favors  $p_1 = \pm p_2 = \pm p_3$  with relative signs determined by the sign of  $w_{pT} T_7$ . Examination of Eq. (5.51) shows that similar considerations apply to  $Q_3$ ,  $Q_4$ , and  $Q_5$ . Thus, the vector  $\mathbf{p}$

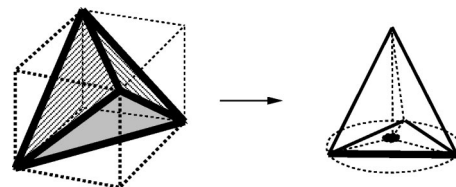


FIG. 28. A schematic representation of the  $T \rightarrow V+3$  transition.

will align along the (1,1,1) or a symmetry equivalent axes, i.e., along a threefold axis of the tetrahedron characterizing the  $T$  phase. Thus, to discuss the phase transition signaled by the onset of  $p$ - $Q$  order, it is useful to transform to a new coordinate system with  $\mathbf{n}'$  along the (1,1,1) axis, which is most easily achieved by a rotation about the (1, -1, 0) axis. Under this rotation we find that our basis transforms according to

$$\mathbf{m} = \frac{1}{2} \left( 1 + \frac{1}{\sqrt{3}} \right) \mathbf{m}' - \frac{1}{2} \left( 1 - \frac{1}{\sqrt{3}} \right) \mathbf{l}' - \frac{1}{\sqrt{3}} \mathbf{n}', \quad (5.52a)$$

$$\mathbf{l} = -\frac{1}{2} \left( 1 - \frac{1}{\sqrt{3}} \right) \mathbf{m}' + \frac{1}{2} \left( 1 + \frac{1}{\sqrt{3}} \right) \mathbf{l}' - \frac{1}{\sqrt{3}} \mathbf{n}', \quad (5.52b)$$

$$\mathbf{n} = \frac{1}{\sqrt{3}} (\mathbf{m}' + \mathbf{l}' + \mathbf{n}'). \quad (5.52c)$$

Straightforward algebraic manipulations then yield

$$I_7^{ijk} = \frac{\sqrt{5}}{3} I_1^{ijk} - \frac{\sqrt{2}}{3} (I_2^{ijk} + I_3^{ijk}), \quad (5.53)$$

so that in the rotated coordinate system,

$$T_1' = \frac{\sqrt{5}}{3} T_7, \quad (5.54a)$$

$$T_2' = -\frac{\sqrt{2}}{3} T_7, \quad (5.54b)$$

$$T_3' = -\frac{\sqrt{2}}{3} T_7. \quad (5.54c)$$

In this rotated basis the polar order is described by  $\mathbf{p} = p_3' \mathbf{n}'$ , also inducing the nematic order  $S'$  through the  $f_{pQ}$  coupling. Thus, the phase produced by such  $p$ - $Q$  ordering from the  $T$  phase has nonvanishing  $p_3'$ ,  $S'$ ,  $T_1'$ ,  $T_2'$ , and  $T_3'$  order, which describes polar order along the  $\mathbf{n}'$  axis and triaxial order in the  $\mathbf{m}'$ - $\mathbf{l}'$  plane perpendicular to it; a rotation by  $\pi/12$  about the (1,1,1) axis can be used to remove  $T_3'$  component of the triaxial order. Thus, the phase produced by  $p$ - $Q$  ordering inside the tetrahedral  $T$  phase is indeed the previously discussed  $V+3$  phase.

### G. Transitions from the $N_T$ phase

The  $N_T$  phase is characterized by nonvanishing nematic order parameter,  $S$ , and an arbitrary linear combination of the tetrahedral order parameters,  $T_6$  and  $T_7$ , which we collectively call  $\vec{T}_{6,7}$ . These define the directions of the orthonormal triad  $(\mathbf{m}, \mathbf{l}, \mathbf{n})$ , which we can for convenience always pick to have  $T_6$  vanish, with the tetrahedral order completely characterized by the value of  $T_7$ .

The free energy  $\tilde{f}^{(N_T)}$  describing *harmonic* fluctuations in the  $N_T$  phase can be expressed as a sum of three independent parts,

$$\tilde{f}^{(N_T)} = \tilde{f}_{B_1}^{(N_T)} + \tilde{f}_{p_3, B_2, T_1}^{(N_T)} + \tilde{f}_{p_{1,2}, Q_{3,4}, T_{2,3}, T_{4,5}}^{(N_T)}, \quad (5.55)$$

where

$$\tilde{f}_{B_1}^{(N_T)} = \frac{1}{2} \tilde{r}_{B_1}^{(N_T)} B_1^2,$$

$$\begin{aligned} \tilde{f}_{p_3, T_1, B_2}^{(N_T)} &= \frac{1}{2} \tilde{r}_{p_3}^{(N)} p_3^2 + \frac{1}{2} \tilde{r}_{B_2}^{(N_T)} B_2^2 + \frac{1}{2} \tilde{r}_{T_1}^{(N_T)} T_1^2 \\ &\quad + \tilde{\alpha}_{p_3, B_2}^{(N_T)} p_3 B_2 + \tilde{\alpha}_{p_1, T_3}^{(N)} p_3 T_1 + \tilde{\alpha}_{B_2, T_1}^{(N_T)} B_2 T_1, \end{aligned}$$

$$\begin{aligned} \tilde{f}_{p_{1,2}, Q_{3,4}, T_{2,3}, T_{4,5}}^{(N_T)} &= \frac{1}{2} \tilde{r}_{p_{1,2}}^{(N)} (p_1^2 + p_2^2) + \frac{1}{2} \tilde{r}_{Q_{3,4}}^{(N_T)} (Q_3^2 + Q_4^2) \\ &\quad + \frac{1}{2} \tilde{r}_{T_{2,3}}^{(N_T)} (T_2^2 + T_3^2) + \frac{1}{2} \tilde{r}_{T_{4,5}}^{(N_T)} (T_4^2 + T_5^2) \\ &\quad + \tilde{\alpha}_{p_{1,2}, Q_{3,4}}^{(N_T)} (p_1 Q_4 + p_2 Q_3) \\ &\quad + \tilde{\alpha}_{p_{1,2}, T_{4,5}}^{(N)} (p_1 T_4 + p_2 T_5) \\ &\quad + \tilde{\alpha}_{B_2', T_1'}^{(N_T)} \left[ Q_3 \left( \frac{1}{\sqrt{3}} T_3 - \frac{1}{\sqrt{5}} T_5 \right) \right. \\ &\quad \left. + Q_4 \left( \frac{1}{\sqrt{3}} T_2 - \frac{1}{\sqrt{5}} T_4 \right) \right], \\ &\quad + \tilde{\alpha}_{Q_{3,4}, T_{4,5}}^{(N_T)} (Q_3 T_5 + Q_4 T_4) \\ &\quad + \tilde{\alpha}_{T_{2,3}, T_{4,5}}^{(N_T)} (T_2 T_4 + T_3 T_5), \end{aligned} \quad (5.56)$$

with

$$\tilde{r}_{B_1}^{(N_T)} = \tilde{r}_{B_{1,2}}^{(N)} - \frac{2}{3} (2w_1 - w_3) T_7^2,$$

$$\tilde{r}_{B_2}^{(N_T)} = \tilde{r}_{B_{1,2}}^{(N)} - \frac{2}{3} (2w_1 + 2w_2 + w_3) T_7^2,$$

$$\tilde{r}_{T_1}^{(N_T)} = \tilde{r}_{T_1}^{(N)} + (4u_T - \frac{2}{5}v_T) T_7^2,$$

$$\tilde{\alpha}_{p_3, B_2}^{(N_T)} = -\sqrt{\frac{2}{3}} w_{pQT} T_7,$$

$$\tilde{\alpha}_{B_2, T_1}^{(N_T)} = \frac{4}{\sqrt{15}} w_{QT} T_7 - \frac{4}{3\sqrt{15}} (2w_1 + 3w_2 - w_3) S T_7,$$

$$\tilde{r}_{Q_{3,4}}^{(N_T)} = 2r_Q + \frac{8}{3} u_Q S^2 - \frac{1}{3} (2w_1 + 2w_2 + w_3) T_7^2,$$

$$\tilde{r}_{T_{2,3}}^{(N_T)} = \tilde{r}_{T_{2,3}}^{(N)} + 4u_T T_7^2,$$

$$\tilde{r}_{T_{4,5}}^{(N_T)} = \tilde{r}_{T_{4,5}}^{(N)} + (4u_T + \frac{4}{15}v_T) T_7^2,$$

$$\begin{aligned}
\tilde{\alpha}_{p_{1,2}, Q_{3,4}}^{(N_T)} &= -\frac{1}{\sqrt{3}} w_{pQT} T_7, \\
\tilde{\alpha}_{B'_2, T'_1}^{(N_T)} &= w_{QT} T_7 + \frac{1}{3} (w_1 - 2w_3) S T_7, \\
\tilde{\alpha}_{Q_{3,4}, T_{4,5}}^{(N_T)} &= -\frac{4}{3\sqrt{5}} w_2 S T_7, \\
\tilde{\alpha}_{T_{2,3}, T_{4,5}}^{(N_T)} &= \frac{2}{\sqrt{15}} v_T T_7^2.
\end{aligned} \tag{5.57}$$

As can be seen from the structure of  $\tilde{f}^{(N_T)}$  above, there are three possible symmetry-reducing transitions that can take place out of the  $N_T$  phase. In contrast to the nematic phase with  $D_{\infty h}$  symmetry in which fluctuations in the biaxial fields  $B_1$  and  $B_2$  are degenerate, the  $N_T$  phase with nonvanishing  $\vec{T}_{6,7}$  order breaks the degeneracy of fluctuations in  $B_1$  and  $B_2$ . For our choice of  $\mathbf{m}$ -I axes, with  $T_6=0$ , the tetrahedric order parameter  $T_7$  couples the biaxial order parameter  $B_2$  to the vector order along  $\mathbf{n}$ , described by  $p_3$  and its third harmonic  $T_1$ . Hence two (of the three) transitions are the ordering of  $B_1$ , and the ordering of a linear combination of  $p_3$ ,  $B_2$ , and  $T_1$ . A third possible transition out of the  $N_T$  phase is the development of vector order *transverse* to nematic axis  $\mathbf{n}$  described by an arbitrary linear combination of  $p_1$  and  $p_2$ . In the  $N_T$  phase with nonzero  $T_7$ , harmonic fluctuations in  $p_1$  are coupled to those of  $Q_4$  and  $T_4$ , and harmonic fluctuations in  $p_2$  are coupled to those of  $Q_3$  and  $T_5$ . As a result, the development of transverse vector order from the  $N_T$  phase is accompanied by a specific linear combination of these higher-order order parameters.

Which of these three transitions takes place first is determined by minimum determinant in the set  $\mathcal{S}_{N_T} = \{\Delta_{B_1}, \Delta_{p_3, B_2, T_1}^{(N_T)}, \Delta_{p_{1,2}, Q_{3,4}, T_{2,3}, T_{4,5}}^{(N_T)}\}$  of determinants of the harmonic coefficients, that can be read off from  $\tilde{f}^{(N_T)}$  above.

### 1. $N_T \rightarrow (N_T+2)^*$ transition

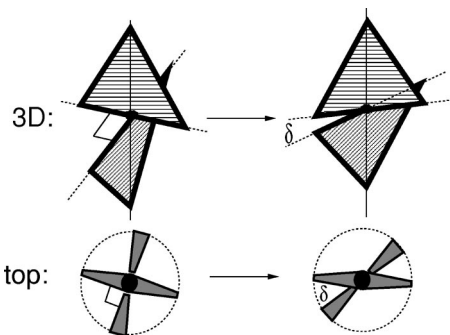


FIG. 29. A schematic representation of the  $N_T \rightarrow (N_T+2)^*$  transition.

Development of biaxial order,  $B_1$ , in the presence of  $T_7$  (with  $T_6=0$ ) and  $S$  order is quite similar to the development of  $T_7$  order in the presence of  $B_1$  order, discussed in Sec. VD 2, and corresponds to spontaneous chiral symmetry breaking of the  $N_T \rightarrow (N_T+2)^*$  transition (Fig. 29). As can be seen from the structure of  $\tilde{f}^{(N_T)}$ , no other order parameters are induced at this transition and, as discussed above, the resulting  $(N_T+2)^*$  phase is characterized by nonzero  $S$ ,  $B_1$ , and  $T_7$  order parameters. Because it is the underlying  $B_1 \rightarrow -B_1$ ,  $Z_2$  symmetry of the  $N_T$  phase, that is broken when  $B_1$  orders, the  $N_T \rightarrow (N_T+2)^*$  transition is in the Ising universality class if the linear gradient coupling proportional to  $\Xi_{ijk}$  is ignored. The latter term, aside from potentially modifying the critical properties of this transition, leads to a pitch wave number in the cholesteric  $(N_T+2)^*$  phase that scales in mean-field theory as  $q_0 \sim B_1 \sim |\Delta T|^{1/2}$  just below the  $N_T \rightarrow (N_T+2)^*$  transition.

### 2. $N_T \rightarrow V+2$ transition

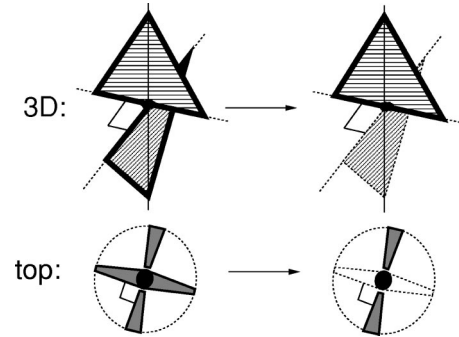


FIG. 30. A schematic representation of the  $N_T \rightarrow V+2$  transition.

The  $N_T \rightarrow V+2$  transition takes place via the development of vector order  $\mathbf{p} = p_3 \mathbf{n}$  along the nematically ordered  $\mathbf{n}$  axis. Since in the presence of  $T_7$  and  $S$  such longitudinal vector order is coupled to  $B_2$  and  $T_1$ , the  $N_T \rightarrow V+2$  is also accompanied by the development of  $B_2$  and the  $T_1$  order parameter. Because the free energy of the  $N_T$  phase is invariant under  $\mathbf{n} \rightarrow -\mathbf{n}$ , the development of  $p_3$  longitudinal order can be of either sign and the transition is in the Ising universality class (Fig. 30).

### 3. $N_T \rightarrow N+V$ transition

A third possible transition out of the  $N_T$  phase takes place when *transverse* vector order  $\vec{p}_{1,2}$  develops. As can be seen from the form of  $\tilde{f}^{(N_T)}$ , the development of  $\vec{p}_{1,2}$  is accompanied by biaxial order  $\vec{Q}_{3,4}$  and a linear combination of  $\vec{T}_{2,3}$  and  $\vec{T}_{4,5}$  order parameters. The resulting phase has a  $C_{1h}$  symmetry, and we therefore identify it with the previously discussed  $N+V$  phase. At the harmonic level, the free energy appears to be  $O(2)$  invariant, with respect to rotation of  $\vec{p}_{1,2}$ . However, in the presence of  $T_7$ , nonlinearities in  $\vec{p}_{1,2}$ , break this rotational invariance. A lowest order such symmetry breaking nonlinearity is given by

$$f_{\text{symm. breaking}}^{N_T} = Q^{i_1, i_2} T^{j_1, j_2} p^{k_1} p^{k_2} p^{j_1} p^{j_2} p^{k_2},$$

$$= \frac{4}{9} S T_7^2 p_1^2 p_2^2. \quad (5.58)$$

It introduces into the  $O(2)$  symmetry harmonic free energy of  $\vec{p}_{1,2}$  a well-studied cubic symmetry breaking anisotropy. Based on these studies [32], we therefore expect the  $N_T \rightarrow N+V$  transition to be driven first order by thermal fluctuations [33].

**H. Transitions from the  $V+2$  phase**

As can be seen from the flow-chart, Fig. 7, the biaxial vector  $V+2$  phase, characterized, for example, by finite  $p_3, S, B_1, T_1, T_6$  order parameters and by  $C_{2v}$  symmetry, can further lower its symmetry in two ways. It can undergo a transition to the  $N+V$  phase via the development of polar order, characterized by  $\vec{p}_{1,2}, \vec{Q}_{3,4},$  and  $\vec{T}_{4,5}$  order parameters along one of the biaxial axis perpendicular to the  $V(p_3)$  order. Alternatively, it can undergo a transition to the  $(V_T+2)^*$  phase via the development of  $T_7$  order. Both the  $V+2 \rightarrow N+V$  and the  $V+2 \rightarrow (V_T+2)^*$  are expected to be in the Ising universality class because in both cases it is  $\mathcal{Z}_2$  symmetry that is being broken.

**I.  $V+3 \rightarrow N+V$  transition**

The threefold symmetry in the plane transverse to the vector ( $p_3$ ) axis of the  $V+3$  phase can be spontaneously broken with, e.g., biaxial order in this plane driving the transition and other parameters (listed in Table I) also condensing. We therefore expect the  $V+3 \rightarrow N+V$  transition to be in the three-state Potts model universality class.

**J.  $(N_T+2)^* \rightarrow (V_T+2)^*$  transition**

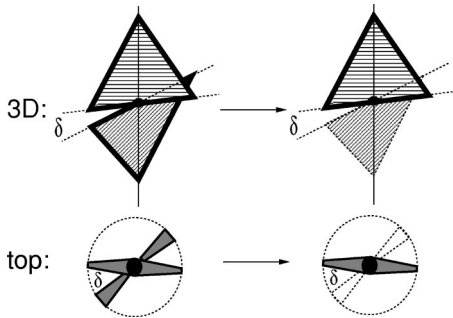


FIG. 31. A schematic representation of the  $(N_T+2)^* \rightarrow (V_T+2)^*$  transition.

The final transition that we will comment on is polar ordering transition from the nonpolar  $N_T+2^*$  phase. Because of the present nematic order in  $N_T+2^*$  state, polar order breaks  $\mathcal{Z}_2$  symmetry and we expect  $(N_T+2)^* \rightarrow (V_T+2)^*$  transition to be in the Ising universality class (Fig. 31).

**VI. NEW SMECTIC PHASES**

Our primary interest in this paper has been in fluid (spatially homogeneous) but anisotropic liquid-crystalline phases of bent-core molecules, particularly in phases with exotic symmetries not encountered in systems of rodlike or plate-like mesogens. Our work, however, suggests the possibility of smectic or layered analogs of these exotic fluid phases. In these putative phases, which we will explore in more detail in a separate publication [17] the smectic layer normal  $\mathbf{N}$  provides an additional direction that may or may not coincide with a symmetry direction of the fluid phase. Most of the banana-shaped smectic phases classified to date are based upon  $V+2$  order embedded in smectic layers either in identical configurations (as in the  $\text{Sm } C_S P_F$  phase in the notation [4] of Ref. [3]) in neighboring layers or in alternating configurations (as in the  $\text{Sm } C_A P_A$  phase) in neighboring layers. Each layer is then characterized by the molecular directions  $\mathbf{n}, \mathbf{m},$  and  $\mathbf{l}$  and by  $\mathbf{N}$ . Though the  $V+2$  fluid phase is not chiral, each layer of smectic phases derived from it can be chiral if, for example,  $\mathbf{m}$  lies in the smectic layer and  $\mathbf{n}$  is tilted relative to  $\mathbf{N}$  as is the case in the globally chiral  $\text{Sm } C_A P_A$  and  $\text{Sm } C_S P_F$  phases, and in the  $\text{Sm } C_S P_A$  and  $\text{Sm } C_A P_F$  phases where chirality alternates in adjacent layers [4].

New types of smectics can arise from layering of  $N_T, (N_T+2)^*,$  and  $(V_T+2)^*$  fluid phases. In the simplest of

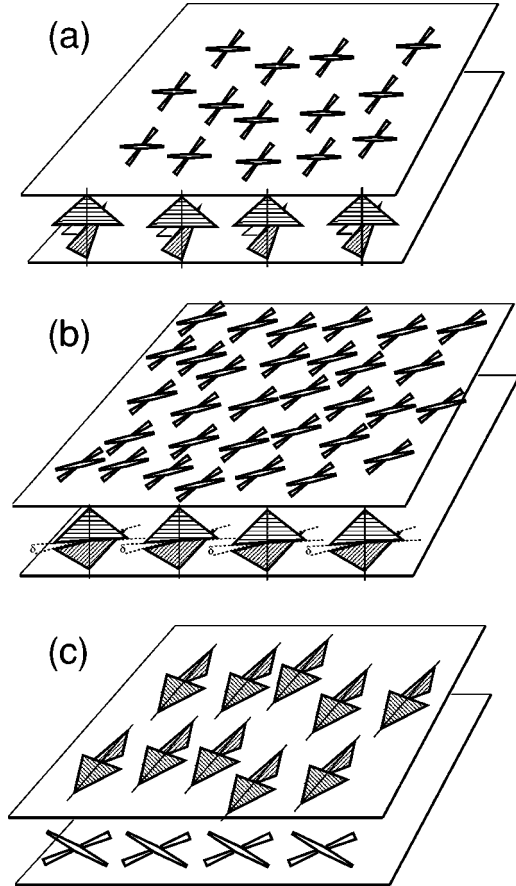


FIG. 32. A schematic representation of smectic phases (a)  $\text{Sm } A_{N_T},$  (b)  $\text{Sm } A_{||}^*(N_T+2),$  (c)  $\text{Sm } A_{\perp}^*(N_T+2).$



these phases, which we label  $\text{Sm}A_{N_T}$  and depict in Fig. 32(a), each layer has  $N_T$  symmetry with  $\mathbf{n}$  parallel to  $\mathbf{N}$  and  $\mathbf{m}$  along a common direction in each layer. This phase has  $D_{2d}$  point group symmetry. Many variants of it are imaginable. For example, the  $\mathbf{m}$  axis could rotate by  $\pi/2$  from layer to layer, or the  $\mathbf{n}$  axis could tilt relative to  $\mathbf{N}$  to produce a  $\text{Sm}C^*(N_T)$  phase, which like the  $\text{Sm}C^*$  phase would be chiral. Layered phases formed from the  $(N_T+2)^*$  fluid phase are chiral. In one such phase, the  $\text{Sm}A_{\parallel}^*(N_T+2)$  phase, a layer of which is depicted in Fig. 32(b), the  $\mathbf{n}$  axis is parallel to  $\mathbf{N}$ , and the biaxial  $\mathbf{m}$  axis rotates from layer to layer like the  $\mathbf{c}$  director in the  $\text{Sm}C^*$  phase. If the pitch of the twist structure is very long, this phase would appear to be a biaxial smectic. The recently identified biaxial  $\text{Sm}A$  phase [37] in mixtures of banana-shaped and rodlike mesogens may correspond to the very long-pitch  $\text{Sm}A_{\parallel}^*(N_T+2)$  phase. An alternative version of a smectic  $(N_T+2)^*$  phase, the  $\text{Sm}A_{\perp}^*(N_T+2)$  phase has  $\mathbf{n}$  in the plane of the layers as depicted for a single layer in Fig. 32(c). Since this phase is chiral,  $\mathbf{n}$  will rotate in a helical fashion from layer to layer. A more complex  $(N_T+2)$  smectic-C like phase, with  $\mathbf{n}$  making an angle other than 0 or  $\pi/2$  with respect to  $\mathbf{N}$  is also possible.

## VII. SUMMARY AND CONCLUSIONS

In this paper, we have presented a comprehensive study of liquid phases of achiral bent-core liquid-crystal molecules. Using symmetry we enumerated all possible orientationally-ordered liquid phases, classified them by subgroups of the rotation group  $O(3)$  under which they are invariant, and constructed Landau mean-field theory describing these phases and transitions between them. One primary conclusion of our work is that in addition to the vector ( $p^i$ ) and second-rank nematic ( $Q^{ij}$ ) order parameters, a third-rank tensor order parameter  $T^{ijk}$ , representing third-mass moment, is necessary to characterize the liquid-crystal phases of banana-shaped molecules, such as, for example, the  $N_T$  phase with  $D_{2d}$  symmetry, the tetrahedric  $T$  phase, and the spontaneously chiral nematic  $(N_T+2)^*$  and its chiral polar analog  $(V_T+2)^*$ . In these phases the chiral symmetry is spontaneously broken by “condensation” of the biaxial  $\vec{B}_{1,2}$  and tetrahedric  $\vec{T}_{6,7}$  order parameters with a nonvanishing angle  $0 < \delta < \pi/2$  between their respective principal axes  $\mathbf{m}$ - $\mathbf{l}$  [see Fig. 6(b)].

The  $N_T$  phase is neither uniaxial nor biaxial but instead exhibits an invariance with respect to a fourfold improper rotation consisting of a rotation through  $\pi/2$  about the  $z$ -axis followed by a reflection  $z \rightarrow -z$ . The  $T$  phase is invariant under the  $T_d$  symmetry group of a tetrahedron. Like the isotropic phase, its second-rank dielectric tensor is isotropic, making it optically isotropic, but unlike the isotropic phase, it has a nonvanishing second-order nonlinear susceptibility  $\chi_{ijk}^{(2)} \sim T^{ijk}$  such that there is a second-order contribution to the polarization  $P_i^{(2)} = \chi_{ijk}^{(2)} E_j E_k$  where  $E_i$  is the electric field.

The chiral nematic  $(N_T+2)^*$  phase, like the traditional chiral cholesteric and blue phases, will exhibit periodic spatial modulations of the direction of molecular alignment. Un-

like the transition from the isotropic to the cholesteric phase, the transitions to the  $(N_T+2)^*$  phase (from the biaxial  $N+2$  phase, the tetrahedric  $T$  phase, and the  $N_T$  phase with  $D_{2d}$  symmetry) are second order, at least in mean-field theory. The pitch of the cholesteric structure of the  $(N_T+2)^*$  phase diverges as these second-order transitions are approached and thus changes rapidly with temperature. Since the  $(N_T+2)^*$  phase spontaneously breaks chiral symmetry, the state initially formed upon cooling from the higher-symmetry phase will consist of domains of opposite chirality separated by domain wall that will coarsen over time. Chiral dopants (or distortions of bent-core mesogens to make them chiral) render all phases chiral and, in particular, induce a cholesteric pitch of a particular sign on the chiral extensions  $(N+2)^*$ ,  $T^*$ , and  $N_T^*$ , of the  $(N+2)$ ,  $T$ , and  $N_T$  phases. Thus chiral dopants act like an external field in an Ising ferromagnet, favoring a particular sign of chirality (rather than a particular sign of spin), and the transitions from the  $(N+2)^*$ ,  $T^*$ , and  $N_T^*$  phases to the  $(N_T+2)^*$  phase will be analogous to the Ising transition in an external magnetic field. In principle, for sufficiently large chirality, blue phases, with two orthogonal twist axes can also appear in  $(N_T+2)^*$ . In addition to these properties of the nonpolar  $(N_T+2)^*$  phase, the chiral *polar*  $(V_T+2)^*$  phase will exhibit spontaneous ferroelectricity, a liquid state that has been a holy grail in liquid-crystal research dating back to Louis Pasteur. Light scattering, circular dichroism, and switching with a weak electric field would be natural experimental probes for these spontaneously chiral states.

These chiral phases are particularly interesting because their smectic analogs, the chiral  $\text{Sm}C_A P_A$ ,  $\text{Sm}C_S P_A$ ,  $\text{Sm}C_A P_F$ , and  $\text{Sm}C_S P_F$  (the four  $B_2$  phases) [3,4,7] have been realized in banana-shaped liquid-crystal molecules, generating significant excitement in the ferroelectric liquid-crystal community. Our work suggests that smectic positional order is not necessary and that spatially homogeneous spontaneously chiral liquid-crystal phases are generically possible.

Although, most [16] experimental systems of banana-shaped molecules studied so far, appear to undergo direct first-order transitions into smectic phases, our work suggests that this situation does not have to be the case, and a rich phase structure and hierarchy of continuous transitions studied here is possible. We hope that the results presented here will stimulate searches in experiments and simulations for banana-shaped materials that exhibit orientationally-ordered liquid phases predicted here.

## ACKNOWLEDGMENTS

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- [1] R. B. Meyer, L. Liébert, L. Strzelecki, and P. Keller, *J. Phys. (France) Lett.* **36**, 69 (1975).
- [2] T. Niori, T. Sekine, J. Watanabe, T. Furukawa, and H. Takezoe, *J. Mater. Chem.* **6**, 1231 (1996).
- [3] D. R. Link, G. Natale, R. Shao, J. E. Maclennan, N. A. Clark, E. Korblova, and D. M. Walba, *Science* **278**, 1924 (1997).
- [4] In a more faithful nomenclature put forth by Link *et al.* in Ref. [3], the so-called  $B_2$  phase actually refers to four different smectic- $C$  phases  $\text{Sm } C_i P_j$  of banana-shaped molecules. These are distinguished by the values of the  $i, j$  labels. The  $i$  label is either  $S$  for synclinic or  $A$  for anticlinic indicating, respectively, that molecules in neighboring layers tilt in the same or opposite directions. The  $j$  label is either  $F$  for ferro or  $A$  for antiferro indicating, respectively, that dipoles in neighboring layers are either parallel or antiparallel. The corresponding four phases are: the interlayer synclinic (same tilt from layer to layer) and ferroelectric  $\text{Sm } C_S P_F$  (homochiral) phase, the interlayer anticlinic and ferroelectric  $\text{Sm } C_A P_F$  phase, the interlayer synclinic and antiferroelectric  $\text{Sm } C_S P_A$  phase, and the interlayer anticlinic and antiferroelectric  $\text{Sm } C_A P_A$  phase, all of which have now been observed.
- [5] G. Pelzl, S. Diele, and W. Weissflog, *Adv. Mater.* **11**, 707 (1999).
- [6] J. P. Bedel, J. C. Rouillon, J. P. Marcerou, M. Laguerre, H. T. Nguyen, and M. F. Achard, *Liq. Cryst.* **28**, 1285 (2001).
- [7] D. M. Walba, E. Korblova, R. Shao, J. E. Maclennan, D. R. Link, M. A. Glaser, and N. A. Clark, *Science* **288**, 2181 (2000).
- [8] Technical University of Berlin Report No. Afb 335, 1997 (unpublished).
- [9] H. R. Brand, P. E. Cladis, and H. Pleiner, *Eur. Phys. J. B* **6**, 347 (1998).
- [10] A. Roy, N. V. Madhusudana, P. Toledano, and A. M. Figueiredo Neto, *Phys. Rev. Lett.* **82**, 1466 (1999).
- [11] M. P. Neal, A. P. Parker, and C. M. Care, *Mol. Phys.* **91**, 603 (1997).
- [12] P. J. Camp, M. P. Allen, and A. J. Masters, *J. Chem. Phys.* **111**, 9871 (1999).
- [13] J. L. Billeter and R. A. Pelcovits, *Liq. Cryst.* **27**, 1151 (2000).
- [14] R. Memmer, *Liq. Cryst.* **29**, 483 (2002).
- [15] Y. Lansac, P. K. Maiti, N. A. Clark, and M. A. Glaser, e-print cond-mat/0202154.
- [16] K. Kishikawa *et al.*, *Chem. Mater.* **11**, 867 (1999); D. Shen, S. Diele, G. Pelzl, I. Wirth, and C. Tschierske, *J. Mater. Chem.* **9**, 661 (1999); J. Matraszek *et al.*, *Liq. Cryst.* **27**, 429 (2000).
- [17] T. C. Lubensky and L. Radzihovsky (unpublished).
- [18] See, for example, Michael Tinkham, *Group Theory and Quantum Mechanics* (McGraw-Hill, New York, 1964).
- [19] John Toner, *Phys. Rev. A* **27**, 1157 (1983).
- [20] By “anisotropic” we mean an orientationally ordered phase, which, as in the case of a tetrahedric phase  $T$ , characterized by  $S=0$  and isotropic dielectric tensor, should appear isotropic in *linear* optics experiments. It is, nevertheless, an anisotropic phase since its rotational symmetry is smaller than that of fully disordered isotropic liquid, a distinction that can in principle be experimentally observed in nonlinear optical experiments, such as optical second harmonic generation.
- [21] P. G. de Gennes and J. Prost, *The Physics of Liquid Crystals* (Clarendon Press, Oxford, 1993).
- [22] P. Chaikin and T. C. Lubensky, *Principles of Condensed Matter Physics* (Cambridge University Press, Cambridge, 1995).
- [23] R. Alben, *Phys. Rev. Lett.* **30**, 778 (1973).
- [24] In mean-field theory, a noncritical order parameter explicitly induced by spontaneous ordering of another order parameter has its growth with reduced temperature and field, completely determined by the critical exponents controlling the behavior of the critical order parameter. Canonical example is an  $XY$  model where ordering of  $\psi_1$  explicitly induces higher harmonic order parameters, such as, e.g.,  $\psi_n$  through coupling  $\psi_1^n \psi_n^* + \text{c.c.}$  However, despite the irrelevance of this coupling for the critical behavior of  $\psi_1$  (noncritical  $\psi_n$  can be simply integrated out, finitely renormalizing bare parameters of the  $H[\psi_1]$ ), because of the nonlinear nature of this coupling operator, beyond mean-field theory, it, as well as susceptibility  $\chi_n$  for  $\psi_n$  generically receive nontrivial fluctuation corrections and therefore have independent and nontrivial scaling dimensions. These can be shown to lead [25] to breakdown of mean-field  $\beta_n = n\beta_1$  relation, as is most strikingly seen for an  $XY$  model in two dimensions.
- [25] A. Aharony, R. J. Birgeneau, J. D. Brock, and J. D. Litster, *Phys. Rev. Lett.* **57**, 1012 (1986).
- [26] L. G. Fel, *Phys. Rev. E* **702**, 702 (1995).
- [27] In the preceding reference, Fel studied the  $I \rightarrow T$  transitions and many of the interesting properties of the  $T$  phase using a Landau theory for a third-rank symmetric-traceless tensor order parameter. He failed, however, to identify all of the invariants in the Landau theory and, therefore, failed to identify the  $I \rightarrow N+3$  transition. He also missed the second quartic invariant in  $T^{ijk}$  [the  $v_T$  term in our Eq. (4.4)], and therefore incorrectly identified the  $I \rightarrow T$  transition as being in the  $O(7)$  universality class. For correct analysis, see Ref. [29].
- [28] R. G. Priest and T. C. Lubensky, *Phys. Rev. B* **13**, 4159 (1976).
- [29] Thermal fluctuations drive the  $I$ - $T$  transition first order as shown in L. Radzihovsky and T. C. Lubensky, *Europhys. Lett.* **54**, 206 (2001).
- [30] The reduced transition temperatures for ordering from the nematic into polar states with one of the three order parameters  $p_3$ ,  $p_2$ , and  $p_1$  finite are, respectively, determined by  $r_{p_3}^{eff} \equiv r_p + 4w_{pQ}S/3$ ,  $r_{p_2}^{eff} \equiv r_p - 2w_{pQ}S/3$ ,  $r_{p_1}^{eff} \equiv r_p - 2w_{pQ}S/3$ . Nematic ordering along  $\mathbf{n}$ , therefore obviously raises  $T_c$  for  $p_3$ , and lowers it equally for  $p_1$  and  $p_2$ .
- [31] K. G. Wilson and J. Kogut, *Phys. Rev. C* **12**, 77 (1977).
- [32] J. Rudnick, *Phys. Rev. B* **18**, 1406 (1978).
- [33] The nature of the ordered phase is determined by the sign of the coefficient of the cubic symmetry breaking term. If positive, the  $XY$ -order parameter  $\vec{p}_{1,2}$  will order along either the  $\mathbf{m}$  or  $\mathbf{l}$  axis, leading to  $\vec{p}_{1,2}=p_1(1,0)$  or  $\vec{p}_{1,2}=p_2(0,1)$  order. For negative value of the cubic anisotropy coefficient, the ordering is along the diagonal with  $\vec{p}_{1,2}=p(1,1)$ . With the  $N_T$  phase characterized by nonzero  $T_7$  and  $T_6=0$ , it is only the latter (1,1) ordering that leads to the  $N+V$  phase. In the former case of (1,0) or (0,1) order, the resulting state is the chiral  $(N+V)^*$  state characterized by triclinic  $C_1$  symmetry. Evidence for the smectic version of this state, the so-called  $\text{Sm } C_G$ , proposed by de Gennes [21] has recently been presented in freely suspended films and in the bulk, and identified with the  $B_7$  texture [34].

- [34] N. A. Clark, Abstract Book of the ALCOM Symposium on Liquid Crystals and Polymers: Past, Present, and Future, 2000, p. 15; D. M. Walba, E. Korblova, R. Shao, D. N. Coleman, N. Chattham, and N. A. Clark, Abstract Book of the Eighth International Conference on Ferroelectric Liquid Crystals, 2001, p. 29; N. Chattham, E. Kor-blova, R. Shao, D. M. Walba, J. E. Maclennan, and N. A. Clark, *ibid.*, p. 32; A. Jáklí, D. Kruerke, H. Sawade, and G. Heppke, Phys. Rev. Lett. **86**, 5715 (2001).
- [35] E. Brezin, J. C. LeGuillou, and J. Zinn-Justin, Phys. Rev. B **10**, 892 (1974).
- [36] It is easy to show using Eq. (5.22) for  $\tilde{r}_{B_{1,2}}^{(N)}$  that within the quartic  $f_Q$  model, Eq. (4.3), valid only close to the  $I \rightarrow N$  transition (and even then, only if it is weakly first order, so that  $S$  is small), the  $\tilde{r}_{B_{1,2}}^{(N)} = 6w_Q S$  is strictly positive, precluding an  $N \rightarrow N+2$  transition. However, a more general free energy density of  $Q^{ij}$  (e.g., including higher order nonlinearities in  $Q^{ij}$ ) can be shown to lead to  $\tilde{r}_{B_{1,2}}^{(N)}$  that does go negative, thereby triggering the transition to a biaxial  $N+2$  state [21,23].
- [37] R. Pratibha, N. V. Madhusudana, and B. K. Sadashiva, Science **288**, 2184 (2000).