Pre- and Post-Transitional Behavior of the Flow Alignment and Flow-Induced Phase Transition in Liquid Crystals

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The flow alignment in the isotropic and nematic phases of a liquid crystal is studied theoretically with special emphasis on temperatures close to the transition temperature. The point of departure is a nonlinear, inhomogeneous relaxation equation for the alignment tensor which is applicable to both phases. The stationary solutions of this equation are analysed. In addition to some well-known results which are recovered as limiting cases for small velocity gradients, it is found that a sufficiently large velocity gradient can induce a transition into an ordered phase if the temperature is between the transition temperature for equilibrium conditions and a somewhat larger critical temperature. In the nematic phase, a weak dependence of the flow alignment angle on the magnitude of the velocity gradient is obtained. The relaxation towards a steady state is also considered.

Recently, nonlinear constitutive laws have been derived[1, 2] which govern the relaxation of the alignment and determine the flow alignment and the friction pressure tensor both in the isotropic phase and in the nematic phase of liquid crystals. These equations were obtained within the framework of irreversible thermodynamics modified in essentially two points, viz. the specific energy was assumed to contain a term quadratic in the alignment and in the entropy terms up to 4-th order in the alignment were included. In the absence of a viscous flow, the nonlinear relaxation equation for the alignment yields zero and nonzero steady state solutions if the temperature is above or below the characteristic temperature T_K where the transition from the isotropic to the nematic phase occurs. In the presence of a viscous flow, the equation of de Gennes[3, 4] for the pretransitional behavior of the flow birefringence in the isotropic phase and the Ericksen-Leslie equation[4, 5] for the flow alignment in the nematic phases are comprised as special cases.

Nonequilibrium phenomena in the vicinity of T_K are of particular interest. In Ref.[2], it has been noticed that for the flow alignment in the isotropic phase close to T_K, a steady state and spatially homogenous solution could only be found if the velocity gradient (flow rate) did not exceed a certain value which is proportional to $(T-T^*)^2$. The temperature T^* (with $T^* < T_K$) marks the limit of existence of the metastable isotropic phase. The theoretical treatment of this specific point in Ref.[2] was based on an approximation to the nonlinear equations. Consequently, the question what happens if the velocity gradient does exceed its critical value could not be answered. In this paper the full nonlinear equations are used. For small velocity gradients, the flow alignment behaves as described in Reference[2]. If the velocity gradient is larger than a critical value, the liquid undergoes a transition to a nematic phase with the director in the plane determined by the direction of the velocity and its gradient. It is remarkable that a transition into an ordered phase can still be induced by application of a velocity gradient if the temperature is above T_K but below a critical temperature T_c which is determined by $T_c - T_K \approx \frac{1}{2}(T_K - T^*)$. A similar behavior is expected for lyotropic liquid crystals where the number density of the solute molecules rather than the temperature is the relevant thermodynamic variable.

This paper is divided into 6 sections. Firstly, some general remarks are made on the description of the alignment and on the relation between alignment and birefringence. Then, in Sect. 2, the relaxation equation for the alignment tensor is presented. For a special geometry, viz. flow between plane parallel plates, the alignment tensor can be characterized by 3 scalar variables. The choice of these variables and their physical meaning (one of them is the flow alignment angle) is discussed in Section 3. The relaxation equations for these scalar variables following from the tensor relaxation equation are stated in Section 4. The stationary solutions of these equations (which are the main result of this paper) are discussed in Section 5. The dependence of the

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magnitude of the relevant scalar order parameter and the flow alignment angle on the velocity gradient is shown graphically for some cases of special interest. Finally, in Section 6, the relaxation towards the stationary state is considered briefly.

1. General Remarks on the Alignment and on Birefringence

The alignment of a liquid composed of (effectively) axisymmetric molecules is characterized by the second rank tensor

$$\mathbf{a} = \zeta \langle \overline{\boldsymbol{u}\boldsymbol{u}} \rangle . \qquad (1)$$

Here $\boldsymbol{u}$ is a unit vector parallel to the figure axis of a molecule and the bracket $\langle \ldots \rangle$ refers to an average over the molecules in the liquid. The symbol $\overline{\ldots}$ indicates the symmetric traceless part of a tensor, e. g. one has $\overline{\boldsymbol{u}\boldsymbol{u}} = \boldsymbol{u}\boldsymbol{u} - \frac{1}{3}\boldsymbol{\delta}$ where $\boldsymbol{\delta}$ is the unit tensor. The quantity ζ is a numerical factor which can be chosen conveniently. Following Refs. [1, 2], $\zeta = (15/2)^{1/2}$ is used here. Of course, physically observable quantities must be independent of any specific choise for ζ.

For the special case of an unaxial alignment, $\mathbf{a}$ is of the form

$$\mathbf{a} = \sqrt{\tfrac{3}{2}}\, a\, \overline{\boldsymbol{n}\boldsymbol{n}} \qquad (2)$$

where $\boldsymbol{n}$ is a (space fixed) unit vector. The factor $\sqrt{\frac{3}{2}}$ has been inserted such that $\mathbf{a} : \mathbf{a} = a^2$. With the special choice for ζ mentioned above, the scalar order parameter a is given by $a = \sqrt{5}\,\langle P_2(\boldsymbol{u}\cdot\boldsymbol{n})\rangle = \sqrt{5}\,S$ where P_2 is the 2nd Legendre polynomial; S is the order parameter of Maier and Saupe [6]. The alignment induced in an isotropic liquid by application of a (spatially homogeneous) magnetic or electric field, as well as the alignment occurring in the nematic phase of a liquid crystal is of the unaxial type (2). It must be stressed, however, that this is not the case in general. The alignment caused by a gradient of the flow velocity (which leads to flow birefringence) is of biaxial type.

A medium is birefringent whenever the anisotropic, i. e. symmetric traceless part $\overline{\boldsymbol{\epsilon}}$ of the dielectric tensor $\boldsymbol{\epsilon}$ is nonzero. In a liquid composed of optically anisotropic particles as considered here, $\overline{\boldsymbol{\epsilon}}$ can be assumed to be proportional to the alignment tensor, viz.

$$\overline{\boldsymbol{\epsilon}} = \varepsilon_{\mathrm{a}}\, \mathbf{a} \qquad (3)$$

where ε_{a} is the relevant proportionality coefficient. On account of relation (3), the alignment tensor determines the directions of the principal axes of the dielectric tensor and the magnitude of the birefringence.

2. Relaxation Equation for the Alignment

In Ref. [1], a nonlinear (inhomogeneous) relaxation equation for the alignment tensor has been obtained by the methods of irreversible thermodynamics. In the presence of a viscous flow, this equation can be written as

$$\tau_{\mathrm{a}} \left(\frac{\partial \mathbf{a}}{\partial t} - 2\, \overline{\boldsymbol{\omega} \times \mathbf{a}} \right) + \boldsymbol{\Sigma} = -\sqrt{2}\, \tau_{\mathrm{ap}} \overline{\boldsymbol{\nabla} \boldsymbol{v}} , \qquad (4)$$

with $\boldsymbol{\omega} = \frac{1}{2}\operatorname{rot}\boldsymbol{v}$, $\boldsymbol{v}$ is the flow velocity. The "relaxation" times τ_{a} and τ_{ap} are phenomenological coefficients; τ_{a} is positive, τ_{ap} may have either sign. In Ref. [7], where an equation very similar to (4) has been derived by a Fokker-Planck equation approach, τ_{a} and τ_{ap} have been related to molecular parameters. The quantity $\boldsymbol{\Sigma}$ occurring in (4) is a nonlinear function of $\mathbf{a}$, viz.

$$\boldsymbol{\Sigma} = A\,\mathbf{a} - \sqrt{6}\, B\, \overline{\mathbf{a}\cdot\mathbf{a}} + C_1\, \mathbf{a}\,(\mathbf{a} : \mathbf{a}) + C_2\, \overline{\mathbf{a}\cdot\mathbf{a}\cdot\mathbf{a}} ,$$
$$A = A_0\,(1 - T^*/T) , \qquad (5)$$

where T is the temperature of the liquid and T^* is a characteristic temperature related to the mean field energy. The coefficients A_0, B, C_1, C_2 are positive. Their temperature dependence is assumed to be weak such that it can be ignored. It has already been pointed out earlier that the equation of de Gennes [3, 4] for the pretransitional behavior of the flow birefringence in the isotropic phase, and the Ericksen-Leslie [5] equation for the flow alignment in the nematic phase are special cases of Equation (4).

In the absence of a flow field, the stationary solutions of (4) are determined by $\boldsymbol{\Sigma}\ (\mathbf{a}) = 0$. The stable equilibrium solutions are $\mathbf{a} = 0$ for $T > T_{\mathrm{K}}$ (isotropic phase) and $\mathbf{a} = \sqrt{\frac{3}{2}}\, a_{\mathrm{eq}}\, \overline{\boldsymbol{n}\boldsymbol{n}}$ (nematic phase) for $T < T_{\mathrm{K}}$. The temperature T_{K} where the transition from the isotropic to the nematic phase takes place is determined by

$$\delta_{\mathrm{K}} \equiv 1 - \frac{T^*}{T_{\mathrm{K}}} = \frac{2}{9}\, \frac{B^2}{A_0\, C} \qquad (6)$$

with $C = C_1 + \frac{1}{2} C_2$. Notice that $T_K > T^*$. At $T = T_{\mathrm{K}}$, the equilibrium value a_{eq} of the order parameter is $a_{\mathrm{K}} = \frac{2}{3}\frac{B}{C}$. With the dimensionless temperature variable

$$\vartheta = \left(1 - \frac{T^*}{T}\right) \delta_{\mathrm{K}}{}^{-1} = \frac{T - T^*}{T_{\mathrm{K}} - T^*} \cdot \frac{T_{\mathrm{K}}}{T} , \qquad (7)$$

the temperature dependence of a_{eq} is given by

$$a_{\text{eq}} = a_{\text{K}}\, s(\vartheta)\,, \quad s(\vartheta) = \tfrac{3}{4}\left(1 + \sqrt{1 - \tfrac{8}{9}\vartheta}\right). \qquad (8)$$

Notice that $\vartheta = 1$ and $\vartheta = 0$ correspond to $T = T_{\text{K}}$ and $T = T^*$, respectively. It should be mentioned, that the isotropic and the nematic phases are metastable in the temperature ranges corresponding to $0 < \vartheta < 1$ and $1 < \vartheta < 9/8$..

With due modifications, the present theory can also be applied to lyotropic liquid crystals where the number density n of solute particles rather than the temperature is the relevant thermodynamic variable. In this case, A occurring in (5) is assumed to be of the form $A = A_0\ (1 - n/n^*)$ with a characteristic number density n^*. Then ϑ is equal to $(n^* - n)/(n^* - n_{\text{K}})$, n_{K} (with $n_{\text{K}} < n^*$) is the number density where the transition into a nematic occurs under equilibrium conditions.

3. Special Geometry, Scalar Variables

The tensor equation (4) is equivalent to 5 equations for 5 linearly independent scalar variables (e. g. the spherical components of $\mathbf{a}$). For the special geometry to be considered in the following, it is sufficient to take 3 scalar variables into account.

To obtain some feeling for a convenient choice of these variables, the flow alignment problem is considered for a flow between plane parallel plates of Couette or of Poiseuille type. If the x- and y-directions of a cartesian coordinate system are chosen parallel to the flow velocity $\boldsymbol{v}$ and to its gradient (with $\partial v_x/\partial y > 0$), one has

$$\overline{\nabla \boldsymbol{v}} = \overline{\boldsymbol{e}^x \boldsymbol{e}^y}\, \frac{\partial v_x}{\partial y}\,, \quad \boldsymbol{\omega} = \frac{1}{2}\, \text{rot}\, \boldsymbol{v} = -\frac{1}{2}\, \frac{\partial v_x}{\partial y}\, \boldsymbol{e}^z\,,$$

where $\boldsymbol{e}^{x,y,z}$ are unit vectors parallel to the axes of the coordinate system. The linearized version of Eq. (4) with $\boldsymbol{\omega} = 0$ yields the steady state solution $\mathbf{a} \sim \overline{\boldsymbol{e}^x \boldsymbol{e}^y}\, \partial v_x/\partial y$. This result can be considered as a first step in an iterative solution of (4) corresponding to increasing powers of $\partial v_x/\partial y$. The terms involving $\boldsymbol{\omega}$ and B in $\boldsymbol{\Sigma}$ generate, in 2nd order in $\partial v_x/\partial y$, contributions to $\mathbf{a}$ which are proportional to $\boldsymbol{e}^x \boldsymbol{e}^x - \boldsymbol{e}^y \boldsymbol{e}^y$ and to $\overline{\boldsymbol{e}^x \boldsymbol{e}^x} + \overline{\boldsymbol{e}^y \boldsymbol{e}^y} = -\overline{\boldsymbol{e}^z \boldsymbol{e}^z}$, respectively. Higher order iterations generate terms of the same tensor character als already occurred in first and second order. Thus the following ansatz (which could also have been inferred from symmetry arguments without recourse to the iteration scheme) can be made for the alignment tensor:

$$\mathbf{a} = \tfrac{1}{2}\sqrt{3}\, a_{\text{K}} (Q_+ \mathbf{T}_+ + Q_- \mathbf{T}_-) + a_{\text{K}} R\, \mathbf{T}_0\,, \qquad (9)$$

with

$$\mathbf{T}_+ = \sqrt{2}\, \overline{\boldsymbol{e}^x \boldsymbol{e}^y}\,, \quad \mathbf{T}_- = \tfrac{1}{2}\sqrt{2}\, (\boldsymbol{e}^x \boldsymbol{e}^x - \boldsymbol{e}^y \boldsymbol{e}^y)\,,$$

$$\mathbf{T}_0 = \sqrt{\tfrac{3}{2}}\, \overline{\boldsymbol{e}^z \boldsymbol{e}^z}\,. \qquad (10)$$

These tensors are orthogonal and normalized i. e. one has

$$\mathbf{T}_l : \mathbf{T}_k = \delta_{lk} \qquad (11)$$

where l and k stand for "+, −, 0". The variables Q_+, Q_-, R are scalar order parameters (in units of $a_{\text{K}} = \frac{2}{3} B/C$). For later reference, it is noted that the unaxial alignment $\mathbf{a} = \sqrt{\frac{3}{2}}\, a_{\text{eq}}\, \overline{\boldsymbol{n}\boldsymbol{n}}$ as it occurs in the nematic phase is of the form (9) with $Q_+ = Q_- = 0$, $a_{\text{K}} R = a_{\text{eq}}$, if $\boldsymbol{n}$ is parallel to $\boldsymbol{e}^z$, and $a_{\text{K}} Q_+ = a_{\text{eq}} \sin 2\chi$, $a_{\text{K}} Q_- = a_{\text{eq}} \cos 2\chi$, $a_{\text{K}} R = -\frac{1}{2} a_{\text{eq}}$ if one has $\boldsymbol{n} = \cos\chi\, \boldsymbol{e}^x + \sin\chi\, \boldsymbol{e}^y$.

In general, Q_+ and Q_- can be written as

$$Q_+ = Q \sin 2\chi\,, \quad Q_- = Q \cos 2\chi\,, \qquad (12)$$

with

$$Q = (Q_+^2 + Q_-^2)^{1/2}, \quad \text{tg}\, 2\chi = Q_+/Q_-\,. \qquad (13)$$

The angle χ is related the directions of the principal axes of $\mathbf{a}$ and consequently of the dielectric tensor. More specifically, the ansatz (9) implies that two of the principal axes are in the x-y-plane and enclose the angles χ and $\chi + \pi/2$ with the x-direction; then, of course, the third one is parallel to the z-axis.

4. Relaxation Equations for the Scalar Variables

Insertion of the ansatz (9) into Eq. (4), use of (11) and of $\overline{\boldsymbol{e}^z \times \mathbf{T}_+} = -\mathbf{T}_-$, $\overline{\boldsymbol{e}^z \times \mathbf{T}_-} = \mathbf{T}_+$, yields the following equations for Q_+, Q_- and R

$$\tau_{\text{K}} \frac{\partial Q_+}{\partial t} + \Gamma Q_- + \tilde{\vartheta} Q_+ = \lambda_{\text{K}} \Gamma, \qquad (14)$$

$$\tau_{\text{K}} \frac{\partial Q_-}{\partial t} - \Gamma Q_+ + \tilde{\vartheta} Q_- = 0\,, \qquad (15)$$

$$\tau_{\text{K}} \frac{\partial R}{\partial t} + \tilde{\vartheta} R + \tfrac{9}{4}(Q^2 - 4R^2) = 0\,, \qquad (16)$$

with

$$\tilde{\vartheta} = \vartheta + 6R + 2R^2 + \tfrac{3}{2} Q^2\,, \qquad (17)$$

and

$$\Gamma = \tau_{\text{K}} \frac{\partial v_x}{\partial y}\,. \qquad (18)$$

Here $\tau_{\text{K}} = \tau_{\text{a}} (A_0\, \delta_{\text{K}})^{-1}$ is the relaxation time of the alignment in the isotropic phase for $T = T_{\text{K}}$. It is related to the Leslie coefficient [2] γ_1 by

$$\tau_{\mathrm{K}} = (A_0\,\delta_{\mathrm{K}}\,3\,a_{\mathrm{eq}}^2\,P_{\mathrm{k}})^{-1}\,\gamma_1\,, \quad P_{\mathrm{k}} = n\,k_{\mathrm{B}}\,T\,, \quad (19)$$

where n is the number density of the liquid. Notice that one has $\Gamma > 0$ if the y-direction is chosen such that $\partial v_x/\partial y$ is positive.

The quantity λ_{K} is given by

$$\lambda_{\mathrm{K}} = -2\,\tau_{\mathrm{ap}}\,(\sqrt{3}\,a_{\mathrm{K}}\,\tau_{\mathrm{a}})^{-1} = -(\gamma_2/\gamma_1)_{\mathrm{K}}\,. \quad (20)$$

The subscript "K" indicates that the ratio between the Leslie coefficients [2–5] γ_2 and γ_1 has to be taken at the transition temperature T_{K}.

For prolate (rod-like) particles, one has $\tau_{\mathrm{ap}} < 0$ and consequently $\lambda_{\mathrm{K}} > 0$.

The Equations (14, 15) for Q_+ and Q_- are equivalent to two equations for the variables Q and χ, viz.

$$\tau_{\mathrm{K}}\,\partial Q/\partial t + \tilde{\vartheta}\,Q = \lambda_{\mathrm{K}}\,\Gamma \sin 2\chi\,, \quad (21)$$

$$\tau_{\mathrm{K}}\,\partial\, 2\chi/\partial t + \Gamma = Q^{-1}\,\lambda_{\mathrm{K}}\,\Gamma \cos 2\chi\,. \quad (22)$$

Notice that for $T < T_{\mathrm{K}}$ the stationary solutions of (14–16) and (21, 22) in the absence of a flow field ($\Gamma = 0$) are $R = s(\vartheta)$, $Q = 0$, cf. (8), and $R = -\frac{1}{2}s(\vartheta)$, $Q = Q_{\mathrm{eq}} = s(\vartheta)$ corresponding to a nematic phase with the director $\boldsymbol{n}$ parallel to the z-axis and somewhere in the x-y-plane, respectively. In the latter case one has $\tilde{\vartheta} = 0$.

5. Stationary Solution, Flow-Induced Phase Transition

a) General Remarks

The stationary solution of Eqs. (14–16) or equivalently of Eqs. (16, 21, 22) for a time independent velocity gradient can be obtained from these equations with all time derivatives put equal to zero. Then (22) reduces to

$$\cos 2\chi = Q\,\lambda_{\mathrm{K}}^{-1}\,. \quad (23)$$

Clearly, such a stationary solution exists only if the inequality

$$Q \leqq |\lambda_{\mathrm{K}}| \quad (24)$$

is fulfilled. The following discussions are restricted to the case $\lambda_{\mathrm{K}} > 0$ (prolate particles).

Similarly, elimination of $\sin 2\chi$ from (21) with the help of (22) yields

$$\lambda_{\mathrm{K}}\,\Gamma = \tilde{\vartheta}\,Q\,(1 - Q^2\,\lambda_{\mathrm{K}}^{-2})^{-1/2}\,, \quad (25)$$

for $\tilde{\vartheta} = \tilde{\vartheta}(R, Q)$ see (17). Since $\lambda_{\mathrm{K}}\,\Gamma \geqq 0$ is assumed, Eq. (24) has a physically meaningful solution only if $\tilde{\vartheta}$ is positive. Finally, Eq. (16) leads to a relation between R and Q, viz.

$$Q^2 = -\tfrac{4}{9}\,R\,(\vartheta - 3\,R + 2\,R^2)\,(1 + \tfrac{2}{3}\,R)^{-1}\,. \quad (26)$$

The physical range of R values is restricted by the obvious condition $Q^2 > 0$. The problem of determining $Q = Q(\Gamma)$ and $\chi = \chi(\Gamma)$ for a steady state situation is now solved, in principle, if R occurring in $\tilde{\vartheta}$ is eliminated with the help of Eq. (26). Before this point is discussed any further, it seems to be instructive to consider Eqs. (23, 25) for two limiting cases.

b) Special Limiting Cases

In the isotropic phase for temperatures T well above the transition temperature, $\tilde{\vartheta}$ can be approximated by $\tilde{\vartheta} \approx \vartheta$, $\vartheta \sim (1 - T^*/T)$, cf. (7). Then (25) yields (see also Ref. [2]).

$$Q = \vartheta^{-1}\,\lambda_{\mathrm{K}}\,\Gamma\,(1 + \vartheta^{-2}\,\Gamma^2)^{-1/2}\,, \quad (27)$$

and (23) becomes equivalent to $\operatorname{tg} 2\chi = \vartheta\,\Gamma^{-1}$. Notice that the expression (27) fulfills the inequality (24) for all values of Γ. In the limit $\Gamma \to 0$, i. e. for small velocity gradients, (27) essentially reduces to the expression of de Gennes [3] for flow alignment in the isotropic phase, viz.

$$Q_+ = \vartheta^{-1}\,\lambda_{\mathrm{K}}\,\Gamma\,, \quad \chi = \pi/4\,. \quad (28)$$

Deviations from (27) which show up at temperatures close to T_{K} will be discussed later.

Next, the nematic phase ($T < T_{\mathrm{K}}$) is considered with the director in the x-y-plane. If it is assumed that Q and R are equal to their equilibrium values $Q_{\mathrm{eq}} = s(\vartheta)$ and $R_{\mathrm{eq}} = -\frac{1}{2}Q_{\mathrm{eq}}$, for $s(\vartheta)$ see (8), Eq. (26) is fulfilled, and (23) reduces to the Ericksen-Leslie expression

$$\cos 2\chi = \lambda^{-1}\,, \quad \Gamma = Q_{\mathrm{eq}}^{-1}\,\lambda_{\mathrm{K}} \quad (29)$$

for the flow alignment angle. Notice, however, that one has $\tilde{\vartheta} = 0$ in this case, i. e. Eq. (25) is obeyed only in the limit $\Gamma \to 0$. Another special case to be mentioned briefly is the nematic phase with the director parallel to the z-axis and $R = R_{\mathrm{eq}} = s(\vartheta)$. Then $\tilde{\vartheta}$ can be approximated by $\vartheta - 6\,R_{\mathrm{eq}} + 2\,R_{\mathrm{eq}}^2 = 9\,R_{\mathrm{eq}}$ and Q is given by an expression of the form (27) but with ϑ replaced by $9\,R_{\mathrm{eq}}$.

c) General Solution, Flow-Induced Phase Transition, Critical Behavior

Now, the discussion of the full Equations (23, 25, 26) is resumed. To obtain an appreciation for the relation between Q and R as given by (26), Q is plotted as function of R with the temperature variable ϑ as parameter in Figure 1. For $\vartheta \geqq 9/8$, R has always to be negative; for $\vartheta < 9/8$ also positive values for R are allowed if R is within the range indicated by the loops on the right hand side of Figure 1. A nematic equilibrium alignment with the director parallel to the z-axis corresponds to $Q=0$, and R given by the intersections of the loops with the R-axis marked by crosses in Figure 1. Similarly, an unaxial alignment with the director in the x-y-plane corresponds to pairs of Q, R values obtained by the intersections of the curves on the left side of Fig. 1 with the dashed straight line $Q = -\frac{1}{2} R$.

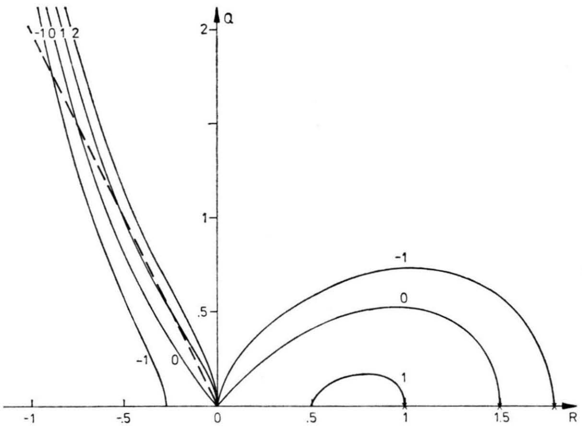

Fig. 1. The functional relation between the order parameters Q and R as given by Equation (26). The various curves are labeled with the pertaining value of the parameter ϑ.

It is evident from Eq. (26) and from a glance at Fig. 1, that the elimination of R from $\tilde{\vartheta}$ (R, Q) with the help of (26) which is required to obtain $Q = Q(\vartheta, \Gamma)$ from (25) is not a simple task unless the above mentioned special cases are considered. To treat the general case, it is more convenient to express Q in (25) as function of R with the help of (26). Notice that Q also occurs in $\tilde{\vartheta}$, cf. (17). This yields $\Gamma = \Gamma(\vartheta, R)$. With $Q = Q(\vartheta, R)$ determined by (26), one has now a parameter representation for the desired functional interrelation between Q and Γ. This procedure has been used to plot $\vartheta^{-1} \lambda_K \Gamma$ as function of Q for $\vartheta = 1$, 1.2, 1.5, as shown in Figure 2. It is recalled that $\vartheta = 1$ corresponds to the transition temperature T_K. The fully drawn curves are for $\lambda_K = 2$, the dashed-dotted lines are for $\lambda_K \rightarrow \infty$ where (25) reduces to $\lambda_K \Gamma \approx \tilde{\vartheta} Q$. The dashed straight line through the origin corresponds to de Gennes' result (28). Though this is a good approximation for $\vartheta \geqq 1.5$ and small Γ, the curves displayed in Fig. 2 are drastically different from this simple straight line behavior. In fact, they are reminiscent of van der Waals curves occurring in connection with gas-liquid phase transition. Notice, however, that the influence of a velocity gradient on the order parameter Q considered here is a nonequilibrium phenomenon. To discuss the curves shown in Fig. 2 further, the case $\vartheta = 1$ is considered first where, under equilibrium conditions ($\Gamma = 0$), the isotropic ($Q = 0$) and nematic ($Q = 1$) phases are in coexistence. Application of a velocity gradient in the isotropic phase leads to an increase of Q still Γ reaches a value where one has $\partial \Gamma / \partial Q = 0$. This marks the limit of existence of a metastable phase. The parts of the curve $\Gamma = \Gamma(Q)$ with $\partial \Gamma / \partial Q < 0$ correspond to an unstable situation and are dashed in Figure 2. It can be seen from the right hand part of the curve for $\vartheta = 1$ that application of a velocity gradient in the nematic phase leads to an increase of the order parameter from its equilibrium value $Q = 1$. This influence of Γ on the magnitude of the order parameter in the nematic phase is, however, rather weak. The curve for $\vartheta = 1.2$ clearly shows that a transition from an isotropic to an ordered phase can be expected if Γ exceeds a certain value. The two phases are in coexistence for a Γ which lies between the maximum and minimum values of $\Gamma = \Gamma(Q)$. This behavior is remarkable because $\vartheta = 1.2$ already lies above $\vartheta_K{}^* = 9/8$ which determines the limit of existence of a (superheated) metastable nematic phase for $\Gamma = 0$. The critical isotherm goes through the critical point characterized by $\partial^2 \Gamma / \partial Q^2 = 0$. As can be seen from a comparison of the full and the dashed-dotted curves which are for $\lambda_K = 2$ and $\lambda_K \rightarrow \infty$, respectively, the critical values ϑ_c, Q_c, $\lambda_K \Gamma_c$ for ϑ, Q, $\lambda_K \Gamma$ do not depend strongly on λ_K. Approximately, one has

$$\vartheta_c \approx 1.5\,, \quad Q_c \approx .5\,, \quad \lambda_K \Gamma_c \approx .35\,. \quad (30)$$

With $\Gamma = \Gamma(Q)$ determined as described aboved, the flow alignment angle given by (23) can be plotted as function of Γ. In Fig. 3, this has been done $\lambda_K = 2$ and $\vartheta = 1$, 1.2, 1.5. The parts of the curves corresponding to an unstable situation are dashed. In the limit $\Gamma \rightarrow 0$, χ is equal to 45° in the isotropic phase and, in the nematic phase (with $\boldsymbol{n}$

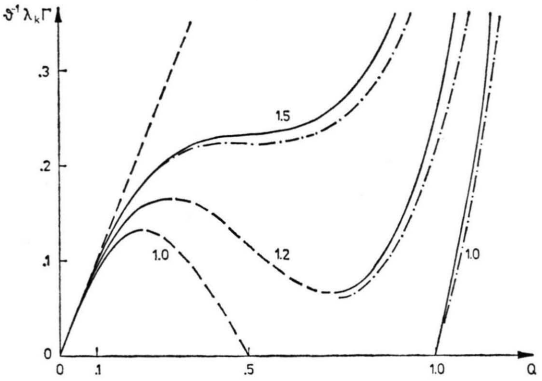

Fig. 2. The quantity $\vartheta^{-1}\,\lambda_{\mathrm{K}}\,\Gamma$, where Γ is the dimensionless velocity gradient variable, as function of Q for the values 1.0, 1.2, and 1.5 of the parameter ϑ. The full and dashed-dotted curves are for $\lambda_{\mathrm{K}}=2$ and $\lambda_{\mathrm{K}} \gg 1$, respectively. The straight line through the origin corresponds to de Gennes' result, cf. Equation (28).

in the x-y-plane) it is given by (29). Many of the features shown in Fig. 3 are similar to those of Figure 2. The curve for $\vartheta=1.2$, e. g. indicates that a jump of the flow alignment angle to a smaller value can be expected for a certain value of Γ where a transition into an ordered phase occurs. The dashed-dotted line in Fig. 3 is obtained from the approximate expression tg $2\,\chi=\vartheta^{-1}\,\Gamma$ (cf. 27) for the angle χ with $\vartheta=1.5$. Clearly, even for $\vartheta=1.5$, the fully drawn curve $\chi=\chi(\Gamma)$ deviates significantly from the approximate curve if Γ is not too small.

Next, an estimate of the magnitude of the velocity gradient $(\partial v_x/\partial y)_{\mathrm{c}}$ associated with the critical value Γ_{c} for Γ is in order. According to Eqs. (18, 30), one has $(\partial v_x/\partial y)_{\mathrm{c}} \approx .35 \quad (\lambda_{\mathrm{K}}\,\tau_{\mathrm{K}})^{-1}$. Thus for ordinary (nematic) liquid crystals like PAA and MBBA with $\lambda_{\mathrm{K}} \geqq 1$ and $\tau_{\mathrm{K}} \approx 10^{-6}\,\mathrm{s}-10^{-7}\,\mathrm{s}$, a critical velocity gradient of $10^5\,\mathrm{s}^{-1}-10^6\,\mathrm{s}^{-1}$ is found. This value is rather large. Shear rates up to $10^6\,\mathrm{s}^{-1}$, however, are used in high-shear-viscometry [8]. Notice that discontinuities of Q and χ (cf. Figs. 2, 3) indicating a flow-induced transition into an ordered phase should already occur for smaller velocity gradients if the temperature T is closer to T_{K}. Furthermore, the chances to observe such a phenomenon and the critical behavior for $\vartheta=\vartheta_{\mathrm{c}}$, $\Gamma=\Gamma_{\mathrm{c}}$ are much better for liquids composed of larger molecules where the relaxation time τ_{K} is larger. In particular, lyotropic liquid crystals, i. e. solutions of (relatively stiff) macromolecules should be good candidates. In that case, the number density or the concentration of the solute molecules rather than the temperature is the relevant thermodynamic variable, cf. the comments at the end of Section 2. In fact, a flow-induced transition into an ordered phase has been noticed in connection with viscosity measurements of polymer solutions [9] performed at concentrations below the value where a transition into the nematic phase occurs under equilibrium conditions.

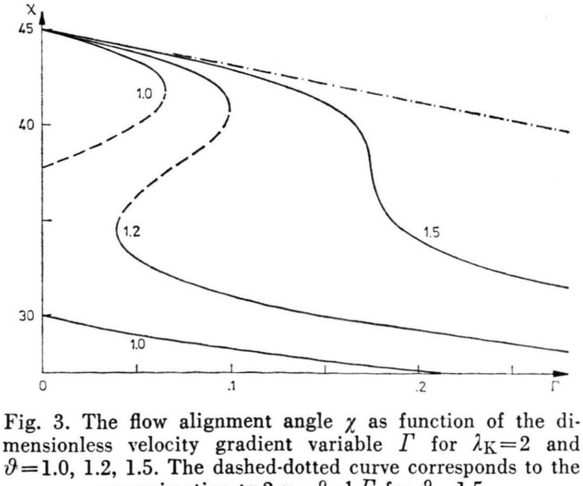

Fig. 3. The flow alignment angle χ as function of the dimensionless velocity gradient variable Γ for $\lambda_{\mathrm{K}}=2$ and $\vartheta=1.0$, 1.2, 1.5. The dashed-dotted curve corresponds to the approximation tg $2\,\chi=\vartheta^{-1}\,\Gamma$ for $\vartheta=1.5$.

6. Relaxation towards Steady State, Stability

To study the approach towards a steady situation, in equations (16, 21, 22) the variables R, Q, χ are replaced by $R_0+\delta R$, $Q_0+\delta Q$, $\chi_0+\delta\chi$ where R_0, Q_0, χ_0 are assumed to be stationary solutions of these equations. If terms nonlinear in the deviations are disregarded, one finds the following relaxations equations

$$\tau_{\mathrm{K}}\frac{\partial}{\partial t}\,\delta R+\Phi_{RR}\,\delta R+\Phi_{RQ}\,\delta Q \qquad =0, \quad (31)$$

$$\tau_{\mathrm{K}}\frac{\partial}{\partial t}\,\delta Q+\Phi_{QR}\,\delta R+\Phi_{QQ}\,\delta Q-2\,Q\,\Gamma\,\delta\chi=0, \quad (32)$$

$$\tau_{\mathrm{K}}\frac{\partial}{\partial t}\,\delta\chi \qquad +\tfrac{1}{2}\,Q^{-1}\,\Gamma\,\delta Q+\tilde{\vartheta}\,\delta\chi=0, \quad (33)$$

with

$$\Phi_{RR}=\tilde{\vartheta}-12\,R+4\,R^2, \quad \Phi_{RQ}=\tfrac{9}{2}\,Q(1+\tfrac{2}{3}\,R)\,,$$
$$\Phi_{QR}=6\,Q(1+\tfrac{2}{3}\,R)\,, \qquad \Phi_{QQ}=\tilde{\vartheta}+3\,Q^2, \qquad (34)$$

for $\tilde{\vartheta}$ see (17). Notice that the subscript "0" referring to the stationary solution has been dropped in order to simplify the notation. The coefficient matrix of Eqs. (31, 32, 33) has to be positive definite. In particular, this implies that the inequalities $\tilde{\vartheta} > 0$ and

$$\Delta_{RQ} \equiv \Phi_{RR}\, \Phi_{QQ} - \Phi_{RQ}\, \Phi_{QR} > 0 \qquad (35)$$

have to hold true in order that a relaxation towards the stationary state occurs. If, for the isotropic phase, the approximations $\Phi_{RR} = \Phi_{QQ} \approx \vartheta$, $\Phi_{RQ}\, \Phi_{QR} \approx 27\, Q^2$ and $Q = \vartheta^{-1} \lambda_{\mathrm{K}}\, \Gamma$ (cf. Eq. (28)) are used, the inequality (35) becomes equivalent to $3\sqrt{3}\, \lambda_{\mathrm{K}} < \vartheta^2$. Notice, however, that this stability limit which has also been obtained in Ref.[2] by a somewhat different analysis, is based on an approximation where only terms in the lowest order in Q are taken into account. The stability limits for Γ based on the full expressions for $\Phi \ldots$ can also be inferred from the extrema of $\Gamma = \Gamma(Q)$, cf. Figure 2.

Of specific interest is the relaxation of the angle χ. For small Γ, the relaxation equation (33) for χ is decoupled from those for R and Q. In this case, χ decays exponentially towards its steady state value with the effective relaxation time

$$\tau_{\mathrm{eff}} = \tau_{\mathrm{K}}\, \tilde{\vartheta}^{-1}. \qquad (36)$$

In the isotropic phase, τ_{eff} becomes equal to the relaxation time $\tau = \tau_{\mathrm{K}}\, \vartheta^{-1}$ of the alignment tensor if $\tilde{\vartheta}$ is approximated by ϑ. In the nematic phase, on the other hand, one has $\tilde{\vartheta} \approx \lambda\, \Gamma \sqrt{1 - \lambda^{-2}}$, cf. (25) with $\lambda = Q_{-1}^{\mathrm{eq}}\, \lambda_{\mathrm{K}}$ if Q is replaced by its equilibrium value Q_{eq}. Notice that the effective relaxation time for the flow alignment angle χ is proportional to Γ^{-1} in this case, viz.

$$\tau_{\mathrm{eff}} = \tau_{\mathrm{K}} (\lambda^2 - 1)^{-1/2}\, \Gamma^{-1}. \qquad (37)$$

Incidentally, (37) also indicates that no (spatially homogeneous) steady state can be reached for $\lambda < 1$.

Concluding Remarks

In this paper, spatial inhomogeneities of the alignment tensor associated with fluctuations, boundary effects, disclinations and domain formation have been disregarded. Furthermore, laminar flow only has been considered. Within these limitations, the following results have been obtained from the stationary solution of the inhomogeneous nonlinear relaxation equation (4) for the alignment tensor (which reduces to the Eqs. (14 – 16) or (16, 21, 22) for scalar variables). For temperatures T above the transition temperature T_{K}, the results of de Gennes for flow birefringence in the isotropic phase are recovered in the limit of small velocity gradients. For sufficiently large shear rates, a drastically different behavior is found, in particular for temperatures T with $T_{\mathrm{K}} < T \leqq T_{\mathrm{c}}$ where T_{c} is a critical temperature. In this temperature intervall, a transition into ordered phase can be induced by the flow field. This ordered phase is essentially of nematic type with the director in the plane determined by the directions of the flow velocity and its gradient. For $T < T_{\mathrm{K}}$ i. e. in the nematic phase, the order parameter and the flow alignment angle depend weakly on the flow rate. In the limit of small velocity gradients, the Ericksen-Leslie expression is obtained for the latter quantitity. Similar remarks apply to lyotropic liquid crystals where the number density of solute molecules rather than the temperature is the relevant variable. Finally, the relaxation towards a steady state situation has been considered.

Experimental investigations on the flow-induced phase transition, e. g. through a study of the dependence of flow alignment angle χ on the shear rate, are desirable both for thermotropic and lyotropic liquid crystals.

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[1] S. Hess, Z. Naturforsch. **30 a**, 728 [1975].

[2] S. Hess, Z. Naturforsch. **30 a**, 1224 [1975].

[3] P. G. de Gennes, Phys. Lett. **30 A**, 454 [1969].

[4] M. J. Stephen and J. P. Strayley, Rev. Mod. Phys. **46**, 617 [1974]; P. G. de Gennes, The Physics of Liquid Crystals, Clarendon Press, Oxford 1974.

[5] J. L. Ericksen, Arc. Rat. Mech. Anal. **23**, 266 [1966]; in Liquid Crystals 2, part 1 (ed. G. H. Brown), Gordon and Breach; London, New York 1969; F. M. Leslie, Quart. J. Mech. Appl. Math. **19**, 357 [1966].

[6] W. Maier and A. Saupe, Z. Naturforsch. **13 a**, 564 [1958]; **14 a**, 882 [1959); **15 a**, 287 [1960].

[7] S. Hess, Z. Naturforsch. **31 a**, 1034 [1976].

[8] A. Ram, in Rheology, Theory and Applications, vol. **4**, p. 251 (ed. F. R. Eirich), Academic Press, New York 1967.

[9] J. Hermans, Jr., J. Polymer Sci. **C 2**, 129 [1963].