Irreversible Thermodynamics of Nonequilibrium Alignment Phenomena in Molecular Liquids and in Liquid Crystals

I. Derivation of Nonlinear Constitutive Laws, Relaxation of the Alignment, Phase Transition

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To treat nonequilibrium alignment phenomena in molecular liquids and in liquids crystals two points of the usual irreversible thermodynamics have to be modified. Firstly, in the specific energy a term quadratic in the alignment tensor is included. Secondly, terms up to 4th order in the alignment are taken into account in the entropy for a nonequilibrium situation. Then the entropy production is calculated. Constitutive laws are set up for the friction pressure tensor and for the tensor which characterizes the decay and the production of the alignment in the balance equation for the alignment tensor. As a first application, the nonlinear relaxation equation for the alignment is considered. For a uni-axial alignment zero and nonzero stable stationary values of the order parameter are found for temperatures above and below the temperature T_K at which the transition from the isotropic to the nematic phase takes place. Small deviations from the equilibrium alignment decay exponentially. For temperatures below T_K the relaxation time turns out to be anisotropic. In the appendix, the entropy associated with the alignment is calculated for a special case.

Introduction

In molecular fluids, nonequilibrium alignment phenomena such as flow birefringence and the relaxation of the alignment occur in addition to the standard transport processes. In this and in a following paper, these phenomena are treated theoretically within the framework of irreversible thermodynamics. Special attention is paid to nematic liquid crystals.

Point of departure is an expression for the entropy in the nonequilibrium situation where terms up to 4-th order in the alignment are taken into account. Furthermore, it is assumed that the total energy of the fluid contains a term quadratic in the alignment. Then the entropy production and the constitutive laws are obtained by standard techniques. The nonlinearity of the constitutive laws is of crucial importance for the occurence of the phase transition "isotropic-nematic" and for the description of nonequilibrium processes at temperatures T close to the transition temperature T_K. The nonlinear constitutive laws contain those derived by de Gennes [1, 2] for $T > T_K$ (isotropic phase) and those proposed previously [2, 3–7] for $T < T_K$ (nematic phase) as special cases.

This paper is divided into 8 sections. Section 1 is devoted to a discussion of the description of the alignment. In Sect. 2, the basic assumptions underlying the present theory are introduced. Firstly, it is assumed that the specific energy of the fluid contains a term proportional to $\mathbf{a}:\mathbf{a}$ where $\mathbf{a}$ is the alignment tensor. Secondly, it is assumed that the entropy in a nonequilibrium situation is the sum of the usual entropy plus a term associated with the alignment. The most general expression for the alignment entropy up to terms of 4th order in the alignment tensor is introduced in Section 3. It contains 4 characteristic coefficients which reduce to 3 coefficients for an unaxial alignment. In Sect. 4, the local conservation laws and the balance equation for the alignment tensor are formulated. The latter contains a term associated with the relaxation and the production of the alignment which has to be determined by a constitutive law. The entropy production is calculated in Section 5. It contains two force-flux pairs which are 2nd rank tensors, viz., the gradient of the velocity and the friction pressure tensor, a tensor which is a nonlinear function of the alignment and a tensor which occurs in the balance equation for the alignment tensor. The constitutive laws involving these 2nd rank tensors are set up in Section 6. They are nonlinear with respect to the alignment. As a first application, the relaxation of the alignment is discussed in Section 7. For small

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alignment and for temperatures $T > T^*$ where T^* is a characteristic temperature, the relaxation equation can be linearized. It contains a relaxation time which is inversely proportional to $1 - T^* T^{-1}$ just as in the theory of de Gennes[1,2]. Then the relaxation of an unaxial alignment is studied in more detail. The stable stationary solutions of the nonlinear relaxation equation for the order parameter are zero for $T > T_K$ and nonzero for $T < T_K$. Here $T_K > T^*$ is the temperature at which the transition from the isotropic to the nematic phase occurs. The transition is of first order. Furthermore, there exist metastable stationary solutions in certain temperature intervals. The relaxation of small deviations of the order parameter from its stable stationary values is exponential. The same is true for small deviations from the metastable stationary values except at the critical temperatures which specify the limits of existence of the metastable states. Then the relaxation of a special biaxial alignment is studied. A stationary solution with finite alignment is found for $T < T^*$. The transition from the isotropic to this special biaxial type of alignment would be of 2nd order. This state, however, has a larger free energy than the nematic phase, i. e. it is metastable. In Sect. 8, the relaxation of the deviation of the alignment tensor from its constant equilibrium value in the nematic phase is considered. For small deviations, a linear relaxation equation is obtained with an anisotropic relaxation time. Applications of the constitutive laws to flow alignment and viscous flow will be studied in a subsequent paper. In the appendix, the entropy associated with the alignment is calculated for uncorrelated particles.

§ 1. Description of the Alignment

Before the foundations of the irreversible thermodynamics of alignment phenomena are discussed, the description of the alignment has to be specified.

In this paper, liquids of axisymmetric molecules are considered. Their alignment is characterized by the 2nd rank tensor.

$$\mathbf{a} = \zeta \langle \overline{\boldsymbol{u}\boldsymbol{u}} \rangle \, . \tag{1.1}$$

Here $\boldsymbol{u}$ is a unit vector parallel to the figure axis of a molecule and $\langle \ldots \rangle$ refers to a local average. The symbol $\overline{\ldots}$ indicates the symmetric traceless part of a tensor. In particular, one has

$$\overline{\boldsymbol{u}\boldsymbol{u}} = \boldsymbol{u}\boldsymbol{u} - \tfrac{1}{3}\boldsymbol{\delta} \tag{1.2}$$

where $\boldsymbol{\delta}$ is the unit tensor. In Eq. (1.1), ζ is a numerical factor which can be chosen conveniently. Some specific choices for ζ will be mentioned later.

The part of the anisotropic dielectric tensor which is associated with the alignment of the molecules is proportional to $\mathbf{a}$. Hence the alignment tensor $\mathbf{a}$ is of crucial importance for the birefringence and for the depolarized Rayleigh scattering. The anisotropic part of the magnetic susceptibility tensor is also proportional to $\mathbf{a}$. In fact, this relation can be used to introduce the alignment tensor on a macroscopic basis[3] rather than through Equation (1.1).

In general, the tensor $\mathbf{a}$ can be written as

$$\mathbf{a} = \sum_{i=1}^{3} a_i \, \boldsymbol{e}^{(i)} \boldsymbol{e}^{(i)} \tag{1.3}$$

where the $\boldsymbol{e}^{(i)}$ are unit vectors parallel to the principal axes of the tensor $\mathbf{a}$ and a_i are its eigenvalues (i. e. diagonal elements of $\mathbf{a}$ in the principal axes system). Due to

$$\sum_{i=1}^{3} a_i = 0 \, , \tag{1.4}$$

($\mathbf{a}$ is a traceless tensor), only two of the 3 eigenvalues a_i are linearly independent. In connection with some applications, two special types of alignment are of interest.

i) Unaxial Alignment

If the alignment is of unaxial type, $\mathbf{a}$ can be written as

$$\mathbf{a} = \sqrt{\tfrac{3}{2}} \, a \, \overline{\boldsymbol{n}\boldsymbol{n}} \tag{1.5}$$

where $\boldsymbol{n}$ is a spacefixed unit vector termed "director". The scalar alignment parameter a is given by (notice that $\overline{\boldsymbol{n}\boldsymbol{n}} : \overline{\boldsymbol{n}\boldsymbol{n}} = \boldsymbol{n} \cdot \overline{\boldsymbol{n}\boldsymbol{n}} \cdot \boldsymbol{n} = 2/3$)

$$a = \sqrt{\tfrac{3}{2}} \, \boldsymbol{n} \cdot \mathbf{a} \cdot \boldsymbol{n} = \sqrt{\tfrac{2}{3}} \, \zeta \langle P_2(\boldsymbol{u} \cdot \boldsymbol{n}) \rangle \, , \tag{1.6}$$

where P_2 is the 2nd Legendre polynomiacl. If ζ is put equal to $\zeta_{\mathrm{MS}} \equiv \sqrt{3/2}$, a is the order parameter used in the Maier-Saupe theory of liquid crystals[2,8]. In (1.5), the factor $\sqrt{3/2}$ has been inserted such that one has

$$\mathbf{a} : \mathbf{a} = a^2 \tag{1.7}$$

for the unaxial alignment. Incidentally, (1.6) implies that a is bounded according to

$$-\tfrac{1}{2} \sqrt{\tfrac{2}{3}} \, \zeta \leqq a \leqq \sqrt{\tfrac{2}{3}} \, \zeta \, . \tag{1.8}$$

This follows from $-\frac{1}{2} \leqq P_2(\boldsymbol{u} \cdot \boldsymbol{n}) \leqq 1$.

For a tensor of the type (1.5), one of the principal axes is parallel to $\boldsymbol{n} \equiv \boldsymbol{e}^{(3)}$, the two other axes are anywhere in the plane perpendicular to $\boldsymbol{n}$.

The pertaining eigenvalues are

$$a_1 = a_2 = -\tfrac{1}{2}\, a_3\,, \quad a_3 = \sqrt{\tfrac{2}{3}}\, a\,. \tag{1.9}$$

The spontaneous alignment set up in a nematic liquid crystal is of the type (1.5).

ii) Special Biaxial Alignment

A special biaxial alignment which, e. g. occurs in connection with flow birefringence [9–11], is described by

$$\mathbf{a} = \sqrt{2}\, a\, \overline{\boldsymbol{n}^{(1)} \boldsymbol{n}^{(2)}}\,, \tag{1.10}$$

where $\boldsymbol{n}^{(1)}$ and $\boldsymbol{n}^{(2)}$ are unit vectors which are perpendicular to each other $(\boldsymbol{n}^{(1)} \cdot \boldsymbol{n}^{(2)} = 0)$. In this case, the "magnitude" of the alignment is also characterized by a single scalar parameter, viz. a. The factor $\sqrt{2}$ has been inserted in (1.10) such that

$$\mathbf{a} : \mathbf{a} = a^2 \tag{1.11}$$

provided that the alignment is of the special type (1.10). The principal axes of the tensor (1.10) are parellel to

$$\boldsymbol{e}^{(1,2)} = \frac{1}{\sqrt{2}}\, (\boldsymbol{n}^{(1)} \pm \boldsymbol{n}^{(2)})\,, \quad \boldsymbol{e}^{(3)} = \boldsymbol{n}^{(1)} \times \boldsymbol{n}^{(2)}\,. \tag{1.12}$$

The pertaining eigenvalues are

$$a_1 = \tfrac{1}{2} \sqrt{2}\, a\,, \quad a_2 = -a_1\,, \quad a_3 = 0\,. \tag{1.13}$$

Due to $a_3 = 0$, this special type of alignment will be referred to as "planar" alignment.

§ 2. The Basic Assumptions

The expression for the entropy production required to set up the constitutive laws for irreversible processes is derived subject to two assumptions.

Firstly, the total specific energie e shall be given by

$$e = \tfrac{1}{2} v^2 + \frac{1}{2\,m}\, \boldsymbol{\omega} \cdot \boldsymbol{\Theta} \cdot \boldsymbol{\omega} - \tfrac{1}{2}\, \varepsilon\, \mathbf{a} : \mathbf{a} + u \tag{2.1}$$

where $\boldsymbol{v}$ is the flow velocity, $\boldsymbol{\omega}$ is the average angular velocity, $\boldsymbol{\Theta}$ is the moment of inertia tensor of a molecule, and u is the specific internal energy. The quantitity ε characterizes the energy associated with the alignment. The addition of a term proportional to $\mathbf{a} : \mathbf{a}$ can be justified as follows. In the presence of an electric field $\boldsymbol{E}$ a term proportional to $\overline{\boldsymbol{E}\boldsymbol{E}} : \mathbf{a}$ will contribute to e provided that the molecules possess an anisotropic molecular polarizability. Here, in the spirit of a mean field theory, $\overline{\boldsymbol{E}\boldsymbol{E}}$ is replaced by an internal field tensor proportional to $\mathbf{a}$. The sign of ε has been chosen such that $\varepsilon > 0$ if the ordered state $(\mathbf{a} \neq 0)$ is energetically more favorable than the isotropic phase $(\mathbf{a} = 0)$. For a liquid crystal, ε can be inferred from the latent heat released when it undergoes a transition from the isotropic to the nematic phase.

Secondly, it is assumed that the specific entropy s is, in a nonequilibrium situation, given by

$$s = s_{\text{eq}}(u, \varrho) + s_{\text{a}}(\mathbf{a})\,. \tag{2.2}$$

Here ϱ is the mass density. The subscript "eq" indicates that the functional dependence of s_{eq} on u and ϱ is the same as in thermal equilibrium. In particular, s_{eq} obeys the Gibbs relation

$$\mathrm{d}s_{\text{eq}} = T^{-1}\, (\mathrm{d}u + P_{\text{eq}}\, \mathrm{d}\varrho^{-1})\,, \tag{2.3}$$

where T and $P_{\text{eq}} = P_{\text{eq}}(T, \varrho)$ are the temperature and the thermodynamic pressure of the liquid. The quantity $s_{\text{a}}(\mathbf{a})$ is the contribution to the nonequilibrium entropy associated with the alignment. For $s_{\text{a}} = 0$, (2.2) reduces to the standard assumption underlying the irreversible thermodynamics of transport processes [12, 13]. An explicit expression for s_{a} is introduced in the following section.

§ 3. Alignment Entropy

Up to terms of 4th order in $\mathbf{a}$, the most general expression for the specific entropy s_{a} associated with the alignment is

$$s_{\text{a}} = -\frac{k_{\text{B}}}{m} \left[\tfrac{1}{2} A_0\, a_{\mu\nu}\, a_{\mu\nu} - \tfrac{1}{3} \sqrt{6}\, B\, a_{\mu\nu}\, a_{\nu\lambda}\, a_{\lambda\mu} + \tfrac{1}{4}\, C_1 (a_{\mu\nu}\, a_{\mu\nu})^2 + \tfrac{1}{4}\, C_2\, a_{\mu\nu}\, a_{\nu\lambda}\, a_{\lambda\varkappa}\, a_{\varkappa\mu}\right], \tag{3.1}$$

where k_{B} is Boltzmann's constant. Greek subscripts refer to Cartesian components. The summation convention is used. The characteristic (dimensionless) coefficients, A_0, B, C_1, C_2 in general, are functions of the thermodynamic variables, e. g. of T and ϱ. Their values depend on the choice of the numerical factor ζ occurring in (1.1). Later, they will be related to measurable quantities.

An expression for the alignment entropy can be calculated from the one-particle distribution function in the nonequilibrium state according to Boltzmann's prescription[14]; for an application to multipole relaxation see Ref.[15]. This procedure is only valid for dilute systems (e. g. dilute gases, dilute suspensions) where the interparticle correlation plays no dominant role. Yet it seems worth mentioning that the entropy calculated in this manner (see the appendix) is of the form (3.1) with the coefficients $A_0, \ldots, C_2$ given by

$$A_0 = 1, \quad B = \sqrt{\tfrac{5}{7}}, \quad C_1 = \tfrac{5}{7}, \quad C_2 = 0, \tag{3.2}$$

if ζ is put equal to $\sqrt{\tfrac{15}{2}}$. For a liquid, these coefficients will certainly deviate from the special values (3.2). However, it can be assumed that A_0, B, C_1, are positive and practically independent of the temperature over a reasonable temperature range.

Next, the alignment entropy is considered for the special types of alignment discussed in Section 1. For an unaxial alignment (cf. 1.5), (3.1) reduces to

$$s_{\text{a}} = -\frac{k_{\text{B}}}{m}\left[\tfrac{1}{2} A_0 a^2 - \tfrac{1}{3} B a^3 + \tfrac{1}{4} C a^4\right], \tag{3.3}$$

with

$$C = C_1 + \tfrac{1}{2} C_2 . \tag{3.4}$$

Notice that s_{a} is always negative (higher order implies lower entropy) provided that

$$A_0 > 0, \quad C > 0, \quad \text{and} \quad B^2 < \tfrac{9}{2} A_0 C . \tag{3.5}$$

The special values (3.2) indeed fulfill, these inequalities.

For the planar biaxial alignment (1.10), Eq. 63.1) reduces to

$$s_a = -(k_{\text{B}}/m)\left[\tfrac{1}{2} A_0 a^2 + \tfrac{1}{4} C a^4\right] . \tag{3.6}$$

Notice that no third order term occurs in this case.

§ 4. Local Conservation Laws, Balance Equations for the Alignment and the Internal Energy

Of fundamental importance for the irreversible thermodynamics are the local conservation laws for the mass density, the energy, the linear momentum and the angular momentum. The first three of these equations can be written as[13]

$$\mathrm{d}\varrho/\mathrm{d}t + \varrho \nabla \cdot \boldsymbol{v} = 0 , \tag{4.1}$$

$$\varrho\, \mathrm{d}e/\mathrm{d}t + \nabla \cdot (\boldsymbol{e} - \varrho\, e\, \boldsymbol{v}) = 0 , \tag{4.2}$$

$$\varrho\, \mathrm{d}\boldsymbol{v}/\mathrm{d}t + \nabla \cdot \mathbf{P} = 0 . \tag{4.3}$$

Here

$$\mathrm{d}/\mathrm{d}t \equiv \partial/\partial t + \boldsymbol{v} \cdot \nabla \tag{4.4}$$

is the substantial derivative. In (4.2) and (4.3), $\boldsymbol{e}$ and $\mathbf{P}$ denote the total energy flux density and the total pressure tensor, respectively, As a consequence of the conservation of the total angular momentum, the internal angular momentum obeys the following balance equation[13, 16]:

$$(1/m)\, \varrho\, \mathrm{d}j_\mu/\mathrm{d}t - \varepsilon_{\mu\nu\lambda} P_{\nu\lambda} = 0 \tag{4.5}$$

where $\boldsymbol{j} = \boldsymbol{\Theta} \cdot \boldsymbol{\omega}$ is the average internal angular momentum and $\varepsilon_{\mu\nu\lambda}$ is the Levi-Civita tensor. Notice that $\varepsilon_{\mu\nu\lambda} P_{\nu\lambda} = \varepsilon_{\mu\nu\lambda} p^{a}_{\nu\lambda}$ where $p^{a}_{\nu\lambda}$ is the antisymmetric part of the pressure tensor.

The alignment tensor obeys a balance equation of the form

$$\mathrm{d}a_{\mu\nu}/\mathrm{d}t - \omega_\lambda (\varepsilon_{\mu\lambda\varkappa} a_{\varkappa\nu} + \varepsilon_{\nu\lambda\varkappa} a_{\varkappa\mu}) = A_{\mu\nu} . \tag{4.6}$$

The 2nd term in Eq. (4.8) describes the change of **a** due to the rotation of the molecular axes in the presence of a nonvanishing average angular velocity $\boldsymbol{\omega}$. The quantity $A_{\mu\nu}$ is associated with the decay and production of the alignment. In Eq. (4.6) the alignment flux is disregarded, i. e. the alignment is assumed to be spatially homogeneous.

A balance equation for the internal energy is also needed. Use of relation (2.1) and of Eqs. (4.2, 3, 6) leads to

$$\begin{aligned} \varrho\, \mathrm{d}u/\mathrm{d}t + \nabla \cdot q = & -P_{\mu\nu} \nabla_\mu v_\nu \\ & - \omega_\mu \varepsilon_{\mu\nu\lambda} P_{\nu\lambda} + \varrho\, \varepsilon\, a_{\mu\nu} A_{\mu\nu} , \end{aligned} \tag{4.7}$$

with the heat flux

$$q_\mu = e_\mu - \varrho\, e\, v_\mu - P_{\mu\nu} v_\nu . \tag{4.8}$$

The Eqs. (4.1 – 3), (4.6, 7) have to be supplemented by constitutive laws for the heat flux, the friction pressure tensor and for the tensor $A_{\mu\nu}$. The entropy production to be derived in the following section provides the guide to set up these constitutive laws.

§ 5. Entropy Production

According to Eqs. (2.2, 3), the time change of the specific entropy is given by

$$\varrho \frac{\mathrm{d}s}{\mathrm{d}t} = T^{-1}\left(\varrho \frac{\mathrm{d}u}{\mathrm{d}t} + P_{\text{eq}}\, \varrho \frac{\mathrm{d}\varrho^{-1}}{\mathrm{d}t}\right) + \varrho\, s_{\mu\nu} \frac{\mathrm{d}a_{\mu\nu}}{\mathrm{d}t} \tag{5.1}$$

with

$$s_{\mu\nu} = \partial s_{\text{a}}/\partial a_{\mu\nu} . \tag{5.2}$$

With the help of Eqs. (4.1, 6, 7), Eq. (5.1) can be cast into the form

$$\varrho \, \mathrm{d}s/\mathrm{d}t + \nabla_\mu (T^{-1} q_\mu) = \varrho (\delta s/\delta t)_{\text{irrev.}} . \qquad (5.3)$$

The 2nd term represents the entropy flow. The entropy production due to irreversible processes is the sum of the usual entropy production $(\delta s/\delta t)^{\text{iso}}_{\text{irrev}}$ and of terms associated with the alignment, viz.

$$\varrho \left(\frac{\delta s}{\delta t}\right)_{\text{irrev}} = \varrho \left(\frac{\delta s}{\delta t}\right)^{\text{iso}}_{\text{irrev}} - \varrho \, \frac{k_{\text{B}}}{m} \, \Sigma_{\mu\nu} A_{\mu\nu} . \qquad (5.4)$$

Here the quantity

$$\Sigma_{\mu\nu} = - (m/k_{\text{B}}) (s_{\mu\nu} + T^{-1} \varepsilon \, a_{\mu\nu}) \qquad (5.5)$$

has been introduced. Up to terms of 4th order in **a**, the tensor $\Sigma_{\mu\nu}$ is given by [cf. Eq. (4.1)]

$$\Sigma_{\mu\nu} = A \, a_{\mu\nu} - \sqrt{6} \, B \, \overline{a_{\mu\lambda} \, a_{\lambda\nu}} + C_1 \, a_{\mu\nu} \, a_{\lambda\varkappa} \, a_{\lambda\varkappa} + C_2 \, \overline{a_{\mu\lambda} \, a_{\lambda\varkappa} \, a_{\varkappa\nu}} , \qquad (5.6)$$

with

$$A = A_0 - m \, \varepsilon / k_{\text{B}} T = A_0 (1 - T^*/T) . \qquad (5.7)$$

The characteristic temperature T^* is defined by

$$k_{\text{B}} T^* = m \, \varepsilon \, A_0{}^{-1} . \qquad (5.8)$$

Since A_0 is positive, the coefficient A is positive for $T > T^*$. Notice that $\Sigma_{\mu\nu}$, as given by (5.6), can be written as

$$\Sigma_{\mu\nu} = \partial \Sigma / \partial a_{\mu\nu} \qquad (5.9)$$

with

$$\Sigma = \tfrac{1}{2} A \, a_{\mu\nu} \, a_{\mu\nu} - \tfrac{1}{3} \sqrt{6} \, B \, a_{\mu\nu} \, a_{\nu\lambda} \, a_{\lambda\mu} + \tfrac{1}{4} C_1 (a_{\mu\nu} \, a_{\mu\nu})^2 + \tfrac{1}{4} C_2 \, a_{\mu\nu} \, a_{\nu\lambda} \, a_{\lambda\varkappa} \, a_{\varkappa\mu} . \qquad (5.10)$$

Comparison with Eq. (3.1) shows that Σ is equal to $-(m/k_{\text{B}}) s_{\text{a}}$ with A_0 replaced by A, cf. Eq. (5.7). The quantity $(k_{\text{B}} T/m) \Sigma$ is the specific free energy associated with the alignment. An expresion for the entropy production in liquid crystals similar to (5.4) but with $\Sigma_{\mu\nu}$ approximated by the linear term $A \, a_{\mu\nu}$ has been proposed by de Gennes [1, 2].

The term $(\delta s/\delta t)^{\text{iso}}_{\text{irrev}}$ occurring in Eq. (5.4) is given by [13] (the superscript "iso" refers to isotropic)

$$\varrho \left(\frac{\delta s}{\delta t}\right)^{\text{iso}}_{\text{irrev}} = - T^{-2} q_\mu \nabla_\mu T - T^{-1} p \nabla_\mu v_\mu - T^{-1} p^a_{\mu\nu} (\nabla_\nu v_\mu + \varepsilon_{\mu\nu\lambda} \, \omega_\lambda) - T^{-1} \overline{p_{\mu\nu}} \, \overline{\nabla_\mu v_\nu} . \qquad (5.11)$$

Here

$$p = \tfrac{1}{3} p_{\lambda\lambda} , \quad p^a_{\mu\nu} = \tfrac{1}{2} (p_{\mu\nu} - p_{\nu\mu}) , \qquad (5.12)$$

$$\overline{p_{\mu\nu}} = \tfrac{1}{2} (p_{\mu\nu} + p_{\nu\mu}) - \tfrac{1}{3} p_{\lambda\lambda} \, \delta_{\mu\nu} \qquad (5.13)$$

are the scalar (spherical), antisymmetric and symmetric traceless parts of the friction pressure tensor

$$p_{\mu\nu} = P_{\nu\mu} - P_{\text{eq}} \, \delta_{\mu\nu} . \qquad (5.14)$$

In this paper, the imphasis is on the constitutive laws for the quantities $\overline{p_{\mu\nu}}$, $A_{\mu\nu}$ which are set up such that the entropy production is positive.

Before these points are discussed, a remark on the antisymmetric part $p^a_{\mu\nu}$ of the pressure tensor is in order. The linear constitutive law for $p^a_{\mu\nu}$ can be written as [13, 16]

$$\boldsymbol{p}^{\text{a}} = - (\varrho/m) \, \tau_{\text{r}}{}^{-1} \, \boldsymbol{\Theta} \cdot (\boldsymbol{\omega} - \tfrac{1}{2} \operatorname{rot} \boldsymbol{v}) \qquad (5.15)$$

with $p^a_\mu = \varepsilon_{\mu\nu\lambda} \, p^a_{\nu\lambda}$. This relation is also of importance for the time development of the alignment since the Eq. (4.6) involves the molecular angular velocity $\boldsymbol{\omega}$. Insertion of (5.15) into (4.5) leads to

$$\mathrm{d}\boldsymbol{\omega}/\mathrm{d}t + \tau_{\text{r}}{}^{-1} (\boldsymbol{\omega} - \tfrac{1}{2} \operatorname{rot} \boldsymbol{v}) = 0 . \qquad (5.16)$$

Clearly, τ_{r} introduced in (5.15), is the rotational relaxation time. In liquid crystals and in most ordinary liquids τ_{r} is very short compared with the orientational relaxation time which characterizes the decay of the alignment. Thus for the applications to be considered here $p^a_{\mu\nu} = 0$ and consequently

$$\boldsymbol{\omega} = \tfrac{1}{2} \operatorname{rot} \boldsymbol{v} \qquad (5.17)$$

can be assumed safely.

§ 6. Constitutive Laws for the Alignment and the Friction Pressure Tensor

The entropy production (5.4) contains two force-flux pairs which are symmetric traceless tensors, viz. $\overline{p_{\mu\nu}}$, $\overline{\nabla_\mu v_\nu}$, and $A_{\mu\nu}$, $\Sigma_{\mu\nu}$. The part of the entropy production associated with these tensors of rank 2 can be written as

$$\left(\frac{\delta s}{\mathrm{d}t}\right)^{(2)}_{\text{irrev}} = - \frac{k_{\text{B}}}{m} \, [A_{\mu\nu} \Sigma_{\mu\nu} + P_k{}^{-1} \overline{p_{\mu\nu}} \, \overline{\nabla_\mu v_\nu}] , \qquad (6.1)$$

where

$$P_k = (1/m) \, \varrho \, k_{\text{B}} T \qquad (6.2)$$

is the "kinetic pressure". If $A_{\mu\nu}$ and $\sqrt{2} \, \overline{\nabla_\mu v_\nu}$ are considered as "fluxes", $\Sigma_{\mu\nu}$ and $(\sqrt{2} P_k)^{-1} \overline{p_{\mu\nu}}$

as the pertaining forces, the constitutive laws are

$$A_{\mu\nu} = \omega_{\mathrm{a}} \Sigma_{\mu\nu} + \omega_{\mathrm{a}p} (\sqrt{2}\, P_k)^{-1} \overline{p_{\mu\nu}}, \tag{6.3}$$

$$-\sqrt{2}\, \overline{\nabla_\mu v_\nu} = \omega_{p\mathrm{a}} \Sigma_{\mu\nu} + (\sqrt{2}\, P_k)^{-1} \overline{p_{\mu\nu}}. \tag{6.4}$$

The relaxation coefficients $\omega_{\mathrm{a}}, \ldots$ occurring in Eqs. (6.3, 4) have the properties

$$\omega_{\mathrm{a}} > 0, \quad \omega_p > 0, \quad \omega_{\mathrm{a}}\, \omega_p > \omega_{\mathrm{a}p}\, \omega_{p\mathrm{a}}, \tag{6.5}$$

and

$$\omega_{\mathrm{a}p} = \omega_{p\mathrm{a}}. \tag{6.6}$$

The inequalities (6.5) guarantee that the entropy production (6.1) is positive. Note that $\omega_{\mathrm{a}p}$ can either be positive or negative. Equation (6.6) is an Onsager symmetry relation which is due to time reversal invariance of the molecular interaction.

Notice that the constitutive laws (6.3, 4) are nonlinear with respect to the alignment tensor **a**, cf. Equation (5.6). If $\Sigma_{\mu\nu}$ is approximated by its linear term $A\, a_{\mu\nu}$ Eqs. (6.3, 4) are very similar to the previously derived equations [17] governing the flow birefringence in gases [18].

Solution of Eqs. (6.3, 4) for $\Sigma_{\mu\nu}$ and $\overline{p_{\mu\nu}}$ yields

$$-\Sigma_{\mu\nu} = \tau_{\mathrm{a}} A_{\mu\nu} + \sqrt{2}\, \tau_{\mathrm{a}p} \overline{\nabla_\mu v_\nu} \tag{6.7}$$

$$-\overline{p_{\mu\nu}} = \sqrt{2}\, P_k \tau_{p\mathrm{a}} A_{\mu\nu} + 2 P_k \tau_p \overline{\nabla_\mu v_\nu}. \tag{6.8}$$

The relaxation times $\tau_{..}$ are related to the relaxation frequencies $\omega_{..}$ by

$$\tau_{\mathrm{a}} = \omega_{\mathrm{a}}^{-1} \left(1 - \frac{\omega_{\mathrm{a}p}\, \omega_{p\mathrm{a}}}{\omega_{\mathrm{a}}\, \omega_p}\right)^{-1}, \quad \tau_p = \frac{\omega_{\mathrm{a}}}{\omega_p} \tau_{\mathrm{a}}, \tag{6.9}$$

$$\tau_{\mathrm{a}p} = -\frac{\omega_{\mathrm{a}p}}{\omega_p} \tau_{\mathrm{a}}, \quad \tau_{p\mathrm{a}} = -\frac{\omega_{\mathrm{a}p}}{\omega_p} \tau_{\mathrm{a}}. \tag{6.10}$$

The Onsager symmetry relation (6.6) implies

$$\tau_{\mathrm{a}p} = \tau_{p\mathrm{a}}. \tag{6.11}$$

Due to (6.5), the $\tau_{..}$ obey the inequalities

$$\tau_{\mathrm{a}} > 0, \quad \tau_p > 0, \quad \tau_{\mathrm{a}}\, \tau_p > \tau_{\mathrm{a}p}\, \tau_{p\mathrm{a}}. \tag{6.12}$$

The Eqs. (6.7, 8) can be inferred from (6.1) directly if $\Sigma_{\mu\nu}$ and $(\sqrt{2}\, P_k)^{-1} \overline{p_{\mu\nu}}$ are considered as fluxes, then $A_{\mu\nu}$ and $\sqrt{2}\, \overline{\nabla_\mu v_\nu}$ are the pertaining forces. The factor $\sqrt{2}$ has been inserted in (6.3, 4) and (6.7, 8) such that the shear viscosity η is related to τ_p by $\eta = P_k \tau_p$ (without any numerical factor).

The application of Eqs. (6.3, 4) or (6.7, 8) to the relaxation of the alignment will be discussed in the following sections. Applications to flow birefringence and its reciprocal phenomenon, and viscous flow will be discussed in a subsequent paper.

§ 7. Relaxation of the Alignment, Phase Transitions

a) General Remarks

For $\boldsymbol{v} = 0$ (no flow) Eqs. (6.3, 4) or Eq. (6.7) imply $A_{\mu\nu} = \tau_{\mathrm{a}}^{-1} \Sigma_{\mu\nu}$. Insertion of $A_{\mu\nu}$ into Eq. (4.6) yields

$$\partial a_{\mu\nu}/\partial t + \tau_{\mathrm{a}}^{-1} \Sigma_{\mu\nu} = 0; \tag{7.1}$$

for τ_{a} see (6.9). Notice that (7.1) is a nonlinear relaxation equation since $\Sigma_{\mu\nu}$ as given by (5.6) is nonlinear with respect to $a_{\mu\nu}$. If $\Sigma_{\mu\nu}$ is replaced by its linear approximation $A\, a_{\mu\nu}$, Eq. (7.1) reduces to the linear relaxation equation

$$\partial a_{\mu\nu}/\partial t + \tau^{-1} a_{\mu\nu} = 0, \tag{7.2}$$

with the relaxation time

$$\tau = A^{-1} \tau_{\mathrm{a}} = A_0^{-1} (1 - T^*/T)^{-1} \tau_{\mathrm{a}}. \tag{7.3}$$

This linear approximation is applicable for small alignment and for $T > T^*$ where A and consequently τ is positive. According to Eq. (7.2), the alignment relaxes to zero. This occurs in ordinary liquids and in liquid crystals at temperatures T above the characteristic temperature T_{K} at which the transition from the isotropic to the nematic phase occurs in a liquid crystal. The temperature dependence of the relaxation time τ as found experimentally for the isotropic phase of liquid crystals is indeed of the form (7.3), e. g. see Reference [19].

For $T < T_{\mathrm{K}}$, the linear relaxation Eq. (7.2) is certainly inappropriate. The reason is that the alignment does not relax to zero but to a finite value. Next, it is demonstrated that the full nonlinear Eq. (7.1) describes such a behavior. To this purpose an unaxial alignment is studied. The alignment of nematic liquid crystals is of this type.

b) Relaxation of an Unaxial Alignment, Phase Transition

For an unaxial alignment with a constant director but with a time dependent order parameter a, cf. Eq. (1.5), Eq. (7.1) is equivalent to

$$\partial a/\partial t + \tau_{\mathrm{a}}^{-1} (A\, a - B\, a^2 + C\, a^3) = 0; \tag{7.4}$$

for C see Eq. (3.4). Firstly, it is noted that Eq. (7.4) has 3 solutions $a = 0$ and $a = a_{\mathrm{I,\,II}}$ for a stationary situation i. e. for $\partial a/\partial t = 0$. The nonzero stationary solutions are.

$$a_{\mathrm{I,\,II}} = \frac{1}{2}\,\frac{B}{C}\left(1 \pm \sqrt{1-\frac{4\,A\,C}{B^2}}\right). \qquad (7.5)$$

The order parameter is real. Hence the values (7.5) for $a_{\mathrm{I,\,II}}$ are of physical relevance only if the inequality $B^2 \leqq 4\,A\,C$ is fulfilled. In the following, A_0, B, and C are assumed to be independent of the temperature; for A see Equation (5.7). Then this inequality is fulfilled for temperatures $T \leqq T_{\mathrm{K}}{}^*$ where $T_{\mathrm{K}}{}^*$ is defined by

$$T_{\mathrm{K}}{}^* = T^*\,(1 - B^2/4\,A_0\,C)^{-1}\,. \qquad (7.6)$$

In order to discuss the stability of the stationary solutions, it is noticed that Eq. (7.4) can be written as

$$\partial a/\partial t + \tau_{\mathrm{a}}{}^{-1}\;\mathrm{d}\Sigma/\mathrm{d}a = 0\,, \qquad (7.7)$$

with effective potential

$$\Sigma = \tfrac{1}{2}\,A\,a^2 - \tfrac{1}{3}\,B\,a^3 + \tfrac{1}{4}\,C\,a^4; \qquad (7.8)$$

cf. Eq. (5.10); $(k_{\mathrm{B}}\,T/m)\,\Sigma$ is recalled as the specific free energy associated with the alignment. Thus the mathematical analysis of the stability of the stationary solution of Eq. (7.4) is equivalent to the analysis of the equilibrium states of a liquid crystal based on a Landau expression for the free energy analogous to (7.8); cf. Ref. [20]. States for which Σ assumes minimal values are (locally) stable. The stationary value of the order parameter for which Σ has an absolute minimum corresponds to a globally stable situation (thermal equilibrium).

At the transition temperature

$$T_{\mathrm{K}} = T^*\,(1 - \tfrac{2}{9}\,B^2/A_0\,C)^{-1} \qquad (7.9)$$

Σ possesses two minima of equal height for $a = 0$ and

$$a = a_{\mathrm{K}} \equiv \tfrac{2}{3}\,B/C\,. \qquad (7.10)$$

Note that $T^* < T_{\mathrm{K}} < T_{\mathrm{K}}{}^*$. The thermal equilibrium values of a are

$$a = 0 \quad \text{for} \quad T > T_{\mathrm{K}} \quad \text{and} \quad a = a_{\mathrm{eq}} \quad \text{with}$$

$$a_{\mathrm{eq}} = a_{\mathrm{I}} = a_{\mathrm{K}}\,[\tfrac{3}{4} + \tfrac{1}{4}\,\sqrt{1 + 8\,(T_{\mathrm{K}}/T - 1)\;(T_{\mathrm{K}}/T^* - 1)^{-1}}] \qquad (7.11)$$

for $T < T_{\mathrm{K}}$. Metastable values of a corresponding to local but not global minima of Σ are

$a = a_{\mathrm{I}}$ for $T_{\mathrm{K}} < T \leqq T_{\mathrm{K}}{}^*$, $a = 0$ for $T^* < T < T_{\mathrm{K}}$,

and $a = a_{\mathrm{II}}$ for $T < T^*$.

Equation (7.11) cannot be expected to describe the temperature dependence of the equilibrium alignment too far below T_{K}. Terms of higher than 4th order in the alignment will contribute to the alignment entropy if the alignment increases. Furthermore, Eq. (7.11) is based on the assumption that the temperature dependence of A_0, B, and C can be ignored. On the other hand, the temperature intervall in which the nematic phase exists is not too large either.

With the help of Eqs. (7.9, 10), the coefficients A_0, B, C are related to the measurable quantities T_{K}, T^*, and a_{K}. The latent heat (per particle) is

$$-T_{\mathrm{K}}\,m\,s_{\mathrm{a}}(a_{\mathrm{K}}) = \tfrac{1}{2}\,a_{\mathrm{K}}{}^2\,A_0\,k_{\mathrm{B}}\,T^* = \tfrac{1}{2}\,\varepsilon\,a_{\mathrm{K}}{}^2; \qquad (7.12)$$

cf. Eqs. (3.3) and (5.8). It seems worth mentioning that the special values (3.2) for the coefficients A_0, B, C yield $\delta_{\mathrm{K}} = (T_{\mathrm{K}} - T^*)\,T_{\mathrm{K}}{}^{-1} = 2/63$ and a value for a_{K} corresponding to $\langle P_2 \rangle_{\mathrm{K}} = 2/15$, cf. Equation (1.6). The experimentally observed values for δ_{K} und $\langle P_2 \rangle_{\mathrm{K}}$ are smaller and larger by factors of about 0.1 and 3, respectively. It is surprising that the discrepancy is not larger since the special values (3.2) were obtained subject to the assumption that the effect of intermolecular correlations on the alignment entropy can be ignored.

The dynamic behaviour of the order parameter is governed by Equation (7.4). Though this nonlinear equation can be solved in general, only some features of special interest are discussed here. In particular, it is noticed that small deviations of the order parameter from its equilibrium values $a = 0$ $(T > T_{\mathrm{K}})$ and $a = a_{\mathrm{I}}$ ($T < T_{\mathrm{K}}$ decay exponentially with a relaxation time τ given by Eq. (7.3) for $T > T_{\mathrm{K}}$ and by

$$\begin{aligned}\tau &= \tau_{\mathrm{a}}\,(A - 2\,B\,a_{\mathrm{I}} + 3\,C\,a_{\mathrm{I}}{}^2)^{-1}\\ &= \tau_{\mathrm{a}}\,(2\,C\,a_{\mathrm{I}}{}^2 - B\,a_{\mathrm{I}})^{-1}\,,\end{aligned} \qquad (7.13)$$

for $T < T_{\mathrm{K}}$. For $T = T_{\mathrm{K}}$, τ as given by (7.3) is equal to the expression (7.13).

So far, the relaxation of the alignment in a spatially homogeneous system has tacitly been treated as isothermal, i. e. the heat conductivity has been assumed to be practically infinite. For an adiabatically isolated system, Eq. (4.7) implies

$$c_p\,T - \tfrac{1}{2}\,\varepsilon\,a_{\mu\nu}\,a_{\mu\nu} = \text{const} \qquad (7.14)$$

where c_p is the specific heat. Thus $A = A_0(1 - T^*/T)$ occurring in the relaxation equation is time dependent. However, if terms nonlinear in the alignment are ignored as in Eq. (7.2), A can still be considered as constant, i. e. the relaxation time (7.3) is also applicable to an adiabatic process. The situation is slighly different for the relaxation of a small deviation of the order parameter from its equilibrium value a_I in the nematic phase. In this case, the adiabatic relaxation time is given by an expression of the form (7.13) with $3\,C$ replaced by

$$3\,C + A_0 \frac{T^*}{T}\,\frac{\varepsilon}{c_p\,T} = 3\,C + \frac{k_\mathrm{B}}{m\,c_p}\left(\frac{T^*}{T}\right)^2 A_0{}^2\,.$$

Next, the isothermal relaxation of the order parameter is considered for the temperature T^* where Eq. (7.4) reduces to

$$\partial a/\partial t + \tau_\mathrm{a}{}^{-1}\,C\,a^2\,(a - a^*) = 0\,, \qquad (7.15)$$

with $a^* = B/C = \frac{3}{2} a_\mathrm{K}$. The asymptotic solutions ($t \gg \tau_\mathrm{a}$) of Eq. (7.15) are quite different for positive and negative initial values a_0 (at $t = 0$). In the first case a approaches a^* exponentially. For $a_0 < 0$, $a \sim \mathrm{t}^{-1}$ is found. At the temperature $T_\mathrm{K}{}^*$ which specifies the limit of existence of the superheated metastable nematic phase, a similar semicritical behavior is encountered. In particular, a decays exponentially to zero for $a_0 < a_\mathrm{K}{}^*$ and one has $a - a_\mathrm{K}{}^* \sim t^{-1}$ for $a_0 > a_\mathrm{K}{}^*$ with $a_\mathrm{K}{}^* = \frac{1}{2} B/C = \frac{3}{4}\,a_\mathrm{K}$. Notice that the nonexponential decay occurs in connection with the approach of metastable stationary states.

c) Relaxation and Stationary States for a Planar (Biaxial) Alignment

For a planar alignment with the order parameter α cf. Eq. (1.10), the nonlinear relaxation equation corresponding to (7.7) is

$$\partial \alpha/\partial t + \tau_\mathrm{a}{}^{-1}\,\mathrm{d}\Sigma_\alpha/\mathrm{d}\alpha = 0 \qquad (7.16)$$

with

$$\Sigma_\alpha = \tfrac{1}{2} A\,\alpha^2 + \tfrac{1}{4}\,C\,\alpha^4; \qquad (7.17)$$

cf. Equation (3.6). In this case, the stationary values are $\alpha = 0$ for $T > T^*$ and

$$\alpha = \sqrt{\frac{-A}{C}} = \sqrt{\frac{A_0}{C}\left(\frac{T^*}{T} - 1\right)} \qquad (7.17)$$

for $T < T^*$. The transition from the isotropic phase to a phase with biaxial planar alignment is of second order in contradistinction to the first order transition which occurs for the unaxial alignment. Biaxial nematics have previously been considered in Ref. [21, 22]. The planar alignment state of the liquid crystal, however, is not stable. For the temperature T^*, e. g. one has $\Sigma_\alpha = 0$ whereas Σ as given by (7.8) for the unaxial phase assumes the smaller value $-\frac{1}{12} B (B/C)^3$.

The dynamical behavior of the order parameter is particularly interesting at the temperature T^* where Eq. (7.16) reduces to $\partial\alpha/\partial t + \tau_\mathrm{a}{}^{-1}\,C\,\alpha^3 = 0$. The solution of this nonlinear equation is

$$\alpha(t) = \alpha(0)\,[1 + 2\,C\,\alpha^2(0)\,\tau_\mathrm{a}{}^{-1}\,t]^{-1/2},$$

i. e. $\alpha(t) \sim t^{-1/2}$ for large times. This slowing down of the relaxation (nonexponential decay) is typical for 2nd order phase transitions. It should be pointed out, however, that Eq. (7.16) is subject to the assumption that the alignment is of pure planar biaxial type. The relaxation is different if the alignmen tensor **a** is a sum of an unaxial type of alignment as in the nematic phase plus a biaxial alignment. This case is considered in some detail in the next section.

§ 8. Relaxation of the Alignment in the Nematic Phase

a) Linearized Relaxation Equation for $T < T_\mathrm{K}$

For temperatures T below the transition temperature T_K the alignment tensor $a_{\mu\nu}$ decays to the constant equilibrium alignment $\sqrt{3/2}\,a_\mathrm{I}\,\overline{n_\mu\,n_\nu}$ where a is given by (7.5) or (7.11). To describe this relaxation process, it is convenient to introduce the tensor $\tilde{a}_{\mu\nu}$ by

$$a_{\mu\nu} = \sqrt{\tfrac{3}{2}}\,a_\mathrm{I}\,\overline{n_\mu\,n_\nu} + \tilde{a}_{\mu\nu}\,. \qquad (8.1)$$

Clearly, $\tilde{a}_{\mu\nu}$ is the deviation of the alignment tensor from its equilibrium value. Insertion of (8.1) into Eq. (7.1) yields a nonlinear equation. For small deviations $\tilde{a}_{\mu\nu}$ it is sufficient to study the linearized version of this relaxation equation, viz.

$$\partial\tilde{a}_{\mu\nu}/\partial t + \tau_\mathrm{a}{}^{-1}\,\{[A + (C_1 + C_2)\,a_\mathrm{I}{}^2]\,\tilde{a}_{\mu\nu} + 3\,C_1\,a_\mathrm{I}{}^2\,\overline{n_\mu\,n_\nu}\,n_\lambda\,n_\varkappa\,\tilde{a}_{\lambda\varkappa} + (\tfrac{3}{2}\,C_2\,a_\mathrm{I}{}^2 - 6\,B\,a_\mathrm{I})\,\overline{\overline{n_\mu\,n_\lambda}\,\tilde{a}_{\lambda\nu}}\} = 0\,. \qquad (8.2)$$

According to Eq. (8.2), $\tilde{a}_{\mu\nu}$ will decay exponentially with an anisotropic relaxation time. The anisotropy is due to the constant equilibrium alignment which is proportional to $\overline{n_\mu\,n_\nu}$. The direction of $\boldsymbol{n}$ is assumed to be fixed (e. g. by application of an external magnetic field).

b) Solution of Eq. (8.2), Anisotropy of the Relaxation Time

To solve Eq. (8.2), spherical components of 2nd rank tensors are introduced. For any symmetric traceless tensor $T_{\mu\nu}$, tensors $T^{(m)}_{\mu\nu}$ $(m=0, \pm 1 \; \pm 2)$ are defined by

$$T^{(m)}_{\mu\nu} = \mathcal{P}^{(m)}_{\mu\nu,\mu'\nu'}(\boldsymbol{n}) T_{\mu'\nu'} . \tag{8.3}$$

In (8.3) $\mathcal{P}^{(m)}_{\mu\nu,\mu'\nu'}(\boldsymbol{n})$ is a 4-th rank projection tensor which describes the infinitesimal rotation of the 2nd rank tensor about an axis parallel to $\boldsymbol{n}$ (if $\boldsymbol{n}$ is replaced by an axial vector parallel to it); cf. Ref. [23]. These tensors have the properties [23]

$$\mathcal{P}^{(m)}_{\mu\nu,\lambda\varkappa} \mathcal{P}^{(m')}_{\lambda\varkappa,\mu'\nu'} = \mathcal{P}^{(m)}_{\mu\nu,\mu'\nu'} \delta_{mm'} , \tag{8.4}$$

$$\sum_{m=-2}^{2} \mathcal{P}^{(m)}_{\mu\nu,\mu'\nu'} T_{\mu'\nu'} = \sum_{m=-2}^{2} T^{(m)}_{\mu\nu} = T_{\mu\nu} , \tag{8.5}$$

$$\mathcal{P}^{(m)}_{\mu\nu,\mu'\nu'} \overline{\overline{n_{\mu'} n_\lambda} T_{\lambda\nu'}} = (\tfrac{1}{3} - m^2/6) T^{(m)}_{\mu\nu} , \tag{8.6}$$

$$n_\mu n_\nu n_\lambda n_\varkappa T_{\lambda\varkappa} = \tfrac{2}{3} T^{(0)}_{\mu\nu} . \tag{8.7}$$

Multiplication of Eq. (8.2) by the projection tensor $\mathcal{P}^{(m)}$ leads to

$$\partial \tilde{a}^{(m)}_{\mu\nu} / \partial t + \tau_m^{-1} \tilde{a}^{(m)}_{\mu\nu} = 0 , \tag{8.8}$$

which implies, according to (8.5),

$$\tilde{a}_{\mu\nu}(t) = \sum_{m=-2}^{2} e^{-t/\tau_m} \tilde{a}^{(m)}_{\mu\nu}(0) ; \quad t \geqq 0 . \tag{8.9}$$

Use of Eqs. (8.6, 7) yields for the relaxation times τ_m:

$$\tau_m = \tau_{\text{a}} [A - 2 B a_{\text{I}} (1 - \tfrac{1}{2} m^2) + (C_1 + \tfrac{3}{2} C_2 - \tfrac{1}{4} C_2 m^2) a_{\text{I}}^2 + 2 C_1 a_{\text{I}}^2 \delta_{m,0}]^{-1} . \tag{8.10}$$

Notice that $\tau_m = \tau_{-m}$. In particular, one infers from (8.10) $\tau_0 = \tau$ where τ is given by Eq. (7.13) and

$$\tau_1 = \tau_{-1} = \tau_{\text{a}} (\tfrac{3}{4} C_2 a_{\text{I}}^2)^{-1} , \tag{8.11}$$

$$\tau_2 = \tau_{-2} = \tau_{\text{a}} (3 B a_{\text{I}})^{-1} . \tag{8.12}$$

To obtain (8.11, 12) from (8.10), use has been made of $A - B a_{\text{I}} + C a_{\text{I}}^2 = 0$, $C = C_1 + \frac{1}{2} C_2$.

For the temperatures T_{K} (transition temperature) and T^*, e. g., one has

$$\tau_0/\tau_1 = \tfrac{3}{2} C_2/C , \quad \tau_0/\tau_2 = 9 , \tag{8.13}$$

and

$$\tau_0/\tau_1 = \tfrac{3}{4} C_2/C , \quad \tau_0/\tau_2 = 3 , \tag{8.14}$$

respectively.

The results (8.11 – 14) are remarkable with regards to two aspects. Firstly, τ_1^{-1} is proportional to C_2, the coefficient which vanishes for the simple model (3.2) based on an expression for the alignment entropy where the interparticle correlations were ignored. Thus τ_1 is particularly sensitive to these correlations. Secondly, the anisotropy of the relaxation time, e. g. expressed by the ratio τ_0/τ_2 is rather large. It should be emphasized, however, that Eqs. (8.2, 8.10 – 14) follow from Eq. (6.7) where the relaxation time τ_{a} was assumed to isotropic, i. e. independent of the alignment.

c) Relaxation of Unaxial and of Planar Biaxial Alignment

To assess the consequences of Eq. (8.9) [which is the solution of Eq. (8.2)] two special cases are considered:

i) $$\tilde{a}_{\mu\nu}(0) = \sqrt{\tfrac{3}{2}} \, \tilde{a}_0 \overline{e_\mu e_\nu} , \tag{8.15}$$

ii) $$\tilde{a}_{\mu\nu}(0) = \sqrt{2} \, a_0 \overline{e_\mu c_\nu} , \quad \boldsymbol{e} \cdot \boldsymbol{c} = 0 , \tag{8.16}$$

where $\boldsymbol{e}$ and $\boldsymbol{c}$ are unit vectors. In cases i) and ii), $\tilde{a}_{\mu\nu}$ is of unaxial and of planar biaxial type, respectively. The latter case is of importance for the inertia of the flow-birefringence and the broadening of the depolarized Rayleigh line (in particular for scattering in the forward direction). Next it is noticed that

$$\begin{aligned} T^{(0)}_{\mu\nu} &= \tfrac{3}{2} \overline{n_\mu n_\nu} n_\lambda n_\varkappa T_{\lambda\varkappa} , \\ T^{(1)}_{\mu\nu} + T^{(-1)}_{\mu\nu} &= n_\mu n_\lambda T_{\lambda\nu} + n_\nu n_\lambda T_{\lambda\mu} - 2 n_\mu n_\nu n_\lambda n_\varkappa T_{\lambda\varkappa} , \\ T^{(2)}_{\mu\nu} + T^{(-2)}_{\mu\nu} &= T_{\mu\nu} - T^{(0)}_{\mu\nu} - (T^{(1)}_{\mu\nu} + T^{(-1)}_{\mu\nu}) , \end{aligned} \tag{8.17}$$

for any symmetric traceless tensor $T_{\mu\nu}$. Thus for the case of an unaxial alignment one has

$$\begin{aligned} \tilde{a}^{(0)}_{\mu\nu}(0) &= \sqrt{\tfrac{3}{2}} \, \tilde{a}_0 [(\boldsymbol{e} \cdot \boldsymbol{n})^2 - \tfrac{1}{3}] \tfrac{3}{2} \overline{n_\mu n_\nu} , \\ \tilde{a}^{(1)}_{\mu\nu}(0) + \tilde{a}^{(-1)}_{\mu\nu}(0) &= \sqrt{\tfrac{3}{2}} \, \tilde{a}_0 [(n_\mu e_\nu + e_\nu n_\mu) \boldsymbol{e} \cdot \boldsymbol{n} - 2 n_\mu n_\nu (\boldsymbol{e} \cdot \boldsymbol{n})^2] . \end{aligned} \tag{8.18}$$

Hence the relaxation times $\tau_0 = \tau$ and both τ_0 and τ_2 occur for $\boldsymbol{e} \parallel \boldsymbol{n}$ and $\boldsymbol{e} \perp \boldsymbol{n}$, respectively. For $(\boldsymbol{e} \cdot \boldsymbol{n})^2 = \frac{1}{3}$, the relaxation times τ_1 and τ_2 show up in Equation (8.9).

For the case of a planar biaxial alignment [cf. Eq. (8.16)], Eq. (8.17) reduce to

$$\tilde{a}^{(0)}_{\mu\nu}(0) = \sqrt{2}\, a_0\, \tfrac{3}{2}\, n_\mu n_\nu\, \boldsymbol{n}\cdot\boldsymbol{e}\, \boldsymbol{n}\cdot\boldsymbol{c}\,, \tag{8.19}$$

$$\tilde{a}^{(1)}_{\mu\nu}(0) + \tilde{a}^{(-1)}_{\mu\nu}(0) = \sqrt{2}\, a_0 \left[\tfrac{1}{2}(n_\mu c_\nu + c_\mu n_\nu)\,\boldsymbol{n}\cdot\boldsymbol{e} + \tfrac{1}{2}(n_\mu e_\nu + e_\nu n_\mu)\,\boldsymbol{n}\cdot\boldsymbol{c} - 2\, n_\mu n_\nu\, \boldsymbol{n}\cdot\boldsymbol{e}\, \boldsymbol{n}\cdot\boldsymbol{c}\right].$$

Hence for $\boldsymbol{e} \perp \boldsymbol{n}$, $\boldsymbol{c} \parallel \boldsymbol{n}$ and for $\boldsymbol{e} \perp \boldsymbol{n}$, $\boldsymbol{c} \perp \boldsymbol{n}$ one has

$$\tilde{a}_{\mu\nu}(0) = \tilde{a}^{(1)}_{\mu\nu}(0) + \tilde{a}^{(-1)}_{\mu\nu}(0) \quad \text{and} \quad \tilde{a}_{\mu\nu}(0) = \tilde{a}^{(2)}_{\mu\nu} + \tilde{a}^{(-2)}_{\mu\nu}\,,$$

respectively. In both these cases just one relaxation time, viz. τ_1 and τ_2, respectively, occurs in Equation (8.9).

These remarks indicate that it should be possible to measure the three relaxation times τ_0, τ_1, τ_2 separately.

Concluding Remarks

The first part of this article (Sects. 1 – 6) was devoted to the derivation of the constitutive laws (6.3, 4) or (6.7, 8). Their application was restricted to the relaxation of the alignment. The nonlinearity of the relaxation equation accounts for the fact that the alignment of liquid crystals relaxes to zero and to a finite value at temperatures T above and below the temperature T_K at which the transition from the isotropic to the nematic phase occurs. For $T < T_K$, the relaxation time for the alignment becomes anisotropic. An experimental investigation of this anisotropy would be desirable. Further applications of the constitutive laws to flow alignment and its reciprocal phenomenon, as well as to viscous flow will be studied in a subsequent paper. Ordinary molecular liquids, the isotropic and the nematic phases of liquid crystals will be considered.

Finally, a few remarks on the limitations of the present approach are in order. Firstly, fluctuations which can be expected to be of importance at temperatures very close to the transition temperature T_K have been disregarded. Secondly, the alignment tensor was assumed to be spatially homogeneous. This limitation can be overcome rather easily. To this purpose a term proportional to $(\nabla \mathbf{a})^2$ associated with the elastic energy has to be included in Eq. (2.1) and the gradient of the flux of the alignment tensor has to be taken into account in Equation (4.6). A constitutive law for the alignment flux tensor can then be derived. As a consequence, the relaxation equation for the alignment contains a term proportional to the 2nd spatial derivative of the alignment tensor. This term, e. g., determines the diffusional contribution to the width of the depolarized Rayleigh line.

Appendix
Calculations of the Entropy Associated with the Alignment

The orientation of a symmetric top molecule is specified by the unit vector $\boldsymbol{u}$ which is parallel to its figure axis. Let $\varrho = \varrho(t, \boldsymbol{u})$ be the orientational (one-particle) distribution function with the normalization

$$\int \varrho\, \mathrm{d}^2 u = 1\,. \tag{A.1}$$

Then the average $\langle \Psi \rangle$ of a quantity $\Psi = \Psi(\boldsymbol{u})$ is given by

$$\langle \Psi \rangle = \int \Psi(\boldsymbol{u})\, \varrho(t, \boldsymbol{u})\, \mathrm{d}^2 u\,. \tag{A.2}$$

The distribution function and the pertaining average for an equilibrium state are denoted by ϱ_0 and $\langle \ldots \rangle_0$. According to Boltzmann[14], the specific entropy associated with the alignment is determined by

$$s_\mathrm{a} = -(k_\mathrm{B}/m)\left[\int \varrho \ln \varrho\, \mathrm{d}^2 u - \int \varrho_0 \ln \varrho_0\, \mathrm{d}^2 u\right], \tag{A.3}$$

where k_B is the Boltzmann constant and m is the mass of a molecule. Notice that this expression for s_a is associated with the one-particle distribution function. Hence interparticle correlations are ignored in (A.3). Yet, it seems worthwhile to study this simple case.

In general, ϱ can be written as

$$\varrho = \varrho_0 (1 + \varphi)\,, \tag{A.4}$$

with

$$\langle \varphi \rangle_0 = 0\,. \tag{A.5}$$

The quantity φ characterizes the deviation of ϱ from ϱ_0. In the absence of external orienting fields one has

$$\varrho_0 = (4\pi)^{-1}\,, \tag{A.6}$$

i. e. in equilibrium all directions of $\boldsymbol{u}$ occur with equal probability. Insertion of (A.4) into (A.3) and use of (A.5, 6) leads to

$$s_{\mathrm{a}} = -\frac{k_{\mathrm{B}}}{m} \langle (1+\varphi)\ln(1+\varphi) \rangle_0 = -\frac{k_{\mathrm{B}}}{m} \sum_{n=2}^{\infty} (-1)^n \frac{1}{n(n-1)} \langle \varphi^n \rangle_0 . \tag{A.7}$$

Up to terms of 4-th order in φ, Eq. (A.7) is equivalent to

$$s_a = -(k_{\mathrm{B}}/m)\left[\tfrac{1}{2}\langle\varphi^2\rangle_0 - \tfrac{1}{6}\langle\varphi^3\rangle_0 + \tfrac{1}{12}\langle\varphi^4\rangle_0\right] . \tag{A.8}$$

Next, it is assumed that the deviation of ϱ from ϱ_0 is solely due to an alignment of the type (1.1). Then φ can be written as

$$\varphi = a_{\mu\nu}\,\Phi_{\mu\nu} \tag{A.9}$$

with

$$\Phi_{\mu\nu} = \sqrt{\tfrac{15}{2}}\,\overline{u_\mu u_\nu}\,, \quad a_{\mu\nu} = \langle \Phi_{\mu\nu} \rangle . \tag{A.10}$$

The factor $\sqrt{15/2}$ has been inserted such that

$$\langle \Phi_{\mu\nu}\,\Phi_{\mu'\nu'} \rangle_0 = \Delta_{\mu\nu,\mu'\nu'}\,, \tag{A.11}$$

where

$$\Delta_{\mu\nu,\mu'\nu'} = \tfrac{1}{2}(\delta_{\mu\mu'}\,\delta_{\nu\nu} + \delta_{\mu\nu'}\,\delta_{\nu\mu'}) - \tfrac{1}{3}\,\delta_{\mu\nu}\,\delta_{\mu'\nu'} . \tag{A.12}$$

Equation (A.10) implies that the factor ζ occurring in Eq. (1.1) is equal to $\sqrt{15/2}$. Insertion of (A.9) into (A.8), use of (A.11) and of

$$\langle \Phi_{\mu\nu}\,\Phi_{\mu'\nu'}\,\Phi_{\mu''\nu''} \rangle_0 = \tfrac{2}{7}\sqrt{30}\,\Delta_{\mu\nu,\lambda\varkappa}\,\Delta_{\mu'\nu',\lambda\tau}\,\Delta_{\mu''\nu'',\tau\varkappa} \tag{A.13}$$

$$\begin{aligned}\langle \Phi_{\mu\nu}\,\Phi_{\mu'\nu'}\,\Phi_{\lambda\varkappa}\,\Phi_{\lambda'\varkappa'} \rangle_0 &= \tfrac{5}{7}\,(\Delta_{\mu\nu,\mu'\nu'}\,\Delta_{\lambda\varkappa,\lambda'\varkappa'} + \Delta_{\mu\nu,\lambda\varkappa}\,\Delta_{\mu'\nu',\lambda'\varkappa'} \\ &\quad + \Delta_{\mu\nu,\lambda'\varkappa'}\,\Delta_{\mu'\nu',\lambda\varkappa})\end{aligned} \tag{A.14}$$

leads to an expression for s_{a} of the form (3.1) with the coefficients A_0, B, C_1, C_2 given by (3.2).

For an unaxial alignment (A.9) reduces to

$$\varphi = \sqrt{5}\,a\,P_2(\boldsymbol{n}\cdot\boldsymbol{u}) \tag{A.15}$$

cf. Equations (1.5, 6). In this case, an expression for s_{a} of the form (3.3) can be obtained directly from (A.8) with the help of the relations

$$\langle P_2 \rangle_0 = 0\,, \quad \langle P_2^{\,2} \rangle_0 = \tfrac{1}{5}\,, \quad \langle P_2^{\,3} \rangle_0 = \tfrac{2}{35}\,, \quad \langle P_2^{\,4} \rangle_0 = \tfrac{3}{35} \tag{A.16}$$

This again yields the values (3.2) for the coefficients A_0, B, and $C = C_1$.

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