*Ferroelectrics,* 2005, Vol. 315, pp. 165-172

DOI: 10.1080/00150190509656
Received in final form: January 26, 2004

# Selected Macroscopic Consequences of Tetrahedratic Order

H.R. BRAND[1,2,3], P.E. CLADIS[2] AND H. PLEINER[3]

1. Theoretische Physik III, Universität Bayreuth, 95440 Bayreuth
2. ALCT, POB 1314, Summit, NJ 07902, USA
3. Max-Planck-Institute for Polymer Research, 55021 Mainz

*We discuss for tetrahedratic phases a number of cross-coupling terms not considered before and we analyse their macroscopic physical consequences. In particular we show that if a tetrahedratic phase is acted on by an electric field that is perpendicular to a temperature gradient, an electric current perpendicular to both forces results. We also demonstrate that spatial variations of the tetrahedratic order, as can arise e.g. near phase transitions, generate reversible stresses and can thus induce flows.*

**Keywords:** Symmetries; tetrahedratic order; banana smectics; macroscopic dynamics; cross-coupling terms; chiral invariants; field effects.

## Introduction

Traditional liquid crystalline phases show quadrupolar orientational order [1,2]. More recently, in connection with the study of liquid crystalline phases formed by banana-shaped or bent-core molecules [3–16], the question asked was whether tetrahedratic (octupolar) order also played a role. The answer now emerging is that tetrahedratic order plays an essential role in describing the multitude of new effects exhibited by banana liquid crystals.

After pioneering work by Fel [17, 18], the following investigations [19–22] focused on phase transitions [19,21] and on the flow properties of a tetrahedratic phase, which has no simultaneous quadrupolar orientational order [20]. We also investigated the changes of the flow behavior assuming that, in the absence of an external flow and/or external fields, there is only tetrahedratic symmetry in a ground state that is lost when such forces are present [22]. Our interest in the field of tetrahedratic phases was originally triggered by the observation of flow in the optically isotropic phase [23, 24] above the B7 - isotropic phase transition [16].

Quite recently several additional phenomena were described for liquid crystalline phases formed by banana-shaped molecules, which cannot be understood using only the classical quadrupolar orientational order parameter, $Q_{ij}$. In one case [25] it was found that a liquid crystalline phase can be induced by an electric field up to about ten degrees above the liquid crystalline ($B2$) - isotropic phase transition. In addition, it was reported [25], that the shift in transition

temperature ($T - T_{B2,iso}$) is linear in the applied electric field. The other class of phenomena consists of the spontaneous formation of left- and right-handed domains in nematic [26–28] and smectic $C$-type [29] LC phases composed of nonchiral bent-core molecules. Very recently we have suggested an explanation [30] of these experimentally observed phenomena using static cross-coupling terms between quadrupolar and tetrahedratic (octupolar) order.

In the present paper we explore additional static cross-coupling terms between quadrupolar and octupolar order. The main emphasis, however, is on the investigation of reversible and dissipative dynamic cross-coupling terms involving either both, tetrahedratic *and* quadrupolar order, or tetrahedratic order and its gradients. We find, for example, that an electric field applied in the $x-$direction, say, and a temperature gradient applied in the $y-$direction, leads in a tetrahedratic phase to an electric current in the $z-$direction, that is in a direction perpendicular to both external forces.

## New Cross-Coupling Terms in the Macroscopic Description of the Tetrahedratic Phase

To make the following presentation self-contained, we will make use of some of the material presented in ref. [20]. For the tetrahedratic phase one has the same hydrodynamic variables as for an isotropic liquid, namely the density, $\rho$, the energy density, $\epsilon$, the density of linear momentum, $g_i$, and, in mixtures, the concentration, $c$. In addition one has a third rank tensor $T_{ijk}$ characterizing the tetrahedratic order. $T_{ijk}$ is symmetric in all indices and traceless $T_{iik} = 0$, i.e. it does not contain any vectorial quantity. Since it transforms under an $l = 3$ representation, it is odd under parity and thus allows coupling terms not possible in ordinary simple liquids.

The statics of a macroscopic system is governed by its energy density, $f$. Due to the Gibbs relation (the local manifestation of the first and second law of thermodynamics)

$$df = \mu\, d\rho + T\, d\sigma + \mu_c\, dc \tag{1}$$

the conjugate quantities follow from the energy density by partial differentiation

$$\delta T \equiv \frac{\partial f}{\partial \sigma} = \frac{T}{C_V}\,\delta\sigma + \frac{1}{\rho\alpha_s}\,\delta\rho + \beta_\sigma \delta c \tag{2}$$

$$\delta\mu \equiv \frac{\partial f}{\partial \rho} = \frac{1}{\rho^2\kappa_s}\,\delta\rho + \frac{1}{\rho\alpha_s}\,\delta\sigma + \beta_\rho \delta c \tag{3}$$

$$\delta\mu_c \equiv \frac{\partial f}{\partial c} = \gamma\,\delta c + \beta_\sigma\delta\sigma + \beta_\rho\delta\rho \tag{4}$$

The pressure is related to the other conjugate quantities by the Gibbs-Duhem relation [31]

$$\delta p = \rho\delta\mu + \sigma\delta T - \mu_c\delta c \tag{5}$$

neglecting contributions quadratic in the velocity.

For the statics of tetrahedratics, we have found for the energy density [20]

$$f = f_0 + \epsilon_1 T_{ijk} D_i D_j D_k + \epsilon_2 T_{ijk} D_i H_j H_k + f_T \tag{6}$$

where $f_0$ denotes the energy density of an isotropic fluid, $f_T$ denotes the density of the analogue of the Frank energy for the tetrahedratic phase discussed by Fel [17], and $D_i$ denotes the dielectric displacement field.

Very recently we found [30] that the energy density, $f$, also contains the contribution $f_{QT}$

$$f_{QT} = \mathcal{D} T_{ijk} \nabla_k Q_{ij} - \Gamma T_{ijk} D_i Q_{jk} \tag{7}$$

when one allows bilinear cross-coupling terms between tetrahedratic (octupolar) order and the usual quadrupolar orientational order, $Q_{ij}$, [1, 2] in a truly tetrahedratic phase. Physical consequences of these two contributions have been elucidated in ref. [30]. In particular we have shown [30], that the application of an electric field to an isotropic tetrahedratic phase can lead to the induction of quadrupolar orientational order of the type familiar from nematics and thus to an optically uniaxial phase.

In addition to an induced orientational order, smectic layering can be induced simultaneously via terms coupling the smectic order parameter $\psi$ to the order parameters $T_{ijk}$ and $Q_{ij}$. As cross-coupling contributions in the generalized energy, which are linear in $|\psi|^2$ we find

$$f_{Sm} = |\psi|^2 (\tau_1 T_{ijk} T_{ijk} + \tau_2 Q_{ij} Q_{ij} + \tau_3 T_{ijk} D_i Q_{jk}) \tag{8}$$

For suitable values of the coefficients of the coupling terms to smectic order, layering can be induced simultaneously with the onset of $Q_{ij}$. We note, that the same type of analysis as for the coupling to smectic order also applies to that for columnar order.

The results of our analysis show that the experimental observations described in ref. [25] would find an explanation if the 'isotropic' phase observed in [25] is actually tetrahedratic. We are not aware of any other explanation which could account for the experimental results. In contrast to the explanation suggested in ref. [25], there is no macroscopic polarization in an isotropic liquid. If there is a liquid phase with a macroscopic polarization $\mathbf{P}$, it would be uniaxial due to the preferred direction set by $\mathbf{P}$. To further test our suggestion it would be important to study the 'isotropic' phase in detail, for example via x-ray investigations of well oriented samples.

To construct a pseudoscalar for a system with tetrahedratic and orientational order necessitates, in the absence of an external electric field, the inclusion of two spatial gradients

$$\zeta_T = \epsilon_{jml} \nabla_i T_{ijk} \nabla_l Q_{mk} \tag{9}$$

Using the pseudoscalar $\zeta_T$ - containing two spatial gradients - one can then construct the analog of the term familiar from cholesterics and chiral smectics

$$f_{q_T} = \tilde{c}\ \zeta_T \epsilon_{ijk} Q_{i\ell} \nabla_k Q_{j\ell} \tag{10}$$

We note that $\zeta_T$ has the dimension $m^{-2}$ and thus $\tilde{c}$ has the dimension of an energy from the way the pseudoscalar quantity has been constructed.

We also note that in an applied electric field it is possible to construct a pseudoscalar quantity without spatial gradients by replacing the gradients by the dielectric displacement field

$$\zeta_{TE} = \epsilon_{jml} D_i D_l T_{ijk} Q_{mk} \tag{11}$$

Two additional pseudoscalar quantities can be generated by incorporating an electric field as well as one spatial gradient into the construction.

$$\zeta_{TE2} = \epsilon_{ijn} D_k Q_{nl} \nabla_i T_{jkl} \tag{12}$$

$$\zeta_{TE3} = \epsilon_{jmn} D_m Q_{nl} \nabla_i T_{ijl} \tag{13}$$

Such terms as well as the existence of $\zeta_{TE}$ might explain why chiral domains are observed to be most pronounced when the preparation and the sample history involved the application of external electric fields [32].

For a simple liquid, one has as hydrodynamic variables - as already mentioned briefly above - the density $\rho$, the momentum density $\rho\boldsymbol{v}$ related to the velocity $\boldsymbol{v}$, and the entropy density $\sigma$, or equivalently the free energy density $f$. In the case of mixtures one has as an additional conserved quantity the concentration $c$. The hydrodynamic equations are [31, 33, 34]

$$\left(\frac{\partial}{\partial t} + v_i \nabla_i\right) \rho + \rho \, div \, \boldsymbol{v} = 0 \tag{14}$$

$$\rho \left(\frac{\partial}{\partial t} + v_j \nabla_j\right) v_i + \nabla_j \sigma_{ij} = 0 \tag{15}$$

$$\rho \left(\frac{\partial}{\partial t} + v_j \nabla_j\right) c + div \, \boldsymbol{j}^c = 0 \tag{16}$$

$$\left(\frac{\partial}{\partial t} + v_j \nabla_j\right) \rho^e + div \, \boldsymbol{j}^e = 0 \tag{17}$$

$$\left(\frac{\partial}{\partial t} + v_i \nabla_i\right) \sigma + \sigma div \, \boldsymbol{v} + div \, \boldsymbol{j}^\sigma = \frac{R}{T} \tag{18}$$

where we have also included the dynamic equation for the electric charge density $\rho^e$.

The electric current density has the form

$$j_i^e = \sigma_{ij}^E E_j + D_{ij}^E \nabla_j \mu_c + \kappa_{ij}^E \nabla_j T \tag{19}$$

where $\sigma_{ij}^E$, $D_{ij}^E$ and $\kappa_{ij}^E$ have the structure

$$\kappa_{ij}^E = \kappa^E \delta_{ij} \tag{20}$$

with the Kronecker symbol $\delta_{ij}$. For the detailed conventional expressions and the structure of the other currents we refer to ref. [20]

Since $T_{ijk}$ is associated with the spontaneously broken orientational symmetry of the tetrahedratic phase, it serves as an additional hydrodynamic variable [34] and leads to the following quasi-conservation law for $T_{ijk}$

$$\dot{T}_{ijk} + Y_{ijk} = 0 \tag{21}$$

As usual the reversible and the dissipative parts of the quasi-current, $Y_{ijk}$, are expanded into thermodynamic forces, that is, the gradients of eqs.(2-4), $\delta f/\delta T_{ijk}$, and $A_{ij} = \frac{1}{2}(\nabla_i v_j + \nabla_j v_i)$. Since $T_{ijk}$ is not directly observable, we refrain from writing down explicitly all expressions, but concentrate on the cross-coupling terms of $T_{ijk}$ to other hydrodynamic variables.

A similar quasi-conservation law arises for the usual nematic order parameter $Q_{ij}$

$$\dot{Q}_{ij} + Y_{ij} = 0 \tag{22}$$

an equation well-known near the isotropic - nematic transition [1, 2].

The Gibbs relation taking into account quadrupolar order $Q_{ij}$ and tetrahedratic order, $T_{ijk}$ assumes the form

$$\begin{aligned} df &= \mu\, d\rho + T\, d\sigma + \mu_c\, dc + S_{ij} dQ_{ij} + V_{ijk} dT_{ijk} \\ &\quad + E_i dD_i + v_i dg_i \end{aligned} \tag{23}$$

with the momentum density $g_i = \rho v_i$, the thermodynamic conjugates $S_{ij}$ (for quadrupolar order) and $V_{ijk}$ (for tetrahedratic order), and the dielectric displacement vector connected to the electric charge density by $\mathrm{div}\mathbf{D} = \rho^e$. The conjugates inherit the symmetries of the variables, i.e. $S_{ij} = S_{ji}$ and $V_{ijk} = V_{jik} = V_{kji} = V_{ikj}$.

In addition to the reversible currents discussed previously [20] describing a coupling between the stress tensor and electric fields or gradients of temperature (or concentration in mixtures) involving one factor $T_{ijk}$, we find also a direct coupling between gradients of $T_{ijk}$ and the stress tensor

$$\sigma^R_{ij} = \cdots + \alpha \nabla_k V_{ijk} \tag{24}$$

$$Y_{ijk}{}^R = \cdots - \frac{\alpha}{3}(\nabla_k A_{ij} + \nabla_i A_{kj} + \nabla_j A_{ik}) \tag{25}$$

We note that there is also the analog of the reversible couplings considered previously to the stress tensor [20] for the conjugate associated with the quadrupolar order, $S_{ij}$

$$\sigma^R_{ij} = \cdots + \gamma T_{ijk} \nabla_l S_{lk} \tag{26}$$

$$Y_{ij}{}^R = \cdots - \frac{\gamma}{2}(\nabla_i T_{jkl} A_{lk} + \nabla_j T_{ikl} A_{lk}) \tag{27}$$

When we consider the effect of an external electric field on the macroscopic dynamics, we find additional contributions to the dissipative part of the electric current

$$\begin{aligned} j^{eD}_i &= \cdots + \Delta_1 T_{ijk} E_j E_k + \Delta_2 T_{ijk} E_j \nabla_k T + \Delta_3 T_{ijk} E_j \nabla_k c \\ &\quad + \Delta_4 T_{ijk} (\nabla_j c)(\nabla_k T) + \Delta_5 T_{ijk} (\nabla_j c)(\nabla_k c) \\ &\quad + \Delta_6 T_{ijk} (\nabla_j T)(\nabla_k T) \end{aligned} \tag{28}$$

The experimental consequences of these cross-coupling terms will be investigated in more detail in the next section.

For the irreversible contributions associated with the coupling between the conjugates of the two order parameter fields we have in the entropy production in addition

$$R = \cdots + \beta V_{ijk} \nabla_i S_{jk} \tag{29}$$

which gives rise to cross-coupling terms in the two quasi-currents

$$Y^D_{ijk} = \cdots + \frac{\beta}{3}(\nabla_i S_{jk} + \nabla_j S_{ik} + \nabla_k S_{ji}) \tag{30}$$

and

$$Y^D_{ij} = \cdots - \beta \nabla_k V_{ijk} \tag{31}$$

This cross-coupling term is the dissipative analog of the static cross-coupling term $\sim T_{ijk}\nabla_i Q_{jk}$ whose implications for the ground state of phases showing both, quadrupolar and tetrahedratic order, have been discussed very recently [30]. Finally there are dissipative contributions describing the coupling of $S_{ij}$ to an electric field as well as to temperature and concentration gradients

$$R = \cdots + T_{ijk} S_{jk}(\lambda_1 E_i + \lambda_2 \nabla_i T + \lambda_3 \nabla_i c) \tag{32}$$

We note that the first term in eq.(32) is similar in structure to the term $\sim T_{ijk} D_i Q_{jk}$ in the generalized energy whose importance has been discussed recently in the context of field induced transitions [30].

**Experimental Consequences**

Equation (28) suggests a very simple experiment to evaluate the magnitude of one of the effects predicted here: if one applies an electric field $E$ in $x$-direction and a temperature gradient in $y$-direction, the prediction of this equation is that an electric current should appear in $z$-direction, that is orthogonal to the directions of the applied electric field and of the temperature gradient.

$$j^{eD}_z = \cdots + \Delta_2 T_{zxy} E_x \nabla_y T \tag{33}$$

Making use of the explicit form of $T_{ijk}$ used in ref. [22], this leads to, with $E_x = E_0 \hat{x}$ and $|\nabla_y T| = G$

$$j^{eD}_z = -\Delta_2 \frac{4 E_0 G}{3\sqrt{3}} \tag{34}$$

and vanishing components of the electric current in the other two directions, $j^{eD}_x$ and $j^{eD}_y$ (Fig. 1). We note, that the sign in eq.(34) depends on the specific representation used to calculate $T_{ijk}$. This component arises in addition to the Ohmic contribution one expects for an isotropic liquid in the $\hat{x}-$ direction

$$j^{eD}_x = \sigma E_x \tag{35}$$

with the electric conductivity $\sigma$, when the electric field is applied in the $\hat{x}-$direction.

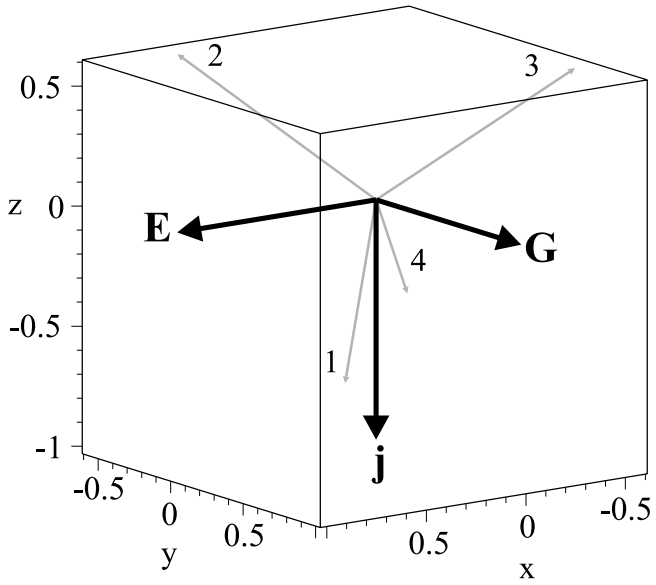


**Figure 1** : An electric field in the $\hat{x}$-direction combined with a temperature gradient in the $\hat{y}$-direction generates an electric current in the $\hat{z}$ direction.

Another experiment is suggested by eq.(24) for the reversible contribution to the stress tensor presented here for the first time: spatial variations of the tetrahedratic order will generate stresses, which can trigger flows. For example, for spatial variations of $T_{ijk}$ in $\hat{z}-$direction, eq.(24) gives

$$\sigma^R_{ij} = \alpha \nabla_z V_{ijz} \tag{36}$$

an expression, which can give rise to shear flow. For example, for $i = x$ and $j = y$ we have

$$\sigma^R_{xy} = \alpha \nabla_z V_{xyz} \tag{37}$$

This effect should be observed experimentally, for example, near the truly isotropic-tetrahedratic transition.

**Acknowledgements**
It is a pleasure for H.R.B. to thank the Deutsche Forschungsgemeinschaft for partial support of this work through Sonderforschungsbereich 481 'Polymere und Hybridmaterialien in inneren und äußeren Feldern'.

## References

[1] P.G. de Gennes, *Mol. Cryst. Liq. Cryst.* **12**, 191 (1971).

[2] P.G. De Gennes, *The Physics of Liquid Crystals* (Clarendon Press, Oxford, 1975).

[3] H.R. Brand, P.E. Cladis and H. Pleiner, *Macromolecules* **25**, 7223 (1992).

[4] P.E. Cladis and H.R. Brand, *Liq. Cryst.* **14**, 1327 (1993).

[5] T. Niori, T. Sekine, J. Watanabe, T. Furukawa, H. Takezoe, *J. Mat. Chem.* **6**, 1231 (1996).

[6] T. Sekine, T. Niori, J. Watanabe, T. Furukawa, S.W. Choi, H. Takezoe, *J. Mat. Chem.* **7**, 1307 (1997).

[7] D.R. Link, G. Natale, R. Shao, J.E. Mclennan, N.A. Clark, E. Körblova, D.M. Walba, *Science* **278**, 1924 (1997).

[8] H.R. Brand, P.E. Cladis and H. Pleiner, *Eur. Phys. J. B* **6**, 347 (1998).

[9] R. Macdonald, F. Kentischer, P. Warnick, and G. Heppke, *Phys. Rev. Lett.* **81**, 4408 (1998).

[10] D. Shen, S. Diele, I. Wirth, and C. Tschierske, *Chem. Commun.* **1998**, 2573 (1998).

[11] G. Pelzl, S. Diele and W. Weissflog, *Adv. Mat.* **11**, 707 (1999).

[12] P.E. Cladis, H.R. Brand and H. Pleiner, *Liquid Crystals Today* **9 (3/4)**, 1 (1999).

[13] H.R. Brand, P.E. Cladis and H. Pleiner *Int. J. Eng. Sci.* **38**, 1099 (2000).

[14] P.E. Cladis, H. Pleiner and H.R. Brand, *Ferroelectrics* **243**, 221 (2000).

[15] H. Pleiner, H.R. Brand and P.E. Cladis, *Ferroelectrics* **243**, 291 (2000).

[16] G. Pelzl, S. Diele, S. Grande, A. Jakli, Ch. Lischka, H. Kresse, H. Schmalfuss, I. Wirth and W. Weissflog, *Liq. Cryst.* **26**, 401 (1999).

[17] L.G. Fel, *Phys. Rev. E* **52**, 702 (1995).

[18] Throughout the present manuscript we focus on the nonchiral tetrahedratic phase, $T_d$ [17]. We note, however, that our analysis is also useful for the blue phase version of its chiral analogue, the $T$ phase [17].

[19] L. Radzihovsky and T.C. Lubensky, *Europhys. Lett.* **54**, 206 (2001).

[20] H.R. Brand, H. Pleiner and P.E. Cladis, *Eur. Phys. J. E* **7**, 163 (2002).

[21] T.C. Lubensky and L. Radzihovsky, *Phys. Rev. E* **66**, 0310704 (2002).

[22] P.E. Cladis, H. Pleiner and H.R. Brand, *Eur. Phys. J. E* **11**, 283 (2003).

[23] P.E. Cladis, W. Weissflog, G. Pelzl and H.R. Brand, to be published.

[24] Y. Yusuf, Y. Hidaka, S. Kai, H.R. Brand, P.E. Cladis, W. Weissflog and G. Pelzl, *Ferroelectrics* **276**, 171 (2002).

[25] W. Weissflog, M.W. Schröder, S. Diele and G. Pelzl, *Adv. Mat.* **15**, 630 (2003).

[26] G. Pelzl, A. Eremin, S. Diele, H. Kresse and W. Weissflog, *J. Mat. Chem.* **12**, 2591 (2002).

[27] T. Niori, J. Yamamoto and H. Yokoyama, *Mol. Cryst. Liq. Cryst.*, in print (2003).

[28] M. Hird, Y. Raoul, J.W. Goodby, and H.F. Gleeson, Abstract PL6, presented at the 9th International Ferroelectric Liquid Crystal Conference in Dublin, Aug.24-29, 2003.

[29] J.W. Goodby, A.W. Hall, S.J. Cowling, M. Hird, and R. Tuffin, Abstract PL3, presented at the 9th International Ferroelectric Liquid Crystal Conference in Dublin, Aug.24-29, 2003.

[30] H.R. Brand, H. Pleiner and P.E. Cladis, submitted for publication.

[31] H. Pleiner and H.R. Brand, Hydrodynamics and Electrohydrodynamics of Nematic Liquid Crystals, in *Pattern Formation in Liquid Crystals*, eds. A. Buka and L. Kramer (Springer, New York, 1996) p. 15ff.

[32] A. Eremin, private communication (2003).

[33] P. C. Martin, O. Parodi and P.S. Pershan, *Phys. Rev.* **A6**, 2401 (1972).

[34] D. Forster, *Hydrodynamic Fluctuations, Broken Symmetry and Correlation Functions* (Benjamin, Reading, Mass. 1975).