

# Low Symmetry Tetrahedral Nematic Liquid Crystal Phases: Ambidextrous Chirality and Ambidextrous Helicity

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**Abstract.** We discuss the symmetry properties as well as the dynamic behavior of various non-polar nematic liquid crystal phases with tetrahedral order. We concentrate on systems that show biaxial nematic order coexisting with octupolar (tetrahedral) order. Non-polar examples are phases with  $D_2$  and  $S_4$  symmetries, which can be characterized as biaxial nematics lacking inversion symmetry. It is this combination that allows for new features in the statics and dynamics of these phases. The  $D_2$ -symmetric phase is chiral, even for achiral molecules, and shows ambidextrous chirality in all three preferred directions. The achiral  $S_4$ -symmetric phase allows for ambidextrous helicity, similar to the higher-symmetric  $D_{2d}$  symmetric phase. Such phases are candidates for nematic phases made from banana-shaped molecules.

## 1 Introduction

Ordinary nematic liquid crystal phases are described by the symmetric, traceless second-rank (quadrupolar) order parameter  $Q_{ij}$  [1, 2]. The use of tetrahedral (octupolar) order by a rank-3 order parameter tensor,  $T_{ijk}$  [3–5] to describe bent-core liquid crystal phases [6, 7] has by now a long tradition [8–13]. Here, we will discuss low symmetry phases that have both, tetrahedral and nematic order, and are non-polar. We only consider cases where the relative orientation of nematic and tetrahedral order is fixed, i.e. by strong coupling terms in the appropriate Ginzburg-Landau description. Opposite cases have been discussed in Ref. [11, 13].

The optically isotropic  $T_d$  phase shows a spontaneous breaking of orientational symmetry due to  $T_{ijk}$ , only, and serves to explain optically detected isotropic to isotropic phase transitions. When the tetrahedral order parameter is combined with a uniaxial nematic one, with the nematic director along one of the four-fold improper rotation axes of  $T_{ijk}$ , an optically uniaxial  $D_{2d}$ -symmetric phase (called D2d) results [14] that can explain the phase transition between two optically uniaxial bent-core liquid crystal phases. The symmetries and dynamics of the D2d phase has recently be discussed in detail by the present authors [14]. In the present manuscript we will discuss the hydrodynamics of phases that show a combination of tetrahedral order and biaxial nematic order, with one of the nematic directors along an improper four-fold tetrahedral symmetry axis, in particular phases of  $D_2$  and  $S_4$

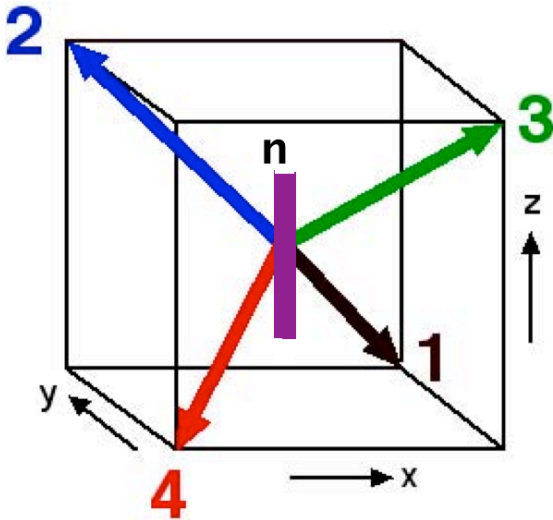
symmetry [3], which we will call D2 and S4 phases, respectively.

The principal difference between the conventional isotropic, uniaxial nematic and biaxial nematic phases on the one hand, and the  $T_d$ , D2d, and D2 and S4 phases on the other, is the lack of inversion symmetry in the latter ones due to their tetrahedral order, which changes sign,  $T_{ijk}$  to  $-T_{ijk}$ , under inversion. Somewhat less important, but manifest in some details is the overall lower symmetry that the tetrahedral phases have compared to their conventional, inversion-symmetric counter-parts. Both aspects will be dealt with in detail below. Another common feature of all these phases is their non-polarity, which is a result of the special mutual orientation of the nematic and tetrahedral axes. If a nematic axis is oriented along some (proper) tetrahedral rotation axes, which are described by polar vectors, the resulting phases (e.g. of  $C_{3v}$  and  $C_{2v}$ ) are polar. We will discuss those cases elsewhere.

The hydrodynamics of (these low symmetry) phases is solely based on their symmetry. Therefore, we first discuss those symmetries and the structures of the tetrahedral and nematic directors involved without relying on any model for a possible molecular packing. For the simpler phases there are some intuitive packing models, which we, however, do not explicitly need to use. It is also obvious that we only consider symmetry properties of the phases, not those of specific molecules, since it is well-known that the latter not necessarily coincide with the former, e.g. biaxial calamitic molecules rarely form biaxial nematic phases, or polar calamitic molecules mostly form non-polar nematic phases.

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**Fig. 1.** The 4 tetrahedral vectors  $\mathbf{n}^\alpha$  ( $\alpha = 1, 2, 3, 4$ ) from the origin to the tetrahedral corners. In the D2d phase the director  $\mathbf{n}$  is along the  $z$  axis, which remains to be an improper  $\bar{4}$  axis: rotation by  $\pi/2$  leads to a (non-equivalent) inverted structure, while an additional inversion (e.g.  $z \rightarrow -z$ ) restores the original structure. The  $x$  and  $y$  axes are 2-fold symmetry axes and the planes spanned by  $\mathbf{n}^1/\mathbf{n}^4$  and  $\mathbf{n}^2/\mathbf{n}^3$  are mirror planes (both contain  $\mathbf{n}$ ).

We only deal with phases made of achiral molecules, except for Sec. 4, where we briefly make the connection with the  $T$ -symmetric chiral tetrahedral phase T and where we make use of a specific packing model.

## 2 Symmetries

### 2.1 The D2d Phase

The tetrahedral order parameter  $T_{ijk} = \sum_{\alpha=1}^4 n_i^\alpha n_j^\alpha n_k^\alpha$  is expressed by 4 unit vectors,  $\mathbf{n}^\alpha$ , with  $\alpha = 1, 2, 3$  and 4, the position vectors of a tetrahedron. It is fully symmetric in all three indices and odd under parity, since the  $n^\alpha$ 's are (polar) vectors. Tetrahedral order by itself is non-polar, since  $T_{ikk} \equiv 0$ .  $T_{ijk}$  breaks rotational symmetry completely and the associated Goldstone modes (hydrodynamic variables) are its three (properly normalized) rotations  $\delta T_i \sim \epsilon_{ipq} T_{pkl} \delta T_{qkl}$ . In the D2d phase with the director,  $\mathbf{n}$ , rigidly attached to an improper  $\bar{4}$  axis, the broken rotational symmetry is the same. However, in that case it is more appropriate to use, as hydrodynamic variables, two rotations of the director,  $\delta \mathbf{n}$  with  $\mathbf{n} \cdot \delta \mathbf{n} = 0$ , and one rotation about  $\mathbf{n}$  [14]. The former are similar to those of ordinary uniaxial nematics, while the latter does not exist there, since rotational symmetry is not broken in the plane perpendicular to  $\mathbf{n}$  and  $\mathbf{n}$  is a continuous rotation axis. As a result, the overall symmetry is  $D_{\infty h}$  for uniaxial nematics and  $D_{2d}$  for the D2d phase where  $\mathbf{n}$  is an improper 4-fold axis. In both phases there are additionally 2 (degenerate and perpendicular) two-fold rotation axes, both perpendicular to  $\mathbf{n}$ , and 2 (degenerate)

mirror planes that include  $\mathbf{n}$  and – in the case of D2d – two opposite tetrahedral vectors, respectively, as depicted in Fig. 1. The presence of the director  $\mathbf{n}$  removes all 3-fold tetrahedral symmetry axes. The lower transverse symmetry of the D2d (compared to the uniaxial nematic) phase has some implications on the structure of several material tensors, e.g. there are 7 genuine quadratic Frank coefficients (rather than 3) and 6 ordinary viscosities (rather than 5) reflecting similarities to a tetragonal biaxial nematic phase. There are some specific nonlinear effects in the transverse rotational dynamics of the D2d phase, for which we refer to Ref. [14].

A more profound difference between a standard nematic and the D2d phase arises from the broken inversion symmetry in the latter. The outstanding feature is the existence of a linear gradient term in the free energy

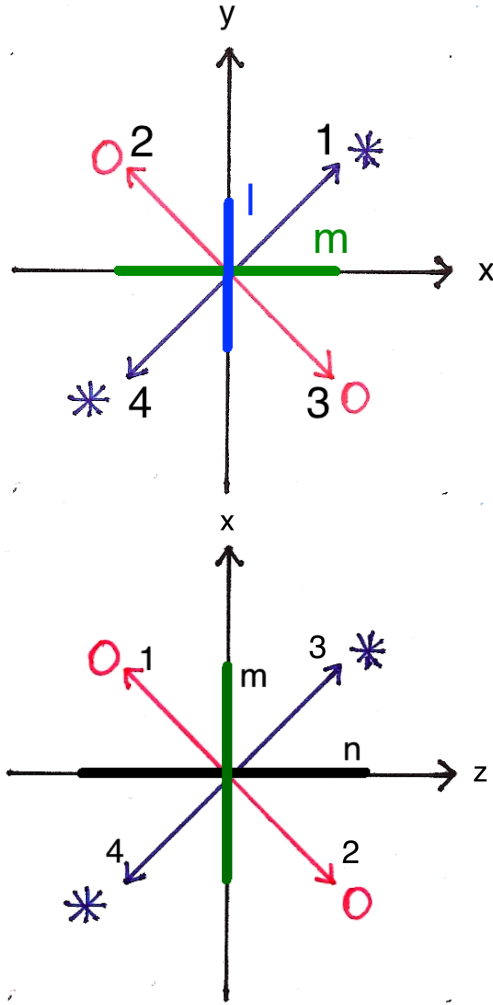
$$\varepsilon_l = \xi T_{ijk} n_i \nabla_j n_k, \quad (1)$$

which is neither related to linear splay (as in polar nematics), nor to linear twist, (as in chiral nematics), but involves the combination  $\nabla_x n_y + \nabla_y n_x$ . Generally, linear gradient terms have the tendency to favor energetically non-homogeneous ground states. In the D2d case these are helical structures of the director and the tetrahedral vectors along the  $x$  or the  $y$  axis (in Fig. 1). Left and right handed helices can be discriminated based on the distinction of a tetrahedron and its inverted structure. All these possible helices are energetically degenerate and the phenomenon has been called "ambidextrous chirality" in Ref. [14]. However, since D2d is not chiral, the name "ambidextrous helicity" is more appropriate.

There are hydrodynamic effects of the broken inversion symmetry already in the (optically) isotropic  $T_d$  phase, namely reversible cross-couplings between flow and the thermal, electrical, and solute degrees of freedom, i.e. electric fields, temperature and concentration gradients produce stresses, while symmetric velocity gradients give rise to electric, thermal, and concentration currents [8]. These effects are also present (in a uniaxial manner) in the D2d phase and can be expected in the lower symmetry tetrahedral nematic phases as well. To this group of broken-inversion effects also belong the odd-powered electric,  $\varepsilon_E \sim T_{ijk} E_i E_j E_k$ , and magnetic external field effect,  $\varepsilon_H \sim T_{ijk} H_i H_j E_k$  that give rise to electric field dependent effective dielectric and magnetic susceptibilities (and second harmonic generation). In the D2d phase there is a competition between the ordinary nematic dielectric anisotropy that aligns the director parallel or perpendicular to the field, and  $\varepsilon_E$  that favors alignment of a tetrahedral vector along the field – a situation incompatible with the structure of D2d leading to frustration and to possible reorientation effects as a function of the field strength [14].

### 2.2 The D2 Phase

A D2 phase is obtained by combining rigidly the tetrahedral vectors  $\mathbf{n}^\alpha$  ( $\alpha = 1, 2, 3, 4$ ) with an orthorhombic



**Fig. 2.** Two projections of the 4 tetrahedral vectors  $n^\alpha$  ( $\alpha = 1, 2, 3, 4$ ) and the orthorhombic directors  $l, m, n$  in the D2 phase. A circle (asterisk) denotes tetrahedral vectors that also have a component sticking out of (pointing into) the projection plane. Only three 2-fold symmetry axes (the  $x, y, z$  axes) are left, but no mirror planes.

biaxial nematic such that the (mutually orthogonal) directors  $l, m, n$  are along the three (improper)  $\bar{4}$  axes of the tetrahedron. In a Ginzburg-Landau description with the tetrahedral order parameter and the biaxial nematic one, the fourth order coupling term  $D_4 Q_{ij} Q_{kl} T_{mik} T_{mjl}$  exactly leads to this configuration as the minimum for  $D_4 > 0$ . In Fig. 2 2-dimensional projections of this structure with the nematic directors along the  $x, y, z$  axes are shown. Since the nematic directors in the orthorhombic case are not equivalent (e.g. there is no  $n \Leftrightarrow m$  invariance), the (improper) 4-fold symmetry axes are reduced to (proper) 2-fold ones. For the same reason, the mirror planes of the  $D_{2d}$  phase ( $n^1/n^4$  and  $n^2/n^3$ ) are removed and no mirror planes exist. A phase that only has (proper) rotation axes as symmetry elements is chiral, even if only achiral molecules are involved. Another example of this structural chirality would be the smectic  $C_{B2}$  ( $B2$ ) phase

of bent-core liquid crystals [15]. In the D2 phase the chirality is manifest by the existence of a pseudoscalar quantity

$$q_0 = n_i n_j m_k m_p l_q l_r \epsilon_{ikq} T_{jpr} \quad (2)$$

This definition is not unique and could have been replaced by  $q'_0 = n_i n_j m_k m_p l_q l_r \epsilon_{iqk} T_{jpr}$ , which is just  $-q_0$  denoting opposite handedness. It is a hallmark of these structurally chiral phases that both types of handedness are equal in the sense that there is no energetic preference for one or the other; this has been called "ambidextrous chirality" [16].

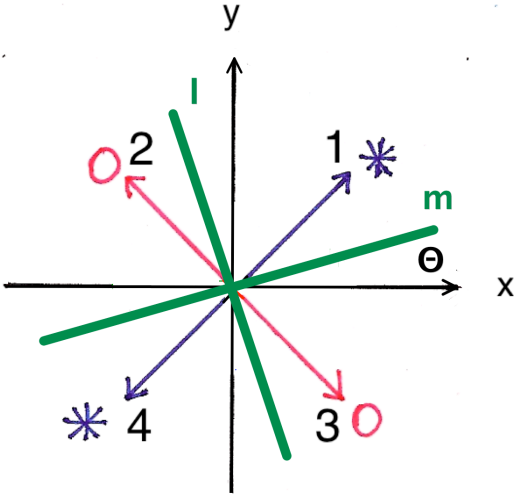
In the D2 phase the three independent rotations of the rigid structure are the hydrodynamic degrees of freedom (Goldstone modes), like in the D2d and in the biaxial nematic phases [17, 18]. We will use the biaxial nematic picture and describe these rotations by rotations of the directors  $l, m, n$  under the condition that their mutual orientation, and their orientation w.r.t. the tetrahedral vectors remains constant. This guarantees that only rigid rotations are involved, since internal deformations of the structure and relative rotations among parts of the structure are non-hydrodynamic and will not be considered here. However, compared to ordinary orthorhombic biaxial nematics, we have to take into account additional effects due to the broken inversion symmetry (because of  $T_{ijk}$ ) and due to chirality (because of  $q_0$ ). We can expect linear gradient terms in the free energy of the type present in the D2d phase ( $\epsilon_l$ ) as well as chiral linear twist terms of the cholesteric type. A full discussion of all broken inversion- and chirality-related hydrodynamic aspects will be given below.

### 2.3 The S4 Phase

Above, we have introduced the structure of the D2d phase as a uniaxial nematic director being along one of the  $\bar{4}$  axes of the tetrahedron. Equally well, the D2d phase can be described by adding a tetragonal biaxial nematic to the tetrahedron with the nematic preferred directions along the three  $\bar{4}$  tetrahedral directions. Since the two transverse directors  $m$  and  $l$  are equivalent (there is a  $m \Leftrightarrow l$  invariance), the tetragonal preferred direction  $n$  is the (improper) 4-fold rotation axis,  $m$  and  $l$  are the 2-fold symmetry axes and the planes set by  $n^1/n^4$  and  $n^2/n^3$  are the mirror planes.

Using this picture of the D2d phase it is easy to get to the S4 phase: Rotate the directors  $m$  and  $l$  in the plane transverse to  $n$  by a finite angle (other than  $\pi/4$  and  $\pi/2$ ) as in Fig. 3. It is obvious to see that due to this rotation the mirror planes are removed as well as both 2-fold rotation axes ( $x, y$  axes). Only the (improper) 4-fold symmetry axis ( $n$  or  $z$  axis) is left.

This phase is rather similar to the D2d phase. There is broken inversion symmetry due to  $T_{ijk}$  and ambidextrous helicity due to a linear gradient term in the free energy similar to Eq. (1). There is no chirality due to the existence of an improper rotation axis. It is easy to see that the pseudoscalar of the D2 phase,  $q_0$  Eq. (2), has to be zero



**Fig. 3.** The projection of the 4 tetrahedral vectors into the  $x, y$  plane perpendicular to the director  $\mathbf{n}$  in the S4 phase. The tetragonal nematic directors  $\mathbf{m}$  and  $\mathbf{l}$  are equivalent and rotated by an angle other than  $\pi/4$ , thereby removing any mirror planes as well as the 2-fold axes. The  $z$  axis remains to be an improper  $\bar{4}$  axis

in the S4 phase, because of the  $\mathbf{m} \Leftrightarrow \mathbf{l}$  equivalence (that requires  $q_0 = -q_0 = 0$ ).

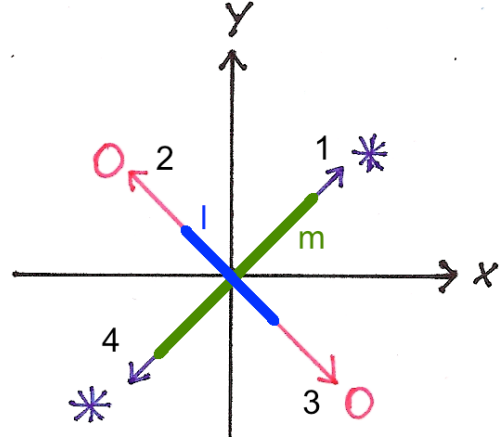
## 2.4 The $C_{2v}$ Phase

We have discussed the symmetry change from a D2d to a D2 phase by replacing the uniaxial nematic director with a orthorhombic biaxial one, such that the nematic preferred directions are along the  $\bar{4}$  axes of the tetrahedron. If the two biaxial directors  $\mathbf{m}$  and  $\mathbf{l}$  are along the projections of the tetrahedral vectors (i.e. rotated by  $\pi/4$  compared to the D2 case), a  $C_{2v}$ -symmetric phase ( $C_{2v}$ ) is obtained, Fig. 4. The former  $\bar{4}$  axis along  $\mathbf{n}$  is reduced to a (proper) 2-fold symmetry axis and the planes spanned by  $\mathbf{n}^1/\mathbf{n}^4$  and  $\mathbf{n}^2/\mathbf{n}^3$  are still mirror planes. Therefore, the  $C_{2v}$  phase is achiral, and the  $q_0$  defined in Eq. (2) vanishes, because  $n_i m_j l_k T_{ijk}$  is zero for this special orientation of the biaxial directors.

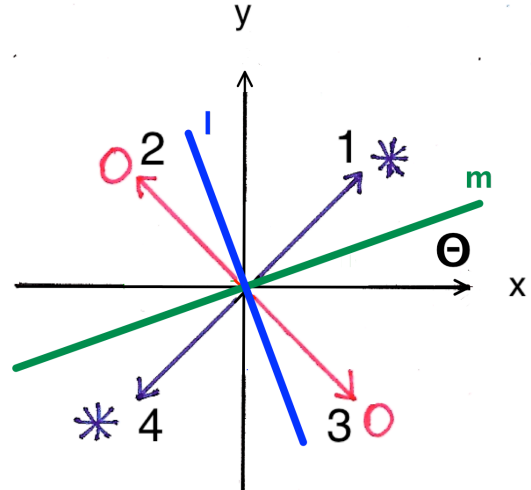
The  $C_{2v}$  phase is polar, with the polar axis along  $\mathbf{n}$  and given by  $T_{ijk}(m_j m_k - l_j l_k)$ . This polarity is neither connected to the polarity of the molecules, nor to that of external fields. In the S4 phase, such a vector does not exist, because of the tetragonal  $\mathbf{m} \Leftrightarrow \mathbf{l}$  invariance.

## 2.5 The $C_2$ Phase

The mirror planes of the  $C_{2v}$  phase can be removed, and the symmetry further reduced to  $C_2$ , if the biaxial directors are neither along the tetrahedral projections, nor along the  $x, y$  direction, Fig. 5. Only the 2-fold symmetry axis is left and therefore, the  $C_2$  phase is chiral with a nonzero pseudoscalar  $q_0$  given by Eq.(2). The 2-fold axis



**Fig. 4.** The projection of the  $C_{2v}$  structure into the  $x, y$  plane perpendicular to the director  $\mathbf{n}$ . The orthorhombic nematic directors  $\mathbf{m}$  and  $\mathbf{l}$  are rotated by  $\pi/4$  w.r.t. the  $x, y$  axes, thereby preserving the mirror planes  $\mathbf{n}^1/\mathbf{n}^4$  and  $\mathbf{n}^2/\mathbf{n}^3$ .



**Fig. 5.** As in Fig. 4, but with the orthorhombic nematic directors  $\mathbf{m}$  and  $\mathbf{l}$  rotated by an angle other than  $\pi/4$ , thereby removing any mirror planes. Only a 2-fold (proper) rotation axis, the  $z$  axis, remains as a symmetry element in the  $C_2$  phase.

is polar, as in the  $C_{2v}$  phase. Starting from an S4 phase, such a  $C_2$  phase is obtained by replacing the tetragonal biaxial directors by orthorhombic ones.

In smectic liquid crystals  $C_{2v}$ - and  $C_2$ -symmetric phases are rather frequent, e.g. the tilted smectic C phases, made of achiral and chiral calamitic molecules, respectively [2]. For bent-core smectic phases with a molecular polar axis within the layer, the untilted  $C_P$  [6]) and the tilted  $C_{B2}$  [15] also show these symmetries, respectively. In the following, however, we will not discuss the hydrodynamics of polar phases but concentrate on the non-polar ones.

### 3 Hydrodynamics

#### 3.1 D2 Hydrodynamics

##### 3.1.1 Hydrodynamic Variables D2

In Sec. 2.2 the structure of the D2 phase is discussed. It is an orthorhombic biaxial nematic phase that lacks inversion symmetry and is chiral. The hydrodynamics of conventional orthorhombic biaxial nematics has been described in Ref. [17] (for less symmetric biaxial nematics cf. also [18]) using rotations  $\delta\mathbf{n}$ ,  $\delta\mathbf{m}$ , and  $\delta\mathbf{l}$  (with  $\mathbf{n} \cdot \delta\mathbf{n} = 0$ ,  $\mathbf{m} \cdot \delta\mathbf{m} = 0$ , and  $\mathbf{l} \cdot \delta\mathbf{l} = 0$ ,) of the three mutually orthogonal preferred directions as the hydrodynamic Goldstone variables due to the broken rotational symmetry. Of course, only rigid rotations are hydrodynamic, since any internal deformations of the structure cost energy and lead to nonhydrodynamic excitations, which are excluded by the additional conditions  $\mathbf{m} \cdot \delta\mathbf{n} + \mathbf{n} \cdot \delta\mathbf{m} = 0$  and  $\mathbf{l} \equiv \mathbf{n} \times \mathbf{m}$ . Since there is a  $\mathbf{l} \rightarrow -\mathbf{l}$  equivalence, the alternative definition  $\mathbf{l} \equiv \mathbf{m} \times \mathbf{n}$  is also possible, and the results must not depend on which definition has been used.

In the D2 phase inversion symmetry is broken by the existence of a tetrahedral tensor  $T_{ijk}$  that is rigidly coupled to the triad of nematic directors ( $\mathbf{n}$ ,  $\mathbf{m}$ , and  $\mathbf{l}$  are along the three 4 axes of the tetrahedron). Therefore, rotations of  $T_{ijk}$  are no independent hydrodynamic variables, and the orientation of  $T_{ijk}$  is always given by the actual orientation of the director triad. Nevertheless,  $T_{ijk}$  can give rise to additional material tensors (or parts of them) due to the lack of a  $T_{ijk} \rightarrow -T_{ijk}$  equivalence, in contrast to the conventional  $\mathbf{n} \rightarrow -\mathbf{n}$ ,  $\mathbf{m} \rightarrow -\mathbf{m}$ , and  $\mathbf{l} \rightarrow -\mathbf{l}$  equivalence of the nematic directors. Similarly, the chirality of the D2 phase does not give rise to additional hydrodynamic variables, but allows for additional couplings between the hydrodynamic fields due to the existence of the pseudoscalar  $q_0$ , defined in Eq. (2).

There are several ways of setting up the hydrodynamic description of the D2 phase. One can use as variables, e.g., the three-dimensional rotations of the tetrahedral structure,  $\delta\Gamma_i \sim \epsilon_{ipq} T_{pkl} \delta T_{qkl}$  (as in the Td phase [14]), or the three independent director rotations, e.g.  $\mathbf{m} \cdot \delta\mathbf{n}$ ,  $(\mathbf{n} \times \mathbf{m}) \cdot \delta\mathbf{n}$ , and  $(\mathbf{m} \times \mathbf{n}) \cdot \delta\mathbf{m}$  (as is common in the liquid crystal literature). We will choose the latter one, in order to make easier contact to the local equilibrium frame in terms of the directors ( $\mathbf{n}^0 = \mathbf{e}_z$  and  $\mathbf{m}^0 = \mathbf{e}_y$ ).

The Gibbs relation, connecting changes of the total energy density  $d\varepsilon$  with those of all hydrodynamic variables (entropy density  $\sigma$ , mass density  $\rho$ , momentum density  $g_i$ , concentration  $c$ , and the director rotations) [19,20] can be written as

$$d\varepsilon = Td\sigma + \mu d\rho + v_i dg_i + \mu_c dc + \bar{h}_i^n dn_i + \bar{h}_i^m dm_i + \Phi_{ij}^n d\nabla_j n_i + \Phi_{ij}^m d\nabla_j m_i \quad (3)$$

thereby defining the conjugate quantities (temperature  $T$ , chemical potential  $\mu$ , velocity  $v_i$ , relative chemical potential  $\mu_c$ , and the 'molecular fields'  $\bar{h}_i^{n,m}$  and  $\nabla_j \Phi_{ij}^{n,m}$ ) as appropriate partial derivatives of  $\varepsilon$ . When combining the molecular fields into  $h_i^{n,m} \equiv \bar{h}_i^{n,m} - \nabla_j \Phi_{ij}^{n,m}$  one has

to take into account that  $d\nabla_j n_i \neq \nabla_j dn_i$  (for details cf. [17,21]), since finite three-dimensional rotations generally do not commute; the same phenomenon occurs when using  $\delta\Gamma_i$  as variables [14].

##### 3.1.2 Statics D2

We will not repeat the hydrodynamics of ordinary biaxial nematics, but concentrate on the differences in the D2 phase related to chirality and the lack of inversion symmetry. It is obvious that the form of the quadratic, Frank-type gradient energy of the director rotations is not affected by the lack of inversion symmetry, nor by the chirality. Therefore, the expression for ordinary orthorhombic biaxial nematics (Eq. (3.15) of [17]) is valid for the D2 phase, as well. It has the form

$$d\varepsilon_g = A_{ijkl}^{(1-8)} (\nabla_j n_i) (\nabla_l m_k) + A_{ijkl}^{(9-11)} (\nabla_j m_i) (\nabla_l m_k) + A_{ijkl}^{(12-15)} (\nabla_j n_i) (\nabla_l m_k) \quad (4)$$

The material tensors  $A_{ijkl}$  are functions of the nematic directors and contain 15 (rotational) elastic coefficients, three of which denote surface contributions [22]. The latter can be eliminated by choosing  $A_3 = A_6$ ,  $A_{12} = A_{13}$ , and  $A_{14} = A_{15}$  [23].

On the other hand, linear gradient terms, absent in ordinary biaxial nematics, are possible in the D2 phase, due to the existence of both,  $T_{ijk}$  (as in the D2d phase) and  $q_0$  (as in the cholesteric phase). We get six contributions

$$d\varepsilon_{lg} = T_{ijk} (\xi_1 n_i \nabla_j n_k + \xi_2 m_i \nabla_j m_k + \xi_3 l_i \nabla_j l_k) + q_0 \epsilon_{ijk} (k_1 n_i \nabla_j n_k + k_2 m_i \nabla_j m_k + k_3 l_i \nabla_j l_k) \quad (5)$$

The terms of the first line are the generalization of Eq. (1) of the D2d phase and describe ambidextrous helicity (cf. Sec.2.1), since the inverted structure is different from the non-inverted one, but leads to the same energy reduction. The terms of the second line are known for biaxial cholesterics [24] and are the generalization of the well-known linear twist terms of chiral uniaxial nematics (cholesterics). In the D2 phase, they describe ambidextrous chirality [16], since the pseudoscalar  $q_0$  is not due to a molecular chirality, but originates from the ordered structure, Eq. (2). Both signs of  $q_0$  belong to different structures, but lead to the same energy reduction. This situation is similar to that of the smectic B2 phase of bent-core liquid crystals [15]. In those phases that have only one linear gradient term, the helical structure is a defect-free energetic minimum state. However, in the D2 phase each of the six terms individually minimizes the energy by a helix perpendicular to the appropriate director. Obviously, it is impossible to have a common helix axis for all of them and defects necessarily occur. Only simple helices of two of the directors with the (constant) helix axis given by the third one are defect-free patterns and reduce the energy. Of the three different possibilities one of the minima might be the lowest, but none of them involves all the linear terms of Eq. (5). In that sense, the D2 phase is frustrated.

If linearized about a homogeneous state with  $\mathbf{n}^0$ ,  $\mathbf{m}^0$ ,  $\mathbf{l}^0$ , and  $T_{ijk}^0$  all constant, only two of the three terms in the first line are independent of each other. In that limit the terms in the two lines have a different structure, e.g.  $\nabla_x n_y + \nabla_y n_x$  versus  $\nabla_x n_y - \nabla_y n_x$ , although the full non-linear expressions give rise to helical structures in both cases.

If there are linear gradient terms, there are also static Lehmann-type energy contributions [25,26], bilinear in linear director gradients and variations of the scalar variables,  $S \in \{\sigma, \rho, c\}$

$$d\varepsilon_F = \sum_S \delta S \left( T_{ijk}^S \left[ \xi_1^S n_i \nabla_j n_k + \xi_2^S m_i \nabla_j m_k + \xi_3^S l_i \nabla_j l_k \right] + q_0 \epsilon_{ijk} \left[ k_1^S n_i \nabla_j n_k + k_2^S m_i \nabla_j m_k + k_3^S l_i \nabla_j l_k \right] \right) \quad (6)$$

where the sum over  $S$  comprises all scalar variables. Nine of these terms ( $\xi_{1,2,3}^S$ ) have their origin in the lack of inversion symmetry, and the other nine ( $k_{1,2,3}^S$ ) are due to the chirality of the D2 phase.

### 3.1.3 Dynamics D2

The dynamics is described by conservation laws for the conserved variables and balance equations for the non-conserved ones [17]. The former contain (the divergence of) the currents (e.g. the stress tensor,  $\sigma_{ij}$ , in the momentum conservation law, the heat current), while in the latter case a quasi-current balances the temporal changes of the variable (e.g.  $\dot{n}_i + X_i^n = 0$ ). Both, currents and quasi-currents are additively split into a reversible (superscript  $R$ ) and a dissipative part (superscript  $D$ ). The irreversible part of the dynamics can be derived from the dissipation function (or the entropy production  $R$ , which acts as the source term in the entropy balance), while the reversible part is non-potential, requires  $R = 0$  (conserved entropy), and often (but not always) follows from general invariance principles [20].

The dissipative dynamics of the D2 phase is rather similar to that of biaxial nematics. In particular, there are nine flow viscosities, three rotational viscosities according to the three director degrees of freedom, and each second rank material tensor (e.g. describing heat conduction, diffusion, and thermo-diffusion) contains three material coefficients [17]. In addition, there are dissipative Lehmann-type terms due to the lack of inversion symmetry (as in the D2d phase) and due to chirality (as in cholesterics)

$$2R_L = \sum_Q (\nabla_k Q) (T_{ijk}^Q h_{ij}^Q + q_0 \epsilon_{ijk} H_{ij}^Q) \quad (7)$$

where

$$h_{ij}^Q = (\psi_1^Q m_j m_p + \psi_2^Q l_j l_p) n_i h_p^n + \psi_3^Q l_j l_p m_i h_p^m \quad (8)$$

and  $H_{ij}^Q$  with the same structure as  $h_{ij}^Q$ , but the coefficients  $\psi_{1,2,3}^Q$  replaced by different ones  $\Psi_{1,2,3}^Q$ . The sum over  $Q$  comprises  $\nabla_k Q \in \{\nabla_k T, \nabla_k \mu_c\}$ , the thermodynamic

forces related to the thermal degree of freedom and the concentration. Variational derivatives of  $R$  with respect to these forces and  $h_i^n, h_i^m$  lead to the appropriate dissipative contributions in the heat and concentration currents, and the quasi-currents  $X_i^{n,D}, X_i^{m,D}$ , respectively [20]. Together with the static Lehmann-type contribution, they lead to the different Lehmann effects, rotations of the directors due to applied thermodynamic forces [25,26], and the inverse effects [27].

One part of the reversible dynamics, in particular transport contributions in the total time derivatives and couplings to rotational flow,  $\Omega_{ij} \equiv (1/2)(\nabla_j v_i - \nabla_i v_j)$ , is due to general invariance principles, like Galilean invariance and rotational covariance [19,20]. For biaxial nematics this has been investigated in detail in Ref. [17], where it has been shown that the requirement of zero entropy production  $R = 0$ , not only leads to counter terms in the stress tensor (the isotropic pressure and the nonlinear Ericksen stresses due to nematic deformations), but also allows - with the help of the non-commutativity relations of finite rotations - to write the anisotropic part of the stress tensor in the form of a total divergence, thus guaranteeing angular momentum conservation, locally. This also applies to the D2 phase and will not be repeated here. In nematics there is a phenomenological reversible coupling between director reorientation and symmetrized flow,  $A_{ij} \equiv (1/2)(\nabla_j v_i + \nabla_i v_j)$ , known as 'flow alignment' and 'back flow'. In uniaxial nematics there is one phenomenological parameter (related to the flow alignment angle under shear flow), in the D2d phase there are two of them and orthorhombic biaxial nematics as well as the D2 phase have three such parameters [17].

In the phases with tetrahedral order there are reversible couplings between the currents of the scalar conserved quantities (except the total density) and symmetrized flow of the form

$$j_i^{S,R} = \Gamma_{ip}^S T_{pjk} A_{jk} \quad (9)$$

where each  $\Gamma_{ij}^S$  contains one and two parameters for the  $T_d$  and the D2d phase respectively, while for the D2 phase

$$\Gamma_{ij}^S = \Gamma_1^S n_i n_j + \Gamma_2^S m_i m_j + \Gamma_3^S l_i l_j \quad (10)$$

contains three parameters for each  $S \in \{\sigma, c\}$ . Zero entropy production requires the counter terms in the stress tensor

$$\sigma_{ij} = -T_{pij} (\Gamma_{kp}^c \nabla_k \mu_c + \Gamma_{kp}^\sigma \nabla_k T) \quad (11)$$

There are no additional reversible contributions to the dynamics in the D2d phase that are based on the chirality of that phase. In particular, a chiral version of Eq.(11),  $T_{pij}$  replaced by  $q_0 \epsilon_{pij}$ , is not possible due to the rotational covariance that does not allow for phenomenological couplings between  $j_i^S$  and  $\Omega_{ij}$ .

### 3.1.4 External Fields D2

Generally, external fields can orient liquid crystals. Electric  $E_i$  and magnetic fields  $H_i$  reorient the nematic director either along the field or perpendicular to it, depending

on the sign of the dielectric or magnetic anisotropy. In biaxial nematics (and in the D2 phase as well) there are two orienting free energy terms for each field (in the first line with  $U \in \{E, H\}$ ),

$$\begin{aligned} \varepsilon_f^{quad} = & -\frac{1}{2} (\epsilon_1^U n_i n_j + \epsilon_2^U m_i m_j) U_i U_j \\ & + \frac{1}{2} q_0 \epsilon_{ipq} T_{ijk} (\chi_1^U n_p n_j + \chi_2^U m_p m_j) U_k U_q \end{aligned} \quad (12)$$

since a possible third term  $\sim l_i l_j = \delta_{ij} - n_i n_j - m_i m_j$  would only lead to an additional isotropic contribution. In the D2 phase with both, tetrahedral order and chirality, there is a second class of director orienting terms (second line), which allows for an orientation of  $\mathbf{n}$  (or  $\mathbf{m}$ ) perpendicular to the fields, even for positive  $\epsilon_{1,2}^U$ , if  $|\chi_{1,2}^U q_0 T_0|$  is large enough. Obviously, not all directors can be aligned simultaneously.

In any phase with a tetrahedral structure, there are energy contributions cubic in the field strengths

$$\begin{aligned} \varepsilon_f^{cub} = & -T_{ijk} (\zeta_1^E n_i n_p + \zeta_2^E m_i m_p + \zeta_3^E l_i l_p) E_p E_j E_k \\ & + T_{ijk} (\zeta_1^{EH} n_i n_p + \zeta_2^{EH} m_i m_p + \zeta_3^{EH} l_i l_p) E_p H_j H_k \\ & + q_0 \epsilon_{pi k} (\zeta_3^{EH} n_j n_p + \zeta_4^{EH} m_j m_p) E_i H_j H_k \end{aligned} \quad (13)$$

They orient the tetrahedral structure such that one tetrahedral vector is along the electric field direction, with the three others symmetrically off by the tetrahedral angle  $\theta_T = 2\arccos(-1/3)$ . The mixed electric-magnetic terms are non-zero for parallel as well as perpendicular fields. The chirality of the D2 phase allows for another cubic energy contribution, linear in the electric and quadratic in the magnetic field. It orients the directors perpendicular to the electric field, if the magnetic field is also perpendicular to the electric one, but oblique to the directors. In all these cases the orientation of  $T_{ijk}$  is in conflict with the dielectric director orientation leading to an unconventional field dependence of the director orientation [14].

Like in a biaxial nematic phase, there are flexoelectric energy contributions due to an external electric field

$$\begin{aligned} \varepsilon_{fl} = & e_1 E_i n_j \nabla_j n_i + e_2 E_i n_i \nabla_j n_j \\ & + e_3 E_i m_j \nabla_j m_i + e_4 E_i m_i \nabla_j m_j \\ & + e_5 q_0 T_{jkq} E_i n_k \epsilon_{ijp} \nabla_q n_p + e_6 q_0 T_{jkq} E_i m_k \epsilon_{ijp} \nabla_q m_p. \end{aligned} \quad (14)$$

For a constant electric field, there is only one independent term in the first line and one in the second line (up to surface contributions). The terms of the third line are due to both, the chirality and the lack of inversion symmetry. If linearized these terms involve  $\nabla_x n_x - \nabla_y n_y$  for  $\mathbf{E}$  and  $\mathbf{n}^0$  along the  $z$  axis (and  $\nabla_y m_y - \nabla_z m_z$  for  $\mathbf{E}$  and  $\mathbf{m}^0$  along the  $x$  axis), which is quite different from the usual nematic flexoelectric contributions  $\sim \text{div } \mathbf{n}$  (or  $\sim \text{div } \mathbf{m}$ ).

Boundaries also act as orienting means in liquid crystals. Generally, boundaries can be described by their normal vector,  $\mathbf{b}$ . Since  $\mathbf{b}$  is a polar vector with the same symmetry properties as the electric field, all electrical terms in Eqs. (12) and (13) describe the orientation by boundaries, if  $\mathbf{E}$  is replaced by  $\mathbf{b}$ . In particular, directors and

the tetrahedral structure are oriented differently, incompatible with the structure of the D2 phase, which prevents a homogeneous, defect-free orientation of that phase at boundaries.

If there are electric charges in the material, charge conservation can be added to the list of hydrodynamic equations,  $\dot{\rho}_e + \nabla_i j_i^E = 0$ . In that case the dissipative Lehmann effect, Eq. (7), and the reversible flow-current coupling, Eqs. (9) and (11), also contain linear electric field contributions

$$2R_L = E_k (T_{ijk} h_{ij}^E + q_0 \epsilon_{ijk} H_{ij}^E) \quad (15)$$

$$j_i^{E,R} = (\Gamma_1^E n_i n_j + \Gamma_2^E m_i m_j + \Gamma_3^E l_i l_j) T_{pj k} A_{jk} \quad (16)$$

$$\sigma_{ij} = -T_{pij} (\Gamma_1^E n_k n_p + \Gamma_2^E m_k m_p + \Gamma_3^E l_k l_p) E_k \quad (17)$$

with  $H_{ij}^E$  and  $h_{ij}^E$  of the structure defined in Eq. (8).

### 3.2 S4 Hydrodynamics

The S4 phase has the same hydrodynamic variables as the D2d phase, in particular rotations of the preferred direction  $\mathbf{n}$  (the tetragonal axis) and a rotation about this axis. The latter can be described either by appropriate rotations of the tetrahedral structure,  $\delta\Omega \equiv (1/4\alpha) n_i \epsilon_{ipq} T_{pj k} \delta T_{qjk}$ , with  $\alpha = (32/27) T_0^2$ , or by (in-plane) rotations of  $\mathbf{m}$  or  $\mathbf{l}$ . We will use  $\delta\Omega$  to make close contact with the D2d hydrodynamics [14]. The only difference is the reduced symmetry of S4 compared to D2d, which is manifest in more complicated structures of material tensors or in some additional cross couplings.

We start with the discussion of the statics. The gradient free energy reads

$$\begin{aligned} \varepsilon_g = & \frac{1}{2} K_{ikjl} (\nabla_i n_k) (\nabla_j n_l) + K_7 \delta_{ik}^{\perp} \epsilon_{lij} (\nabla_l \Omega) (\nabla_j n_k) \\ & + \frac{1}{2} (K_5 n_i n_j + K_6 \delta_{ij}^{\perp}) (\nabla_i \Omega) (\nabla_j \Omega) \end{aligned} \quad (18)$$

with  $\delta_{ij}^{\perp} \equiv m_i m_j + l_i l_j$ . It contains 8 Frank-type bulk orientational elastic coefficients according to the  $S_4$  symmetry. Five of them are related to the preferred direction  $\mathbf{n}$

$$\begin{aligned} K_{ijkl} = & K_3 n_i n_j \delta_{kl}^{\perp} + (K_1 - 2K_2) \delta_{ik}^{\perp} \delta_{jl}^{\perp} \\ & + K_2 (\delta_{il}^{\perp} \delta_{jk}^{\perp} + \delta_{ij}^{\perp} \delta_{kl}^{\perp}) + K_4 n_p n_q T_{ijp} T_{qkl} \\ & + K_8 \delta_{rk}^{\perp} \delta_{il}^{\perp} T_{ijp} T_{rtp}, \end{aligned} \quad (19)$$

while  $K_{5,6}$  are transverse coefficients and  $K_7$  is a mixed one. The  $K_8$  term, which does not exist in the D2d phase, gives rise to new combinations of director variations of the form  $\cos 2\Theta \sin 2\Theta (\nabla_x n_x - \nabla_y n_y) (\nabla_y n_x + \nabla_x n_y)$ , if linearized, where  $\Theta$  is the in-plane rotation vector as described in Fig. 3.

However, there is only one linear gradient energy term as in the D2d phase

$$\varepsilon_{lg} = \xi_1 n_i T_{ijk} \nabla_j n_k, \quad (20)$$

giving rise to ambidextrous helicity. If linearized, it involves two different director combinations,  $(\nabla_x n_y +$

$\nabla_y n_x \cos 2\Theta + (\nabla_x n_x - \nabla_y n_y) \sin 2\Theta$ . There is no additional linear gradient term w.r.t.  $\nabla_i \Omega$ , because of the invariance under  $\mathbf{m} \leftrightarrow \mathbf{l}$ . The same applies to the static Lehmann-type energy contributions

$$\varepsilon_F = \xi_1^S n_i T_{ijk} (\delta S) \nabla_j n_k, \quad (21)$$

with  $S \in \{\rho, \sigma, c\}$ .

Generally, only material tensors of fourth order (or higher) have a different structure (different number of independent components) in the S4 and the D2d phase. In particular, the viscosity tensor, relating the stress tensor with the symmetric flow tensor,  $\sigma_{ij} = -\nu_{ijkl} \nabla_l v_k$  has an additional 7th term,  $\nu_{ijkl} \sim \nu_7 \delta_{rk}^\perp \delta_{tl}^\perp T_{ijp} T_{rtp}$  in the S4 phase - quite similar to the  $K_8$  Frank-type term discussed above.

All other material tensors occurring in the static or dynamic part of the S4 hydrodynamics are of a rank less than 4 and have the same structure as in the D2d phase [14]. Therefore, the form of the hydrodynamic equations is the same and will not be repeated here. However, in the S4 phase the linearized tensor  $T_{ijk}$  has a few more non-vanishing elements with the effect that there are more elements coupled than in the D2d phase. An example we already have presented is the linear gradient term, Eq. (20), that couples additionally to  $\nabla_x n_x - \nabla_y n_y$ . In the following we will discuss similar cases of new coupling elements in the S4 phase compared to the D2d phase. We will restrict us here to linear hydrodynamics.

In the D2d phase (Eqs. (22)-(25) of [14]) there is a reversible coupling between shear flow and currents (of temperature, concentration and charge), and vice versa, between shear stresses and gradients (of temperature and concentration) and electric fields, such that shear planes are perpendicular to the vector quantities. In the S4 phase also hyperbolic flows and stresses and oblique currents are involved

$$\begin{aligned} j_x^{\sigma,R} &= \Gamma_\perp (\cos 2\Theta A_{yz} + \sin 2\Theta A_{xz}) \\ j_y^{\sigma,R} &= \Gamma_\perp (\cos 2\Theta A_{xz} - \sin 2\Theta A_{yz}) \\ j_z^{\sigma,R} &= \Gamma_\parallel (\cos 2\Theta A_{xy} + \sin 2\Theta [A_{xx} - A_{yy}]) \end{aligned} \quad (22)$$

and

$$\begin{aligned} \sigma_{xz} &= -\Gamma_\perp (\cos 2\Theta \nabla_y T + \sin 2\Theta \nabla_x T) \\ \sigma_{yz} &= -\Gamma_\perp (\cos 2\Theta \nabla_x T - \sin 2\Theta \nabla_y T) \\ \sigma_{xy} &= -\Gamma_\parallel \cos 2\Theta \nabla_z T \\ \sigma_{xx} &= -\sigma_{yy} = -\Gamma_\parallel \sin 2\Theta \nabla_z T \end{aligned} \quad (23)$$

The dissipative Lehmann-type couplings of the D2d phase (Eq. (26) of [14]) acquire more coupling elements in the S4 phase

$$\begin{aligned} j_x^{\sigma,D} &= -\psi^T (\cos 2\Theta h_y + \sin 2\Theta h_x) \\ j_y^{\sigma,D} &= -\psi^T (\cos 2\Theta h_x - \sin 2\Theta h_y) \end{aligned} \quad (24)$$

and

$$\begin{aligned} \dot{n}_x &= -\psi^T (\cos 2\Theta \nabla_y T + \sin 2\Theta \nabla_x T) \\ \dot{n}_y &= -\psi^T (\cos 2\Theta \nabla_x T - \sin 2\Theta \nabla_y T) \end{aligned} \quad (25)$$

with  $h_{x,y} = \delta\varepsilon/\delta n_{x,y}$ . Similar sets of equations (with different material parameters) are obtained by replacing the temperature current  $\mathbf{j}^\sigma$  by a concentration current (superscript  $c$ ) or a charge current (superscript  $e$ ) and appropriately, the temperature gradient by a concentration gradient or an electric field in Eqs. (22) - (25).

The orientation of the director (and the tetrahedral structure) in an external electric field is basically the same as on the D2d phase. The dielectric anisotropy favors the director to be parallel or perpendicular to the field, while the cubic free energy contributions  $\sim T_{ijk} E_i E_j E_k$  has its minimum, if one of the tetrahedral axes is along the field, leading to frustration. Assuming that the dielectric anisotropy effect is the dominant one in the S4 phase and orienting the director (and thus the  $\bar{4}$  axis) along the  $z$  direction by a strong static electric field, a small oscillating electric transverse field will lead to a reorienting force on  $\mathbf{n}$ , which is proportional to  $E_x^2 + E_y^2$  due to the dielectric anisotropy, while for the tetrahedral orientation the reorientation force is of the form  $\cos 2\Theta E_x E_y + \sin 2\Theta (E_x^2 - E_y^2)$ . Thus, this response to an external field can experimentally reveal the transverse anisotropy in that case.

## 4 Summary

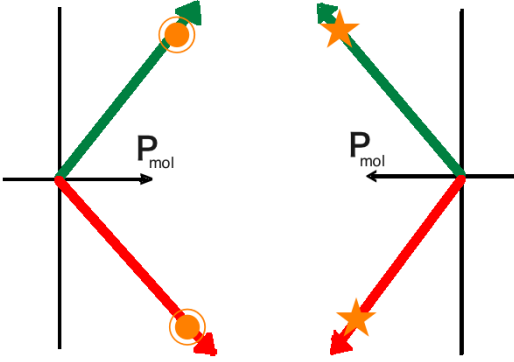
We have investigated the symmetry properties and the macroscopic behavior of nonpolar nematic and isotropic phases with tetrahedral order. The two optically isotropic phases,  $T_d$  and  $T$ , have cubic symmetry and can possess a simple ground state that is spatially homogeneous ( $T_d$ ) or a simple helix due to its handedness ( $T$ ). The nonpolar nematic phases found are optically uniaxial (D2d and S4) or optically biaxial (D2) and belong to the tetragonal and orthorhombic symmetry system, respectively.

D2d, D2 and S4 all possess *linear* gradient terms in their generalized energies, which are not related to the existence of a pseudoscalar. Such linear gradient terms lead to the lowering of the energy by the formation of spatially inhomogeneous ground states. In the present case these are left- and right-handed helical structures that can be discriminated based on the difference between the tetrahedron and its inverted structure: *ambidextrous helicity*.

In the D2 phase, which possesses a chiral structure, one can construct a pseudoscalar,  $q_0$ . It turns out that the definition of  $q_0$  is not unique in D2 and one can equally well replace  $q_0$  by  $-q_0$ . The reason is that D2 is structurally chiral: there is no energetic preference for one type of handedness over the other. Thus one encounters in D2 *ambidextrous chirality*. This property comes in D2 in addition to the ambidextrous helicity also present in D2d and S4.

As a rather unique feature we have demonstrated that the chiral  $T$  phase shows flow alignment in a cubic system. One finds a stationary alignment of the tetrahedral order in simple shear that is independent of the flow rate, but depends linearly on the helical wave vector,  $q_0$ , associated with the linear chiral term in the energy. This simple situation is obtained when one of the 3-fold axes is in the vorticity direction. We would like to emphasize that this





**Fig. A.1.** Model of a symmetrically chiralized bent-core molecule (left) with its mirror image (right); filled (orange) circles mean e.g. positive chirality, while the (orange) stars indicate negative chirality.

type of flow alignment is difficult to detect optically due to the high symmetry of the system in the shear plane. In the  $T_d$  phase this type of flow alignment is not possible because of its higher symmetry.

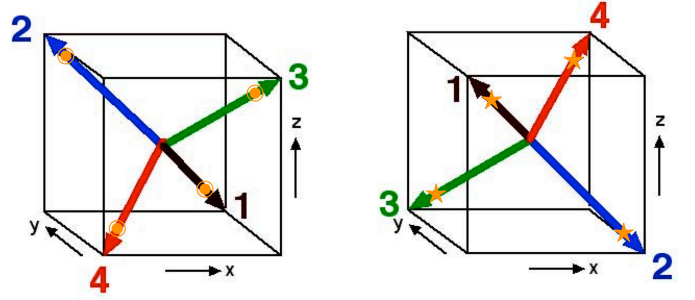
*Acknowledgment* - Early versions of Figs. 1 and A.2 by P.E. Cladis [28] served as inspirations for the plots presented here.

## Appendices

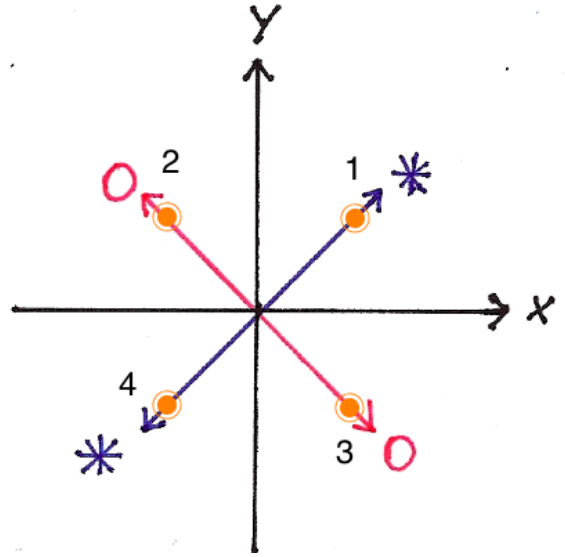
### Appendix A.1: The chiral tetrahedral T phase

In the main body of this manuscript we have dealt with achiral molecules. Nevertheless, due to the low symmetry of e.g. the  $D_2$  phase, there is structural (ambidextrous) chirality. In this Appendix we assume chiral molecules and elucidate the relation between chirality due to chiral molecules and structural chirality found for achiral molecules. There are certainly many ways of chiralizing bent-core molecules, but for our purposes it is convenient to assume that the two tails of such molecules are symmetrically chiralized, Fig. A.1 (left). If such a molecule is mirrored at a plane or inverted, the chirality is changed, Fig. A.1 (right), and the two forms cannot be brought into coincidence by mere rotations.

To get the symmetry of the phase made of such molecules, one has to employ a specific model. Assuming that two bent-core molecules of the same chirality are combined in a steric arrangement similar to the tetrahedral vectors 1-4 and 2-3, Fig. A.2, a  $T$ -symmetric phase (T phase) is obtained [4]. Due to the chirality of the molecules, the  $\bar{4}$  axes of the  $T_d$  phase are reduced to (proper) 2-fold symmetry axes, and the planes spanned



**Fig. A.2.** Model of two bent-core molecules (1-4 and 2-3) with the same chirality, arranged to fit into the tetrahedral geometry (left) with its mirror image (right); not only is the tetrahedral geometry inverted, but also the molecular chirality has changed.



**Fig. A.3.** Projection of the tetrahedral structure of Fig. A.2 onto the  $x/y$  plane. The  $z$  axis is reduced to a 2-fold axis, since a  $\pi/4$  rotation with an additional inversion preserves the structure, but changes the chirality. For the same reason, the planes spanned by vectors 1/4 or 2/3 are no mirror planes.

by vectors 1/4 and 2/3 are no longer mirror planes, Fig. A.3, with the result that only three 2-fold and four 3-fold symmetry axes exist. The former are the  $x, y, z$  directions, while the latter are the tetrahedral axes 1-4, which are equivalent despite the chirality. Such an arrangement of bent-core molecules ensures the compensation of the molecular polarity and results in the T phase being non-polar. This T phase made of chiral molecules is related to the achiral  $T_d$  phase in the same spirit as a chiral smectic  $C^*$  phase is related to an achiral smectic C phase.

The hydrodynamics of the achiral  $T_d$  phase has been given in Ref. [14] and is also briefly mentioned in Sec. 2.1. We therefore concentrate on the differences between the hydrodynamics of the T compared to the  $T_d$  phase. Those differences are solely due to the chirality of the former. Describing the rotations of the tetrahedral structure by  $\delta\Gamma_i \equiv \frac{1}{4\alpha} \epsilon_{ipq} T_{pkl} \delta T_{qkl}$  with a proper norm  $\alpha$ , the rota-

tional elastic free energy

$$\varepsilon_g = \frac{1}{2} K_{ijkl}^T (\nabla_j \Gamma_i) (\nabla_l \Gamma_k) + q_0 K_1^{lin} \nabla_i \Gamma_i \quad (\text{A.1})$$

contains three quadratic achiral contributions  $K_{ijkl}^T = K_1^T (\delta_{ij} \delta_{kl} + \delta_{il} \delta_{jk}) + K_2^T \delta_{ik} \delta_{jl} + K_3^T T_{jlp} T_{ikp}$  and one linear chiral term  $\sim q_0 K_1^{lin}$ . Generally, a linear gradient term favors a spatially inhomogeneous structure. In the present case, a helical rotation of  $T_{ijk}$  about any of the 3-fold axes (the tetragonal vectors) reduces the free energy by  $\Delta\varepsilon = -\frac{1}{2} (q_0 K_1^{lin})^2 / (2K_1^T + K_2^T)$ . What looks like a linear splay term is physically a linear twist contribution, quite similar to the familiar case of chiral nematics (cholesterics). The optimum helical pitch,  $q_h = \frac{3}{2} q_0 K_1^{lin} / (2K_1^T + K_2^T)$ , is generally different from the chiral pseudoscalar of the phase,  $q_0$ , since there is no a priori reason that  $K_1^{lin}$  is related to  $K_{1,2}^T$ . An analogous statement holds for ordinary cholesterics [29]. Helical rotations about the 2-fold axes do not lower the free energy, since the linear gradient term is zero in that case and the quadratic term,  $\sim K_3$ , increases the free energy.

The similarity to the cholesteric phase also holds for chiral Lehmann-type contributions, both static in the free energy,  $\varepsilon_c = q_0 (\xi^\rho \delta \rho + \xi^\sigma \delta \sigma + \xi^c \delta c) \nabla_i \Gamma_i$ , and dynamic in the dissipation function,  $R = q_0 (\Psi^E E_k + \Psi^T \nabla_k T + \Psi^c \nabla_k c) \nabla_i h_i^T$ . They relate the scalar degrees of freedom (temperature, concentration, density etc.) with the rotations of the tetrahedron.

The dynamics of the rotations,  $\dot{\Gamma}_i + Y_i^T = 0$ , contains, as in the  $T_d$  phase, the (reversible) advective and convective parts and an dissipative isotropic relaxation [14], but in addition a chiral, reversible coupling to the rate of strain tensor

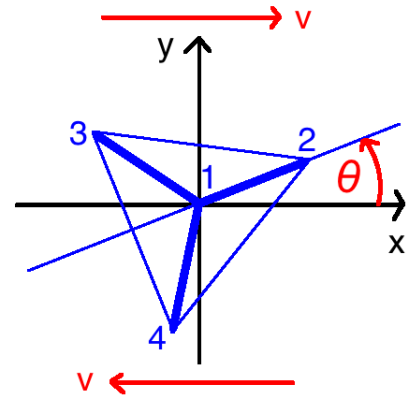
$$Y_i^T = q_0 \lambda T_{ijk} A_{jk}. \quad (\text{A.2})$$

This coupling to both, rotational and symmetric shear flows, allows for a stationary alignment of  $T_{ijk}$  in simple shear that is independent of the flow rate and only depends on  $q_0 \lambda$ . In particular, if one of the 3-fold tetrahedral axis is in the vorticity direction, the tetrahedron is rotated about this direction by an angle  $\theta$ , Fig. A.4, given by

$$\frac{1}{\cos 2\theta} = \frac{16}{27} q_0 \lambda \quad (\text{A.3})$$

This alignment by shear flow resembles very much the flow alignment in nematics, although there it is an achiral effect. On the other hand, however, it might be difficult to orient the T phase properly and to detect its rotation under shear. There is no flow alignment of a 2-fold axis by shear, since there is no stationary homogeneous solution possible for that geometry. It is rather remarkable that chiralization allows the tetrahedral vectors to act as preferred directions (albeit all equivalently), e.g. as helical axis or as rotation axis in flow alignment. In the achiral phase the tetrahedral vectors are only preferred directions, when an electric field is applied.

The remainder of the dynamics is as in the achiral  $T_d$  phase: 2-rank material tensors (e.g. heat conduction, diffusion, electric conductivity) are isotropic leaving the system optically isotropic, while the viscosity tensor contains



**Fig. A.4.** Projection of the tetrahedral structure onto the  $x/y$  plane with one of the tetrahedral axes ( $\mathbf{n}^1$ ) along the  $z$ -axis (corners 2,3,4 lie below the  $x/y$  plane). This is also the vorticity direction of the simple shear  $\nabla_y v_x = S$ . The structure is rotated in the shear plane by an angle  $\theta$  that is independent of the shear rate  $S$ .

three independent viscosities in accordance with the cubic symmetry class. There is also the reversible crosscoupling between flow and the currents of heat, concentration and charge and their reverse effects, stresses due to temperature or concentration currents or electric fields [8], which is possible by the broken inversion symmetry of  $T_{ijk}$ .

## Appendix A.2: The D2' and D2'' phases

One can further reduce the symmetry of the T phase by adding a uniaxial nematic director along one of the 2-fold symmetry axis (e.g. the  $z$  axis). This removes all 3-fold axes and a  $D_2$ -symmetric phase (D2') with only three mutually orthogonal 2-fold axes, is obtained. The same effect can be obtained, when the tetrahedron formed by the vectors 1-4 is stretched or dilated uniaxially along a 2-fold axis. This D2' phase has the same symmetry as the D2 phase described in Sec. 2.2, but differs in the origin of the chirality. In the D2' phase there is a definite handedness coming from the chiral molecules (denoted by the pseudoscalar  $q_0'$ ), while the D2 phase chirality is structural and both types of handedness are possible ( $q_0$  and  $-q_0$  of Eq. (2)). Adding orthorhombic biaxial nematic directors to the T phase (with the directors along the 2-fold axes) does not change the symmetry. This D2'' phase, however, shows both, ambidextrous chirality of D2 and the definite chirality of the T phase.

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