Deformable tetrahedratic phases: the effects of external fields and flows

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Abstract. We discuss changes in the symmetry and physical properties of an isotropic phase which has initially tetrahedral symmetry characterized by four unit vectors. In its undeformed state, these four vectors are at the tetrahedral angle (109.47^o) to each other. We find that this optically isotropic phase becomes uniaxial under the influence of an external electric field, $\mathbf{E}$, resulting in a phase with C_{3v}-symmetry. For an applied simple shear flow, the system becomes biaxial and a time-dependent state with C_1 symmetry arises. We discuss to what extent deformations induced by external forces and flows on this optically isotropic phase, which we call a "deformable tetrahedratic phase", are consistent with observations at the isotropic-B7 transition found recently in compounds composed of banana-shaped molecules and suggest a number of experiments to test the conclusions of this model.

PACS. 61.30.Gd Orientational order of liquid crystals; electric and magnetic field effects on order – 64.70.Md Transitions in liquid crystals – 05.70.Ln Nonequilibrium irreversible thermodynamics

1 Introduction

In 3D, the tetrahedratic phase, T, is depicted by four unit vectors (Fig. 1a), $\mathbf{n^1}$ to $\mathbf{n^4}$, oriented along the four tetrahedral corners of a cube with the property that $T_d(-\mathbf{n}^\alpha) = -T_d(\mathbf{n}^\alpha)$ (no inversion symmetry) and $\alpha = 1, 2, 3, 4$. One of the reasons for increasing interest in the optically isotropic tetrahedratic phase is its unusual property that it can spontaneously flow in the presence of a static external force such as an electric field or a temperature gradient [1]. This unusual feature arises because a third rank tensor, $T_{ijk} = \sum_\alpha n_i^\alpha n_j^\alpha n_k^\alpha$, is required as an order parameter to characterize tetrahedratics [1–4]. T_{ijk} can couple to physical properties described by first (e.g. electric fields, E_i) and second rank (e.g. orientational order, Q_{ij}), tensors [5].

For example, with an electric field, $\mathbf{E}$, parallel to $\mathbf{n^1}$, say, the coupling, $\pm\varsigma E_i T_{ijk}$, gives rise to the second rank tensor, Q_{jk}, which is just the order parameter for rod-like $(-)$ or for disc-like $(+)$ orientational order as shown in Fig.1b.

In an electric field then, tetrahedratics can give rise to lamellar and/or columnar mesophases equally well. Ap-plying a field parallel to a cube face, gives symmetric off-diagonal components that describe biaxial orientational order. As this coupling term, $\pm\varsigma E_i T_{ijk}$, is linear in T, superposition of states applies leading to novel states where an optically isotropic tetrahedratic phase and an optically anisotropic state with orientational order effectively coexist in the presence of external force fields e.g. electric field: the deformable tetrahedratic. When the field is turned off, the optically anisotropic states fade away.

We also point out that there are terms linear in the gradient coupling Q_{ij} and T_{ijk} [5]. These terms have a form similar to the term familiar from cholesterics: $\epsilon_{ijk}Q_{i\ell}\partial_k Q_{j\ell}$. However, while this term is odd under parity in cholesterics because of the chirality of the molecules - i.e. cholesterics have only one hand, this is not the case for deformable tetrahedratics where both hands are possible (ambidextrous chirality, [3]). The novel gradient terms and their further physical implications will be discussed in detail in ref. [5].

Tetrahedratics are thus interesting as a model system to study frustrated lamellar and columnar liquid crystal phases with many different condensed states that are energetically very close together [6–11].

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(a)

(b)
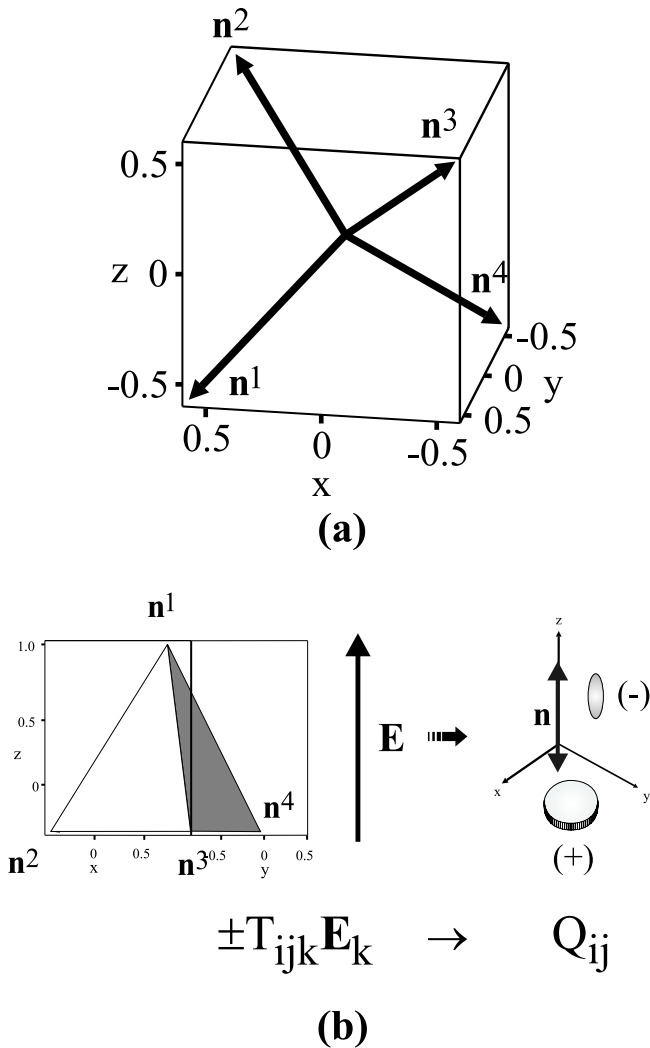
Fig. 1. a) The four tetrahedral vectors of the optically isotropic tetrahedratic phase: $\mathbf{n}^1$, $\mathbf{n}^2$, $\mathbf{n}^3$ and $\mathbf{n}^4$. $T_d(-\mathbf{n}^\alpha) = -T_d(\mathbf{n}^\alpha)$: no inversion symmetry where $\alpha = 1, 2, 3, 4$. b) The four unit vectors are rotated so that $\mathbf{n}^1$ is parallel to an electric field, $\mathbf{E}$. Then, depending on the sign of this term, either disc-like or rod-like orientational order may appear [5].

Recent work on tetrahedratics has covered phase transitions [2, 4], the behavior in an electric field [2] and the hydrodynamic behavior [1]. Up to now, it has been assumed that the symmetry of the tetrahedratic phase is unchanged under the influence of external forces like flow, temperature gradients and electric fields. Here we consider possible changes when we allow the tetrahedral symmetry to be reduced by the action of external forces. That is, we now assume that the tetrahedral angle can be modified by external fields and flow. We argue that this is a possibility because of the linear nature of the coupling terms available to T_{ijk}.

The present investigation has been triggered by puzzling observations for liquid crystalline phases formed by compounds composed of achiral banana-shaped molecules. Indeed, the experimental evidence to date suggests that compounds with banana-shaped molecular structure rep-

resent a new subfield of thermotropic liquid crystals [12]. When there are no mirror planes, for example when achiral banana-shaped molecules are tilted in layers, they have the novel property of ambidextrous chirality, i.e. both left-handed and right-handed spirals are observed [8–11].

Here, we focus on the phase transition of achiral banana-shaped compounds from an optically isotropic liquid phase to a condensed state known as B7. Between crossed polarizers, B7 exhibits a wide variety of patterns on cooling from the isotropic liquid [12, 13] including spirals of both hands growing into the isotropic phase [13], myelin patterns and patterns showing spatial modulations, sometimes regular, in a second direction. All these optically anisotropic patterns grow vigorously when the system is far from equilibrium e.g. after a temperature decrease, then shrink once equilibrium is reached leaving behind in many instances an isotropic liquid [14, 15]. Furthermore, there is a remarkable variety of transitions between growth forms with the result that none matures to a mono-domain B7 which is essential for e.g. systematic high resolution x-ray investigations.

B7 phases also have rich dynamics both with and without applied fields. Recent experiments on the effect of temperature variations and of an AC (30Hz and larger) electric field have revealed the occurrence of flow close to and in the isotropic phase near the B7-isotropic phase transition. While the field untwisted some spirals and coarsened the less mobile myelin textures, it stimulated even more flow and an anisotropic B7 texture with variable but exceedingly small length scales [15].

Very recently, in a step towards understanding these features of the B7 phase, we found [1] that flow can occur in the isotropic tetrahedratic phase in the presence of external forces such as electric fields and temperature gradients. In this analysis, we assumed the symmetry of the tetrahedratic phase is unchanged by the external forces i.e. the tetrahedral angle is conserved and the system remains isotropic.

X-ray diffraction finds some banana compounds with ambidextrous spirals growing into the isotropic liquid are simple layered structures [16, 17]. For at least two others, the original phase called B7 in a compound called NB8 [12, 13] and a composite material that is ferroelectric [18], x-ray investigations find many diffraction peaks that could not be indexed by a standard smectic or columnar phase known to form for many other low molecular weight liquid crystalline compounds [13].

Because freely suspended films of B7 decompose into strands [13, 19], the conclusion is that B7 is not a well-formed smectic phase. This observation led us to investigate very recently [20] possible symmetries of columnar phases possessing a macroscopic polarization. It turns out [20] that C_1 symmetry (meaning no symmetry) results, as soon as the macroscopic polarization is inclined to any of the preferred axes of the columnar structure.

In summary, neither the symmetry nor the physical properties of the B7 ground state are understood. Indeed, the evidence so far is that it does not have a simple ground state. Consequently, there is a need to look for models to

describe the B7 phase exhibited by achiral banana-shaped liquid crystals and their transitions to the isotropic phase.

Here, we consider a new type of phase that we call a deformable tetrahedratic phase. We assume that, in the absence of external forces and flows, the 4 unit vectors of the undeformed state include the tetrahedral angle between each other. When external fields or forces are applied, we allow the initial tetrahedral angle between the 4 unit vectors to change.

The motivation for this model arises from experimental observations made for the B7 phase [12–15]. We argue that this model is helpful to understand various unusual features observed in the B7 phase: e.g. the appearance then subsequent disappearance of the optically anisotropic growth forms, the appearance of flows, even the transitions between the many different growth forms of B7 and, in the case of B7 grown in AC fields, a texture with variable but exceedingly small length scales [15].

As we will show, our analysis allows an interpretation of the isotropic-B7 transition as the phase transition from the optically isotropic deformable tetrahedratic phase to a variety of condensed states mediated by a deformed tetrahedratic phase. These condensed phases may be columnar, lamellar and/or ambidextrously chiral.

The paper is organized as follows. In section 2 we analyze the deformations of a deformable tetrahedratic phase in an external electric field. In section 3 we consider the effects of an imposed shear flow and in section 4 we discuss how the deformations of a deformable tetrahedratic phase could mediate the transition to the B7 phase observed in a number of compounds as well as suggest some experiments to test the conclusions of this model.

2 Distortions of a deformable tetrahedratic phase by an electric field

In this section we consider how torques from an external electric field, $\mathbf{E}$, deform the tetrahedra. The starting point is the free energy density in an electric field [1, 2]

$$f_E = f_0 - \frac{\epsilon_1}{2} T_{ijk} E_i E_j E_k \qquad (1)$$

where f_0 denotes the free energy density of an isotropic fluid [1, 21] and $T_{ijk} = \Sigma_{\alpha=1}^{4} n_i^\alpha n_j^\alpha n_k^\alpha$ is the tetrahedratic order parameter that can be expressed by the 4 unit vectors $\mathbf{n}^\alpha$ defining a tetrahedron [2] with $\alpha = 1, 2, 3$ or 4) (Fig. 1).

We note that, while this form of the field energy coincides with what is known as the leading term for a truly tetrahedratic phase, we use it here as a simple model for the field behavior of a deformable tetrahedratic phase in the spirit introduced above.

In terms of the unit vectors $\mathbf{n}^\alpha$, eq.(1) takes the form [2]

$$f_E = f_0 - \frac{\epsilon_1}{2} \sum_{\alpha=1}^{4} (\mathbf{E} \cdot \mathbf{n}^\alpha)^3 \qquad (2)$$

where we chose the following set of tetrahedral unit vectors

$$\mathbf{n^1} = \frac{1}{\sqrt{3}}(1, 1, -1) \qquad (3)$$

$$\mathbf{n^2} = \frac{1}{\sqrt{3}}(1, -1, 1) \qquad (4)$$

$$\mathbf{n^3} = \frac{1}{\sqrt{3}}(-1, 1, 1) \qquad (5)$$

$$\mathbf{n^4} = \frac{1}{\sqrt{3}}(-1, -1, -1). \qquad (6)$$

In the undistorted case, the $\mathbf{n}^\alpha$ are at an angle ϕ with $\cos \phi = -1/3$ ($\phi = 109.47°$) to each other.

The electric part of the free energy has an orienting effect on tetrahedratic order. It can be shown that the orientation of one of the $\mathbf{n}^\alpha$ parallel (antiparallel) to the field is the minimal energy state for $\epsilon_1 > 0$ ($\epsilon_1 < 0$), with

$$f_E = f_0 - \frac{4}{9}\epsilon_1 E_0^3. \qquad (7)$$

For definiteness, we consider the stable case where an electric field $\mathbf{E}$ is applied $\parallel \mathbf{n^1}$ i.e. $\mathbf{E} = E_0 \mathbf{n^1}$, $E_0 \geq 0$ and $\epsilon_1 > 0$.

It should be mentioned that an analogous orienting effect of a magnetic field does not exist as the magnetic field is an axial vector that is odd under time reversal while an electric field is a polar vector that is even under time reversal.

While there is no torque on $\mathbf{n^1}$ when it is parallel or anti-parallel to $\mathbf{E}$, there are non-zero electric torques on $\mathbf{n^{2,3,4}}$ "frustrating" the tetrahedral order:

$$\mathbf{n^2} \times \frac{\partial f_E}{\partial \mathbf{n^2}} \sim (0, 1, 1) \qquad (8)$$

$$\mathbf{n^3} \times \frac{\partial f_E}{\partial \mathbf{n^3}} \sim (-1, 0, -1) \qquad (9)$$

$$\mathbf{n^4} \times \frac{\partial f_E}{\partial \mathbf{n^4}} \sim (1, -1, 0) \qquad (10)$$

These torques are perpendicular to $\mathbf{n^1}$ and tend to rotate $\mathbf{n^{2,3,4}}$ with a given sense.

Assuming as an ansatz such a rotation of (yet undetermined) finite amplitude b, the distorted set of unit vectors is given by:

$$\mathbf{n^{1E}} = \frac{1}{\sqrt{3}}(1, 1, -1) \qquad (11)$$

$$\mathbf{n^{2E}} = \frac{1}{\sqrt{3}} \frac{1}{\sqrt{1+2b^2}}(1, -1+\sqrt{3}b, 1+\sqrt{3}b) \qquad (12)$$

$$\mathbf{n^{3E}} = \frac{1}{\sqrt{3}} \frac{1}{\sqrt{1+2b^2}}(-1-\sqrt{3}b, 1, 1-\sqrt{3}b) \qquad (13)$$

$$\mathbf{n^{4E}} = \frac{1}{\sqrt{3}} \frac{1}{\sqrt{1+2b^2}}(-1+\sqrt{3}b, -1-\sqrt{3}b, -1). \qquad (14)$$

That these unit vectors represent a distorted tetrahedron is easily seen from the scalar products

$$\mathbf{n^{1E}} \cdot \mathbf{n^{\alpha E}} = -\frac{1}{3} \frac{1}{\sqrt{1+2b^2}} \qquad (15)$$

for $\alpha = 2, 3, 4$ and

$$\mathbf{n^{2E}} \cdot \mathbf{n^{3E}} = \mathbf{n^{2E}} \cdot \mathbf{n^{4E}} = \mathbf{n^{3E}} \cdot \mathbf{n^{4E}} = -\frac{1}{3}\frac{1 + 3b^2}{1 + 2b^2} \quad (16)$$

which is different from the undistorted case $-1/3$. The only 3-fold axis left is $\mathbf{n^1}$. As $\mathbf{n^{2E}}$, $\mathbf{n^{3E}}$ and $\mathbf{n^{4E}}$ are not 3-fold rotation axes when $b \neq 0$, the deformed tetrahedratic has no 2-fold axes. Thus, from Eqs.(15,16), it follows that the $b \neq 0$ distortions lead to an optically uniaxial system, where the preferred direction, set by the external field, is the 3-fold axis, $\mathbf{n^1}$: the T_d symmetry of the undeformed tetrahedratic has been reduced to C_{3v} [22].

We now argue that this $b \neq 0$ distortion of the tetrahedra lowers the electric part of the free energy further, as $\Delta f_E = f_E(\mathbf{n^{\alpha E}}) - f_E(\mathbf{n^\alpha})$ where f_E given in (2) is always negative:

$$\Delta f_E = -\frac{1}{2}\epsilon_1 E_0^3 \frac{(1 + 2b^2)^{3/2} - \frac{1}{9}}{(1 + 2b^2)^{3/2}} + \frac{4}{9}\epsilon_1 E_0^3 < 0. \quad (17)$$

Of course, the distortion of the tetrahedral structure costs deformation energy, which can be expressed in a harmonic approximation by:

$$f_{def} = \frac{B_1}{2} \sum_{\alpha, \beta > \alpha} (n_i^{\alpha E} n_i^{\beta E} + \frac{1}{3})^2 \quad (18)$$

$$= \frac{B_1}{6}\left[(1 - \frac{1}{\sqrt{1 + 2b^2}})^2 + (\frac{b^2}{1 + 2b^2})^2\right]. \quad (19)$$

It is positive and vanishes for an undeformed tetrahedratic structure (3-6) with $b = 0$. If the deformation energy is the largest one in the system ($B_1 \to \infty$) no deformation will take place. In case, however, this energy is comparable to the electric part of the free energy, a finite deformation can occur. Minimizing the total free energy

$$f = f_0 + f_{def} + \Delta f_E - \frac{4}{9}\epsilon_1 E_0^3 \quad (20)$$

with respect to b^2 the equilibrium deformation amplitude b_0 in the presence of an external field is obtained. The condition is:

$$\sqrt{1 + 2b_0^2}\ (2 + 4b_0^2 - \alpha) = 2 + 2b_0^2 \quad (21)$$

with $\alpha = \frac{\epsilon_1 E_0^3}{B_1}$. In the limit of low ($\alpha \ll 1$) as well as of high electric fields ($\alpha \gg 1$) eq.(21) leads to
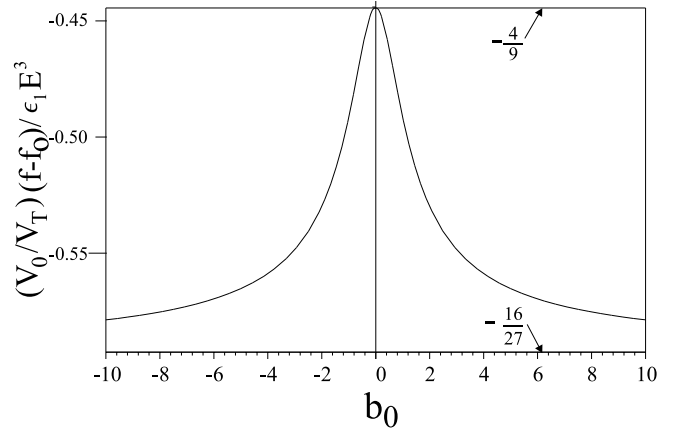
$$b_0^2 = \frac{\alpha}{4} = \frac{\epsilon_1 E_0^3}{4B_1}. \quad (22)$$

which applies approximately also for intermediate values of α. The total energy f from eq.(20) is

$$f = f_0 - \frac{4}{9}\epsilon_1 E_0^3 (1 + \frac{3\alpha}{64}) \quad (23)$$

for $\alpha << 1$ and

$$f = f_0 - \frac{1}{2}\epsilon_1 E_0^3 (1 - \frac{5}{12\alpha}) \quad (24)$$

Fig. 2. The free energy (20), $\Delta f = f - f_0$, in units of $\epsilon_1 E_0^3$ normalized by the relative volume change, V_T/V_0 (25), as a function of b_0. In the limits $b_0^2 \to 0$, $\Delta f \to -\frac{4}{9}$ and $b_0^2 \to \infty$, $\Delta f \to -\frac{16}{27}$.

for $\alpha >> 1$. While $f - f_0$ is symmetric in b_0, it monotonically decreases for $E_0 > 0$ (while $E_0 < 0$ is the unstable case for $\epsilon > 0$). The energy can be lowered by 12.5% maximum.

In addition to the decrease in energy, there is a volume change of the individual tetrahedra due to the deformations caused by the external field. Geometry leads to

$$\frac{V_T}{V_0} = \frac{1 + \frac{9}{4}b_0^2}{1 + 2b_0^2}\frac{1 + 3\sqrt{1 + 2b_0^2}}{4\sqrt{1 + 2b_0^2}} \quad (25)$$

with V_T and V_0 the volume of the deformed and the undeformed tetrahedra, respectively. The field dependence is contained in b_0^2, which is a function of α and given by (21). The volume is reduced by $\approx 15.6\%$ maximum. The energy change normalized by the volume change is shown in Fig.2. The energy reduction and the volume changes are smooth functions of the electric field and no threshold is found.

This is also manifest in the distortion (15) of the angles between $\mathbf{n^1}$ and the others, which approaches 90° in the high field limit, but is a smooth function everywhere (Fig. 3). Similarly, the angle between $\mathbf{n^1}$ and the other directions $\mathbf{n^2}$, $\mathbf{n^3}$ and $\mathbf{n^4}$ (16) increases to 120° for b or $E_0 \to \infty$ indicating the 3-fold rotational symmetry about the external field. Interestingly, the rotation of $\mathbf{n^{2E}}$, $\mathbf{n^{3E}}$ and $\mathbf{n^{4E}}$ with increasing external field into the plane perpendicular to $\mathbf{E}$ is accompanied by a rotation of the 3 vectors about the field. Thus, an electric field with slowly varying field strength gives rise to a rotation of the tetrahedra about the field direction, a manifestation of the lack of inversion symmetry of C_{3v}.

For $E_0 \to \infty$ the total rotation of the n^α is 90° as can be seen by projecting $\mathbf{n^{2\infty}}$, $\mathbf{n^{3\infty}}$ and $\mathbf{n^{4\infty}}$ in the high field limit onto the zero field limit:

$$\mathbf{n^{2,0}} \cdot \mathbf{n^{2\infty}} = \mathbf{n^{3,0}} \cdot \mathbf{n^{3\infty}} = \mathbf{n^{4,0}} \cdot \mathbf{n^{4\infty}} = 0. \quad (26)$$
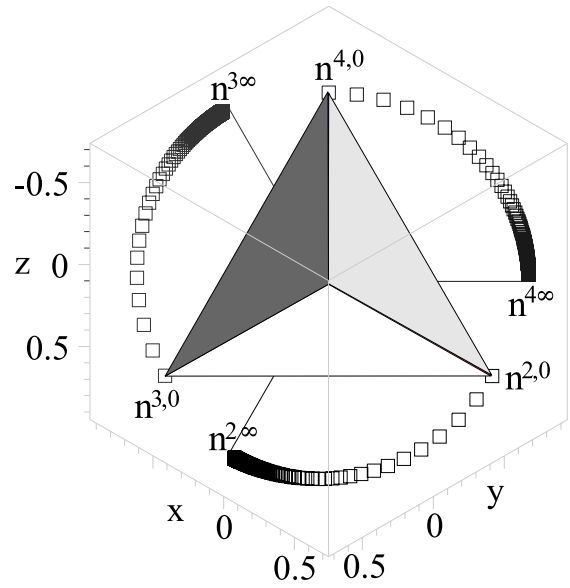
This analysis is summarized in Fig.4.
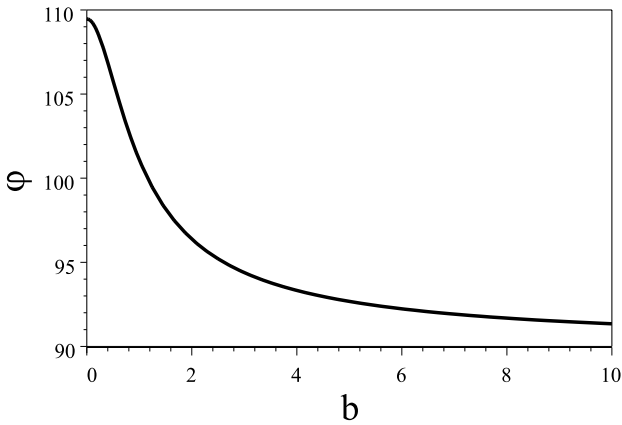
Fig. 3. From Eq. 15, the angle (in degrees), $\varphi = \cos^{-1}(\mathbf{n}^{\beta\mathbf{E}} \cdot \mathbf{n}^1)$ $(\beta = 2,3,4)$ vs. b. As $E_0 \to \infty$, $\mathbf{n^{2E}}$, $\mathbf{n^{3E}}$ and $\mathbf{n^{4E}}$ spiral clockwise $(b > 0)$ to lie in the plane $\perp \mathbf{n^1} \parallel \mathbf{E}$.

Fig. 4. (a) View looking down $\mathbf{n^1} \parallel \mathbf{E}$, with increasing b (200 points shown as □) for $\mathbf{n^{\beta,0}} \to \mathbf{n^{\beta\infty}}$ $(\beta = 2,3,4)$. With increasing E (or equivalently b), the $\mathbf{n^{\beta\mathbf{E}}}$ spiral clockwise towards the tetrahedron center. $\mathbf{n^1}$ is unchanged and, in this perspective, is a point at the tetrahedron apex shown here for the case $E_0 = 0$. The structure is C_{3v} with the property that $C_{3v}(-\mathbf{n}^\alpha) = -C_{3v}(\mathbf{n}^\alpha)$. (b) Tetrahedron viewed with $\mathbf{n^1} \parallel \mathbf{E}$ in the plane of the figure for $b = 0$ and $b \to \infty$. In the limit $b \to \infty$, the $\mathbf{n^{\beta\infty}}$ are 120° apart and in the plane $\perp \mathbf{n^1}$.

We stress that the minimization of the free energy does not fix the sign of b_0: in (21) only b_0^2 appears as a function of the external field. Thus the system is free to choose either sign for b_0. The sign of b_0, however, governs the rotation sense of the tetrahedra in a field. As clockwise and counterclockwise rotations cost the same energy, both can occur in the same sample when a field is switched on. This feature mimics "ambidextrous chirality" found in those banana liquid crystal phases that exhibit both left and right handed helix structures. The tetrahedra deformed by an electric field have C_{3v} symmetry which has mirror planes and is achiral [22]. See Fig.5.
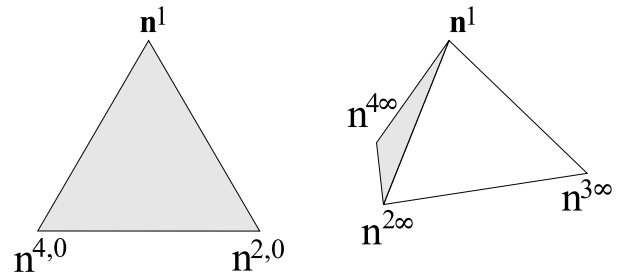
As the main result, we conclude that there is no threshold for deformations of a spatially homogeneous deformable tetrahedratic phase when an electric field is applied parallel to one of the unit vectors $\mathbf{n}^\alpha$. In this connection, it is important to point out that Fel [2] found a finite threshold for the Frederiksz transition in this geometry assuming, however, that the tetrahedratic phase is non-deformable.

The analysis given so far has taken into account the effects of external electric fields only via the expression given in eq.(1). Once the uniaxial deformation is established, it could be necessary to take into account the classical orientational order parameter Q_{ij} [23] as well, where the strength of uniaxial order S is proportional to the field strength E_0^2.

The reduction in symmetry from T_d to C_{3v} has a number of important consequences for the macroscopic properties. As an external field effect, the deformed tetrahedratic phase has induced pyroelectricity and an induced macroscopic polarization. In addition, there are reversible dynamic cross coupling terms between extensional flow on the one hand, and electric fields as well as temperature and concentration gradients, on the other.

## 3 Distortions of a deformable tetrahedratic phase by shear flow

In [1] we have shown that a shear flow can couple to both, the order parameter of the tetrahedratic phase as well as to electric fields and temperature gradients. As we have seen in the previous section electric fields have profound effects on deformable tetrahedratics. Complementing the investigation of field effects, we examine in this section the consequences of an applied shear flow as well as of an applied extensional flow.

First we analyze how the unit vectors $\mathbf{n}^\alpha$ of the deformable tetrahedratic phase couple to flow. The part of
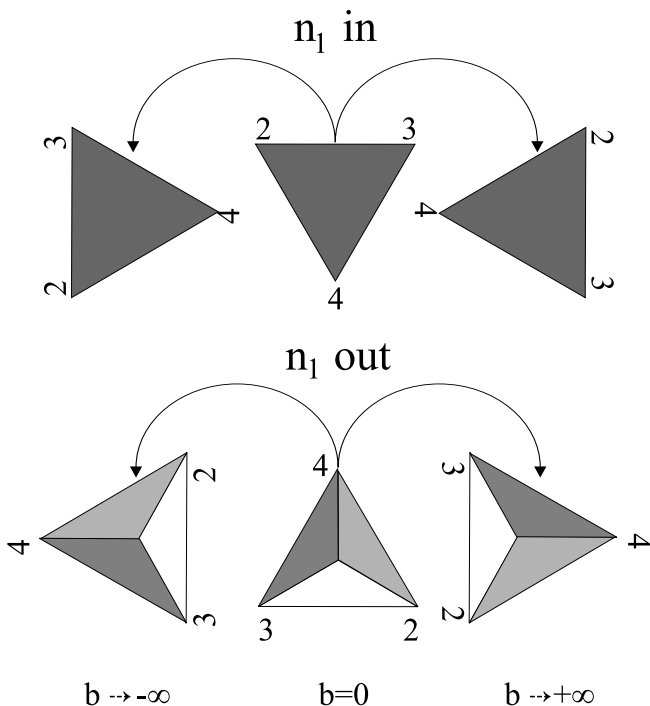
Fig. 5. When $b > 0$ ($b < 0$), the rotation sense is clockwise (counterclockwise) whether the tetrahedra are viewed along $\mathbf{n}^1$ ($\mathbf{n}^1$ in) or against $\mathbf{n}^1$ ($\mathbf{n}^1$ out). As $\mathbf{n}^\beta$, $\beta = 2, 3, 4$ rotate around $\mathbf{n}^1$ into the plane $\perp \mathbf{n}^1$, the sense is right-handed (left-handed) for $b > 0$ ($b < 0$) when viewed along $\mathbf{n}^1$ ($\mathbf{n}^1$ in) but of opposite hand when viewed against $\mathbf{n}^1$ ($\mathbf{n}^1$ out).

the dynamic equations for $\mathbf{n}^\alpha$

$$\dot{n}_i^\alpha + Y_i^{\alpha R} + Y_i^{\alpha D} = 0 \tag{27}$$

that describes these reversible contributions is:

$$Y_i^{\alpha R} = v_l \nabla_l n_i^\alpha + \lambda_{ijk}^\alpha A_{jk} + \epsilon_{ijk} n_j^\alpha \omega_k \tag{28}$$

with $\omega_k = \frac{1}{2}\epsilon_{klm}\nabla_l v_m$ and $A_{jk} = \frac{1}{2}(\nabla_j v_k + \nabla_j v_k)$. Eqs.(27) and (28) contain only three independent variables, since the $\mathbf{n}^\alpha$ are not linearly independent. The last term in eq.(28) describes the behavior of the $\mathbf{n}^\alpha$ under rigid rotations. The contribution $\sim \lambda_{ijk}^\alpha$ represents the analog of the coupling to extensional flow well known from uniaxial and biaxial nematics. However, the contribution $\sim \lambda_{ijk}^\alpha$ vanishes identically due to the high symmetry of the tetrahedratic phase [24], Thus, we conclude that in a non-deformable tetrahedratic phase, an applied shear flow leads to a solid-body rotation of the tetrahedratic structure. This implies that there is no stationary state in the presence of shear flow - unlike the flow-aligned state in a usual nematic. In an extensional flow, which is irrotational ($\omega_i = 0$), non-deformable tetrahedratics are unaffected, i.e. they do not rotate.

For a deformable tetrahedratic, external fields such as an electric field (cf. the preceding section) can lead to changes in the structure and thus of the symmetry. For the case of an external flow field, a similar possibility arises.

As noted, deformable tetrahedratic means that we still have in equilibrium (no fields, no flows) the tetrahedratic

unit vectors as before, but that their relative angles are no longer fixed to $cos^{-1}(-1/3)$ and they do not sum to zero, $\Sigma_{\alpha=1}^4 n_i^\alpha \neq 0$ once the phase is driven out of equilibrium.

In that case the λ-tensor in (28) does not have to vanish and takes the usual nematic form

$$\lambda_{ijk}^\alpha = \lambda^\alpha(\delta_{ij}^{tr,\alpha} n_k^\alpha + \delta_{ik}^{tr,\alpha} n_j^\alpha) \tag{29}$$

(with $\delta_{ij}^{tr,\alpha} = \delta_{ij} - n_i^\alpha n_j^\alpha$) describing the behavior of n_i^α under shear and elongational flow. Since without external flow all $\mathbf{n}^\alpha$ are equivalent and the flow dependence of λ^α is probably small, one can expect the λ^α to be equal, $\lambda^\alpha = \lambda$. In addition there is a relaxation towards the undeformed equilibrium tetrahedratic structure, which is expressed by the dissipative contribution

$$Y_i^{\alpha D} = \frac{1}{\gamma_1} \frac{\partial f_{def}}{\partial n_j^\alpha} \delta_{ij}^{tr,\alpha} \tag{30}$$

with f_{def} the deformation energy (18). Again, the rotational viscosity is the same for all unit vectors due to their equivalence for vanishing fields.

In a shear flow, apart from the solid body rotation, there is an additional response to flow of the individual $\mathbf{n}^\alpha$ due to the existence of the λ-tensor. This response depends on their orientation relative to the flow direction and its gradient and leads to a deformation of the tetrahedral structure. However, this deformation is superimposed on the solid body rotation and might therefore be difficult to detect experimentally. Therefore we investigate how the relative angles between the unit vectors are affected by shear flow. They are no longer preserved but obey a relaxing dynamic equation. For $\alpha \neq \beta$ there are six additional macroscopic variables $B^{\alpha\beta} = \mathbf{n}^\alpha \cdot \mathbf{n}^\beta$ whose dynamic equations follow from that of the n_i^α and read:

$$\begin{aligned}
&\dot{B}^{\alpha\beta} + v_l \nabla_l B^{\alpha\beta} \\
&+ 2\lambda\big(n_i^\alpha n_j^\beta + n_j^\alpha n_i^\beta - B^{\alpha\beta}(n_i^\alpha n_j^\alpha + n_i^\beta n_j^\beta)\big)A_{ij} \\
&+ \frac{1}{\tau}\sum_{\gamma\neq\alpha}(B^{\alpha\gamma} - B_0^{\alpha\gamma})(B^{\beta\gamma} - B^{\alpha\beta}B^{\alpha\gamma}) \\
&+ \frac{1}{\tau}\sum_{\gamma\neq\beta}(B^{\beta\gamma} - B_0^{\beta\gamma})(B^{\alpha\gamma} - B^{\beta\alpha}B^{\beta\gamma}) = 0 \tag{31}
\end{aligned}$$

where $B_0^{\alpha\beta} = -\frac{1}{3}$ is the equilibrium value [2]. There is no coupling to the vorticity ω_k (rotational flow), since the $B^{\alpha\beta}$ are scalar quantities. The relaxation time $\tau = \gamma_1/B_1$. For non-deformable tetrahedratics $\lambda = 0$ and $\tau = 0$. Note that the system of equations (31) is not closed, but still contains individual $\mathbf{n}^\alpha$'s in the coupling term to A_{ij}. Therefore we will solve these equations only approximately for two special cases.

First we study the effect of an external shear flow in the $x - y$ plane. Taking a velocity field of the form

$$\mathbf{v} = S(0, x, 0) \tag{32}$$

it is appropriate to choose one of the tetrahedratic unit vectors, $\mathbf{n}^1$, to be parallel to the $\hat{\mathbf{e}}_z-$ direction in equilibrium. To achieve this the equilibrium unit vectors in

eqs.(3-6) are suitably rotated

$$\mathbf{n^1} = (0,0,1) \tag{33}$$

$$\mathbf{n^2} = \frac{1}{3}(-\sqrt{2}, -\sqrt{6}, -1) \tag{34}$$

$$\mathbf{n^3} = \frac{1}{3}(-\sqrt{2}, \sqrt{6}, -1) \tag{35}$$

$$\mathbf{n^4} = \frac{1}{3}(2\sqrt{2}, 0, -1) \tag{36}$$

Then to leading order (that is, discarding λ_{ijk}^{α} in (28)) $\mathbf{n^2}, \mathbf{n^3}$ and $\mathbf{n^4}$ rotate together about $\hat{\mathbf{e}}_z$ with a frequency $\omega = S/2$ and a phase difference of $2\pi/3$ between them

$$\mathbf{n^{1s}} = (0,0,1) \tag{37}$$

$$\mathbf{n^{2s}} = \frac{1}{3}(2\sqrt{2}\cos(\tfrac{S}{2}t + \tfrac{4\pi}{3}), 2\sqrt{2}\sin(\tfrac{S}{2}t + \tfrac{4\pi}{3}), -1) \tag{38}$$

$$\mathbf{n^{3s}} = \frac{1}{3}(2\sqrt{2}\cos(\tfrac{S}{2}t + \tfrac{2\pi}{3}), 2\sqrt{2}\sin(\tfrac{S}{2}t + \tfrac{2\pi}{3}), -1) \tag{39}$$

$$\mathbf{n^{4s}} = \frac{1}{3}(2\sqrt{2}\cos(\tfrac{S}{2}t), 2\sqrt{2}\sin(\tfrac{S}{2}t), -1) \tag{40}$$

Using this as input in eq.(31) the λ term acts as driving force $F^{\alpha\beta}$ for oscillations of $B^{\alpha\beta}$ about the equilibrium value $-1/3$ describing oscillating deformations of the tetrahedra. Since this driving force is quadratic in $\mathbf{n^{\alpha s}}$ it oscillates with twice the frequency

$$F^{\alpha\beta} = \frac{8}{27}f^{\alpha\beta}\lambda S \sin(St + \varphi^{\alpha\beta}) \tag{41}$$

with $\varphi^{\alpha\beta} = 2\pi/3, 4\pi/3, 0, 0, 4\pi/3, 2\pi/3$ and $f^{\alpha\beta} = 1, 1, 1, 5, 5, 5$ for $\{\alpha\beta\} = \{12, 13, 14, 23, 24,$ and $34\}$, respectively. Linearizing in the amplitude of the fluctuations around the equilibrium value, we get $(1 \neq \alpha \neq \beta \neq 1)$

$$B^{\alpha\beta} + \frac{1}{3} = A(S)\sin(St + \varphi^{\alpha\beta} + \varphi(S)) \tag{42}$$

The shear dependent amplitude and phase shift are

$$A(S) = \frac{2}{3}\lambda\tau S\Big(1 + \big(\frac{3\tau S}{8}\big)^2\Big)^{-1/2} \tag{43}$$

$$\varphi(S) = -\tan^{-1}\big(\frac{3\tau S}{8}\big) \tag{44}$$

The angles B^{12}, B^{13}, and B^{14} oscillate around their equilibrium value $-1/3$ with a smaller amplitude $\sim \lambda(\tau S)^2$.

Thus we find that an applied shear leads to an oscillatory distortion of the tetrahedratic structure with a maximum amplitude $\sim S\lambda\tau$. At any given time, the deformations are such that no symmetry of the tetrahedron is left and a distorted C_1-symmetric structure is locally present. However, when averaged over an oscillation period, tetrahedratic symmetry is conserved (see Fig. 6).

A direct way to observe this deformation experimentally is the following. In rotational shear, non-deformable tetrahedratics stay optically isotropic as the $\mathbf{n^\alpha}$, $\alpha = 2, 3, 4$, rotate rigidly around n^1 conserving the overall symmetry. Eq. 42 shows that the situation is different for
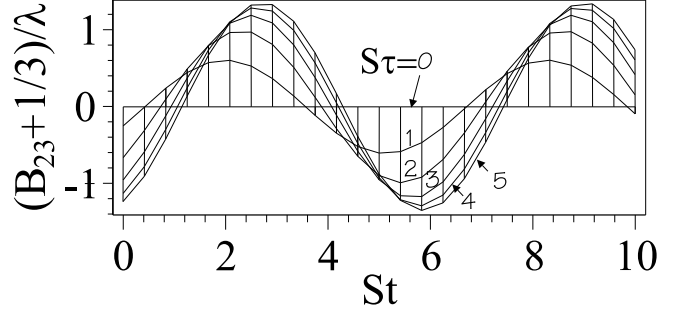
Fig. 6. Eq. (42) scaled by λ vs. St for $\{\alpha\beta\} = \{23\}$ and $S\tau = 0, \ldots 5$.

deformable tetrahedratics. Due to the oscillating values of the angles between the $\mathbf{n^\alpha}$ (see e.g. Fig. 6), the system has a time dependent biaxiality and therefore an oscillating birefringence, Δn:

$$\Delta n = (\Delta n)_0 \, sin(2\omega t + \phi). \tag{45}$$

The prediction is that if a shear with corresponding frequency ω is applied, one should be able to detect the system response blinking at frequency 2ω. Measuring the amplitude and the phase shift of the response as a function of shear could lead to direct determinations of λ and τ (cf Fig. 6).

In an extensional flow the tetrahedra do not rotate. There is, however, a deformation due to the term proportional to the λ tensor, which is balanced by the dissipative contribution associated with the elastic forces. We now study the effect of steady extensional flow on the angles $B^{\alpha\beta}$ in a linear approximation. Linearizing (31) in $\Delta^{\alpha\beta} = B^{\alpha\beta} - B_0^{\alpha\beta}$ and in the flow field one finds $(\alpha \neq \beta)$

$$\dot{\Delta}^{\alpha\beta} + 2\lambda\left(n_i^\alpha n_j^\beta + n_j^\alpha n_i^\beta + \tfrac{1}{3}(n_i^\alpha n_j^\alpha + n_i^\beta n_j^\beta)\right)A_{ij}$$
$$+\frac{16}{9\tau}\Big(\Delta^{\alpha\beta} - \tfrac{1}{4}\sum_{\substack{\gamma\neq\beta\\\gamma\neq\alpha}}(\Delta^{\alpha\gamma} + \Delta^{\beta\gamma})\Big) = 0 \tag{46}$$

where the n_i^α are to be taken at their equilibrium values. To obtain a consistent approximation in eq.(46), only terms up to linear order in δn_i^α are included in $\Delta^{\alpha\beta}$. We also note that the $\Delta^{\alpha\beta}$ are not linearly independent, as $\sum_{\alpha,\beta\neq\alpha}\Delta^{\alpha\beta} = 0$. The structure of (46) preserves that relation for all times.

The stationary deformations of the relative angles between the unit tetrahedral vectors can be obtained from (46) by putting $\dot{\Delta}^{\alpha\beta} = 0$. For definiteness, we assume a flow of the form

$$\mathbf{v} = S(y, x, 0) \tag{47}$$

which is irrotational and in the $x-y$-plane. The symmetric velocity gradient A_{ij} then has only two non-vanishing components $A_{xy} = A_{yx} = S$ while $A_{ij} \equiv 0$ otherwise.
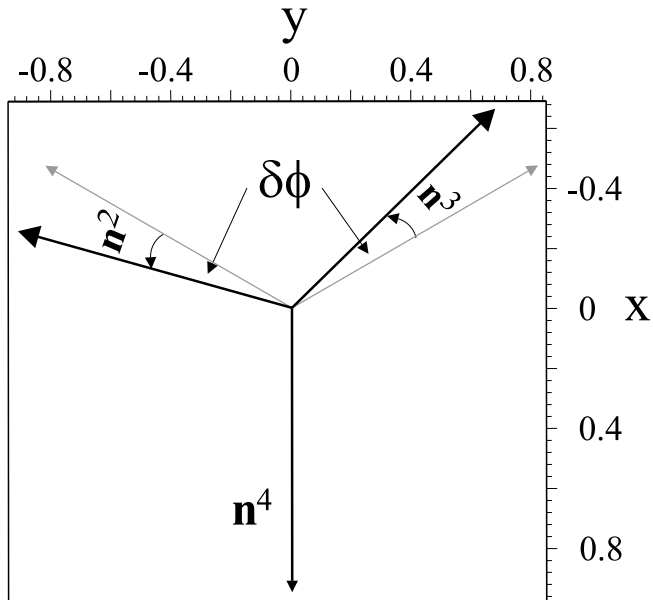
Using (47,33-36) and the condition $\sum_{\alpha,\beta\neq\alpha}\Delta^{\alpha\beta} = 0$ the five independent equations (46) give with $\tau = \gamma_1/B_1$

$$\Delta^{12} = \Delta^{13} = \Delta^{14} = \Delta^{23} = 0 \tag{48}$$

$$\Delta^{24} = -\Delta^{34} = \frac{2\sqrt{3}}{3}S\lambda\tau \tag{49}$$

demonstrating the stationary non-equilibrium deformation of the tetrahedra by extensional flow.

The interpretation of the deformations (49) is the following (See Fig. 7). The unit vectors $\mathbf{n^1}$ and $\mathbf{n^4}$ stay at

Fig. 7. The black arrows depict the stationary deformed state for deformable tetrahedratics in elongational shear (viewed against $\mathbf{n^1}$). $\mathbf{n^2}$ and $\mathbf{n^3}$ rigidly rotate $\delta\phi \approx S\lambda\tau$ while $\mathbf{n^1}$ and $\mathbf{n^4}$ remain fixed. Small grey arrows show the orientation of $\mathbf{n^2}$ and $\mathbf{n^3}$ at equilibrium. Here, $\delta\phi = 0.25$.

their equilibrium directions (thus conserving the relative angle B^{14}), while $\mathbf{n^2}$ and $\mathbf{n^3}$ rotate as a rigid entity (conserving the relative angle B^{23}) about $\mathbf{n^1}$ (thus conserving the relative angles B^{12} and B^{13}) by an angle $\delta\phi \approx S\lambda\tau$. These skewed tetrahedra have lost all equilibrium tetrahedral symmetries, such as the 2- and 3-fold symmetry axes and the mirror planes, thus giving rise to C_1 (i.e. no) symmetry.

4 Does a deformed tetrahedratic phase mediate the isotropic - B7 transition?

In the bulk of this paper we have discussed the influence of an external electric field and of an external flow on a deformable tetrahedratic phase. We found that both external forces lead to a reduction in symmetry: in the case of an electric field to a static C_{3v}-symmetry and for simple shear, to a time dependent C_1-symmetric local structure.

As we have investigated recently the flow properties of a tetrahedratic phase [1] and the symmetry and macroscopic properties of columnar phases with a macroscopic polarization [20], we combine these results with the ones presented here and compare them with experimental observations in the vicinity of the isotropic - B7 phase transition observed in compounds made of banana-shaped

molecules [12, 13]. This leads us to suggest the following scenario.

As temperature is lowered above an isotropic - B7 phase transition, one generates flow if an electric field or temperature variations are applied, provided the optically isotropic phase observed is tetrahedratic. For a deformable tetrahedratic phase the symmetry is then reduced drastically to C_1 in the presence of flow. Given the fact that the heat of transition observed for this phase transition is rather large [12, 13, 15] and comparable in magnitude to that observed for isotropic - pyramidic transitions [25], this leads us to suggest that the B7 phase could have locally a columnar structure with a macroscopic polarization [18]. This suggestion is further supported by the observation that in B7 freely suspended films decompose into strands [13, 19] . We also note that the same local C_1 symmetry (or rather the absence of any symmetry) will facilitate locally the transition from a deformed tetrahedratic structure to a columnar structure with an 'oblique' polarization.

To experimentally test the scenario outlined above a few crucial experiments are important. First, the question whether the B7 phase has a macroscopic polarization must be addressed. At this time there is no clear-cut experimental result in the literature concerning this point. Second, it would be important to study in detail the physical properties of the optically isotropic phase above the B7 phase. Key question: is its symmetry reduced drastically when external forces are applied? Third, we predict in this scenario a phase transition from a classical isotropic fluid to a tetrahedratic or a deformable tetrahedratic phase. In this general respect, it is important to measure the specific heat of all the banana phases for anomalous temperature dependence recently predicted for tetrahedral spin ice [26] and first observed for water-ice [27], as it appears to be a physical signature of condensed phases with frustrated tetrahedral order.

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