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Chirality and Biaxiality in Cholesteric Liquid Crystals

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We investigate the statistical mechanics of chirality and biaxiality in liquid crystals through a variety of theoretical approaches, including Monte Carlo simulations, lattice mean-field theory, and Landau theory. All of these calculations show that there is an important interaction between cholesteric twist and biaxial order: The twist acts as a field on the biaxial order, and conversely, the biaxial order increases the twist, i.e. reduces the pitch. We model the behavior of chiral biaxial liquid crystals as a function of temperature, and discuss how the predictions can be tested in experiments.

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In liquid crystals, there is a close connection between *chirality*, asymmetry under reflection, and *biaxiality*, orientational order in the plane perpendicular to the director. In the 1970s, Priest and Lubensky [1] recognized that a cholesteric liquid crystal must have some slight biaxial order because of the difference between the directions along and perpendicular to the helical axis. Brand and Pleiner [2] showed theoretically that chirality can smear out the transition between uniaxial and biaxial phases, and Kroin et al. [3] confirmed this smearing experimentally in lyotropic liquid crystals. Later, Harris, Kamien, and Lubensky [4] developed a microscopic model of molecules interacting through classical central-force interatomic potentials, and found that cholesteric twist can only form if there are at least short-range biaxial correlations between molecules. By comparison, in a system with quantum dispersive interactions, cholesteric twist can form even without such correlations [5–7].

In recent years, there has been a resurgence of interest in biaxial liquid crystals—driven in part by experimental reports of the discovery of a biaxial nematic phase in thermotropic liquid crystals [8, 9], and in part by prospects for using biaxial liquid crystals for fast-switching display devices [10]. For that reason, it is now important to re-examine the interplay between chirality and biaxiality in liquid crystals. The key issue is: How is the cholesteric pitch affected by biaxial order—either by long-range biaxial order or by short-range biaxial correlations?

In this paper, we investigate this issue through three theoretical approaches: (1) Monte Carlo simulations of a lattice model for chiral molecules interacting via anisotropic van der Waals forces. (2) Mean-field theory for the same lattice model. (3) Landau theory based on symmetry-allowed couplings between twist and biaxial order. Through all three approaches, we calculate the cholesteric twist as a function of molecular chirality, molecular biaxiality, and temperature. These calculations show that chirality acts as an effective field on the biaxial order, which changes the second-order uniaxial-biaxial transition into a rapid but nonsingular evolution. Conversely, biaxial order enhances the cholesteric twist, i.e. reduces the pitch, so that the pitch greatly decreases in the low-temperature, highly biaxial state. The calculations also allow us to reconsider the relationship between twist and short-range biaxial correlations. Based on this theoretical work, we discuss opportunities for experimental studies of chiral biaxial liquid crystals.

For the simulations, we need a model molecular structure that can exhibit biaxial order with or without chirality. Inspired by van der Meer et al. [5], we consider a structure with two ellipsoids arranged rigidly in the shape of the letter H. Each ellipsoid represents an extended, anisotropic charge distribution within the molecule. If the two ellipsoids are parallel, as in Fig. 1(a), this is an achiral biaxial structure, with a biaxiality characterized by the separation h. By contrast, if the ellipsoids are twisted about the central connector, as in Fig. 1(b), this is a chiral biaxial structure. The molecular chirality is measured by the twist angle 2χ between the ellipsoids, with χ as the angle of each ellipsoid from the parallel configuration. The connector is only a guide to the eye, and does not have any

FIG. 1: (a) Achiral and (b) chiral biaxial molecular structures studied in this work. (c) Cholesteric phase of chiral molecules, showing the macroscopic twist.

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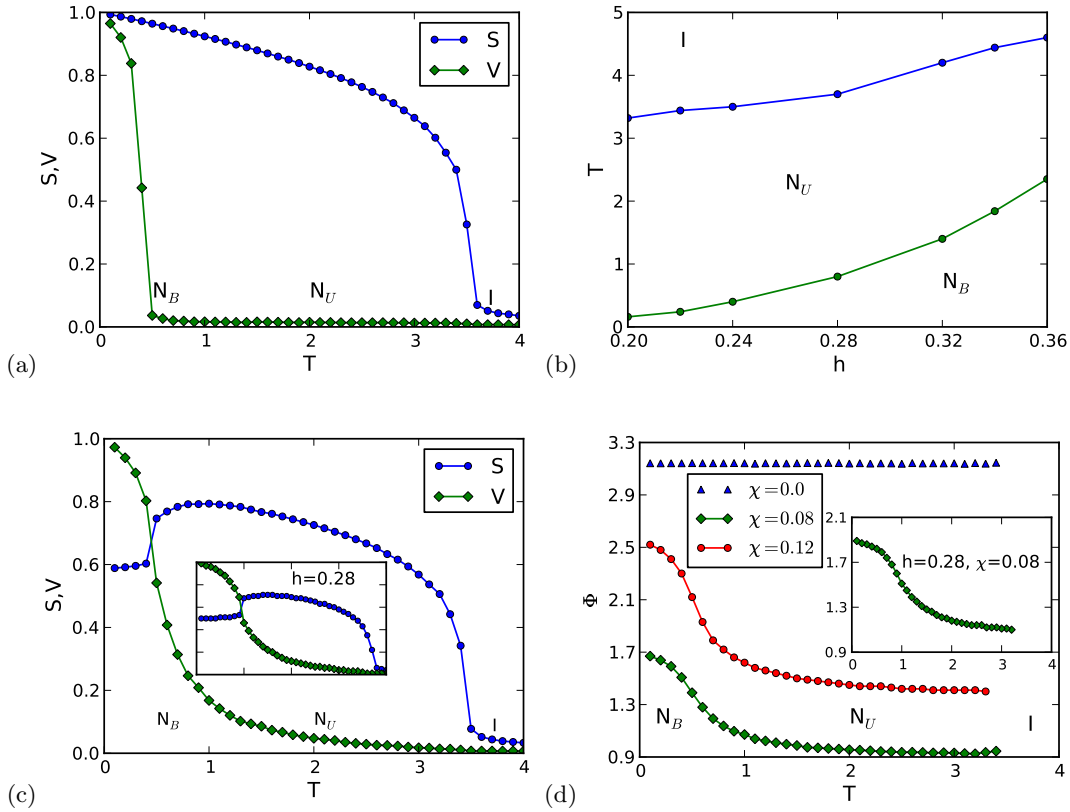

FIG. 2: Monte Carlo results: (a) Uniaxial and biaxial order parameters as functions of temperature T, for achiral biaxial molecules with ellipsoid separation $h = 0.24$. (b) Phase diagram for achiral biaxial molecules, in terms of h and T. (c) Order parameters as functions of T, for chiral biaxial molecules with $h = 0.24$ and molecular twist angle $\chi = 0.08$. (Inset shows results for $h = 0.28$ and $\chi = 0.08$, with axis labels same as main figure.) (d) Boundary twist angle Φ as a function of T. For achiral molecules, Φ is locked at π, indicating that system is not twisted. For chiral molecules, Φ is not a multiple of π, indicating that system is twisted, and cholesteric twist increases as T decreases. (Inset shows results for $h = 0.28$ and $\chi = 0.08$.)

interactions. The interaction between ellipsoids on neighboring molecules is the van der Waals dipole-induced-dipole interaction. Hence, the total interaction between two molecules i and j is the sum of four pairwise interactions among constituent ellipsoids,

$$U_{ij} = -A \sum_{\alpha,\beta=1,2} \frac{(\hat{\boldsymbol{e}}_{i\alpha} \cdot \hat{\boldsymbol{e}}_{j\beta})^2}{r^6_{i\alpha,j\beta}}, \tag{1}$$

where $\hat{\boldsymbol{e}}_{i\alpha}$ is the orientation of ellipsoid α on molecule i, and $r_{i\alpha,j\beta} = |\boldsymbol{r}_{j\beta} - \boldsymbol{r}_{i\alpha}|$ is the center-to-center distance between two interacting ellipsoids $i\alpha$ and $j\beta$.

Initially, we perform Monte Carlo simulations of *achiral* biaxial molecules. We simulate a simple cubic lattice of size $16 \times 16 \times 16$, with a molecule centered on each lattice site. In each Monte Carlo step, a molecule is randomly selected and its orientation is changed, following the standard Metropolis algorithm. The uniaxial order parameter S and biaxial order parameter V are calculated as described by Bates and Luckhurst [11]. For small ellipsoid separation h, we find a first-order transition from isotropic (I) to uniaxial nematic (N_u), followed by a second-order transition to biaxial nematic (N_b) at lower temperature. The temperature range of the biaxial nematic phase increases with h, as expected for board-shaped molecules. Figure 2(a) shows a sample plot of the order parameters for $h = 0.24$, and Fig. 2(b) shows the full simulated phase diagram.

We now use the same approach to simulate *chiral* biaxial molecules. In this system, we expect molecular chirality to induce a cholesteric twist. This twist is generally not consistent with periodic boundary conditions. Hence, we use self-adjusting twisted boundary conditions in the z-direction, following the method of Memmer [12]. In this method, the boundary twist angle Φ from the top to bottom of the cell is a free simulation variable, determined by the Monte Carlo process. In an untwisted system, Φ must be a multiple of π. Hence, the deviation of Φ from a multiple of π is

a measure of the twist across the system, i.e. the inverse pitch. With this method, the simulation forms a cholesteric phase over a wide temperature range. A sample configuration showing the molecular orientations along the z-axis is shown in Fig. 1(c).

Using these simulations, we determine the uniaxial and biaxial order parameters for systems of chiral molecules. Figure 2(c) shows S and V as functions of temperature T for ellipsoid separation $h = 0.24$ and molecular twist angle $\chi = 0.08$. At $T = 3.4$ there is a first-order transition from isotropic to cholesteric, as seen from the jump in S. In the cholesteric phase there is a slight nonzero value of V, as expected from Ref. [1]. As T decreases further, V gradually increases toward its maximum value of 1. There is no phase transition between uniaxial and biaxial, but only a nonsingular increase in V. Apparently the chirality acts as an effective field on the biaxial order, which smears out the N_u-N_b transition. (For comparision, the inset shows simulation results for a larger $h = 0.28$, which are consistent with the results for $h = 0.24$.)

We also determine the boundary twist angle Φ as a function of T, as shown in Fig. 2(d). For achiral molecules, this angle is locked at $\Phi = \pi$, indicating that the system is in a uniform nematic phase, either uniaxial or biaxial. By contrast, for chiral molecules with $\chi = 0.08$ or 0.12, the results for Φ show a twisted cholesteric phase. The cholesteric twist is substantial just below the isotropic-cholesteric transition, although the biaxial order parameter is very small there. The twist increases further as T decreases, and becomes largest in the temperature range that *would be* the biaxial phase for an achiral system. Thus, we see that the cholesteric twist and the biaxial order increase together, reinforcing each other, as T decreases. (The inset shows similar behavior is observed for molecules with a larger $h = 0.28$.)

In addition to the long-range biaxial order, we measure the short-range biaxial correlations as a function of distance between nearby lattice sites. Through most of the cholesteric temperature range, these biaxial correlations are very small; they do not become noticeable until slightly above the achiral N_u-N_b transition temperature.

To compare with the simulations, we construct a Maier-Saupe-type mean-field theory for the same lattice model, following a method similar to our calculation for the flexoelectric effect [13]. Here, we assume the system has perfect order of the long axes of the molecules, but variable biaxial order and variable cholesteric twist. Suppose that site i has its long axis along the x-direction, as do the four neighbors in the xy-plane, while the two neighbors in the z-direction have long axes twisted about the z-axis. The long axis at site i is $\hat{\boldsymbol{n}}_i = (1, 0, 0)$, while the long axes of the neighbors are $\hat{\boldsymbol{n}}_{\pm x} = (1, 0, 0)$, $\hat{\boldsymbol{n}}_{\pm y} = (1, 0, 0)$, and $\hat{\boldsymbol{n}}_{\pm z} = R_z(\pm\Delta\theta)(1, 0, 0)$, where $\Delta\theta$ is the cholesteric twist from one layer to the next and $R_z(\Delta\theta)$ is the rotation operator about the z-axis. At each site, the molecular short axis must be in the plane perpendicular to the long axis. Hence, the short axis at site i is $\hat{\boldsymbol{b}}_i = (0, \sin\phi_i, \cos\phi_i)$, while the short axes of the neighbors are $\hat{\boldsymbol{b}}_{\pm x} = (0, \sin\phi_{\pm x}, \cos\phi_{\pm x})$, $\hat{\boldsymbol{b}}_{\pm y} = (0, \sin\phi_{\pm y}, \cos\phi_{\pm y})$, and $\hat{\boldsymbol{b}}_{\pm z} = R_z(\pm\Delta\theta)(0, \sin\phi_{\pm z}, \cos\phi_{\pm z})$, where the local angle ϕ represents the azimuthal angle of the short axis.

We now construct a distribution function for the local azimuthal angle ϕ, which can be written as

$$\rho(\phi) = \frac{\exp(C\cos 2\phi)}{\int_0^{2\pi} d\phi \exp(C\cos 2\phi)}, \tag{2}$$

where C is a variational parameter representing the effective biaxial potential. It is related to the biaxial order parameter by $V = \int_0^{2\pi} \cos(2\phi)\rho(\phi)d\phi$. With this distribution function, the mean-field free energy per site can be written as the sum of energetic and entropic terms,

$$F = \langle H \rangle + k_B T \langle \log \rho \rangle, \tag{3}$$

where $\langle H \rangle$ is the average interaction energy of Eq. (1) between site i and its six neighbors. This free energy depends on two variational parameters (effective biaxial potential C and cholesteric twist $\Delta\theta$), two molecular parameters (ellipsoid separation h and molecular chirality χ), and temperature T (in units of interaction strength A). We numerically minimize the free energy over the variational parameters for each set of molecular parameters and temperature, to find the biaxial order and twist.

The numerical mean-field results are consistent with the Monte Carlo simulations. For *achiral* biaxial molecules, the system has a uniaxial phase with $V = 0$ at high temperature. As a critical temperature, it undergoes a second-order transition to a biaxial phase with $V \neq 0$, and the biaxial order parameter increases as a power law as T decreases. This achiral system is untwisted, with $\Delta\theta = 0$ for all T. By contrast, for *chiral* biaxial molecules, the system has a high-temperature cholesteric phase with a small but nonzero value of V. As T decreases, V increases gradually, without any phase transition between uniaxial and biaxial. The cholesteric twist $\Delta\theta$ is substantial at high temperature, even when V is small, and it increases further as T decreases, as shown by crosses in Fig. 3. Thus, as in the simulations, we see that the chirality acts as a field that induces biaxial order and smears out the N_u-N_b transition, and conversely, the biaxial order increases the cholesteric twist.

For further insight into the relationship between cholesteric twist and biaxial order, we construct a Landau theory for a chiral biaxial liquid crystal. As in the mean-field theory above, we suppose the system has perfect uniaxial order along

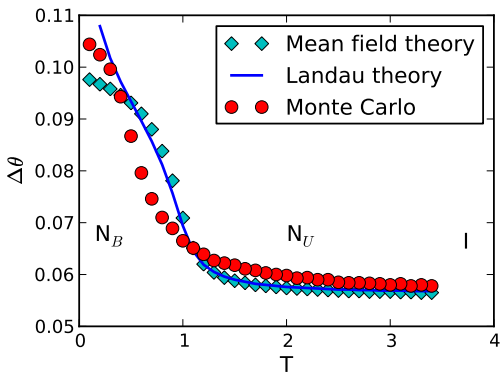

FIG. 3: Theoretical results for cholesteric twist as a function of temperature (in units of interaction strength A): Monte Carlo simulations, mean-field theory, and Landau theory.

the local axis $\hat{\boldsymbol{n}}(\boldsymbol{r})$, but variable biaxial order. The biaxial order can be described by the tensor $B_{ij} = V(b_i b_j - c_i c_j)$, where V is the magnitude of the order, and $\hat{\boldsymbol{b}}(\boldsymbol{r})$ and $\hat{\boldsymbol{c}}(\boldsymbol{r})$ are the two principal axes orthogonal to $\hat{\boldsymbol{n}}(\boldsymbol{r})$. The free energy can then be expanded in B_{ij} and in gradients of $\hat{\boldsymbol{n}}(\boldsymbol{r})$, to obtain

$$\begin{aligned} F &= \tfrac{1}{2}K(\partial_i n_j)(\partial_i n_j) - Kq_0\epsilon_{ijk}n_i\partial_j n_k \\ &\quad + \tfrac{1}{4}r(T - T_{\rm UB})\mathrm{Tr}(B^2) + \tfrac{1}{8}s\mathrm{Tr}(B^4) + \tfrac{1}{12}t\mathrm{Tr}(B^6) \\ &\quad - u\epsilon_{ijk}B_{jl}n_i\partial_l n_k - w\epsilon_{ijk}B_{jl}n_i\partial_k n_l \end{aligned} \tag{4}$$

In this expression, the first line is the Frank free energy for director gradients in a chiral liquid crystal, the second line is a power series expansion in B_{ij}, and the third line is a pair of chiral couplings between B_{ij} and director gradients. If we now assume a cholesteric modulation of the form $\hat{\boldsymbol{n}} = (\cos qz, \sin qz, 0)$, $\hat{\boldsymbol{b}} = (0, 0, 1)$, and $\hat{\boldsymbol{c}} = (-\sin qz, \cos qz, 0)$, with an arbitrary twist wave vector q, the free energy simplifies to

$$\begin{aligned} F &= \tfrac{1}{2}Kq^2 - Kq_0 q + \tfrac{1}{2}r(T - T_{\rm UB})V^2 + \tfrac{1}{4}sV^4 + \tfrac{1}{6}tV^6 \\ &\quad - (u + w)Vq. \end{aligned} \tag{5}$$

In the limit of high temperature, where biaxial order is small and the s and t terms are negligible, we minimize this free energy over V and q to obtain

$$V \approx \frac{(u + w)q_0}{r(T - T_{\rm UB})}, \tag{6a}$$

$$q \approx q_0 + \frac{(u + w)^2 q_0}{Kr(T - T_{\rm UB})}. \tag{6b}$$

Equations (6) demonstrate that the twist q acts as a field on the biaxial order V, and conversely, the biaxial order increases the twist, and hence reduces the pitch.

Instead of treating the Landau coefficients as purely phenomenological, we can derive them from the lattice model presented in this paper, by expanding the free energy (3) in powers of biaxial order and twist. For example, the Vq coupling coefficient is $u + w \approx 14Ah^3 \sin 2\chi + 12Ah \sin 4\chi + 105Ah^3 \sin 4\chi$. Results of this calculation are shown by the solid line in Fig. 3. The predictions of Landau theory are consistent with simulation and mean-field results, except at low temperature where biaxial order is large and series expansion is unreliable.

To interpret these results, it is important to distinguish between *short-range* biaxial correlations between neighboring molecules and *long-range* biaxial order:

(a) For systems with classical central-force interactions, Ref. [4] argued that short-range biaxial correlations are needed to produce a cholesteric twist. By contrast, for systems with quantum dispersive interactions, Refs. [5–7] found that such correlations are not needed for a cholesteric twist. Here, using non-central-force, dispersive interactions, we find a cholesteric twist even within mean-field theory, even without short-range biaxial correlations, consistent with Refs. [5–7]. This result draws attention to the fact that most liquid crystals have quantum dispersive interactions, while central-force interactions are unusual. (To be sure, quantum dispersive interactions are derived from fluctuating microscopic central-force interactions among electrons, and these electrons might have some biaxial correlations, but this microscopic origin of the interactions is not observable in experiments or simulations.)

(b) Our results show there is not a cause-and-effect relationship between long-range biaxial order and cholesteric twist, but rather a mutually reinforcing interaction between them. Twist acts as a field on biaxial order, so any twist gives nonzero biaxial order. Conversely, biaxial order combined with molecular chirality increases the twist; it does not induce twist in an achiral system but enhances twist in a chiral system. As temperature decreases, biaxial order and twist increase together.

The theory presented here has implications for experiments on biaxial liquid crystals, either thermotropic or lyotropic. It should be possible to choose an achiral host that has a uniaxial-biaxial transition, and add a chiral dopant. The theory predicts that the dopant will induce a small twist (large pitch) in the uniaxial phase, but the twist will increase (pitch will decrease) as the uniaxial-biaxial transition is approached. For low dopant concentration the twist will diverge as $(T - T_{\mathrm{UB}})^{-1}$, while for larger concentration the divergence will be more rounded. At the same time, the chiral dopant will smear out the uniaxial-biaxial transition. The chirality-induced rounding of the uniaxial-biaxial transition has been observed in lyotropics [3], but has not yet been investigated in thermotropics. Moreover, to our knowledge, no experiments have yet examined the cholesteric twist around the uniaxial-biaxial transition in either thermotropics or lyotropics. This should be a promising area for experimental research, to further characterize the close relationship between chirality and biaxiality.

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