

# Macroscopic behavior of non-polar tetrahedratic nematic liquid crystals

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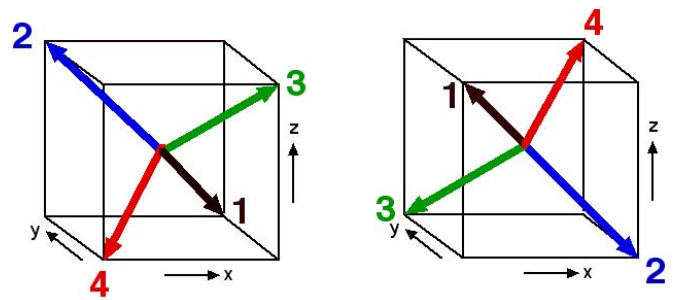
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**Abstract.** We discuss the symmetry properties and the macroscopic behavior of a nematic liquid crystal phase with  $D_{2d}$  symmetry. Such a phase is a prime candidate for nematic phases made from banana-shaped molecules where the usual quadrupolar order coexists with octupolar (tetrahedratic) order. The resulting nematic phase is non-polar. While this phase could resemble the classic  $D_{\infty h}$  nematic in the polarizing microscope, it has many static as well as reversible and irreversible properties unknown to non-polar nematics without octupolar order. In particular, there is a linear gradient term in the free energy that selects parity leading to ambidextrously helical ground states when the molecules are achiral. In addition, there are static and irreversible coupling terms of a type only met otherwise in macroscopically chiral liquid crystals, e.g. the ambidextrous analogues of Lehmann-type effects known from cholesteric liquid crystals. We also discuss the role of hydrodynamic rotations about the nematic director. For example, we show how strong external fields could alter the  $D_{2d}$  symmetry, and describe the non-hydrodynamic aspects of the dynamics, if the two order structures, the nematic and the tetrahedratic one, rotate relative to each other. Finally, we discuss certain nonlinear aspects of the dynamics related to the non-commutativity of three-dimensional finite rotations as well as other structural nonlinear hydrodynamic effects.

## 1 Introduction

Fel [1, 2] was the first to consider tetrahedral (octupolar) order,  $T_{ijk}$ , in the context of liquid crystals. He considered the regular tetrahedron which belongs to the symmetry group  $T_d$  [3–5]. Under the parity operation,  $\mathbf{r} \rightarrow -\mathbf{r}$ ,  $T_{ijk}$  transforms to  $-T_{ijk}$  (fig. 1). An important implication of this observation is that at a tetrahedratic-isotropic liquid phase transition,  $T_{ijk}$  and  $-T_{ijk}$  simultaneously condense from  $O(3)$ , the usual isotropic liquid. On the other hand, nematic (quadrupolar) order,  $Q_{ij}$  well-known for liquid crystals [6, 7], introduces one (or two) preferred orientations thus breaking rotational symmetry at the isotropic to nematic phase transition. Here we are interested in a phase, where both, tetrahedral and nematic order coexist, in particular a  $D_{2d}$ -symmetric phase (D2d) (called  $N_T$  in ref. [8]) where the uniaxial director,  $\mathbf{n}$ , is along one of the 4 axes of the tetrahedral structure (e.g. the  $z$  axis in fig. 1).

While we are studying here a D2d nematic, which is non-polar, there are many other options for the macroscopic and molecular symmetries of unconventional nematic phases (for a recent review we refer to ref. [9]). Another outstanding candidate for the superposition of quadrupolar and octupolar order is a phase with  $C_{2v}$  symmetry. Such a phase would be polar and can lead to ferroelectric and/or antiferroelectric order. In the



**Fig. 1.** (Colour on-line)  $T_{ijk}$  (left) and its inverse  $-T_{ijk}$  (right). The tetrahedron,  $T_d$ , is described by four unit vectors,  $\mathbf{n}^\alpha$  ( $\alpha = 1, 2, 3$  and 4) to alternate corners of a cube:  $T_{ijk} = \sum_{\alpha=1}^4 n_i^\alpha n_j^\alpha n_k^\alpha$ . The spatially inverted system is equivalent to a  $\pi/2$  rotation about (here) the  $y$  axis making this axis (and generally also the  $x$  and  $z$  axis) a  $\bar{4}$  improper rotation axis with  $S_4$  the appropriate symmetry element of  $T_d$  [4, 14].

context of liquid crystal phases formed by bent-core molecules it has been suggested first in the context of fluid smectic phases in ref. [10].

In contrast to optically isotropic liquid crystals with  $T_d$  symmetry, D2d is (locally) optically uniaxial and in contrast to uniaxial nematics with  $D_{\infty h}$  symmetry, D2d is not inversion symmetric. The question is then, how can we differentiate this

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D2d phase from other non-polar biaxial or uniaxial nematics and from the  $T_d$  phase?

In the polarizing microscope, a homogeneously oriented D2d could resemble the usual uniaxial nematic,  $D_{\infty h}$ . But, the full structure, nematic and tetrahedric, breaks continuous rotational symmetry in all three directions. In particular, there are three hydrodynamic degrees of freedom (Goldstone modes) as in biaxial nematic phases [11, 12]. Two of these modes are associated with rotations of  $\mathbf{n}$  about the two axes  $\perp \mathbf{n}$  and the third with rotations around  $\mathbf{n}$ .

Octupolar order introduces several effects unknown in usual nematics. For example, we showed that  $T_{ijk}$  has reversible couplings between velocity gradients (deformational flows), electric fields and gradients in concentration, and temperature giving rise to stresses [13]. There are also additional static and dissipative effects not known in usual nematics which have only an axis of orientation [15]. These include irreversible coupling terms between director rotations on the one hand and electric fields and temperature and concentration gradients on the other. In addition, there are static contributions coupling director deformations to density, concentration and temperature variations unknown in quadrupolar nematics [15]. All these effects can be checked but so far have not been, perhaps, because of material scarcity.

As we have pointed out earlier [16–18], symmetry allows a linear gradient term in the free energy,  $T_{ijk}\nabla_k Q_{ij}$ , when both types of order are present. Both  $\nabla_k$  and  $T_{ijk}$  are odd under parity so the product,  $T_{ijk}\nabla_k Q_{ij}$ , conserves parity. Put simply, coupling spatial gradients in an order parameter that conserves parity with an order parameter that does not provide a mechanism for local parity selection. In the following we will show that for the D2d phase this linear gradient term allows for an ambidextrous helical ground state structure, where both types of handedness occur equally likely, since the tetrahedral structure and its inverted variant are present simultaneously, if there is no preferred parity due to external fields or surfaces. Optically, this would resemble a cholesteric phase.

The behavior in an electric field gives rise to additional possibilities to distinguish a D2d from usual nematics. First, a D2d phase allows second harmonic generation and novel electro-mechanical effects as it breaks parity symmetry. Secondly, it has an unusual reorientation behavior: Below a threshold field, the director is oriented in the usual uniaxial nematic way. Above this threshold value the director turns away continuously from its original orientation to a direction oblique to the field, a phenomenon unknown in a usual uniaxial nematic.

D2d is a good candidate for nematics formed by banana-shaped molecules. Recently [19], an isotropic to isotropic phase transition has been observed above a nematic phase formed by banana-shaped molecules. In the context of D2d, the following scenario comes to mind. The higher temperature isotropic phase is  $O(3)$  (the usual isotropic phase), the lower temperature (optically) isotropic phase is  $T_d$  [1, 2] ( $B7$  as in [20–23]), and the (optically) uniaxial nematic phase is D2d.

Generally a director,  $\mathbf{n}$ , can be uniformly oriented between parallel glass plates, either parallel or homeotropic. Generally, also the tetrahedral vectors could be oriented by boundaries, however, the coexistence of  $T_{ijk}$  and its inverse cannot lead to

a homogeneous structure. In addition, the director surface orientation and the surface orientation of (one of) the tetrahedral vectors (parallel or antiparallel) are incompatible. Only if the nematic surface ordering is dominating, a homogeneous structure can be expected. But similar to  $B7$  which has single parity traveling domains that grow or shrink but never coarsen, alternating parity convection rolls in D2d can't coalesce or annihilate with each other [24].

In sect. 2 we start with an overview on this topic and how it is related to current experiments and to previous theoretical work (sect. 2.1). Then we give the hydrodynamics of a  $T_d$  phase (not given previously in full completeness), in order to set the notation and to facilitate comparison with the D2d phase (sect. 2.2).

In sect. 3, the main body of this paper, we derive the unusual linear hydrodynamics of the D2d phase (sects. 3.1 and 3.3) and show how this is different from the familiar uniaxial or tetragonal biaxial nematic case. The new hydrodynamic variable (compared to uniaxial nematics), rotations about the nematic director, is discussed in detail in sect. 3.5. The complexity of the D2d phase allows for the possibility that the lowest energy state is an inhomogeneous one, in particular a helical state, where the helical sense can be of either handedness (ambidextrous chirality, sect. 3.2). The very unusual orientation effects of a D2d phase in an external electric field are elaborated in sect. 3.4. In addition, we describe the non-hydrodynamic aspects of the dynamics, if the two order structures, the nematic and the tetrahedric one, are rotating relative to each other. Relative rotations, important in other liquid crystalline systems, may play a role when different kinds of external fields or different types of boundary conditions are present. Finally, in sect. 4, we discuss nonlinear aspects of the dynamics related to the non-commutativity of three-dimensional finite rotations as well as other structural nonlinear hydrodynamic effects.

## 2 Review of Previous Results

### 2.1 General

A current fundamental question in liquid crystal and soft matter research is to what extent polar order and fluidity can co-exist. To date, no examples of polar order and 3D fluidity are known. In [10, 25–27], we showed that 2D fluidity in biaxial smectic layers was sufficient to stabilize polar order. Since the prediction and demonstration [28–30] of the existence of novel liquid crystal phases made of bent-core and banana-shaped molecules, this issue has drawn considerable attention. Subsequently, it was found that there are many smectic phases formed by banana-shaped molecules revealing anti-ferroelectric order [21, 22, 26, 27, 31–36].

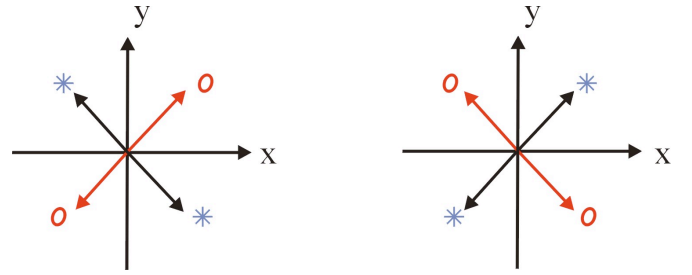
Fairly early on, symmetry arguments were given [37] that the low symmetry of the bent core molecules allowed nematic phases not only of the usual uniaxial non-polar nematic type as found by [38, 39], but also biaxial phases of the orthorhombic type [11, 12] and that even polar biaxial nematic phases were possible. While polar uniaxial nematic phases for which the polar direction is parallel to the usual nematic director have been investigated for about two decades [40], interest in these systems has recently become more intense in connection with

polypeptides showing polar order [41–44] as well as for the field of active driven systems in actin filament gels [45]. The macroscopic dynamic behavior of such phases has been given [46, 47].

Very recently several studies of the physical properties of nematic phases formed by banana-shaped molecules have revealed properties unknown from usual uniaxial nematics including giant flexoelectricity [48], nonstandard electroconvection [24] as well as unusual behavior near the transition from an optically isotropic phase to a nematic phase [19, 49]. These experimental results underscore all previous conclusions that liquid crystal phases formed by banana-shaped molecules are different from those obtained from rod-like or disc-like molecules. Previously it had been shown that one can obtain chiral domains of both hands for nematic phases formed by achiral molecules [50, 51] and also the induction of a liquid crystal phase in an optically isotropic phase by an external electric field showing an upward shift in the phase transition temperature by up to ten degrees with a shift, which varied linearly in the applied electric field [52].

After liquid crystalline phases composed of banana-shaped molecules were found and experimentally characterized, the influence of tetrahedric order on the physical properties of such LC phases was theoretically investigated considering phase transitions [8, 53] and the coupling between flow and various external fields in an optically isotropic situation [13]. More recently, these early studies were complemented by the analysis of the coupling terms between quadrupolar and octupolar order [15–18] elucidating in particular the role played by a linear gradient term between the two types of order and its physical consequences [16–18]. The latter include the appearance of spontaneous chiral domains of either hand (ambidextrous chirality), the formation of spontaneous defect-free splay-bend textures [18], which could play a key role in the explanation of the textures observed for Weissflog’s B7 phase [21, 22, 28, 54] as well as more recent results on electro-convection in banana nematics [24]. An explanation for the observed shift in the liquid crystal - optically isotropic phase transition temperature [52] has also been suggested [17] assuming that the ‘isotropic’ phase is actually tetrahedric: in this case a tri-linear static coupling in the generalized energy of an external electric field and the quadrupolar as well as the octupolar order parameter leads to a shift of the phase transition temperature, which is linear in the electric field,  $\mathbf{E}$ .

In the previous theoretical studies we considered the unlocked case, where the nematic director and the tetrahedral structure were allowed to rotate freely with respect to each other; this is very likely a good approximation close to a phase transition where the order parameters are still small. Far inside a given phase, a Ginzburg-Landau argument reveals that there are two thermodynamic phases, where the two types of orientation are locked: Either the director is along one of the 3-fold axes (the tetrahedral vectors) or is along one of the improper  $\bar{4}$  axes. The former case has  $C_{3V}$  symmetry and is a polar, trigonal biaxial nematic with macroscopic properties resembling optically the case of a uniaxial polar nematic. Such a type of symmetry is also obtained, if one allows the tetrahedral structure (of the  $T_d$  phase) to deform due to a strong external electric field. In this paper we will take the tetrahedral structure as rigid



**Fig. 2.** Left: The 4 tetrahedric vectors of Eq.(1) are shown in a projection onto the  $x/y$  plane. Those vectors pointing out of (into) the drawing plane are red (blue) and decorated by a circle (asterisk); the  $z$ -axis sticks out. Right: The spatially inverted system equivalent to a  $\pi/2$  rotation (about the  $z$  axis).

and consider only the  $D_{2d}$  phase, where the director is along the improper  $\bar{4}$  axis and the nematic and tetrahedral structures are rigidly locked. Only in sect. 3.6 we allow for a finite, but large energy for rotations of the tetrahedral structure relative to the nematic director. First we start with the  $T_d$  hydrodynamics.

## 2.2 Tetrahedric Hydrodynamics

The tetrahedric phase is characterized by the existence of the octupolar order parameter  $T \equiv T_{ijk} = \sum_{\alpha=1}^4 n_i^\alpha n_j^\alpha n_k^\alpha$  expressed by the 4 unit vectors,  $\mathbf{n}^\alpha$ , with  $\alpha = 1, 2, 3$  and 4 defining a tetrahedron.  $T$  is fully symmetric in all three indices and odd under parity, since the  $\mathbf{n}^\alpha$ 's are vectors, or, in physical terms, are polar. Only 2-, 3- and 4-fold symmetry axes are allowed by the tetrahedric  $T_d$  symmetry. The 4-fold symmetry axes are improper (accompanied by an inversion of their direction), thus destroying inversion symmetry. There are two mirror planes defined by two non-adjacent tetrahedral vectors, thus excluding chirality. The orientation of the tetrahedron in laboratory space is arbitrary, but the matrix representation

$$T_{ijk} = \frac{1}{\sqrt{3}} \begin{pmatrix} 1 & 1 & -1 & -1 \\ 1 & -1 & 1 & -1 \\ -1 & 1 & 1 & -1 \end{pmatrix} \quad (1)$$

is very convenient for the discussion of the  $D_{2d}$  phase. The columns in the matrix Eq.(1) are the four unit vectors with their  $x$ ,  $y$ , and  $z$  components in the first, second and third row, respectively. This is shown in fig. 2 on the left. The spatially inverted system, where all signs in Eq.(1) are reversed, describes an orientation that is different from the original one, but completely equivalent. This is the meaning of the statements that the  $D_{2d}$  phase lacks inversion symmetry, or inversion symmetry is spontaneously broken. This is shown in fig. 2 on the right. Obviously, an inversion is equivalent to a  $\pi/2$  rotation of the structure about the  $z$ -axis. Performing simultaneously, inversion with a  $\pi/2$  rotation, leaves the structure invariant rendering the  $z$ -axis an improper  $\bar{4}$  axes.

Generally the order parameter strength  $T$  shows a relaxational type of dynamics, which is relevant close to a phase transition or for defect topology to be discussed separately [54]. Consequently, throughout this paper it will be treated as a constant  $T_0$ . Formally, the two possibilities, original and inverted

orientation, can be dealt with by always using Eq.(1), but assigning a positive and negative sign to  $T_0$ , respectively. The absence of a  $T_0 \rightarrow -T_0$  invariance is then the manifestation of the absence of inversion symmetry. The sum of the 4 tetrahedron vectors vanishes,  $T_{ijj} = 0$ , making sure that no polar order is present. There is also no quadrupolar (nematic) order present, since  $T_{ikl}T_{jkl} = \alpha \delta_{ij}$ , which is isotropic ( $\alpha = (32/27) T_0^2$ ).

Changes of the order parameter  $\delta T_{ijk} = T_{ijk} - T_{ijk}^{eq}$  from its equilibrium value are the candidates for being variables.  $\delta T_{ijk}$  is restricted by the special properties of  $T_{ijk}$  discussed above leading to the requirements  $\delta T_{ijj} = 0$  and  $\delta T_{ikl}T_{jkl} + T_{ikl}\delta T_{jkl} = 0$ . Thus, we are left with three (properly normalized) hydrodynamic variables

$$\delta \Gamma_i \equiv \frac{1}{4\alpha} \epsilon_{ipq} T_{pkl} \delta T_{qkl} \quad (2)$$

describing the 3-dimensional rotations of the tetrahedric structure and reflecting the 3-fold broken rotational symmetry. Equation (2) is not integrable and  $\delta \Gamma_i$  is not a vector, nor are its components rotation angles (except in linear approximation). Thus, two subsequent changes cannot be interchanged

$$\begin{aligned} (\delta_1 \delta_2 - \delta_2 \delta_1) \Gamma_i &= \frac{1}{2\alpha} \epsilon_{ipq} (\delta_1 T_{pjk}) (\delta_2 T_{qjk}) \\ &= 2\epsilon_{ipq} (\delta_1 \Gamma_p) (\delta_2 \Gamma_q) \end{aligned} \quad (3)$$

because finite 3-dimensional rotations in space do not commute. This is similar to e.g. rotations of the preferred direction in superfluid  $^3\text{He-A}$  (Mermin-Ho relation [55]), rotations in biaxial nematics [11, 12] or rotations of a biaxial nematic structure for models of the core of neutron stars [56]. Equation (2) can be inverted to give  $\delta T_{qkl} = 2\epsilon_{ipq} T_{pkl} \delta \Gamma_i$ .

In a linearized theory, where only infinitesimal rotations are considered, the hydrodynamic variable  $\delta \Gamma_i^{lin} \equiv 1/(4\alpha) \epsilon_{ipq} T_{pkl}^{eq} \delta T_{qkl}$  is a true vector and  $(\delta_1 \delta_2 - \delta_2 \delta_1) \Gamma_i^{lin} = 0$ .

Since homogeneous rotations of the tetrahedric structure must not cost energy, only gradients of the rotations enter the (gradient) free energy

$$f_g = \frac{1}{2} K_{ijkl}^{\Gamma} (\nabla_j \Gamma_i) (\nabla_l \Gamma_k) \quad (4)$$

where

$$\begin{aligned} K_{ijkl}^{\Gamma} &= K_1^{\Gamma} (\delta_{ij} \delta_{kl} + \delta_{il} \delta_{jk}) + K_2^{\Gamma} \delta_{ik} \delta_{jl} \\ &+ K_3^{\Gamma} T_{jlp} T_{ikp}. \end{aligned} \quad (5)$$

A possible fourth term  $\sim (T_{ijp} T_{klp} + T_{jkp} T_{ilp})$  is not independent, but apart from a surface energy contribution, equivalent to a certain linear combination of the terms kept in Eq.(5).

The dynamic equation is a simple balance equation

$$\frac{\partial}{\partial t} \Gamma_i + Y_i = 0 \quad (6)$$

where  $Y_i = Y_i^R + Y_i^D$  contains reversible crosscouplings to the velocity  $\mathbf{v}$ ,

$$Y_i^R = +v_j \nabla_j \Gamma_i - \frac{1}{2} \omega_i + \frac{1}{2\alpha} \epsilon_{ipq} T_{pjk} T_{qlk} \epsilon_{mjl} \omega_m. \quad (7)$$

Here,  $\omega_i = (1/2) \epsilon_{ijk} \nabla_j v_k$  is the vorticity.

In Eq.(7) these couplings arise from the behavior of tensors under rigid rotations, in particular of  $T_{ijk}$ . The term  $\sim v_i \nabla_i$  can be viewed as the transport part of the time derivative. All these terms are universal and do not depend on material properties. If linearized, the reversible current simplifies to  $Y_i^R = -\omega_i$  showing that  $\delta \Gamma_i$  does not transform like a vector under rotations, but resembles the case of director dynamics in biaxial nematic systems which also has non-commuting variables. Note that there is, in contrast to the nematic case, no phenomenological coupling to deformational flow,  $A_{ij} = (1/2)(\nabla_j v_i + \nabla_i v_j)$  of the form  $Y_i^R = \lambda_{ijk} A_{jk}$ , since the flow alignment tensor  $\lambda_{ijk}$  should be even under parity and thus cannot be proportional to  $T_{ijk}$ . The symmetry of  $T_d$  does not allow a coupling to shear flow.

The entropy production due to the reversible rotational flow contributions to  $Y_i^R$  in Eq.(6) is zero, as required by thermodynamics, due to the requirement that the energy is a scalar quantity (cf. the procedure described in sec.2 of [57]) with the result that the stress tensor does not contain a contribution from  $\delta \Gamma_i$ . The transport term in Eq.(7) is balanced, together with all transport terms in the other dynamic equations, by the pressure in the stress tensor [57].

The dissipative current only contains a self-coupling term

$$Y_i^D = -\frac{1}{\gamma_1} h_i^{\Gamma}$$

which is governed by the material dependent ‘rotational viscosity’,  $\gamma_1$ . The diffusion of  $\delta \Gamma_i$  is due to its thermodynamic conjugate quantity, the ‘molecular field’

$$h_i^{\Gamma} \equiv \left( \frac{\partial}{\partial \Gamma_i} - \nabla_j \frac{\partial}{\partial \nabla_j \Gamma_i} \right) f$$

where  $f$  is the sum of all energy contributions. Clearly, if no gradients are present,  $h_i^{\Gamma}$  is zero demonstrating the hydrodynamic nature of  $\delta \Gamma_i$ . However, for energy minimum, one needs to balance torques i.e.  $\mathbf{h}^{\Gamma} \times \mathbf{E}^{\alpha} = 0$ .

There are no further couplings of the rotations  $\delta \Gamma_i$  to other variables (like mass density, energy density) and vice versa. Due to the lack of flow alignment, there are no ‘back flow’ effects, i.e. no coupling of the stress tensor to  $\delta \Gamma_i$ . However, there are several additional observables and new effects in the hydrodynamics of the usual variables because of the existence of  $T_{ijk}$ , which we have described in [13].

It is well known [1, 2] that an electric field  $\mathbf{E}$  orients the tetrahedral structure due to the generalized dielectric energy,

$$f_E = -\frac{\zeta^E}{2} T_{ijk} E_i E_j E_k. \quad (8)$$

This energy is minimal, if one of the tetrahedral vectors (a 3-fold symmetry axis, say  $\mathbf{n}^1$ ) is parallel or antiparallel to  $\mathbf{E}$  depending on the sign of  $\zeta^E$ . In this geometry  $T_{ijk}$  takes the form [17]

$$T_{ijk} = \frac{1}{3} \begin{pmatrix} 0 & -\sqrt{2} & -\sqrt{2} & 2\sqrt{2} \\ 0 & -\sqrt{6} & \sqrt{6} & 0 \\ 3 & -1 & -1 & -1 \end{pmatrix}. \quad (9)$$

For deviations from this ground state there is an energy penalty

$$f_E^{(1)} = \frac{16}{9} |\zeta^E T_0| E^3 (\delta \mathbf{\Gamma}_\perp)^2 \quad (10)$$

with  $\delta \mathbf{\Gamma}_\perp = \{\delta \Gamma_x, \delta \Gamma_y\}$  and the z-axis defined by the external field. Thus, a rotation of  $T_{ijk}$  about the field axis,  $\delta \Gamma_z$ , does not cost energy and this rotation is still hydrodynamic. The two other rotations,  $\delta \Gamma_x$  and  $\delta \Gamma_y$ , are non-hydrodynamic and relax to zero even in the homogeneous limit. Obviously, the external field  $\mathbf{E}$  breaks the appropriate rotational symmetries externally. Note that the orienting free energy is cubic in the field strength  $E = |\mathbf{E}|$  and the total energy of the system decreases [17].

There is also a flexoelectric type of free energy

$$f_E^{(2)} = e_1 E_j E_k \nabla_i T_{ijk} = \frac{32}{9} e_1 T_0 E^2 (\text{curl } \mathbf{\Gamma}_\perp)_z \quad (11)$$

which is quadratic in  $E$  and involves  $\nabla_x \Gamma_y - \nabla_y \Gamma_x$  in the geometry chosen. In addition, there is an energy contribution linear in the field, but with second order gradients of  $\delta \Gamma_i$

$$\begin{aligned} f_E^{(3)} &= e_2 E_i \nabla_j \nabla_k T_{ijk} \\ &= -\frac{4}{9} e_2 T_0 E (4 \nabla_z [\nabla_y \Gamma_x - \nabla_x \Gamma_y] \\ &\quad + 2\sqrt{2} [\nabla_y^2 - \nabla_x^2] \Gamma_y - 4\sqrt{2} \nabla_x \nabla_y \Gamma_x) \\ &\quad + O((\nabla \Gamma)^2). \end{aligned} \quad (12)$$

A magnetic field  $\mathbf{H}$  cannot orient the tetrahedral structure, since an energy contribution  $\sim T_{ijk} H_i H_j H_k$  is impossible because magnetic fields changes sign under time reversal while energy does not. What is possible however is a term  $\zeta^{EH} T_{ijk} E_i H_j H_k$ . But even for crossed fields,  $\mathbf{E} \perp \mathbf{H}$ , no orientation is fixed in the plane perpendicular to the electric field, since the  $\zeta^{EH}$  term only involves  $(\delta \mathbf{\Gamma}_\perp)^2$ , similar to Eq.(10). Orientation by an external magnetic field can only be provided by higher order terms, e.g. quadratic in  $T_{ijk}$  and fourth order in  $H_i$ , which however, are very likely rather small. Anyhow, terms of fourth order (in the magnetic or the electric field) are known to orient phases with cubic symmetry, as is known for example for cholesteric blue phases in electric fields.

Comparing the  $T_d$  phase with an isotropic liquid, we find material tensors of third or higher rank are more complicated (have more independent components), e.g. the viscosity tensor contains three viscosities rather than two. Second, there are completely new cross couplings between the standard hydrodynamic variables: density, energy density and density of linear momentum, in particular a reversible dynamic coupling between shear and elongational flow on the one hand, and temperature, concentration gradients and electric fields on the other [13]. Finally, the existence of the tetrahedral structure gives rise to additional hydrodynamic variables. The orientation of this structure in space is arbitrary, and any rotation of it is a Goldstone variable associated with a spontaneously broken continuous symmetry. This is analogous to biaxial nematic phases, where three rotational hydrodynamic degrees of freedom are also present. As the rotations of the tetrahedral structure are not optically observable in  $T_d$  but are in D2d, we discussed this aspect only very briefly in [13] for  $T_d$  and expanded on this topic in more detail for D2d in sect. 2.2.

### 3 Linear Hydrodynamics of the D2d phase

We model the D2d phase as a tetrahedric phase that has acquired an additional uniaxial nematic order,  $Q_{ij}$ . Here,  $Q_{ij}$  is a traceless symmetric second rank tensor  $Q_{ij} = \frac{S_0}{2} (n_i n_j - \frac{1}{3} \delta_{ij})$  with the nematic order parameter strength  $S$ , which we will take to be constant ( $S_0 = 1$ ) (since its dynamics is fast and non-hydrodynamic), and the director  $\mathbf{n}$  [6,7]. The latter can be used as a unit vector,  $\mathbf{n}^2 = 1$ , under the proviso that all equations are invariant under the replacement of  $\mathbf{n}$  with  $-\mathbf{n}$ . In the D2d phase the director is oriented along one (improper) 4-fold axis of the tetrahedric structure. Denoting this axis, which is still a  $\bar{4}$  symmetry axis, as the z-direction (in fig. 1), the orientation of the tetrahedric vectors is given by Eq.(1), where the orientations of the two former  $\bar{4}$  axes of the tetrahedric phase are along the x and y direction. The director  $\mathbf{n}$  makes an angle of  $\Theta_T/2$  or  $\pi - \Theta_T/2$  with the tetrahedric directions  $\mathbf{n}^\alpha$ , where  $\Theta_T$  is the tetrahedric angle with  $\cos \Theta_T = -1/3$ . All 3-fold symmetry axes (of  $T_d$ ) are removed by the existence of the nematic director. The remaining 2-fold, the (improper) 4-fold symmetry axis, and the nematic orientation all lie at the intersection of the two vertical symmetry planes, which guarantee the absence of (usual) chirality.

As in the tetrahedric phase there are three rotational symmetry variables, which are here the rotations of the rigidly combined  $T_{ijk}$  and  $Q_{ij}$  structure. In this section we will not consider the non-hydrodynamic relative rotations among them (but see sect. 4). The common existence of octupolar and quadrupolar order does not imply the D2d phase to be polar (i.e. there is no polar vector present), since  $T_{ijk} Q_{jk} = 0 = T_{ijk} n_j n_k$  for the equilibrium structure.

The important and qualitatively new feature is that rotations of the director are directly observable in the microscope. Those of the tetrahedric structure are not but can be inferred from observations of a rigidly attached  $\mathbf{n}$ .

There are only two rotations of  $\mathbf{n}$ , since  $\mathbf{n} \cdot \delta \mathbf{n} = 0$ . Instead of using  $\delta \mathbf{n}$  one could also use  $\delta \mathbf{\Gamma}$  to describe those rotations, where  $\delta \Gamma_i \sim (\mathbf{n} \times \delta \mathbf{n})_i$  for  $i = \{x, y\}$ . The third rotation, about  $\mathbf{n}$ , is described by  $\delta \Gamma_z$  or more generally, by  $\mathbf{n} \cdot \delta \mathbf{\Gamma}$ . Since this variable is not detectable optically and is only slightly coupled to the other hydrodynamic variables, we will first disregard it and discuss its behavior at the end of this section. Thus, we are left with a system that has the same number and type of variables as a conventional uniaxial nematic. The difference is that the D2d phase is not transversely isotropic but has a structure perpendicular to  $\mathbf{n}$  expressed by  $T_{ijk}$  which does not conserve parity.

This difference to conventional uniaxial nematics will be investigated in detail next. The case of external electric and magnetic fields is dealt with, separately. We also restrict ourselves first to a linear hydrodynamic description, then describe nonlinear effects in sect. 4.

#### 3.1 Static Properties

In addition to the rotational degrees of freedom described above and for which we take the nematic "language"  $\delta n_i$ , there are those variables characteristic of an isotropic fluid, namely the mass density  $\rho$ , entropy density  $\sigma$ , and momentum density

*g.* The statics is described by setting up an energy density function  $\varepsilon = \varepsilon_0 + \varepsilon_g + \varepsilon_l + \varepsilon_c + \varepsilon_\Omega + \varepsilon_J$ , where  $\varepsilon_0$  is the part of isotropic liquids. The gradient free energy

$$\varepsilon_g = \frac{1}{2} K_{ijkl} (\nabla_i n_k) (\nabla_j n_l) \quad (13)$$

contains 4 Frank-type orientational elastic coefficients

$$K_{ijkl} = K_3 n_i n_j \delta_{kl}^{tr} + (K_1 - 2K_2) \delta_{ik}^{tr} \delta_{jl}^{tr} + K_2 (\delta_{il}^{tr} \delta_{jk}^{tr} + \delta_{ij}^{tr} \delta_{kl}^{tr}) + K_4 n_p n_q T_{ijp} T_{qkl}. \quad (14)$$

In Eq.(14) as well as in the following equations, we have expanded into  $n_i$ , the transverse Kronecker delta,  $\delta_{ij}^{tr} = \delta_{ij} - n_i n_j$ , projecting onto the plane perpendicular to  $n_i$ , and  $T_{ijk}$  making sure simultaneously that only independent terms are taken into account. In the limit of a usual uniaxial nematic this expression reduces to the Frank free energy with the Frank constants splay, bend and twist. In linear order  $T_{ijk}$  is the equilibrium one given e.g. by Eq.(1). In the D2d phase all 4 Frank-type coefficients depend on the degree of tetrahedric order,  $T_0$ , one of them vanishing at the transition to the (uniaxial) nematic phase.

As required, also the new term ( $\sim K_4$ ) contains only gradients of the director with  $n_i \nabla_j n_i = 0$ , in particular the combination  $(\nabla_x n_x) (\nabla_y n_y)$ .

There is also a linear gradient energy

$$\varepsilon_l = \xi T_{ijk} n_i \nabla_j n_k \quad (15)$$

which is related neither to linear splay,  $\nabla_x n_x + \nabla_y n_y$  (present in polar nematics), nor to linear twist,  $\nabla_x n_y - \nabla_y n_x$  (present in chiral nematics), but involves the combination  $\nabla_x n_y + \nabla_y n_x$ . As it is well known from cholesteric liquid crystals [7], polar nematics [40, 46, 58] and from polar cholesterics [54] the appearance of linear gradient terms in the deformation energy of a director field signals the possibility of an inhomogeneous ground state. Clearly this is also an option for the macroscopic behavior of the D2d-phase described here and will be discussed in the next subsection.

Finally there are cross-couplings between director deformations of the  $\xi$ -type (Eq.(15)) and all the scalar hydrodynamic variables

$$\varepsilon_c = T_{ijk} n_i \nabla_j n_k (\xi^\rho \delta \rho + \xi^\sigma \delta \sigma) \quad (16)$$

unknown for usual nematics. Analogous terms for possible additional scalar variables, like concentration variations  $\delta c$  in mixtures, or variations of the order parameters  $\delta T$  or  $\delta S$ , can be written down straightforwardly. These terms resembles the static Lehmann terms in cholesteric liquid crystals [59], although here they do not involve a simple rigid rotation of the director structure. The contribution  $\varepsilon_\Omega$  containing the third symmetry variable associated with the broken symmetry around  $\mathbf{n}$  and  $\varepsilon_J$  related to relative rotations will be given and discussed below.

Instead of using  $n_i$ ,  $\delta_{ij}^{tr} = \delta_{ij} - n_i n_j$  and  $T_{ijk}$ , one can also express the structure of the Frank tensor (as well as those of other property tensors) by a triad of orthogonal unit vectors  $n_i$ ,  $m_i$  and  $l_i$  as it has been done for orthorhombic biaxial nematics

[11]. Thereby making contact with the description given in ref. [8]  $T_{ijk}$  reads

$$T_{ijk} = T_0 (n_i m_j l_k + n_i l_j m_k + m_i l_j n_k + m_i n_j l_k + l_i n_j m_k + l_i m_j n_k) \quad (17)$$

and the  $K_4$  term in Eq.(14) is given by  $K_4 T_0^2 (m_i l_j + l_i m_j) (m_k l_l + l_k m_l)$ .

### 3.2 Ambidextrous Chirality

The linear gradient energy contribution Eq.(15) allows for a non-homogenous ground state. Indeed, it is straightforward to show that a helical state has a lower free energy than the homogeneous state. In this helical state the director (and thus the  $\bar{4}$  axis of the D2d phase) rotates about one of the other  $\bar{4}$  axes of the pure tetrahedric phase. These are the  $x$  or  $y$  axis in the geometry of Eq.(1), where the director is along the  $z$  axis. Choosing the  $x$  axis as helical axis for definiteness, the director (and the  $\bar{4}$  axis) is given by

$$n_i = \delta_{iz} \cos(q_0 x) + \delta_{iy} \sin(q_0 x) \quad (18)$$

while for the tetrahedral vectors one finds

$$\frac{1}{\sqrt{3}} \begin{pmatrix} 1 & 1 & -1 & -1 \\ C - S & -C + S & C + S & -C - S \\ -C - S & C + S & C - S & -C + S \end{pmatrix} \quad (19)$$

with  $C = \cos(q_0 x)$  and  $S = \sin(q_0 x)$ .

This state has a free energy, which is by

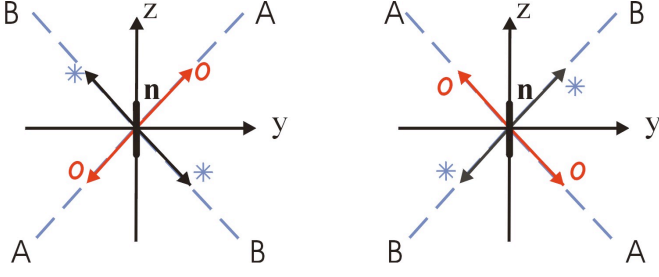
$$\Delta \varepsilon = \frac{1}{2} \frac{\xi^2 T_0^2}{K_2} \quad (20)$$

smaller than that of the homogeneous state, independent of the sign of the modulus,  $\xi$ , of the linear gradient term and that of  $T_0$ . The sign of  $\xi T_0$ , however, governs the rotation sense of the helix, since for the helical wave vector one gets, for the geometry chosen,

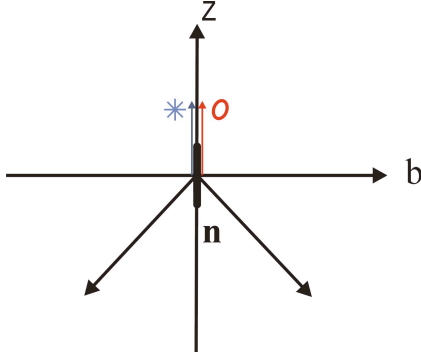
$$q_0 = -\frac{\xi T_0}{K_2} \quad (21)$$

leading to a left- (right-) handed helix for  $\xi T_0 > 0$  ( $< 0$ ). The sign of  $\xi$  is fixed for a given material (and, of course, not related to molecular chirality because there is none), while the sign of  $T_0$  depends on the tetrahedric orientation (original or inverted). In fig. 3 it is shown, how the rotation sense changes when going from the original (left) to the inverted (right) system, equivalently, going from  $T_0$  to  $-T_0$ . For a rotation about the  $y$  axis (the other  $\bar{4}$  axis of the pure tetrahedric state) the sequence  $A \rightarrow z \rightarrow B$  in fig. 3 constitutes a left (right) helical sense the original (inverted) system, just opposite to the case of a rotation about the  $x$ -axis, and  $q_0 = \xi T_0 / K_2$ . The energy reduction is still given by Eq.(20).

On the contrary, a rotation about a direction that bisects the  $x$  and  $y$  (or  $-y$ ) axes (the two extra  $\bar{4}$  axes of the pure tetrahedric state), does not lead to an energy reduction due to the linear gradient term, and no helical sense can be defined (fig. 4). Of course, a rotation about the director,  $\mathbf{n}$ , (the  $z$ -axis) does not



**Fig. 3.** Projection of the D2d structure onto the  $y/z$  plane. The director  $\mathbf{n}$  is along the  $z$  axis, the  $x$  axis sticks out of the drawing plane, and circles and asterisks are as in fig. 2. A rotation about the  $x$  axis with the sequence  $A \rightarrow z \rightarrow B$  constitutes a right (left) helical sense for the original system on the left (inverted system on the right), while the sequence  $B \rightarrow z \rightarrow A$  gives the opposite rotating sense.



**Fig. 4.** Projection of the D2d structure onto the  $b/z$  plane (with  $\mathbf{b} = \mathbf{e}_x + \mathbf{e}_y$ ). The director  $\mathbf{n}$  is along the  $z$  axis; circles and asterisks as in fig. 2. A rotation about the axis perpendicular to the drawing plane does not allow the identification of any rotation sense, (since the sequence  $b \rightarrow z \rightarrow b$  is identical to  $z \rightarrow b \rightarrow z$ ) neither does a rotation about the  $b$  axis.

lead to an energy reduction as the linear gradient term makes no contribution.

In a spontaneous formation of the D2d phase helices of different rotation sense and about different orthogonal axes might occur at different places of the sample, since all the possibilities discussed above are equally likely. This is a manifestation of ambidextrous chirality [35]. Where regions of different helicity or different orientation of the helical axis meet, there are defects (distortions of the D2d structure), which cost energy thus reducing the gain due to the helix formation.

We would like to emphasize that the two senses of rotation are exclusively due to the structure of the linear gradient term (Eq.(15)), which is specific to systems showing quadrupolar and octupolar order simultaneously. Therefore the ambidextrous chirality arising here is qualitatively different from the ambidextrous chirality in the  $C_{B2}$  ( $B_2$ ) phase, where the energetically equivalent left and right handed helices are due to the tilt of the tetrahedric structure to two different sides [26, 27]. Of course, in usual chiral liquid crystals such as cholesteric liquid crystals, for which the molecular chirality is transferred to a large-scale, collective level, only one kind of handedness results as the energetic minimum.

If in a D2d phase a pure helical state (with a single helicity and single helix orientation) can form over a sufficiently large domain, it has a lower energy compared to the homogeneous state. Averaging such a structure over a length scale large compared to the pitch, the resulting symmetry of the phase is that of a smectic A phase, since all informations about the helix are eliminated (since there is no molecular chirality).

However, a description on the global level, i.e. on length scales much larger than the pitch, loses information of the special properties on length scales smaller than the pitch. Therefore, we will use the local description in the following. This means, we assume locally D2d symmetry, which is tetragonal biaxial nematic-like, but with the  $\xi$ -term in the free energy (Eq.(15)) due to the lack of inversion symmetry. This procedure is frequently used in cholesterics, which are locally described as nematics with the additional linear twist energy term. If the D2d phase is in a homogeneous state, the linear gradient free energy term always leads to the tendency of forming localized helical domains.

### 3.3 Dynamic Properties

In the D2d phase the structure of the director dynamics is the same as in uniaxial nematics. There is flow alignment, the coupling to deformational flow, and the appropriate back flow terms in the stress tensor, as well as director relaxation or diffusion due the molecular field  $h_i = \delta\varepsilon/\delta n_i$  giving rise to one reversible and one irreversible transport parameter [60–63].

The conserved variables generally obey conservation laws involving currents, e.g.  $(\partial\rho/\partial t) + \nabla_i j_i = 0$  for the density or  $(\partial g_i/\partial t) + \nabla_j \sigma_{ij} = 0$  for the momentum density. There are structurally new couplings in the currents of charge, entropy (or heat) and concentration to deformational flow

$$j_i^{e,R} = \dots + (\Gamma_{11} \delta_{ii}^{tr} + \Gamma_{12} n_i n_i) T_{ljk} A_{jk} \quad (22)$$

$$j_i^{\sigma,R} = \dots + (\Gamma_{21} \delta_{ii}^{tr} + \Gamma_{22} n_i n_i) T_{ljk} A_{jk} \quad (23)$$

$$j_i^{c,R} = \dots + (\Gamma_{31} \delta_{ii}^{tr} + \Gamma_{32} n_i n_i) T_{ljk} A_{jk} \quad (24)$$

not present in nematics, but found also in the tetrahedric phase. In the latter case, there is only one reversible transport parameter per current, while here there are two,  $\Gamma_{x1}$  and  $\Gamma_{x2}$ , due to the anisotropy. The physical meaning of these terms has already been discussed extensively in [13], e.g. a shear flow leads to an electric, heat and concentration current. In a homogeneous D2d state the induced currents are perpendicular to the shear plane defined by the deformational flow  $A_{ij}$ . Since  $T_0$  can have either sign (for the original and inverted tetrahedric order), the induced currents will point in opposite directions, what could be viewed as induced ambi-polarity. If both variants are present in different parts of the same sample, this ambi-polarity shows up directly. For a pure helical state (along the  $x$  axis) the induced currents are modulated by the factor  $\cos(2q_0 x)$ . However, a strong flow destroys the helix due to the flow alignment effect acting on the nematic part of the D2d structure.

The counter terms guaranteeing zero entropy production are in the stress tensor

$$\begin{aligned} \sigma_{ij}^R = & \dots - (\Gamma_{11}\delta_{lk}^{tr} + \Gamma_{12}n_l n_k)T_{ijk}E_l \\ & - (\Gamma_{21}\delta_{lk}^{tr} + \Gamma_{22}n_l n_k)T_{ijk}\nabla_l T \\ & - (\Gamma_{31}\delta_{lk}^{tr} + \Gamma_{32}n_l n_k)T_{ijk}\nabla_l c \end{aligned} \quad (25)$$

and describe, for a homogeneous state, induced stresses in the plane perpendicular to temperature and concentration gradients or an electric field.

In the dissipative parts of the currents there are the following structurally new couplings of electric fields, gradients of the temperature, concentration, and  $W$ , the thermodynamic conjugate to the modulus  $S$ , to the nematic molecular field  $h_i$

$$R \sim (\Psi^E E_k + \Psi^T \nabla_k T + \Psi^c \nabla_k c + \Psi^S \nabla_k W)T_{ijk}n_j h_i. \quad (26)$$

We note that the opening of these new dissipative channels are of the same order as director diffusion  $R \sim \gamma_1^{-1}h_i^2$  and, for example, thermal conductivity,  $R \sim \kappa_{ij}(\nabla_i T)(\nabla_j T)$ , or electric conductivity,  $R \sim \sigma_{ij}^E E_i E_j$  in usual uniaxial nematics. Physically speaking, they are similar in structure to the Lehmann effect in cholesteric liquid crystals [59]. In cholesteric liquid crystals the wave vector of the helix, a pseudoscalar,  $q_0$ , guarantees the appropriate behavior of the dissipation function under parity while here it is  $T_{ijk}$ . Thus a nematic with octupolar order can generate director rotations under external fields including electric fields, temperature and concentration gradients.

The viscosity tensor is more complicated and has one coefficient more than in the nematic case. The viscous part of the entropy production reads

$$\begin{aligned} 2R = & \nu_{ijkl}(\nabla_i v_k)(\nabla_j v_l) \\ = & \nu_1 [(\nabla_x v_x)^2 + (\nabla_y v_y)^2] + \nu_2 [(\nabla_x v_y)^2 + (\nabla_y v_x)^2] \\ & + 2\nu_3 [(\nabla_x v_z)^2 + (\nabla_y v_z)^2 + (\nabla_z v_x)^2 + (\nabla_z v_y)^2] \\ & + \nu_4 (\nabla_z v_z)^2 + 2\nu_5 (\nabla_z v_z)(\nabla_y v_y + \nabla_x v_x) \\ & + 2\nu_6 (\nabla_y v_y)(\nabla_x v_x) \end{aligned} \quad (27)$$

with the viscosity tensor

$$\begin{aligned} \nu_{ijkl} = & (\nu_1 - 2\nu_2)\delta_{ik}^{tr}\delta_{jl}^{tr} + \nu_2(\delta_{ij}^{tr}\delta_{kl}^{tr} + \delta_{il}^{tr}\delta_{jk}^{tr}) \\ & + \nu_3(\delta_{ij}^{tr}n_k n_l + \delta_{il}^{tr}n_j n_k + \delta_{kl}^{tr}n_i n_j + \delta_{jk}^{tr}n_i n_l) \\ & + \nu_4 n_i n_j n_k n_l + \nu_5(\delta_{ik}^{tr}n_j n_l + \delta_{jl}^{tr}n_i n_k) \\ & + \nu_6 n_p n_q T_{pij}T_{qkl} \end{aligned} \quad (28)$$

containing 6 viscous coefficients in accord with general symmetry considerations [64]. Possible additional terms  $\sim \delta_{pq}^{tr}T_{pij}T_{qkl}$ ,  $\sim n_p n_q(T_{pik}T_{qjl} + T_{pil}T_{qjk})$ , and  $\sim \delta_{pq}^{tr}(T_{pik}T_{qjl} + T_{pil}T_{qjk})$  are not independent, but equivalent to certain linear combinations of the terms kept in Eq.(28). In the D2d phase all six viscous coefficients depend on the degree of tetrahedric order,  $T_0$ , one of them vanishing at the transition to the (uniaxial) nematic phase.

### 3.4 External Field Effects

It is well known that external fields have an orienting effect on liquid crystalline phases, in particular the dielectric anisotropy

orients the director of the nematic phase, while the tetrahedric structure is aligned by a cubic generalization of the dielectric energy, as discussed above. The homogeneous part of the field-induced free energy reads

$$\begin{aligned} \varepsilon_E = & -\frac{\tilde{\varepsilon}_a}{2}n_i n_j D_i D_j - \frac{\tilde{\zeta}^E}{2}T_{ijk}D_i D_j D_k \\ & + (\zeta_1^{EH}T_{ijk}\delta_{il}^{tr} + \zeta_2^{EH}T_{ijk}n_i n_l)D_i H_j H_k. \end{aligned} \quad (29)$$

There is only one coefficient in  $\tilde{\zeta}^E$  due to the high symmetry of this term; we note, that the contribution  $\sim \tilde{\zeta}^E$  gives rise to second harmonic generation and can thus serve as a useful experimental tool to distinguish a D2d phase from a usual uniaxial nematic phase. The term  $\sim T_{ijk}n_i n_j D_k$ , which is linear in the displacement field,  $D_i$ , is zero in the D2d phase, because  $(\mathbf{n} \cdot \mathbf{n}^\alpha)^2 = 1/3$  for any  $\alpha$  and  $\sum_{\alpha=1}^4 \mathbf{n}^\alpha = 0$ . The terms  $\sim DH^2$  have no analog in usual uniaxial nematics, but only in the tetrahedric  $T_d$  phase where one contribution exists. There is no need to incorporate fourth order terms in  $\varepsilon_E$  to guarantee convexity, since we study external fields here.

We have used the electric displacement field  $\mathbf{D}$  rather than the electric field  $\mathbf{E}$ , since it is suitable to take the former as variable and the latter as conjugate quantity, if charge density conservation is taken into account as a hydrodynamic equation. This gives the susceptibilities a slightly different meaning, which is indicated by the tilde. The first term is minimized for  $\mathbf{n}$  parallel or perpendicular to the field (for  $\tilde{\varepsilon}_a \geq 0$ ), while the second term forces one of the tetrahedric unit vectors to be parallel or antiparallel to  $\mathbf{D}$  depending on  $\tilde{\zeta}^E \geq 0$ . However, in the D2d phase these two cases are incompatible, since the director always makes an angle of  $\Theta_T/2$  or  $\pi - \Theta_T/2$  (e.g.  $\cos(\Theta_T/2) = \pm 1/\sqrt{3}$ ) with any of the tetrahedric vectors, disproving the possibility for zero or 90 degrees. At small fields the first term is dominant and the director orientation is the usual nematic one, while the tetrahedric orientation is completely frustrated. Above a threshold field  $D_c$  it is energetically favorable to tilt the director away from the dielectrically optimal orientation and at the same time tilt one of the tetrahedric vectors by the same angle towards the field (or its negative). For positive dielectric coupling,  $\tilde{\varepsilon}_a > 0$ , this tilt angle  $\theta_E$  depends on the external field  $D = |\mathbf{D}|$  through

$$6 \cos \theta_E = \beta \pm (\beta^2 + 12)^{1/2} \quad \text{with} \quad \beta = \pm \frac{\sqrt{3}}{4} \frac{\tilde{\varepsilon}_a}{\tilde{\zeta}^E T_0 D} \quad (30)$$

where  $T_0 > 0$  ( $< 0$ ) refers to parallel (antiparallel) tetrahedric field orientation. Upper and lower signs in eq. (30) refer to the possibility to call the dielectric orientation angle between the director and the field, either zero or  $\pi$ , respectively. Such a degeneracy does not exist with respect to the tetrahedric vectors, where ‘parallel’ and ‘antiparallel’ are well defined. The threshold field is given by

$$D_c = \frac{\sqrt{3}}{8} \frac{\tilde{\varepsilon}_a}{\tilde{\zeta}^E T_0} \quad \text{or} \quad \beta_c = \pm 2 \quad (31)$$

and basically depends on the ratio of the dielectric anisotropy and the tetrahedric cubic ‘electricity’.

The tilt angle  $\theta_E$  is zero at the threshold meaning there is no jump. For very large fields or if  $\tilde{\varepsilon}_a \rightarrow 0$  the tilt angle



approaches asymptotically the value  $\Theta_T/2$ , where the tetrahedral orientation is perfect. If  $\tilde{\epsilon}_a \equiv 0$  any infinitesimally small external field reorients the whole structure in the tetrahedral way ( $\theta_E = \theta_T/2$ ) without any threshold. Here we assume  $\tilde{\epsilon}_a$  to be positive and the nematic dielectric anisotropy to be the dominant effect such that the system is below the threshold for reasonable applied fields. In that case the symmetry of the D2d phase is preserved and the hydrodynamic description given above (and below) is valid when the z-axis is taken as the external field direction. In this case rotations of the structure about the electric field direction cost energy

$$\varepsilon_E = \frac{1}{2} \left( \tilde{\epsilon}_a + \frac{32}{9} \tilde{\zeta}^E T_0 D \right) D^2 (\delta \mathbf{n})^2$$

with an effective, field dependent susceptibility (in the big parentheses). The mixed electric and magnetic field terms, the last ones of Eq.(29), do not have any additional orienting effect.

If  $\tilde{\zeta}^E$  is large enough to reach the threshold field experimentally, there is a unique way of identifying the D2d phase: Below the threshold, the director is oriented parallel to  $\mathbf{D}$ . Increasing the field beyond the threshold, the director turns away to a direction oblique to the field - something that cannot happen in a conventional uniaxial nematic phase. The presence of a helix further complicates the behavior. Any homogeneous external field is incompatible with the combined helical structure of director and tetrahedral vectors and tends to distort that structure. Therefore the quadratic and cubic electric field energies compete.

### 3.5 Influence of the third broken symmetry variable

As discussed above the third variable associated with broken rotational symmetry is a rotation around  $\mathbf{n}$ . This is not a hydrodynamic variable for usual uniaxial nematics, but is present in biaxial nematics, where a second director  $\mathbf{m}$  can rotate orthogonally to  $\mathbf{n}$ . In the D2d phase the structure  $T_{ijk}$  rotates about  $\mathbf{n}$ , which is described by  $\delta\Omega \equiv n_i \delta\Gamma_i = \frac{1}{4\alpha} n_i \epsilon_{ipq} T_{pjk} \delta T_{qjk}$ . By construction  $\delta\Omega$  is even under parity and time reversal and odd in  $\mathbf{n}$ , but is not a true scalar (concerning its behavior under rotations - see below). It obeys the dynamic equation

$$\frac{\partial}{\partial t} \Omega + Y^\Omega = 0 \quad (32)$$

where the quasicurrent is split into a reversible and irreversible part  $Y^\Omega = Y^{\Omega R} + Y^{\Omega D}$ . The former contains the transport derivative and the coupling to rotational flow in the perpendicular plane

$$Y^{\Omega R} = v_i \nabla_i \Omega - n_i \omega_i \quad (33)$$

The latter term shows that  $\delta\Omega$  is not constant under rotations (as a true scalar is), but behaves like the component  $\delta \mathbf{m} \cdot (\mathbf{n} \times \mathbf{m})$  in biaxial nematics. There is no coupling to deformational flow and therefore, no flow alignment in the plane perpendicular to  $\mathbf{n}$ . Of the counter terms in the stress tensor, necessary to guarantee zero entropy production, one (the transport term) is hidden in the isotropic pressure term and the other

is removed by the requirement that the energy is a scalar quantity (cf. the procedure described in sect. 2 of [57]) with the result that the stress tensor does not contain a contribution from  $\delta\Omega$ .

Dissipation is described by the appropriate entropy production

$$R^\Omega = \frac{1}{2\gamma_2} Z^2 \quad (34)$$

which leads to  $Y^{\Omega D} = (1/\gamma_2)Z$ . Compared to usual uniaxial nematics and to the tetrahedral phase,  $\gamma_2$  constitutes a second rotational viscosity generally different from the first one  $\gamma_1$  due to the anisotropy of the different rotations. The thermodynamic conjugate  $Z = \delta\varepsilon_\Omega/\delta\Omega$  follows from the free energy

$$\varepsilon_\Omega = (K_5 n_i n_j + K_6 \delta_{ij}^{tr})(\nabla_i \Omega)(\nabla_j \Omega) + K_7 \delta_{ik}^{tr} \epsilon_{lij} (\nabla_l \Omega)(\nabla_j n_k) \quad (35)$$

which contains two Frank-like rotational elastic coefficients with respect to  $\delta\Omega$  and one for the coupling to  $n_i$ . Together with the 4 coefficients of Eq.(14) there are in total 7 rotational elastic moduli in accordance with the known number of such moduli for tetragonal biaxial nematics. For fourth order material tensors the lack of inversion symmetry in D2d does not influence the number of coefficients.

There are no further cross-coupling terms to other variables. Since this degree of freedom is not optically visible in a polarizing microscope and the only coupling to other degrees of freedom is provided by  $K_7$ , it is not easy to detect it. The  $K_7$  coupling links inhomogeneous  $\Omega$  rotations  $\nabla_z \Omega$  with director twist  $\nabla_x n_y - \nabla_y n_x$ . Assuming that the tetrahedral structure is clamped at solid surfaces with  $\mathbf{n}$  homeotropic, a circular Couette cell with a fixed plate at  $z = 0$  and a rotating one at  $z = z_0$  will create a finite  $\nabla_z \Omega$ . By the  $K_7$  coupling, which enters the director dynamics via  $h_i = \delta\varepsilon/\delta n_i$ , twist of the director is induced in the x-y-plane.

Phase winding,  $\delta\Omega$ , of D2d is expected in non-equilibrium situations such as directional solidification in cholesterics [65, 66] which have an intrinsic length scale as D2d has in Eq.(21). In D2d we have the analogue of the Lehmann effect in cholesteric liquid crystals. Indeed, in B7 many examples of phase winding have been observed, for example, during non-equilibrium spiral formation with a doubling of the spiral pitch [21]. Splay-bend in D2d can have many wavelengths not necessarily harmonically related [18] so could be less coherent and more in the orientational glass limit [66].

### 3.6 Relative Rotations

We think relative rotations are important because they can lead to new tetrahedral liquid crystal phases. In the D2d phase the orientation of the director relative to the tetrahedral structure is fixed. This is similar to the smectic A phase, where the layer normal and the director are locked to be parallel. Under certain conditions, like the vicinity to the nematic phase transition [67] or strong external shear [68], this coupling can weaken allowing the two preferred directions to differ from each other for some time before they relax back. Another example of relative rotations arises for mixtures of a rod-like and a disk-like uniaxial nematic phase [69]. Such relative rotations play a prominent

role in nematic elastomers [70,71], where they are responsible for elastic anomalies [72]. In the D2d phase relative rotations between  $\mathbf{n}$  and  $T_{ijk}$  are possible, if the relative orienting energy is weak enough. For rigid combined rotations of the two structures, there is  $\delta\mathbf{T}_\perp = \mathbf{n} \times \delta\mathbf{n}$ . Thus we can define relative rotations

$$J_i = \delta_{ik}^\perp \delta\Gamma_k - (\mathbf{n} \times \delta\mathbf{n})_i \quad (36)$$

as non-hydrodynamic variables. This definition of relative rotations is suitable for a linear theory, while a method for a nonlinear generalization is given in [73]. These relative rotations are even under spatial inversion, even under the replacement of  $\mathbf{n}$  by  $-\mathbf{n}$ , and are invariant under rigid rotations.

The free energy of relative rotations

$$\varepsilon_J = \frac{1}{2} D_1 \mathbf{J}^2 + \gamma_{ijk}^E J_k \nabla_i D_j + \gamma_{ijk}^n J_k \nabla_i n_j + \gamma_{ijk}^\Omega J_k \nabla_i \Omega \quad (37)$$

contains the stiffness coefficient  $D_1$ , which has to be taken as infinite for the rigidly locked case, as well as cross-couplings to gradients of the electric field, the director, and the third rotation. The tensor  $\gamma_{ijk}^E$  has the same symmetry as  $J_k$  and reads  $\gamma_E(\epsilon_{ikp} n_p n_j + \epsilon_{jkp} n_p n_i)$ , while  $\gamma_{ijk}^n$  and  $\gamma_{ijk}^\Omega$  are odd under inversion and odd in powers of  $\mathbf{n}$  and given by  $\gamma_{n1} \delta_{kl}^\perp \epsilon_{ipq} n_p T_{qjl} + \gamma_{n2} n_p \epsilon_{pkl} T_{ijl}$  and  $\gamma_{\Omega} n_p T_{pik}$ , respectively.

The dynamics is given by the balance equation

$$\frac{\partial}{\partial t} J_i + Y_i^J = 0 \quad (38)$$

where the quasi-current is split into a reversible and irreversible part  $Y_i^J = Y_i^{JR} + Y_i^{JD}$ . The former contains the transport derivative and the coupling to deformational flow

$$Y_i^{JR} = v_k \nabla_k J_i + \lambda_{ijk}^J A_{jk} \quad (39)$$

where  $\lambda_{ijk}^J = \lambda_J(\epsilon_{ikp} n_p n_j + \epsilon_{ijp} n_p n_k)$  contains one "flow alignment" parameter. There is no coupling to rotational flow, since  $\delta\Gamma_i$  transforms as  $\omega_i$  under rigid rotations (cf. sec.2.2), identical to what  $(\mathbf{n} \times \delta\mathbf{n})_i$  does. Lacking the coupling to rotational flow, shear flow does not lead to an alignment of  $J_i$ .

The dissipative dynamics can be derived from the appropriate part of the dissipation function,  $Y_i^{JD} = (\partial/\partial L_i) R^J$  where

$$R^J = \frac{1}{2} \zeta^\perp \delta_{ij}^\perp L_i L_j + \zeta_{ij}^n L_i h_j + \zeta_{ijk}^E L_i \nabla_j E_k \quad (40)$$

with  $\zeta_{ij}^n = \zeta_n n_k \epsilon_{ijk}$  and  $\zeta_{ijk}^E = \zeta_E(\epsilon_{ikp} n_p n_j + \epsilon_{ijp} n_p n_k)$ , where  $L_i = (\partial/\partial J_i) \varepsilon_J$  is the thermodynamic conjugate of the relative rotations. The transport parameter  $\zeta^\perp$  governs the relaxation of relative rotations with the relaxation time  $1/(\zeta^\perp D_1)$ . There is a dissipative coupling between relative rotations and 'combined' rotations,  $J_x/n_y$  and  $J_y/n_x$ , due to the  $\zeta_n$  term.

## 4 Nonlinear Hydrodynamics and Macroscopic Dynamics of a D2d phase

Complex fluids and soft matter are known to frequently show nonlinear behavior. This is manifest e.g. in the large number of

instabilities possible in such materials. To generalize the linear description of the preceding section into the nonlinear domain, several different aspects have to be taken into account.

First, all the material parameters, the static susceptibilities as well as the dynamic transport parameters, can depend on the state variables pertinent to the system. These are density (or pressure), entropy density (or temperature), and concentration, but also the nematic and tetrahedric order parameters. The latter are tensors and their tensorial implications to the material properties have already been made explicit in the linear description (cf. e.g. the viscosity tensor Eq.(28)), while the various coefficients (e.g. viscosities) can still depend on the scalar order parameters,  $S$  and  $T$ . A dependence on the velocity (or rather the kinetic energy density) is forbidden by Galilean invariance, while a dependence on the vorticity (squared),  $\omega^2$ , is possible. In addition one must guarantee the correct behavior under rigid rotations for such terms.

A second line of generalization into the nonlinear domain comes from the continuation of the phenomenological expansions to higher orders. In statics this amounts to setting up a free energy expression that goes beyond a harmonic expansion in the conjugate quantities. Well-known examples are rubber elasticity, where the linear elastic Hooke law is generalized, or the second harmonic generation in certain materials, where energy contributions cubic in the electric field are important, or the thermal anomaly of water, where the linear thermal expansion coefficient vanishes (at a certain temperature and pressure) and a second order one comes into play. For nematics and similar systems such effects are less important and we will not write down such nonlinearities here. The dissipative dynamics is obtained by expansion of the entropy production (or dissipation function) in terms of the thermodynamic forces. The linear order (linear irreversible thermodynamics) is well established and founded on microscopic grounds (linear response theory) and the appropriate material parameters are related to statistical properties of the system (close to equilibrium). A phenomenological generalization of that expansion to higher orders is prone to be ill-defined, unphysical and basically unnecessary as effects very far from equilibrium (like turbulence) are still captured by hydrodynamic descriptions based on linear irreversible thermodynamics. Thus, we consider in the irreversible dynamics of the D2d phase only nonlinearities arising from statics.

The third class of nonlinearities is related to the reversible dynamics of the system and has its roots in general symmetry, geometry, and thermodynamic laws. Due to their fundamental nature these nonlinearities do not come with a possibly small phenomenological prefactor, in contrast to those nonlinearities described above. Examples are the transport derivatives dictated by Galilean invariance and the corrotational derivatives due the transformation behavior of vectors under rigid rotations, as is well-known from reversible nematodynamics,  $\dot{n}_i + v_k \nabla_k n_i + (\boldsymbol{\omega} \times \mathbf{n})_i = 0$ . Being reversible, these terms have to be compensated in order not to lead to entropy production. This is achieved by the hydrostatic pressure contribution to the stress tensor,  $\sigma_{ij} = \delta_{ij} p$ , since the thermodynamic pressure is a nonlinear quantity by definition  $p = -\varepsilon + \sigma T + \mu \rho + \mathbf{v} \cdot \mathbf{g}$  (here  $\sigma$  is the entropy density,  $\mu$  the chemical potential,  $\rho$  the density, and  $\mathbf{g}$  the momentum density). For systems where gradients

are important as in nematics, a nonlinear gradient term (Ericksen stress) arises in the stress tensor  $\sigma_{ij} = \phi_{kj} \nabla_i n_k$  ( $\phi_{ij}$  is the conjugate to  $\nabla_j n_i$ ). Apart from those features known from usual nematics, here we concentrate on the additional complications in a D2d phase due to the non-commutativity of finite 3-dimensional rotations, Eq.(3), and the condition that the nematic and tetrahedric structure have to rotate rigidly together. The latter point is relevant in a nonlinear description, where the material tensors have to be taken with the actual orientations of  $T_{ijk}$  and  $n_i$ , rather than at their equilibrium ones. To avoid clumsy compatibility conditions, it is conceptually and technically easier to treat rotations of the tetrahedric and nematic structures as independent ones and link them by a free energy term, whose coefficient can be taken as infinite at the end regaining the rigid coupling limit of a true D2d phase. Writing down the Gibbs relation (suppressing additional degrees of freedom)

$$d\varepsilon = v_i dg_i + h'_i dn_i + \phi_{ij} d\nabla_j n_i + h_i^{\Gamma'} d\Gamma_i + \psi_{ij} d\nabla_j \Gamma_i \quad (41)$$

one realizes the other complication in the nonlinear description of the D2d phase, since  $d\nabla_j \Gamma_i \neq \nabla_j d\Gamma_i$ . To overcome this problem one can replace  $h_i^{\Gamma'} d\Gamma_i + \psi_{ij} d\nabla_j \Gamma_i$  by the appropriate expressions for the full tetrahedric tensor  $M_{ijk} dT_{ijk} + L_{ijkl} d\nabla_l T_{ijk}$ , since  $T_{ijk}$  is an ordinary tensor and behaves rotationally like a vector in all of its indices. At the end one projects back to the relevant rotations  $\delta\Gamma_i$  using Eq.(2).

By this procedure we get for the reversible dynamics

$$\begin{aligned} \dot{\Gamma}_i + v_j \nabla_j \Gamma_i - \frac{1}{2} \omega_i \\ + \frac{1}{2\alpha} \epsilon_{ipq} \epsilon_{mjl} T_{pjkl} T_{qlk} \omega_m + Y_i^{R,p} = 0 \end{aligned} \quad (42)$$

$$\dot{n}_i + v_k \nabla_k n_i + (\boldsymbol{\omega} \times \mathbf{n})_i + X_i^{R,p} = 0 \quad (43)$$

$$\dot{g}_i + v_k \nabla_k g_i + \nabla_i p + \nabla_j [\sigma_{ij}^E + \sigma_{ij}^{R,p}] = 0 \quad (44)$$

with

$$\begin{aligned} \nabla_i p = \sigma \nabla_i T + \rho \nabla_i \mu + g_j \nabla_i v_j - h_j \nabla_i n_j - h_j^{\Gamma} \nabla_i \Gamma_j \\ - 2\psi_{kj} \epsilon_{kpq} (\nabla_i \Gamma_p) (\nabla_j \Gamma_q) \end{aligned} \quad (45)$$

where  $h_j^{\Gamma} = h_j^{\Gamma'} - \nabla_j \psi_{ij}$  and  $h_i = h'_i - \nabla_j \phi_{ij}$ .

For the generalized Ericksen stress we find (properly symmetrized)

$$\begin{aligned} 2\sigma_{ij}^E = \phi_{kj} \nabla_i n_k + \phi_{ki} \nabla_j n_k + \nabla_k (\phi_{kj} n_i - \phi_{ki} n_j) \\ + \psi_{kj} \nabla_i \Gamma_k + \psi_{ki} \nabla_j \Gamma_k - \frac{3}{2} \epsilon_{ijk} \nabla_l \psi_{kl} \end{aligned} \quad (46)$$

Angular momentum is conserved as the stress tensor is either manifestly symmetric, or is the divergence of an antisymmetric tensor [61].

The remaining phenomenological parts of the reversible dynamics involve deformational flow and are the origin of flow alignment and backflow

$$Y_i^{R,p} = \lambda_{ijk}^{\Gamma} A_{jk} \quad (47)$$

$$X_i^{R,p} = \lambda_{ijk} A_{jk} \quad (48)$$

$$\sigma_{ij}^{R,p} = -\lambda_{kji} h_k - \lambda_{kji}^{\Gamma} (h_k^{\Gamma} + 2\epsilon_{lkq} \psi_{lp} \nabla_p \Gamma_q) \quad (49)$$

with

$$\lambda_{ijk} = \lambda (\delta_{ij}^{tr} n_k + \delta_{ik}^{tr} n_j) \quad (50)$$

$$\lambda_{ijk}^{\Gamma} = \lambda^{\Gamma} n_p (\epsilon_{ikp} n_j + \epsilon_{ijp} n_k). \quad (51)$$

Due to the non-commutativity there is a genuinely nonlinear contribution in Eq.(49).

The free energy that couples the (transverse) rotations of the tetrahedric structure with director rotations is

$$\varepsilon_J = \frac{1}{2} D_1 (\delta \boldsymbol{\Gamma}_{\perp} - \mathbf{n} \times \delta \mathbf{n})^2 \quad (52)$$

For  $D_1 \rightarrow \infty$  the rigid coupling of the D2d phase is regained, while for finite  $D_1$  relative rotations are allowed.

## 5 Conclusions and Experimentally Relevant Results

We have analyzed the macroscopic behavior of a nematic phase with local  $D_{2d}$  symmetry. This phase, we have called D2d, is a tetrahedric nematic which breaks parity and therefore represents a type of nematic not considered before. It is described as a combination of a tetrahedric  $T_d$  phase with a uniaxial nematic, where the nematic director is along one of the improper 4 axes. Such a tetrahedric nematic phase could be a good description for nematics formed by banana-shaped molecules. D2d has three rotational hydrodynamic degrees of freedom giving rise to three Goldstone modes. Two of these modes associated with spontaneously broken rotational symmetries are connected to variations of the usual nematic director while the third describes rotations of the tetrahedral structure about the director. As a result, the former two can be optically observed. The linear gradient term in the generalized Frank elastic free energy, possible due to the inversion-breaking tetrahedral structure, gives rise to ambidextrous chirality. However, with a helical structure two of those modes acquire a gap and only rotations about the helical axis remain truly hydrodynamic. If only the nematic director is detectable (e.g. under crossed polarizers in the microscope) the helically structured D2d phase could look similar to a cholesteric phase.

In contrast to usual uniaxial and biaxial nematic phases with only quadrupolar order, velocity gradients (extensional flows) reversibly generate in D2d concentration-, heat- and electric currents and, vice versa, electric fields, temperature and concentration gradients give rise to stresses.

There are also additional static and dissipative effects not known from usual nematics. These include irreversible coupling terms between director rotations on the one hand and electric fields and temperature and concentration gradients on the other. In addition, there are static contributions coupling director deformations to density, concentration and temperature variations unknown in quadrupolar nematics.

The behavior in a static electric field gives rise to additional possibilities to distinguish a tetrahedric nematic from more usual nematic phases. First, it allows second harmonic generation as it breaks parity. Second, there is a rather unusual reorientation behavior. Below a threshold field, the director is oriented parallel to the field (for positive dielectric anisotropy).

Above this threshold value the director turns away continuously from its original orientation to a direction oblique to the field, a phenomenon unknown to uniaxial nematics with positive dielectric anisotropy.

Of course, a  $D_{2d}$  phase is not the only possibility for tetrahedral nematic phases [8]. If the nematic director is along one of the 3-fold tetrahedral axes, a polar biaxial nematic phase of  $C_{3V}$  symmetry arise. Its properties are very close to that of a uniaxial polar nematic, since the transverse structure of  $C_{3V}$  is hardly detectable in optical measurements. The linear gradient term in the generalized Frank elastic free energy reduces in this phase to a linear splay term, already well-known from uniaxial polar nematics.

Another possibility would be to add to the tetrahedral structure a biaxial nematic (of tetragonal symmetry) leading to a phase of  $D_2$  symmetry. It has three equivalent, orthogonal 2-fold rotation axes and no mirror planes left. Thus, it is chiral, i.e., a pseudoscalar quantity exists, whose sign governs the helical sense and which is due to the internal structure. However, for this pseudoscalar both signs are possible depending on whether the tetrahedral structure or its inverted one is present. Thus, ambidextrous chirality is obtained in the same way as it is found in the  $C_{B2}$  smectic banana phase [26, 27].

Finally, a  $S_4$  symmetric phase is obtained, where one improper  $\bar{4}$  axis is the sole symmetry element, if one adds to a  $D_{2d}$  phase an appropriate additional rank-3 order parameter.

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