

Flow properties of the optically isotropic tetrahedric phase

Helmut R. Brand^{1 a}, Harald Pleiner² and P.E. Cladis³,

¹Theoretische Physik III, Universität Bayreuth, 95440 Bayreuth, Germany;

²Max-Planck-Institute for Polymer Research, POBox 3148, 55021 Mainz, Germany;

³Advanced Liquid Crystal Technologies, Summit, POB 1314, NJ 07902, U.S.A.

Received: July 30, 2001

Abstract. We discuss the coupling between flow and other hydrodynamic variables that can occur in the optically isotropic tetrahedric phase (T_d) characterized by a third rank tensor order parameter T_{ijk} . We point out that an applied electric field or an applied temperature gradient will lead to flow. Reciprocally we predict that, for example, a shear flow applied to a tetrahedric phase leads to an induced electric field and a temperature gradient. Similarities to recent experimental observations in the vicinity of the isotropic - B7 phase transitions in materials formed by banana-shaped molecules are discussed.

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

Recently the liquid crystalline phases formed in compounds composed of achiral banana-shaped molecules have attracted considerable attention [1–13]. One of the most puzzling phenomena observed in this area is the phase transition from an optically isotropic liquid phase to the B7 phase [9, 14] for which neither the symmetry nor the properties of the ground state are understood. It is not a well formed smectic phase, since one cannot draw freely suspended films in it. Instead these films decompose into strands [14]. In addition, x-ray investigations give rise to 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 [14]. We also note that so far one has not successfully grown large monodomains in the B7 phase, which are essential for systematic high resolution x-ray investigations. Instead, one has optically observed many different patterns on cooling including spirals of both hands growing into the isotropic phase, myelinic patterns and patterns showing spatial modulations, sometimes regular, in a second direction [9, 14]. Recent experiments on the effect of an external electric field and of temperature variations have also revealed the occurrence of flow close to and in the isotropic phase near the B7 - isotropic phase transition [15].

Consequently, there is a need to look for models which can describe the B7 phase and its transition to the isotropic phase. From a general perspective, the question

to what extent phases that are optically isotropic but not cubic can show coupling effects between flow and electric fields and/or temperature gradients has never been addressed. It is the goal of this manuscript to analyze the macroscopic behavior of such a phase with high symmetry, namely the tetrahedric phase of T_d symmetry, which has been studied recently mainly in connection with its phase transition behavior [16–18].

2 Hydrodynamics of the tetrahedric phase

For the tetrahedric phase one has the same hydrodynamic variables as for an isotropic liquid, namely the density, ρ , the energy density, ϵ , 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 tetrahedric 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 free energy. For an isotropic fluid the free energy density, in harmonic approximation, is [19, 20]

$$f = \frac{T}{2C_V} (\delta\sigma)^2 + \frac{1}{2\rho^2\kappa_s} (\delta\rho)^2 + \frac{\gamma}{2} (\delta c)^2 + \frac{1}{\rho\alpha_s} (\delta\sigma)(\delta\rho) + \beta_\sigma(\delta c)(\delta\sigma) + \beta_\rho(\delta c)(\delta\rho) + \frac{\rho}{2} v_i^2 \quad (1)$$

where the static susceptibilities contained in (1) are the specific heat (at constant density) C_V , the isentropic com-

^a e-mail: brand@uni-bayreuth.de

compressibility κ_s , the adiabatic volume expansion coefficient α_s and the appropriate susceptibilities γ , β_σ and β_ρ related to the concentration instead of the total mass density.

Due to the Gibbs relation (the local manifestation of the first and second law of thermodynamics)

$$df = \mu d\rho + T d\sigma + \mu_c dc \quad (2)$$

the conjugate quantities follow from the free energy density by partial differentiation

$$\delta T \equiv \frac{\partial f}{\partial \sigma} = \frac{T}{C_V} \delta\sigma + \frac{1}{\rho\alpha_s} \delta\rho + \beta_\sigma \delta c \quad (3)$$

$$\delta\mu \equiv \frac{\partial f}{\partial \rho} = \frac{1}{\rho^2\kappa_s} \delta\rho + \frac{1}{\rho\alpha_s} \delta\sigma + \beta_\rho \delta c \quad (4)$$

$$\delta\mu_c \equiv \frac{\partial f}{\partial c} = \gamma \delta c + \beta_\sigma \delta\sigma + \beta_\rho \delta\rho \quad (5)$$

The pressure is related to the other conjugate quantities by the Gibbs-Duhem relation [21]

$$\delta p = \rho \delta\mu + \sigma \delta T - \mu_c \delta c \quad (6)$$

neglecting contributions quadratic in the velocity.

For the statics of tetrahedratics, we find for the free energy density

$$f = f_0 + \epsilon_1 T_{ijk} D_i D_j D_k + \epsilon_2 T_{ijk} D_i H_j H_k + f_T \quad (7)$$

where f_0 denotes the free energy density of the isotropic fluid given in eq.(1) and where f_T denotes the density of the analogue of the Frank energy for the tetrahedric phase discussed by Fel [16]. We note that the term cubic in the dielectric displacement field \mathbf{D} in eq.(7) has been given first in [16], where also its physical implications have been studied in detail. The term quadratic in the magnetic field \mathbf{H} presented in eq.(7) has been overlooked and is not possible in a simple liquid for parity reasons.

For a simple liquid, one has as hydrodynamic variables - as already mentioned briefly above - the density ρ , the momentum density $\rho\mathbf{v}$ related to the velocity \mathbf{v} , and the entropy density σ , 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 [19–21]

$$\left(\frac{\partial}{\partial t} + v_i \nabla_i \right) \rho + \rho \operatorname{div} \mathbf{v} = 0 \quad (8)$$

$$\rho \left(\frac{\partial}{\partial t} + v_j \nabla_j \right) v_i + \nabla_j \sigma_{ij} = 0 \quad (9)$$

$$\rho \left(\frac{\partial}{\partial t} + v_j \nabla_j \right) c + \operatorname{div} \mathbf{j}^c = 0 \quad (10)$$

$$\left(\frac{\partial}{\partial t} + v_j \nabla_j \right) \rho^e + \operatorname{div} \mathbf{j}^e = 0 \quad (11)$$

$$\left(\frac{\partial}{\partial t} + v_i \nabla_i \right) \sigma + \sigma \operatorname{div} \mathbf{v} + \operatorname{div} \mathbf{j}^\sigma = \frac{R}{T} \quad (12)$$

where we have also included the dynamic equation for the electric charge density ρ^e .

The densities of the currents for heat \mathbf{j}^σ , concentration \mathbf{j}^c , electric charge \mathbf{j}^e , and momentum σ_{ij} are

$$\sigma_{ij} = p \delta_{ij} - \nu_{ijkl} \nabla_l v_k \quad (13)$$

$$j_i^\sigma = -\kappa_{ij} \nabla_j T - D_{ij}^T \nabla_j \mu_c - \kappa_{ij}^E E_j \quad (14)$$

$$j_i^e = \sigma_{ij}^E E_j + D_{ij}^E \nabla_j \mu_c + \kappa_{ij}^E \nabla_j T \quad (15)$$

$$j_i^c = -D_{ij} \nabla_j \mu_c - D_{ij}^T \nabla_j T - D_{ij}^E E_j \quad (16)$$

with the Kronecker symbol δ_{ij} .

The heat conduction tensor, κ_{ij} , the electric conductivity tensor, σ_{ij}^E , the diffusion tensor, D_{ij} , as well as thermodiffusion tensor, D_{ij}^T , (related to the Soret/Dufour effects), the thermoelectric tensor, κ_{ij}^E , and its analogue for concentration variations, D_{ij}^E , are symmetric and have the following form containing together six coefficients, including, thermal conductivity, diffusivity and Soret/Dufour,

$$\kappa_{ij} = \kappa \delta_{ij} \quad (17)$$

and the fourth rank viscosity tensor contains three viscosities [22, 23]

$$\begin{aligned} \nu_{ijkl} = & \eta_1 (\delta_{jl} \delta_{ik} + \delta_{il} \delta_{jk} - \frac{2}{3} \delta_{ij} \delta_{kl}) \\ & + \eta_2 T_{ijp} T_{klp} + \zeta \delta_{ij} \delta_{lk} \end{aligned} \quad (18)$$

Since T_{ijk} is associated with the spontaneously broken orientational symmetry of the tetrahedric phase, it serves as an additional hydrodynamic variable [20] and leads to the following quasi-conservation law for T_{ijk}

$$\dot{T}_{ijk} + Y_{ijk} = 0 \quad (19)$$

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.(3-5), $\delta f / \delta T_{ijk}$, 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. When comparing the tetrahedric phase to an ordinary isotropic phase in the dynamic regime, we have for the additional reversible currents

$$\sigma_{ij}^R = \dots - \Gamma_1 T_{ijk} E_i - \Gamma_2 T_{ijk} \nabla_i T - \Gamma_3 T_{ijk} \nabla_i c \quad (20)$$

$$j_i^{eR} = \dots + \Gamma_1 T_{ijk} A_{jk} \quad (21)$$

$$j_i^{\sigma R} = \dots + \Gamma_2 T_{ijk} A_{jk} \quad (22)$$

$$j_i^{cR} = \dots + \Gamma_3 T_{ijk} A_{jk} \quad (23)$$

From inspecting eqs.(20–23), we see that velocity gradients - including shear and extensional flows - couple to electric fields as well as temperature and concentration gradients. The experimental consequences of these cross coupling terms will be investigated in more detail in the next section.

For the irreversible contributions, we have in the entropy production in addition

$$R = \dots + \Psi_1 T_{ijk} E_i M_j M_k + \Psi_2 T_{ijk} E_i E_j E_k \quad (24)$$

Inspecting eq.(24) in detail, it is clear that these terms are the dissipative analogues of the two cubic static contributions given in eq.(7) above.

3 Experimental consequences

A number of implications for the static term cubic in the field (eq.(7)) has been discussed in the paper by Fel [16]. In this section, we outline some of the simple experimentally testable predictions to enable a distinction between the novel tetrahedric phase and the usual isotropic liquid.

We focus on the implications of the reversible dynamic cross-coupling terms presented in eqs.(20–23) of the last section. Applying, for example, a simple shear flow in the $y - z$ -plane, that is $A_{jk} = S\delta_{jy}\delta_{kz}$ with the shear rate S , to a tetrahedric phase, we read off from eq.(22) that this results in a reversible heat current of the form

$$j_i^{\sigma R} = \Gamma_2 T_{iyz} S \quad (25)$$

Making use of the explicit form of T_{ijk} [16], this leads to

$$j_x^{\sigma R} = \Gamma_2 \frac{4S}{3\sqrt{3}} \quad (26)$$

and vanishing components $j_y^{\sigma R}$ and $j_z^{\sigma R}$. This result shows that a shear flow applied in a given plane leads to a heat current in the direction perpendicular to this plane. Analogously we obtain from eq.(21)

$$j_x^{eR} = \Gamma_1 \frac{4S}{3\sqrt{3}} \quad (27)$$

and $j_y^{eR} = 0$ and $j_z^{eR} = 0$. This demonstrates that there is, in addition to the heat current, also a reversible electric current set up in the direction perpendicular to the shear plane. The same applies for the appearance of a concentration current in mixtures: in a tetrahedric phase a shear flow leads to a segregation of the subspecies involved.

Reciprocally, one can apply an electric field or a temperature gradient (or a concentration gradient) to a sample in the tetrahedric phase and ask how the flow behavior is affected. Applying, for example, an electric field \mathbf{E} in the z -direction, one obtains for the only non-vanishing component of the stress tensor (eq.(20))

$$\sigma_{yx}^R = \sigma_{xy}^R = -\Gamma_1 \frac{4E_z}{3\sqrt{3}} \quad (28)$$

This result shows that an electric field applied in a specific direction gives rise to a shear stress in the plane perpendicular to this direction. And this shear stress can in turn lead for spatially varying situations - via the dynamic equation for the linear momentum density or the velocity field - to a flow in the plane perpendicular to the direction of the applied field. The same applies to external gradients of temperature and concentration. As an example

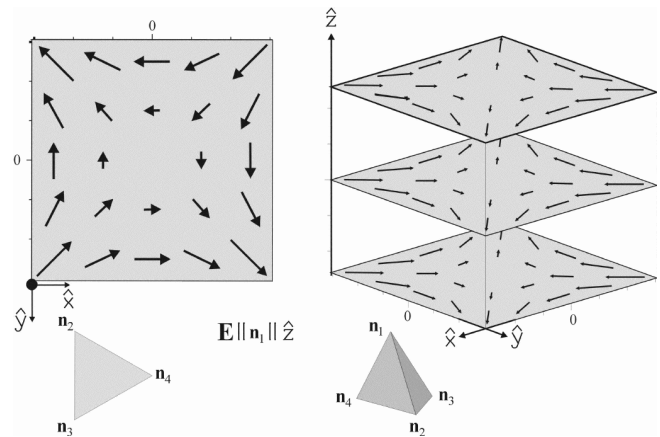


Fig. 1. Plot demonstrating the effect of the cross-coupling term $\propto \Gamma_1$ between an electric field, \mathbf{E} , and flow in the plane perpendicular to the electric field in the case of extensional flow. The view on the left is along the electric field, \mathbf{E} , with $\mathbf{E} \parallel \hat{z} \parallel \mathbf{n}_1$ (where \mathbf{n}_1 denotes one of the tetrahedral directions using the notation of Fel [16]). On the right we have plotted a three-dimensional view of both, the flow pattern and the tetrahedral directions. In a simple isotropic fluid, an electric field cannot generate any flow and vice versa.

we have plotted in Fig.1 the case of an electric field in the \hat{z} -direction and of pure extensional flow in the $\hat{x} - \hat{y}$ -plane.

An important implication of the new reversible dynamic contributions discussed here, is that the analysis of the electric Frederiks transition must include also dynamic effects. A static analysis based on energy considerations only as that given in [16] is insufficient for the tetrahedric phase.

4 Similarities to phenomena observed in the vicinity of the B7 - isotropic transition

In the last section we discussed how the new terms in the tetrahedric phase coupling flow to an external electric field as well as to temperature gradients could be experimentally detected. Here we suggest that a good candidate for the tetrahedric phase may be the isotropic liquid state above the B7 phase for the following reasons.

First of all, we note that all experiments undertaken so far show, that the B7 phase has several types of local order. This includes some degree of positional order, be it smectic or columnar. Simultaneously, with the onset of translational order there is also an onset of orientational order - typically characterized by the order parameter Q_{ij} , a traceless second rank tensor [24, 25]. Therefore to describe the isotropic - B7 phase transition minimal ingredients include order parameters for the onset of translational and orientational order, just as for the only recently studied case of the smectic A - isotropic phase transition in Landau approximation [26].

Second, the transition enthalpy observed at the B7 - isotropic transition [14, 15] is comparable to that typically obtained for isotropic - columnar phase transitions

in other classes of low molecular weight materials including compounds made of pyramidic molecules [27]. This points to the fact that major rearrangements in the degree of order take place at this transition.

Third, one observes pronounced dielectric behaviour along with flow [15]. A completely open question for the B7 phase is the role and importance of a macroscopic polarization, \mathbf{P} . There appears to be no conclusive experimental evidence as yet for the occurrence of a substantial linear electro-optic effect.

The most significant similarity is clearly the response of the isotropic phase in the vicinity of the isotropic - B7 phase boundary. Applying an electric field leads to hydrodynamic flow of significant strength [15]. When the field is turned off, this flow subsides. The same is true for temperature variations. When temperature changes are applied to a sample in the vicinity of the isotropic - B7 phase transition, this leads again to a considerable amount of flow, which stops after the temperature gradients have disappeared [15]. Such phenomena are not observed at the phase transitions between the isotropic phase and a large number of other liquid crystalline phases including, for example, nematic, smectic *A*, smectic *C*, smectic *B* and hexagonal columnar phases.

To decide unequivocally whether the isotropic phase above the B7 phase is actually a good candidate for the tetrahedric phase or not, two steps seem to be important. First, the nature of the ordering in the B7 phase must be identified, in particular with respect to the existence of a macroscopic polarization \mathbf{P} . And second, it would be crucial to investigate in detail the behavior of the isotropic phase above the B7 phase under external electric fields and temperature gradients in the absence of the B7 phase.

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. H.R. Brand, P.E. Cladis and H. Pleiner, *Macromolecules* **25**, 7223 (1992).
2. P.E. Cladis and H.R. Brand, *Liq. Cryst.* **14**, 1327 (1993).
3. T. Niori, T. Sekine, J. Watanabe, T. Furukawa, H. Takezoe, *J. Mat. Chem.* **6**, 1231 (1996).
4. T. Sekine, T. Niori, J. Watanabe, T. Furukawa, S.W. Choi, H. Takezoe, *J. Mat. Chem.* **7**, 1307 (1997).
5. D.R. Link, G. Natale, R. Shao, J.E. McLennan, N.A. Clark, E. Körblova, D.M. Walba, *Science* **278**, 1924 (1997).
6. H.R. Brand, P.E. Cladis and H. Pleiner, *Eur. Phys. J. B* **6**, 347 (1998).
7. R. Macdonald, F. Kentischer, P. Warnick, and G. Heppke, *Phys. Rev. Lett.* **81**, 4408 (1998).
8. D. Shen, S. Diele, I. Wirth, and C. Tschierske, *Chem. Commun.* **1998**, 2573 (1998).
9. G. Pelzl, S. Diele and W. Weissflog, *Adv. Mat.* **11**, 707 (1999).
10. P.E. Cladis, H.R. Brand and H. Pleiner, *Liquid Crystals Today* **9** (3/4), 1 (1999).
11. H.R. Brand, P.E. Cladis and H. Pleiner *Int. J. Eng. Sci.* **38**, 1099 (2000).
12. P.E. Cladis, H. Pleiner and H.R. Brand, *Ferroelectrics* **243**, 221 (2000).
13. H. Pleiner, H.R. Brand and P.E. Cladis, *Ferroelectrics* **243**, 291 (2000).
14. G. Pelzl, S. Diele, S. Grande, A. Jakli, Ch. Lischka, H. Kresse, H. Schmalfuss, I. Wirth and W. Weissflog, *Liq. Cryst.* **26**, 401 (1999).
15. Y. Yusuf, Y. Hidaka, S. Kai, H.R. Brand, P.E. Cladis, W. Weissflog and G. Pelzl, to be published.
16. L.G. Fel, *Phys. Rev. E* **52**, 702 (1995).
17. L. Radzihovsky and T.C. Lubensky, *Europhys. Lett.* **54**, 206 (2001).
18. Throughout the present manuscript we focus on the nonchiral tetrahedric phase, T_d [16]. We note, however, that our analysis is also useful for the blue phase version of its chiral analogue, the T phase [16].
19. P. C. Martin, O. Parodi and P.S. Pershan, *Phys. Rev.* **A6**, 2401 (1972).
20. D. Forster, *Hydrodynamic Fluctuations, Broken Symmetry and Correlation Functions* (Benjamin, Reading, Mass. 1975).
21. 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.
22. L.D. Landau and E.M. Lifshitz, *Hydrodynamics* (Pergamon, London, England, 1959).
23. L.G. Fel, *Mol. Cryst. Liq. Cryst.* **206**, 1 (1991).
24. P.G. de Gennes, *Mol. Cryst. Liq. Cryst.* **12**, 191 (1971).
25. P.G. de Gennes, *The Physics of Liquid Crystals* (Clarendon Press, Oxford, 1975).
26. P.K. Mukherjee, H.R. Brand and H. Pleiner, *Eur. Phys. J. E* **4**, 293 (2001).
27. H. Zimmermann, R. Poupko, Z. Luz and J. Billard, *Z. Naturf. A* **40**, 149 (1985); **41**, 1137 (1986).