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Tetrahedric cross-couplings: novel physics for banana liquid crystals

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Abstract

Liquid crystal phases (LCs) formed by achiral bent-core molecules (banana LCs) are distinguishable from those of their classical (i.e., rod/disc-shaped) counterparts with only quadrupolar order. We argue that the interplay between tetrahedric (octupolar) and quadrupolar order clarifies the physics of banana LCs sufficiently to account for two effects only observed in achiral banana LCs: a 100 times larger field-induced anisotropy than observed in classical LCs and ambidextrous chirality where left- and right-handed chiral domains co-exist.

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1. Introduction

Symmetry allowed cross-coupling terms in a free energy are often the driving forces, behind new physical phenomena studied in complex systems such as liquid crystals, polymers and elastomers, colloidal suspensions and biologically relevant fluids. Here, we analyze the consequences of symmetry allowed cross-couplings with [1,2] and without electric fields, between the octupolar tetrahedric order parameter, T_{ijk} [3], and the familiar quadrupolar orientational order parameter, Q_{ij} , of rod and/or disc-shaped liquid crystals [4]. With this analysis, we account for two observations that have only been observed in liquid crystal phases exhibited by achiral bent-core molecules (banana liquid crystals) [5–8] and which cannot be understood using only the physics developed for rod/disc liquid crystals, i.e., Q_{ij} .

The first observation is that an external electric field (\mathbf{E}) can induce in an ‘isotropic’ liquid an anisotropic liquid (i.e., $Q_{ij} \neq 0$) [5]. The remarkable aspects of this observation are the size of the effect (nearly two orders of magnitude larger than observed in field-induced enhancements of rod/disc-shaped liquid crystals) and that the increase in transition temperature to the isotropic liquid state, ΔT_c , scaled with E . When the field was switched off, the isotropic phase reappeared within seconds. Such an enhancement of a liquid crystal phase, linear in the electric field, cannot be understood invoking only quadrupolar order. However, it can be understood by assuming that the ‘isotropic’ phase is actually tetrahedric. (This allows a transition into the genuine isotropic phase at an even higher temperature.) The classical orientational order parameter, Q_{ij} , can then arise because of a coupling between the tetrahedric order parameter, T_{ijk} , and an external electric field, \mathbf{E} [2].

In the second example, left- and right-handed chiral domains have been reported for a nematic phase in compounds composed of achiral bent-core molecules [6,7]. Very recently, the Hull group has seen this behavior for another class of compounds as well [8,9]. Here, we show that by including in the free energy a term coupling quadrupolar orientational order with tetrahedric octupolar order provides an explanation for ambidextrous chirality. This term contains one spatial gradient and leads to an overall energy reduction that is the same for left- and right-handed helices. As a result, achiral banana liquid crystals can show coexisting left- and right-handed domains.

Clearly, the classical way of obtaining spontaneous twist as in cholesteric (chiral molecules with no positional order) or chiral smectic liquid crystals (layered, i.e., 1D positional order) [10] does not apply to achiral banana compounds. The key issue is: how does this picture change when going to liquid crystalline phases formed by achiral banana-shaped molecules? Being achiral, in the absence of an external field, a pseudoscalar corresponding to a helix structure cannot be associated with terms involving only one gradient.

Starting with the prediction of liquid crystalline phases with lower symmetries composed of achiral bent-core molecules [11], the field of banana liquid crystals rapidly expanded [12–21]. In particular, the B7 phase [14], whose ground state is still puzzling, attracted a great deal of attention [13,14,16–19,22–26] because it exhibited effects not observed in classical liquid crystal phases. Stimulated by the experimental

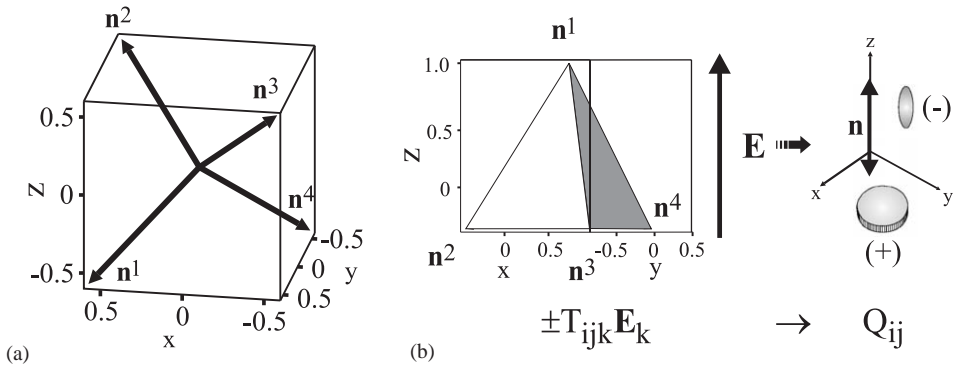


Fig. 1. Tetrahedral order parameter, T_{ijk} , lacks inversion symmetry. (a) The Fel orientation [3], (b) T_{ijk} is oriented with $\mathbf{n}^1 \parallel \hat{z}$. Applying a field, $\mathbf{E} \parallel \hat{z}$, results in uniaxial orientational order $\parallel \hat{z}$ [2].

observations on the B7 phase, as well as by the multitude of new liquid crystalline phases formed by banana-shaped molecules in general, the issue of possible tetrahedral order and its consequences came into focus (Fig. 1). It became clear that quadrupolar order alone was not enough to organize phenomena observed in achiral banana liquid crystals [1,2,27,28]. Tetrahedral banana liquid crystals thus opens a new field of complex materials research.

2. Phase transitions induced by an electric field

The order parameter of a tetrahedral phase is a third-rank tensor,

$$T_{ijk} = \sum_{\alpha=1}^4 n_i^\alpha n_j^\alpha n_k^\alpha \tag{1}$$

with $\alpha = 1, 2, 3$ or 4 [3] (Fig. 1). T_{ijk} is symmetric in all indices and odd under parity.

At first, static properties of the tetrahedral phase were studied [3]. In Refs. [3,27,28], the tetrahedral–nematic phase transition and possible nematic phases were investigated using a Landau expansion and renormalization group analysis. Following our observations on the B7 phase [23,24], we analyzed tetrahedral dynamics under fields and flow [1]. This was the first hint of the large variety of symmetry allowed coupling terms available to T_{ijk} . Very recently, in the framework of macroscopic dynamics, we studied what happens to a tetrahedral phase should it be deformable, i.e., a phase that is tetrahedral in the absence of an electric field, but for which external electric fields and flows can change the tetrahedral angles [2].

We now focus on the remarkable observation described in Ref. [5], using a DC electric field, where it was possible to induce a liquid crystalline phase up to about 10K above the isotropic-liquid crystal phase transition temperature, T_c^0 in the

field-free case. To leading order, the generalized energy of the tetrahedric phase takes the form

$$f_t = f_0 + f_T + f_Q - \Gamma T_{ijk} E_i Q_{jk}, \quad (2)$$

where we consider only spatially homogeneous terms. Later, in the discussion on ambidextrous chirality, we include terms containing one spatial gradient. f_0 is associated with terms not containing T_{ijk} or the usual quadrupolar orientational order parameter, Q_{ij} [4]. f_T contains the usual terms that are quadratic and quartic in T [3,27,28] and f_Q has the form

$$f_Q = \frac{\epsilon}{2} Q_{ij} Q_{ij} + O(Q^3). \quad (3)$$

Terms of cubic and higher order, well-known from studies of the isotropic–nematic phase transition [4], are not explicitly written here because we assume that we start out in the tetrahedric phase so only need lowest order coupling terms. The last term in Eq. (2) is new and couples an electric field to the tetrahedric order parameter, T_{ijk} , and the usual orientational order parameter, Q_{ij} . Its coefficient, $\sim \Gamma$, is a true scalar, as Q_{ij} is even under parity, while both E_i and T_{ijk} are odd under parity. This term does not exist for magnetic fields which are even under parity and odd under time reversal.

To investigate the implications of this coupling term, we analyze what happens when an electric field is applied to an optically isotropic tetrahedric phase. Minimizing Eq. (2) with respect to Q_{ij} we find

$$Q_{ij} = \frac{\Gamma}{\epsilon} E_k T_{ijk}. \quad (4)$$

To make this result more explicit, we consider an electric field applied $\parallel \hat{z}$, $\mathbf{E} = E_0 \hat{z}$. For the four unit vectors of the tetrahedric phase we use the [2] orientation (Fig. 1b), which minimizes the energy [2], where \mathbf{n}^1 is also $\parallel \hat{z}$: $\mathbf{n}^1 = (0, 0, 1)$, $\mathbf{n}^2 = \frac{1}{3}(-\sqrt{2}, -\sqrt{6}, -1)$, $\mathbf{n}^3 = \frac{1}{3}(-\sqrt{2}, \sqrt{6}, -1)$ and $\mathbf{n}^4 = \frac{1}{3}(2\sqrt{2}, 0, -1)$. Then from Eq. (4), we obtain for the diagonal elements of Q_{ij} :

$$Q_{xx} = Q_{yy} = -\frac{1}{2} Q_{zz} = \frac{4\Gamma}{9\epsilon} E_0 \quad (5)$$

while all off-diagonal elements of Q_{ij} vanish. The structure of Eq. (5) is that of a uniaxial nematic [4]. Depending on the sign of Γ the induced nematic order is rod- or disk-like (Fig. 1b).

From this analysis, we arrive at three main conclusions: (1) the application of a DC electric field to an optically isotropic tetrahedric phase leads to the generation of quadrupolar orientational order of the type familiar from nematic liquid crystals formed by rod/disc-shaped molecules; (2) the degree of induced orientational order is proportional to the strength of the applied electric field, E_0 ; and (3) putting $\epsilon = \epsilon_o(T_c^E - T_c^0)/T_c^0$, we find the enhancement in the liquid crystal transition temperature, $\Delta T_c \sim E_0$, as observed [5].

Once quadrupolar order is established, it is well documented where conditions must be met in a Landau approach to obtain simultaneously a density wave thus giving rise to a smectic phase. Depending on the coefficients one gets a transition

from an isotropic phase to a nematic phase, a smectic A phase or a smectic C phase [29]. Birefringence found in Ref. [5] suggests that a tilted phase is present.

We note that the explanation of the field-induced transition given in Ref. [5] does not apply, since it uses a $\vec{P} \cdot \vec{E}$ term. In an optically isotropic system, there can be no vector like \vec{P} , which would make the phase uniaxial and no longer isotropic. In addition, we are not dealing with a ferroelectric phase transition, where \vec{P} would be the order parameter.

In summary, the application of an electric field to an isotropic tetrahedric phase induces quadrupolar orientation order, i.e., an optically uniaxial or biaxial phase. Thus, the experimental observations in Ref. [5], finds an explanation if the ‘isotropic’ phase observed in Ref. [5] is actually tetrahedric. To test this, it would be important to study the ‘isotropic’ phase as well as the field-induced liquid crystal phase by, for example, X-ray investigations of well oriented samples. Furthermore, we suggest measuring directly the quadrupolar order parameter as a function of the electric field, \vec{E} , would confirm the validity of Eq. (5). An additional tool to distinguish between an optically isotropic tetrahedric phase and a truly isotropic liquid would be the observation of second harmonic generation (SHG). In contrast to a truly isotropic phase, SHG can occur in an isotropic tetrahedric phase because it lacks inversion symmetry.

3. Ambidextrous chirality: counter-rotating helices of tetrahedric and quadrupolar order

We now turn to the challenge posed by ambidextrous chirality. First we recall that classical cholesteric phases composed of chiral molecules are never ambidextrous. Rather, the director, \mathbf{n} , spontaneously twists with a preferred hand always. Taking the helix wave vector $\mathbf{q}_o \parallel \hat{z}$ ($q_o > 0$ describes a right-handed helix), we put $\mathbf{n} = (\cos q_o z, \sin q_o z, 0)$ and $Q_{ij} = Q(T)(\mathbf{n}_i \mathbf{n}_j - \frac{1}{3} \delta_{ij})$ to get an additional term in the generalized energy [4,10] of the form $f_{chol} = K_2 q_o \varepsilon_{ijk} Q_{it} \nabla_k Q_{jt} = K_2 q_o \mathbf{n} \cdot (\nabla \times \mathbf{n})$. K_2 is the twist elastic constant and $q_o = 2\pi/P_o$ with P_o the helix pitch. Here, q_o is a pseudoscalar because cholesterics have no mirror planes.

In the following, we assume that the existence of tetrahedric order is important for nematic phases formed by banana-shaped molecules and we explore possible gradient terms in the generalized energy, in particular a coupling between the tetrahedric order parameter, T_{ijk} , and the orientational order parameter, Q_{ij} , containing only one spatial gradient.

Without an external electric field, we find one such cross-coupling term

$$f_{grad} = \mathcal{D} T_{ijk} \nabla_k Q_{ij}. \quad (6)$$

The structure of this new contribution [30], Eq. (6), is clearly very different from the spontaneous twist term familiar from cholesterics [10]. A pseudoscalar such as q_o does not emerge. The coefficient, $\sim \mathcal{D}$, is a true scalar as T_{ijk} and $\nabla_k Q_{ij}$ are odd under parity. A hand is not associated with Eq. (6) and the phase is achiral.

To check if Eq. (6) provides an explanation for the observation of the coexistence of left- and right-handed chiral domains (ambidextrous chirality) in the nematic order parameter Q_{ij} , we start with a helical director (with pitch q and arbitrary phase shift ϕ with respect to the orientation of the tetrahedra): $\mathbf{n} = (\cos[qz + \phi], \sin[qz + \phi], 0)$. Next we rotate the tetrahedric (Fig. 1a) also about the \hat{z} -axis, but by kz , and get the only non-vanishing elements for T_{ijk} : $T_{113} = -\frac{4}{3\sqrt{3}} \sin 2kz$, $T_{223} = \frac{4}{3\sqrt{3}} \sin 2kz$ and $T_{123} = -\frac{4}{3\sqrt{3}} \cos 2kz$. Finally, we evaluate the expression $T_{ijk} \nabla_k Q_{ij}$ using the rotating tetrahedric and director given above to get

$$\mathcal{D}T_{ijk} \nabla_k Q_{ij} = -\frac{8}{3\sqrt{3}} \mathcal{D}q \cos(2qz + 2kz + 2\phi). \tag{7}$$

For $q = -k$, Eq. (7) is a scalar invariant of the energy density:

$$\mathcal{D}T_{ijk} \nabla_k Q_{ij} = -\frac{8}{3\sqrt{3}} \mathcal{D}q \cos(2\phi). \tag{8}$$

Physically, Eq. (8) describes two counterrotating helices (Fig. 2). If the helix for Q_{ij} is right-handed, the helix for tetrahedric order is left-handed and vice versa.

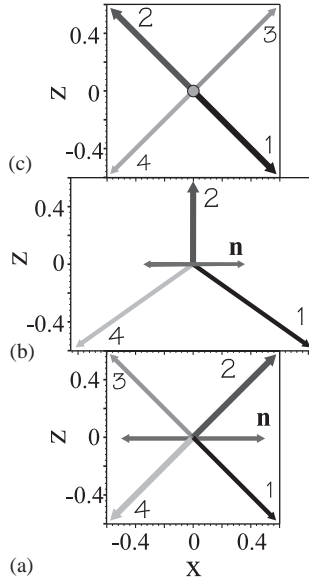


Fig. 2. A quarter pitch left-handed rotation for the isotropic tetrahedric (1, 2, 3 and 4 refer to the vectors in Fig. 1a) and a right-handed rotation of discs/rods for \mathbf{n} (2-headed arrow) shown in the \hat{x} - \hat{z} -plane ($\phi = 0$). (a) $qz = 0$: \mathbf{n} is in the \hat{x} - \hat{z} plane and $\pm\pi/4$ to the projections of the [2,3] and [1,4] tetrahedric 2-fold axes in this plane. (b) $qz = \pi/4$: the [1,4]-2-fold axis is in the \hat{x} - \hat{z} plane and the [2, 3] 2-fold axis is \perp to it. (c) $qz = \pi/2$: \mathbf{n} is \perp \hat{x} - \hat{z} plane.

To check the energy change relative to the homogeneous state associated with the formation of two counter-rotating helices, we analyze the energy up to quadratic order in the gradients:

$$F = F_0 + \mathcal{D}T_{ijk}\nabla_k Q_{ij} + \gamma(\nabla_k Q_{ij})^2 + \delta(\nabla_k T_{ijl})^2, \quad (9)$$

where F_0 contains the spatially homogeneous terms in T_{ijk} and Q_{ij} . Minimization with respect to the wave vector, q , gives the result

$$q_c = \frac{2\mathcal{D}}{3\sqrt{3}} \frac{\cos(2\phi)}{\gamma + 64\delta/27}, \quad (10)$$

which is a wave vector directly proportional to \mathcal{D} —or, equivalently, a length scale that diverges for $\mathcal{D} \rightarrow 0$. Inserting the value for q_c in Eq. (9), we find an energy reduction, $\Delta f = -8(\mathcal{D} \cos(2\phi))^2/(27\gamma + 64\delta)$, independent of the sign of \mathcal{D} . This energy reduction is maximum (the energy minimum) for $\cos 2\phi = \pm 1$, or a phase shift of 0 and $\pi/2$ between the (opposite) rotations of Q_{ij} and T_{ijk} . The two cases belong to two different hands of q_c (Eq. (10)), but equal $|q_c|$.

We have shown that the generation of counter-rotating helices for the usual orientational order parameter, Q_{ij} , and the tetrahedric order parameter, T_{ijk} , always leads to a reduction of the energy provided tetrahedric order is present. Both hands are equally likely for T_{ijk} and Q_{ij} with the same reduction in energy. This provides an explanation for the observations described in Refs. [6–8].

The contribution from the rotation of T_{ijk} to optical anisotropy is presumed to be very small as without a helix structure, T_{ijk} is optically isotropic. As a result, the anisotropy of the refractive index for this system is dominated by the orientational order parameter Q_{ij} .

From this analysis, we conclude that the coexistence of left- and right-handed chiral domains is compatible with the simultaneous presence of tetrahedric and the classical orientational order. With only orientational order and achiral molecules, co-existing chiral domains of both hands cannot be explained.

Cubic terms that could produce lock-in between orientations contained in Q_{ij} and T_{ijk} , for example, $Q_{ij}T_{ikl}T_{jkl}$, must vanish identically. This is because a second rank tensor cannot be constructed out of T_{ijk} [31], thus, $T_{ikl}T_{jkl} \sim \delta_{ij}$. And, as Q_{ij} is traceless, $\delta_{ij}Q_{ij} \sim 0$.

We point out that the analysis given for the lowest-order gradient terms can be carried over to orthorhombic non-polar biaxial nematic phases as well as to biaxial orthogonal fluid smectic phases [9]. If one observes ambidextrous chiral domains in a material composed of nonchiral molecules, then the coupling mechanism presented above can apply. One candidate for this type of behavior has been discussed very recently by the Hull group for a ‘smectic C type’ liquid crystal phase [32].

In contrast to other work on chiral phases for tetrahedratics [28], we deal with achiral phases. In the present manuscript, we have shown that counter-rotating helices for tetrahedric and quadrupolar order can reduce the energy of the system due to a linear gradient term not considered before. In Ref. [28] chiral phases have been considered with a fixed sense of rotation of the helices in each given phase.

4. Conclusions and perspective

We have discussed two coupling terms between the classical quadrupolar orientation order parameter and an isotropic octupolar order parameter. We found that an electric field can induce a liquid crystal phase in a tetrahedric liquid which is optically isotropic when the field is turned off. This analysis provides an explanation for recent experimental observations of a field-induced enhancement (up to 10 K) of the isotropic-liquid crystal transition temperature. In addition, we found that for a nematic phase where quadrupolar and tetrahedric order coexist, the lowest order gradient term leads to the induction of counter-rotating helices of the two types of order. As this structure is energetically more favorable than the uniform state, chiral domains of both hands can spontaneously appear giving rise to ambidextrous chirality. While this result provides an explanation—the only one known—for the recent experimental observation of ambidextrous chirality in various nematic phases formed by achiral banana-shaped molecules, it applies to any system where tetrahedric and quadrupolar order may simultaneously exist including layered and columnar liquid crystalline phases, biologically relevant lyotropic liquid crystals and colloidal suspensions.

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