

Chiral symmetry breaking in bent-core liquid crystals

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By molecular modeling we demonstrate that the nematic long-range order discovered in bent-core liquid-crystal systems should reveal further spatially homogeneous phases. Two of them are identified as a tetrahedric nematic (N_T) phase with D_{2d} symmetry and a chiral tetrahedric nematic (N_T^*) phase with D_2 symmetry. These phases were found for a lattice model with quadrupolar and octupolar anisotropic interactions using mean-field theory and Monte Carlo simulations. The phase diagrams exhibit tetrahedric (T), N_T , and N_T^* phases, in addition to ordinary isotropic (I), uniaxial nematic (N_U), and biaxial nematic (N_B) phases.

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The chirality of liquid crystals is commonly attributed to the presence of optically active (chiral) molecules [1]. Such *intrinsic molecular chirality* distinguishes right-handed and left-handed molecules, leading to a rich variety of chiral phases, where cholesteric phase [1] and blue phases [2] serve as typical examples.

Interestingly, this classical liquid crystalline chirality should be revised for *achiral* bent-core (banana-shaped) liquid crystalline molecules [3–11]. These fascinating compounds have substantially different physical properties than the molecules of the traditional calamitic materials, and have recently been a source of discoveries that are changing our view on molecular self-organization in liquid crystals [3,4,6,8,10].

Several observations indicate that achiral bent-core molecules can acquire conformational chirality in layered (smectic) mesophases [3,10]. They can form ferroelectric and *homogeneously* chiral states [4], or coexisting left- and right-handed chiral domains in a nematic phase [6,8]. Some theoretical interpretations of these observations introduce at a macroscopic scale a tetrahedric order-parameter field. The interplay between this order parameter and the (nematic) quadrupolar tensor order parameter [12,13] appears to be essential for the emergence of the chirality of the achiral bent-core molecules [7,9]. In the bent-core molecular systems this coupling generates not only the most interesting chiral symmetry breaking. The tetrahedric (T) and tetrahedric nematic (N_T) phases should also be stabilized [7]. Recently, the experimental indication of stable T and N_T phases was indeed reported [14], along with earlier discovery of the biaxial nematic phase [15,16].

This Rapid Communication analyzes some consequences of molecular interactions that have tetrahedric, uniaxial, and biaxial components. For a complete understanding of the macroscopic properties of mesophases in the bent-core systems, a first-rank tensor generating structures with polar order is also required. To simplify the analysis, the microscopic model being discussed is limited to quadrupolar and octupolar

interactions. In addition to isotropic and nematic phases, the model is shown to stabilize T , N_T , and chiral tetrahedric nematic (N_T^*) phases. These results are what we believe a first microscopic demonstration of spontaneous chiral symmetry breaking in nonlayered bent-core liquid crystals.

We assume the molecules to occupy the sites of a three-dimensional simple cubic lattice with interactions limited to nearest neighbors (coordination number: $d=6$). The total interaction potential is then given by $H = \frac{1}{2} \sum_{\langle i,j \rangle} V(\mathbf{\Omega}_i, \mathbf{\Omega}_j)$, where $V(\mathbf{\Omega}_i, \mathbf{\Omega}_j)$ is the orientational interaction between a pair of molecules (or molecular complexes in general) and $\langle i,j \rangle$ denotes the nearest-neighbor molecules i and j . Our calculations are based on the simplest attractive $O(3)$ -invariant interaction $V(\mathbf{\Omega}_i, \mathbf{\Omega}_j)$ that involves second-rank quadrupolar tensor with uniaxial ($\hat{\mathbf{T}}_0^{(2)}$) and biaxial ($\hat{\mathbf{T}}_2^{(2)}$) components, and a third-rank octupolar tensor ($\hat{\mathbf{T}}_2^{(3)}$). The tensors are built out of the orthonormal tripod $\mathbf{\Omega}_k$ of vectors $\{\hat{\mathbf{a}}_k, \hat{\mathbf{b}}_k, \hat{\mathbf{c}}_k\}$ defining the orientational degrees of freedom of the k th molecule. Under these assumptions $V(\mathbf{\Omega}_i, \mathbf{\Omega}_j)$ takes the form

$$V(\mathbf{\Omega}_i, \mathbf{\Omega}_j) = -\epsilon [\{\hat{\mathbf{T}}_0^{(2)}(\mathbf{\Omega}_i) + \sqrt{2}\lambda \hat{\mathbf{T}}_2^{(2)}(\mathbf{\Omega}_i)\} \cdot \{\hat{\mathbf{T}}_0^{(2)}(\mathbf{\Omega}_j) + \sqrt{2}\lambda \hat{\mathbf{T}}_2^{(2)}(\mathbf{\Omega}_j)\} + \tau \hat{\mathbf{T}}_2^{(3)}(\mathbf{\Omega}_i) \cdot \hat{\mathbf{T}}_2^{(3)}(\mathbf{\Omega}_j)], \quad (1)$$

where [18]

$$\hat{\mathbf{T}}_0^{(2)}(\mathbf{\Omega}_k) = \sqrt{\frac{3}{2}} \left(\hat{\mathbf{c}}_k \otimes \hat{\mathbf{c}}_k - \frac{1}{3} \mathbf{1} \right),$$

$$\hat{\mathbf{T}}_2^{(2)}(\mathbf{\Omega}_k) = \frac{1}{\sqrt{2}} (\hat{\mathbf{a}}_k \otimes \hat{\mathbf{a}}_k - \hat{\mathbf{b}}_k \otimes \hat{\mathbf{b}}_k),$$

$$\hat{\mathbf{T}}_2^{(3)}(\mathbf{\Omega}_k) = \frac{1}{\sqrt{6}} \sum_{(\hat{\mathbf{x}}, \hat{\mathbf{y}}, \hat{\mathbf{z}}) \in \pi(\hat{\mathbf{a}}_k, \hat{\mathbf{b}}_k, \hat{\mathbf{c}}_k)} \hat{\mathbf{x}} \otimes \hat{\mathbf{y}} \otimes \hat{\mathbf{z}}, \quad (2)$$

and where $\hat{\mathbf{T}}_m^{(L)} \cdot \hat{\mathbf{T}}_{m'}^{(L)} = \delta_{mm'}$ [17]. The summation in $\hat{\mathbf{T}}_2^{(3)}$ runs over all permutations of $(\hat{\mathbf{a}}_k, \hat{\mathbf{b}}_k, \hat{\mathbf{c}}_k)$. The symbol “ \cdot ” denotes the scalar product formed by a full contraction of the Carte-

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sian indices, and $\hat{\mathbf{T}}_m^{(L)}(\boldsymbol{\Omega}_i) \cdot \hat{\mathbf{T}}_{m'}^{(L)}(\boldsymbol{\Omega}_j) = \Delta_{mm'}^{(L)}$, are linear combinations of Wigner rotation matrices [18].

Interaction (1) can be interpreted within point dispersion forces approximation. The quadrupolar tensor $\hat{\mathbf{T}}_0^{(2)} + \sqrt{2}\lambda\hat{\mathbf{T}}_2^{(2)}$ is then proportional to the anisotropic part of the dielectric polarizability tensor of a molecule, while $\hat{\mathbf{T}}_2^{(3)}$ is the T_d -symmetric component of the third-order polarizability tensor. The model parameters $\{\epsilon, \lambda, \tau\}$ are related to the molecular absorption frequencies.

Special cases of the model have already been studied. For $\tau = \lambda = 0$ the potential in Eq. (1) reduces to the well-known Maier-Saupe or Lebwohl-Lasher [19] potential, which describes a phase diagram with isotropic and uniaxial nematic phases connected by a first-order phase transition. Second is the one where $\lambda \neq 0$ and $\tau = 0$. Potential (1) then reduces to the model proposed by Luckhurst *et al.* [20], which was extensively studied by Biscarini *et al.* [21]. The model describes a phase diagram with uniaxial nematic and biaxial nematic phases connected by the second-order phase transition. The phases include: a prolate uniaxial (N_{U+}) phase, an oblate uniaxial (N_{U-}) phase, a biaxial (N_B) phase, and an isotropic (I) phase. A self-dual point for which $\lambda = 1/\sqrt{6}$ [18,21] separates a phase in which the molecules are of distorted prolate form ($\lambda < 1/\sqrt{6}$) from a phase in which the molecules are of distorted oblate form ($\lambda > 1/\sqrt{6}$). Bates and Luckhurst proposed a simple relation between ϵ , λ and the opening angle for bent-core molecules based on segmental second-rank interactions [22].

When only the term proportional to $\epsilon\tau$ is retained in Eq. (1), the resulting model corresponds to a purely tetrahedric coupling. It was introduced by Fel [23] and studied via mean-field (MF) and Monte Carlo (MC) simulations by Romano [24]. For this model, MF theory predicts a second-order phase transition from I to T phase and MC simulations indicate a weak first-order transition from I to T .

Combining quadrupolar and octupolar interactions in Eq. (1) yields possibilities of which the most notable one is the spontaneous breaking of chiral symmetry. Such a symmetry breaking is already manifested in the ground-state properties of the interaction of Eq. (1). Indeed, to be consistent with Eq. (1), the average molecular configurations of two bent-core molecules in a chiral phase must belong to one of two configurations of opposite chirality ($0 < \delta < \pi/2$), as shown in Fig. 1. Due to the global $O(3)$ invariance of H , the two configurations of different chirality are the source of two homochiral domains, which are present with equal probability in the system's configuration space. When $\tau = 0$ ($\delta = 0$) or $\lambda = 0$ ($\delta = \pi/2$) the molecular configurations are nonchiral and can be brought into coincidence by a rotation. In particular, these configurations produce N_U , N_B , T , and N_T phases. In order for both chiral configurations to be equivalent, the degrees of freedom of the k th molecule should involve a rotation $\boldsymbol{\Omega}_k$ and parity $p_k = \hat{\mathbf{a}}_k \cdot (\hat{\mathbf{b}}_k \times \hat{\mathbf{c}}_k) = \pm 1$, thereby reflecting an $O(3)$ symmetry. Consequently, the free energy for the system composed of N such molecules is given by $\beta F = -\ln Z$, where $Z = \prod_{k=1}^N (\frac{1}{2} \sum_{p_k = \pm 1} \int d\boldsymbol{\Omega}_k) \exp[-\beta H]$, and $\beta = 1/(k_B T)$ is the inverse temperature.

We will apply two methods to determine phase diagrams

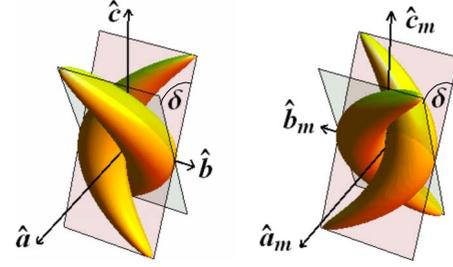


FIG. 1. (Color online) Ground-state configurations of opposite chirality ($0 < \delta < \pi/2$) for a pair of bent-core molecules in N_T^* phase; the configurations for $0 < \delta < \pi/2$ cannot be brought into coincidence by a proper rotation. $(\hat{\mathbf{a}}_m, \hat{\mathbf{b}}_m, \hat{\mathbf{c}}_m)$ are mirror images of $(\hat{\mathbf{a}}, \hat{\mathbf{b}}, \hat{\mathbf{c}})$.

from F . The methods are the MF approximation and the Metropolis MC simulations with a crucial step being the identification of the order parameters. The identification is achieved by expanding the one-particle distribution function $P(p, \boldsymbol{\Omega})$ in a series of symmetry adapted real Δ functions,

$$P(p, \boldsymbol{\Omega}) = \sum_{L, m, m', s} \frac{2L+1}{8\pi^2} \overline{p_s \Delta_{mm'}^{(L)}} p_s \Delta_{mm'}^{(L)}(\boldsymbol{\Omega}), \quad (3)$$

with $\overline{\mathbf{X}} = \frac{1}{2} \sum_{p=\pm 1} \int \mathbf{X}(p, \boldsymbol{\Omega}) P(p, \boldsymbol{\Omega}) d\boldsymbol{\Omega}$, $p_s = (1, p)$, and

$$\begin{aligned} & \frac{1}{2} \sum_{p=\pm 1} \int d\boldsymbol{\Omega} p_s \Delta_{mn}^{(L)}(\boldsymbol{\Omega}) p_{s'} \Delta_{m'n'}^{(L')}(\boldsymbol{\Omega}) \\ &= \frac{8\pi^2}{(2L+1)} \delta_{LL'} \delta_{mm'} \delta_{nn'} \delta_{ss'}. \end{aligned} \quad (4)$$

For the interaction of Eq. (1), the allowed symmetry reduction is shown in Fig. 2 along with the primary order

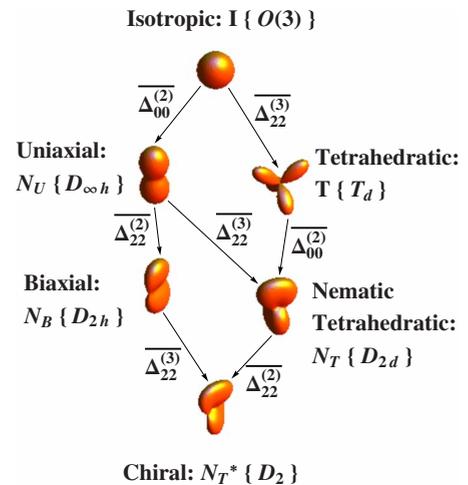


FIG. 2. (Color online) A flowchart of phase transitions between liquid-crystal phases for molecules interacting through pair potential, Eq. (1). Primary order parameters, which become nonzero at the transitions, their symmetry groups and abbreviated notation for the structures are indicated. In addition, sketched are one-particle spherical distribution functions $P \sim \text{const} + aY_{20} + b(Y_{22} + Y_{2-2}) + ci(Y_{32} - Y_{3-2})$ illustrating symmetries considered.

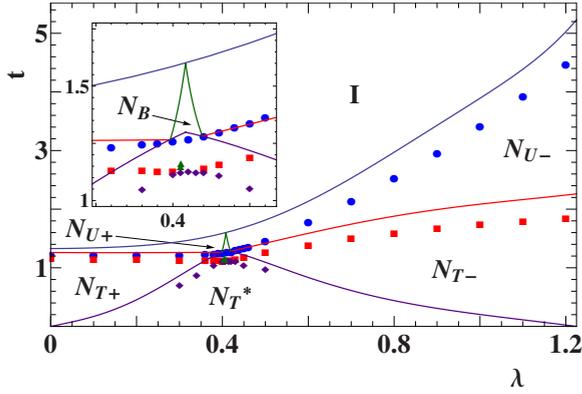


FIG. 3. (Color online) Phase diagram for $\tau=1$. Lines represent MF results; points are from MC simulations for the three-dimensional cubic lattice ($16 \times 16 \times 16$); $t = (\beta\epsilon)^{-1}$.

parameters that acquire nonzero averages when crossing various phase transitions. In order to be consistent with $L=3$ primary tetrahedratic order parameter, we list all remaining (secondary) molecular order parameters of rank $L \leq 3$. These are: (a) $\Delta_{02}^{(2)}$ for N_U ; (b) $\Delta_{20}^{(2)}$ and $p\Delta_{22}^{(3)}$ for N_B ; (c) $p\Delta_{20}^{(2)}$ and $p\Delta_{22}^{(2)}$, along with N_U secondary order parameters, for N_T ; and finally (d) for N_T^* all aforementioned order parameters are nonzero, in addition to \bar{p} , $p\Delta_{00}^{(2)}$, and $p\Delta_{02}^{(2)}$. Here

$$\Delta_{mm'}^{(L)} = \left(\frac{1}{\sqrt{2}} \right)^{2+\delta_{0m}+\delta_{0m'}} \sum_{s,s'=\pm 1} [\delta_{ss'} + (-1)^L \delta_{-ss'}] D_{sms'm'}^L, \quad (5)$$

where D are the Wigner rotation matrices.

We are now in position to evaluate the MF approximation to F and obtain the equilibrium properties of our system. We have identified six stable phases of model (1) that cover the whole symmetry reduction flowchart of Fig. 2. The phases are (a) the isotropic phase; (b) the uniaxial prolate or oblate nematic phase; (c) the biaxial phase; (d) the tetrahedratic phase; (e) the prolate or oblate tetrahedratic nematic phase; and (f) the chiral tetrahedratic nematic phase. Exemplary

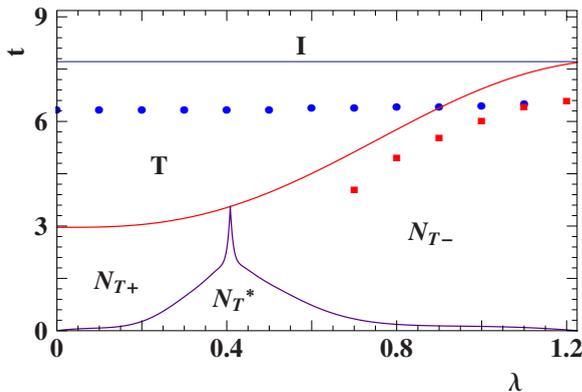


FIG. 4. (Color online) MF phase diagram for $\tau=9$ (see captions to Fig. 3). Simulations here are difficult since parity degrees of freedom condense to a glassy state. The N_T^* phase cannot be reached by standard Metropolis simulations.

phase diagrams for $\tau=1$ and for $\tau=9$ are shown in Figs. 3 and 4, respectively. Figure 3 shows a phase diagram in which the high-temperature region is dominated by the nematic phases. Figure 4 shows a phase diagram in which occurs a direct I - T phase transition. Phase diagrams for intermediate values of τ can partly be deduced by extrapolation. One of them is of particular interest. Namely, for $\tau = \frac{28}{15}$ six phases: I , T , N_{T+} , N_T^* , N_{T-} , and N_{U-} meet at a single multicritical Landau point. All phase transitions found are of second order except when more than one order parameter acquires a nonzero value at a bifurcation. Such first-order phase transitions occur at I - N_T , T - N_T , or I - N_{U-} . A fuller account of the properties of this model is deferred to our future publication.

To check the validity of the MF predictions the phase diagrams were also determined from MC simulations. The simulations were performed on a $16 \times 16 \times 16$ lattice with periodic boundary conditions. Each MC move included a rotation of a molecule's orientation and a parity inversion. The size of MC rotational moves was selected to produce an acceptance ratio between 30% and 40% in the ordered phases. Typically, 50 000 to 200 000 lattice sweeps were used to thermalize the system and 60 000 to 200 000 sweeps for measurements. In the MC simulations, phase transitions were detected by observing the temperature dependence of the order parameters. In turn, these quantities were determined from the asymptotic behaviors of the correlation functions $G_{mm'}^{(L)}(|i-j|) = \overline{\hat{\mathbf{T}}_m^{(L)}(\mathbf{\Omega}_i) \cdot \hat{\mathbf{T}}_{m'}^{(L)}(\mathbf{\Omega}_j)}$ and $G_{pp}(|i-j|) = \overline{p_i p_j}$ for large $|i-j|$. Here the overline indicates an ensemble average. In the simulations, the temperature resolution δt satisfied $\delta t = 0.01$. At the above resolution (and system's size) our simulations were unable to distinguish between weakly first-order and second-order phase transitions. The MC transition curves lie below those obtained from MF. The MF results worsen from a discrepancy of 8% to about 20% as λ increases from $\lambda=0$ (I - N_U) to $\lambda=0.3$ (N_T - N_T^*). The I - N_U part of our MC diagram agrees with MC results of Biscarini *et al.* [21].

The liquid-crystal phases appear due to the combination of octupolar interactions with quadrupolar contributions. In addition to a tetrahedratic nematic phase, existing in prolate (N_{T+}) and oblate (N_{T-}) versions, the N_T^* phase appears stable. It does not appear for $\lambda=0$ or $\lambda = \sqrt{3}/2$, which correspond to a uniaxial limit. From the leading MF contribution to the parity order parameter, \bar{p} , an induced homogeneous chirality is seen to emerge when both biaxial and tetrahedratic orders condense. The estimation gives

$$\bar{p} \cong \frac{\sqrt{2}}{210t^4} \tau \lambda (-3 + 2\lambda^2) \overline{\Delta_{22}^{(3)}} (\overline{\Delta_{20}^{(2)}} + \sqrt{2\lambda} \overline{\Delta_{22}^{(2)}})^3, \quad (6)$$

which vanishes when biaxial or tetrahedratic order parameters are zero. A maximal transition temperature to a chiral phase is achieved for the self-dual point of $\lambda = 1/\sqrt{6}$.

To conclude, bent-core liquid crystals can stabilize the elusive thermotropic biaxial nematic phase [15,16], and reveal a path to a series of spatially homogeneous but anisotropic liquids [7]. Of these liquids the most interesting one is the N_T^* phase, which should emerge from a nonchiral liquid as a result of spontaneous chiral symmetry breaking. The

simplest “spin-spin”-type of molecular model of Eq. (1), with quadrupolar and octupolar interactions supports this scenario, but, unlike chiral phases of ordinary chiral materials, the orientational order in N_T^* appears spatially uniform. It is worth noting, however, that inclusion of higher-order cross-coupling terms between uniaxial, biaxial, and tetrahedral interactions can superimpose a spatial modulation to N_T and N_T^* [17]. Thus the structures stabilized in our model can serve as the long-wavelength limits to a family of spatially modulated chiral structures that can possibly condense

in the presence of higher-order interactions. Owing to general form of the interaction, Eq. (1), these conclusions should apply to any system where tetrahedral and quadrupolar order may simultaneously coexist.

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