A Simplified Thermodynamic Theory for Biaxial Nematics

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Z. Naturforsch. **50a,** 795–804 (1995); received June 3, 1994

A continuum theory of a biaxial nematic phase in liquid crystals is presented. The liquid crystalline ordering is described by a field of three unit vectors. Because these are macroscopic directors, the present approach is a generalization of the Ericksen-Leslie theory to biaxial nematics. The applied tools from nonequilibrium thermodynamics are classical Linear Irreversible Thermodynamics and Gyarmati's variational principle.

Key words: Liquid crystals; biaxial nematics; Linear Irreversible Thermodynamics; Onsager reciprocity relations; Gyarmati's variational principle.

1. Introduction

It is known since a long time, that in certain materials a uniaxial nematic phase exits at temperatures below the clearing point. At higher temperatures the material is an isotropic liquid. All liquid crystalline phases exhibit no long range positional order in three dimensions, in contrast to the crystalline phase. They are distinguished from the isotropic phase by the fact that there is long range order of molecular orientations. At lower temperatures there may exist smectic liquid crystalline phases, which exhibit a one dimensional periodicity of the mass density.

Liquid crystals consist of formanisotropic molecules. If the effective molecular shape is uniaxial, the particle orientation can be described by the orientation of one axis, the microscopic director (see Figure 1). The different molecular orientations give rise to an orientation distribution function, defined on the unit sphere S^2. This distribution function can be uniaxial or biaxial (see Figure 1), i.e. there may exist a symmetry axis of rotation for the orientation distribution function or not. In both cases the distribution function can be expanded in terms of cartesian tensors [1]. Because of the head-tail symmetry of the molecules the orientation distribution function is symmetric under inversion. Consequently odd order tensors do not enter into the expansion. The first anisotropic moment of the orientation distribution function is the second order alignment tensors **a**, a symmetric traceless tensor. In the case of uniaxial symmetry of the orientation distribution function the alignment tensor has two equal eigenvalues and can be written as

$$\mathbf{a} = a(\boldsymbol{n}\boldsymbol{n} - 1/3\,\boldsymbol{\delta}). \tag{1.1}$$

The vector $\boldsymbol{n}$ is called macroscopic director and a is the scalar order parameter. If the orientation distribution function is uniaxial, the macroscopic director is given by the symmetry axis of the orientation distribution function.

In most cases the nematic phase is observed to be uniaxial (i.e. the orientation distribution function is uniaxial). The possibility of a biaxial nematic phase has been predicted more than twenty years ago [2], [3]. Later a biaxial nematic phase has been found in a mixture [4] as well as in a pure system [5]. The present paper is concerned with the theoretical description of such biaxial nematic phases. The deviation of the molecular shape from rotation symmetry will not be taken into account, because the orientation of biaxial particles cannot be described by a single unit vector (the microscopic director). Rotation matrices are needed, or equivalently unit vectors in four dimensional space [6]. This will not be done here.

If the phase is biaxial, the second order alignment tensor does not have the simple form of (1.1), but three eigenvalues are different. The corresponding eigenvectors will be denoted by $\boldsymbol{n}$, $\boldsymbol{l}$ and $\boldsymbol{m}$.

The continuum theory of uniaxial nematics with a (macroscopic) director of unit length has been developed by Oseen [7], Franck [8], Ericksen [9] and Leslie [10]. The Ericksen-Leslie-approach has been applied

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0932-0784 / 95 / 0900-0795 $ 06.00 © – Verlag der Zeitschrift für Naturforschung, D-72027 Tübingen

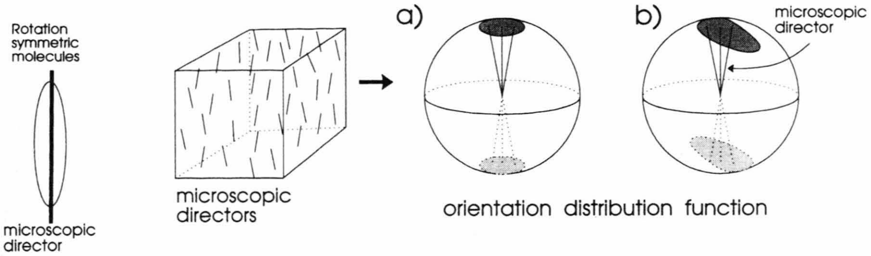

Fig. 1. The orientation of rotation symmetrical molecules is described by a microscopic director. The microscopic directors in an volume element give rise to an orientation distribution function which can be a) uniaxial or b) biaxial.

to biaxial nematics too [11], yielding the differential equations governing elastic and flow behaviour. The constitutive equations derived using the Ericksen-Leslie-theory have been compared with the theory developed by Saupe [12]. In [13], the linearized hydrodynamic equations have been used to predict the attenuation of low frequency sound waves. The hydrodynamics of biaxial nematics in an external magnetic field have been treated in [14] in terms of thermodynamical forces and fluxes. In a recent work [15] the phenomenological theory of the viscosity of biaxial liquid crystals has been developed, and experimental geometries which allow the different coefficients to be measured have been discussed. The linear combinations of the viscosity coefficients which should be accessible to experiments, have also been discussed in [15]. The particles are described as ellipsoids. By the affine transformation model all viscosity coefficients are expressed in terms of the two viscosities of an isotropic reference system and the axis ratios of the particles. Applying the theory to the problem of flow alignment, the alignment angle has been expressed in terms of the axis ratio of the ellipsoidal particles. All these aproaches, including the presented here, cannot describe variations of the degree of order in the liquid crystal.

The present work is a generalisation to biaxial nematics of an earlier publication [16] on uniaxial nematic liquid crystals. Gyarmati's variational principle [17] is applied to deduce the equations of equilibrium as well as those of motion. The hypothesis of local equilibrium is accepted. For the methods of linear Onsager theory the book of the De Groot and Mazur [18] is referred to.

2. The Choice of the Relevant Variables and the Entropy of Biaxial Nematic Liquid Crystals

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 a biaxial liquid crystal the state space includes in addition to the internal energy u, the velocity $\boldsymbol{v}$, the gradient of the velocity $\nabla \boldsymbol{v}$ and the specific polarisation $\boldsymbol{P}$ some other variables connected with the alignment tensor of second order $\mathbf{a}$. We consider only rigid rotations of the orientational distribution function mentioned in the introduction. In this case the eigenvalues of the alignment tensor are constant and the eigenvectors $\boldsymbol{l}$, $\boldsymbol{m}$ and $\boldsymbol{n}$ can be taken as additional variables. With this choice of variables we have to take into account the constraints

$$\begin{aligned} \boldsymbol{m}\cdot\boldsymbol{m} &\equiv 1, \quad \boldsymbol{n}\cdot\boldsymbol{n} \equiv 1, \quad \boldsymbol{l}\cdot\boldsymbol{l} \equiv 1, \\ \boldsymbol{m}\cdot\boldsymbol{n} &\equiv 0, \quad \boldsymbol{m}\cdot\boldsymbol{l} \equiv 0, \quad \boldsymbol{n}\cdot\boldsymbol{l} \equiv 0. \end{aligned} \tag{2.1}$$

$\boldsymbol{m}$, $\boldsymbol{n}$, and $\boldsymbol{l}$ 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 a 3×3-matrix $\mathbf{Q}$ as an element of the state space. The orthogonal mapping $\mathbf{Q}$ is defined by the equation

$$\mathbf{a}(\boldsymbol{r}) = \mathbf{Q}(\boldsymbol{r}, \boldsymbol{r}^O)\cdot\mathbf{a}(\boldsymbol{r}^O)\cdot\mathbf{Q}^{\mathrm{T}}(\boldsymbol{r}, \boldsymbol{r}^O), \tag{2.2}$$

where $\mathbf{a}(\boldsymbol{r}^O)$ is the alignment tensor at some reference point $\boldsymbol{r}^O$. If the the coordinate system in the reference point is chosen such that the eigenvectors $\boldsymbol{l}(\boldsymbol{r}^O)$, $\boldsymbol{m}(\boldsymbol{r}^O)$ and $\boldsymbol{n}(\boldsymbol{r}^O)$ are along the x-, y- and z-axis, the rows of the matrix $\mathbf{Q}(\boldsymbol{r}, \boldsymbol{r}^O)$ are the eigenvectors $\boldsymbol{l}(\boldsymbol{r})$, $\boldsymbol{m}(\boldsymbol{r})$ and $\boldsymbol{n}(\boldsymbol{r})$ at the point $\boldsymbol{r}$ with the coordinates x_i, $i=1, 2, 3$.

The gradient of $\mathbf{Q}$ is a relevant variable, too, describing the inhomogeneity of the orientation. We define

$$\boldsymbol{O}_i := \boldsymbol{w}\left(\frac{\partial \mathbf{Q}}{\partial x_i} \cdot \mathbf{Q}^{\mathrm{T}}\right), \quad i = 1, 2, 3 \tag{2.3}$$

and the angular distortion mapping

$$\mathbf{O} := (\boldsymbol{O}_1\, \boldsymbol{O}_2\, \boldsymbol{O}_3). \tag{2.4}$$

The vector invariant $\boldsymbol{w}(\mathbf{F})$ of a tensor $\mathbf{F}$ occuring in (2.3) is defined by

$$\frac{1}{2}(\mathbf{F} - \mathbf{F}^{\mathrm{T}}) =: \boldsymbol{w}(\mathbf{F}) \times \boldsymbol{\delta} \leftrightarrow \frac{1}{2}(F_{kl} - F_{lk}) =: \varepsilon_{kjl}\, w_j, \tag{2.5}$$

where $\mathbf{F}^{\mathrm{T}}$ denotes the transposed of $\mathbf{F}$. The above definition (2.3), cast into rectangular components, reads

$$O_{ik} = -\frac{1}{2}\varepsilon_{irl}\frac{\partial Q_{rs}}{\partial x_k} Q_{ls}, \tag{2.6}$$

where ε_{irl} stands for the components of the total antisymmetric tensor of third order. From here the relation

$$\frac{\partial Q_{ij}}{\partial x_k} = \varepsilon_{isr} O_{sk} Q_{rj} \tag{2.7}$$

follows for the cartesian components of the gradient of $\mathbf{Q}$ (see Appendix C).

Finally, the relevant variables are

$$Z = (u, \boldsymbol{v}, \nabla \boldsymbol{v}, \boldsymbol{P}, \mathbf{Q}, \mathbf{O}) \tag{2.8}$$

or equivalently

$$Z' = (u, \boldsymbol{v}, \nabla \boldsymbol{v}, \boldsymbol{P}, \boldsymbol{l}, \boldsymbol{m}, \boldsymbol{n}, \nabla \boldsymbol{l}, \nabla \boldsymbol{m}, \nabla \boldsymbol{n}) \tag{2.9}$$

with the constraints (2.1). For the gradients of the directors, the relations

$$\nabla \boldsymbol{l} = -\boldsymbol{l} \times \mathbf{O}, \quad \nabla \boldsymbol{m} = -\boldsymbol{m} \times \mathbf{O}, \quad \nabla \boldsymbol{n} = -\boldsymbol{n} \times \mathbf{O} \tag{2.10}$$

hold.

The requirement that the form of the constitutive equations should be independent of the motion of the observer is expressed in the principle of objectivity. Mathematically it means that a constitutive quantity transforms like a tensor under Galilei-transformations [19]. For the scalar entropy this reads

$$\begin{aligned} &s(u, \boldsymbol{v}, \nabla \boldsymbol{v}, \boldsymbol{P}, \mathbf{Q}, \mathbf{O}) \\ &= s(u, \mathbf{R} \cdot \boldsymbol{v}, \mathbf{R} \cdot \nabla \boldsymbol{v} \cdot \mathbf{R}^{\mathrm{T}}, \mathbf{R} \cdot \boldsymbol{P}, \mathbf{R} \cdot \mathbf{O}, \mathbf{R} \cdot \mathbf{O} \cdot \mathbf{R}^{\mathrm{T}}) \end{aligned} \tag{2.11}$$

with any orthogonal tensor $\mathbf{R}$. In addition, the form of the constitutive equations is restricted by the material symmetry. For the biaxial nematic liquid crystal the three directors have the mirror symmetry for the three planes perpendicular to the directors $\boldsymbol{l}$, $\boldsymbol{m}$, and $\boldsymbol{n}$, respectively:

$$\boldsymbol{l} \to -\boldsymbol{l}, \ \boldsymbol{m} \to -\boldsymbol{m}, \ \boldsymbol{n} \to -\boldsymbol{n} \tag{2.12}$$

are symmetry operations. If we use a cartesian frame with the axes in the direction of the directors, the transformations read

$$\begin{aligned} &x_1 \to -x_1, \ x_2 \to x_2, \ x_3 \to x_3, \\ &x_1 \to x_1, \ x_2 \to -x_2, \ x_3 \to x_3, \\ &x_1 \to x_1, \ x_2 \to x_2, \ x_3 \to -x_3. \end{aligned} \tag{2.13}$$

For the cholesteric phase of a chiral biaxial liquid crystal the material symmetry is lowered to the 180° rotations around the three directors:

$$\begin{aligned} &x_1 \to -x_1, \ x_2 \to x_2, \ x_3 \to -x_3, \\ &x_1 \to -x_1, \ x_2 \to -x_2, \ x_3 \to x_3, \\ &x_1 \to x_1, \ x_2 \to -x_2, \ x_3 \to -x_3. \end{aligned} \tag{2.14}$$

One of the most important constitutive equations is the one for the entropy. Following Oseen [7] and Frank [5], the entropy is approximated by a quadratic polynomial of the components of the angular distortion mapping $\mathbf{O}$ and the polarisation $\boldsymbol{P}$, which is invariant under the symmetry operations (2.13):

$$\begin{aligned} s = s_0 &- \tfrac{1}{2} s^{\mathrm{oo}}_{1111} O_{ll} O_{ll} - \tfrac{1}{2} s^{\mathrm{oo}}_{2222} O_{mm} O_{mm} \\ &- \tfrac{1}{2} s^{\mathrm{oo}}_{3333} O_{nn} O_{nn} - \tfrac{1}{2} s^{\mathrm{oo}}_{1122} O_{ll} O_{mm} \\ &- \tfrac{1}{2} s^{\mathrm{oo}}_{1133} O_{ll} O_{nn} - \tfrac{1}{2} s^{\mathrm{oo}}_{2233} O_{mm} O_{nn} \\ &- \tfrac{1}{2} s^{\mathrm{oo}}_{1212} O_{lm} O_{lm} - \tfrac{1}{2} s^{\mathrm{oo}}_{1221} O_{lm} O_{ml} \\ &- \tfrac{1}{2} s^{\mathrm{oo}}_{2121} O_{ml} O_{ml} - \tfrac{1}{2} s^{\mathrm{oo}}_{1313} O_{ln} O_{ln} \\ &- \tfrac{1}{2} s^{\mathrm{oo}}_{1331} O_{ln} O_{nl} - \tfrac{1}{2} s^{\mathrm{oo}}_{3131} O_{nl} O_{nl} \\ &- \tfrac{1}{2} s^{\mathrm{oo}}_{2323} O_{mn} O_{mn} - \tfrac{1}{2} s^{\mathrm{oo}}_{2332} O_{mn} O_{nm} \\ &- \tfrac{1}{2} s^{\mathrm{oo}}_{3232} O_{nm} O_{nm} - \tfrac{1}{2} s^{\mathrm{pp}}_{11} P_1^2 \\ &- \tfrac{1}{2} s^{\mathrm{pp}}_{22} P_m^2 - \tfrac{1}{2} s^{\mathrm{pp}}_{33} P_n^2. \end{aligned} \tag{2.15}$$

For a biaxial cholesteric phase, terms linear in O_{ll}, O_{mm}, and O_{nn} also enter into the entropy function which are not allowd by the symmetry transformations (2.13) but by the transformations (2.14).

Here we have chosen the vectors $\boldsymbol{l}$, $\boldsymbol{m}$, and $\boldsymbol{n}$ as the basis of the coordinate system, e.g.

$$O_{lm} := \boldsymbol{l} \cdot \mathbf{O} \cdot \boldsymbol{m}, \quad P_l := \boldsymbol{P} \cdot \boldsymbol{l}, \tag{2.16}$$

and analogously for the other components. The absolut term s_0 and all the coefficients depend on u, $\boldsymbol{v}$ and $\nabla \boldsymbol{v}$. In (2.15) terms bilinear in the angular distortion and the polarisation are neglected, i.e. we do not take into account flexoelectric effects. The coefficients s^{OO}_{ijkl}

are proportional to 15 independent elastic constants. In terms of **Q** instead of the three directors, the polynomial of second degree in the components of **O** and ***P***, which is invariant under the symmetry transformations, is

$$\begin{aligned} s = s_0 &- \tfrac{1}{2} s^{\mathrm{oo}}_{1111} (\mathbf{Q}^{\mathrm{T}} \cdot \mathbf{O} \cdot \mathbf{Q})^2_{11} - \tfrac{1}{2} s^{\mathrm{oo}}_{2222} (\mathbf{Q}^{\mathrm{T}} \cdot \mathbf{O} \cdot \mathbf{Q})^2_{22} \\ &- \tfrac{1}{2} s^{\mathrm{oo}}_{3333} (\mathbf{Q}^{\mathrm{T}} \cdot \mathbf{O} \cdot \mathbf{Q})^2_{33} \\ &- \tfrac{1}{2} s^{\mathrm{oo}}_{1122} (\mathbf{Q}^{\mathrm{T}} \cdot \mathbf{O} \cdot \mathbf{Q})_{11} (\mathbf{Q}^{\mathrm{T}} \cdot \mathbf{O} \cdot \mathbf{Q})_{22} \\ &- \tfrac{1}{2} s^{\mathrm{oo}}_{1133} (\mathbf{Q}^{\mathrm{T}} \cdot \mathbf{O} \cdot \mathbf{Q})_{11} (\mathbf{Q}^{\mathrm{T}} \cdot \mathbf{O} \cdot \mathbf{Q})_{33} \\ &- \tfrac{1}{2} s^{\mathrm{oo}}_{2233} (\mathbf{Q}^{\mathrm{T}} \cdot \mathbf{O} \cdot \mathbf{Q})_{22} (\mathbf{Q}^{\mathrm{T}} \cdot \mathbf{O} \cdot \mathbf{Q})_{33} \\ &- \tfrac{1}{2} s^{\mathrm{oo}}_{1212} (\mathbf{Q}^{\mathrm{T}} \cdot \mathbf{O} \cdot \mathbf{Q})_{12} (\mathbf{Q}^{\mathrm{T}} \cdot \mathbf{O} \cdot \mathbf{Q})_{12} \\ &- \tfrac{1}{2} s^{\mathrm{oo}}_{1221} (\mathbf{Q}^{\mathrm{T}} \cdot \mathbf{O} \cdot \mathbf{Q})_{12} (\mathbf{Q}^{\mathrm{T}} \cdot \mathbf{O} \cdot \mathbf{Q})_{21} \\ &- \tfrac{1}{2} s^{\mathrm{oo}}_{2121} (\mathbf{Q}^{\mathrm{T}} \cdot \mathbf{O} \cdot \mathbf{Q})_{21} (\mathbf{Q}^{\mathrm{T}} \cdot \mathbf{O} \cdot \mathbf{Q})_{21} \\ &- \tfrac{1}{2} s^{\mathrm{oo}}_{1313} (\mathbf{Q}^{\mathrm{T}} \cdot \mathbf{O} \cdot \mathbf{Q})_{13} (\mathbf{Q}^{\mathrm{T}} \cdot \mathbf{O} \cdot \mathbf{Q})_{13} \\ &- \tfrac{1}{2} s^{\mathrm{oo}}_{1331} (\mathbf{Q}^{\mathrm{T}} \cdot \mathbf{O} \cdot \mathbf{Q})_{13} (\mathbf{Q}^{\mathrm{T}} \cdot \mathbf{O} \cdot \mathbf{Q})_{31} \\ &- \tfrac{1}{2} s^{\mathrm{oo}}_{3131} (\mathbf{Q}^{\mathrm{T}} \cdot \mathbf{O} \cdot \mathbf{Q})_{31} (\mathbf{Q}^{\mathrm{T}} \cdot \mathbf{O} \cdot \mathbf{Q})_{31} \\ &- \tfrac{1}{2} s^{\mathrm{oo}}_{2323} (\mathbf{Q}^{\mathrm{T}} \cdot \mathbf{O} \cdot \mathbf{Q})_{23} (\mathbf{Q}^{\mathrm{T}} \cdot \mathbf{O} \cdot \mathbf{Q})_{23} \\ &- \tfrac{1}{2} s^{\mathrm{oo}}_{2332} (\mathbf{Q}^{\mathrm{T}} \cdot \mathbf{O} \cdot \mathbf{Q})_{23} (\mathbf{Q}^{\mathrm{T}} \cdot \mathbf{O} \cdot \mathbf{Q})_{32} \\ &- \tfrac{1}{2} s^{\mathrm{oo}}_{3232} (\mathbf{Q}^{\mathrm{T}} \cdot \mathbf{O} \cdot \mathbf{Q})_{32} (\mathbf{Q}^{\mathrm{T}} \cdot \mathbf{O} \cdot \mathbf{Q})_{32} \\ &- \tfrac{1}{2} s^{\mathrm{pp}}_{ii} (\mathbf{Q}^{\mathrm{T}} \cdot \boldsymbol{P})^2_1 - \tfrac{1}{2} s^{\mathrm{pp}}_{22} (\mathbf{Q}^{\mathrm{T}} \cdot \boldsymbol{P})^2_2 \\ &- \tfrac{1}{2} s^{\mathrm{pp}}_{33} (\mathbf{Q}^{\mathrm{T}} \cdot \boldsymbol{P})^2_3 . \end{aligned} \tag{2.17}$$

It has been used that

$$\begin{aligned} &\boldsymbol{e}_1 \cdot \mathbf{O} \cdot \boldsymbol{e}_2 = \boldsymbol{e}^O_1 \cdot (\mathbf{Q}^{\mathrm{T}} \cdot \mathbf{O} \cdot \mathbf{Q}) \cdot \boldsymbol{e}^O_2 , \\ &\boldsymbol{e}_1 , \boldsymbol{e}_2 \in \{\boldsymbol{l}, \boldsymbol{m}, \boldsymbol{n}\} \end{aligned} \tag{2.18}$$

with the eigenvectors $\boldsymbol{l}^O$, $\boldsymbol{m}^O$ and $\boldsymbol{n}^O$ of the alignment tensor $\mathbf{a}(\boldsymbol{r}^O)$ in the reference point $\boldsymbol{r}^O$, $\boldsymbol{l}^O$ is chosen along the x_1 axis, $\boldsymbol{m}^O$ along the x_2 axis and $\boldsymbol{n}^O$ along the x_3 axis. Again flexoelectric effects have been neglected. In equilibrium $\boldsymbol{P} = \mathbf{0}$ with no external electric field, and $\mathbf{O} = \mathbf{0}$ for a nonchiral liquid crystal if there are no boundary conditions inducing a distortion. As for an adiabatic system the entropy is maximal in equilibrium, the following stability conditions hold:

$$\begin{aligned} &s^{\mathrm{oo}}_{iiii} \geq 0, \quad i \in \{1, 2, 3\}, \\ &s^{\mathrm{oo}}_{ijij} \geq 0, \quad i, j \in \{1, 2, 3\}, \\ &s^{\mathrm{oo}}_{iiii} \, s^{\mathrm{oo}}_{jjjj} \geq (s^{\mathrm{oo}}_{iijj})^2, \quad i, j \in \{1, 2, 3\}, \\ &\begin{vmatrix} s^{\mathrm{oo}}_{1111} & s^{\mathrm{oo}}_{1122} & s^{\mathrm{oo}}_{1133} \\ s^{\mathrm{oo}}_{1122} & s^{\mathrm{oo}}_{2222} & s^{\mathrm{oo}}_{2233} \\ s^{\mathrm{oo}}_{1133} & s^{\mathrm{oo}}_{2233} & s^{\mathrm{oo}}_{3333} \end{vmatrix} \geq 0, \\ &s^{\mathrm{oo}}_{ijij} \, s^{\mathrm{oo}}_{jiji} \geq (s^{\mathrm{oo}}_{ijji})^2, \quad i, j \in \{1, 2, 3\}, \\ &s^{\mathrm{pp}}_{ii} \geq 0, \quad i \in \{1, 2, 3\}. \end{aligned} \tag{2.19}$$

3. Balance Equations and Dissipation Inequality

The following notations are used: ϱ is the mass density, $\boldsymbol{v}$ the velocity, $\mathbf{t}$ the stress tensor and $\boldsymbol{f}$ the force density exerted by external fields, $\boldsymbol{r}$ the position vector, $\boldsymbol{s}$ the internal angular momentum (spin), $\boldsymbol{\Pi}$ the couple stress tensor, $\boldsymbol{m}$ the couple density, $\boldsymbol{J}_q$ the heat current density, u the internal energy, $\boldsymbol{\Omega}$ the angular velocity of the directors, $\boldsymbol{E}$ the electric field and $\boldsymbol{P}$ the polarisation density.

The conservation laws of mass,

$$\frac{\mathrm{d}\varrho}{\mathrm{d}t} + \varrho \nabla \cdot \boldsymbol{v} = 0, \tag{3.1}$$

and momentum,

$$\varrho \frac{\mathrm{d}\boldsymbol{v}}{\mathrm{d}t} = \nabla \cdot \mathbf{t} + \varrho \boldsymbol{f}, \tag{3.2}$$

are the same as for a simple fluid [20]. The balance equation of the angular momentum has the form

$$\varrho \frac{\mathrm{d}}{\mathrm{d}t} (\boldsymbol{r} \times \boldsymbol{v} + \boldsymbol{s}) = \nabla \cdot (\boldsymbol{r} \times \mathbf{t} + \boldsymbol{\Pi}) + \varrho \boldsymbol{r} \times \boldsymbol{f} + \varrho \boldsymbol{m}, \tag{3.3}$$

and the balance equation for the total energy is assumed to be

$$\begin{aligned} &\varrho \frac{\mathrm{d}}{\mathrm{d}t} \left(u + \frac{\boldsymbol{v}^2}{2} + \frac{1}{2} \boldsymbol{s} \cdot \boldsymbol{\Omega} \right) + \nabla \cdot \boldsymbol{J}_q \\ &= \nabla \cdot (\boldsymbol{v} \cdot \mathbf{t} + \boldsymbol{\Omega} \cdot \boldsymbol{\Pi}) + \varrho \boldsymbol{f} \cdot \boldsymbol{v} + \varrho \boldsymbol{E} \cdot \frac{\mathrm{d}\boldsymbol{P}}{\mathrm{d}t} . \end{aligned} \tag{3.4}$$

The last term on the right hand side gives the energy supply from the electric field. The nonconvective energy flux is the sum of a mechanical part $\boldsymbol{J}_q$ and an electromagnetic part. Just so the energy and the stress tensor can be decomposed into mechanical and electromagnetic parts. It is shown in Appendix A that for an incompressible fluid in an electric field, (3.4) is correct for the energy balance if the model of Grot and Eringen [21] is accepted.

In (3.3) and (3.4) the terms with the couple stress tensor and the couple density and the spin are included due to the internal structure of the liquid crystal.

These are the balance equations for a micropolar fluid [19]. They have been derived within an alignmenttensor theory of liquid crystals, which has been founded statistically [22]. The angular velocity $\boldsymbol{\Omega}$ has been defined so that

$$\frac{\mathrm{d}\boldsymbol{l}}{\mathrm{d}t} = \boldsymbol{\Omega} \times \boldsymbol{l}, \quad \frac{\mathrm{d}\boldsymbol{m}}{\mathrm{d}t} = \boldsymbol{\Omega} \times \boldsymbol{m}, \quad \frac{\mathrm{d}\boldsymbol{n}}{\mathrm{d}t} = \boldsymbol{\Omega} \times \boldsymbol{n}, \tag{3.5}$$

which is possible with one vector $\boldsymbol{\Omega}$ because we consider only rigid rotations of the angular distribution function. The balance equation of the angular momentum is equivalent to the spin balance

$$2\,\boldsymbol{w}(\mathbf{t}) + \nabla \cdot \boldsymbol{\Pi} + \varrho\, \boldsymbol{m} = \frac{\mathrm{d}\boldsymbol{s}}{\mathrm{d}t}. \tag{3.6}$$

With the balance equation (3.2) of linear momentum and (3.6) the internal energy balance is obtained from the conservation law of total energy (3.4):

$$\varrho \frac{\mathrm{d}u}{\mathrm{d}t} + \nabla \cdot \boldsymbol{J}_q = \mathbf{t} : \mathring{\mathbf{d}} + \nabla \cdot (\boldsymbol{\Omega}' \cdot \boldsymbol{\Pi}) + \boldsymbol{\Pi} : \nabla \boldsymbol{\omega} + \varrho \boldsymbol{E} \cdot \mathring{\boldsymbol{P}} - \frac{\mathrm{d}\boldsymbol{s}}{\mathrm{d}t} \cdot \Omega', \tag{3.7}$$

where the notations

$$\mathring{\mathbf{d}} = \frac{1}{2}[\nabla \boldsymbol{v} + (\nabla \boldsymbol{v})^{\mathrm{T}}], \quad \boldsymbol{\omega} = \frac{1}{2} \nabla \times \boldsymbol{v},$$

$$\boldsymbol{\Omega}' = \boldsymbol{\Omega} - \boldsymbol{\omega}, \quad \mathring{\boldsymbol{P}} = \frac{\mathrm{d}\boldsymbol{P}}{\mathrm{d}t} - \boldsymbol{\omega} \times \boldsymbol{P} \tag{3.8}$$

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

$$\boldsymbol{m} = \boldsymbol{P} \times \boldsymbol{E}. \tag{3.9}$$

The vector $\boldsymbol{\Omega}'$ is the angular velocity in a cartesian frame corotating with the body, and $\mathring{\mathbf{d}}$ and $\mathring{\boldsymbol{P}}$ are the time derivatives of $\mathbf{d}$ and $\boldsymbol{P}$ in this frame. The time derivatives of the directors in this frame are

$$\mathring{\boldsymbol{l}} = \boldsymbol{\Omega}' \times \boldsymbol{l}, \quad \mathring{\boldsymbol{m}} = \boldsymbol{\Omega}' \times \boldsymbol{m}, \quad \mathring{\boldsymbol{n}} = \boldsymbol{\Omega}' \times \boldsymbol{n}, \tag{3.10}$$

It follows from this equation that

$$\mathring{\mathbf{O}} = \boldsymbol{\Omega}' \times \mathbf{Q}, \tag{3.11}$$

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

The second law of thermodynamics is expressed in the dissipation inequality

$$\varrho \frac{\mathrm{d}s}{\mathrm{d}t} + \nabla \cdot \boldsymbol{J}_s = \sigma_s \geq 0, \tag{3.12}$$

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

$$\boldsymbol{J}_s = \frac{1}{T} \boldsymbol{J}_q, \tag{3.13}$$

which holds always in a local equilibrium state.

With the state space Z' the time derivative of the entropy in the corotating frame is

$$\frac{\mathrm{d}s}{\mathrm{d}t} = \frac{1}{T}\frac{\mathrm{d}u}{\mathrm{d}t} + \frac{\partial s}{\partial \boldsymbol{l}} \cdot \mathring{\boldsymbol{l}} + \frac{\partial s}{\partial \boldsymbol{m}} \cdot \mathring{\boldsymbol{m}} + \frac{\partial s}{\partial \boldsymbol{n}} \cdot \mathring{\boldsymbol{n}} + \frac{\partial s}{\partial \mathbf{O}} : \mathring{\mathbf{O}} + \frac{\partial s}{\partial \boldsymbol{P}} \cdot \mathring{\boldsymbol{P}}. \tag{3.14}$$

As the entropy is a scalar, it has the same form in any other frame. Equivalently with the choice of the relevant variables Z:

$$\frac{\mathrm{d}s}{\mathrm{d}t} = \frac{1}{T}\frac{\mathrm{d}u}{\mathrm{d}t} + \frac{\partial s}{\partial \mathbf{Q}} : \mathring{\mathbf{Q}} + \frac{\partial s}{\partial \mathbf{O}} : \mathring{\mathbf{O}} + \frac{\partial s}{\partial \boldsymbol{P}} \cdot \mathring{\boldsymbol{P}}. \tag{3.15}$$

It has been used that the velocity is not an objective variable and that therefore by the principle of objectivity it appears only in the corotating time derivatives which are objective. Moreover, use has been made of the fact that the entropy does no depend on the deformation rate in a local equilibrium situation. The relation

$$\frac{\partial s}{\partial u} = \frac{1}{T}, \tag{3.16}$$

known to be valid in equilibrium, has also been used. The derivations can be carried out explicitly using the constitutive relations (2.15) or (2.17) for the entropy. Examples of this calculation are given in the appendix. Substituting (3.15), (3.13) and (3.7) into the dissipation inequality (3.12) results in

$$T\,\sigma_s = \mathbf{t} : \mathring{\mathbf{d}} + \nabla \cdot (\boldsymbol{\Omega}' \cdot \boldsymbol{\Pi}) + \boldsymbol{\Pi} : (\nabla \boldsymbol{\omega}) + \varrho\, T \frac{\partial s}{\partial \mathbf{Q}} : \mathring{\mathbf{Q}} + \varrho\, T \frac{\partial s}{\partial \mathbf{O}} : \mathring{\mathbf{O}} + \left(\varrho\, T \frac{\partial s}{\partial \boldsymbol{P}} + \varrho\, \boldsymbol{E}\right) \cdot \mathring{\boldsymbol{P}} - \frac{\mathrm{d}\boldsymbol{s}}{\mathrm{d}t} \cdot \boldsymbol{\Omega}'. \tag{3.17}$$

In the first term of the right hand side only the symmetric part of the stress tensor is relevant. Inserting the spin balance for $\mathrm{d}\boldsymbol{s}/\mathrm{d}t$ in the last term, one sees that also the antisymmetric part of the stress tensor contributes to the entropy production.

The following identities are used to simplify this expression:

$$\frac{\partial s}{\partial \mathbf{Q}} : \mathring{\mathbf{Q}} = \frac{\partial s}{\partial \mathbf{Q}} : (\boldsymbol{\Omega}' \times \mathbf{Q}) = 2\, \boldsymbol{\Omega}' \cdot \boldsymbol{w}\left(\frac{\partial s}{\partial \mathbf{Q}} \cdot \mathbf{Q}^{\mathrm{T}}\right),$$

$$\nabla \cdot (\boldsymbol{\Omega}' \cdot \boldsymbol{\Pi}) + \boldsymbol{\Pi} : \nabla \boldsymbol{\omega} = (\nabla \boldsymbol{\Omega}) : \boldsymbol{\Pi} + \boldsymbol{\Omega}' \cdot \nabla \cdot \boldsymbol{\Pi},$$

$$\nabla \boldsymbol{\Omega} = \mathring{\mathbf{O}} + \mathbf{O} \cdot \mathring{\mathbf{d}} - \boldsymbol{\Omega}' \times \mathbf{O}. \tag{3.18}$$

The derivation of the last identity is given in the appendix.

For the energy dissipation function we get

$$T\,\sigma_s = \boldsymbol{\Omega}'\cdot\left\{2\,\boldsymbol{w}\left[\varrho\,T\left(\frac{\partial s}{\partial \mathbf{Q}}\cdot\mathbf{Q}^{\mathrm{T}}\right)-\boldsymbol{\Pi}\cdot\mathbf{O}^{\mathrm{T}}\right]+\nabla\cdot\boldsymbol{\Pi}\right\} + \overset{\circ}{\mathbf{O}}:\left\{\boldsymbol{\Pi}+\varrho\,T\,\frac{\partial s}{\partial\mathbf{O}}\right\}+\overset{\circ}{\mathbf{d}}:\{\mathbf{t}+\mathbf{O}^{\mathrm{T}}\cdot\boldsymbol{\Pi}\} + \overset{\circ}{\boldsymbol{P}}\cdot\left\{\varrho\,T\,\frac{\partial s}{\partial \boldsymbol{P}}+\varrho\,\boldsymbol{E}\right\}-\frac{\mathrm{d}s}{\mathrm{d}t}\cdot\boldsymbol{\Omega}'. \tag{3.19}$$

The energy dissipation function fulfils the inequality

$$T\,\sigma_s \geq 0 \tag{3.20}$$

with $T\,\sigma_s = 0$ in and only in an equilibrium.

4. The Equilibrium Conditions

In equilibrium the objective rates of processes $\boldsymbol{\Omega}'$, $\overset{\circ}{\mathbf{O}}$, $\overset{\circ}{\mathbf{d}}$, and $\overset{\circ}{\boldsymbol{P}}$ vanish. As the energy dissipation function (3.19) is linear in these fluxes, the equilibrium conditions are that the corresponding forces are equal to zero [18]. The only constraint to be taken into account is that $\overset{\circ}{\mathbf{d}}$ is a symmetric traceless tensor as we consider only volume preserving motions:

$$\overset{\circ}{\mathbf{d}}:\boldsymbol{\delta} = 0, \quad \overset{\circ}{\mathbf{d}}:\mathbf{A} = 0 \tag{4.1}$$

with any antisymmetric tensor $\mathbf{A}$. The components of $\boldsymbol{\Omega}'$ and $\overset{\circ}{\mathbf{O}}$ are all independent. The auxiliary function, taking also the constraints (4.1) into account, is

$$L^* = T\,\sigma_s + \overset{\circ}{\mathbf{d}}:(p\,\boldsymbol{\delta}+\mathbf{A}) = \boldsymbol{\Omega}'\cdot\left\{2\,\boldsymbol{w}\left[\varrho\,T\left(\frac{\partial s}{\partial \mathbf{Q}}\cdot\mathbf{Q}^{\mathrm{T}}\right)-\boldsymbol{\Pi}\cdot\mathbf{O}^{\mathrm{T}}\right]+\nabla\cdot\boldsymbol{\Pi}\right\} + \overset{\circ}{\mathbf{O}}:\left\{\boldsymbol{\Pi}+\varrho\,T\,\frac{\partial s}{\partial\mathbf{O}}\right\}+\overset{\circ}{\boldsymbol{P}}\cdot\left\{\varrho\,T\,\frac{\partial s}{\partial \boldsymbol{P}}+\varrho\,\boldsymbol{E}\right\} + \overset{\circ}{\mathbf{d}}:\{\mathbf{t}+\mathbf{O}^{\mathrm{T}}\cdot\boldsymbol{\Pi}+p\,\boldsymbol{\delta}+\mathbf{A}\}, \tag{4.2}$$

where it has already been used that $\mathrm{d}s/\mathrm{d}t = 0$ in equilibrium.

p and $\mathbf{A}$ are Lagrange multipliers, which have to be eliminated from the resulting equilibrium conditions. These equations for equilibrium are

$$2\,\boldsymbol{w}\left[\varrho\,T\,\frac{\partial s}{\partial \mathbf{Q}}\cdot\mathbf{Q}^{\mathrm{T}}-\boldsymbol{\Pi}\cdot\mathbf{O}^{\mathrm{T}}\right]+\nabla\cdot\boldsymbol{\Pi} = 0, \tag{4.3}$$

$$\boldsymbol{\Pi}+\varrho\,T\,\frac{\partial s}{\partial\mathbf{O}} = 0, \tag{4.4}$$

$$\mathbf{t}+\mathbf{O}^{\mathrm{T}}\cdot\boldsymbol{\Pi}+p\,\boldsymbol{\delta}+\mathbf{A} = 0, \tag{4.5}$$

$$T\,\frac{\partial s}{\partial \boldsymbol{P}}+\boldsymbol{E} = 0. \tag{4.6}$$

The term $\boldsymbol{\Pi}\cdot\mathbf{O}^{\mathrm{T}}$ in (4.3) has no analogon in the case of a uniaxial nematic liquid crystal [16].

Equation (4.6) gains the form

$$\varrho\,\boldsymbol{P} = \chi_l\,\boldsymbol{l}\,\boldsymbol{E}\cdot\boldsymbol{l}+\chi_m\,\boldsymbol{m}\,\boldsymbol{E}\cdot\boldsymbol{m}+\chi_n\,\boldsymbol{n}\,\boldsymbol{E}\cdot\boldsymbol{n} \tag{4.7}$$

with $\chi_l^{-1} = T\,s^{\mathrm{pp}}_{11}$, $\chi_m^{-1} = T\,s^{\mathrm{pp}}_{22}$, $\chi_n^{-1} = T\,s^{\mathrm{pp}}_{33}$, (4.8)

when determining the derivative $\frac{\partial s}{\partial \boldsymbol{P}}$ from (2.15). This expression for the electric polarisation is the usual one. Equation (4.4) is rather explicit for the couple stress, and only the large number of material coefficients in the entropy function (2.15) can cause difficulties.

To determine the equilibrium stress, we combine (4.3), (4.4), (3.6), (3.9) and (4.6). In the balance of angular momentum (3.6) it is used that in equilibrium $\mathrm{d}s/\mathrm{d}t = 0$. We get first

$$2\,\varrho\,T\,\boldsymbol{w}\left[\frac{\partial s}{\partial \mathbf{Q}}\cdot\mathbf{Q}^{\mathrm{T}}+\frac{\partial s}{\partial \mathbf{O}}\cdot\mathbf{O}^{\mathrm{T}}\right]+\nabla\cdot\boldsymbol{\Pi} = 0, \tag{4.9}$$

$$2\,\boldsymbol{w}(\mathbf{t})+\nabla\cdot\boldsymbol{\Pi} = \varrho\,T\,\boldsymbol{P}\times\frac{\partial s}{\partial \boldsymbol{P}} = 2\,\varrho\,T\,\boldsymbol{w}\left[\frac{\partial s}{\partial \boldsymbol{P}}\,\boldsymbol{P}\right] \tag{4.10}$$

and then

$$2\,\boldsymbol{w}(\mathbf{t}) = 2\,\varrho\,T\,\boldsymbol{w}\left[\frac{\partial s}{\partial \boldsymbol{P}}\,\boldsymbol{P}+\frac{\partial s}{\partial \mathbf{Q}}\cdot\mathbf{Q}^{\mathrm{T}}+\frac{\partial s}{\partial \mathbf{O}}\cdot\mathbf{O}^{\mathrm{T}}\right]. \tag{4.11}$$

Making use of the indentity

$$\frac{\partial s}{\partial \mathbf{Q}}\cdot\mathbf{Q}^{\mathrm{T}} = \boldsymbol{P}\,\frac{\partial s}{\partial \boldsymbol{P}}+\mathbf{O}\cdot\left(\frac{\partial s}{\partial \mathbf{O}}\right)^{\mathrm{T}}+\mathbf{O}^{\mathrm{T}}\cdot\left(\frac{\partial s}{\partial \mathbf{O}}\right), \tag{4.12}$$

which is a consequence of the fact that the entropy is an objective quantity, we arrive at

$$\boldsymbol{w}[\mathbf{t}+\mathbf{O}^{\mathrm{T}}\cdot\boldsymbol{\Pi}] = 0, \tag{4.13}$$

from which

$$\mathbf{t} = p\,\boldsymbol{\delta}+\varrho\,T\,\mathbf{O}^{\mathrm{T}}\cdot\frac{\partial s}{\partial \mathbf{O}} \tag{4.14}$$

is obtained. The scalar pressure p is available only when integrating the differential equation. It is worth mentioning that the right hand side of the expression for the stress is quadratic in the components of the angular distortion tensor, so, in linear approximation the distortion does not contribute to Cauchy's stress.

5. The Motion of Biaxial Nematic liquid crystals

The equations of motion in the linear Onsager theory have a very simple form if the generalized forces and fluxes are independent and the body is of high symmetry. This is not so in our case because the constraint equations (4.1) hold and the symmetry of a biaxial nematic liquid crystal is rather low. A further difficulty is that a transformation of fluxes producing independent variables spoils the frame independent notation and makes the calculations clumsy. The variational principles of thermodynamics worked out by Gyarmati [17] in the 60's offer a more elegant and easier procedure. The most convenient representation for dealing with biaxial nematic liquid crystals is the flux representation of the local principle in the energy picture.

To apply the variational principle we have to look for the actual form of the dissipation potential φ. It is a homogenous 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 $\boldsymbol{\Omega}'$, $\mathring{\mathbf{O}}$, $\mathring{\mathbf{d}}$, and $\mathring{\boldsymbol{P}}$ and contains the local state variables u, $\boldsymbol{P}$, $\mathbf{O}$, and $\mathbf{Q}$ as parameters. To make the task a bit easier we suppose that the dielectric losses are negligible, i.e. (4.6) holds also for dissipative processes. In this way φ does not depend on $\mathring{\boldsymbol{P}}$. Moreover, we supose that the sample of the liquid crystal is large enough to neglect the angular distorsion $\mathbf{O}$ and its time derivative in the dissipation potential. This supposition is encouraged by the thermodynamic theory of uniaxial nematics, where the same simplification leads to the Ericksen-Leslie-Parodi theory [16]. In this way the function we are looking for is of the form

$$\varphi = \varphi(\boldsymbol{\Omega}', \mathring{\mathbf{d}}, \mathbf{Q}). \tag{5.1}$$

This function has to be objective, i.e. the equality

$$\varphi(\mathbf{R}\cdot\boldsymbol{\Omega}', \mathbf{R}\cdot\mathring{\mathbf{d}}\cdot\mathbf{R}^{\mathrm{T}}, \mathbf{R}\cdot\mathbf{Q}) = \varphi(\boldsymbol{\Omega}', \mathring{\mathbf{d}}, \mathbf{Q}) \tag{5.2}$$

holds for any proper orthogonal tensor $\mathbf{R}$. Moreover, it has to be invariant under the transformations (2.13). The special choice of $\mathbf{R}=\mathbf{Q}^{\mathrm{T}}$ leads to

$$\varphi = \varphi(\mathbf{Q}^{\mathrm{T}}\cdot\boldsymbol{\Omega}', \mathbf{Q}^{\mathrm{T}}\cdot\mathring{\mathbf{d}}\cdot\mathbf{Q}, \boldsymbol{\delta}), \tag{5.3}$$

making use of which we conclude that φ consists of three kinds of terms, terms quadratic in $\mathbf{Q}^{\mathrm{T}}\cdot\boldsymbol{\Omega}'$, terms bilinear in $\mathbf{Q}^{\mathrm{T}}\cdot\boldsymbol{\Omega}'$ and $\mathbf{Q}^{\mathrm{T}}\cdot\mathring{\mathbf{d}}\cdot\mathbf{Q}$ and quadratic in $\mathbf{Q}^{\mathrm{T}}\cdot\mathring{\mathbf{d}}\cdot\mathbf{Q}$. As the mapping $\mathbf{Q}^{\mathrm{T}}$ transforms the axial vector $\boldsymbol{\Omega}'$ and the tensor $\mathring{\mathbf{d}}$ into the abstract reference frame, we put down the dissipation potential as a function of the vector and tensor components in the reference frame. The invariant form of φ is

$$\begin{aligned}\varphi = {}&\tfrac{1}{2}(\mathbf{Q}^{\mathrm{T}}\cdot\boldsymbol{\Omega}')\cdot\mathbf{R}^{\Omega\Omega}\cdot(\mathbf{Q}^{\mathrm{T}}\cdot\boldsymbol{\Omega}') + (\mathbf{Q}^{\mathrm{T}}\cdot\boldsymbol{\Omega}')\\ &\cdot\mathbf{R}^{\Omega d}:(\mathbf{Q}^{\mathrm{T}}\cdot\mathring{\mathbf{d}}\cdot\mathbf{Q}) + \tfrac{1}{2}(\mathbf{Q}^{\mathrm{T}}\cdot\mathring{\mathbf{d}}\cdot\mathbf{Q}):\mathbf{R}^{dd}:(\mathbf{Q}^{\mathrm{T}}\cdot\mathring{\mathbf{d}}\cdot\mathbf{Q}).\end{aligned} \tag{5.4}$$

Here $\mathbf{R}^{\Omega\Omega}$ is a second order tensor, $\mathbf{R}^{\Omega d}$ is a third order one (remember that $\mathbf{R}^{\Omega d}$ is an axial tensor) and $\mathbf{R}^{dd}$ is a fourth order one. To avoid misunderstanding, (5.4) is repeated in cartesian coordinates:

$$\begin{aligned}\varphi = {}&\tfrac{1}{2}\sum_{ijsr} R^{\Omega\Omega}_{ij} Q_{si}\,\Omega'_s\,Q_{jr}\,\Omega'_r + \sum_{ijkrst} R^{\Omega d}_{ijk}\,Q_{si}\,\Omega'_s\,Q_{rj}\,Q_{tk}\,\mathring{d}_{rt}\\ &+\tfrac{1}{2}\sum_{ijklprst} R^{dd}_{ijkl}\,Q_{pi}\,Q_{rj}\,Q_{sk}\,Q_{tl}\,\mathring{d}_{pr}\,\mathring{d}_{st}.\end{aligned} \tag{5.5}$$

We determine the possible form of polynomial (5.5) similarly as it has been done with the entropy function. According to the transformations (2.13) the nonzero coefficients of the phenomenological tensors are listed here:

$$\begin{aligned}&R^{\Omega\Omega}_{11},\ R^{\Omega\Omega}_{22},\ R^{\Omega\Omega}_{33},\\ &R^{\Omega d}_{123},\ R^{\Omega d}_{132},\ R^{\Omega d}_{213},\ R^{\Omega d}_{231},\ R^{\Omega d}_{312},\ R^{\Omega d}_{321},\\ &R^{dd}_{1111},\ R^{dd}_{2222},\ R^{dd}_{3333},\\ &R^{dd}_{1122},\ R^{dd}_{1212},\ R^{dd}_{1221},\ R^{dd}_{2112},\ R^{dd}_{2121},\ R^{dd}_{2211},\\ &R^{dd}_{1133},\ R^{dd}_{1313},\ R^{dd}_{1331},\ R^{dd}_{3113},\ R^{dd}_{3131},\ R^{dd}_{3311},\\ &R^{dd}_{2233},\ R^{dd}_{2323},\ R^{dd}_{2332},\ R^{dd}_{3223},\ R^{dd}_{3232},\ R^{dd}_{3322}.\end{aligned} \tag{5.6}$$

Next we make use of the symmetry relations

$$R^{dd}_{ijkl} = R^{dd}_{klij}, \tag{5.7}$$

which are well known from the algebraic theory of quadratic forms and are equivalent to Onsager's reciprocal relations [2]. Moreover, because $\mathring{\mathbf{d}}$ is a symmetric tensor, the relations

$$R^{dd}_{ijkl} = R^{dd}_{ijlk}, \tag{5.8}$$

can be required without hurting the generality. This way the independent coefficients reduce to

$$\begin{aligned}&R^{\Omega\Omega}_{11},\ R^{\Omega\Omega}_{22},\ R^{\Omega\Omega}_{33},\\ &R^{\Omega d}_{123},\ R^{\Omega d}_{213},\ R^{\Omega d}_{312},\\ &R^{dd}_{1111},\ R^{dd}_{2222},\ R^{dd}_{3333},\\ &R^{dd}_{1122},\ R^{dd}_{1212},\\ &R^{dd}_{1133},\ R^{dd}_{1313},\\ &R^{dd}_{2233},\ R^{dd}_{2323}.\end{aligned} \tag{5.9}$$

The number of the independent coefficients, is further reduced, when regarding the fact that, for volume preserving motions

$$\mathring{d}_{11} + \mathring{d}_{22} + \mathring{d}_{33} = 0. \tag{5.10}$$

For this reason only the 6 coefficients of the 9 elements of $\mathbf{R}^{dd}$ in (5.9) are independent, and the coefficients R^{dd}_{1122}, R^{dd}_{2233}, and R^{dd}_{3311} can be chosen for zero. Now we are able to put down the actual form of the dissipation potential:

$$\begin{aligned}\varphi = {} & \tfrac{1}{2} R^{\Omega\Omega}_{ll} \Omega'^2_l + \tfrac{1}{2} R^{\Omega\Omega}_{mm} \Omega'^2_m + \tfrac{1}{2} R^{\Omega\Omega}_{nn} \Omega'^2_n \\ & + 2 R^{\Omega d}_{lmn} \Omega'_l \mathring{\mathrm{d}}_{mn} + 2 R^{\Omega d}_{mnl} \Omega'_m \mathring{\mathrm{d}}_{nl} + 2 R^{\Omega d}_{nlm} \Omega'_n \mathring{\mathrm{d}}_{lm} \\ & + \tfrac{1}{2} R^{dd}_{llll} \mathring{\mathrm{d}}^2_{ll} + \tfrac{1}{2} R^{dd}_{mmmm} \mathring{\mathrm{d}}^2_{mm} + \tfrac{1}{2} R^{dd}_{nnnn} \mathring{\mathrm{d}}^2_{nn} \\ & + 2 R^{dd}_{lmlm} \mathring{\mathrm{d}}^2_{lm} + 2 R^{dd}_{lnln} \mathring{\mathrm{d}}^2_{ln} + 2 R^{dd}_{mnmn} \mathring{\mathrm{d}}^2_{mn},\end{aligned} \tag{5.11}$$

where again the directors $\boldsymbol{l}$, $\boldsymbol{m}$, and $\boldsymbol{n}$ are chosen to be parallel to the coordinate axes. As the dissipation potential is always positive except for equilibrium, when it is zero, the following inequalities hold:

$$\begin{aligned} & R^{\Omega\Omega}_{11} \geq 0, \quad R^{\Omega\Omega}_{22} \geq 0, \quad R^{\Omega\Omega}_{33} \geq 0, \\ & R^{dd}_{2323} \geq 0, \quad R^{dd}_{1313} \geq 0, \quad R^{dd}_{1212} \geq 0, \\ & R^{\Omega\Omega}_{11} R^{dd}_{2323} \geq (R^{\Omega d}_{123})^2, \quad R^{\Omega\Omega}_{22} R^{dd}_{1313} \geq (R^{\Omega d}_{231})^2, \\ & R^{\Omega\Omega}_{33} R^{dd}_{1212} \geq (R^{\Omega d}_{312})^2, \\ & R^{dd}_{1111} + R^{dd}_{2222} \geq 0, \quad R^{dd}_{1111} + R^{dd}_{3333} \geq 0, \\ & R^{dd}_{2222} + R^{dd}_{3333} \geq 0, \\ & R^{dd}_{1111} R^{dd}_{2222} + R^{dd}_{1111} R^{dd}_{3333} + R^{dd}_{2222} R^{dd}_{3333} \geq 0,\end{aligned} \tag{5.12}$$

The coefficients appearing in the dissipation potential are material coefficients depending on the chemical composition of the biaxial nematic liquid crystal and on the temperature. 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 [17]. Applying the variational principle, the constraint conditions (4.1) have to be kept in mind. The auxiliary function of the variational problem is of the form

$$L^* = T\sigma_s - \varphi + (p\,\boldsymbol{\delta} + \mathbf{A}) : \mathring{\mathbf{d}}, \tag{5.13}$$

where p and $\mathbf{A}$ are Lagrange multipliers; the latter is an antisymmetric tensor. The differential equations describing the processes are obtained from here. First of all notice that neither the components of $\mathring{\boldsymbol{P}}$ nor $\mathring{\mathbf{O}}$ enter the dissipation potential; consequently, the derivatives of the Lagrangian L^* with respect to them exhibit the same equations as in equilibrium, i.e. (4.4) and (4.6) remain valid for nonequilibrium situations. Making use of these, we can reduce the actual form of the dissipation function. Combining (3.6), (3.9) and (4.6) so as it was done in the case of equilibrium, moreover applying the identity (4.12), we arrive at

$$\begin{aligned}T\sigma_s = {} & -2\boldsymbol{\Omega}' \cdot \left\{ \boldsymbol{w}\left[\mathbf{t} - \varrho T\, \mathbf{O}^{\mathrm{T}} \cdot \frac{\partial s}{\partial \mathbf{O}} \right] - \varrho \frac{\mathrm{d}\boldsymbol{s}}{\mathrm{d}t} \right\} \\ & + \mathring{\mathbf{d}} : \left[\mathbf{t} - \sigma T\, \mathbf{O}^{\mathrm{T}} \cdot \frac{\partial s}{\partial \mathbf{O}} \right].\end{aligned} \tag{5.14}$$

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

$$\mathbf{t} =: \varrho T\, \mathbf{O}^{\mathrm{T}} \cdot \frac{\partial s}{\partial \mathbf{O}} + \mathbf{t}^{\mathrm{vs}} + \boldsymbol{t}^{\mathrm{va}} \times \boldsymbol{\delta}, \tag{5.15}$$

where $\mathbf{t}^{\mathrm{vs}}$ is a symmetric second order tensor and $\mathbf{t}^{\mathrm{va}}$ is an axial vector. The energy dissipation function gets the form

$$T\sigma_s = -2\boldsymbol{\Omega}' \cdot \boldsymbol{t}^{\mathrm{va}} + \mathring{\mathbf{d}} : \mathbf{t}^{\mathrm{vs}}, \tag{5.16}$$

or in components

$$\begin{aligned}T\sigma_s = {} & -2(\Omega'_l \cdot t^{\mathrm{va}}_l + \Omega'_m \cdot t^{\mathrm{va}}_m + \Omega'_n \cdot t^{\mathrm{va}}_n) \\ & + \mathring{\mathrm{d}}_{ll} t^{\mathrm{vs}}_{ll} + \mathring{\mathrm{d}}_{mm} t^{\mathrm{vs}}_{mm} + \mathring{\mathrm{d}}_{nn} t^{\mathrm{vs}}_{nn} \\ & + 2\mathring{\mathrm{d}}_{lm} t^{\mathrm{vs}}_{lm} + 2\mathring{\mathrm{d}}_{mn} t^{\mathrm{vs}}_{mn} + 2\mathring{\mathrm{d}}_{nl} t^{\mathrm{vs}}_{nl}.\end{aligned} \tag{5.17}$$

The axial vector $\boldsymbol{t}^{\mathrm{va}}$ includes the term $\varrho\,\mathrm{d}\boldsymbol{s}/\mathrm{d}t$ of the time derivative of the internal angular momentum. Within a statistically founded alignment-tensor theory [22] this term can be identified with the expression

$$\varrho \frac{\mathrm{d}\boldsymbol{s}}{\mathrm{d}t} = \frac{1}{2} \boldsymbol{w}\left[\frac{\mathrm{d}}{\mathrm{d}t}\mathbf{a} - 2\boldsymbol{\omega} \times \mathbf{a} \right] = \frac{1}{2} \boldsymbol{w}[\mathring{\mathbf{a}}], \tag{5.18}$$

where $\mathring{\mathbf{a}}$ is the time derivative of the alignment-tensor in the corotating frame. From here it can be seen that $\mathrm{d}\boldsymbol{s}/\mathrm{d}t$ is an axial vector. On the other hand there is some evidence 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. $\mathrm{d}\boldsymbol{s}/\mathrm{d}t = 0$.

The constitutive equations are determined as

$$\begin{aligned} t^{\mathrm{va}}_l &= -\tfrac{1}{2} R^{\Omega\Omega}_{ll} \Omega'_l - R^{\Omega d}_{lmn} \mathring{d}_{mn}, \\ t^{\mathrm{va}}_m &= -\tfrac{1}{2} R^{\Omega\Omega}_{mm} \Omega'_m - R^{\Omega d}_{mnl} \mathring{d}_{nl}, \\ t^{\mathrm{va}}_n &= -\tfrac{1}{2} R^{\Omega\Omega}_{nn} \Omega'_n - R^{\Omega d}_{nlm} \mathring{d}_{lm},\end{aligned} \tag{5.19}$$

$$\begin{aligned} t^{\mathrm{vs}}_{ll} + p &= R^{dd}_{llll} \mathring{d}_{ll}, \\ t^{\mathrm{vs}}_{mm} + p &= R^{dd}_{mmmm} \mathring{d}_{mm}, \\ t^{\mathrm{vs}}_{nn} + p &= R^{dd}_{nnnn} \mathring{d}_{nn},\end{aligned} \tag{5.20}$$

$$\begin{aligned} t^{\mathrm{vs}}_{lm} + A_{lm} &= R^{\Omega d}_{nml} \Omega'_n + 2 R^{dd}_{lmlm} \mathring{d}_{lm}, \\ t^{\mathrm{vs}}_{mn} + A_{mn} &= R^{\Omega d}_{lmn} \Omega'_l + 2 R^{dd}_{mnmn} \mathring{d}_{mn}, \\ t^{\mathrm{vs}}_{nl} + A_{nl} &= R^{\Omega d}_{mln} \Omega'_m + 2 R^{dd}_{nlnl} \mathring{d}_{nl},\end{aligned} \tag{5.21}$$

As all tensors in (5.22) are symmetric, the multiplicator **A** turns out to be zero:

$$\begin{aligned} t^{\mathrm{vs}}_{lm} &= R^{\Omega d}_{nml}\,\Omega'_n + 2\,R^{dd}_{lmlm}\,\mathring{d}_{lm}, \\ t^{\mathrm{vs}}_{mn} &= R^{\Omega d}_{lnm}\,\Omega'_l + 2\,R^{dd}_{mnmn}\,\mathring{d}_{mn}, \\ t^{\mathrm{vs}}_{nl} &= R^{\Omega d}_{mln}\,\Omega'_m + 2\,R^{dd}_{nlnl}\,\mathring{d}_{nl}, \end{aligned} \tag{5.22}$$

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 balance equations. It can be seen that both the deformation and the rotation of the director have influence both on the symmetric and on the antisymmetric parts of the viscous stress tensor. The number of independent viscosity coefficients is 12, the same number as in the ansatz used by Carlsson, Leslie and Laverty [23]. It is very interesting that the structure of the equations is more transparent than in the theory of uniaxial liquid crystals. This may be due to the fact that neither the direction of the angular velocity of the director 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.

The assumptions we have made in the derivation of these constitutive equations can be summarized as follows:

Gyarmati's variational principle has been used, the validity of which can be proved only in the case of linear relations between the thermodynamical forces and the fluxes [14, 24]. The relations

$$\boldsymbol{J}_s = \frac{1}{T}\boldsymbol{J}_q \quad \text{and} \quad \frac{\partial s}{\partial u} = \frac{1}{T}$$

have been assumed, which are valid in a situation of local equilibrium. It has been shown that in some examples the first of these relations is not valid [25]. But this equation does not mean that we have neglected the contribution of the pointing vector to the nonconvective energy flux, as $\boldsymbol{J}_q$ is only the mechanical heat flux. The model of Grot and Eringen [21] has been accepted for the interaction of the electromagnetic field with matter. It is shown in appendix A how the form of the energy balance used in the present work follows. The couple stress exerted by the electromagnetic field has been assumed to be

$$\boldsymbol{m} = \boldsymbol{P} \times \boldsymbol{E}.$$

The eigenvalues of the alignment-tensor are taken to be constant, i.e. we consider only rigid rotations of the angular distribution function.

The entropy has been approximated by a polynomial quadratic in the components of $\mathbf{O}$ and $\boldsymbol{P}$, and flexoelectric terms have been neglected. These simplifications are only made for the sake of convenience.

$\mathring{\mathbf{O}}$ and $\mathring{\boldsymbol{P}}$ have been neglected in the dissipation potential with the argumentation given above.

Acknowledgements

Many helpful discussions with H. Ehrentraut und Dr. S. Sellers are greatfully acknowledged. We thank the Technical University of Budapest and the Technical University of Berlin for financial support of the cooperation. Financial support by the DAAD sponsoring the co-operation between both our departments is gratefully acknowledged.

Appendix

A) The Balance of Energy in the Electric Field

The energy e, the nonconvective energy flux $\boldsymbol{q}$ and the stress tensor $\mathbf{T}$ can be decomposed into mechanical parts u, $\boldsymbol{J}_q$, $\mathbf{t}$ and electromagnetic parts e_{em}, $\boldsymbol{q}_{em}$, $\mathbf{t}_{em}$:

$$e = u + e_{em}, \quad \boldsymbol{q} = \boldsymbol{J}_q + \boldsymbol{q}_{em}, \quad \mathbf{T} = \mathbf{t} + \mathbf{t}_{em},$$

Within the model of Grot and Eringen [21] the electromagnetic parts are in a nonrelativistic approximation

$$\begin{aligned} e_{em} &= \frac{1}{2\mu_0}\boldsymbol{B}\cdot\boldsymbol{B} + \frac{\varepsilon_0}{2}\boldsymbol{\mathcal{E}}\cdot\boldsymbol{\mathcal{E}} + \boldsymbol{\mathcal{E}}\cdot\boldsymbol{P}, \\ \boldsymbol{q}_{em} &= \boldsymbol{\mathcal{E}}\times\boldsymbol{\mathcal{H}}, \\ \mathbf{t}_{em} &= \left[\frac{1}{2\mu_0}\boldsymbol{B}\cdot\boldsymbol{B} - \frac{1}{2}\varepsilon_0\boldsymbol{\mathcal{E}}\cdot\boldsymbol{\mathcal{E}} - \boldsymbol{B}\cdot\boldsymbol{\mathcal{H}}\right]\boldsymbol{\delta} \\ &\quad + \boldsymbol{\mathcal{E}}\boldsymbol{D} + \boldsymbol{\mathcal{H}}\boldsymbol{B} \end{aligned}$$

with

$$\boldsymbol{\mathcal{E}} = \boldsymbol{E} + \boldsymbol{v}\times\boldsymbol{B}, \quad \boldsymbol{\mathcal{H}} = \boldsymbol{H} - \boldsymbol{v}\times\boldsymbol{D}.$$

With these equations the electromagnetic terms in the energy balance are

$$\begin{aligned} &\frac{\mathrm{d}}{\mathrm{d}t}u_{em} + \nabla\cdot\boldsymbol{q}_{em} - \mathbf{t}_{em}:\nabla\boldsymbol{v} \\ &\quad = \frac{\mathrm{d}}{\mathrm{d}t}\left[\frac{1}{2\mu_0}\boldsymbol{B}\cdot\boldsymbol{B} + \frac{\varepsilon_0}{2}\boldsymbol{\mathcal{E}}\cdot\boldsymbol{\mathcal{E}} + \boldsymbol{\mathcal{E}}\cdot\boldsymbol{P}\right] + \nabla\cdot[\boldsymbol{\mathcal{E}}\times\boldsymbol{\mathcal{H}}] \\ &\quad\quad - \left[\left(\frac{1}{2\mu_0}\boldsymbol{B}\cdot\boldsymbol{B} - \frac{1}{2}\boldsymbol{\mathcal{E}}\cdot\boldsymbol{\mathcal{E}} - \boldsymbol{\mathcal{H}}\cdot\boldsymbol{B}\right)\boldsymbol{\delta} + \boldsymbol{\mathcal{E}}\boldsymbol{D} \right. \\ &\quad\quad \left. + \boldsymbol{\mathcal{H}}\boldsymbol{B}\right]:\nabla\boldsymbol{v}. \end{aligned}$$

Using the Maxwell equations in the formulation [26] with the objective quantities $\mathscr{E}$, $\mathscr{H}$ and the objective time derivatives

$$\overset{*}{\boldsymbol{B}} = \dot{\boldsymbol{B}} + \boldsymbol{B}\nabla\cdot\boldsymbol{v} - \boldsymbol{B}\cdot\nabla\boldsymbol{v},$$
$$\overset{*}{\dot{\boldsymbol{D}}} = \dot{\boldsymbol{D}} + \boldsymbol{D}\nabla\cdot\boldsymbol{v} - \boldsymbol{D}\cdot\nabla\boldsymbol{v},$$

and

$$\mathscr{J} = \boldsymbol{J} - \varrho_e\boldsymbol{v}$$

we arrive at

$$\frac{\mathrm{d}}{\mathrm{d}t}u_{em} + \nabla\cdot\boldsymbol{q}_{em} - \mathbf{t}_{em}:\nabla\boldsymbol{v}$$
$$= \frac{1}{\mu_0}\dot{\boldsymbol{B}}\cdot\boldsymbol{B} + \varepsilon_0\dot{\mathscr{E}}\cdot\mathscr{E} + \dot{\mathscr{E}}\cdot\boldsymbol{P} + \mathscr{E}\cdot\overset{:}{\boldsymbol{P}} - \overset{*}{\dot{\boldsymbol{B}}}\cdot\mathscr{H}$$
$$- \overset{*}{\boldsymbol{D}}\cdot\mathscr{E} - \mathscr{J}\cdot\mathscr{E} - \mathbf{t}_{em}:\nabla\boldsymbol{v}.$$

If we assume that the fluid is incompressible and that the constitutive equations

$$\mathscr{H} = \frac{1}{\mu_o}\boldsymbol{B}, \quad \boldsymbol{j} = 0 \quad \text{and} \quad \varrho_e = 0$$

hold and that $\boldsymbol{B} \equiv 0$, this results in

$$\frac{\mathrm{d}}{\mathrm{d}t}u_{em} + \nabla\cdot\boldsymbol{q}_{em} - \mathbf{t}_{em}:\nabla\boldsymbol{v} = \dot{\boldsymbol{E}}\cdot\boldsymbol{P} = \dot{\boldsymbol{E}}\cdot(\boldsymbol{\varepsilon} - \varepsilon_0\boldsymbol{\delta})\cdot\boldsymbol{E}\cdot\dot{\boldsymbol{P}},$$

which is the last term in the energy balance equation (3.4).

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