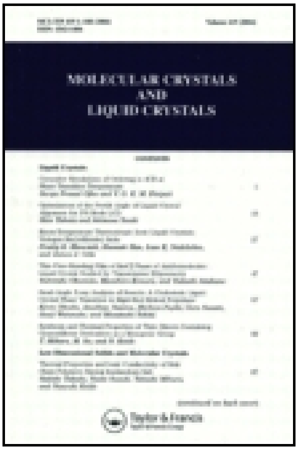

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Macroscopic Dynamic Equations for Nematic Liquid Crystalline Side-Chain Polymers

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We present linear macroscopic dynamic equations for nematic liquid crystalline side-chain polymers. The visco-elastic degree of freedom of the polymeric backbone is taken into account by a strain field, which relaxes on a long but finite time scale. Besides the usual director field to describe the nematic ordering of the side-chains we also keep the nematic order parameter modulus as a variable, in order to describe the intrinsic connection of the polymeric and nematic aspects in nematic side-chain polymers. We discuss two experiments where our concept can be tested.

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Keywords: nematic liquid crystals, side-chain polymers, macroscopic dynamics

1. INTRODUCTION AND MOTIVATION

Synthesis of polymers with mesogenic side-chains has lead in the past years to the appearance of various new liquid crystalline phases.[1–8] They are of great interest for potential applications but also pose a new challenge for basic science. A complete understanding and description of their macroscopic dynamical behaviour does not exist yet. Here we want to take one modest step in that direction by discussing the linear macroscopic dynamics of nematic side-chain polymers. Thus we have to deal with the (linear) visco-elasticity of the polymeric backbone, the nematic ordering of the side-chains and the (dynamic) interaction between them. Using long and flexible spacers between the mesogenic group and the chain segments, this interaction can be made rather weak, so that the polymeric and the nematic aspect can be discussed separately, especially in the static limit. Early considerations of the liquid crystalline influence on polymeric behaviour (and vice versa) can be found in References 9 and 10.

Here we want to use the generalized hydrodynamic method in order to describe the macroscopic dynamics of polymeric side-chain nematic liquid crystals (pscN). The hydrodynamic method[11,12] uses only general symmetry arguments and irreversible thermodynamics[13] to establish phenomenological dynamic equations.[14–17] In the present case this method has to be generalized by taking into account not only the true hydrodynamic variables (which become infinitely slow in the homogeneous limit), but also some slow microscopic variables, which are slow enough to be relevant for the usual hydrodynamic frequency range. Such additional variables are required in order to give a complete dynamic description for low but finite frequencies in systems, where no clear distinction between the time scale of hydrodynamic variables and non-hydrodynamic variables is possible.[18–20] Of course, this approach is useful only, if there is only a small number of slow non-hydrodynamic variables.

In isotropic polymer melts and solutions such non-hydrodynamic variables[21] are necessary to describe hydrodynamically the well-known viscoelastic behaviour.[22] This arises because the long polymer molecules entangle in a rather complicate way giving rise to slowly relaxing stresses and strains,[23] in contrast to ordinary liquids, where such internal stresses and strains relax on a microscopic time scale. Using a non-conserved strain field as additional variable the linear visco-elastic behaviour of polymers can be described adequately, and the resulting equations include the simple Maxwell model,[24] although they are more general. Throughout this paper we will restrict ourselves to linear visco-elasticity.

The fact that in pscN nematic and polymeric aspects are coupled physically has some obvious consequences. First all polymeric features as e.g., viscosity, elasticity etc. become anisotropic (uniaxial) due to the presence of the nematic director. Second all nematic features get renormalized due to the presence of long polymeric molecules, e.g., curvature elastic constants or viscosity parameters may change their magnitude (or their relative magnitude compared to each other). However, this latter kind of interaction between polymeric and nematic aspects does not change the structure of the dynamic equations. Here we propose that for the dynamics this interaction also leads to qualitatively new effects to be described by additional macroscopic variables.

The dynamical interaction between visco-elasticity and nematic order of the side-chains will explicitly be taken into account by using the nematic order parameter modulus as an additional non-hydrodynamic, but slow variable. This variable is usually used in a macroscopic description only for the mean-field dynamics near the nematic to isotropic phase transition, but is discarded in low-molecular weight nematics (lmwN) away from the phase transition, because there it relaxes on a microscopic time scale. The situation is different in polymeric nematics, because of the physical linkage between the backbone and the mesogenic unit. Fluctuations of the position of the backbone may influence the degree of ordering in the nematic side-chains, and vice versa, nematic order fluctuations cannot relax instantaneously (i.e., in a microscopic time), because the process of ordering (or disordering) is slowed down by the hindrance due to the backbone.

Since there is no general rule how to choose necessary additional slow nonhydrodynamic variables, one has to rely on physical intuition and imagination, when selecting the relevant ones. Final proof for the usefulness of a given choice has to come from the verification of experimental consequences that follow from that choice. The set of macroscopic variables we have discussed above to be necessary for the dynamic description of nematic side-chain polymers is in that sense tentative. It is also a minimal set, since there is the possibility that additional variables are relevant under certain circumstances. Especially, we do not consider the dynamic interaction of fluctuations of the direction of the mesogenic side-chains and the (local) direction of the backbone unit, to which it is attached. The statics of this interaction has already been discussed some time ago.[25] In the case of short and stiff spacers between the mesogenic units and the backbone, this interaction requires the introduction of even more slow non-hydrodynamic variables, which will be discussed elsewhere. Here, however we deal with the case of long and flexible spacers, which renders the interaction of the nematic preferred direction of the side chains with the backbone direction weak and allows the fluctuations of the backbone direction to remain local and to be fast internal chain fluctuations, not to be considered in a macroscopic description.

2. THE LINEARIZED MACROSCOPIC EQUATIONS

As already discussed in the Introduction we will focus exclusively on linearized macroscopic equations throughout the present paper. In the truly hydrodynamic regime (i.e., for frequencies ω small compared to all microscopic frequencies $1/\tau_c$: $\omega\tau_c << 1$ and for wavevectors k small compared to all wavevectors associated with microscopic length scales l_c: $kl_c << 1$) the densities of the conserved quantities and the variables associated with spontaneously broken (continuous) symmetries are the appropriate hydrodynamic variables. Thus, for lmwN the dynamics of the following spatio-temporal fields has to be considered: the density ρ associated with the law of mass conservation, the density of linear momentum $\mathbf{g}$ (conservation of linear momentum), the energy density ε (energy conservation) and the director $\hat{\mathbf{n}}$ (unit vector associated with the broken rotational symmetry and with $\hat{\mathbf{n}}$ indistinguishable from $-\hat{\mathbf{n}}$). In binary mixtures without chemical reactions the concentration c of one constituent is an additional hydrodynamic variable.

In pscN the visco-elastic properties of the backbone are described by using the strain field $\varepsilon_{ij}(\mathbf{r}, t)$. This is not a truly hydrodynamic variable as the other variables introduced above, since it relaxes in a large, but finite time (the Maxwell time). Nevertheless we keep the strain field in our list of macroscopic variables to account for the empirical fact, that polymer melts and solutions behave at low frequencies as simple liquids, but on sufficiently high frequencies like solids. On the other hand in solids the strain field (or rather the displacement field $\mathbf{u}$, from which it is derived), is a truly hydrodynamic variable and does not relax even in the long time limit (it only diffuses), since it is connected with the broken translational symmetry characteristic for solids. In polymers the strain field may be regarded as describing strains in the polymeric backbone configuration, which may exist there for short but finite times, because of the various entanglements of the chains. However, our use of the strain field is not based on, nor restricted to, any microscopic model of visco-elasticity. As discussed in the Introduction we will keep the order parameter modulus $S(\mathbf{r}, t)$ in our list of variables, since it describes the intrinsic interaction between the viscoelastic properties and the nematic properties of pscN. Again this is not a hydrodynamic variable and relaxes in a finite time.

Our goal is now to derive for all these macroscopic variables balance equations valid for long wavelengths and for frequencies smaller than all microscopic frequencies. The Maxwell time and the nematic order relaxation time are considered to be macroscopic time scales in this context. The approach used to derive such balance equations is linear irreversible thermodynamics.[15] In the macroscopic regime local thermodynamic equilibrium guarantees the validity of the Gibbs relation

$$T d\sigma = d\epsilon - \mu d\rho - \mu_c dc - \mathbf{v} \cdot d\mathbf{g} - W dS - \Phi_{ij} d\nabla_j n_i - \Psi_{ij} d\epsilon_{ij}. \tag{2.1}$$

This relation can be viewed as a local formulation of the first law of thermodynamics. In deriving Equation (2.1) one has averaged already over many molecules or chain segments, or—to phrase it differently—each fluid particle contains enough material so that a continuum approximation is justified. Equation (2.1) gives a relation between the increments in the macroscopic variables and the entropy density $\sigma(\mathbf{r}\ t)$. Only gradients of $\hat{\mathbf{n}}$ enter Equation (2.1), since homogeneous rotations of $\hat{\mathbf{n}}$ do not cost energy.

The quantities multiplying the increments of the thermodynamic variables in the Gibbs relation are called thermodynamic conjugate quantities or thermodynamic forces. They express how the energy changes, when one thermodynamic variable is changed while all the other ones are kept constant. The thermodynamic forces in Equation (2.1) we have not yet alluded to are the temperature $T(\mathbf{r}, t)$, the relative chemical potential of the mixture $\mu_c(\mathbf{r}, t)$, the restoring forces of nematic order changes and director distortions, W and Φ_{ij} respectively, and the elastic stress $\Psi_{ij}\ (\mathbf{r}, t)$, the quantity which is the thermodynamic conjugate to the strain field $\varepsilon_{ij}\ (\mathbf{r}, t)$. Since $\varepsilon_{ij}\ (\mathbf{r}, t)$ is symmetric, $\Psi_{ij}\ (\mathbf{r}, t)$ can be chosen to be symmetric without loss of generality.

The static behaviour of the system is now obtained by connecting the thermodynamic forces to the macroscopic variables. As we have seen above these forces can be obtained from the energy, by taking variational derivatives with respect to the variables. For linearized thermodynamics it is then sufficient to expand the energy up to second order in the variables. This expansion must preserve all fundamental invariance properties of the system under investigation including for example translational and rotational invariance, time reversal symmetry, symmetry under spatial parity, uniaxiality and $\hat{\mathbf{n}}$ to $-\hat{\mathbf{n}}$ symmetry.

In the present case of pscN we obtain for the energy $E = \int \varepsilon\, d\tau$

$$\begin{aligned} E = E_0 + \int d\tau \big[& \frac{1}{2} c_{ijkl} \epsilon_{ij} \epsilon_{kl} + (\chi_{ij}^{\rho} \delta\rho + \chi_{ij}^{\sigma} \delta\sigma + \chi_{ij}^{c} \delta c + \chi_{ij}^{S} \delta S) \epsilon_{ij} \\ & + \frac{1}{2} K_{ijkl} (\nabla_j n_i)(\nabla_l n_k) + \frac{a}{2} (\delta S)^2 + (b^{\sigma}\, \delta\sigma + b^{\rho}\, \delta\rho + b^{c}\, \delta c) \delta S \big] \end{aligned} \tag{2.2}$$

where E_0 contains all the terms already present in a simple liquid and where the summation convention over repeated indices is implied in Equation (2.2) and all the following equations. The tensor K_{ijkl} is the usual Frank curvature-elastic tensor, $K_{ijkl} = K_1\delta_{ij}^{tr}\delta_{kl}^{tr} + K_2 n_p \varepsilon_{pij} n_q \varepsilon_{qkl} + K_3 n_j n_l \delta_{ik}^{tr}$, where $\delta_{ij}^{tr} = \delta_{ij} - n_i n_j$. The elastic tensor has the form

$$\begin{aligned} c_{ijkl} =& c_1\delta_{ij}^{tr}\delta_{kl}^{tr} + c_2(\delta_{ik}^{tr}\delta_{jl}^{tr} + \delta_{il}^{tr}\delta_{jk}^{tr}) + c_3 n_i n_j n_k n_l \\ &+ c_4(\delta_{ij}^{tr} n_k n_l + \delta_{kl}^{tr} n_i n_j) + c_5(\delta_{ik}^{tr} n_j n_l + \delta_{il}^{tr} n_j n_k + \delta_{jk}^{tr} n_i n_l + \delta_{jl}^{tr} n_i n_k) \end{aligned} \qquad (2.3)$$

Cross-couplings between elements of the diagonal part of the strain tensor and the density, entropy density, concentration and nematic order variations are expressed by the static susceptibility tensors χ_{ij}^{ρ}, χ_{ij}^{σ}, χ_{ij}^{c} and χ_{ij}^{S}, respectively, which have the uniaxial form $\chi_{ij} = \chi_{\|} n_i n_j + \chi_{\perp}\delta_{ij}^{tr}$. Note that in Equation (2.2) we have to use explicitly the deviations of the variables from their equilibrium values (e.g., $\delta\rho(\mathbf{r}, t) = \rho(\mathbf{r}, t) - \rho_{eq}$), while under gradients or time derivatives this distinction is unnecessary (since $(\partial/\partial t)\rho_{eq} = 0 = \nabla_i\rho_{eq}$ etc.). By inspection of Equation (2.2) we see that there is no static cross-coupling between strains and director distortions, only between strains and nematic order variations. The latter cross-coupling describes the possibility to induce stresses (in the back-bone conformation) by changing the nematic order (i.e., making the side-chains better or worse aligned with respect to their average direction) or to have a "force," which changes the nematic order, if a strain in the backbone exists. Of course, this static cross-coupling cannot be seen directly (in an infinitely slow process), since the elastic behaviour disappears on long time scales in pscN. In high frequency experiments this cross-coupling is manifest, but has to be seen in addition to the appropriate dynamical cross-coupling, which will be derived below.

As outlined above the generalized forces are evaluated by taking the variational derivative of the generalized thermodynamic potential with respect to the appropriate variable, while keeping all other variables constant. We find for example

$$\Psi_{ij} = \frac{\delta E}{\delta \epsilon_{ij}}\Big|_{\dots} = c_{ijkl}\epsilon_{kl} + \chi_{ij}^{\rho}\delta\rho + \chi_{ij}^{\sigma}\delta\sigma + \chi_{ij}^{c}\delta c + \chi_{ij}^{S}\delta S \qquad (2.4a)$$

$$\Phi_{ij} = \frac{\delta E}{\delta \nabla_j n_i}\Big|_{\dots} = K_{ijkl}\nabla_l n_k \qquad (2.4b)$$

$$W = \frac{\delta E}{\delta S}\Big|_{\dots} = a\delta S + \chi_{ij}^{S}\epsilon_{ij} + b^{\sigma}\,\delta\sigma + b^{\rho}\,\delta\rho + b^{c}\,\delta c \qquad (2.4c)$$

We can now proceed to the dynamics of pscN. For the conservation laws for density, density of linear momentum and concentration we have

$$\begin{aligned} \dot{\rho} + \nabla_i g_i &= 0 \\ \dot{g}_i + \nabla_j \sigma_{ij} &= 0 \\ \dot{c} + \nabla_i j_i{}^c &= 0 \end{aligned} \qquad (2.5)$$

where σ_{ij} is the stress tensor and j_i^c the concentration current. As we can read off from Equations (2.5) and (2.1) the density of linear momentum serves as both, as a variable and as the current of the density. The balance equations for the non-conserved fields read

$$\begin{aligned} \dot{\sigma} + \nabla_i j_i^\sigma &= \frac{R}{T} \\ \dot{\epsilon}_{ij} + X_{ij} &= 0 \\ \dot{n}_i + Y_i &= 0 \\ \dot{S} + Z &= 0 \end{aligned} \tag{2.6}$$

In Equations (2.6) j_i^σ is the entropy current, Y_i and Z and X_{ij} are the quasi-currents associated with temporal changes of the nematic order, the director orientation and the strain field, respectively. The source term R/T in the dynamic equation for the entropy density is the entropy production. The second law of thermodynamics requires $R > 0$ and $R = 0$ for dissipative and reversible processes, respectively. To guarantee rotational invariance of the dynamic equation for the strain field, its quasi-current X_{ij} must be symmetric $X_{ij} = X_{ji}$. From Equations (2.5) and (2.6) the conservation law for the energy density follows by making use of the Gibbs relation (2.1). Having written down already the dynamic equations for all the other dynamic variables, the form of the energy current is thus fixed completely. To give the currents and quasi-currents (the fluxes) introduced in (2.5) and (2.6) a physical meaning it is necessary to connect them with the thermodynamic forces (or thermodynamic conjugate quantities) taking into account all symmetry properties of the system. In the present paper we concentrate on the linear connection between forces and fluxes, since we are focusing on the linearized macroscopic dynamics.

All the currents written down in Equations (2.5) and (2.6) can be split into dissipative and into reversible parts, depending on whether they give rise to a finite amount of dissipation (or positive entropy production) or to a vanishing entropy production ($R = 0$).

Using general symmetry and invariance arguments (e.g., Galilean invariance) we obtain for the linear, reversible parts of the currents

$$\begin{aligned} g_i^R &= \rho_0 v_i \\ \sigma_{ij}^R &= p\delta_{ij} - \Psi_{ij} - \lambda_{kji}\nabla_l\Phi_{kl} + \frac{1}{2}(n_i\nabla_k\Phi_{jk} - n_j\nabla_k\Phi_{ik}) + \beta_{ij}W \\ j_i^{cR} &= c_0 v_i \\ j_i^{\sigma R} &= \sigma_0 v_i \\ Y_i^R &= \epsilon_{ijk}\omega_j n_k + \lambda_{ijk}A_{jk} \\ Z^R &= \beta_{ij}A_{ij} \\ X_{ij}^R &= -A_{ij} \end{aligned} \tag{2.7}$$

where p is the hydrostatic pressure, A_{ij} is the symmetric velocity gradient $A_{ij} = \frac{1}{2}(\nabla_i v_j + \nabla_j v_i)$ and ω_i is the vorticity $\omega_i = \frac{1}{2}\,\varepsilon_{ijk}\nabla_j v_k$. The reversible current for the strain field reflects the fact that for homogeneous translations (solid body translations) $\dot{\mathbf{u}} = \mathbf{v}$. In the stress tensor there is the elastic contribution from the transient network (Ψ_{ij}), the curvature elastic contribution from director distortions ($\nabla_j \Phi_{ij}$) and a stress due to variations of the order parameter modulus (W). The tensor λ_{ijk} is the flow alignment (or back flow) tensor, $\lambda_{ijk} = \lambda(\delta^{tr}_{ij} n_k + \delta^{tr}_{ik} n_j)$. The quantities ρ_0, c_0, σ_0, and S_0 are the equilibrium values of density, concentration, entropy density, and nematic order, respectively, around which the linearized equations are derived. All the reversible currents given in Equation (2.7) lead to vanishing entropy production $R = 0$.

For the derivation of the dissipative parts of the linearized currents in Equations (2.4) and (2.5) one expands the dissipation function to second order in the thermodynamic forces and then obtains the dissipative currents by taking the variational derivatives of the dissipation function with respect to the forces.

We find for the dissipation function

$$\begin{aligned} R = R_0 + \int d\tau \Big[&\frac{1}{2}\Big(\frac{1}{\tau}\Big)_{ijkl} \Psi_{ij} \Psi_{kl} + \frac{1}{2}\gamma_{ij} (\nabla_k \Psi_{ik})(\nabla_l \Psi_{jl}) + \frac{1}{2}\kappa_w W^2 + \xi_{ij} W \Psi_{ij} \\ &+ (\nabla_j \Psi_{ij})(\zeta^T_{ik} \nabla_k T + \zeta^c_{ik} \nabla_k \mu_c + \zeta^W_{ik} \nabla_k W) + \frac{1}{2\gamma_1}(\nabla_j \Phi_{ij})^2 + \zeta^n_{kji} \Psi_{ij} (\nabla_l \Phi_{kl}) \Big] \end{aligned} \tag{2.8}$$

where R_0 is the part of the dissipation function already present in simple fluids. The strain relaxation tensor τ^{-1} has the same structure as the elastic tensor (2.3) and contains five phenomenological transport coefficients. This strain relaxation is characteristic for polymers but is absent for permanent networks (elastomers[26,27]) or solids. The strain selfdiffusion described by the tensor γ_{ij}, which is of the usual uniaxial form (as the other second rank tensors in (2.8)), can be neglected against strain relaxation in the small k limit. It corresponds to vacancy diffusion in solids or permeation in smectics, although it is neglected in the usual elasticity theory of solids. There are several dissipative crosscouplings in (2.8) between strain or stress in the backbone and the other degrees of freedom. The most important of these, in the small k limit, are the cross-coupling to director distortions and order variations, characterized by the tensors ξ_{ij} and ζ^n_{ijk}, respectively, where ζ^n_{ijk} has the same structure as the flow alignment tensor λ_{ijk} and contains one phenomenological transport parameter ζ_n. The meaning of these cross-couplings is that dilations or compressions of the backbone network are dynamically coupled to fluctuations of the nematic order, while the dynamics of shear strains is coupled to director distortions, both on the dissipative level. Some of the experimental consequences will be discussed in Sec. 3.

All the terms in Equation (2.8) have been chosen in such a way that they guarantee the positivity of the entropy production in accordance with the second law of thermodynamics, if the phenomenological transport parameters satisfy a number of positivity conditions including τ_1, τ_2, τ_3, τ_5, $\tau_4^2 - \tau_1 \tau_2$, $\gamma_{\parallel}$, $\gamma_{\perp}$, κ_w, $\kappa_w - \tau_1 \xi_{\perp}^2$, $\kappa_w - \tau_3 \xi_{\parallel}^2$, and $1 - \tau_5 \gamma_1 \zeta_n^2$ being all positive. In addition all contributions to R transform like a scalar, that is they must be invariant under translations, rotations, under time reversal and operations including spatial parity and under $\hat{\mathbf{n}}$ to $-\hat{\mathbf{n}}$ symmetry.

As already mentioned above we get the dissipative parts of the currents by taking the variational derivative of the dissipation function with respect to the appropriate thermodynamic force. We find for example

$$\begin{aligned} Z^D &= \frac{\delta R}{\delta W}|_{\dots} = \kappa_w W + \xi_{ij}\Psi_{ij} - \zeta^W_{ik}\nabla_k\nabla_j\Psi_{ij} \\ Y_i^D &= \frac{\delta R}{\delta\nabla_j\Phi_{ij}}|_{\dots} = \frac{1}{\gamma_1}\nabla_j\Phi_{ij} + \zeta^n_{ijk}\Psi_{jk} \\ X^D_{ij} &= \frac{\delta R}{\delta\Psi_{ij}}|_{\dots} = (\frac{1}{\tau})_{ijkl}\Psi_{kl} + \xi_{ij}W + \zeta^n_{kji}\nabla_l\Phi_{kl} \\ &\quad -\frac{1}{2}[\nabla_j(\gamma_{ik}\nabla_l\Psi_{kl} + \zeta^T_{ik}\nabla_k T + \zeta^c_{ik}\nabla_k\mu_c + \zeta^W_{ik}\nabla_k W) + (i \leftrightarrow j)] \end{aligned} \tag{2.9}$$

From Equation (2.9) we read off immediately that X^D_{ij} can be split into two parts, the source terms (first line) and the symmetrized gradient terms (second line) of the form $\nabla_j X_i + \nabla_i X_j$. In a solid the source terms all vanish, since the displacement is a true hydrodynamical variable there. From classical elasticity theory of solids[28] one knows that the strain tensor must satisfy a compatibility condition to guarantee that a continuous displacement field $\mathbf{u}(\mathbf{r}, t)$ exists. This condition reads

$$\epsilon_{ijk}\epsilon_{lmn}\nabla_j\nabla_m\epsilon_{kn} = 0 \tag{2.10}$$

and applies, because of Equation (2.6), also to X_{ij} ($\varepsilon_{ijk}\varepsilon_{lmn}\nabla_j\nabla_m X_{kn} = 0$). Obviously, the reversible part X^R_{ij} and the symmetrized gradient part of X^D_{ij} fulfill this condition, but not the source terms. Thus, we are lead to the conclusion, that in polymers the compatibility condition does not apply. This means that in polymers a displacement field in the usual sense does not exist. Strains in the backbone conformation are not relaxed by displacing some lattice points to their equilibrium position (as in solids), but rather by the (slow) motion of the entangled chains. The elasticity of polymers is therefore described by (six independent) nonhydrodynamic variables ε_{ij}, while the elasticity of solids can be reduced to (three independent) hydrodynamic variables $\mathbf{u}$.*

3. POSSIBLE EXPERIMENTAL TESTS OF THE MACROSCOPIC DYNAMICS APPROACH

In this section we briefly discuss how two standard experiments in pseN differ from the analogous experiments in lmwN on the one hand and conventional polymers on the other. First we look at sound propagation. In lmwM the velocity of ordinary

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* In Reference 21 the application of the compatibility condition on isotropic polymers has lead to some restrictions for the elastic moduli (Equation (2.13) there), which we now believe to be unnecessary. As a consequence the Maxwell time for bulk compressional or dilational strains is no longer equal to that for shear strains.

(first) sound is isotropic (in the absence of external fields), despite the fact that the phase itself is uniaxial. The reason is that the curvature elasticity of the director couples to the bulk compression or dilation of the liquid only in order k^2 and gives, thus, only a contribution to the sound dispersion ($\omega \sim k^2$) but not to the sound velocity ($\omega \sim k$). On the contrary, the velocity of first sound in pscN *is* anisotropic at high frequencies, what has already been verified experimentally,[29,30] but becomes isotropic when sound is excited at low frequencies (this prediction is yet to be confirmed experimentally). From Equation (2.7) it is easily seen that the elastic stress (Ψ_{ij}) and the nematic order "force" (W) contribute to the stress tensor on equal footing with the ordinary compressibility and thus enter the sound velocity. But both additional contributions depend manifestly on the direction $\hat{\mathbf{n}}$ rendering the sound velocity anisotropic. However, both the elastic strain and the nematic order are relaxational variables and for frequencies smaller than the inverse Maxwell and the order relaxation time they die out and their contribution to the sound velocity is ineffective. The first sound dispersion relation has the following structure (neglecting viscosity and other ordinary sound damping mechanisms as well as the static and dynamic cross-coupling terms proportional to χ_{ij} and ξ_{ij})

$$\omega^2 = k^2 \left[\frac{\partial p}{\partial \rho} + \frac{c_3}{\rho_0} \frac{\omega^2 - i\omega f_1}{\omega^2 - i\omega f_2 - {f_3}^2} + \frac{\beta_{\parallel}^2}{\rho_0} \frac{ai\omega}{i\omega + a\kappa_w} \right] \tag{3.1a}$$

$$\omega^2 = k^2 \left[\frac{\partial p}{\partial \rho} + \frac{c_1 + 2c_2}{\rho_0} \frac{\omega^2 - i\omega f_4}{\omega^2 - i\omega f_2 - {f_3}^2} + \frac{\beta_{\perp}^2}{\rho_0} \frac{ai\omega}{i\omega + a\kappa_w} \right] \tag{3.1b}$$

for $\mathbf{k} \| \hat{\mathbf{n}}$ ($\phi = 0$) and $\mathbf{k} \perp \hat{\mathbf{n}}$ ($\phi = \pi/2$), respectively. The coefficients f_α are some linear combinations of elastic constants c_α divided by some transport parameters τ_α. From Equation (3.1) the following picture emerges: For large frequencies, both, elastic strains and the nematic order fluctuations contribute to sound propagation and these contributions depend on ϕ, the angle between the wave vector and the director, thus rendering first sound anisotropic. At $\omega = a\kappa_w$ the sound velocity changes (dispersion) and, below, nematic order fluctuations no longer contribute to the sound velocity (only to the damping). A second dispersion step is reached at the inverse Maxwell time, which is a function of the f_α's and which depends on ϕ, and below which only (the isotropic) compressibility supports sound propagation. Taking into account the cross-coupling terms ($\sim \chi_{ij}$ and $\sim \xi_{ij}$) the dispersion relation becomes even more involved and we refrain from writing down explicit results.

This picture is also different from that in conventional polymers, where sound is always isotropic (because of the lack of a director) and where only one dispersion step exists in the validity range of a macroscopic description (because there are no nematic order fluctuations).

In addition to ordinary first sound, there is also transverse sound in conventional polymers above the inverse Maxwell time.[21,23] On the other hand in lmwN there is no transverse sound at all, since director fluctuations do not lead to propagating waves.[12] In pscN the transverse sound dispersion relation is found from (2.5)–(2.8) for either $\phi = 0$ and $\mathbf{v} \perp \hat{\mathbf{n}}$ or $\phi = \pi/2$ and $\mathbf{v} \| \hat{\mathbf{n}}$

$$\omega^2 = \frac{c_5}{\rho_0} \frac{i\omega}{i\omega + 4\frac{c_5}{\tau_5}} k^2, \tag{3.2}$$

which describes a propagating (anisotropic) mode in the high frequency limit only. Again there is a dispersion step at $\omega = 4c_5/\tau_5$, while below this Maxwell frequency, which is different from the Maxwell frequencies relevant for first sound, there is no propagation at all and the dissipative behaviour of lmwN is regained. For general wave vector directions also the transverse sound velocity becomes anisotropic, while on the contrary, in conventional polymers transverse sound velocity is isotropic.

The second example of different behaviour of lmwN, conventional polymers and pscN we discuss briefly is flow alignment. In lmwN application of a stationary shear leads to a stationary state, where the director is, within the shear plane, tilted from the shear velocity direction by a constant angle Θ with $\cos 2\Theta = 1/\lambda$ (except for some boundary layer), if the flow alignment parameter fulfils $|\lambda| > 1$. Of course, this effect has no counterpart in conventional polymers. In pscN a stationary flow alignment effect is possible. However, the externally applied shear Γ ($= \nabla_x v_z$, where the director was parallel to the z-axis before shearing) not only tilts the director, but also creates a (constant) elastic stress and a (constant) nematic order "force" (cf. (2.6)–(2.9))

$$\Psi_{xz} = \frac{1}{2}\Gamma\left(\frac{1}{\tau_2} + \frac{2}{\tau_5}\right)^{-1} \tag{3.3a}$$

$$\Psi_{xx} = -\Gamma\xi_a\kappa_w^{-1}(B_1\xi_\perp + B_2\xi_\parallel)\sin 2\Theta + O(\xi^3) \tag{3.3b}$$

$$\Psi_{zz} = -\Gamma\xi_a\kappa_w^{-1}(B_3\xi_\perp + B_4\xi_\parallel)\sin 2\Theta + O(\xi^3) \tag{3.3c}$$

$$W = -\Gamma\kappa_w^{-1}\left[\beta_a + \xi_a\left(\frac{1}{\tau_2} + \frac{2}{\tau_5}\right)^{-1}\right]\sin 2\Theta + O(\xi^3) \tag{3.3d}$$

Here the B_α's stand for some complicated combinations of the transport parameters τ_α, $\beta_\parallel$, and $\beta_\perp$ and $O(\xi^3)$ characterizes terms cubic in the cross-coupling coefficients ξ_α. Subscripts a denote anisotropic parts of second rank tensors, like $\xi_a \equiv \xi_\parallel - \xi_\perp$. Due to the dynamic cross-coupling between elasticity and nematic order fluctuations, not only the elastic shear stresses, but also elastic bulk stresses are created (3.3b, c). The flow alignment angle is given by

$$(\cos 2\Theta)^{-1} = \lambda + \frac{1}{2}\zeta_n\left[\left(\frac{1}{\tau_2} + \frac{2}{\tau_5}\right) + O(\xi^2)\right] \tag{3.4}$$

and acquire a contribution due to the dynamic cross-coupling between elasticity and nematic orientation.

Apparently the solution (3.3) not only enhances the energy dissipation (cf. (2.8)), but also leads to non-vanishing elastic stresses and a change in the nematic order.

However it is doubtful, whether the latter two effects can directly be detected by experiments. A possibility to see the change in the energy dissipation seems to be studying oscillatory shear, $\Gamma \sim \exp(i\omega t)$. In that case the induced elastic strains and nematic order changes are frequency dependent $\sim 1/(i\omega T + 1)$, where T is the appropriate Maxwell time and the order relaxation time, respectively. For frequencies e.g., smaller than the Maxwell frequency, the induced strain is in phase with the shear flow, giving rise to additional energy dissipation, while well above, it is out of phase by π, as it would be in a gel or solid, and is not dissipative. Thus, the energy dissipation, which is a measure for the energy that has to be supplied to the system in order to maintain the shear flow, drops (mainly) at the resonance frequency. The same happens at the inverse nematic order relaxation time. Other experimentally detectable consequences of this macroscopic dynamics approach will be discussed elsewhere.

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