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Cholesteric Liquid Crystals: Flow Properties, Thermo- and Electromechanical Coupling

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Developments in the macroscopic behavior of cholesteric liquid crystals, focusing mainly on low molecular weight materials, are reviewed in this article. Among the topics covered are experimental and theoretical results on Lehmann-type effects, which are only possible for fluid phases that possess a handedness macroscopically. It is summarized how such effects can be obtained using an electric field as well as gradients of temperature and concentration as external forces. The static analogues of these effects involving variations of density, entropy density and concentration in mixtures are also discussed.

Other aspects covered are nonequilibrium phenomena at a moving cholesteric - isotropic interface as well as (static and dynamic) flexoelectric effects including a critical discussion how these flexoelectric effects can be determined

experimentally.

Finally various types of electromechanical couplings in cholesteric liquid crystalline polymers and elastomers including piezoelectricity and the novel concept of rotato-electricity, which cannot exist in low molecular weight cholesteric liquid crystals, are briefly discussed. For reviews summarizing earlier work on the flow behavior of cholesteric liquid crystals as well as the thermo- and electromechanical properties see de Gennes and Prost (1993), Chandrasekhar (1992), and Coles (1997).

1 Lehmann-type Effects

Lehmann (1900) described the observation of a rather unusual effect in a cholesteric liquid crystal: when a cholesteric droplet is submitted to a thermal temperature gradient parallel to its helical axis, the director, $\hat{\mathbf{n}}$, the average molecular orientation, shows a uniform rotation. This observation was not confirmed until the 1980s (Madhusudana and Pratibha, 1987) when a similar phenomenon was observed in an external DC electric field for flat cholesteric drops completely immersed in the isotropic liquid phase. In a subsequent paper (Madhusudana and Pratibha, 1989) analyzed in detail how sensitive the phenomenon of Lehmann rotation is with respect to the difficulty of obtaining a sufficiently weak anchoring boundary condition for the director at the cholesteric surface. Only in the case of practically zero anchoring energy a Lehmann rotation could be observed in a controlled way.

Classically (e.g., de Gennes and Prost 1993, and Chandrasekhar 1992) the Lehmann phenomenon is described in the framework of Leslie's equations. For a layer of a cholesteric liquid crystal under the influence of a field \mathbf{E} parallel to the helical axis (z -direction) there is no macroscopic flow. The dynamic equation for the angle $\phi(z, t)$ between the director $\hat{\mathbf{n}}$ and a fixed axis (say x) in the plane of the layer then reads

$$\gamma_1 \frac{\partial \phi}{\partial t} = K_2 \frac{\partial^2 \phi}{\partial z^2} - \nu E \quad (1)$$

where K_2 is the twist elastic constant, $1/\gamma_1$ the director diffusion coefficient, E the strength of the applied field and ν the dissipative dynamic cross-coupling coefficient associated with the Lehmann rotation. This cross-coupling is only possible for systems having a ground state which violates parity macroscopically: the cholesteric differs from its mirror image. To extract the Lehmann rotation phenomenon from eq.(1), one considers a film with thickness D with 'free' boundary conditions, meaning that there is zero surface torque on the director. For sample surfaces located at $z = 0$ and $z = D$ this condition yields the following boundary conditions for ϕ

$$\left. \frac{\partial \phi}{\partial z} \right|_{z=0} = \left. \frac{\partial \phi}{\partial z} \right|_{z=D} = q_0 \quad (2)$$

where q_0 is the equilibrium wave vector associated with the helical pitch P_0 . As a solution of eq.(1) satisfying the boundary conditions given in eq.(2) one

obtains

$$\phi = q_0 z - \frac{\nu E}{\gamma_1} t + C \quad (3)$$

From eq.(3) one reads off that the director rotates at a constant rate $\nu E/\gamma_1$.

Following the observation of the Lehmann rotation in DC electric fields Brand and Pleiner (1988) reanalyzed the Lehmann phenomenon in the framework of hydrodynamics, which had been developed for cholesteric liquid crystals by Lubensky (1972) and by Martin, Parodi and Pershan (1972). It emerges from their study that the classical Lehmann effect arising when a temperature gradient is applied parallel to the helical axis of the cholesteric droplet is not only due to a dissipative dynamic cross-coupling, but that there is also a static contribution coupling temperature and director orientation. Specifically Brand and Pleiner (1988) find for the generalized free energy the contributions (using the local description, which is appropriate for cholesteric phases with a large pitch and for cholesteric films with a sample thickness small compared to the pitch)

$$F = F_N + K_2 q_0 (\hat{\mathbf{n}} \cdot \text{curl} \hat{\mathbf{n}} + q_0) - (\tau_\sigma \delta\sigma + \tau_\rho \delta\rho + \tau_c \delta c) q_0 (\hat{\mathbf{n}} \cdot \text{curl} \hat{\mathbf{n}} + q_0) \quad (4)$$

Here $\delta\sigma$, $\delta\rho$ and δc are the variations of entropy, density and concentration (in mixtures of thermotropics and for lyotropic materials). F_N contains all the terms already present in nematic liquid crystals. As it turns out (see below) the contributions proportional to τ_σ , τ_ρ and τ_c enter into Lehmann-type effects. For

the dissipative parts relevant to Lehmann-type effects the entropy production takes the form in lowest order

$$R = R_N + q_0(\psi_T \nabla T + \psi_c \nabla \mu + \psi_E \mathbf{E}) \cdot (\hat{\mathbf{n}}^0 \times \mathbf{h}) \quad (5)$$

where R_N contains all the contributions present in a nematic phase. The molecular field \mathbf{h} is obtained via $\mathbf{h} \equiv -(\delta/\delta\hat{\mathbf{n}}) \int F dV$, μ is the chemical potential, and ψ_T , ψ_c and ψ_E are the coefficients of the contributions associated with Lehmann-type effects. Note that $\psi_T = \nu/\gamma_1$ for ν in eq.(1).

Using again free boundary conditions, one obtains for the angular velocity $\omega \equiv \dot{\phi}$ of the director for an applied temperature gradient:

$$\omega = q_0(\psi_T + C_V T_0^{-1} \tau_\sigma / \gamma_1) \quad (6)$$

where C_V is the specific heat at constant volume. As one reads off immediately from eq.(6), the static ($\sim \tau_\sigma$) as well as the dissipative dynamic ($\sim \psi_T$) contributions enter. Therefore these two contributions cannot be separated by the classical Lehmann experiment in a temperature gradient parallel to the helical axis. The same situation arises for concentration gradients or gradients in the chemical potential (see sect. 2). The situation is different for the case of an external electric field studied experimentally by Madhusudana and Pratibha (1987,1989). In this case there is no static contribution and one obtains for the angular velocity ω :

$$\omega = q_0 \psi_E \quad (7)$$

and thus ψ_E can be determined directly. For an external density gradient there is no dissipative cross-coupling and the rotation velocity ω reads:

$$\omega = q_0(\tau_\rho - C_V T_0^{-1} \tau_\sigma \frac{\partial T}{\partial \rho}) / \gamma_1 \quad (8)$$

This result is a prediction so far, which one could test by applying small pressure gradients. Further details can be found in Brand and Pleiner (1988).

All results presented for cholesteric liquid crystals are applicable equally well for chiral smectic phases with a helical superstructure and complete or partial in-plane fluidity.

2 Nonequilibrium Phenomena at a Moving Cholesteric - Isotropic Interface

Interfacial pattern formation during directional growth from the isotropic liquid to the cholesteric liquid crystal has been studied by Cladis et al. (1991) and by Brand and Cladis (1994). While in equilibrium a cholesteric liquid crystal is characterized by its handedness and a characteristic length scale, the pitch P_0 , for an isotropic-cholesteric interface moving in a temperature gradient G , an instability with a characteristic length and time scale can set in for a certain range of temperature gradients G and pulling speeds v . When the wavenumber q_0 associated with the helical pitch becomes comparable but incommensurate with the wavenumber q arising due to the nonequilibrium driving force, the elastic response of the cholesteric state is out of phase with the driving force and an oscillatory mode can result. As the pulling speed

is increased several instabilities are observed. While the first instability is a Hopf bifurcation associated with a finite frequency and a finite wave vector at onset, the second instability gives rise to a breathing mode, which is shown in Fig.1. From Figs.1 and 2 one can see that the helical twist axis is not constant in space, but varies on a surface. In Fig.1 one observes an array of λ -defect lines (one of the characteristic type of defect lines for cholesteric liquid crystals (e.g., de Gennes and Prost 1993) shed by the interface. In this state oscillations of neighboring defect lines are in antiphase whereas next-nearest neighbors are in phase. We note that for Fig.1 the defect oscillatory motion is nearly 1D, while for higher pulling speeds, v , it becomes 2D. One observes space-time helices and a dislocation (Fig.2). It is important to note that none of these phenomena can be observed in achiral liquid crystalline phases such as nematic liquid crystals, which have neither a handedness nor a macroscopic intrinsic length scale.

At sufficiently high pulling speeds and temperature gradients the isotropic - cholesteric interface flattens out again. It turns out, however, that in this case one can obtain for cholesteric liquid crystals nonequilibrium states that are characterized by long spatial correlations of the director phase that rotates at fixed frequency. This regime has been called the forced phase winding regime (Brand and Cladis 1994) (Fig.3). Analysis of the pattern depicted in Fig.3 reveals a large coherence length both parallel and perpendicular to the interface. This director rotation about an axis parallel to the applied temperature

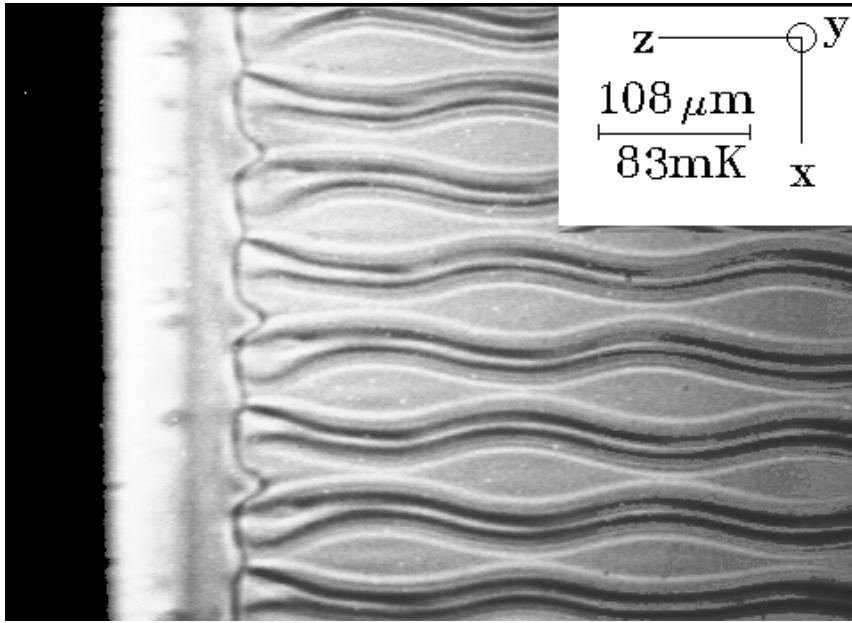


Fig. 1. One video frame showing the breathing-mode pattern decorated behind the interface by disclination lines viewed with polarizers crossed at 45° to the sides of the frame. The λ -defect is seen as the wavy bright line surrounded by two wavy dark lines. The black region at the extreme left is the isotropic phase. The bright band next to it is the cholesteric - isotropic meniscus. Inset: The temperature and length scale as well as the frame of reference used in this section. (Fig2a of Cladis et al.(1991))

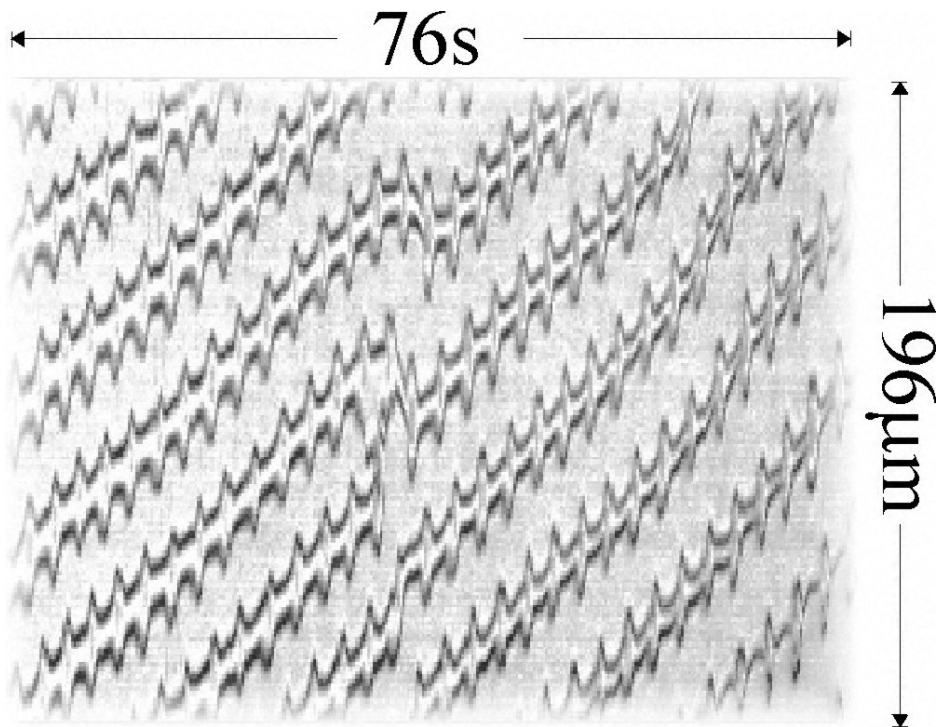


Fig. 2. Space-time helices of the breathing mode decorated by oscillating λ -defects observed for $v = 70 \mu\text{m}/\text{s}$ and $v_x \sim 3.45 \mu\text{m}/\text{s}$. (Fig.2b of Cladis et al. (1991))

gradient, which is reminiscent of the Lehmann effect, is possible in cholesteric liquid crystals, because – as discussed above – symmetry allows for the couplings between temporal variations of the director phase and temperature as well as concentration gradients. It turns out that the latter are dominant in the present system: the thermal length scale set externally is much larger than the length scale due to impurity diffusion. In fact this experiment can be used to extract an estimate for the coupling constant. At even higher pulling speed the wavelength of the pattern emerging behind the interface increases, but the coherence of the pattern decreases. Above a critical speed phase coherence is lost and a disordered liquid crystalline state emerges (Fig.4). That this state, which is disordered and has a frozen-in structure, is similar to a glassy state is revealed when the relaxing defect structures anneal (right hand side of Fig.4). This state has been called an orientational glass by Brand and Cladis (1994), since the system does not have enough time to organize itself in the coherent fashion observed at equilibrium or at smaller pulling speeds. The quenched state results, when there is insufficient time to pass the information about the orientational order across the interface over macroscopic distances.

3 Static and Dynamic Flexoelectric Effects

Flexoelectricity in nematic liquid crystals is a well studied field in liquid crystal science (e.g., de Gennes and Prost 1993, and Chandrasekhar 1992). In the

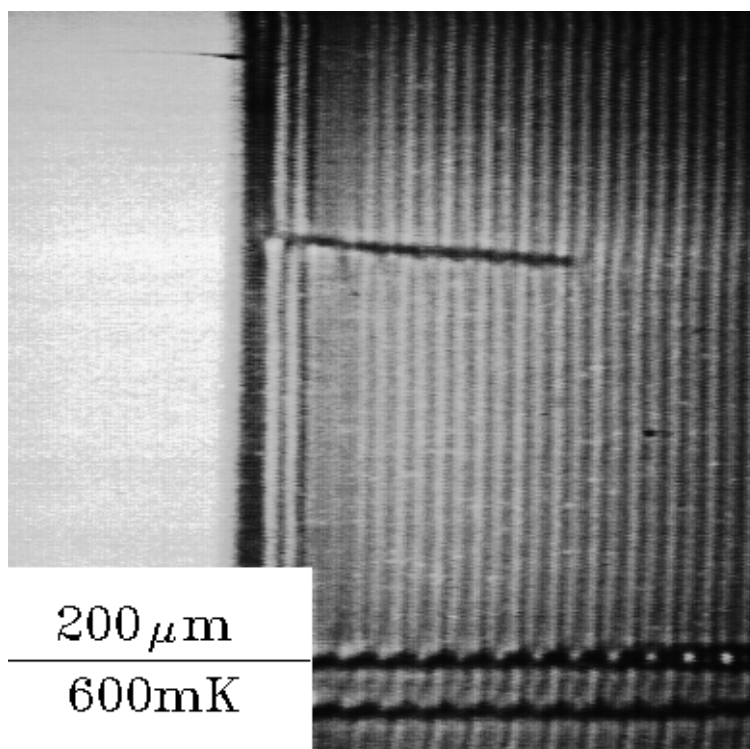


Fig. 3. Pattern behind flat interface for a sample thickness $d = 63\mu\text{m}$, $v = 40\mu\text{m}/\text{s}$, and $G = 30\text{K}/\text{cm}$. The isotropic liquid is the featureless region to the left and the regular forced phase winding with large coherence length perpendicular to the interface is to the right. The lines perpendicular to the interface are localized regions with an apparent phase mismatch of the director. (Fig.1 of Brand and Cladis (1994))

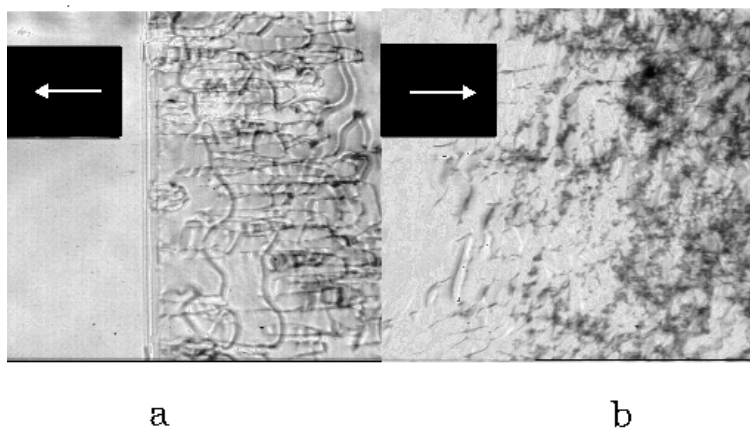


Fig. 4. Orientational glass patterns behind the flat interface in a constant temperature gradient. Higher temperatures are to the left. (a) Growing the orientational glass state at $v = 70\mu\text{m}/\text{s} \parallel \mathbf{G}$. (b) Defect structures observed as the orientational glass anneals in the temperature gradient during directional melting at $v = 70\mu\text{m}/\text{s}$. Sample thickness, $d = 80\mu\text{m}$, temperature gradient, $G = 45\text{K}/\text{cm}$. The arrow in the black box gives the direction of motion of the interface, which is outside the field of view in (b). (Fig.2 of Brand and Cladis(1994))

generalized energy flexoelectricity leads to an additional term

$$F_f = \int dV e_{ijk} E_k \nabla_i n_j \quad (9)$$

where e_{ijk} is given for uniaxial nematics by $e_{ijk} = e_1 \delta_{ij}^\perp n_k + e_3 \delta_{jk}^\perp n_i$. In the local description of cholesteric liquid crystals flexoelectricity takes the same form.

Flexoelectricity complements Frank's free energy for director deformations and the dielectric term.

Experimentally Patel and Meyer (1987) have investigated flexoelectricity in cholesterics by applying a static electric field \mathbf{E} perpendicular to the helix axis. According to the Patel and Meyer this leads to a periodic splay-bend pattern in the helix, which allows the determination of the flexoelectric coefficient. An analysis by Brand and Pleiner (1997) shows that the situation in the geometry studied by Patel and Meyer is, in general, rather complicated. First, Brand and Pleiner found that the flexoelectric contribution to the generalized energy is a surface effect. Second, it turns out that depending on the boundary conditions and geometry one can find experimentally a rotation of the optical axis or not. Such a rotation of the optical axis with respect to the laboratory frame set by the helix in the field-free case and the external field has been found by Patel and Meyer.

Features that add to the complexity of the behavior of cholesteric liquid crystals in an electric field are the dynamic effects coupling director orientation to the external electric field and its gradients. There is a dissipative analogue of

the flexoelectric effect already in nematic liquid crystals (Brand and Pleiner 1984), which as a contribution to the dissipation function takes the form

$$R_f = -\zeta_{ijk}^E h_i \nabla_j E_k \quad (10)$$

where ζ_{ijk}^E has the structure $\zeta_{ijk}^E = \zeta^E (\delta_{ij}^\perp n_k + \delta_{ik}^\perp n_j)$ assuming the quasi-static condition $\text{curl} \mathbf{E} = 0$ holds. In the local description of cholesterics one has the same dissipative contribution. As discussed in detail by Pleiner and Brand (1997) the static and dynamic flexoelectric effects appear as linear combinations in all dynamic measurements aimed at measuring the static flexoelectric coefficients.

In cholesteric liquid crystals the situation becomes even more complex due to the Lehmann-type effects discussed above. One has in the dissipation function related to electric effects the cross-coupling term

$$R_L = q_0 \psi_E \mathbf{E} \cdot (\hat{\mathbf{n}}^0 \times \mathbf{h}) \quad (11)$$

It must be emphasized that this Lehmann-type dissipative cross-coupling contains even one gradient less than the dynamic analogue of the flexoelectric effect. The detailed analysis by Brand and Pleiner (1997) shows that the term $\sim \psi_E$ is crucial for the interpretation of the experiments done by Patel and Meyer (1987). While Patel and Meyer just minimized the sum of the elastic and the flexoelectric energies to deduce the flexoelectric coefficient in a cholesteric, Brand and Pleiner showed that there is no static, but rather a

stationary solution only, which also involves the Lehmann-type term $\sim \psi_E$. As a consequence it is not possible to extract $e_1 + e_3$ from these experiments without knowledge of ψ_E . For a detailed discussion the interested reader is referred to Brand and Pleiner (1997).

4 *Rotato-Electricity and Piezoelectricity in Cholesteric Polymers and Elastomers*

In cholesteric liquid crystalline polymers and elastomers, in addition to the usual conserved quantities and the orientational degrees of freedom, one has macroscopic variables, which are associated with the deformations of the transient network and - for liquid crystalline elastomers - with the permanent network. A recent review of the physical properties of liquid crystalline elastomers can be found in Brand and Finkelmann (1997). As pointed out by de Gennes (1980) for nematic gels there are relative rotations between the director and the gel as macroscopic variables - in addition to the director $\hat{\mathbf{n}}$ and the strain tensor ϵ_{ij} familiar from the elasticity of solids and gels. These relative rotations lead to coupling terms which exist neither in low molecular weight liquid crystalline systems nor in solids and gels. The corresponding contributions in the generalized energy take up to quadratic order the form (de Gennes 1980):

$$F_{rel} = \int dV \left(\frac{1}{2} D_1 \tilde{\Omega}_i \tilde{\Omega}_i + D_2 \tilde{\Omega}_i \epsilon_{jk} n_j \delta_{ik}^\perp \right) \quad (12)$$

where u_i is the displacement vector, $\epsilon_{ij} = \frac{1}{2}(\nabla_i u_j + \nabla_j u_i)$ the strain tensor, $\Omega_{ij} = \frac{1}{2}(\nabla_i u_j - \nabla_j u_i)$ and where $\Omega_i^\perp = n_j \Omega_{ij}$ with $n_i \Omega_i^\perp = 0$. The relative rotations $\tilde{\Omega}_i$ are then introduced via $\tilde{\Omega}_i = \delta n_i - \Omega_i^\perp$ with $\hat{\mathbf{n}} \cdot \delta \mathbf{n} = 0$.

In systems which break mirror symmetry spontaneously such as cholesteric and chiral smectic liquid crystals the existence of relative rotations for their elastomeric counterparts allows electromechanical cross-couplings, which are not possible in other systems. The most unusual effect among these is certainly rotato-electricity (Brand, 1989), which in the generalized energy for a cholesteric elastomer gives rise to the contribution ($\sim \zeta^R$)

$$F_{rot} = \int dV [\zeta^R (\delta\phi - \Omega) q_0 p_j D_j + \frac{1}{2} D_1 (\delta\phi - \Omega)^2] \quad (13)$$

where $\delta\phi$ and $\Omega = p_i \epsilon_{ijk} \Omega_{jk}$ are the variables characterizing, respectively, the rotation of the director and of the polymer network around p_i , the helical axis in the cholesteric phase. D_i is the dielectric displacement conjugate to the electric field E_i . The second contribution $\sim D_1$, too, is specific to liquid crystalline polymers and elastomers, has no counterpart in low molecular weight systems and contains one of the contributions proportional to D_1 in eq.(12). There is a dissipative analogue to rotato-electricity expressed by the contributions to the dissipation function

$$R_{rot} = \frac{1}{2\gamma} W^2 + \xi^R W q_0 p_i E_i \quad (14)$$

with W the conjugate to the relative rotations $\delta\phi - \Omega$. To study the effect of rotato-electricity one applies an electric field parallel to the helical axis. A stationary state is found, which incorporates the static and dissipative rotato-electric effects for relative rotations

$$(\delta\phi - \Omega) = -\frac{q_0 p_j E_j}{D_{1E}} (\epsilon_{\parallel} \zeta^R + \gamma \xi^R) \quad (15)$$

where ϵ_{\parallel} is the dielectric constant taken along the helical axis and $D_{1E} = D_1 - \epsilon_{\parallel} (\zeta^R q_0)^2$. Depending on the boundary conditions eq.(15) predicts a rotation of the director or the network. In samples with a thickness small compared to the pitch it should be easy to detect this relative rotation optically.

The other group of electromechanical effects, which is of potential interest for applications as soft sensors, is related to piezoelectricity. This effect is well known for crystals lacking inversion symmetry such as quartz. They represent in crystals a direct coupling between the strain tensor and the electric field. For cholesteric liquid crystalline polymers and elastomers the interest derives from the fact that they have reduced fluidity compared to low molecular weight systems. In a generalized energy piezoelectricity gives a contribution of the structure

$$F_{piezo} = \int dV \zeta_{ijk}^P q_0 E_i \epsilon_{jk} \quad (16)$$

As discussed by Pleiner and Brand (1993) such a contribution exists for polar cholesterics for which the polar axis coincides with the helical axis. In such a

case one has globally C_∞ symmetry in contrast to the ordinary case of non-polar cholesterics for which the helical axis is nonpolar and which has D_∞ symmetry. To realize this low symmetry globally (which corresponds locally to C_1 or C_2 symmetry) is much easier to achieve in cholesteric liquid crystalline polymers and elastomers (see Pleiner and Brand (1993) for details). For polar cholesterics, which are globally of uniaxial symmetry, ζ_{ijk}^P takes the form $\zeta_{ijk}^P = \zeta_1^P p_i p_j p_k + \zeta_2^P p_i \delta_{jk}^\perp + \zeta_3^P (p_j \delta_{ik}^\perp + p_k \delta_{ij}^\perp)$. In such a phase one thus encounters longitudinal piezoelectricity with respect to the helical axis, transverse piezoelectricity and shear piezoelectricity in any plane containing the helical axis.

For polar cholesterics with a finite electric conductivity there exists a dissipative analogue of the static piezoelectric effect in the entropy production. As a consequence an applied external electric field leads to stationary (rather than static) deformation states, which are given both by the static as well as the dissipative piezoelectric coefficients.

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