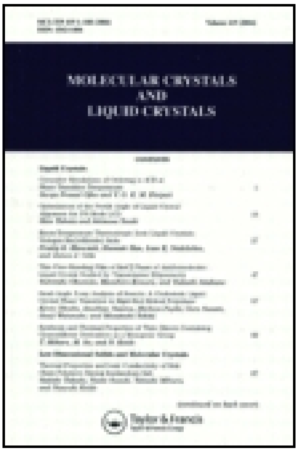

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A Simplified Thermodynamic Theory for Biaxial Nematics Using Gyarmati's Principle

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A SIMPLIFIED THERMODYNAMIC THEORY FOR BIAXIAL NEMATICS USING GYARMATI' S PRINCIPLE

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Abstract Gyarmati's variational principle of thermodynamics is used to derive the equilibrium conditions as well as the equations of motion for biaxial nematic liquid crystals. From the equations of motion the nonequilibrium stress tensor is derived. The resulting equations are much easier than in the case of uniaxial nematics. This is probably a consequence of the fact that the state space can be chosen in such a way that no constraints for the generalized directors and their gradients have to be taken into account.

Keywords: biaxial nematics, thermodynamic theory

INTRODUCTION

Recently a biaxial nematic phase has been found in a mixture[1] as well as in a pure system[2]. The continuum theory of uniaxial nematics with a director of unit length has been developed by Oseen, Frank, Ericksen and Leslie. The present work is a generalisation to biaxial nematics of an earlier publication[3] in which Gyarmati's variational principle[4] has been applied to uniaxial nematics. This variational principle exploits the second law of thermodynamics in the form of the dissipation inequality. It yields the constitutive equations and the equations of motion. The fact is used that the entropy production is the sum of products of fluxes and forces. If the fluxes depend linearly on the forces the Irreversible Thermodynamics established by Onsager is obtained. In an equivalent approach the forces depend linearly on the fluxes. Both forms of the Onsager Theory are included in the universal form of Gyarmati's principle, but Gyarmati's Governing Principle of Thermodynamics[6] is not restricted to the case of linear constitutive relations. In this sense it is a generalisation of the Onsager Theory.

This technique has not yet been applied to biaxial liquid crystals. Part of the literature[7,8] is a generalisation of the Ericksen Leslie theory which is an application of the Coleman Noll technique[11] to exploit the dissipation inequality. Saupe[9] on the other hand restricts himself in the first part of his work to thermostatics using the minimum principle for the free energy. To describe viscous flow he introduces the dissipation function which is a quadratic function of the time derivatives of the variables that occur in the free energy. This Irreversible Thermodynamics approach has been applied also by Govers and Vertogen[10].

It should be noted that in the case of uniaxial nematics the relaxation times for a distorted director field in a cell with strong anchoring at the parallel walls determined from Gyarmati' s principle tends to a finite value for very thin layers, whereas the Ericksen Leslie theory lead to vanishing relaxation times with vanishing cell thickness. This comparison would be interesting for biaxial nematics too, but the discussion of solutions for the director field in special exemples must remain for a future work.

THE CHOICE OF THE RELEVANT VARIABLES

To handle the derivatives of the constitutive functions it is necessary to chose the relevant variables, on which the constitutive functions may depend. In the case of an incompressible biaxial liquid crystal the state space includes in addition to the internal energy u, the velocity $\underline{v}$, the gradient of the velocity $\nabla\underline{v}$ and the specific polarisation $\underline{P}$ some other variables connected with the orientational order. There is a distibution of molecular orientations associated with every volume element. We consider only rigid rotations of this orientational distribution function which can be approximated by the alignmenttensor $\underline{\underline{a}}$. We neglect changes of the degree of order. In this case the eigenvalues of the alignmenttensor are constant and the eigenvectors $\underline{l}$, $\underline{m}$ and $\underline{n}$ can be taken as the additional variables. With this choice of variables we have to take into account the constraints

$$\underline{m}\cdot\underline{m} \equiv 1,\quad \underline{n}\cdot\underline{n} \equiv 1,\quad \underline{l}\cdot\underline{l} \equiv 1,\quad \underline{m}\cdot\underline{n} \equiv 0,\quad \underline{m}\cdot\underline{l} \equiv 0,\quad \underline{n}\cdot\underline{l} \equiv 0 \qquad (2.1)$$

$\underline{m}$, $\underline{n}$ and $\underline{l}$ will be called directors in analogy to the theory of uniaxial nematic liquid crystals. Instead of three vectors with six constraints it is more convenient to use the orientational configuration map $\underline{\underline{Q}}$ as an element of the state space. $\underline{\underline{Q}}$ is defined by the equation

$$\underline{\underline{a}}(\underline{r}) = \underline{\underline{Q}}(\underline{r}, \underline{r}^0)\cdot\underline{\underline{a}}(\underline{r}^0)\cdot\underline{\underline{Q}}^T(\underline{r}, \underline{r}^0) \qquad (2.2)$$

where $\underline{\underline{a}}(\underline{r}^0)$ is the alignmenttensor at some reference point $\underline{r}^0$. The gradient of $\underline{\underline{Q}}$ is a relevant variable describing the inhomogeneity of the orientation. We define

$$\underline{G}_i := \underline{w}\left(\frac{\partial \underline{\underline{Q}}}{\partial x_i}\cdot\underline{\underline{Q}}^T\right) \quad (i = x, y, z) \quad , \qquad \underline{\underline{G}} := (\underline{G}_x, \underline{G}_y, \underline{G}_z) \, , \qquad (2.3)$$

where $\underline{w}(\underline{\underline{F}})$ is the vector invariant of $\underline{\underline{F}}$. In summary the relevant variables are $\mathcal{Z}$ or equivalently $\mathcal{Z}'$ with the constraints (2.1):

$$\mathcal{Z} = (u, \underline{v}, \nabla\underline{v}, \underline{P}, \underline{\underline{Q}}, \underline{\underline{G}}) \qquad \mathcal{Z}' = (u, \underline{v}, \nabla\underline{v}, \underline{P}, \underline{l}, \underline{m}, \underline{n}, \nabla\underline{l}, \nabla\underline{m}, \nabla\underline{n}) \qquad (2.4)$$

Note that not the electric field but the polarisation has been chosen as the variable. This corresponds to an experiment, where the charge on a condenser is changed keeping the voltage constant.

For the gradients of the directors, the relations

$$\nabla\underline{l} = -\,\underline{l}\times\underline{\underline{G}}, \qquad \nabla\underline{m} = -\,\underline{m}\times\underline{\underline{G}}, \qquad \nabla\underline{n} = -\,\underline{n}\times\underline{\underline{G}} \qquad (2.5)$$

hold.

BALANCE EQUATIONS

The conservation laws of mass and momentum are the same as for a simple fluid. The balance equation of angular momentum has the form ($\underline{\underline{t}}$: stress tensor, $\underline{f}$: force density exerted by external fields, $\underline{r}$: position vector, $\underline{\underline{\Pi}}$: couple stress tensor, $\underline{c}$: couple density, $\underline{S}$: spin density, ρ: mass density):

$$\rho \frac{d}{dt} (\underline{r} \times \underline{v} + \underline{S}) = \nabla\cdot(\underline{r} \times \underline{\underline{t}} + \underline{\underline{\Pi}}) + \rho\, \underline{r} \times \underline{f} + \rho\, \underline{c} \tag{3.1}$$

or with the balance of momentum

$$2\, \underline{w}(\underline{\underline{t}}) + \nabla\cdot\underline{\underline{\Pi}} + \rho\, \underline{c} = \frac{d\underline{S}}{dt} \tag{3.2}$$

and the balance equation for the internal energy reads[5] ($\underline{J}_q$: heat current, $\underline{E}$: electric field)

$$\rho \frac{du}{dt} + \nabla\cdot\underline{J}_q = \underline{\underline{t}} : \overset{o}{\underline{\underline{d}}} + \nabla\cdot(\underline{\Omega}'\cdot\underline{\underline{\Pi}}) + \underline{\underline{\Pi}} : \nabla\underline{\omega} + \rho\, \underline{E}\cdot\overset{o}{\underline{P}} \tag{3.3}$$

where the notations

$$\overset{o}{\underline{\underline{d}}} = \frac{1}{2}\left[\nabla\underline{v} + (\nabla\underline{v})^T\right], \quad \underline{\omega} = \frac{1}{2}\nabla\times\underline{v}, \quad \underline{\Omega}' = \underline{\Omega} - \underline{\omega}, \quad \overset{o}{\underline{P}} = \frac{d\underline{P}}{dt} - \underline{\omega}\times\underline{P} \tag{3.4}$$

have been introduced and the couple density is regarded to be exerted by the electric field alone:

$$\underline{c} = \underline{P} \times \underline{E} \tag{3.5}$$

The angular velocity $\underline{\Omega}$ has been defined so that

$$\frac{d\underline{l}}{dt} = \underline{\Omega}\times\underline{l}, \quad \frac{d\underline{m}}{dt} = \underline{\Omega}\times\underline{m}, \quad \frac{d\underline{n}}{dt} = \underline{\Omega}\times\underline{n} \tag{3.6}$$

which is possible with one vector $\underline{\Omega}$, because we consider only rigid rotations of the orientational distribution function. The vector $\underline{\Omega}'$ is the angular velocity in a cartesian frame corotating with the body and $\overset{o}{\underline{\underline{d}}}$ and $\overset{o}{\underline{P}}$ are the time derivatives of $\underline{\underline{d}}$ and $\underline{P}$ in this frame. The time derivatives of the directors and of the orientational configuration map in this frame are

$$\overset{o}{\underline{l}} = \underline{\Omega}'\times\underline{l}, \quad \overset{o}{\underline{m}} = \underline{\Omega}'\times\underline{m}, \quad \overset{o}{\underline{n}} = \underline{\Omega}'\times\underline{n}, \quad \overset{o}{\underline{\underline{Q}}} = \underline{\Omega}'\times\underline{\underline{Q}} \tag{3.7}$$

The corotational time derivatives and $\underline{\Omega}'$ are objective quantities.

The second law of thermodynamics is expressed in the dissipation inequality

$$\rho \frac{ds}{dt} + \nabla\cdot\underline{J}_s = \sigma_s \geq 0 \tag{3.8}$$

where s is the entropy density, $\underline{J}_s$ is the entropy current and σ_s is the entropy production. We assume the validity of the relations

$$\underline{J}_s = \frac{1}{T}\underline{J}_q \, , \qquad \frac{\partial s}{\partial u} = \frac{1}{T}. \tag{3.9}$$

The time derivative of the entropy has the form

$$\frac{ds}{dt} = \frac{1}{T}\frac{du}{dt} + \frac{\partial s}{\partial \underline{\underline{Q}}} : \mathring{\underline{\underline{Q}}} + \frac{\partial s}{\partial \underline{\underline{G}}} : \mathring{\underline{\underline{G}}} + \frac{\partial s}{\partial \underline{P}} \cdot \mathring{\underline{P}} \;. \tag{3.10}$$

It has been used, that by the principle of objectivity the velocity appears only in the corotating time derivatives, moreover, that the entropy does not depend on the deformation rate in a local equilibrium situation. Substituting (3.10), (3.9) and (3.3) into the dissipation inequality (3.10) results in

$$T\sigma_s = \underline{\underline{t}} : \mathring{\underline{\underline{d}}} + \nabla\cdot(\underline{\Omega}'\cdot\underline{\underline{\Pi}}) + \underline{\underline{\Pi}}:(\nabla\underline{\omega}) + \rho T\frac{\partial s}{\partial \underline{\underline{Q}}} : \mathring{\underline{\underline{Q}}} + \rho T\frac{\partial s}{\partial \underline{\underline{G}}} : \mathring{\underline{\underline{G}}} + \left(\rho T\frac{\partial s}{\partial \underline{P}} + \rho\underline{E}\right)\cdot\mathring{\underline{P}} \tag{3.11}$$

After some manipulations[5] we get

$$T\sigma_s = \underline{\Omega}'\cdot\left\{2\,\underline{w}\left[\rho T\left(\frac{\partial s}{\partial \underline{\underline{Q}}}\cdot\underline{\underline{Q}}^T\right) - \underline{\underline{\Pi}}\cdot\underline{\underline{G}}^T\right] + \nabla\cdot\underline{\underline{\Pi}}\right\} + \mathring{\underline{\underline{G}}}:\left\{\underline{\underline{\Pi}} + \rho T\frac{\partial s}{\partial \underline{\underline{G}}}\right\} +$$
$$+\, \mathring{\underline{\underline{d}}}:\left\{\underline{\underline{t}} + \underline{\underline{G}}^T\cdot\underline{\underline{\Pi}}\right\} + \mathring{\underline{P}}\cdot\left\{\rho T\frac{\partial s}{\partial \underline{P}} + \rho\underline{E}\right\} \geq 0 \tag{3.12}$$

THE EQUILIBRIUM CONDITIONS

In equilibrium the objective rates of processes $\underline{\Omega}'$, $\mathring{\underline{\underline{G}}}$, $\mathring{\underline{\underline{d}}}$ and $\mathring{\underline{P}}$ vanish. As we have shown that the energy dissipation function (3.12) is linear in these fluxes the equilibrium conditions are, that the corresponding forces are equal to zero. The only constraint to be taken into accout is that $\overset{\circ}{\underline{d}}$ is a symmetric traceless tensor as we consider only volume preserving motions. p and an antisymmetric tensor $\underline{A}$ are the corresponding Lagrange multipliers, which have to be eliminated from the resulting equilibrium conditions. These resulting equations are

$$2\underline{w}\left[\rho T\frac{\partial s}{\partial \mathbf{Q}}\cdot\underline{Q}^{T}-\underline{\Pi}\cdot\underline{G}^{T}\right]+\nabla\cdot\underline{\Pi}=0 \tag{4.1}$$

$$\underline{\Pi}+\rho T\frac{\partial s}{\partial \underline{\underline{G}}}=0 \tag{4.2}$$

$$\underline{t}+\underline{G}^{T}\cdot\underline{\Pi}+p\underline{\delta}+\underline{A}=0 \tag{4.3}$$

$$T\frac{\partial s}{\partial \underline{P}}+\underline{E}=0 \tag{4.4}$$

The term $\underline{G}^{T}\cdot\underline{\Pi}$ in equation (4.3) has no analogon in the case of uniaxial nematics. When an expression for the entropy as a function of the relevant variables taking into account the symmetry of the phase is given[5], the derivative $\frac{\partial s}{\partial \underline{P}}$ can be calculated. Equation (4.4) then gives the relation between the electric field and the polarization, which is the usual one if the entropy is quadratic in the polarization. The equation (4.2) is rather explicit for the couple stress. To determine the equilibrium stress, we combine equations (4.1) and (4.2) moreover equations (3.2), (3.5) and (4.4) and we make use of the fact that the entropy is an objective quantity. In the balance of angular momentum it is used that in equilibrium $d\underline{S}/dt = 0$. We get[5]

$$\underline{t}=p\underline{\delta}+\rho T\underline{G}^{T}\cdot\frac{\partial s}{\partial \underline{\underline{G}}} \tag{4.5}$$

Making an explicit ansatz for s as a function of $\underline{G}$ and $\underline{P}$ one has 15 independent elastic terms (quadratic in $\underline{G}$) and 3 terms proportional to $\underline{P}^{2}$, i. e. 18 independent terms contribute to the traceless part of the stress tensor[5]. The number of these terms is given by the symmetry and is therefore the same as in other publications[8].

THE MOTION OF BIAXIAL NEMATIC LIQUID CRYSTALS

The variational principle worked out by Gyarmati[4] in the flux representation is used to derive the equations of motion. The dissipation potential φ is a homogeneous quadratic function of the fluxes and the derivatives of φ with respect to the fluxes are equal to the generalized forces. In our case the dissipation function depends on the fluxes $\underline{\Omega}'$, $\underline{\underline{\mathring{G}}}$, $\underline{\underline{\mathring{d}}}$ and $\underline{\mathring{P}}$ and contains the local state variables u, $\underline{P}$, $\underline{\underline{G}}$ and $\underline{\underline{Q}}$ as parameters. We suppose that the dielectric losses are neglegible, i. e. the equation (4.4) holds also for dissipative processes. In this way φ does not depend on $\underline{\mathring{P}}$. Moreover, we suppose that the angular distorsion and its time derivative are small enough to be neglected in the dissipation potential. This could be wrong even in equilibrium for very thin samples, where the boundaries induce a non neglegable distorsion. It would also be wrong for chiral molecules. On the other hand in the case of uniaxial nematics the same simplification leads to the Ericksen Leslie Parodi theory. In this way the function we are looking for is of the form $\varphi(\underline{\Omega}', \underline{\underline{\mathring{d}}}, \underline{\underline{Q}})$. Making use of the principle of objectivity we conclude that φ is of the form

$$\varphi = \frac{1}{2}\,(\underline{\underline{Q}}^{T}\cdot\underline{\Omega}')\cdot\underline{\underline{R}}^{\Omega\Omega}\cdot(\underline{\underline{Q}}^{T}\cdot\underline{\Omega}') + (\underline{\underline{Q}}^{T}\cdot\underline{\Omega}')\cdot\underline{\underline{\underline{R}}}^{\Omega d}:(\underline{\underline{Q}}^{T}\cdot\underline{\underline{\mathring{d}}}\cdot\underline{\underline{Q}}) +$$

$$+ \frac{1}{2}\,(\underline{\underline{Q}}^{T}\cdot\underline{\underline{\mathring{d}}}\cdot\underline{\underline{Q}}):\underline{\underline{\underline{\underline{R}}}}^{dd}:(\underline{\underline{Q}}^{T}\cdot\underline{\underline{\mathring{d}}}\cdot\underline{\underline{Q}}) \tag{5.3}$$

An explicit ansatz for the dissipation potential taking into account the symmetry has 15 independent viscosity coefficients, which is the same number as found by Saupe[5] or Govers and Vertogen[10]. These coefficients have to fulfill some inequalities resulting from the second law.

The equations of motion are obtained from a partial form (flux representation) of Gyarmati's local variational principle, which says that $L^{*} = T\sigma_{s} - \varphi$ is maximal if the fluxes belong to real processes.[4] Applying the variational principle the constraint conditions have to be kept in mind. The auxiliary function of the variational problem is of the form

$$L^{*} = t\sigma_{s} - \varphi + (p\underline{\underline{\delta}} + \underline{\underline{A}}):\underline{\underline{\mathring{d}}}\ , \tag{5.4}$$

symmetric parts of the viscous stress tensor. It is very interesting that the structure of the equations is more transparent than in the theory of uniaxial liquid crystals[3]. It may be due to the fact, that neither the direction of the angular velocity of the directors nor the couple stress tensor are restricted. In the light of the present theory, it seems worth reformulating the thermodynamic theory of uniaxial liquid crystals.

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First of all notice that neither the components of $\overset{\circ}{\underline{P}}$ nor $\overset{\circ}{\underline{\underline{G}}}$ enter the dissipation potential, consequently, the derivatives of the Lagrangian L^* with respect to them exhibit the same equations as in equilibrium, i. e. equations (4.2) and (4.4) remain valid for nonequilibrium situations. Making use of these we can reduce the actual form of the dissipation function. Combining equations (3.2), (3.5) and (4.4) so as it was done in the case of equilibrium we arrive at

$$T\sigma_s = -2\,\underline{\Omega}'\cdot\left\{\underline{w}\left[\underline{\underline{t}} - \rho T\underline{\underline{G}}^T\cdot\frac{\partial s}{\partial \underline{\underline{G}}}\right] - \rho\frac{d\underline{S}}{dt}\right\} + \overset{\circ}{\underline{\underline{d}}}:\left[\underline{\underline{t}} - \rho T\underline{\underline{G}}^T\cdot\frac{\partial s}{\partial \underline{\underline{G}}}\right]. \tag{5.5}$$

This form of the energy dissipation function shows that it is useful to introduce the viscous stress tensor by

$$\underline{\underline{t}} =: \rho T\underline{\underline{G}}^T\cdot\frac{\partial s}{\partial \underline{\underline{G}}} + \underline{\underline{t}}^{vs} + \underline{t}^{va}\times\underline{\underline{\delta}}, \tag{5.6}$$

where $\underline{\underline{t}}^{vs}$ is a symmetric second order tensor and $\underline{t}^{va}$ is an axial vector. We assume here, that the relaxation of the spin is so fast, that for experimentally observable times the spin balance can be assumed to be stationary, i. e. $d\underline{s}/dt = 0$. In a more general consideration the time derivative of the spin can be taken into account[5].

The constitutive equations are determined as (without summation convention)

$$t_i^{va} = -\frac{1}{2}R_{ii}^{\Omega\Omega}\Omega'_i - R_{ilm}^{\Omega d}\overset{\circ}{d}_{lm} \qquad i,\ l,\ m \in \{1,\ 2,\ 3\} \tag{5.7}$$

ilm a cyclic permutation of 123

$$t_{ii}^{vs} + p = R_{iiii}^{dd}\overset{\circ}{d}_{ii} \qquad i \in \{1,\ 2,\ 3\} \tag{5.8}$$

$$t_{il}^{vs} = R_{mil}^{\Omega d}\Omega'_m + 2\,R_{ilil}^{dd}\overset{\circ}{d}_{il} \qquad i,\ l,\ m \in \{1,\ 2,\ 3\} \tag{5.9}$$

ilm a cyclic permutation of 123

The Lagrange multiplier $\underline{\underline{A}}$ appearing first in the equations for the antisymmetric part of the viscous stress tensor has turned out to be zero as all the other terms in the equations are symmetric. The above equations completely determine the traceless part of the viscous stress tensor. The scalar multiplicator p i. e. the scalar pressure can be determined during the integration of the equations. It can be seen that both the deformation rate $\overset{\circ}{\underline{\underline{d}}}$ and the rotation of the directors have influence on the symmetric and on the anti-