Fluctuation-driven 1st-order isotropic-to-tetrahedratic phase transition

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(received 1 September 2000; accepted in final form 13 February 2001)

PACS. 64.60.Ak – Renormalization-group, fractal, and percolation studies of phase transitions.
PACS. 64.70.Md – Transitions in liquid crystals.
PACS. 61.30.Cz – Molecular and microscopic models and theories of liquid crystal structure.

Abstract. – Motivated in part by recent experiments on liquid crystals with bent-core molecules, which are observed to display a spontaneous chiral symmetry breaking, we introduce a field theory of a 3rd-rank tensor order parameter $T^{ijk}$ to describe the isotropic-to-tetrahedratic phase transition that we predict to take place in these materials. We study the critical properties of the corresponding phase transition and find that this transition, continuous at the mean-field level, is generically driven 1st-order by thermal fluctuations.

Experimental studies of liquid crystals, systems that exhibit phases that are intermediate (both in their properties and the symmetries that they break) between ordinary liquids and solids, continue to present new surprises and theoretical challenges. The experimental discovery in achiral bent-core molecules of polar-ordered smectic layers by the Tokyo Tech group [1] and of spontaneous chiral symmetry breaking by the Boulder group [2] is the latest important example of such a challenge. Bent-core molecules are V-shaped with $C_{2v}$ symmetry [3] characterized by a non-polar direction $n$ pointing from one endpoint of the V to the other and an orthogonal polar direction $p$ pointing to the vertex of the V. Seven distinct phases of bent-core molecules tentatively labeled $B_1$ to $B_7$ have been identified [4], though not all have been fully characterized. Two phases, the $B_2$ and $B_7$ phases, are smectic phases consisting of stacks of fluid layers with some internal tilt order. The Boulder group [2] has shown that the $B_2$ phase is an anti-ferroelectric smectic-$C$ phase in which the configuration of molecules in each layer is chiral with chirality alternating in sign from one layer to the next. A material of achiral nematogens having a ground state which is ferroelectric and homogeneously chiral has also recently been discovered [5]. Within smectic phases, such spontaneous breaking of chiral symmetry is possible because layers provide an anisotropic environment, defined by the layer normal, relative to which molecules can tilt and rotate.

Though most bent-core molecules do not exhibit nematic phases, some do [6], and it is of some interest to develop the minimal theory capable of exhibiting isotropic, nematic,
and the various smectic phases of bent-core molecules. Homogeneous (i.e., translationally invariant) phases composed of achiral molecules and characterized only by two orthogonal axes cannot be chiral. Clearly, then, a theory whose orientational order is based only on the Maier-Saupe symmetric-traceless 2nd-rank tensor order parameter $Q_{ij}$ cannot describe the exotic orientational order of the $B_2$ phase. In bulk liquid crystals, electric dipoles play an insignificant role in determining the development of order, and it is appropriate to consider models in which molecular properties are described entirely by their mass-moment tensors. Since the first mass-moment tensor relative to the center of mass is zero, these molecules do not have mass-moment vector order parameter. They do, however, have a third-rank mass-moment tensor that does contain information about the polar shape of a bent-core molecule.

The simplest model capable of describing both the nematic and the orientational order of the aforementioned smectic phases of bent-core molecules is one with both 2nd-rank and 3rd-rank order parameters. Arbitrary symmetric third-rank tensors can be decomposed into a symmetric-traceless part $T_{ijk}$, which transforms under the $l = 3$ representation of the group $SO(3)$, and a part that transforms like a vector $p^l$ ($l = 1$) under $SO(3)$.

A model with $p^i$, $Q^{ij}$ and $T^{ijk}$ order parameters produces an incredibly rich phase diagram at the mean-field level [7]. It predicts, in particular, translationally invariant nematic phases with $D_{3h}$, $D_{2d}$ and even chiral $D_2$ symmetry in addition to the usual uniaxial and biaxial nematic phases with respective $D_{3h}$ and $D_{2h}$ symmetry. The latter phases are characterized by $p^i = 0$, $T^{ijk} = 0$, and $Q^{ij} \neq 0$, whereas the former, more unfamiliar phases have both $T^{ijk}$ and $Q^{ij}$ non-zero, but $p^i = 0$. There is also a novel tetrahedral (T) phase with $p^i = 0$, $Q^{ij} = 0$, and only $T^{ijk}$ non-zero. As discussed in ref. [7], its basic building block is a structure consisting of two oppositely $p$-directed and crossed “V”-shaped banana molecules, that lie in the orthogonal planes and whose 4 ends generically form a uniaxially distorted tetrahedron. In the putative tetrahedral phase such two-molecule tetrahedral subunits have their uniaxial axes equally distributed among a spontaneously chosen orthonormal triad $\{m, l, n\}$, thereby guaranteeing the vanishing of $Q^{ij}$. Consistent with this, a simple analysis [7] shows that $T^{ijk}T^{ipj} \propto \delta^{kl}$ in the tetrahedral phase; hence the coupling $T^{ijk}T^{ijl}Q_{kl}$ vanishes by virtue of the tracelessness of $Q^{kl}$ and therefore does not induce the nematic order $Q^{kl}$, as one might have naively thought.

The direct transition from the isotropic phase to the tetrahedral phase [8] can be described by a simpler model depending only on the 3rd-rank tensor order parameter $T^{ijk}$. Since there are no odd-order invariants of $T^{ijk}$, this transition can be continuous in mean-field theory [7]. In this note, we study fluctuation corrections to the mean-field isotropic-to-tetrahedral (IT) transition within an $\epsilon$-expansion about the upper critical dimension $d_c = 4$. Our principal result is that the presence of two distinct fourth-order invariants (see eq. (1) below) leads to a runaway within the $\epsilon$-expansion whose effect, in analogy with charged superconductors [9] and a ferromagnet in a cubic field [10], is to convert this mean-field 2nd-order transition to a 1st-order one.

Our starting point is the Landau free-energy density functional $\mathcal{H}[T_{ijk}]$, controlling the direct transition into the tetrahedral phase:

$$\mathcal{H} = \frac{1}{2} (\partial_i T^{ijk} \partial_j T^{ijk}) + \frac{1}{2} v T^{ijk} T^{ijk} + u (T^{ijk} T^{ijk})^2 + v T^{i12i31} T^{i14i5} T^{i24i6} T^{i35i6} . \tag{1}$$

In the above expressions we have used the Einstein summation convention, and have left out the “space-spin”–like gradient terms $\partial_i T_{ijk} \partial_j T_{ijk}$ that couple the internal indices of $T_{ijk}$ to that of the spatial coordinate $x$ [11]. We have also omitted couplings of $T^{ijk}$ to other order parameters. Since here we are interested in the direct transition to the $T$ phase, all other order parameters (e.g., the nematic $Q_{ij}$) are generically non-critical and can, therefore, be
safely integrated out, only finitely renormalizing the Landau parameters in $\mathcal{H}$. As usual the quadratic parameter $r \sim T - T_c$ vanishes at the mean-field transition temperatures $T_c$, which is determined predominantly by the interaction potential between molecules. In writing down quartic non-linearities in $\mathcal{H}$ we have used a non-obvious relation,

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

valid when the dimension $d_R$ of the space in which $T^{ijk}$ rotates is three, to reduce the number of independent quartic couplings in $\mathcal{H}[T]$ from three to two. The coupling $v$ was incorrectly omitted in the analysis of Fel [8]. If $v = 0$, the model described by eq. (1) has $O(7)$ symmetry. Thus, it is analogous to an $O(N)$ Heisenberg ferromagnet with an $N$-dimensional vector order parameter $T_{\alpha}$ in a cubic crystal field, giving rise to a $v \sum_{\alpha} T_{\alpha}^4$ quartic potential in addition to the $O(N)$ invariant potential $u(\sum_{\alpha} T_{\alpha}^2)^2$.

As discussed extensively in ref. [7], the IT transition is generically continuous at the mean-field level since rotational invariance forbids the appearance of a cubic invariant in $T^{ijk}$. Its nature, however, depends on the sign of $v$. For $v > 0$, the stable low-temperature phase has $D_{3h}$ symmetry, whereas for $v < 0$, it has tetrahedral ($T_d$) symmetry. Similar behavior is seen in $O(N)$ ferromagnets in a cubic crystal field. When the cubic coupling $v$ is non-zero, the low-temperature phase has $T_{\alpha} \sim (1,0,...,0)$ for $v < 0$ and $T_{\alpha} \sim (1,1,...,1)/\sqrt{N}$ for $v > 0$. Our main goal then is to go beyond this mean-field theory [7] and study effects of thermal fluctuations on this heretofore unexplored IT transition.

Before analyzing fluctuations in this model, it is useful to introduce a tensor representation for the 7 independent components of $T^{ijk}$. Any third-rank symmetric-traceless field $T^{ijk}(x)$ can be expressed as $T^{ijk}(x) = \sum_{\alpha=1}^{7} T_{\alpha}(x) i_{\alpha}^{ijk}$, where

$$I_{1}^{ijk} = \sqrt{\frac{5}{2}}(n^i n^j n^k - \frac{1}{5}(\delta^{ij} n^k + \delta^{jk} n^i + \delta^{ki} n^j)), \quad (3a)$$

$$I_{2}^{ijk} = \frac{1}{2}(m^i m^j m^k - m^i \delta^{jk} - m^j \delta^{ik} - m^k \delta^{ij}), \quad (3b)$$

$$I_{3}^{ijk} = \frac{1}{2}(l^i l^j l^k - \delta^{ij} l^k - \delta^{jk} l^i - \delta^{ki} l^j), \quad (3c)$$

$$I_{4}^{ijk} = \sqrt{\frac{5}{2}}(m^i m^j n^k + m^j n^i n^k + m^k n^i n^j - \frac{1}{5}(m^i \delta^{jk} + m^j \delta^{ik} + m^k \delta^{ij})), \quad (3d)$$

$$I_{5}^{ijk} = \sqrt{\frac{5}{2}}(l^i n^j n^k + l^j n^i n^k + l^k n^i n^j - \frac{1}{5}(l^i \delta^{jk} + l^j \delta^{ik} + l^k \delta^{ij})), \quad (3e)$$

$$I_{6}^{ijk} = \frac{1}{\sqrt{6}}(n^i (m^j m^k - l^j l^k) + n^j (m^i m^k - l^i l^k) + n^k (m^i m^j - l^i l^j)), \quad (3f)$$

$$I_{7}^{ijk} = \frac{1}{\sqrt{6}}(n^i m^j l^k + n^j m^i l^k + m^i l^j n^k + m^j l^i n^k + l^i n^j m^k + l^j n^i m^k) \quad (3g)$$

are an orthonormal set of basis tensors with $n^i$, $m^i$, and $l^i$ forming a space-fixed right-handed orthonormal basis. The $O(7)$ invariance of the eq. (1) when $v = 0$ follows easily from the relation $T^{ijk}T^{ijk} = \sum_{\alpha=1}^{7} T_{\alpha}^2$.

The effective Hamiltonian $H = \int d^d x \mathcal{H}$ in $d$ spatial dimensions can be conveniently rewritten in terms of Fourier-transformed $T$-fields

$$H = \frac{1}{2} \int_k (k^2 + r)|T_{\alpha}(k)|^2 + \int_x V^{ij_1j_2k_1,ij_3j_4k_2}_{ij_1j_2k_1} T_{i_1j_1k_1} T_{i_2j_2k_2} T_{i_3j_3k_3} T_{i_4j_4k_4}, \quad (4)$$
where $V_{i_1j_1k_1,i_2j_2k_2} = V_{i_3,i_4}^{i_1j_1,k_1}$ is a fully symmetrized quartic potential (consisting of products of 3 Kronecker $\delta$-functions), containing the $u$ and $v$ vertex couplings and is too complicated to be reproduced here. There are at least two ways to generalize our model, originally defined in 3 dimensions to arbitrary spatial dimension $d$. We can either fix the dimension $d_T$ of the space in which $T^{ijk}$ “lives” to be three and let the dimension $d$ of space be arbitrary, or we could lock $d_T$ and $d$ together. Here, we adopt the former option, keeping $d_T = 3$. The advantage of the symmetrized representation in eq. (4) is that the averages of any pair of $T^{ijk}$ fields appearing in the quartic operator are equivalent, and the field theory part of the calculation is effectively mapped onto a standard analysis of a scalar $\phi^4$ field theory.

It is not difficult to show that a corresponding tensor part of the $T$-$T$ propagator $G_{ijk}^{lmn}$ defined by

$$\langle T_{ijk}(k)T_{lmn}(k') \rangle = (2\pi)^d \delta^{(d)}(k + k') \frac{G_{ijk}^{lmn}}{k^2 + r}$$

is given by

$$6G_{ijk}^{lmn} = \left[ \delta_{il} \delta_{jm} \delta_{kn} + 5 \text{ permutations of } (ijk) \right] - \frac{2}{3} \left[ \delta_{ij} \left( \delta_{lm} \delta_{kn} + \delta_{lk} \delta_{mn} + \delta_{ln} \delta_{km} \right) + (i \leftrightarrow k) + (i \leftrightarrow j) \right],$$

(6)

The tensor $G_{ijk}^{lmn}$ is uniquely constrained by the rotational invariance to be a sum of products of Kronecker $\delta$-functions, with two non-trivial coefficients uniquely determined by the various traces of $G_{ijk}^{lmn}$. Another more systematic way of obtaining $G_{ijk}^{lmn}$ is to use the $O(7)$ representation of $T_{ijk}(k)$, eq. (3) inside the left-hand side of eq. (5), to produce

$$\langle T_{ijk}(k)T_{lmn}(k') \rangle = \sum_{\alpha,\alpha'} \frac{G_{ijk}^{lmn}}{T_{\alpha'}(k')T_{\alpha}(k)}.$$

(7)

Using the $O(7)$ representation of $H$ along with equipartition, we obtain $\langle T_{\alpha}(k)T_{\alpha'}(k') \rangle = (2\pi)^d \delta^{(d)}(k + k') (k^2 + r)$, which, when used inside eq. (7), gives $G_{ijk}^{lmn} = \sum_{\alpha = 1}^{7} T_{\alpha}^{ijk} T_{\alpha}^{lmn}$ that can be shown to be equivalent to our expression for $G_{ijk}^{lmn}$ in eq. (6).

To assess the role of thermal fluctuations, we need to compute the total free energy by integrating over the field $T^{ijk}(x)$ rather than by simply minimizing the effective Hamiltonian above, as we did in ref. [7]. As usual, because of the non-linear quartic interaction, this cannot be done exactly, and near a critical point ($r \approx 0$) a perturbative calculation in $V_{i_1,i_2}^{i_3,i_4}$ diverges (for $d < 4$), thereby indicating that the nature of the IT transition is qualitatively modified by thermal fluctuations.

To make sense of these divergences, we employ the standard perturbative momentum-shell RG calculation [12], in which we integrate out an infinitesimal fraction (a momentum shell) of degrees of freedom at a time near the shortest length scales, at the lattice cutoff $\Lambda^{-1}$. More concretely, we separate the $T_{ijk}$ order parameter field into high- and low-wavevector components $T_{ijk}(x) = T_{ijk}^>(x) + T_{ijk}^<$, with $T_{ijk}^>$ having support in the wavevector range $\Lambda e^{-\ell} < k < \Lambda$ and $\Lambda$ is an ultraviolet (uv) cutoff of order of the inverse of molecular size. We integrate out the high-wavevector part $T_{ijk}^>(x)$, perturbatively in $V_{i_1,i_2}^{i_3,i_4}$, and rescale the lengths and long-wavelength part of the fields according to $x = e^\ell x'$, $T_{ijk}^>(x) = e^{(2-d)/2}T_{ijk}(x')$, so as to restore the uv cutoff back to $\Lambda$ and to (1-loop order) keep the coefficient of the $k^2 |T_{ijk}(k)|^2$
in $H$ fixed at 1. Under this transformation the resulting effective free-energy functional $H$ can be restored into its original form, eq. (4), with effective $\ell$-dependent couplings.

Standard perturbative 1-loop RG analysis, represented graphically in fig. 1, leads to the following flow equations:

$$
\frac{d}{d\ell} G_{\ell_1, \ell_2}^{-1} = 2 G_{\ell_1, \ell_2}^{-1} + \frac{12 \Lambda^{d-2} C_d}{(1 + r/\Lambda^2)^2} V_{\ell_1, \ell_2}^{i_1, i_4} G_{i_3, i_4}, \tag{8}
$$

$$
\frac{d}{d\ell} V_{\ell_1, \ell_2}^{i_1, i_4} = \epsilon V_{\ell_1, \ell_2}^{i_1, i_4} - \frac{36 \Lambda^{d-4} C_d}{(1 + r/\Lambda^2)^2} V_{\ell_1, \ell_2}^{i_1, i_4} V_{\ell_1, \ell_2}^{i_1, i_4} G_{i_3, i_4} G_{i_3, i_4}, \tag{9}
$$

where $\epsilon = 4 - d$. These equations describe the evolution of the reduced temperature $r(\ell)$ (determined by the $q = 0$ part of the 2-point inverse propagator $G_{\ell_1, \ell_2}^{-1}(q = 0, r)$) and the quartic vertex $V_{\ell_1, \ell_2}^{i_1, i_4} (\ell)$ after a fraction $e^{\ell}$ of high-wavevector modes has been integrated out. In above $C_d = 2\pi^{d/2}/((2\pi)^d \Gamma(d/2))$ is a surface area of a $d$-dimensional sphere divided by $(2\pi)^d$, an obvious extension of Einstein convention was employed, and $\epsilon$ was taken to be small so as to allow higher-order corrections in $V_{\ell_1, \ell_2}^{i_1, i_4}$ to be neglected. We note in passing that for the fully symmetrized $V_{\ell_1, \ell_2}^{i_1, i_4}$ vertex the factors 12 and 36 of the respective second term in eqs. (8) and (9) are identical to the corresponding coefficients in the equations for the reduced temperature and quartic coupling constant in the scalar $\phi^4$ (Ising) model [12].

After technically tedious but conceptually straightforward tensor contraction in eq. (9), we find that the RG flow equations at criticality ($r = 0$) for the two dimensionless couplings of our theory $\tilde{u} \equiv u \Lambda^{d-4} C_d$ and $\tilde{v} \equiv v \Lambda^{4-d} C_d$, with $u$ and $v$ defined in eq. (1), are

$$
\frac{d\tilde{u}(\ell)}{d\ell} = \epsilon \tilde{u} - 60 \tilde{u}^2 - \frac{28}{5} \tilde{u} \tilde{v} - \frac{17}{25} \tilde{v}^2, \tag{10a}
$$

$$
\frac{d\tilde{v}(\ell)}{d\ell} = \tilde{v} \left( \epsilon - \frac{116}{25} \tilde{v} - 48 \tilde{u} \right). \tag{10b}
$$

The flow off the critical surface, controlled by $\tilde{r}(\ell) \equiv r(\ell)/\Lambda^2$, is determined by the equation

$$
\frac{d\tilde{r}(\ell)}{d\ell} = 2\tilde{r} + \frac{1}{1 + \tilde{r}} \left( 36 \tilde{u} + \frac{76}{5} \tilde{v} \right). \tag{11}
$$
Fig. 2 – RG flow characterizing the IT phase transition. The Gaussian and O(7) ($u = \epsilon/60, v = 0$) critical points are indicated by black circles. In a generic model, with $v \neq 0$, the flow runs away into the region of $u < 0$, suggesting a fluctuation-driven 1st-order IT transition.

As a simple check on our results, we first note that the flow for $\tilde{v}$, eq. (10), has an obvious fixed-point solution of $\tilde{v} = 0$. This property of the flow for $\tilde{v}$ is a rigorous consequence of an exact O(7) invariance of our theory for $\tilde{v} = 0$, as can be easily seen from eq. (1).

Standard fixed-point analysis of the above equations leads to two physical critical points given by: i) Gaussian with $\tilde{u} = 0, \tilde{v} = 0$, and ii) O(7) with $\tilde{u} = \epsilon/60, \tilde{v} = 0$. As a further check, we also note that for $v = 0$, the above flow equations, eqs. (11) and (10), reduce exactly to the flow equations for the O($N$) Heisenberg model with $N = 7$ (the model which our Hamiltonian $H$ explicitly reduces to for $v = 0$), with corresponding universal coefficients 36 and 60, in the above equations, identical to the well-known $4(N + 2)$ and $4(N + 8)$ coefficient for the O($N$) Heisenberg model with $N = 7$.

As expected and discussed above, for $d < 4$ the Gaussian critical point is unstable. For the special $v = 0$ O(7) invariant subspace, this instability terminates at the well-known $N = 7$ Heisenberg model critical point characterized by (1-loop) exponents: $\nu = 1/(2 - 3\epsilon/5)$, $\gamma = 2\nu$ and $\eta = 0$. This O(7) critical point is also unstable with respect to turning on $v$. Standard linear analysis of eqs. (10) around the O(7) ($v = 0$) critical point leads to two eigenvectors and eigenvalues that characterize the instability to turning on the O(7)-symmetry breaking perturbation $v$

$$
(\delta u, \delta v)_u = \tilde{u}(1, 0), \quad \lambda_{\tilde{u}} = -\epsilon, \quad \lambda_{\tilde{v}} = \epsilon/5. \quad (12a)
$$

$$
(\delta u, \delta v)_v = \tilde{v}\left(-\frac{7}{90}, 1\right), \quad \lambda_{\tilde{v}} = \epsilon/5. \quad (12b)
$$

As is graphically displayed in fig. 2 for the critical surface $r_c(\ell)$, we find that in the full model the effective couplings $u(\ell)$ and $v(\ell)$ run off to infinity.

The absence of a stable fixed point and the runaway towards negative values of $u$ is analogous to the situation encountered in model superconductors [9] with $(N/2)$-component $U(1)$ symmetry in which there is runaway from an O($N$)-symmetric Heisenberg fixed point towards negative $u$ when the charge is turned on. In the latter system, the runaway near $d = 4$ can be identified with a fluctuation-induced 1st-order phase transition [9]. It is likely that the runaway in the current problem is also a signal of a fluctuation-induced 1st-order IT
transition, although extension of such analysis to \( d = 3 \) has been known to fail [13]. In the
case of the superconductor, an effective free energy indicating a 1st-order transition could be
obtained by integrating out the vector potential. In the model considered here, there is no
obvious analog of the vector potential. As a result, the detailed analysis of the 1st-order IT
transition is likely to be more similar to that of the fluctuation-induced 1st-order transition,
which exists for appropriate values of the potentials, in \( O(N) \) magnets in a cubic field [14],
analyzed for \( N = 2 \) by Rudnick [10].

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LR acknowledges support by the NSF through the CAREER grant DMR96-25111, the
MRSEC grant DMR98-09555, and by the A. P. Sloan and David and Lucile Packard Foundations. TL was supported by the NSF through grant DMR97-30405.

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