Local Rotational Degrees of Freedom in Nematic Liquid-Crystalline Side-Chain Polymers

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ABSTRACT: In nematic side-chain polymers the side chains are oriented in the mean along a certain direction (the director). Rotations of backbone segments relative to the director are degrees of freedom characteristic for such polymeric nematic systems. We investigate theoretically the influence of these relative rotations on the linear mode spectrum. We discuss longitudinal and transverse sound excitations and propose experiments, in which qualitatively new features due to these relative rotations are to be expected. We show that recent unexpected findings in director relaxation experiments can be explained with the help of these new degrees of freedom as well as by elasticity.

1. Introduction and Discussion of Results

Since the first synthesis of liquid-crystalline side-chain polymers,[1] the number of investigations of this new class of material has grown rapidly (cf. refs 2 and 3 and references cited therein). Apart from the technological importance of these materials, there is also a profound purely scientific interest in such materials; e.g., they facilitate certain experiments due to the longer time scales involved in polymeric systems compared to low molecular weight systems. Here we are interested in the possibility of getting access to rotational degrees of freedom connected to viscoelasticity with the help of the hydrodynamic liquid-crystalline degrees of freedom.

In hydrodynamics each degree of freedom is represented by an appropriate dynamical field[4] in contrast to phenomenological models for polymers (Maxwell, Jeffries, etc.), where only the conventional fields of simple liquids are used and the additional dynamical complexity is put into frequency-dependent transport parameters. The hydrodynamic method, however, has the advantage that cross couplings between the dynamical fields are much more apparent and their derivation is more systematic.[5] This is even more important for liquid-crystalline polymers, where additional degrees of freedom have to be accounted for, as has successfully been demonstrated for nematic side-chain polymers in ref 6. Having identified all relevant dynamical variables (i.e., the truly hydrodynamic ones and those relaxing on a macroscopic time scale), the hydrodynamic method is exact and sets a framework for microscopic and phenomenological models. It consists of an analytical gradient expansion in the statics and dynamics. Usually such an expansion exists at least for the lowest order terms (with the critical dynamics very close to phase transitions as an exception). In the following we will restrict ourselves to linear hydrodynamics.

In contrast to polymeric main-chain nematics, where the nematic order takes place in the backbone itself, in side-chain nematics the nematic order and the polymeric behavior are separated spatially and coupled through the flexible spacers between mesogenic units of the side chains and backbone segments only. Thus, in a hydrodynamic description the specific polymeric degrees of freedom (transient elasticity[5]) and the specific nematic degrees of freedom (director rotations[7]) can still be treated as independent dynamic variables. Their mutual interaction is then described explicitly by static and dynamic cross couplings[6] similar to the interaction between tempera-

ture and concentration in binary mixtures.

The physical linkage between side chains and the backbone has additional consequences. First, the degree of nematic order (nematic order parameter) is influenced by backbone fluctuations, and, vice versa, any change in the degree of the nematic order may require some movement of the backbone. Thus, in nematic side-chain polymers the nematic order parameter is an additional macroscopic (i.e., slow) variable,[6] whereas in low molecular weight nematics it is fast and discarded in a hydrodynamic description (except near the phase transition to the isotropic phase). In addition, rotations of the side chains can influence the orientation of the backbone segment to which they are attached and vice versa. Since the orientation of the side chains (the director) can be manipulated by external fields,[7] this gives access to the dynamics of local rotations of the backbone. In nonmesogenic polymer systems such rotations of the backbone are decoupled from the macroscopic variables and do not show up explicitly in a hydrodynamic description (Appendix A). Thus, the relative rotations between backbone and director are a specific and important additional macroscopic degree of freedom of nematic side-chain polymers, and the main body of this manuscript will be devoted to the derivation of the appropriate hydrodynamic equations (section 2) and to the discussion of its influence on standard experimental situations like sound propagation, flow alignment, and director relaxation (section 3). A discussion of the static properties of these relative rotations for permanently cross-linked polymers (gels or elastomers) has already been given[8] some time ago. A complete listing of the hydrodynamic equations including the other degrees of freedom is given in Appendix B.

Investigating the normal-mode structure of nematic side-chain polymers including relative rotations, we find (section 3) that generally the influence of the latter and their distinction from (transient) elasticity is most pronounced for high-frequency experiments (e.g., sound propagation), while for quasi-static experiments (flow alignment due to shear flow, director relaxation in homogeneous magnetic fields), the influence of elasticity and relative rotations is difficult to disentangle. The velocity of longitudinal sound acquires an additional dispersion step at the relaxation frequency of the relative rotations, which has a characteristic $\sin^2(2\phi)$ dependence on the angle ϕ between the wave vector $\mathbf{k}$ and the director $\hat{\mathbf{n}}^0$. This is in contrast to the dispersion step due to elasticity, which—although direction dependent too—is present for

all directions. For transverse sound (i.e., with the wave vector perpendicular to the velocity amplitude **v**), the influence of relative rotations is manifest except for **v** $\perp$ $\hat{n}^0$ $\perp$ **k**. In flow alignment and in director relaxation experiments both relative rotations and elasticity enter on equal footing and one measures neither the (bare) nematic flow alignment parameter nor the (bare) nematic rotational viscosity by these experiments in polymeric systems. A detailed discussion of these experiments is given in section 3.

2. Hydrodynamic Equations

In elasticity theory[9] and in hydrodynamics[4] the elastic behavior of solids is described by the displacement field **u**(**r**,t), which characterizes the actual position of the medium (i.e., of the molecules) compared to its equilibrium one. The displacement field constitutes three independent additional degrees of freedom (compared to liquids), two of which combine with the vorticity diffusion of liquids to form the transverse sound modes of solids, while the third one can be interpreted as the vacancy diffusion mode.[4] Since homogeneous translations and solid-body rotations do not change the elastic energy of the solid, the strain tensor ϵ_{ij}, a symmetric second rank tensor, is usually used to describe elasticity. It is completely fixed by the displacement field and does not contain additional degrees of freedom. In the linearized version one has

$$\epsilon_{ij} = \frac{1}{2}(\nabla_j u_i + \nabla_i u_j) \qquad (1)$$

Local rotations are described by an antisymmetric second-rank tensor in linearized theory

$$\Omega_{ij} = \frac{1}{2}(\nabla_j u_i - \nabla_i u_j) \qquad (2)$$

where, again, Ω_{ij} does not introduce additional degrees of freedom.

The elasticity of polymers, however, is only transient; i.e., it is manifest on a short time scale only but absent in the long time (stationary) limit. The simplest way to describe this behavior hydrodynamically is to use a relaxing strain field as an additional (compared to simple liquids) macroscopic variable.[5] However, since there is no defined equilibrium position of the molecules in polymers, the notion of a displacement (from the equilibrium position) does not make sense anymore and ϵ_{ij} is no longer restricted by the special form of eq 1. Thus, it contains 6 degrees of freedom, 3 of which are dynamically related to the momentum and 3 of which are local elastic modes. These strainlike fields no longer have a simple molecular interpretation (in terms of displacements of regular lattices) in polymers, since the transient elasticity there arises from the complicated and entangled motion on the molecular scale, which is even more complicated for side-chain polymers. Nevertheless, we will talk of "backbone elasticity", etc., in the following as a shorthand notation. In addition, Ω_{ij} does not obey eq 2 and, again, cannot be simply interpreted as being due to molecular displacements. In polymers it is related to local torques due to the entangled molecular motion; we will call it "local rotation" in the following. For a discussion of the hydrodynamics of isotropic polymers in terms of ϵ_{ij} and Ω_{ij}, compare Appendix A.

For the description of the dynamics of nematic side-chain polymers we recently[6] used—besides the usual degrees of freedom of liquids (density, momentum density, and energy density) and the nematic director

rotations—the (relaxing) strain field ϵ_{ij} and the (relaxing) order parameter δS as additional hydrodynamic variables in order to describe the dynamic interplay between the viscoelasticity of the backbone and the nematic ordering of the side chains. As discussed in the introduction also relative rotations between local backbone segments and the director are macroscopic degrees of freedom and their hydrodynamic description will now be given.

Local rotations of the polymeric backbone are described by the antisymmetric tensor Ω_{ij}, which in the case of polymers is not restricted to have the form of eq 2. In a nematic (uniaxial) system there are two different cases to be distinguished, namely, the rotation around the preferred direction $\hat{n}^0$ ($\Omega^{\|} = n_i^0 \epsilon_{ijk}\Omega_{jk}$; summation over repeated indices is always implied) and two rotations orthogonal to that ($\Omega_i^{\perp} = n_j^0 \Omega_{ij}$, which implies $n_i^0 \Omega_i^{\perp} \equiv 0$). The former one does not involve a rotation relative to $\hat{n}^0$ and is decoupled from the other hydrodynamic variables. It is rather similar to the local rotations in isotropic polymers (cf. Appendix A) and will not be considered in the following. The latter ones give rise to relative rotations, $\delta n_i - \Omega_i^{\perp}$, which we are interested in. Here δn_i describes rotations of the director from its equilibrium direction, $\delta n_i = n_i - n_i^0$ and $(\partial/\partial t)\delta n_i = \dot{n}_i$. By definition $\Omega_i^{\perp}$ changes sign under the symmetry operation $\hat{n}^0 \rightarrow -\hat{n}^0$.

Since $\delta n_i - \Omega_i^{\perp}$ is not a conserved quantity, the dynamic equations simply read

$$\dot{n}_i - \dot{\Omega}_i^{\perp} + Y_i^{\Omega} = 0 \qquad (3)$$

with $n_i^0 Y_i^{\Omega} = 0$ ($n_i^0 Y_i^{\Omega} = n_i Y_i^{\Omega}$ for the linearized theory). Generally, the quasi-current Y_i^{Ω} can be written as the sum of the irreversible and the reversible parts, $Y_i^{\Omega} = Y_i^{\Omega D} + Y_i^{\Omega R}$, which do or do not contribute to the entropy productio of the system, respectively. The time-reversal behavior of the reversible part is opposite to that of $\delta n_i - \Omega_i^{\perp}$, and the most general form allowed by symmetry is

$$Y_i^{\Omega R} = \lambda^{\perp}(\delta_{ij}^{\perp} n_k^0 + \delta_{ik}^{\perp} n_j^0)\nabla_j v_k \qquad (4)$$

where **v** is the velocity field. The transverse Kronecker symbol $\delta_{ij}^{\perp} = \delta_{ij} - n_i^0 n_j^0$ projects out the direction parallel to $\hat{n}^0$. There is no coupling in eq 4 to the vorticity (the antisymmetric gradients of the velocity), since a global rotation of the system does not affect any relative angle between two directions. The (reversible) transport parameter $\lambda^{\perp}$ resembles the flow alignment parameter λ in nematics and describes how elongational flow (and shear flow) influences the relative rotations. Conversely, relative rotations lead to backflow effects in the stress tensor (cf. eq 8). There are also some similarities with the β terms,[10-12] relating scalar order parameters to elongational flow (and vice versa) in systems close to various liquid-crystalline phase transitions.

Like all transport parameters and static susceptibilities to be defined in the following, $\lambda^{\perp}$ is a (phenomenological) constant in the linearized theory, while in a nonlinear generalization it can be a function of all scalar variables, e.g., temperature, pressure, v^2, etc., but not of frequency, wave vector, or director, since the latter dependencies are made explicit by the hydrodynamic method.

The irreversible part of the quasi-current Y_i^{Ω} can be expressed by the thermodynamic forces via (linear) irreversible thermodynamics.[13] In order to obtain the force associated with the relative rotations, we expand the free

energy density into the variables[8]

$$f = \frac{1}{2}D_1(\delta n_i - \Omega_i^\perp)^2 + D_2(\delta n_i - \Omega_i^\perp)\epsilon_{ij}n_j^0 + ... \quad (5)$$

where the dots contain the contributions not related to the relative rotations (cf. Appendix B). The first term stands for the energy cost of relative rotations, while the second one denotes the cross-coupling energy between a relative rotation and an elongation-like (transient) elasticity. Equation 5 has the same form as for nematic gels.[8] For polymeric systems it is not accessible by static experiments, since in that limit polymers are fluid, but at short time scales the energy cost (eq 5) of relative rotations is manifest. Relative rotations, which enter the macroscopic dynamics even in the static limit, occur in tilted hexatic liquid crystals (smectic F and I)[14,15] and in mixtures of two uniaxial nematic systems with different directors,[16] while relative *translations* strongly influence the macroscopic dynamics of incommensurate solids[17] and other incommensurate systems.[18]

The thermodynamic force due to relative rotations is then given by the derivative of the free energy

$$L_i^\perp = D_1(\delta n_i - \Omega_i^\perp) + D_2\epsilon_{jk}n_j^0\delta_{ik}^\perp \quad (6)$$

The cross-coupling term D_2 describes not only that elastic elongations give rise to a nonvanishing $L_i^\perp$ (the second part of eq 6) but also that relative rotations lead to elastic stresses Ψ_{ij} (the thermodynamic force conjugate to the strain ϵ_{ij})

$$\Psi_{ij} = \frac{1}{2}D_2([\delta n_i - \Omega_i^\perp]n_j^0 + [\delta n_j - \Omega_j^\perp]n_i^0) + ... \quad (7)$$

For the dots, which contain, e.g., the elastic tensor, compare Appendix B. Thermodynamic stability requires $D_1 > 0$ and $D_1 c_5 > D_2^2$, where c_5 is a shear elastic constant. The thermodynamic force conjugate to director rotations (at constant relative rotation), $\nabla_j\Phi_{ij}$, is given by the usual Frank curvature elasticity, $\Phi_{ij} = (\partial f_0/\partial\nabla_j n_i) = K_{ijkl}\nabla_l n_k$. Physically, $n_i^0\epsilon_{ijk}\Omega_j^\perp$ can be interpreted as a torque due to relative rotations. This thermodynamic force adds to the stress tensor

$$\sigma_{ij}^R = -\frac{1}{2}\lambda^\perp(\delta_{kj}^\perp n_i^0 + \delta_{ki}^\perp n_j^0)L_k^\perp + ... \quad (8)$$

where the dots stand for additional stresses due to the other internal degrees of freedom (Appendix B).

With the static relations eqs 6 and 7 now at hand we can return to the dissipative parts of the quasi-currents. Symmetry allows for the expressions

$$Y_i^{\Omega D} = \zeta^\perp L_i^\perp + \zeta_{12}\nabla_j\Phi_{ij} + \zeta_{ijk}^\Omega\Psi_{jk}$$

$$Y_i^D = -\frac{1}{\gamma_1}\nabla_j\Phi_{ij} - \zeta_{12}L_i^\perp - ... \quad (9)$$

$$X_{ij}^D = \left(\frac{1}{\tau}\right)_{ijkl}\Psi_{kl} + \zeta_{ijk}^\Omega L_k^\perp + ...$$

where we have also written down some dissipative contributions to the quasi-currents of the dynamic equations for the director ($\dot{n}_i + Y_i = 0$) and for the transient elasticity ($\dot{\epsilon}_{ij} + X_{ij} = 0$). The diagonal terms $\zeta^\perp$, $1/\gamma_1$, and $1/\tau$ describe the relaxation of relative rotations, director reorientation, and decay of the transient elasticity, respectively. The tensor $\zeta_{ijk}^\Omega = \zeta^\Omega(\delta_{ik}^\perp n_j^0 + \delta_{jk}^\perp n_i^0)$ is of the typical nondiagonal

form that can also be found in eqs 4 and 6, and $(1/\tau)_{ijkl}$ is structurally isomorphic to the elastic tensor c_{ijkl} (cf. Appendix B). For the dissipative cross-coupling coefficients, ζ_{12} and ζ^Ω, the Onsager relations have already been built in. To guarantee positivity of the entropy production, the following expressions have to be positive, $\zeta^\perp$, $\zeta^\perp/\gamma_1 - \zeta_{12}^2$, and $\zeta^\perp/\tau_5 - (\zeta^\Omega)^2$. For permanently cross-linked polymers (elastomers, gels) the elasticity no longer relaxes on finite time scales but diffuses. For that case all τ's have to be infinite, which implies that ζ^Ω is zero, and eq 9 is amended by diffusional terms $\sim\nabla_k\nabla_j\Psi_{ij}$. Equation 9 only contains linear dissipative effects, while nonlinear effects can be incorporated along the lines of ref 19.

There are no orientational effects of spatially homogeneous external (electric or magnetic) fields related to the relative rotations. Only inhomogeneous electric fields couple to relative rotations giving rise to an additional contribution in eq 6 to $L_i^\perp$ of the form $e_{ijk}^\perp\nabla_j E_k$ (with a corresponding contribution to the dielectric displacement vector $D_i = e_{kji}^\perp\nabla_j(\delta n_k - \Omega_k^\perp)$) and in eq 9 to $Y_i^{\Omega D}$ of the form $\zeta_{ijk}^{el}\nabla_j E_k$ (with a corresponding contribution to the electric current density $J_i = -\zeta_{kji}^{el}\nabla_j L_k^\perp$), where the material tensors $e_{ijk}^\perp$ and ζ_{ijk}^{el} are of the form in eq B.7. The flexoelectricity (with respect to relative rotations) $\sim e_{ijk}^\perp$ is not accessible by static measurements in polymers, while elastomeric systems are more suitable for investigating static electric effects.[20,21] For a more general treatment of dynamic electric effects within the macroscopic dynamics, compare refs 22 and 23.

3. Experiments

Having finished the exposition of those parts of the hydrodynamic equations that are related to relative rotations, we will now proceed by discussing how the new degrees of freedom can be detected and identified by experiments. We propose some future experiments and discuss the results of a recent one, where the relative rotations lead to qualitatively new effects, by which their importance for the macroscopic dynamics of nematic side-chain polymers can be demonstrated.

One suitable standard experiment is the measurement of the velocity of (ordinary longitudinal) sound waves, $c(\omega,\phi)$, as function of the frequency and of the orientation between the wave vector **k** and the director $\hat{n}^0$ ($\hat{n}^0\cdot\mathbf{k} = \cos\phi$). Without taking into account relative rotations, we have found[6] that at high frequencies c is anisotropic and especially $c(\phi=0) \neq c(\phi=\pi/2)$. This results from the uniaxiality of the elasticity and from the order parameter, which couples uniaxially to the velocity, as well as from various cross couplings among these variables and the other variables contributing to the sound velocity. At low frequencies the sound velocity is isotropic as for low molecular weight nematic liquid crystals. This general picture has recently been confirmed experimentally.[24-26] For intermediate frequencies there are some dispersion steps, which correspond to the relaxation frequencies of (transient) elasticity, order parameter, and related cross couplings. The dispersion steps depend on the orientation ϕ, and below the lowest one the anisotropy has vanished.

Taking into account the relative rotations, there are additional frequency- and orientation-dependent contributions to the sound velocity. Neglecting the static (D_2) and dissipative cross-coupling terms (ζ^Ω) for the moment, we find for the dispersion relation of first sound (up to

order $\omega \sim k$)

$$\frac{\omega^2}{k^2} = \frac{i\omega}{i\omega + D_1\zeta^\perp}\frac{\lambda^{\perp 2}D_1}{4\rho_0}\sin^2(2\phi) + c_0{}^2(\omega,\phi) \qquad (10)$$

where $c_0{}^2$ denotes the contributions, which are not related to relative rotations. The new contribution due to relative rotations in eq 10 is generally anisotropic but vanishes for both $\phi = 0$ and $\phi = \pi/2$. It introduces an additional dispersion step (at the relaxational frequency of the relative rotations), below which it only adds to the damping of the sound mode but no longer to the velocity. Thus, if in experiments an additional dispersion step is found at some intermediate angle, say $\phi = \pi/4$, but neither for $\phi = 0$ nor for $\phi = \pi/2$, this effect is very likely related to the relative rotations discussed here. This general picture does not change if the cross-coupling terms ζ^Ω and D_2 are taken into account; only eq 10 becomes much more complicated.

The $\sin^2(2\phi)$ signature of the new contribution is quite characteristic for rotational degrees of freedom and can be traced back to the special form of the coupling provided by $\lambda^\perp$ (cf. eq 4). The contributions to the sound dispersion relation due to director rotations (as in low molecular weight nematics) would also have the same ϕ dependence. They are, however, of order $\omega^2 \sim k^4$ and do not contribute to the sound velocity. The difference is that director rotations are true hydrodynamic variables, which can only diffuse but not relax, while the relative rotations are not true hydrodynamic excitations and relax on a finite time scale. The reason is that director rotations are Goldstone modes of the spontaneously broken rotational symmetry in nematics,[27,28] while the relative rotations are not connected to a spontaneously broken continuous symmetry nor to any conservation law.

Other propagative modes in solids (and polymers at high frequencies) are the two transverse sound modes, where the polarization of the mode (i.e., the velocity $\mathbf{v}$) is perpendicular to the wave vector $\mathbf{k}$. In uniaxial systems the two modes (called A and B in the following) have $\mathbf{v} \parallel \hat{\mathbf{n}}^0$ and $\mathbf{v} \perp \hat{\mathbf{n}}^0$, respectively. Without taking into account relative rotations, both modes A and B show one dispersion step[6] in nematic side-chain polymers, below which transverse sound ceases to exist as a propagative mode and is better described as a vorticity diffusion mode common to liquids. The dispersion steps in modes A and B are generally different from each other (and—for B—dependent on ϕ, the angle between $\mathbf{k}$ and $\hat{\mathbf{n}}^0$) but are both given by some elastic relaxation frequencies (e.g., c_2/τ_2, $4c_5/\tau_5$).

The relative rotations are excited by shear flow, except if $\hat{\mathbf{n}}^0$ is perpendicular to the shear plane. This is easily recognized from eq 4: Y_i^Ω is nonzero only, if either $\hat{\mathbf{n}}^0 \cdot \mathbf{v}$ or $\hat{\mathbf{n}}^0 \cdot \mathbf{k}$ or both are nonzero. The reason is that relative rotations about $\hat{\mathbf{n}}^0$ do not exist (rotations about $\hat{\mathbf{n}}^0$ do not change the angle between $\hat{\mathbf{n}}^0$ and the backbone). Thus, relative rotations are generally part of the transverse sound modes A and B, except for $\mathbf{k} \perp \hat{\mathbf{n}}^0$ in case B. Neglecting the cross-coupling terms (D_2 and ζ^Ω) again, which does not alter the general content of the result, the dispersion relations for transverse sound A and B are, respectively

$$\frac{i\omega\rho_0}{k^2} + F_1(\omega) = 0$$

$$\frac{i\omega\rho_0}{k^2} + F_1(\omega)\cos^2\phi + F_2(\omega)\sin^2\phi = 0 \qquad (11)$$

where

$$F_1 = \frac{1}{4}\frac{\lambda^{\perp 2}D_1}{i\omega + \zeta^\perp D_1} + \frac{c_5}{i\omega + 4(c_5/\tau_5)} + \nu_5$$

$$F_2 = \frac{1}{2}\frac{c_2}{i\omega + c_2/\tau_2} + \nu_2 \qquad (12)$$

with $\mathbf{k}\cdot\hat{\mathbf{n}}^0 = \cos\phi$. Relative rotations introduce generally a second dispersion step for the transverse sound velocity at the appropriate relaxation frequency $\zeta^\perp D_1$, below which they only contribute to the relaxation. Only for $\phi = \pi/2$ (case B) is this dispersion step absent. Thus, performing a propagating transverse sound experiment across a layer with planar alignment of the director (i.e., $\hat{\mathbf{n}}^0$ in the layer plane and $\mathbf{k}$ perpendicular) and finding two dispersion steps (one dispersion step) when the flow excitation is parallel (perpendicular) to $\hat{\mathbf{n}}^0$ will be a strong sign that relative rotations are present as important macroscopic excitations.

Relative rotations also influence other experiments involving the dynamics of the director, e.g., director relaxation measurements[29-31] and flow alignment angle measurements. However, in these cases relative rotations do not lead to qualitatively new effects, by which their existence could be demonstrated unambiguously, although their quantitative effects could be rather drastic. These will be discussed in Appendix C.

Appendix A: Local Rotations in Isotropic Polymers

As discussed in the introduction, local rotations in polymeric systems are not related to a displacement field (cf. eq 2) but are described by an antisymmetric second-rank tensor variable Ω_{ij}. It contains three independent fields, which is made apparent by writing $\Omega_i \equiv (1/2)\epsilon_{ijk}\Omega_{jk}$. This axial vector (it transforms even under spatial inversions in contrast to polar vectors, which transform odd) is completely determined by its divergence and curl, div $\vec{\Omega}$ and curl $\vec{\Omega}$. The former is a pseudoscalar quantity (odd under spatial inversion), which cannot couple in an isotropic system to any other macroscopic variable or external field, and is therefore not considered in the following. The latter two variables will be discussed here.

The free energy density related to local rotations reads

$$f_\Omega = \frac{B_1}{2}(\text{curl }\vec{\Omega})^2 + B_2(\text{curl }\vec{\Omega})_i\nabla_j\epsilon_{ij} \qquad (A.1)$$

Equation A.1 resembles the free energy expression for relative rotations in nematic systems (eq 5) with the very important difference that in eq A.1 only gradients of rotations (and gradients of the elastic strain) enter, while in eq 5 already homogeneous relative rotations lead to an increase in energy. Of course, a homogeneous rotation (solid-body rotation) must not alter the free energy of the system. Equation A.1 gives rise not only to the thermodynamic conjugate field with respect to rotations, $\vec{L}_i$, but also to a contribution to the elastic stress Ψ_{ij} (cf. eq 7)

$$\vec{L}_i = B_1(\text{curl }\vec{\Omega})_i + B_2\nabla_j\epsilon_{ij} \qquad (A.2a)$$

$$\Psi_{ij} = -\frac{1}{2}B_2[\nabla_j(\text{curl }\vec{\Omega})_i + (i \to j)] + \dots \qquad (A.2b)$$

The dynamics of local rotations is described by

$$\frac{\partial}{\partial t}\,\mathrm{curl}\,\vec{\Omega} - \mathrm{curl}\,\vec{\omega} + \vec{Z}^{\Omega} = 0 \qquad (A.3)$$

where $\vec{\omega}$ is the vorticity. The dissipative part of the quasi-current, Z_i^{Ω}, is derived from the dissipation function R

$$R = \frac{1}{2}\xi \vec{L}_i^{\,2} + \xi^{\Omega}\vec{L}_i\nabla_j\Psi_{ij} \qquad (A.4)$$

which also gives a contribution to the quasi-current of elastic strains X_{ij} (cf. eq 9), due to the cross coupling $\sim \xi^{\Omega}$

$$X_{ij}^{\,D} = -\frac{1}{2}\xi^{\Omega}(\nabla_j L_i + \nabla_i L_j) + \dots \qquad (A.5a)$$

$$Z_i^{\Omega} = \xi \vec{L}_i + \xi^{\Omega}\nabla_j\Psi_{ij} \qquad (A.5b)$$

Of course, only inhomogeneous rotations lead to entropy production, since a solid-body rotation is an equilibrium state, while homogeneous temporal changes of relative rotations (eq 9) do increase the entropy.

The local rotations are decoupled from longitudinal sound and do not take part in the propagation of transverse sound ($\omega \sim k$), because their coupling to momentum and to other variables contains too many gradients. This is strikingly different from the behavior of relative rotations discussed in the main text.

In solids or permanently cross-linked elastomers local rotations are described by the displacement field and are not independent from the strain field (eqs 1 and 2). In low molecular weight fluids local rotations are completely microscopic excitations (describing rotations of molecules, etc.), which relax on a microscopic time scale, and are, thus, not taken into account in a macroscopic description.

Appendix B: Complete Listing of Hydrodynamic Equations

The relevant macroscopic variables describing the dynamics of nematic side-chain polymers include (mass) density ρ, momentum density g_i, energy density ϵ, elastic strain ϵ_{ij}, director rotations δn_i, nematic order fluctuations δS, relative director – backbone rotations $\delta n_i - \Omega_i^{\perp}$, and in the case of solutions of concentration c. The following complete list of linear equations for these variables is a conjugation of the appropriate equations of refs 5 and 6 and of section 2. Assuming that all internal and microscopic variables not listed explictly above are in thermodynamic equilibrium on the relevant time and length scales, changes of the macroscopic variables are linked to changes of the entropy density σ by the Gibbs relation

$$T\,\mathrm{d}\sigma = \mathrm{d}\epsilon - \mu\,\mathrm{d}\rho - \mu_c\,\mathrm{d}c - v_i\,\mathrm{d}g_i - W\,\mathrm{d}S - \Phi_{ij}\,\mathrm{d}\nabla_j n_i -$$
$$\Psi_{ij}\,\mathrm{d}\epsilon_{ij} - L_i^{\perp}\mathrm{d}(n_i - \Omega_i^{\perp}) \quad (B.1)$$

This equation defines the thermodynamic conjugate quantities temperature T, chemical potential μ, relative chemical potential of the mixture μ_c, velocity v_i, "order parameter field" W, "molecular field" $\nabla_j\Phi_{ij}$, elastic stress Ψ_{ij}, and the "relative molecular field" $L_i^{\perp}$ as partial derivatives of the energy with respect to the associate variable. The relations between these two sets of fields constitute the static part of the macroscopic equations

$$\delta T = T_0 C_V^{-1}\,\delta\sigma - (\alpha_s\rho_0)^{-1}\,\delta\rho + \beta_\sigma\,\delta c +$$
$$\chi_{ij}^{\sigma}\epsilon_{ij} + b^{\sigma}\,\delta S \quad (B.2a)$$

$$\delta\mu = \rho_0^{-2}\kappa_s^{-1}\,\delta\rho + (\alpha_s\rho_0)^{-1}\,\delta\sigma + \beta_\rho\,\delta c +$$
$$\chi_{ij}^{\rho}\epsilon_{ij} + b^{\rho}\,\delta S \quad (B.2b)$$

$$\delta\mu_c = \gamma\,\delta c + \beta_\sigma\,\delta\sigma + \beta_\rho\,\delta\rho + \chi_{ij}^{c}\epsilon_{ij} + b^{c}\,\delta S \quad (B.2c)$$

$$v_i = \rho_0^{-1}g_i \quad (B.2d)$$

$$W = a\,\delta S + \chi_{ij}^{S}\epsilon_{ij} + b^{\sigma}\,\delta\sigma + b^{\rho}\,\delta\rho + b^{c}\,\delta c \quad (B.2e)$$

$$\Phi_{ij} = K_{ijkl}\nabla_l n_k \quad (B.2f)$$

$$\Psi_{ij} = c_{ijkl}\epsilon_{kl} + \chi_{ij}^{\rho}\,\delta\rho + \chi_{ij}^{\sigma}\,\delta\sigma + \chi_{ij}^{c}\,\delta c + \chi_{ij}^{S}\,\delta S +$$
$$\frac{1}{2}D_2[(\delta n_i - \Omega_i^{\perp})n_j^0 + (i \leftrightarrow j)] \quad (B.2g)$$

$$L_i^{\perp} = D_1(\delta n_i - \Omega_i^{\perp}) + D_2\epsilon_{jk}n_j^0\delta_{ik}^{\perp} \quad (B.2h)$$

The δ's denote deviations from the (constant) equilibrium values, which carry a subscript zero. The material tensors are of the uniaxial form

$$z_{ij} = z_{\parallel}n_i^0 n_j^0 + z_{\perp}\delta_{ij}^{\perp} \quad (B.3a)$$

$$c_{ijkl} = c_1\delta_{ij}^{\perp}\delta_{kl}^{\perp} + c_2(\delta_{ik}^{\perp}\delta_{jl}^{\perp} + \delta_{il}^{\perp}\delta_{jk}^{\perp}) + c_3 n_i^0 n_j^0 n_k^0 n_l^0 +$$
$$c_4(\delta_{ij}^{\perp}n_k^0 n_l^0 + \delta_{kl}^{\perp}n_i^0 n_j^0) +$$
$$c_5(\delta_{ik}^{\perp}n_j^0 n_l^0 + \delta_{il}^{\perp}n_j^0 n_k^0 + \delta_{jk}^{\perp}n_i^0 n_l^0 + \delta_{jl}^{\perp}n_i^0 n_k^0) \quad (B.3b)$$

$$K_{ijkl} = K_1\delta_{ij}^{\perp}\delta_{kl}^{\perp} + K_2 n_p^0\epsilon_{pij}n_q^0\epsilon_{qkl} + K_3 n_j^0 n_l^0\delta_{ik}^{\perp} \quad (B.3c)$$

The elastic constants defined here (c_α) are related to those in Voigt notation ($c_{\alpha\beta}$) by $c_{11} = c_{22} = c_1 + 2c_2$, $c_{12} = c_{21} = c_1$, $c_{13} = c_{31} = c_{23} = c_{32} = c_4$, $c_{33} = c_3$, $c_{44} = c_{55} = c_5$, $c_{66} = 2c_2$, and all other $c_{\alpha\beta}$ equal to zero. Thermodynamic stability requires, e.g., $c_1 + 2c_2$, c_3, c_5, $c_3(c_1 + 2c_2) - c_4^2$, $4c_5D_1 - D_2^2$, all to be positive. For the conserved and nonconserved quantities the dynamic equations are

$$\dot{\sigma} + \nabla_i j_i^{\sigma} = R/T \quad (B.4a)$$

$$\dot{\rho} + \nabla_i g_i = 0 \quad (B.4b)$$

$$\dot{c} + \nabla_i j_i^{c} = 0 \quad (B.4c)$$

$$\dot{g}_i + \nabla_j\sigma_{ij} = 0 \quad (B.4d)$$

$$\dot{S} + Z = 0 \quad (B.4e)$$

$$\dot{n}_i + Y_i = 0 \quad (B.4f)$$

$$\dot{\epsilon}_{ij} + X_{ij} = 0 \quad (B.4g)$$

$$\dot{n}_i - \dot{\Omega}_i^{\perp} + Y_i^{\Omega} = 0 \quad (B.4h)$$

The dynamic equation for the energy density follows from eqs B.4 and B.1. The currents and quasi-currents defined in eq B.4 can be written as the sum of a reversible part (superscript R) and a dissipative part (superscript D) leading to zero or positive entropy production ($R \geq 0$), respectively. The two parts of the material equations are

$$j_i^{\sigma R} = \sigma_0 v_i \tag{B.5a}$$

$$g_i^{R} = \rho_0 v_i \tag{B.5b}$$

$$j_i^{cR} = c_0 v_i \tag{B.5c}$$

$$\sigma_{ij}^{R} = p\delta_{ij} + \frac{1}{2}(1 + \lambda)n_j^0 \nabla_k \Phi_{ik} - \frac{1}{2}(1 - \lambda)n_i^0 \nabla_k \Phi_{jk} -$$
$$\frac{\lambda^\perp}{2}(L_j^\perp n_i^0 + L_i^\perp n_j^0) - \Psi_{ij} + \beta_{ij}W \tag{B.5d}$$

$$Z^R = \beta_{ij}A_{ij} \tag{B.5e}$$

$$Y_i^R = -\epsilon_{ijk}\omega_j n_k^0 - \frac{\lambda}{2}(\delta_{ij}^\perp n_k^0 + \delta_{ik}^\perp n_j^0)\nabla_j v_k \tag{B.5f}$$

$$X_{ij}^R = -A_{ij} \tag{B.5g}$$

$$Y_i^{\Omega R} = -\frac{\lambda^\perp}{2}(\delta_{ij}^\perp n_k^0 + \delta_{ik}^\perp n_j^0)\nabla_j v_k \tag{B.5h}$$

and

$$j_i^{\sigma D} = -\kappa_{ij}\nabla_j T - \zeta_{ij}^T\nabla_k\Psi_{jk} - D_{ij}^T\nabla_j\mu_c - D_{ij}^W\nabla_j W \tag{B.6a}$$

$$g_i^{D} = 0 \tag{B.6b}$$

$$j_i^{cD} = -D_{ij}\nabla_j\mu_c - \zeta_{ij}^c\nabla_k\Psi_{jk} - D_{ij}^T\nabla_j T - D_{ij}^c\nabla_j W \tag{B.6c}$$

$$\sigma_{ij}^{D} = -\nu_{ijkl}A_{kl} \tag{B.6d}$$

$$Z^D = \kappa_w W + \xi_{ij}\Psi_{ij} - D_{ij}^W\nabla_i\nabla_j T - D_{ij}^c\nabla_i\nabla_j c \tag{B.6e}$$

$$Y_i^D = -\frac{1}{\gamma_1}\nabla_j\Phi_{ij} - \zeta_{ijk}^n\Psi_{jk} - \zeta_{12}L_i^\perp \tag{B.6f}$$

$$X_{ij}^D = \left(\frac{1}{\tau}\right)_{ijkl}\Psi_{kl} + \xi_{ij}W + \zeta_{kji}^n\nabla_l\Phi_{kl} + \zeta_{kji}^\Omega L_k^\perp -$$
$$\frac{1}{2}[\nabla_j(\zeta_{ik}^T\nabla_k T + \zeta_{ik}^c\nabla_k\mu_c) + (i \leftrightarrow j)] \tag{B.6g}$$

$$Y_i^{\Omega D} = \zeta^\perp L_i^\perp + \zeta_{12}\nabla_j\Phi_{ij} + \zeta_{ijk}^\Omega\Psi_{jk} \tag{B.6h}$$

where we have used the abbreviations $A_{ij} = (1/2)(\nabla_i v_j + \nabla_j v_i)$ and $\omega_i = (1/2)\epsilon_{ijk}\nabla_j v_k$. The second-rank tensors are of the form in eq B.3a, the viscosity tensor ν_{ijkl} and the elastic relaxation tensor $(1/\tau)_{ijkl}$ are of the form in eq B.3b, and the third-rank material tensors read

$$\lambda_{ijk} = \lambda(\delta_{ij}^\perp n_k^0 + \delta_{ik}^\perp n_j^0) \tag{B.7}$$

The viscosity constants defined here (ν_α) by the form in eq B.3b are related to those of the Harvard notation[28] (ν_α^H) by $\nu_1^H = (1/2)(\nu_1 + \nu_3) - \nu_4$, $\nu_2^H = \nu_2$, $\nu_3^H = \nu_5$, $\nu_4^H = \nu_1 + \nu_2$, and $\nu_5^H = \nu_4$. Positivity of entropy production is guaranteed, if the following expressions are positive: $\kappa_\parallel$, $D_\parallel$, $\kappa_\parallel D_\parallel - (D_\parallel^T)^2$, $\kappa_\parallel\kappa_w - (D_\parallel^W)^2$, $\kappa_w D_\parallel - (D_\parallel^c)^2$; all these expressions with subscript $\parallel$ replaced by $\perp$, κ_w, γ_1, $\zeta^\perp$, $1 - \gamma_1\tau_5(\zeta^n)^2$, $\zeta^\perp - \gamma_1\zeta_{12}^2$, $\zeta^\perp - \tau_5(\zeta^\Omega)^2$, $\kappa_w(\tau_2 + 2\tau_1) - \tau_1\tau_2\xi_\perp^2$, $\kappa_w - \tau_3\xi_\parallel^2$; $c_1 + 2c_2$, c_3, c_5, $(c_1 + 2c_2)c_3 - c_4^2$ for either $c_\alpha = \nu_\alpha$ or $c_\alpha = 1/\tau_\alpha$. Equations B.1, B.5, and B.6 only show the contributions of lowest possible order in the gradient expansion. Higher order gradient terms can be incorporated along the lines of ref 32.

Appendix C: Director Relaxation and Flow Alignment Angle Measurements

Recently, director relaxation measurements[29-31] showed a remarkable increase in the relaxation time of nematic side-chain polymers compared to low molecular weight systems. The strong dependence on molecular weight indicated that this was a genuine polymeric effect. Here we want to discuss the origin of this effect within our hydrodynamic description. Applying a homogeneous magnetic field **H** to a well-oriented nematic sample generally results in a (homogeneous) reorientation of the director due to the anisotropy of the magnetic susceptibility. If the latter is positive, $\chi_a > 0$, the director wants to become parallel to **H** and the reorientation force is proportional to the angle θ between $\hat{n}^0$ and **H**, explicitly[7] $\nabla_j\Phi_{ij} = \chi_a H^2 \delta n_i$, with $|\delta n_i| = \sin\theta \approx \theta$. Without the polymeric degrees of freedom and neglecting backflow (cf. eq B.5d), this leads to a simple exponential decay of θ with the relaxation frequency (cf. eq 9) $\Gamma_0 = \chi_a H^2/\gamma_1$. However in polymeric systems also the (transient) elasticity and the relative rotations are excited by this reorientation force (cf. eqs 9 and B.6g). Neglecting again backflow effects, one is left with a coupled system of three linear relaxations, whose eigenfrequencies are related to the relaxation frequency of the elasticity, of the relative rotations, and of the magnetic reorientation, respectively. In recent experiments[29-31] one has observed the magnetic reorientation, which is influenced by the effects of elasticity and relative rotations. It turns out to have the smallest frequency and reads

$$\frac{\Gamma}{\Gamma_0} - 1 = -\gamma_1\frac{(\zeta^n)^2\zeta^\perp + \zeta_{12}^2\frac{1}{\tau_5} - 2\zeta^n\zeta_{12}\zeta^\Omega}{\zeta^\perp\frac{1}{\tau_5} - (\zeta^\Omega)^2} \tag{C.1}$$

where a nonvanishing right-hand side shows the influence of the polymeric degrees of freedom. Neglecting ζ^Ω (the cross coupling between elasticity and relative rotations) for the moment, the polymer influence in eq C.1 can be written as the sum of two contributions, coming from the coupling between the director and the elasticity in the first part and between the director and the relative rotations in the second part. Both parts tend to decrease Γ (i.e., increase the relaxation time), although thermodynamic constraints prevent Γ from becoming exactly zero. However, these two contributions enter eq C.1 on equal footing, and it is impossible at the present stage to decide which one of the two (or both) is (are) responsible for the observed (rather drastic) experimental effect. Of course it is also impossible to disentangle the polymeric effects from the (bare) nematic effect; i.e., what is measured in experiments is not Γ_0 but Γ. In any case this experiment shows that the polymeric degrees of freedom can have a profound effect on the hydrodynamics of the system, even at frequencies which are well below the elastic relaxation frequency and below the relaxation frequency of the relative rotations, where the polymeric system is sometimes supposed to behave like a low molecular weight system. By using longer spacers between the side chains and the backbone, one can expect to reduce the interaction between nematic and polymeric degrees of freedom (i.e., reduce the influence of the cross-coupling terms), which for this experiment means that the relaxation time should decrease. But this experiment is not suitable to disentangle elastic effects from those of the relative rotations.

The flow alignment of the director is another standard experiment in nematic systems. If a shear flow is imposed on a nematic layer with the flow in the direction of the

original director, then the director turns within the shear plane. Subject to the constraint $|\lambda| > 1$, to be fulfilled by the flow alignment parameter λ (eq B.5f), the turning angle θ is constant and independent of the shear rate. For low shear rates this picture is assumed to be valid for polymeric systems too.[6] Since in this geometry elastic strains as well as relative rotations are induced by the flow, these polymeric features both enter the expression for the alignment angle[33] (neglecting contributions quadratic in the dissipative cross-coupling parameters)

$$\frac{1}{\cos 2\theta} = \lambda + \lambda^{\perp}\frac{\zeta_{12}}{\zeta^{\perp}} + \frac{1}{2}\zeta^{n}\tau_5 \qquad (C.2)$$

for the definition of ζ^{n}, compare eq B.6f,g. Of course, flow alignment only occurs if the number on the right-hand side of eq C.2 is larger than 1 (or smaller than -1). This condition may be harder or easier to meet in polymers than $|\lambda| > 1$ in low molecular weight systems, depending on the signs of the cross-coupling parameters $\lambda^{\perp}$, ζ_{12}, and ζ^{n}. One can expect that side chains with longer spacers reduce the polymeric influence on this characteristic nematic effect. Again we find that in this quasi-static experiment the influence of polymeric elasticity and of relative rotations is not qualitatively different and that a clearcut experimental distinction is only possible with high-frequency experiments, as, e.g., sound wave propagation discussed above.

References and Notes

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