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

II. Viscous flow and flow alignment in the isotropic (stable and metastable) and nematic phases

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The previously derived nonlinear constitutive laws for the friction pressure and the alignment tensor are applied to viscous flow, to the flow-induced alignment (flow birefringence) and its reciprocal effect. It is demonstrated that these phenomena may be treated by one set of equations, both in the isotropic and in the nematic phases. The flow alignment in the isotropic phase is also investigated in the temperature range where this phase is metastable.

The preferential orientation of molecules induced by transport processes and the relaxation of the orientation are irreversible processes typical for molecular fluids. A phenomenological theory of such nonequilibrium alignment phenomena which is applicable to molecular liquids and to nematic liquid crystals has been presented in Ref. [1]. In particular, constitutive laws have been derived for the friction pressure tensor and for the tensor which specifies the relaxation of the alignment and its production caused by the gradient of the flow velocity field. As a first application, the relaxation of the alignment was treated. Due to the nonlinearity of the relaxation equation, the order parameter of an unaxial alignment decays to zero and to a nonzero value for temperatures T above and below T_K, respectively. Here T_K is the temperature at which the transition from the isotropic to the nematic phase occurs. For $T < T_K$, the relaxation of the deviation of the alignment tensor from its equilibrium value turned out to be anisotropic. In the present paper, further applications of the constitutive laws are studied, viz. flow alignment (flow birefringence) and its reciprocal phenomenon as well as viscous flow. The constitutive laws obtained by de Gennes [2, 3] for $T > T_K$ (isotropic phase) and essentially those proposed [4] (see also Ref.[3]) for $T < T_K$ (nematic phase) are recovered as special cases. This demonstrates that one set of constitutive laws which are nonlinear with respect to the alignment describes the nonequilibrium alignment phenomena both in the isotropic and in the nematic phases (including the metastable isotropic phase).

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This paper is devided into 6 sections. Firstly, in Sect. 1, the fundamental equations obtained in Ref. [1] are reviewed. These are the relaxation equation for the alignment and the nonlinear constitutive laws for the alignment tensor and the friction pressure tensor. In Sects. 2 and 3, these constitutive laws are applied to ordinary liquids and to the isotropic phase of liquid crystals. In particular, flow alignment and acoustic alignment as well as the ensuing birefringence are discussed (Section 2). Then viscous flow is treated. Special attention is paid to the phenomenon reciprocal to the flow alignment, viz. an anisotropic part of the pressure tensor caused by a preferential orientation (nonequilibrium alignment) of the molecules (Section 3). Sections 4 and 5 deal with the viscous flow and with the flow alignment in the nematic phase of a liquid crystal. The physical meaning of the various viscosity coefficients is elucidated for the special case of a plane Couette flow. Furthermore, it is pointed out that the friction pressure tensor of a nematic liquid crystal possesses "transverse" components which gives rise to a pressure gradient perpendicular to both the flow velocity and its gradient (Section 4). The flow-induced deviations of the alignment tensor from its equilibrium value is treated in Section 5. Section 6, finally, is devoted to a discussion of the flow alignment in the metastable isotropic phase ($T^* < T < T_K$, T^* specifies the limit of existence of the metastable phase). For small velocity gradients, and for temperatures T above the critical temperature T^* the alignment tensor can be expanded in powers of the

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velocity gradient. This expansion diverges for $T \to T^*$. On the other hand, at the temperatur T^*, an alignment proportional to the square root of the velocity gradient is found. A stability analysis, however, reveals that this nonanalytic expression for the alignment does not correspond to a stable situation. For $T \gtrsim T^*$, in the isotropic phase, no stable solution exists for the flow alignment if the magnitude of the velocity gradient exceeds a certain critical value which is proportional to $(T-T^*)^2$.

§ 1. Balance Equation for the Alignment Tensor, Entropy Production, Constitutive Laws

Before further applications of the constitutive laws derived in Ref. [1] are discussed, the notations used in Ref. [1] and some results stated there have to be reviewed.

The alignment of molecules is characterized by the symmetric traceless tensor $a_{\mu\nu}$. Greek subscripts refer to Cartesian components. If the spatial inhomogeneity of the alignment can be disregarded, it obeys the balance equation

$$\frac{\partial}{\partial t} a_{\mu\nu} - \omega_\lambda (\varepsilon_{\mu\lambda\varkappa} a_{\varkappa\nu} + \varepsilon_{\nu\lambda\varkappa} a_{\varkappa\mu}) = A_{\mu\nu}, \qquad (1.1)$$

where $\varepsilon_{\mu\nu\lambda}$ is the Levi-Civita tensor. The 2nd term of Eq. (1.1) describes the change of the alignment tensor due to the rotation of the molecular axes about the average angular velocity

$$\boldsymbol{\omega} = \tfrac{1}{2} \operatorname{rot} \boldsymbol{v}. \qquad (1.2)$$

Here $\boldsymbol{v}$ is the flow velocity. The tensor $A_{\mu\nu}$ specifies the relaxation and the production of the alignment. It is related to the alignment and to the gradient of the flow velocity by a constitutive law.

The specific entropy production due to irreversible processes associated with tensors of rank 2, as derived in Ref. [1], is

$$\left(\frac{\delta s}{\delta t}\right)_{\text{irrev.}} = -\frac{k_B}{m} [A_{\mu\nu} \Sigma_{\mu\nu} + P_k^{-1} \overline{p_{\mu\nu}}\, \overline{\nabla_\mu v_\nu}]. \qquad (1.3)$$

Here k_B is the Boltzmann constant, m is the mass of a molecule; P_k is an abbreviation for

$$P_k = m^{-1} \varrho\, k_B T, \qquad (1.4)$$

where ϱ and T are the mass density and the temperature of the fluid. The friction pressure tensor is denoted by $p_{\mu\nu}$. The symbol $\overline{\ldots}$ refers to the symmetric traceless part of a tensor, e. g. one has

$$p_{\mu\nu} = \overline{\tfrac{1}{2}(p_{\mu\nu} + p_{\nu\mu})} - \tfrac{1}{3} p_{\varrho\varrho} \delta_{\mu\nu}.$$

The tensor $\Sigma_{\mu\nu}$ is related to the alignment tensor by

$$\Sigma_{\mu\nu} = A\, a_{\mu\nu} - \sqrt{6}\, B\, \overline{a_{\mu\lambda} a_{\lambda\nu}} + C_1\, a_{\mu\nu} a_{\lambda\varkappa} a_{\lambda\varkappa} + C_2\, \overline{a_{\mu\lambda} a_{\lambda\varkappa} a_{\varkappa\nu}}, \qquad (1.5)$$

with

$$A = A_0 (1 - T^*/T) \qquad (1.6)$$

where $T^* < T_K$ is a characteristic temperature. The temperature dependence of the coefficients A_0, B, C_1, C_2 is assumed to be rather weak such that it can be disregarded for temperatures T close to T_K. In ordinary molecular liquids which to not possess a nematic phase, T^* is so small that A can be approximated by A_0.

The constitutive laws associated with Eq. (1.3) can be written as [1]

$$-\overline{p_{\mu\nu}} = 2 P_k \tau_p \overline{\nabla_\mu v_\nu} + \sqrt{2}\, P_k \tau_{pa} A_{\mu\nu}, \qquad (1.7)$$

$$-\Sigma_{\mu\nu} = \sqrt{2}\, \tau_{ap} \overline{\nabla_\mu v_\nu} + \tau_a A_{\mu\nu}. \qquad (1.8)$$

Here the $\tau \ldots$ are relaxation times with the properties

$$\tau_{ap} = \tau_{pa} \qquad (1.9)$$

and

$$\tau_p > 0,\ \tau_a > 0, \quad \tau_a \tau_p > \tau_{ap}^2. \qquad (1.10)$$

Notice that τ_{ap} may either be positive or negative. A slightly more general ansatz for $\overline{p_{\mu\nu}}$ which is of importance for the nematic phase is

$$-\overline{p_{\mu\nu}} = 2 P_k \tau_p (\overline{\nabla_\mu v_\nu} + \sqrt{6}\, \sigma_1\, \overline{a_{\mu\nu} \nabla_\mu v_\nu} + \sigma_2\, a_{\mu\nu} a_{\lambda\varkappa} \overline{\nabla_\lambda v_\varkappa}) + \sqrt{2}\, P_k \tau_{ap} A_{\mu\nu}, \qquad (1.11)$$

where σ_1, σ_2 are two additional phenomenological coefficients.

In Ref. [1], the consequences of Eq. (1.8) for the relaxation of the alignment have been studied for $\boldsymbol{v} = 0$. Here, the application of Eqs. (1.7, 8, 11) to flow alignment, its reciprocal phenomenon and viscous flow shall be discussed. Isotropic liquids are considered first.

§ 2. Flow Alignment and Acoustic Alignment in Isotropic Liquids

a) General Remarks

A velocity gradient caused either by a viscous flow or by a sound wave in an isotropic molecular fluid leads to an alignment. If this alignment is de-

tected optically via the ensuing birefringence one talks about flow birefringence [5–7] and acoustic birefringence [6, 8, 9].

Point of departure for the theoretical treatment of these phenomena are Eqs. (1.1) and (1.8). For isotropic liquids $\Sigma_{\mu\nu}$ as given by Eq. (1.5) can be approximated by the linear expression $A\,a_{\mu\nu}$. Insertion of (1.8) into (1.1) then yields

$$\partial a_{\mu\nu}/\partial t - \omega_\lambda(\varepsilon_{\mu\lambda\varkappa}\,a_{\varkappa\nu} + \varepsilon_{\nu\lambda\varkappa}\,a_{\varkappa\mu}) + \tau^{-1}\,a_{\mu\nu} = -\sqrt{2}\,\tau_{\mathrm{ap}}\,\tau_{\mathrm{a}}^{-1}\,\overline{\nabla_\mu v_\nu}\,. \quad (2.1)$$

The relaxation time τ is given by

$$\tau = \tau_{\mathrm{a}} A^{-1} = \tau_{\mathrm{a}} A_0^{-1}(1 - T^*/T)^{-1}\,. \quad (2.2)$$

Notice that τ increases dramatically as T approaches T^*. This is indeed observed in liquid crystals for $T > T_{\mathrm{K}} > T^*$. For $T < T_{\mathrm{K}}$ where τ as given by Eq. (2.2) would become singular and even change sign, Eqs. (2.1) and (2.2) are no longer valid. For $T < T_{\mathrm{K}}$ the full nonlinear expression (1.5) for $\Sigma_{\mu\nu}$ has to be taken into account; cf. Section 6.

b) Flow Alignment

For a steady shear flow ($\overline{\nabla_\mu v_\nu}$ time-independent) the time derivative in Eq. (2.1) can be disregarded. Then

$$a_{\mu\nu} = -\sqrt{2}\,A^{-1}\,\tau_{\mathrm{ap}}\,\overline{\nabla_\mu v_\nu} \quad (2.3)$$

is obtained provided that terms nonlinear in the velocity gradient which stem from $\boldsymbol{\omega} = \frac{1}{2}\,\mathrm{rot}\,\boldsymbol{v}$ are disregarded.

The connection between the anisotropic (symmetric traceless) part of the dielectric tensor $\overline{\varepsilon_{\mu\nu}}$ and the alignment tensor can be written as

$$\overline{\varepsilon_{\mu\nu}} = \varepsilon_{\mathrm{a}}\,a_{\mu\nu} \quad (2.4)$$

where ε_{a} is a proportionality coefficient. Thus Eq. (2.3) implies the constitutive law

$$\overline{\varepsilon_{\mu\nu}} = -2\,\beta\,\overline{\nabla_\mu v_\nu} \quad (2.5)$$

for the flow birefringence where the coefficient β is given by

$$\beta = \varepsilon_{\mathrm{a}}(\sqrt{2}\,A)^{-1}\,\tau_{\mathrm{ap}}\,. \quad (2.6)$$

Equations (2.5), (2.6) are equivalent to the expression derived by de Gennes [2] for flow birefringence in the isotropic phase of liquid crystals. With $A = 1$, Eqs. (2.5), (2.6) are formally equal to the corresponding expression for molecular gases [10, 11] which have been derived within the framework of the kinetic theory based on the Waldmann-Snider equation [12].

Next, some remarks on the consequences of the term of Eq. (2.1) which involves $\boldsymbol{\omega} = \frac{1}{2}\,\mathrm{rot}\,\boldsymbol{v}$ are in order. Formally, Eq. (2.1) is equivalent to the inhomogeneous relaxation equation for the tensor polarization discussed in Ref. [13] where the influence of a magnetic field on the flow birefringence of molecular gas was considered. In Ref. [13], $\boldsymbol{\omega}$ was the frequency for the precession of the rotational angular momentum of a molecule about an applied magnetic field. The result obtained there can easily be adapted to the present situation. To be more specific, flow in x-direction between flat plates parallel to the x-z-plane is considered. Then one has $\overline{\nabla \boldsymbol{v}} = \Gamma\,\overline{\boldsymbol{e}^x\,\boldsymbol{e}^y}$ and $\boldsymbol{\omega} = -\frac{1}{2}\Gamma\,\boldsymbol{e}^z$ with

$$\Gamma = \partial v_x/\partial y\,. \quad (2.7)$$

Here $\boldsymbol{e}^{x,y,z}$ are unit vectors parallel to the axes of the coordinate system. In this case, one of the principle axes of the dielectric tensor is parallel to $\boldsymbol{e}^z$, the others are in the x-y-plane and make the angles

$$\vartheta = \pi/4 - \tfrac{1}{2}\,\mathrm{arc\,tg}\,\Gamma\tau \quad (2.8)$$

and $\vartheta + \pi/2$ with the x-axis. Notice that Eqs. (2.5), (2.6) imply $\vartheta = \pi/4$. Unit vectors parallel to the principal axes are denoted by $\boldsymbol{e}^{(1)}$ ($\boldsymbol{e}^{(1)}\cdot\boldsymbol{e}^x = \cos\vartheta$), $\boldsymbol{e}^{(2)}$ and $\boldsymbol{e}^{(3)} = \boldsymbol{e}^z$. Let ν_{i} be the index of refraction for linearly polarized light with its electric field vector parallel to $\boldsymbol{e}^{(\mathrm{i})}$. Then the difference $\delta\nu = \nu_2 - \nu_1$ is given by

$$\nu\,\delta\nu = [1 + \Gamma^2\tau^2]^{-1/2}\,\beta\,\Gamma\,, \quad (2.9)$$

where ν is the index of refraction for $\Gamma = 0$. Clearly, Eqs. (2.8), (2.9) indicate that Eqs. (2.5), (2.6) are a good approximation for the description of flow birefringence provided that $\Gamma\tau \ll 1$. In ordinary liquids one has typically $\tau < 10^{-10}\,\mathrm{s}$. In the isotropic phase of liquid crystals relaxation times $\tau \lesssim 10^{-6}\,\mathrm{s}$ have been measured [14, 15] for temperatures T close to T_{K}. In both cases, however, the condition $\Gamma\tau \ll 1$ is well satisfied even for $\Gamma \approx 10^3\,\mathrm{s}^{-1}$. This is in contradistinction to macromolecular and colloidal suspensions [6].

c) Acoustic Alignment

Next, the alignment induced by a standing sound wave with frequency Ω, wave vector $\boldsymbol{k}$ and amplitude v_0 is considered. For

$$\boldsymbol{v} = v_0\,k^{-1}\,\boldsymbol{k}\cos\boldsymbol{k}\cdot\boldsymbol{x}\cos\Omega t \quad (2.10)$$

one has

$$\overline{\nabla \boldsymbol{v}} = -v_0 k^{-1} \overline{\boldsymbol{k}\boldsymbol{k}} \sin \boldsymbol{k}\cdot\boldsymbol{x} \cos \Omega t, \boldsymbol{\omega} = \tfrac{1}{2} \operatorname{rot} \boldsymbol{v} = 0 . \tag{2.11}$$

Solution of Eq. (2.1) with (2.11) yields, for times t large compared with the relaxation time τ

$$a_{\mu\nu} = \sqrt{2}\, \tau_{\mathrm{ap}} A^{-1} v_0 k^{-1} \overline{k_\mu k_\nu} \sin \boldsymbol{k}\cdot\boldsymbol{x} \cdot (1+\Omega^2\tau^2)^{-1/2} \cos(\Omega t + \varphi) . \tag{2.12}$$

The phase shift φ is given by $\operatorname{tg}\varphi = -\Omega\tau$ For small frequencies with $\Omega\tau \ll 1$, Eq. (2.12) reduces to the expression which is obtained by inserting (2.10) into Equation (2.3).

The acoustic birefringence is associated with the difference $\delta\nu = \nu_{\|} - \nu_{\perp}$ of the indices of refraction of linearly polarized light with the electric field vector parallel and perpendicular to $\boldsymbol{k}$. Use of Eqs. (2.4) leads to

$$\nu(\nu_{\|} - \nu_{\perp}) = \beta v_0 k \sin \boldsymbol{k}\cdot\boldsymbol{x} \cdot (1+\Omega^2\tau^2)^{-1/2} \cos(\Omega t + \varphi) ,$$

where β is the flow birefringence coefficient (2.6).

§ 3. Viscous flow in Isotropic Liquids, the Effect Reciprocal to flow Alignment

a) Viscosity

For a steady state situation (time independent alignment) and if terms associated with $\boldsymbol{\omega} = \frac{1}{2} \operatorname{rot} \boldsymbol{v}$ can be disregarded, Eq. (1.1) implies $A_{\mu\nu} = 0$. Then the constitutive law (1.7) yields

$$\overline{p_{\mu\nu}} = -2\eta \overline{\nabla_\mu v_\nu} \tag{3.1}$$

where the viscosity η is given by

$$\eta = P_{\mathrm{k}} \tau_{\mathrm{p}} . \tag{3.2}$$

Under the same experimental conditions the alignment tensor $a_{\mu\nu}$ is nonzero, cf. Equation (2.3). According to Eqs. (1.7), (1.8) the viscosity η_{iso} corresponding to a situation where $a_{\mu\nu}$ and consequently $\Sigma_{\mu\nu}$ vanishes, is given by

$$\eta_{\mathrm{iso}} = \eta(1 - \tau_{\mathrm{ap}}^2/\tau_{\mathrm{p}}\tau_{\mathrm{a}}) < \eta . \tag{3.3}$$

Notice that η is different from η_{iso} whenever τ_{ap} which characterizes the coupling between the friction pressure tensor and the alignment is nonzero. Incidentaly, this difference is also of crucial importance for the influence of a magnetic field on the viscosity of molecular gases [16] (Senftleben-Beenaker effect). There, application of a magnetic field and the resulting precessional motion of the rotational angular momentum leads to a partial destruction of the alignment such that the viscosity approaches its isotropic value η_{iso}.

b) The Effect Reciprocal to flow Alignment

Next, it is noticed that Eqs. (1.7), (1,8) lead to a nonzero friction pressure tensor $\overline{p_{\mu\nu}}$ even for $\overline{\nabla_\mu v_\nu} = 0$. In particular, one finds (cf. 1.1)

$$\overline{p_{\mu\nu}} = -\sqrt{2}\, P_{\mathrm{k}} \tau_{\mathrm{pa}} (\partial a_{\mu\nu}/\partial t) . \tag{3.4}$$

This equation describes the effect reciprocal to the flow alignment (2.3). If the system was prepared such the alignment is equal to $a_{\mu\nu}(0)$ at time $t = 0$, the alignment for $t > 0$ is given by $a_{\mu\nu}(t) = e^{-t/\tau} a_{\mu\nu}(0)$. Then Eq. (3.4) yields

$$\overline{p_{\mu\nu}} = \sqrt{2}\, P_{\mathrm{k}} \tau_{\mathrm{pa}} \tau^{-1} e^{-t/\tau} a_{\mu\nu}(0) . \tag{3.5}$$

For the relaxation time τ see Equation (2.2).

Clearly, Eq. (3.5) describes a transient phenomenon; $\overline{p_{\mu\nu}}$ vanishes for $t \gg \tau$. Measurements of the effect reciprocal to the flow alignment and comparison with flow birefringence data could provide an experimental test of the Onsager relation (1.9).

For molecular gases, a relation corresponding to (3.4) has been derived [17] recently within the framework of the kinetic theory based on the Waldmann-Snider equation [12].

§ 4. Viscous flow of a Nematic Liquid Crystal

a) Alignment in the Nematic Phase

In thermal equilibrium, the alignment of a liquid crystal in the nematic phase is of unaxial type. The unit vector parallel to the symmetry axis of the alignment tensor, often referred to as director, is denoted by $\boldsymbol{n}$. In general, the alignment tensor in the nematic phase can be written as

$$a_{\mu\nu} = a_{\mu\nu}^{(\mathrm{eq})} + \tilde{a}_{\mu\nu} , \tag{4.1}$$

where

$$a_{\mu\nu}^{(\mathrm{eq})} = \sqrt{\tfrac{3}{2}}\, a_{\mathrm{eq}} \overline{n_\mu n_\nu} \tag{4.2}$$

is the equilibrium alignment tensor and $\tilde{a}_{\mu\nu}$ specifies the deviation of $a_{\mu\nu}$ from its equilibrium value. In (4.2), a_{eq} is the scalar order parameter for the unaxial alignment in thermal equilibrium. It can be

expressed in terms of the coefficients A, B, and $C = C_1 + \frac{1}{2} C_2$ which occurred in Eq. (1.5); cf. Ref.[1]. The factor $\sqrt{\frac{3}{2}}$ has been inserted such that $a_{\mu\nu}^{(\mathrm{eq})}\, a_{\mu\nu}^{(\mathrm{eq})} = a_{\mathrm{eq}}^2$. With the help of relations (4.1), (4.2), Eq. (1.1) can be rewritten as

$$A_{\mu\nu} = \sqrt{\tfrac{3}{2}}\, a_{\mathrm{eq}}\, 2\, \overline{n_\mu N_\nu} + \frac{\partial \tilde{a}_{\mu\nu}}{\partial t} - \omega_\lambda (\varepsilon_{\mu\lambda\varkappa}\, \tilde{a}_{\varkappa\nu} + \varepsilon_{\nu\lambda\varkappa}\, a_{\varkappa\mu}) \tag{4.3}$$

with

$$\boldsymbol{N} = \partial \boldsymbol{n}/\partial t - \boldsymbol{\omega} \times \boldsymbol{n}\,. \tag{4.4}$$

Note that a_{eq} is time independent.

b) Friction Pressure Tensor, Viscosity

If the terms containing $\tilde{a}_{\mu\nu}$ are disregarded, insertion of (4.3) into (1.11) yields

$$\overline{p_{\mu\nu}} = -2\, \eta_{\mu\nu,\mu'\nu'}\, \overline{\nabla_{\mu'} v_{\nu'}} - 2\, \tilde{\eta}\, \overline{n_\mu N_\nu}\,. \tag{4.5}$$

The viscosity tensor $\eta_{\mu\nu,\mu'\nu'}$ is given by

$$\eta_{\mu\nu,\mu'\nu'} = \eta\,(\Delta_{\mu\nu,\mu'\nu'} + 3\, a_{\mathrm{eq}}\, \sigma_1\, \Delta_{\mu\nu,\lambda\mu'}\, \overline{n_\lambda n_{\nu'}} + \tfrac{3}{2}\, a_{\mathrm{eq}}^2\, \sigma_2\, \overline{n_\mu n_\nu\, n_{\mu'} n_{\nu'}}) \tag{4.6}$$

with $\eta = P_{\mathrm{k}}\, \tau_{\mathrm{p}}$. Here $\Delta_{\mu\nu,\mu'\nu'}$ is the 4-th rank isotropic tensor

$$\Delta_{\mu\nu,\mu'\nu'} = \tfrac{1}{2}(\delta_{\mu\mu'}\, \delta_{\nu\nu'} + \delta_{\mu\nu'}\, \delta_{\nu\mu'}) - \tfrac{1}{3}\, \delta_{\mu\nu}\, \delta_{\mu'\nu'}\,. \tag{4.7}$$

The first term in Eq. (4.5) can be written as [18]

$$\eta_{\mu\nu,\mu'\nu'}\, \overline{\nabla_{\mu'} v_{\nu'}} = \sum_{m=-2}^{2} \eta_m\, \overline{\nabla_\mu v_\nu}^{(m)} \tag{4.8}$$

where $\overline{\nabla_\mu v_\nu}^{(m)}$, $m = 0, \pm 1, \pm 2$ are the spherical components of $\overline{\nabla_\mu v_\nu}$ with $\boldsymbol{n}$ parallel to the reference axis. Due to (4.6), the viscosity coefficients η_m are

$$\begin{aligned} \eta_0 &= \eta\,(1 + a_{\mathrm{eq}}\, \sigma_1 + a_{\mathrm{eq}}^2\, \sigma_2)\,, \\ \eta_1 &= \eta_{-1} = \eta\,(1 + \tfrac{1}{2}\, a_{\mathrm{eq}}\, \sigma_1)\,, \\ \eta_2 &= \eta_{-2} = \eta\,(1 - a_{\mathrm{eq}}\, \sigma_1)\,. \end{aligned} \tag{4.9}$$

Notice that the simpler ansatz (1.7) implies $\eta_0 = \eta_1 = \eta_2 = \eta$. The viscosity tensor (4.6) has the same symmetry properties as the viscosity of a fluid in the presence of an electric field parallel to $\boldsymbol{n}$.

The last term of Eq. (4.5) is typical for nematic liquid crystals. The "rotational viscosity" $\tilde{\eta}$ is given by

$$\tilde{\eta} = \sqrt{3}\, a_{\mathrm{eq}}\, P_{\mathrm{k}}\, \tau_{\mathrm{pa}}\,. \tag{4.10}$$

Here the relaxation time τ_{pa} occurs which is associated with the effect reciprocal to the flow alignment, cf. Equation (3.4).

If the Leslie coefficients $\alpha_1, \ldots, \alpha_6$ are used, the most general ansatz for the symmetric traceless part of the friction pressure tensor of an incompressible nematic liquid crystal is [3]

$$-\overline{p_{\mu\nu}} = \alpha_1\, \overline{n_\mu n_\nu\, n_\lambda n_\varkappa \nabla_\lambda v_\varkappa} + (\alpha_2 + \alpha_3)\, \overline{n_\mu N_\nu} + \alpha_4\, \overline{\nabla_\mu v_\nu} + (\alpha_5 + \alpha_6)\, \overline{n_\mu n_\lambda \nabla_\lambda v_\nu}\,. \tag{4.11}$$

Comparison of (4.5), (4.6) with (4.11) shows that the coefficients used in this paper are related to the Leslie coefficients by

$$\begin{aligned} &\alpha_1 = 3\, \eta\, a_{\mathrm{eq}}^2\, \sigma_2\,,\ \alpha_2 + \alpha_3 = 2\, \tilde{\eta}\,, \\ &\alpha_4 = 2\, \eta\,(1 - a_{\mathrm{eq}}\, \sigma_1)\,,\ \alpha_5 + \alpha_6 = 6\, \eta\, a_{\mathrm{eq}}\, \sigma_1\,; \end{aligned} \tag{4.12}$$

$$\begin{aligned} \eta_0 &= \tfrac{1}{2}\, \alpha_4 + \tfrac{1}{3}\, (\alpha_1 + \alpha_5 + \alpha_6)\,, \\ \eta_1 &= \eta_{-1} = \tfrac{1}{2}\, \alpha_4 + \tfrac{1}{4}\, (\alpha_5 + \alpha_6)\,, \\ \eta_2 &= \eta_{-2} = \tfrac{1}{2}\, \alpha_4\,. \end{aligned} \tag{4.13}$$

For MBBA, α_1 and $\alpha_5 + \alpha_6$ are about one order of magnitude smaller than α_4 and $2\,\tilde{\eta}$, cf. Ref.[3], p. 184. Thus, for some applications, the simpler ansatz (1.7) corresponding to $\sigma_1 = \sigma_2 = 0$ (which implies that the shear viscosity is isotropic) may be a reasonable first approximation to Equation (1.11).

c) Consequences of Eq. (4.5) for Plane Couette Flow

To appreciate the consequences of Eq. (4.5), a flow in x-direction between flat plates parallel to the x-p-plane is considered (cf. Section 2b). As in the viscosity measurements performed by Miesowicz [19] the direction of $\boldsymbol{n}$ is assumed to be fixed by an applied magnetic field.

For this case, one has

$$\boldsymbol{\omega} = \tfrac{1}{2}\, \mathrm{rot}\, \boldsymbol{v} = -\tfrac{1}{2} \frac{\partial v_x}{\partial y}\, \boldsymbol{e}^z$$

and

$$\boldsymbol{N} = \tfrac{1}{2}\, \boldsymbol{e}^z \times \boldsymbol{n}\, \partial v_x/\partial y\,.$$

Now Eq. (4.5) leads to

$$p_{xy} = -\eta_{\mathrm{eff}}\, \partial v_x/\partial y\,, \tag{4.14}$$

with effective viscosity

$$\eta_{\mathrm{eff}} = \eta[1 + \tfrac{3}{2}\, a_{\mathrm{eq}}\, \sigma_1 (n_x^2 - n_y^2 - \tfrac{2}{3}) + 3\, a_{\mathrm{eq}}^2\, \sigma_2\, n_x^2\, n_y^2] + \tilde{\eta}\, \tfrac{1}{2}(n_x^2 - n_y^2)\,. \tag{4.15}$$

Here n_x, n_y are the x- and y-components of the unit vector $\boldsymbol{n}$. For $\boldsymbol{n}$ parallel to the z-axis $\eta_{\mathrm{eff}} = \eta\,(1 - a_{\mathrm{eq}}\, \sigma_1) = \eta_2$ is found. If $\boldsymbol{n}$ is in the x-y-plane

and makes an angle φ with the x-axis, (4.15) reduces to

$$\eta_{\text{eff}} = \eta\,(1 + \tfrac{1}{2}\,a_{\text{eq}}\,\sigma_1 + \tfrac{3}{4}\,a_{\text{eq}}^2\,\sigma_2 \sin^2 2\,\varphi) + \tilde{\eta}\cos 2\,\varphi\,. \tag{4.16}$$

It seems worth to point out that the friction pressure tensor as given by (4.5) contains "transverse" components. In particular, for the special flow field considered above, one finds

$$p_{yz} = -\,[\,(\tfrac{3}{2}\,\eta\,a_{\text{eq}}\,\sigma_1 + \tfrac{1}{2}\,\tilde{\eta})\,n_x\,n_z + 3\,\eta\,a_{\text{eq}}^2\,\sigma_2\,n_x\,n_y^2\,n_z]\,\partial v_x/\partial y\,. \tag{4.17}$$

Due to $\nabla_\mu P + \nabla_\nu \overline{p_{\nu\mu}} = 0$ where P is the hydrostatic pressure, such a term gives rise to a transverse component $\partial P/\partial z = -\,\partial p_{yz}/\partial y$ of the pressure gradient.

Measurements of transverse pressure gradients have been performed for molecular gases in magnetic fields [16, 20] (Senftleben-Beenakker effect). An adaption of these techniques to the study of the flow properties of liquid crystals seems to be worthwhile.

§ 5. Flow Alignment in Nematic Liquid Crystals

a) Constitutive Law for the Molecular Field, Flow Alignment Angle

In addition to Eq. (4.11), Leslie [3, 4] stated a constitutive law for the "molecular field" h_μ which related to $\Sigma_{\mu\nu}$ by

$$h_\mu = -\,2\,\sqrt{\tfrac{3}{2}}\,a_{\text{eq}}\,P_{\text{k}}\,\Sigma_{\mu\nu}\,n_\nu\,. \tag{5.1}$$

This relation can be inferred from the fact that the entropy production (1.3) reduces to the Leslie form

$$\varrho\,m\,T\,(\delta s/\delta t)_{\text{irrev}} = h_\mu\,N_\mu - \overline{p_{\mu\nu}\,\nabla_\mu\,v_\nu}\,, \tag{5.2}$$

with $\boldsymbol{h}$ given by (5.1) if $A_{\mu\nu}$ is approximated by $\sqrt{\tfrac{3}{2}}\,a_{\text{eq}}\,2\,\overline{N_\mu\,n_\nu}$ [cf. Eq. (4.3)].

In the same approximation, multiplication of Eq. (1.8) by $-\,2\,\sqrt{\tfrac{3}{2}}\,a_{\text{eq}}\,P_{\text{k}}\,n_\nu$ leads to

$$h_\mu = \gamma_1\,N_\mu + \gamma_2\,\overline{\nabla_\mu\,v_\nu\,n_\nu} \tag{5.3}$$

(note that $2\,\overline{N_\mu\,n_\nu}\,n_\nu = N_\mu$). The coefficients $\gamma_{1,2}$ are given by

$$\gamma_1 = 3\,a_{\text{eq}}^2\,P_{\text{k}}\,\tau_{\text{a}},\quad \gamma_2 = 2\,\sqrt{3}\,a_{\text{eq}}\,P_{\text{k}}\,\tau_{\text{ap}}\,. \tag{5.4}$$

The Onsager relation (1.9) implies

$$\gamma_2 = 2\,\tilde{\eta}\,. \tag{5.5}$$

Notice that γ_2 and $\tilde{\eta}$ may either be positive or negative. For MBBA, e. g. $\gamma_2 < 0$ is found experimentally (cf. Ref. [3], p. 184). In general, γ_2 as given by (5.4) may be expected to contain an addition term proportional to a_{eq}^2. Such a term is obtained if the isotropic relaxation time τ_{ap} occurring in Eq. (1.8) is replaced by an anisotropic one similar to the replacement of τ_{p} in Eq. (1.7) by the more general expression in Equation (1.11). Then the dependence of γ_1, γ_2 on the order parameter a_{eq} corresponds to that one proposed by Helfrich [21].

For a stationary viscous flow between flat plates as discussed in Sect. 4 c, the director stabilizes in the x-y-plane. The "flow alignment angle" φ between $\boldsymbol{n}$ and the flow direction (parallel to the x-axis) is determined by [3, 4]

$$\cos 2\,\varphi = -\,\gamma_1/\gamma_2\,. \tag{5.6}$$

Of course, this applies only to the cases where $\gamma_1/|\gamma_2| \leqq 1$. For measurements of the angle φ see Ref. [22]. According to (5.4), φ approaches $\pi/4$ for $a_{\text{eq}} \to 0$. An increase of φ with increasing temperature, i. e. with decreasing a_{eq} is found experimentally [22].

b) Alignment Tensor

In the presence of a viscous flow, the alignment tensor $a_{\mu\nu}$ of a nematic liquid crystal is determined by the full constitutive law (1.8). Insertion of (4.3) in (1.8) yields

$$\partial\tilde{a}_{\mu\nu}/\partial t - \omega_\lambda\,(\varepsilon_{\mu\lambda\varkappa}\,\tilde{a}_{\varkappa\nu} + \varepsilon_{\nu\lambda\varkappa}\,\tilde{a}_{\varkappa\mu}) + \tau_{\text{a}}^{-1}\,\Sigma_{\mu\nu} = -\,2\,\sqrt{\tfrac{3}{2}}\,a_{\text{eq}}\,\overline{N_\mu\,n_\nu} - \sqrt{2}\,\tau_{\text{a}}^{-1}\,\tau_{\text{ap}}\,\overline{\nabla_\mu\,v_\nu}\,. \tag{5.7}$$

The quantity $\tilde{a}_{\mu\nu}$, defined by Eq. (4.1), is recalled as the deviation of $a_{\mu\nu}$ from its equilibrium value $a_{\mu\nu}^{(\text{eq})}$. For $\boldsymbol{N}$ see (4.4). Notice that $\Sigma_{\mu\nu}$ vanishes for $\tilde{a}_{\mu\nu} = 0$. For small $\tilde{a}_{\mu\nu}$, the relaxation term $\tau_{\text{a}}^{-1}\,\Sigma_{\mu\nu}$ on the left hand side of Eq. (5.7) is equal to $\sum_{m=-2}^{2} \tau_m^{-1}\,\tilde{a}_{\mu\nu}^{(m)}$. The superscript "$m$" with $m = 0$, $1, \pm 2$ denotes spherical components of a tensor. The reference axis is parallel to $\boldsymbol{n}$. Expressions for the relaxation times τ_0, $\tau_1 = \tau_{-1}$, $\tau_2 = \tau_{-2}$ have been given in Ref. [1].

For a stationary situation and if terms involving $\boldsymbol{\omega}$ are disregarded on the left hand side of (5.7), this equation leads to

$$\tilde{a}_{\mu\nu} = -\,\sqrt{2}\sum_{m=-2}^{2} \tau_m\,\tau_{\text{a}}^{-1}\,\tau_{\text{ap}}\,\overline{\nabla_\mu\,v_\nu}^{(m)} - 2\,\sqrt{\tfrac{3}{2}}\,a_{\text{eq}}\,\tau_1\,\overline{N_\mu\,n_\nu}\,. \tag{5.8}$$

Here, use has been made of $\overline{N_\mu n_\nu} = \overline{N_\mu n_\nu}^{(1)} + \overline{N_\mu n_\nu}^{(-1)}$. The spherical components of (5.8) with $m = 0, \pm 1$ are equivalent to the Leslie relation (5.3). The case $m = \pm 2$, however, is not contained in Equation (5.3). It seems instructive to mention one physical situation where the $m = \pm 2$ components of Eq. (5.8) are of crucial importance.

Consider a flow in x-direction between flat plates which are parallel to the x-z-plane. The director is assumed to be fixed externally as in the Miesowicz flow experiments. Now, for $\boldsymbol{n}$ parallel to the z-direction, the only nonvanishing spherical components of $\tilde{a}_{\mu\nu}^{(m)}$ are those with $m = \pm 2$. In this case, Eq. (5.8) reduces to

$$\tilde{a}_{\mu\nu} = -\sqrt{2}\,(\tau_2/\tau_a)\,\tau_{ap}\,(\partial v_x/\partial y)\,\overline{e_\mu^x\, e_\nu^y} \qquad (5.9)$$

where $\boldsymbol{e}^x$ ($\boldsymbol{e}^y$) is a unit vector parallel to the x-(y)-axis.

As a consequence of Eq. (5.9), the flow birefringence observable for light propagating parallel to the z-direction is similar to the flow birefringence which results from Eq. (2.3). The main difference is that the factor

$$\tau_2/\tau_a = (A + 2\,B\,a_{eq} + C\,a_{eq}^2)^{-1} = (3\,B\,a_{eq})^{-1} \qquad (5.10)$$

occurs instead of A^{-1}.

§ 7. Flow Alignment in the Metastable Isotropic Phase Near T*

a) General Remarks, Power Series Expansion for the Flow Alignment

In Sect. 2, the linearized version of Eq. (1.8) has been employed in order to treat the flow alignment in the isotropic phase. For temperatures T close to the transition temperature T_K and, in particular, in the metastable isotropic phase ($T^* \leqq T < T_K$), the nonlinearity of the constitutive law (1.8) is of crucial importance. Some of the consequences linked with the nonlinearity are studied now.

Firstly, it is noticed that B occurring in Eq. (1.5) can be written as Ca^* where $a^* = B/C$ is the scalar order parameter of the unaxial alignment in the nematic phase at the temperature T^*. Since we are concerned with the flow alignment in the isotropic phase, $a_{\mu\nu}\,a_{\mu\nu} \ll a^{*2}$ can be expected. Thus the terms involving C_1 and C_2 in Eq. (1.5) may be disregarded. If terms associated with the rotational motion of the molecular axes are also disregarded (for a discussion of this point see Sect. 2b), Eq. (1.8) reduces to

$$\tau_a\,\partial\, a_{\mu\nu}/\partial t + A\,a_{\mu\nu} - \sqrt{6}\,B\,\overline{a_{\mu\lambda}\,a_{\lambda\nu}} = -\sqrt{2}\,\tau_{ap}\,\overline{\nabla_\mu v_\nu}\,. \qquad (6.1)$$

The steady state solution of the linearized version of Eq. (6.1) is given by (2.3), viz.

$$a_{\mu\nu} = a_{\mu\nu}^{(1)} \equiv -\sqrt{2}\,A^{-1}\,\tau_{ap}\,\nabla_\mu v_\nu\,.$$

The next higher order terms of a power series expansion in $\overline{\nabla_\mu v_\nu}$ can be inferred from (6.1) with $\partial a_{\mu\nu}/\partial t = 0$. In particular, up to terms of third order in $\overline{\nabla_\mu v_\nu}$ one finds

$$a_{\mu\nu} = a_{\mu\nu}^{(1)} + \sqrt{6}\,A^{-1}\,B\,\overline{a_{\mu\nu}^{(1)}\,a_{\lambda\nu}^{(1)}} + 12\,A^{-2}\,B\,\overline{a_{\mu\lambda}^{(1)}\,a_{\lambda\varkappa}^{(1)}\,a_{\varkappa\nu}^{(1)}}\,. \qquad (6.2)$$

Notice that the various terms in (6.2) are proportional to $A^{-1}\Gamma$, $A^{-3}\Gamma^2$, $A^{-5}\Gamma^3$, respectively, where Γ is the magnitude of the velocity gradient, cf. Equation (2.7). The n-th order terms is proportional to $A^{-(2n-1)}\,\Gamma^n$. Clearly, such an expansion of $a_{\mu\nu}$ diverges for $T \to T^*$, cf. Equation (1.6).

To simplify the further discussion of Eq. (6.1), again the special case of a plane Couette flow is considered.

b) Flow Alignment for a Couette Flow

In the case of a flow velocity parallel to the x-z-plane one has $\overline{\nabla_\mu v_\nu} = \Gamma\,\overline{e_\mu^x\, e_\nu^y}$ with $\Gamma = \partial v_x/\partial y$. For the alignment tensor the ansatz

$$a_{\mu\nu} = \sqrt{2}\,\alpha\,\overline{e_\mu^x\, e_\nu^y} + \sqrt{\tfrac{3}{2}}\,a\,\overline{e_\mu^z\, e_\nu^z} \qquad (6.3)$$

is made. The dependence of the scalar order parameters α and a on Γ has to be determined by Equation (6.1).

With (6.3), the expression $\overline{a_{\mu\lambda}\,a_{\lambda\nu}}$ occurring in (6.1) becomes

$$-\tfrac{2}{3}\sqrt{3}\,\alpha\,a\,\overline{e_\mu^x\, e_\nu^y} + \tfrac{1}{2}(a^2 - \alpha^2)\,\overline{e_\mu^z\, e_\nu^z}\,.$$

Inserting (6.3) into (6.1) and equating the coefficients of $\overline{e_\mu^x\, e_\nu^y}$ and of $\overline{e_\mu^z\, e_\nu^z}$, one obtains

$$\tau_a\,\partial\alpha/\partial t + A\,\alpha + 2\,B\,a\,\alpha = -\tau_{ap}\,\Gamma, \qquad (6.4)$$

$$\tau_a\,\partial a/\partial t + A\,a - B\,a^2 + B\,\alpha^2 = 0\,. \qquad (6.5)$$

In terms of the variables

$$x = 2\,A^{-1}\,B\,\alpha\,,\quad y = 2\,A^{-1}\,B\,a\,,\quad \xi = -2\,A^{-2}\,B\,\tau_{ap}\,\Gamma, \qquad (6.6)$$

Eqs. (6.4), (6.5) can be written as

$$\tau \frac{\partial x}{\partial t} + x + x y = \xi , \tag{6.7}$$

$$\tau \frac{\partial y}{\partial t} + y - \tfrac{1}{2} y^2 + \tfrac{1}{2} x^2 = 0 . \tag{6.8}$$

where $\tau = A^{-1} \tau_a$.

Firstly, these equations are discussed for a steady state situation. In this case, the solution of (6.8) for y which vanishes for $x \to 0$ (and consequently for $\Gamma \to 0$) is

$$y = 1 - \sqrt{1 + x^2} . \tag{6.9}$$

Insertion of this expression into Eq. (6.7) yields, for $\partial x / \partial t = 0$,

$$\varphi(x) \equiv x(2 - \sqrt{1 + x^2}) = \xi . \tag{6.10}$$

In Fig. 1, the curve φ is plotted. The x-values x_i $(i = 1, 2, 3)$ of its intersections with the horizontal line $\varphi = \xi$ are the solutions of Eq. (6.10). For

$$\xi < \xi_0 = \sqrt{\tfrac{1}{2}\sqrt{3}}\,(2 - \sqrt{1 + \tfrac{1}{2}\sqrt{3}}) \lesssim 0.6 \tag{6.11}$$

3 real solutions of (6.10) exist. The solution which becomes equivalent to (6.2) for $\xi \ll \xi_0$ is x_1, the smallest positive value of the x_i. Up to third order in ξ one has

$$x_1 = \xi(1 + \tfrac{1}{2}\xi^2), \quad y_1 = -\tfrac{1}{2}\xi^2 . \tag{6.12}$$

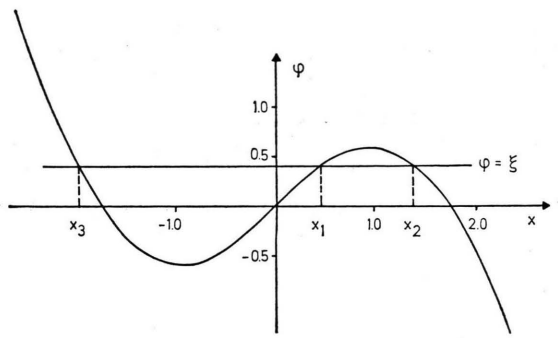

Fig. 1. The quantity φ defined by Eq. (6.10) as function of $x \sim \alpha$. The intersections with the horizontal line $\varphi = \xi \sim \Gamma$ determine the stationary values of the order parameter α in the presence of a velocity gradient Γ.

The inequality (6.11) poses an upper limit on the magnitude of velocity gradient for which the special steady state solution of Eq. (6.1) can exist which reduces to (6.2) for small Γ. This upper limit is determined by

$$|\Gamma| < \Gamma_0 = \frac{A^2}{2B|\tau_{ap}|}\,\xi_0 . \tag{6.13}$$

Notice that $\Gamma_0 \sim (T - T^*)^2$, i. e. Γ_0 decreases rather rapidly if T approaches T^*.

For $\xi > \xi_0$ corresponding to $\Gamma > \Gamma_0$, Eq. (6.10) possesses just the one real solution which has the property $x_3 < 0$. As can be inferred from Fig. 1, for $\xi \to \infty$, x_3 approaches the value of x determined by $-x\sqrt{x^2} = \xi$. This asymptotic solution is equivalent to

$$\alpha = \alpha_\infty \equiv \operatorname{sgn}(\tau_{ap}\,\Gamma) \sqrt{\frac{|\tau_{ap}\,\Gamma|}{2B}} , \tag{6.14}$$

a result which could have been inferred from the steady state version of Eqs. (6.4), (6.5) with $A = 0$.

Next, the stability of the stationary solutions of Eqs. (6.7), (6.8) is investigated. To this purpose, x and y are written as $x_i + \tilde{x}$ and $y_i + \tilde{y}$ where x_i, y_i are the stationary solutions of (6.7), (6.8) and $\tilde{x}$, $\tilde{y}$ are small deviations. Then Eqs. (6.7), (6.8) lead to

$$\begin{aligned} \tau\,\partial\tilde{x}/\partial t + (1 + y_i)x + x_i\tilde{y} &= 0 , \\ \tau\,\partial\tilde{y}/\partial t + x_i\tilde{x} + (1 - y_i)\,\tilde{y} &= 0 , \end{aligned} \tag{6.15}$$

where terms nonlinear in $\tilde{x}$, $\tilde{y}$ have been omitted. It follows from (6.15) that the $\tilde{x}, \tilde{y}$ decay to zero provided that the inequality

$$1 - y_i^2 - x_i^2 > 0 \tag{6.16}$$

is fulfilled. With (6.9), (6.16) implies $x_i^2 < x_0^2 \equiv \frac{1}{2}\sqrt{3}$. This inequality is equivalent to the condition (6.11) specifying the upper limit of the velocity gradient for which the solutions x_1 exists. According to (6.16), the solutions x_2 and x_3 are unstable. This also applies to the asymptotic solution given by (6.14).

Finally, however, a word of caution is in order. It must be emphasized that terms of higher than 2nd order in α and a have been disregarded in Equations (6.4), (6.5). Higher order terms will certainly affect the results (6.11), (6.13), (6.14), and (6.16). The question whether the dramatic behavior of the alignment for a large velocity gradients is indicative of a (kind of a nonequilibrium) phase transition cannot be settled by the present approach based on Eqs. (6.1), (6.4), (6.5).

Concluding Remarks

In this paper, it his been demonstrated that the nonlinear constitutive laws derived in Ref. [1] can be used for the theoretical description of viscous flow, of flow alignment and its reciprocal phenomenon both in the isotropic and nematic phases of liquid crystals. This is also true for the metastable phases where critical behavior can be expected. Flow alignment in the metastable isotropic phase has been discussed in Section 6. For the treatment of nonequilibrium phenomena in the metastable nematic phase, the coupling between the heat flux and the alignment is of importance (cf. Ref. [23]) which has not been considered here.

Finally, it should be emphasized that the constitutive laws derived in Ref. [1] and used in this article are restricted to the case where the alignment is practically spatially homogeneous. The case of a spatially inhomogeneous alignment tensor can be treated by the same approach if some additional terms involving spatial derivatives of the alignment and the flux of the alignment are taken into account in basic equations. For the application of the resulting enlarged set of hydrodynamical equations to specific nonequilibrium phenomena, boundary conditions (in particular also for the alignment tensor) are needed. The required boundary conditions for liquid crystals can be obtained by the appropiate adaption of a method invented by Waldmann [24], which has already been applied successfully to nonequilibrium alignment phenomena in molecular gases [25].

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