Dynamics of the Orientational Tensor Order Parameter in Polymeric Systems

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Introduction

The hydrodynamic description of low-molecular-weight nematic liquid crystals is well established. Nematic-like degrees of freedom are not only relevant for truly thermodynamic nematic phases, but also play a role for isotropic phases close to the transition temperature. To describe these nematic fluctuations a second rank tensor, the full nematic order parameter tensor is required, since there is no director in the isotropic phase and a scalar quantity by itself cannot describe the orientation of the transient patches.

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. 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, thermodynamic and hydrodynamic arguments.

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. The nonlinear convective terms are definitely of the Jaumann type describing the coupling to rotational flow, but there are in addition phenomenological (linear and nonlinear) couplings to elongational flow, which can be of equal importance. The latter, however, have a very definite structure due to the underlying director hydrodynamics.

In addition we discuss the form of the dynamic equations for orientational fluctuations in the isotropic phase of semi-flexible or stiff polymers. 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.

Furthermore we give the form of the appropriate orientational-elastic stresses in the stress tensor. 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 is valid for the isotropic phase only − and only in linear approximation.

A more detailed exposition of these topics including comparison with the literature can be found in [1].

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 [2] by a unit 'vector' n (with $n^2 = 1$) with the additional condition that all equations have to be invariant under the replacement of n by $-n$ (that is why 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 [3, 4]

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

where $\delta_{ik}^{tr} \equiv \delta_{ik} - n_i n_k$ and v is the velocity field, while $\Omega_{kj} \equiv (1/2)\epsilon_{ijk}(curl v)_i = (1/2)(\nabla_j v_k - \nabla_k v_j)$ 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 $2f = K_{ijkl}(\nabla_j n_i)(\nabla_l n_k)$, which contains (de Gennes and Prost 1993) the Frank orientational elastic energy (3 coefficients $K_{1,2,3}$ in K_{ijkl}). 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.

The degree S of the orientational order is defined as the quadrupolar mass moment [2] $S = (1/2) < 3\cos^2 \theta - 1 >$, where θ is the angle between the actual orientation of a particle relative to the mean orientation and $< \ldots >$ 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 [5, 6], a dynamic equation for S is needed. It reads neglecting the thermal and other possible scalar degrees of freedom [4]

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

where the β's [7] 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 n and the scalar order parameter S are combined into a tensor order parameter [2]

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

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

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

with $Q_{ij}^{eq} = (S_{eq}/2)(3n_i n_j - \delta_{ij})$. The viscous effects due to director rotations are represented only by $O(\boldsymbol{\nabla}^2)$, 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}

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

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 $S\delta_{kl} + Q_{kl} = \frac{2}{S}Q_{jk}Q_{jl}$.

Orientational Fluctuations

In the isotropic phase of low molecular weight nematogens [2] and stiff polymers [8] 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)

$$\dot{Q}_{ij} + v_k\nabla_k Q_{ij} + Q_{jk}\Omega_{ki} + Q_{ik}\Omega_{kj}$$
$$-\lambda_{ijkl}A_{kl} = -\frac{1}{\tau_1}Q_{ij} + O(\boldsymbol{\nabla}^2) \quad (6)$$

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 ([2] generalized to compressible flows)

$$\lambda_{ijkl}^{(lin)} = \lambda_1 \left(\delta_{ik}\delta_{jl} + \delta_{jk}\delta_{il} - \frac{2}{3}\delta_{ij}\delta_{kl} \right) \quad (7)$$

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 coefficients

$$\lambda_{ijkl}^{(qua)} = \lambda_2 \left(\delta_{ik}Q_{jl} + \delta_{jk}Q_{il} + \right.$$
$$\left. \delta_{jl}Q_{ik} + \delta_{il}Q_{jk} - \frac{4}{3}\delta_{ij}Q_{kl} \right) + \lambda_3\delta_{kl}Q_{ij} \quad (8)$$

while we will suppress here the higher order terms.

In (6) 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 [2]

$$f = \frac{a}{2}Q_{ij}Q_{ij} + \frac{b}{3}Q_{ij}Q_{jk}Q_{ki} +$$
$$\frac{c_1}{4}(Q_{ij}Q_{ij})^2 + \frac{c_2}{4}Q_{ij}Q_{jk}Q_{kl}Q_{li} + O(\boldsymbol{\nabla}^2) \quad (9)$$

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.

Eqs. (6-9) can be compared with well-known Doi-Edwards equation [8]. The latter is written in the form of an upper convected model. However, there are additional model-dependent couplings to symmetric velocity gradients that allow this equation to be rewritten in the form of our eq.(6), if our coefficient are given special values ($\lambda_1 = 1/2$, $\lambda_2 = 1/2$, and $\lambda_3 = 0$) reflecting the fact that the Doi-Edwards equation are based on a special microscopic model. However, the Doi-Edwards equation cannot be used for the nematic phase, since it is incompatible with eq.(4) and the special form of the λ-tensor (5).

Stress Tensor

In the preceding sections we discussed nonlinear reversible terms in the dynamic equation for the orientational order (6) that describe couplings to flow. In the Navier-Stokes equation, on the other hand, there must be appropriate counter terms describing couplings to orientational order, due to the requirement of zero or positive entropy production, R, in the case of reversible and irreversible terms, respectively [3, 4, 9]. 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

$$
\sigma_{ij} = v_i g_j + p\,\delta_{ij} + \nu_{ijkl}A_{kl} + \sigma_{ij}^{(ad)}
$$
$$
- \lambda_{klij}\psi_{kl} + O(\boldsymbol{\nabla}^2) \quad (10)
$$

containing the transport term, the isotropic pressure, the Newtonian viscosity, and contributions due to additional degrees of freedom not considered here. In addition there are the 'rotational-elastic' stresses described by ψ_{ij}, 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. The Jaumann terms in (6) 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 [3]).

Eq.(10) gives the connection between Q_{ij} and the stress that is induced by it. In the isotropic phase eqs.(7,8,9) give

$$
\sigma_{ij}^{(Q)} = -2\lambda_1 a Q_{ij} - 2(\lambda_1 b + 2\lambda_2 a)Q_{ik}Q_{jk}
$$
$$
- \delta_{ij}(\lambda_3 a - \tfrac{2}{3}\lambda_1 b)Q_{kl}Q_{kl} + O(3) \quad (11)
$$

In linear order, the simple stress-optical law ($\sigma_{ij}^{(Q)} \sim Q_{ij}$) is obtained, while in quadratic order no such simple law is found. Here $\sigma_{ij}^{(Q)}$ is not even traceless indicating that nonlinear orientational fluctuations not only couple to shear and elongation, but also to compression. In the nematic phase eqs.(5,10) lead to

$$
\sigma_{ij}^{(Q)} = -\frac{3}{2}(\beta_\perp \delta_{ij} + \beta_a n_i n_j)n_k n_l \psi_{kl}
$$
$$
- \frac{3}{2}\lambda S(n_k n_i \psi_{kj} + n_j n_k \psi_{ki} - 2n_i n_j n_k n_l \psi_{kl})
$$
$$
= -\frac{1}{2}\lambda S(n_i h_j^\perp + n_j h_i^\perp)
$$
$$
- a(\beta_\perp \delta_{ij} + \beta_a n_i n_j)(S - S_{eq}) \quad (12)
$$

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.

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