

Convective Nonlinearities for the Orientational Tensor Order Parameter in Polymeric Systems

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Rheologica Acta, **41**, 375 (2002)

Abstract

Nonlinear hydrodynamic equations for polymeric fluids with permanent or transient orientational order are discussed. We start from a description that utilizes the well-known nematohydrodynamic equations for low molecular weight uniaxial nematics. We concentrate on the reversible nonlinearities in the dynamic equation for the orientational tensor order parameter. The non-phenomenological part is unambiguously of the 'corotationally convected' or 'Jaumann' type. This holds also for the case of transient orientational order, which occurs in semi-flexible or rigid polymeric systems in the isotropic phase. The phenomenological part of the (nonlinear) reversible dynamics (flow alignment) is different for the isotropic and uniaxial case (the biaxial case is discussed in an Appendix). The corresponding form of the stress tensor is discussed. A comparison with existing phenomenological and mesoscopic models is given.

PACS: 05.70.Ln, 46.05.+b, 83.10.Nn

KEYWORDS: Nematic liquid crystalline polymers, orientational fluctuations, convective nonlinearities, stress tensor

1 Introduction and Results

The hydrodynamic description of low-molecular-weight nematic liquid crystals is well established. It has been derived (Martin et al. 1972) from the fact that the existence of

a mean orientation of the molecules ('director') spontaneously breaks rotational symmetry. Rotations of this director constitute hydrodynamic variables, i.e. they give rise to modes with vanishing frequency in the homogeneous limit. These Goldstone modes come in addition to the usual hydrodynamic excitations of simple fluids, which are based on conservation laws. All other variables are assumed to have already relaxed to their equilibrium states. Only under special circumstances a few of those 'microscopic' variables, e.g. the degree of orientational order (a scalar quantity) near the phase transition, may become slow enough to be relevant on the hydrodynamic time scale. A somewhat different approach ('Leslie-Ericksen') to nematodynamics is based on the rotational particle dynamics in an incompressible continuum. In the relevant limit of vanishing moments of inertia of the particles (or equivalently of fast relaxing angular velocity) this description is equivalent to (incompressible) hydrodynamics (de Gennes and Prost 1993). Characteristic for this approach is the fact that the reversible part of the director dynamics, which is responsible for flow alignment or tumbling, arises as the ratio between the dissipative part of the dynamics of the rotation angle with that of the angular velocity. This detour via an additional dynamic equation (for the angular momentum in the present case), which is then adiabatically eliminated, is also necessary for Poisson-bracket based descriptions of nematics, cf. Dzyaloshinskii and Volovik (1980) and more generally Grmela (1984, 1985a, 1986).

Nematic-like degrees of freedom are not only relevant for true thermodynamic nematic phases, but also play a role for isotropic phases close to the transition temperature. Here, localized patches of nematic order are rather long-lived, i.e. the nematic degree of order is only slowly relaxing (to zero, its equilibrium value). To describe these nematic fluctuations a second rank tensor, the full nematic order parameter tensor (de Gennes and Prost 1993) is required, since there is no director in the isotropic phase and the scalar quantity by itself cannot describe the orientation of the transient patches. Of course, also in the nematic phase, one can use a dynamic equation for the 2nd-rank tensor order parameter (Hess 1975a, 1975b), which then contains the (hydrodynamic) dynamics of the director and the relaxing dynamics of the scalar degree of nematic order.

In polymeric systems, besides the orientational degrees of freedom, there are also elastic degrees of freedom, responsible for the viscoelastic effects. In side-chain polymers these two aspects are clearly separated, since the nematic-like behavior refers to the mesogenic side-chains, while (visco-)elasticity is related to the backbone chain. A linearized hydrodynamic description, with both nematic and elastic degrees of freedom, has been given some time ago (Pleiner and Brand 1991, 1992). For main chain systems there is a much closer connection between orientational and elastic aspects, since both are connected with the polymeric chain. In the following we will concentrate on the orientational degrees of freedom and disregard the elastic aspects. Our goal is to derive nonlinear macroscopic dynamic equations for the nematic-like degrees of freedom using symmetry, hydrodynamic and thermodynamic arguments. The latter include the splitting of the currents into reversible and irreversible parts, which lead to zero and positive entropy production, respectively and which severely restricts the nature and form of the currents. Emphasis is laid on the reversible nonlinearities, some of which do not come with possibly small material-dependent parameters, but are either geometric in nature or determined by the proper transformation behavior of the macroscopic variables under Galilei transformations, rigid rotations etc..

In Sec. 2 we summarize the director hydrodynamics in a nematic phase and combine

this with the relaxing dynamics of the scalar degree of order into an effective dynamic equation for the 2nd rank order parameter tensor (including an external field). The nonlinear convective terms are definitely of the Jaumann type describing the coupling to rotational flow, but there are in addition, and of equal importance, phenomenological (linear and nonlinear) couplings to symmetric velocity gradients, i.e. elongational flow along certain directions. These coupling terms, however, have a very definite structure due to the underlying director hydrodynamics.

In Sec. 3 we discuss the form of the dynamic equations for orientational fluctuations in the isotropic phase of semi-flexible or stiff polymers. Here no director exists and the dynamics is immediately expressed for the tensor order parameter. Again Jaumann-type convective nonlinearities are present, however the phenomenological part of the dynamics is rather different from that in the nematic phase and it is not possible to use the same set of equations for the orientational dynamics in the nematic and the isotropic phase. This hydrodynamic description is different from a (dynamic) Ginzburg-Landau description, which starts from a common energy density functional for the ordered (nematic) and the disordered (isotropic) phase. For the ordered phase the Ginzburg-Landau treatment is valid for very small order parameter, only (close to the phase transition, at best), and does not lead to the full hydrodynamic equations, neither in the statics nor in the dynamics.

In Sec. 4 we give the form of the appropriate stress tensors. Being the current of the momentum density, the stress tensor not only contains isotropic pressure and viscous stresses, but also orientational-elastic stresses, which result from the orientational degrees of freedom. Technically these stresses are the counter terms to the reversible parts of the orientation dynamics ensuring zero entropy production. They are completely fixed by the orientation dynamics and no choices are left. Thus, there are again different expressions for the isotropic and the nematic phase. In particular, a simple stress-optical law, i.e. the stress tensor being proportional to the tensor order parameter, is valid for the isotropic phase only – and only in linear approximation. We show also that the gradient-free part of the stress tensor is manifestly symmetric.

In Sec. 5 we compare our results with equations given previously in the literature. Apparently the distinction between the orientational dynamics in a true nematic phase and in an isotropic phase has not been stressed before. In the Appendix we discuss biaxial fluctuations in a (uniaxial) nematic phase. Again their dynamics is different from the orientational dynamics in the isotropic phase, which intrinsically contains uniaxial as well as biaxial nematic fluctuations.

2 Nematic Order

In the uniaxial nematic phase of low molecular weight systems the mean orientation of long rod-like molecules (or of the normals of plate-like molecules) is described (de Gennes and Prost 1993) by a unit 'vector' \mathbf{n} (with $\mathbf{n}^2 = 1$) with the additional condition that all equations have to be invariant under the replacement of \mathbf{n} by $-\mathbf{n}$ (that is why \mathbf{n} is not a vector in the usual sense and thus called a director). The dynamic equation for the director is well known and conveniently expressed as (Martin et al. 1972; Pleiner and Brand 1996)

$$\dot{n}_i + v_j \nabla_j n_i - n_j (\Omega_{ji} + \lambda \delta_{ik}^{tr} A_{jk}) = -\frac{1}{\gamma_1} h_i^\perp \quad (1)$$

where $\delta_{ik}^{tr} \equiv \delta_{ik} - n_i n_k$ and \mathbf{v} is the velocity field, while $\Omega_{kj} \equiv (1/2)\epsilon_{ijk}(\text{curl}\mathbf{v})_i = (1/2)(\nabla_j v_k - \nabla_k v_j)$ and $A_{kj} \equiv (1/2)(\nabla_j v_k + \nabla_k v_j)$ describe rotational and (generalized) elongational flow, respectively. The 'molecular field' $h_i^\perp \equiv (\delta_{ik} - n_i n_k)\delta F/\delta n_k$ can be inferred from a general free energy $F = \int f dV$, with $2f = K_{ijkl}(\nabla_j n_i)(\nabla_l n_k) - \epsilon_a(\mathbf{E} \cdot \mathbf{n})^2$, which contains (de Gennes and Prost 1993) the Frank orientational elastic energy (3 coefficients $K_{1,2,3}$ in K_{ijkl}) and the dielectric anisotropy energy (ϵ_a).

Eq.(1) contains 2 phenomenological parameters: The reactive flow alignment parameter λ , which describes orientation due to symmetric velocity gradients, and the dissipative orientational viscosity γ_1 representing the orientational diffusion (or relaxation in the presence of an external field) of the director. Most important for the present purposes is the observation that the orientation due to rotational flow is *not* governed by a material dependent coefficient, but given by symmetry: Under a pure rotation one has $\dot{n}_i = \Omega_{ji}n_j$. The same relation is obtained, if angular momentum conservation is employed (Pleiner and Brand 1996). Eq.(1) describes, in the absence of external fields, through its coupling to the velocity field, two hydrodynamic, typically non-propagating diffusive modes (shear-orientational diffusion) characteristic for the spontaneously broken rotational symmetry (Martin et al. 1972). Note that eq.(1) has the most general form allowed by symmetry and thermodynamics up to linear order in the velocity and its gradients.

The degree S of the orientational order is defined as the quadrupolar mass moment (de Gennes and Prost 1993) $S = (1/2) \langle 3 \cos^2 \theta - 1 \rangle$, where θ is the angle between the actual orientation of a particle relative to the mean orientation and $\langle \dots \rangle$ is the ensemble average over the whole system. In low molecular weight nematics far from the isotropic phase transition S is assumed, on the relevant time and length scales, to be relaxed to its equilibrium value S_{eq} (which is a function of the scalar state variables, like temperature and pressure). However, near the phase transition, or in polymeric side-chain systems, where the relaxation of S can become slow enough to be relevant (Pleiner and Brand 1991, 1992), a dynamic equation for S is needed. It reads (Pleiner and Brand 1996) neglecting the thermal and other possible scalar degrees of freedom

$$\dot{S} + v_j \nabla_j S - (\beta_\perp \delta_{ij} + \beta_a n_i n_j) A_{ij} = -\kappa_w a (S - S_{eq}) \quad (2)$$

where the β 's (Liu 1979) are reactive transport coefficients describing linear couplings to symmetric velocity gradients, κ_w is a dissipative one and a is the static susceptibility of order parameter fluctuations. The relaxation time is $\tau = 1/(a\kappa_w)$. Note that eq.(2) has the most general form allowed by symmetry and thermodynamics up to linear order in the velocity and its gradients. Sometimes the director \mathbf{n} and the scalar order parameter S are combined into a tensor order parameter (de Gennes and Prost 1993)

$$Q_{ij} = \frac{S}{2}(3n_i n_j - \delta_{ij}) \quad (3)$$

Using eqs.(1,2) for the field-free case we get

$$\dot{Q}_{ij} + v_k \nabla_k Q_{ij} + Q_{jk} \Omega_{ki} + Q_{ik} \Omega_{kj} - \lambda_{ijkl} A_{kl} = -\frac{1}{\tau}(Q_{ij} - Q_{ij}^{eq}) + O(\nabla^2) \quad (4)$$

with $Q_{ij}^{eq} = (S_{eq}/2)(3n_i n_j - \delta_{ij})$. The viscous effects due to director rotations are represented only by $O(\nabla^2)$, since we are mainly interested here in the nonlinear reversible part of the dynamics. Apart from the trivial transport term there are two terms relating

Q_{ij} with flow, which do not come with a phenomenological parameter, $Q_{jk}\Omega_{ki} + Q_{ik}\Omega_{kj}$. These couplings to rotations are the nonlinear contributions of a 'corotational' or 'Jaumann' derivative, which is the arithmetic mean of the appropriate 'upper convected' and 'lower convected' terms. In contrast to the 'material frame indifference' principle that cannot decide, which linear combination of upper and lower convected terms is correct, our treatment, based on the proper rotational behavior of the director and the scalar order parameter, unambiguously leads to (4). The coupling to symmetric velocity gradients is again phenomenological, i.e. material dependent according to the form of λ_{ijkl}

$$\begin{aligned} 3\lambda_{ijkl} = & \lambda [S\delta_{ik}\delta_{jl} + \frac{1}{2}\delta_{ik}Q_{jl} + \frac{1}{2}\delta_{jl}Q_{ik} - \frac{2}{S}Q_{ik}Q_{jl} + i \leftrightarrow j] \\ & + \frac{1}{S}(3\beta_{\perp} + \beta_a)Q_{ij}\delta_{kl} + \frac{2}{S^2}\beta_a Q_{ij}Q_{kl} \end{aligned} \quad (5)$$

which contains 3 phenomenological coefficients even in linear order (i.e. S taken at S_{eq}); there are no additional nonlinear coefficients. The reason is that (4) does not have the most general form, but has to be compatible with the special (uniaxial) form of Q_{ij} (3). The latter also ensures that Q_{ij} remains traceless for all times, since $\Omega_{ij}Q_{ij} \equiv 0$ and $S\delta_{kl} + Q_{kl} = \frac{2}{S}Q_{jk}Q_{jl}$.

In the case of a static external field \mathbf{E} that is assumed to influence the director dynamics only through the dielectric anisotropy energy mentioned above, there is a second relaxation time involved.¹ For $\epsilon_a > 0$ the equilibrium orientation of the director is $\mathbf{n}_{eq} = \mathbf{E}/E = \hat{\mathbf{E}}$ and $\delta n_i \equiv n_i - \hat{E}_i$ relaxes to zero with the rate $\tau_E^{-1} = \epsilon_a E^2 / \gamma_1$. Then the right hand side of (4) is replaced in linear order by

$$\dot{Q}_{ij} + \dots = -\frac{1}{\tau}\delta Q_{ij} - \left(\frac{1}{\tau_E} - \frac{1}{\tau}\right)(\delta Q_{ik}\hat{E}_k\hat{E}_j + \delta Q_{jk}\hat{E}_k\hat{E}_i - 2\hat{E}_i E_j \delta Q_{lk}\hat{E}_k\hat{E}_l) + O(\nabla^2) \quad (6)$$

where $\delta Q_{ij} = \frac{3}{2}S_{eq}(\hat{E}_j\delta n_i + \hat{E}_i\delta n_j) + \frac{1}{2}(S - S_{eq})(3\hat{E}_i\hat{E}_j - \delta_{ij})$.

In order to use these nematic equations in polymeric systems, they have to be amended by dynamic equations for other degrees of freedom, like the usual conserved quantities (mass, momentum, and energy) and those describing special polymer effects (viscoelasticity, shear thinning etc.). For side-chain nematic liquid crystals that has been discussed in linearized form in Pleiner and Brand (1991, 1992) and eqs.(1-4) are a partial generalization into the nonlinear domain.

3 Orientational Fluctuations

In the isotropic phase of low molecular weight nematogens (de Gennes and Prost 1993) and stiff polymers (Doi and Edwards 1986) orientational fluctuations can become important, especially as pre-transitional effects near the phase transition. Since there is no nematic order in equilibrium ($S_{eq} = 0 = Q_{ij}^{eq}$) a director does not exist (and thus eq.(1) cannot be used), but fluctuations of Q_{ij} are possible. Having the same symmetry properties as Q_{ij} in the nematic phase the structure of the dynamic equation for the orientational fluctuations is that of (4)

$$\dot{Q}_{ij} + v_k \nabla_k Q_{ij} + Q_{jk}\Omega_{ki} + Q_{ik}\Omega_{kj} - \lambda_{ijkl}A_{kl} = -\frac{1}{\tau_1}Q_{ij} + O(\nabla^2) \quad (7)$$

¹For possible effects of an external electric field on the dynamics of \mathbf{n} cf. Pleiner and Brand (1996) and Brand and Pleiner (1984).

Again, the nonlinear reversible terms are of the corotational or Jaumann derivative type, and there is a phenomenological coupling to symmetric velocity gradients. In linear order it has the form ((de Gennes and Prost 1993) generalized to compressible flows)

$$\lambda_{ijkl}^{(lin)} = \lambda_1 (\delta_{ik}\delta_{jl} + \delta_{jk}\delta_{il} - \frac{2}{3}\delta_{ij}\delta_{kl}) \quad (8)$$

and contains one phenomenological, material dependent coefficient. Since the phase transition to the nematic phase is first order (i.e. no smooth transition at $S = 0$), the coefficient λ_1 is not related to the coefficients λ or $\beta_{\perp,a}$ in (5). In quadratic order there are two

$$\lambda_{ijkl}^{(qua)} = \lambda_2 (\delta_{ik}Q_{jl} + \delta_{jk}Q_{il} + \delta_{jl}Q_{ik} + \delta_{il}Q_{jk} - \frac{4}{3}\delta_{ij}Q_{kl}) + \lambda_3\delta_{kl}Q_{ij} \quad (9)$$

and in cubic order 5 phenomenological coefficients

$$\begin{aligned} \lambda_{ijkl}^{(cub)} = & \lambda_4 Q_{kl}Q_{ij} + \lambda_5 (Q_{ik}Q_{jl} + Q_{jk}Q_{il} - \frac{2}{3}\delta_{ij}Q_{kp}Q_{lp}) + \lambda_6\delta_{kl}(Q_{ip}Q_{jp} - \frac{1}{3}\delta_{ij}Q_{pq}Q_{pq}) \\ & + \lambda_7(\delta_{ik}Q_{jp}Q_{lp} + \delta_{jk}Q_{ip}Q_{lp} + \delta_{jl}Q_{ip}Q_{kp} + \delta_{il}Q_{jp}Q_{kp} - \frac{4}{3}\delta_{ij}Q_{pk}Q_{pl}) \\ & + \lambda_8(\delta_{ik}\delta_{jl} + \delta_{jk}\delta_{il} - \frac{2}{3}\delta_{ij}\delta_{kl})Q_{pq}Q_{pq} \end{aligned} \quad (10)$$

The cubic (and higher) order terms are assumed to be rather unimportant and kept here for later comparison, only. There are more phenomenological coefficients involved in (8-10) than in (5), since in the isotropic case Q_{ij} has to be symmetric and traceless only, while in the nematic case it has the special uniaxial form. If in eq.(4) the Jaumann terms are combined with the quadratic contribution (9) for the special value $\lambda_2 = \frac{1}{2}$ ($= -\frac{1}{2}$) one gets something that looks like an upper (lower) convected derivative². However, there is no reason why such a relation should hold for all different materials nor can it hold for all temperatures and pressures, since λ_2 generally depends on all scalar state variables.

In (7) the relaxation on the r.h.s. is written in linear approximation. More generally it can be written as $-\kappa(\delta F[Q]/\delta Q_{ij})$ with the Landau type free energy $F[Q] = \int f dV$ where (de Gennes and Prost 1993)

$$f = \frac{a}{2}Q_{ij}Q_{ij} + \frac{b}{3}Q_{ij}Q_{jk}Q_{ki} + \frac{c_1}{4}(Q_{ij}Q_{ij})^2 + \frac{c_2}{4}Q_{ij}Q_{jk}Q_{kl}Q_{li} + O(\nabla^2) \quad (11)$$

and $a\kappa = 1/\tau_1$. Close to the nematic phase transition a is strongly temperature dependent, $a = \alpha(T - T_c^*)$ with T_c^* the hypothetical transition temperature, if the transition were second order.

4 Stress Tensor

In the preceding sections we discussed nonlinear reversible terms in the dynamic equation for the orientational order (7) that describe couplings to flow. In the Navier-Stokes equation, on the other hand, there must be appropriate counter terms describing couplings

² – with some additional correction terms that ensure $\dot{Q}_{ii} = 0$. Most of the terms in (8-10) show such correction terms, while the Jaumann terms in (4) do not need them.

to orientational order, due to the requirement of zero or positive entropy production, R , in the case of reversible and irreversible terms, respectively (Martin et al. 1972; Grmela 1985b; Pleiner and Brand 1996). Their form can also be derived from Onsager relations. For the stress tensor, defined by $\dot{g}_i + \nabla_j \sigma_{ij} = 0$, where g_i is the momentum density, this leads to the expression

$$\sigma_{ij} = v_i g_j + p \delta_{ij} - \nu_{ijkl} A_{kl} + \sigma_{ij}^{(ad)} - \lambda_{klj} \psi_{kl} + \psi_{ik} Q_{jk} - \psi_{jk} Q_{ik} + O(\nabla^2) \quad (12)$$

where ψ_{ij} is the thermodynamic conjugate to Q_{ij} defined by $\psi_{ij} = \partial f / \partial Q_{ij}$ with f the energy density. Again, gradients of Q_{ij} have been neglected here. Since Q_{ij} is traceless and symmetric, only the traceless and symmetric part of ψ_{ij} is relevant and enters (12).

The free energy density is coupled to all variables by the Gibbs relation (Martin et al. 1972)

$$d\epsilon - T d\sigma = v_i dg_i + \psi_{ij} dQ_{ij} \quad (13)$$

where only the contributions relevant for the present discussion are shown. The total energy density ϵ is a conserved quantity, while σ , the entropy density, contains the entropy production R as source term in its dynamical equation, $\dot{\sigma} + \nabla_i j_i^{(\sigma)} = R/T$. The first three terms in (12) are those of a standard simple fluid, describing momentum convection, isotropic pressure (balancing in the entropy production the transport terms of all dynamic equations (Pleiner and Brand 1996)) and Newtonian viscosity, while $\sigma_{ij}^{(ad)}$ describes the contributions from all additional relevant degrees of freedom for polymers not considered here³. The counter term to the linear elongational flow term in (7), $\sim \lambda_{klj}$, leads to a symmetric part of the stress tensor, while the counter terms to the nonlinear Jaumann terms seem to give an antisymmetric contribution to the stress tensor. However, if we apply the Gibbs relation (13) to solid body rotations, which leave the energy density unchanged ($d\epsilon = 0$), the relation $0 = v_i a_{ik} g_k + \psi_{ij} a_{ik} Q_{kj} + \psi_{ij} a_{jk} Q_{ik}$ is obtained (for an arbitrary antisymmetric a_{ij}), from which we get

$$\psi_{ik} Q_{jk} = \psi_{jk} Q_{ik} \quad (14)$$

This condition on ψ_{ij} ensures that the Jaumann terms in (7) do not at all contribute to the entropy production ($\psi_{ij} \dot{Q}_{ij}$) and do not need counter terms (i.e. these counter terms are identically zero). Thus, the stress tensor is symmetric in its gradient-free part (while the Ericksen stress containing gradients of Q_{ij} is not manifestly symmetric, but can be made effectively symmetric by a well known procedure (Martin et al. 1972)).

Eq.(12) can be used to derive the connection between Q_{ij} and the stress that is induced by it. In the isotropic phase eqs.(8,9,11) give

$$\sigma_{ij}^{(Q)} = -2\lambda_1 a Q_{ij} - 2(\lambda_1 b + 2\lambda_2 a) Q_{ik} Q_{jk} - \delta_{ij} (\lambda_3 a - \frac{2}{3} \lambda_1 b) Q_{kl} Q_{kl} + O(3) \quad (15)$$

where we have refrained from writing down explicitly the third order contributions. In linear order, the simple stress-optical law ($\sigma_{ij}^{(Q)} \sim Q_{ij}$) is obtained, while in the nonlinear regime, already in quadratic order, no such simple law is found. Here $\sigma_{ij}^{(Q)}$ is not even

³One example is the transient elasticity described e.g. by a time evolution equation for the Eulerian strain tensor. The nonlinear elastic stresses related to this degree of freedom are discussed in (Temmen et al. 2000, 2001; Pleiner et al. 2000).

traceless indicating that nonlinear orientational fluctuations not only couple to shear and elongation, but also to compression. In the nematic phase eqs.(5,12) lead to

$$\begin{aligned}\sigma_{ij}^{(Q)} &= -\frac{3}{2}\lambda S(n_k n_i \psi_{kj} + n_j n_k \psi_{ki} - 2n_i n_j n_k n_l \psi_{kl}) - \frac{3}{2}(\beta_{\perp} \delta_{ij} + \beta_a n_i n_j) n_k n_l \psi_{kl} \\ &= -\frac{1}{2}\lambda S(n_i h_j^{\perp} + n_j h_i^{\perp}) - a(\beta_{\perp} \delta_{ij} + \beta_a n_i n_j)(S - S_{eq})\end{aligned}\quad (16)$$

where h_i^{\perp} , defined after (1), is $\sim O(\nabla^2)$ in the absence of external fields. Thus, $\sigma_{ij}^{(Q)}$ does not have the tensorial structure of Q_{ij} and a simple stress-optical law is not valid. This fact could be experimentally used to discriminate fluctuating nematic from director dynamics.

5 Comparison

For low molecular weight liquid crystals the dynamic equation for an alignment tensor (equivalent to Q_{ij}) in the nematic as well as in the isotropic phase has been derived by Hess (1975a, 1975b) a long time ago. From the correct behavior under rigid rotations he gets Jaumann-type quadratic reversible nonlinearities in complete agreement with our eq.(4). The reversible reaction to symmetric velocity gradients is somewhat buried in the irreversible part of an enlarged dynamics, since his approach is in the Leslie-Ericksen spirit, where basically \dot{Q}_{ij} (in addition to Q_{ij}) is taken as a variable. This is completely analogous to the usual nematodynamics (de Gennes and Prost 1993). The flow alignment, which is reversible, is then obtained as the ratio of two irreversible processes and is described by one phenomenological parameter (τ_{ap}/τ_a in Hess (1975a, 1975b)). In the linearized regime this is in agreement with our strictly thermodynamic description concerning the director dynamics (λ for the nematic and λ_1 for the isotropic state), but there is no counterpart in Hess (1975a, 1975b) to our β_a and β_{\perp} contributions related to the reversible dynamics of S . The nonlinearities of eq.(5) and eqs.(9,10) are also not contained in Hess (1975a, 1975b).

However, quite rarely have the equations of Hess (1975a, 1975b) been taken over when orientational effects in polymeric systems have been described (one exception is Tanaka (2000)). Instead, most authors rely on the Doi-Edwards model (Doi and Edwards 1986). This has been developed originally Doi (1981), Kuzuu and Doi (1983) as a microscopic description in terms of a hierarchy of coupled correlation functions. Only after a closure assumption (which can hardly be motivated or controlled by physical considerations) a single equation for the lowest orientational correlation function is obtained, which is then applied to macroscopic situations (e.g. in Larson (1988), Olmsted and Lu (1997, 1999)). Assuming that the Doi-Edwards model is valid for macroscopic situations we can compare their equations (basically (8.149) and (10.75) of Doi and Edwards (1986)) with (4). The Doi-Edwards equation is written in the form of an upper convected model (with a correction to guarantee S_{ij} remaining traceless, where $S_{ij} = (2/3)Q_{ij}$ in our notation). However, there are additional model-dependent couplings to symmetric velocity gradients that allow this equation to be rewritten in the form of our eq.(4) with a λ -tensor of the form

$$\lambda_{ijkl}^{(DE)} = \frac{1}{2}(\delta_{ik}\delta_{jl} + \delta_{ik}Q_{jl} + \delta_{jl}Q_{ik} + [i \leftrightarrow j]) - \frac{2}{3}\delta_{ij}Q_{kl} - \frac{4}{3}Q_{ij}Q_{kl}\quad (17)$$

In the isotropic case comparison with (8-10) reveals that in the Doi-Edwards model the phenomenological parameters have special values, $\lambda_1 = 1/2$, $\lambda_2 = 1/2$, $\lambda_4 = -4/3$, $\lambda_5 = 0 = \lambda_7 = 0 = \lambda_8$, while λ_3 and λ_6 are not defined, because incompressibility $A_{kk} = 0$ is assumed in Doi and Edwards (1986).

The Doi-Edwards model is said (Chapt. 10.4.3 in Doi and Edwards (1986)) to be equally valid for the nematic phase, in which case we have to compare eq.(17) with (5). Apparently (17) is quite different from (5) and cannot be brought into that form by any choice of the parameters involved. The reason is that the Doi-Edwards model, and particularly the form of (17), is not compatible with the uniaxial form (3) of Q_{ij} . The latter requires, e.g.

$$\delta_{iq}^{tr} \delta_{jp}^{tr} \dot{Q}_{ij} = -\frac{1}{2} \delta_{pq}^{tr} n_i n_j \dot{Q}_{ij} \quad (18)$$

which are two equivalent ways of extracting \dot{S} from \dot{Q}_{ij} . It is easy to see that the phenomenological part of the dynamics given by (17) does not fulfill (18), because $\delta_{kp}^{tr} \delta_{lq}^{tr} A_{kl} \neq \delta_{pq}^{tr} \delta_{kl}^{tr} A_{kl}$. Of course, the form of λ_{ijkl} given by (5) is compatible with (18) by construction. In addition, the Doi-Edwards model is also not compatible with biaxial fluctuations (cf. Appendix), since in that case two different relaxation processes are involved (cf. eq.(A.7)).

In Denniston et al. (2000, 2001) and Feng et al. (1998) the dynamic equation for Q_{ij} is written in the form (4) with the coupling to symmetrized velocity gradients given by a λ -tensor of the Doi-Edwards form (17) multiplied by an overall factor (called ξ and λ , respectively) that represents a fudge factor to compensate errors due to the closure approximation and/or takes into account the geometric aspect ratio of the stiff polymers. The comparison to our expressions for λ_{ijkl} , eqs(5, 8-10) is therefore similar to that for the Doi-Edwards expression.

In Beris and Edwards (1994) general dynamic equations for the alignment tensor (equivalent to Q_{ij}) are derived using the Poisson bracket method. This has to be compared to our equations in Sec. 3. In the incompressible limit, where the number of our λ -coefficients in eqs.(8-10) is reduced to one, one, and two, respectively, the results seem to coincide. However, this alignment tensor description is not applicable to the nematic phase, where the existence of the director leads to more specific equations (Sec. 2), especially in the nonlinear domain. Furthermore, the alignment tensor, being symmetric and traceless, contains 5 elements connected to uniaxial (two angles and one degree of order) as well as biaxial (one additional angle and the degree of biaxial order) orientations. Thus, if this description is applied to the (uniaxial) nematic phase, it should be compared with the (uniaxial) hydrodynamic description including biaxial fluctuations (cf. Appendix). In that case, however, two independent relaxation processes are involved, the relaxation of the uniaxial degree of order to its finite equilibrium value as well as the relaxation of the biaxial degree of order to zero (A.7), while the alignment tensor description contains only one relaxation process.

In our hydrodynamic description those parts of the stress tensor that result from the orientational order are fixed by the zero entropy condition, once the equations for the orientational dynamics are derived. Thus, for theories in the literature that use equivalent procedures to get the stress tensor, the comparison to our expressions of the stress tensor (12,15,16) goes along the same lines as the comparisons given above with respect to the orientational dynamics. This is different for cases where the stress tensor has not been connected with the orientational dynamics but derived from, e.g. the free energy (Doi and Edwards 1986; Tanaka 2000). Here typically only a linear contribution is obtained,

but not the nonlinear ones, cf. (15). Thus, a stress-optical law is postulated, while actually such a law only exists in linear approximation. We also notice that nowhere our relation (14) has been given, which ensures the symmetry of the stress tensor and, as a consequence, the conservation of angular momentum density.

Appendix: Biaxial Fluctuations

In the isotropic phase (Sec.(3)) we have discussed the dynamics of the full nematic order parameter Q_{ij} . Being a symmetric traceless tensor it contains 5 independent fields describing uniaxial as well as biaxial nematic fluctuations. In the uniaxial phase (Sec.(2)) we dealt with the orientational dynamics of the (uniaxial) director \mathbf{n} as well as with fluctuations of the strength S of the uniaxial order. In this Appendix we will allow for biaxial fluctuations within the uniaxial nematic phase. Such fluctuations are described (Jacobsen and Swift 1982; Brand and Swift 1983) by a two-dimensional symmetric traceless tensor ξ_{ij} that lives in the plane perpendicular to the (uniaxial) director \mathbf{n} . It describes the strength of biaxial fluctuations (by a scalar field η) as well as the orientation of the transient biaxial preferred direction (by an angle ϕ) by

$$\xi_{11} = -\xi_{22} = \eta \cos 2\phi, \quad \xi_{12} = \xi_{21} = \eta \sin 2\phi \quad (\text{A.1})$$

or $\eta^2 = \xi_{11}^2 + \xi_{12}^2$ and $2\phi = \tan^{-1}(\xi_{12}/\xi_{11})$.

In order to get the nonlinear dynamic equation for ξ_{ij} we digress shortly to a true biaxial nematic phase, where the anisotropy in the plane perpendicular to \mathbf{n} is described (de Gennes and Prost 1993) by a set of two orthogonal unit vectors \mathbf{m} and \mathbf{p}

$$\xi_{ij} = \eta (m_i m_j - p_i p_j) \quad (\text{A.2})$$

whose orientation is given by the angle ϕ (with respect to an arbitrary reference direction). Its dynamics has the form (Brand and Pleiner 1981; Liu 1981)

$$\dot{m}_i + v_k \nabla_k m_i + m_j \Omega_{ji}^\perp - \lambda_{ikl}^{(m)} A_{kl} = -\frac{1}{\gamma^{(m)}} p_i p_k h_k^{(m)} \quad (\text{A.3})$$

with $h_i^{(m)} = \delta F / \delta m_i$ and $\Omega_{ji}^\perp \equiv \delta_{jk}^{tr} \delta_{il}^{tr} \Omega_{kl}$ the projection of the antisymmetric velocity gradients onto the plane perpendicular to \mathbf{n} . There is a similar equation for \dot{p}_i . The phenomenological part of (A.3) contains the coupling to the symmetrized velocity gradients (through $\lambda_{ikl}^{(m)}$) and to the (dissipative) orientational diffusion of m_i (through $\gamma^{(m)}$), the latter of which we do not need explicitly here.

The scalar biaxial order parameter η obeys a relaxation equation resembling (2) for S

$$\dot{\eta} + v_j \nabla_j \eta - \beta_{ij}^{(\eta)} A_{ij} = -\frac{1}{\tau_\eta} (\eta - \eta_{eq}) \quad (\text{A.4})$$

Now, eqs.(A.3) and (A.4) can be combined to give (in the absence of external fields)

$$\dot{\xi}_{ij} + v_k \nabla_k \xi_{ij} + \Omega_{ki}^\perp \xi_{jk} + \Omega_{kj}^\perp \xi_{ik} - \lambda_{ijkl}^{(\xi)} A_{kl} = -\frac{1}{\tau_\eta} (\xi_{ij} - \xi_{ij}^{eq}) + O(\nabla^2) \quad (\text{A.5})$$

with $\xi_{ij}^{eq} = \eta_{eq} (m_i m_j - p_i p_j)$.

In the uniaxial phase the biaxial fluctuations ξ_{ij} follow the dynamic eq.(A.5) with $\eta_{eq} = 0$ and with the phenomenological biaxial flow alignment tensor (up to quadratic order)

$$\begin{aligned} \lambda_{ijkl}^{(\xi)} &= \lambda_1^{(b)}(\delta_{ik}^{tr}\delta_{jl}^{tr} + \delta_{jk}^{tr}\delta_{il}^{tr} - \delta_{ik}^{tr}\delta_{ij}^{tr}) + \xi_{ij}(\lambda_2^{(b)}\delta_{kl}^{tr} + \lambda_3 n_k n_l) \\ &+ \lambda_4^{(b)}(\xi_{ik}\delta_{jl}^{tr} + \xi_{jk}\delta_{il}^{tr} + \xi_{il}\delta_{jk}^{tr} + \xi_{jl}\delta_{ik}^{tr} - 2\delta_{ij}^{tr}\xi_{kl}) + \lambda_5^{(b)}\xi_{ij}\xi_{kl} + O(3) \end{aligned} \quad (\text{A.6})$$

We can now define a biaxial tensorial order parameter $Q_{ij}^{(b)} \equiv Q_{ij} + \xi_{ij}$, where Q_{ij} is of the uniaxial form used in Sec.2. For that quantity the dynamic equation reads combining eq.(4) and (A.5)

$$\begin{aligned} \dot{Q}_{ij}^{(b)} + v_k \nabla_k Q_{ij}^{(b)} + Q_{jk}^{(b)} \Omega_{ki} + Q_{ik}^{(b)} \Omega_{kj} - (\lambda_{ijkl} + \lambda_{ijkl}^{(\xi)}) A_{kl} \\ = -\frac{1}{\tau}(Q_{ij}^{(b)} - Q_{ij}^{eq}) + \left(\frac{1}{\tau} - \frac{1}{\tau_\eta}\right)(Q_{ij}^{(b)} - Q_{ij}) + O(\nabla^2) \end{aligned} \quad (\text{A.7})$$

with λ_{ijkl} given by (5) and $\lambda_{ijkl}^{(\xi)}$ by (A.6), where ξ_{ij} is replaced by $Q_{ij}^{(b)} - Q_{ij}$. Again, the dynamics of $Q_{ij}^{(b)}$ shows a corotational form for the non-phenomenological part of the nonlinear reversible dynamics and in addition, a phenomenological generalized flow alignment-type response to elongational flow. There are now two relaxation processes involved, one related to the S , the uniaxial, and the other related to the η , the biaxial scalar order parameter.

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