Piezoelectricity in Cholesteric Liquid Crystalline Structures

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Abstract – Using symmetry arguments we discuss the various possible helical structures that can show a longitudinal piezoelectric effect. Due to the recent experimental verification of such an effect in some elastomeric cholesteric liquid crystals, we propose that what is called cholesterics could actually represent different helical structures, which can be more complicated than the conventional (i.e. simple screw) model.

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1. Introduction

Conventionally the structure of cholesteric liquid crystals is described as a twisted nematic one [1], i.e. there is orientational order in a given layer, where the preferred direction (the director $\hat{\mathbf{n}}$) rotates helically when going from one layer to the next. This picture is obtained from a Ginzburg-Landau functional using a uniaxal nematic order parameter and D_∞ symmetry for the molecules (i.e. $\hat{\mathbf{n}}$ to $-\hat{\mathbf{n}}$ symmetry). Due to the lack of inversion symmetry a contribution to the energy linear in the twist becomes possible, which leads to the simple helical structure with D_2 symmetry (like an infinite screw). The three 2-fold rotation axes are the helical axis $\hat{\mathbf{p}}$, the director $\hat{\mathbf{n}}$ and $\hat{\mathbf{p}} \times \hat{\mathbf{n}}$, where the latter two are not constant in space, but rotate helically. Thus, there is D_2 symmetry for every layer locally, but with two of the rotationally symmetry axes changing directions when going from one layer to the next. In a coarse grained ("global") description, averaged over many pitch lengths, the symmetry is D_∞, with the helical axis as preferred direction. This picture is not changed qualitatively, if a small local biaxiality is introduced perturbatively [2].

Such a simple screw like structure e.g. is responsible for the strong optical activity (strong optical rotatory power) and the spatially periodic textures well-known in cholesteric liquid crystals [1,3]. Due to the existence of a two-fold rotation axis locally in every layer, which is perpendicular to the helical axis, the latter cannot be a polar axis. This implies that there is no ferroelectricity along the helix axis, nor can be there a longitudinal piezoelectric effect. According to the Curie principle [4] a nonpolar medium subject to a nonpolar external force (like an unidirectional stress along the helical axis) cannot exhibit a polar result (a polarization along the helical axis), which excludes the possibility of a longitudinal piezoelectric effect. In addition, also the shear-piezo effect (the shear plane

contains the helical axis, but the resulting polarization is normal to that plane) is zero for D_∞ symmetry in the electrostatic approximation, where curl **E** must be zero.

Recently, in a series of very thorough investigations [5-7] the existence of a longitudinal piezoelectric effect has been demonstrated experimentally in some elastomeric cholesteric liquid crystals. These experiments have been performed on samples of cylindrical shape for which height and diameter were typically of the order of $1cm$. The samples were obtained by cross-linking a nematic liquid crystalline polymer and by swelling it with a low molecular weight cholesteric liquid crystal. A sufficient amount of static compression gives rise to a cholesteric monodomain [5-7] with the helical axis parallel to the axis of the cylinders. Increasing compression gives rise to a static voltage parallel to the helical axis (longitudinal piezoelectric effect) [5,7]. The variation of this piezoeffect with the cholesteric pitch and with temperature has been measured and it has been demonstrated that in the racemate no piezoelectric effect exists [5]. The vanishing effect in the racemate clearly shows that potential flexoelectric effects due to the presence of deformations of the director field are absent. We also note, that the measured piezoelectric voltage was strictly linear in the applied compression once a mondomain had been formed. Thus electrostrictive effects, which would be quadratic in the electric field, do not contribute [5]. This has also been found to be applicable for the measurement of the inverse piezoelectric effect [6]. Also in this case one does not observe a static linear electromechanical effect in the racemate.

Obviously, these cholesteric systems cannot be of the conventional D_2 symmetry. The following questions immediately arise: What is the actual structure and symmetry of these cholesteric phases? Is the unconventional structure typical for elastomeric or polymeric systems or can it occur in low molecular weight systems as well? In the latter

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case a direct experimental proof for a longitudinal piezo effect seems hardly manageable, because of the fluidity of such systems. There is, however, an additional hint for non-standard cholesteric structures due to the report of an electroclinic effect [8,9] in certain low molecular weight cholesteric liquid crystals, which, again, is not compatible with the D_2 symmetry. The electroclinic response was detected either by switching unwound, large pitch systems, [8] or by dielectric measurements on wound-up, small pitch systems.[9]

In the following we will discuss using symmetry and Ginzburg-Landau type arguments which unconventional structures are possible and under which conditions (which may not always be fulfilled in a real situation) they can occur. A discussion of the hydrodynamic description of the conventional as well as unconventional structures is given in Appendix 2.

2. Conic Structures in Low Molecular Weight Systems

Recently we have shown theoretically [10] that a chiralized biaxial nematic can show either a conic helical structure or the simple screw structure depending on some material parameters (Ginzburg-Landau coefficients). In the former case, generally the two orthogonal nematic directors, $\hat{\mathbf{n}}$ and $\hat{\mathbf{m}}$, spiral together around the helix axis $\hat{\mathbf{p}}$, but are tilted out of the plane perpendicular to $\hat{\mathbf{p}}$. Such a conic helical state generally lacks any two-fold rotational symmetry axis and is of monoclinic (C_1) symmetry (Fig.1). Coarse grained over many pitch lengths it is uniaxial, but polar (C_∞ symmetry) with the helix axis as polar axis. Thus, it shows ferroelectricity (or ferri- or antiferroelectricity) and a longitudinal piezoelectric effect.

We will show now that even for uniaxial nematics, if chiralized, such a conic helical structure is possible. The conventional Ginzburg-Landau description [1] of an isotropic to cholesteric phase transition makes use of the uniaxial nematic order pa-

rameter $Q_{ij} = S(n_i n_j - \frac{1}{3}\delta_{ij})$ by expanding the free energy into powers of Q_{ij} and its gradients. Usually, only one chiral term, $Q_{ij}\epsilon_{ikl}\nabla_k Q_{lj}$, is added to the non-chiral nematic terms. Then minimization leads straightforwardly to the simple screw structure $n_i(\mathbf{r}) = \hat{a}_i \cos\phi + \hat{b}_i \sin\phi$, with $\phi = q_0 \hat{\mathbf{p}} \cdot \mathbf{r}$, where $\hat{\mathbf{a}}$ and $\hat{\mathbf{b}}$ are any pair of orthogonal unit vectors in the plane perpendicular to $\hat{\mathbf{p}}$ and q_0 is the helical wavelength, related to the pitch $d_0 = \pi/q_0$. However, since the isotropic to cholesteric phase transition is generally first order, there is no reason to stop the Ginzburg-Landau expansion after the quadratic order, i.e. the cubic order is necessary, too. In that order additional non-chiral terms occur, e.g. of the form $QQ\nabla Q$, $\nabla Q \nabla Q \nabla Q$ or $\nabla\nabla Q \nabla Q$ (for details cf. App. 1), where the latter are not negligible compared to the former, since we are looking for a spatially non-homogeneous structure and gradients need not be small.

These cubic terms result not only in a more complicated temperature dependence of the pitch, but also in the possibility of a conic helical structure $n_i(\mathbf{r}) = (\hat{a}_i \cos\phi + \hat{b}_i \sin\phi)\cos\Theta_n + (\hat{\mathbf{a}} \times \hat{\mathbf{b}})_i \sin\Theta_n$ with $\Theta_n = const.$ (cf. App.1). This state can have the lower free energy compared to the untilted state, if the Ginzburg-Landau coefficients satisfy certain conditions. There is even a first order phase transition possible between these two states (which also have different q_0). However, for large pitch lengths (small q_0) always the untilted state (the simple screw) occurs.

As in the untilted case [2], also in the conic helical state the helix induces a small biaxiality, characterized by a second preferred direction, $\hat{\mathbf{m}}$, spiraling about $\hat{\mathbf{p}}$, too. Again this direction $\hat{\mathbf{m}}$ can be untilted ($\hat{\mathbf{m}} \perp \hat{\mathbf{p}}$, i.e. $\Theta_m = 0$) or tilted ($\Theta_m \neq 0$) with respect to the plane perpendicular to the helix axis (Fig.1) depending on some Ginzburg-Landau parameters (App.1). In the former case ($\Theta_m = 0$) or if $\hat{\mathbf{n}}$, $\hat{\mathbf{m}}$, and $\hat{\mathbf{p}}$ are coplanar, the structure is of C_2 symmetry locally, with the two-fold rotational axis (symmetry axis)

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perpendicular to $\hat{\mathbf{p}}$. However, only the rotational symmetry axis itself can be a polar direction since all axes perpendicular to the symmetry axis are subject to the two-fold rotational symmetry. Thus, there is no longitudinal piezoelectric effect (i.e. parallel to the helix axis) possible. The (spiraling) polar axis and the accompanying piezoelectric effect along this axis (which can be detected in large pitch or unwound systems) are averaged out on length scales large compared to the pitch leading to D_∞ symmetry globally (as in the simple screw case, where $\hat{\mathbf{n}}$ is untilted).

The other possible state, where also $\hat{\mathbf{m}}$ is tilted ($\hat{\mathbf{m}} \cdot \hat{\mathbf{p}} \neq 0, 1$) and not coplanar with $\hat{\mathbf{n}}$ and $\hat{\mathbf{p}}$, is locally of the C_1 (globally C_∞) symmetry discussed at the beginning of this section, showing a longitudinal piezoelectric effect. Nevertheless, due to the many conditions to be fulfilled, it seems rather unlikely that uniaxial, low molecular weight chiralized nematics will be frequently of C_1 symmetry locally.

3. Oblique Biaxial Nematic Order

Recently it has been proposed [8] to describe certain chiral nematogens not only by the usual uniaxial order parameter $Q_{ij} = S(\hat{n}_i \hat{n}_j - (1/3)\delta_{ij})$, but in addition by a second oblique biaxial one, $t_{ij} = T(\hat{n}_i \hat{n}_j^{(2)} + \hat{n}_j \hat{n}_i^{(2)} - (2/3)\delta_{ij}\hat{n}_k \hat{n}_k^{(2)})$, thus introducing a second director $\hat{\mathbf{n}}^{(2)}$, which is oblique compared to $\hat{\mathbf{n}}$, i.e. $\hat{\mathbf{n}} \cdot \hat{\mathbf{n}}^{(2)} = \cos\theta \neq 0, 1$. It is assumed [8] that the nematic ordering is still given by $\hat{\mathbf{n}}$ (representing the long molecular axis), while $\hat{\mathbf{n}}^{(2)}$ represents a less anisotropic molecular axis and is averaged out in a perfectly ordered nematic state, but becomes manifest in the presence of an electric field (as in ref. [8]) or a helix. Adopting this scenario we will show that the cholesteric state can then support a longitudinal piezoelectric effect.

The Ginzburg-Landau free energy density for t_{ij} can now be written as (note that

the tensors b to $k^{(\nu)}$ in eq.(3.1) are not only functions of δ_{ij} and ϵ_{ijk} as usual, but also of the conventional order parameter Q_{ij})

$$
\begin{aligned}
f = {} & aQ_{ij}t_{ij} + b_{ijkl}\,t_{ij}t_{kl} + c_{ijklm}(t_{lm}\nabla_i Q_{jk} + Q_{lm}\nabla_i t_{jk}) + d_{ijklm}\,t_{ij}\nabla_k t_{lm} \\
& + (e^{(1)}_{ijklmnpq}\nabla_i Q_{jk} + e^{(2)}_{ijklmnpq}\nabla_i t_{jk})t_{lm}\nabla_n Q_{pq} \\
& + (f^{(1)}_{ijklmnpqr}\nabla_i Q_{jk} + f^{(2)}_{ijklmnpqr}\nabla_i t_{jk})t_{lm}\nabla_n \nabla_p Q_{qr} \\
& + g^{(1)}_{ijklmnp}\nabla_i t_{jk}\nabla_l \nabla_m t_{np} + g^{(2)}_{ijklmnp}(\nabla_i Q_{jk}\nabla_l \nabla_m t_{np} + \nabla_i t_{jk}\nabla_l \nabla_m Q_{np}) \\
& + (h^{(1)}_{ijklmp}\nabla_i Q_{jk} + h^{(2)}_{ijklmp}\nabla_i t_{jk})\nabla_l t_{mp} \\
& + (k^{(1)}_{ijklmpqrs}\nabla_i t_{jk} + k^{(2)}_{ijklmpqrs}\nabla_i Q_{jk})\nabla_l Q_{mp}\nabla_q t_{rs} + O(T^3)
\end{aligned}
\tag{3.1}
$$

where we have written down only terms up to order q_0^3 and T^2, since we expect T to be small. Terms linear in $\nabla_i t_{jk}$ are possible due to the existence of Q_{ij}. When evaluating their precise structure, the tensors b to $k^{(\nu)}$ are expanded into the isotropic tensors δ_{ij} and ϵ_{ijk}, as well as into Q_{ij}, whose equilibrium form is given by the usual Ginzburg-Landau expansion in Q_{ij}. Explicitly we have e.g. $b_{ijkl} = b_1\delta_{ik}\delta_{jl} + b_2(Q_{ik}\delta_{jl} + Q_{jl}\delta_{ik}) + b_3 Q_{ij}Q_{kl} + b_4 Q_{ik}Q_{jl}$, $c_{ijklm} = c_1\epsilon_{lij}\delta_{km} + c_2 Q_{pk}\epsilon_{ilp}\delta_{jm} + \dots$ and $d_{ijklm} = d_1\epsilon_{ikl}\delta_{jm} + d_2\epsilon_{ikl}Q_{jm} + \dots$. Although a precise physical meaning cannot be given for all the parameters involved in eq.(3.1), the quantities b_ν/a are related to the biaxial order due to the presence of $\hat{n}_i^{(2)}$, while the others govern the spatial structure (cf. below).

Assuming a simple screw structure for $\hat{\mathbf{n}}$ (a conic structure as discussed in chap. 2 would not alter the conclusions of this chapter) we make the ansatz

$$
\hat{n}_i = \delta_{ix}\cos q_0 z + \delta_{iy}\sin q_0 z
$$

$$
\hat{n}_i^{(2)} = \delta_{ix}(\cos q_0 z \cos\theta - \sin q_0 z \cos\psi \sin\theta)
\tag{3.2}
$$

$$
+ \delta_{iy}(\sin q_0 z \cos\theta + \cos q_0 z \cos\psi \sin\theta) + \delta_{iz}\sin\psi \sin\theta
$$

where $\cos\theta = \hat{\mathbf{n}} \cdot \hat{\mathbf{n}}^{(2)}$ is related to the molecular geometry. Since intramolecular energies are much higher than the orientational energies we are dealing with in the Ginzburg-Landau

expansions, we can keep fixed the molecular angle θ, when determining the orientation of $\hat{\mathbf{n}}$ and $\hat{\mathbf{n}}^{(2)}$. The angle ψ (yet to be determined) governs the direction of $\hat{\mathbf{n}}^{(2)}$ on the cone around $\hat{\mathbf{n}}$, which is accessible for fixed θ, i.e. $\psi = 0$ means $\hat{\mathbf{n}}^{(2)} \perp \hat{\mathbf{p}}$ ($\hat{\mathbf{p}}$ is the helix axis, here taken as the z-direction), while $\psi = \pi/2$ makes $\hat{\mathbf{n}}$, $\hat{\mathbf{m}}$, and $\hat{\mathbf{p}}$ coplanar. With the help of eq.(3.2) and assuming that θ and ψ are spatially homogeneous, the free energy density (eq.(3.1)) reduces to

$$f = \alpha T + (\beta + \gamma \cos^2 \psi)T^2 + O(T^3) \tag{3.3}$$

from which the equilibrium structure is obtained by minimization with respect to T and ψ. The coefficients α, β and γ are complicated functions of the angle θ, the coefficients contained in eq. (3.1) and the helical wave length. There are three different helical states ($q_0 \neq 0$) possible, with i) $\psi = 0$, ii) $\psi = \pi/2$ and iii) $\psi = \psi_0 \neq 0, \pi/2$ (Fig.2). The first structure i) is of C_2 symmetry locally with the two-fold rotation axis being the helix axis, i.e. one obtains C_∞ symmetry globally when coarse grained over many pitch lengths. Thus, this is an untilted, polar phase, which supports a longitudinal piezoelectric effect. The second one also has C_2 symmetry, but the rotation axis is normal to the helix axis (reminiscent of conventional smectic C^* structures) and does not show a longitudinal piezoelectric effect (it is of D_∞ symmetry globally). The latter structure has C_1 symmetry lacking any rotational symmetry axis. Thus, this structure also supports a longitudinal piezoelectric effect, but it is a possible equilibrium state only, if higher order terms (at least cubic in T) in eq.(3.3) are important (i.e. T is not small), while the structures i) and ii) are possible also for small T. Within the truncated expansion (3.3) the polar state i) is stable compared to state ii), if either β and γ are negative, or $\gamma < 0$ and $\beta > -\gamma$, or $\beta < 0$ and $\gamma > -\beta$, respectively, where however, taking into account the cubic terms in eq.(3.3),

the stability relation among the three possible states is much more complicated. A polar axis parallel to the helix axis can be defined by $Q_{kl}\vec{\nabla}t_{kl}$ or $\hat{n}_k\vec{\nabla}\hat{n}_k^{(2)}$, which reads (cf.(3.2))

$$\hat{n}_k\nabla_j\hat{n}_k^{(2)} = -q_0\delta_{jz}\cos\psi\sin\theta \tag{3.4}$$

showing again that a polar axis exists only for case i) and iii).

4. Biaxial Polymeric Systems

The scenarios outlined in the previous chapters are not only applicable for low molecular weight liquid crystals, but are valid for side-chain liquid crystalline polymers as well. However, due to the existence of the polymeric backbone besides the mesogenic side-chains, there are additional features and scenarios possible. We will not deal here with the relative macroscopic variables [11,12] characteristic for the presence of both, polymeric and liquid crystalline subsystems, but rather concentrate on additional equilibrium structures and their symmetries possible in such hybrid systems.

In the isotropic phase of side-chain polymers generally the orientations of the backbone chain as well as those of the side-chains are random and isotropic. However, in the nematic phase, e.g. the orientational order of the side-chain usually also has an orientational (albeit weak) effect on the backbone [13]. The averaged conformation of the polymeric chain is no longer spherical, but slightly uniaxial, where the preferred direction does not necessarily coincide with the nematic direction of the side-chains nor is it related to the angle between individual side-chains and the local backbone segment. We will now discuss what structures can be obtained by chiralizing such a weakly biaxial nematic system.

We will concentrate on two possibilities: Either the averaged angle between the individual side-chain and the local backbone segment is fixed and preserved upon chiral-

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izing, or the conformational anisotropy of the backbone is more or less unaffected by the formation of the helix in the side-chain system. In the latter case (conformational biaxial cholesterics or CBC) the preferred direction of the backbone conformation and the helical axis generally do not coincide, while in the former case (fixed cone cholesterics, FCC) they can be expected to be equal.

4.1 CONFORMATIONAL BIAXIALITY.

In the CBC case it is assumed that the mesogenic side-chains form a helix upon chiralization as they would do without the backbone (i.e. as a low molecular weight system). Thus, the resulting helix is most probably of the simple screw type, although conic structures are possible in principle, too (cf. section 2). However, there is in addition the (weak) conformational anisotropy of the backbone, whose preferred direction, $\hat{\mathbf{l}}$, is independent from, and generically not parallel with, the helix axis $\hat{\mathbf{p}}$. Since this biaxiality may be weak (as it is in appropriate nematic phases), it may be difficult to detect the biaxiality directly in experiments. In the cholesteric phase (even if $\hat{\mathbf{n}}$ is untilted) the symmetry is either C_2 locally (for $\hat{\mathbf{l}} \perp \hat{\mathbf{p}}$) with the axis of rotational symmetry parallel to the helix axis, or C_1 (for $\hat{\mathbf{l}} \cdot \hat{\mathbf{p}} \neq 0, 1$) everywhere, except in the single planes, where $\hat{\mathbf{n}}$ is either perpendicular to both, $\hat{\mathbf{l}}$ and $\hat{\mathbf{p}}$, or coplanar with these two globally preferred directions (Fig.3). Thus, there is a polar preferred direction along the helical axis almost everywhere (in both, the locally C_1 and C_2 symmetric case, which give C_∞ symmetry globally) and a longitudinal piezoelectric effect can be expected.

With the simple screw ansatz for $\hat{\mathbf{n}}$ including an arbitrary helical phase ϕ_0, $\hat{\mathbf{n}} = \hat{\mathbf{a}} \cos(q_0 z + \phi_0) + \hat{\mathbf{b}} \sin(q_0 z + \phi_0)$, and the conformational anisotropy axis $\hat{\mathbf{l}}$ tilted away from the helix axis, $\hat{\mathbf{l}} = \hat{\mathbf{p}} \cos \theta + \hat{\mathbf{b}} \sin \theta$, one can construct the polar vector (along the helix axis

$\hat{\mathbf{p}}$, cf. (Fig. 3), here taken as the z-axis) by

$$\hat{n}_i \hat{l}_i \hat{l}_j \nabla_k \hat{n}_j = \frac{1}{2} q_0 \delta_{kz} \sin(2q_0 z) \sin^2 \theta \qquad (4.1)$$

Obviously this polar direction does not exist for $\theta = 0$ ($\hat{\mathbf{l}} \parallel \hat{\mathbf{p}}$), since then the symmetry is D_2 locally (D_∞ globally). The polar vector changes sign periodically when going along the helix axis (the z-axis), thus representing a polarization wave with the polarization changing sign every half wavelength. Of course, simple coarse graining over many pitch lengths would eliminate this polar axis, but (naive) coarse graining is a procedure that never makes sense in polarization wave states or - more classically - in an antiferroelectric state.

4.2 FIXED CONE CHOLESTERICS:

In the FCC case it is assumed that ψ_0, the angle between the direction of the side-chains and the orientation of the local backbone segment, is fixed in the mean by some local interactions and does not change very much when the side-chains order in a nematic or cholesteric structure giving rise to the macroscopic director $\hat{\mathbf{n}}$. To form a helical arrangement of the side-chains keeping the local angle ψ_0, a large portion of the backbone has to be oriented parallel to the helical axis. Thus, a global anisotropy of the backbone conformation is induced, where the preferred direction due to the backbones, $\hat{\mathbf{l}}$, coincide with the helical axis. If the local angle ψ_0 is accidentally equal to $\pi/2$, then the system is isomorphic to the low molecular weight systems discussed in Chap.2. However, in the general case $\psi_0 \neq \pi/2$, a conic helical structure arises (Fig.4), as is obtained by minimizing

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the gradient free energy density

$$f = \frac{B}{2}(\cos\psi_0 - \hat{\mathbf{l}} \cdot \hat{\mathbf{n}})^2 + C_1\hat{\mathbf{n}} \cdot curl\hat{\mathbf{n}} + C_2(\hat{\mathbf{l}} \times \hat{\mathbf{n}})_i\hat{l}_j\nabla_i\hat{n}_j + C_3(\hat{\mathbf{l}} \times \hat{\mathbf{n}})_i\hat{l}_j\nabla_j\hat{n}_i + \frac{K_1}{2}(div\hat{\mathbf{n}})^2$$
$$+ \frac{K_2}{2}(\hat{\mathbf{n}} \cdot curl\hat{\mathbf{n}})^2 + \frac{K_3}{2}(\hat{\mathbf{n}} \times curl\hat{\mathbf{n}})^2 + \frac{K_4}{2}(\hat{\mathbf{l}} \cdot curl\hat{\mathbf{n}})^2 + \frac{K_5}{2}(\hat{\mathbf{l}} \times curl\hat{\mathbf{n}})^2$$
$$(4.2)$$

where f is written as the sum of an elastic energy, where the coefficient B denotes the strength of the interaction to keep the local angle ψ_0, and a gradient part obtained from general symmetry considerations, where C_ν and K_ν characterize the various chiral and achiral curvature elastic energies, respectively. K_1, K_2, K_3 and C_1 are the elastic coefficients familiar from ordinary cholesterics. With the ansatz $\hat{\mathbf{n}} = (\hat{\mathbf{a}}\cos\phi + \hat{\mathbf{b}}\sin\phi)\sin\psi + \hat{\mathbf{l}}\cos\psi$ where $\phi = q_0\hat{\mathbf{l}} \cdot \mathbf{r}$ and $\hat{\mathbf{a}}$, $\hat{\mathbf{b}}$ and $\hat{\mathbf{l}}$ form an orthogonal triad, the equilibrium structure is found to be always a tilted (conic helical) state, where the cone angle ψ is somewhat different from ψ_0, due to the presence of the helix. For small q_0 (large pitch) or strong B the solution can be simplified into

$$\cos\psi = \cos\psi_0\left(1 + \frac{K_3 + K_5}{B}q_0^2\right)$$
$$q_0 = \frac{C_1 + C_3}{K_3 + K_5 + (K_2 - K_3)\sin^2\psi_0}$$
$$(4.3)$$

Eq.(4.3) represents a locally C_2 symmetric structure (with the symmetry axis perpendicular to the helix axis) quite similar to conventional smectic C^* structures.

However, there is an additional local biaxility due to the different orientations of the side-chains and the backbone. In contrast to the helix induced (small) biaxiality in low molecular weight systems, this biaxiality does not vanish with q_0^2 and does not have to be small. The biaxiality induces a preferred direction, $\hat{\mathbf{m}}^{(0)} \equiv (\hat{\mathbf{n}} \times \hat{\mathbf{l}})/|\hat{\mathbf{n}} \times \hat{\mathbf{l}}|$, in the plane perpendicular to $\hat{\mathbf{n}}$. In a homogeneous (i.e. nematic) state this second preferred direction is also in the plane perpendicular to $\hat{\mathbf{l}}$, while in a helical phase it can be tilted

out of this plane ($\hat{\mathbf{m}}^{(0)} \neq \hat{\mathbf{m}}$ and $\hat{\mathbf{m}} \cdot \hat{\mathbf{l}} \equiv \cos \psi_m \neq 0$, cf. Fig.1 with $\hat{\mathbf{l}}$ instead of $\hat{\mathbf{p}}$) as we will show in the following. Describing the tilted biaxiality perturbatively by an order parameter $M_{ij} \equiv M(\hat{m}_i \hat{m}_j - \hat{m}_i^{(0)} \hat{m}_j^{(0)})$ a Ginzburg-Landau free energy (density) of the form of eq.(3.1) is obtained, where t_{ij} is replaced by M_{ij} and Q_{ij} stands for either, the uniaxial nematic order parameter $Q_{ij} \sim (\hat{n}_i \hat{n}_j - (1/3)\delta_{ij})$ (with $\hat{\mathbf{n}}$ tilted) or the backbone order parameter $L_{ij} \sim (\hat{l}_i \hat{l}_j - (1/3)\delta_{ij})$. In terms of M and $\hat{\mathbf{m}}$ this energy can be written

$$
\begin{aligned}
f_m =& M\big\{ D_1(\hat{\mathbf{l}} \cdot \hat{\mathbf{m}})^2 + E_1 \hat{\mathbf{m}} \cdot curl\hat{\mathbf{m}} + E_2 \hat{n}_i\, (\hat{\mathbf{n}} \times \hat{\mathbf{m}}) \cdot \vec{\nabla} \hat{m}_i + E_3 \hat{m}_i\, (\hat{\mathbf{m}} \times \hat{\mathbf{n}}) \cdot \vec{\nabla} \hat{n}_i \\
&+ E_4 \hat{l}_i\, (\hat{\mathbf{l}} \times \hat{\mathbf{m}}) \cdot \vec{\nabla} \hat{m}_i + \frac{1}{2}F_1(\hat{\mathbf{n}} \cdot curl\hat{\mathbf{m}})^2 + \frac{1}{2}F_2(\hat{\mathbf{l}} \cdot curl\hat{\mathbf{m}})^2 + \frac{1}{2}F_3(\hat{\mathbf{m}} \cdot curl\hat{\mathbf{n}})^2 \\
&+ \frac{1}{2}F_4(\hat{\mathbf{m}} \times curl\hat{\mathbf{n}})^2 + \frac{1}{2}F_5(\hat{\mathbf{l}} \times curl\hat{\mathbf{m}})^2 + \frac{1}{2}F_6(\hat{\mathbf{n}} \times curl\hat{\mathbf{m}})^2 + \frac{1}{2}G_1(div\hat{\mathbf{m}})^2 \big\} \\
&+ M^2\big\{ D_2 + \frac{1}{2}G_2(\hat{\mathbf{m}} \cdot curl\hat{\mathbf{m}})^2 + \frac{1}{2}G_3(\hat{\mathbf{m}} \times curl\hat{\mathbf{m}})^2 + \ldots \big\} + O(M^3, q_0^3)
\end{aligned}
$$

(4.4)

Using an explicit representation for $\hat{\mathbf{m}}$, $\hat{\mathbf{n}}$, and $\hat{\mathbf{l}}$ (e.g. $\hat{l}_i = \delta_{iz}$, $\hat{\mathbf{n}}$ and $\hat{\mathbf{m}}$ given by eq. (A.2) and (A.5), respectively) the free energy is written as

$$
\begin{aligned}
f_m =& M(D_1 \sin^2 \Theta_m + q_0[E_1 + E_2' \sin^2 \Theta_m] + q_0^2[F_1' + F_2' \sin^2 \Theta_m]) \\
&+ M^2(D_2 + q_0^2[G_1' + G_2' \sin^2 \Theta_m + G_3' \sin^4 \Theta_m])
\end{aligned}
$$

(4.5)

Minimizing eq.(4.5) with respect to the tilt order parameter M leads to $f_m = \sin^2 \Theta_m(-\tilde{\alpha} + \tilde{\beta} \sin^2 \Theta_m + \tilde{\gamma} \sin^4 \Theta_m)$. Minimizing with respect to the tilt angle of $\hat{\mathbf{m}}$, Θ_m (Fig.1) then generally gives a non-zero tilt angle. The condition for this to be the case reduces for small q_0 to $q_0 E_1 > 0$, which is always fulfilled under the usual assumption [2] $E_1/G_2 \sim C_1/K_2$ (cf. eq. (4.2)) $\sim q_0$. In that case the tilt order parameter is small of order q_0^2.

This tilted (conic) structure, where both, $\hat{\mathbf{n}}$ and $\hat{\mathbf{m}}$ are tilted, has an overall C_1 symmetry (except in the very special case that $\hat{\mathbf{m}}$, $\hat{\mathbf{n}}$, and $\hat{\mathbf{l}}$ are accidentally coplanar). The polar axis (along the helix axis) can be defined as in eq.(A.7).

There is also the possibility that the local forces, which fix the angle between $\hat{\mathbf{l}}$ and

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$\hat{\mathbf{n}}$, also lead to a preferred angle, ψ_{m0}, between $\hat{\mathbf{l}}$ and $\hat{\mathbf{m}}$, which is then generically different from $\pi/2$. In that case eq.(4.4) carries the term $MB_m(\cos\psi_{m0} - \hat{\mathbf{m}} \cdot \hat{\mathbf{l}})^2$ instead of the term proportional to D_1.

Thus we can expect under the FCC scenario to have conic helical structures with C_1 symmetry locally, although local C_2 symmetry ($\hat{\mathbf{m}} \cdot \hat{\mathbf{l}} = 0$) with the polar axis perpendicular to the helix axis cannot be ruled out completely. The former case supports ferroelectricity and longitudinal piezoelectricity, while the latter does not.

5. Discussion and Conclusion

From the analysis in the last three sections we extract as the major conclusion that there are several possibilities, both for low molecular weight and for polymeric cholesteric liquid crystals, to obtain a globally polar structure with C_∞ symmetry, where the polar axis coincides with the helical axis. For such polar cholesteric structures one obtains [14] for the relation between the macroscopic polarization P_i and the compression of the helix $\nabla_i R_i$ (where R_i is the displacement vector)

$$P_i = \zeta^{(P)} q_0 p_i p_j p_k \nabla_j R_k \tag{5.1}$$

where p_i is the polar direction parallel to the helical axis. For polar cholesteric liquid crystalline elastomers and sidechain polymers above their Maxwell frequency one has in addition [15]

$$P_i = \zeta_{ijk}^{(P)} q_0 \epsilon_{jk} \tag{5.2}$$

where ϵ_{jk} is the strain tensor associated with the permanent (elastomeric) or transient (polymeric) network. The associated piezoelectric tensor $\zeta_{ijk}^{(P)}$ takes for C_∞ symmetry the form

$$\zeta_{ijk}^{(P)} = \zeta_1^{(P)} p_i p_j p_k + \zeta_2^{(P)} p_i \delta_{jk}^{tr} + \zeta_3^{(P)}(p_j \delta_{ik}^{tr} + p_k \delta_{ij}^{tr}) \tag{5.3}$$

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with the transverse Kronecker symbol $\delta_{ij}^{tr} = \delta_{ij} - p_i p_j$ projecting into the plane perpendicular to the polar helical axis p_i. In a local description of cholesteric structures having C_1 symmetry locally (or locally C_2 symmetric ones with the symmetry axis parallel to the helical axis) one finds again a linear relation between the macroscopic polarization P_i and deformations of the helix and the network (the latter for polymeric and elastomeric materials only) similar to equations (5.1) and (5.2) except that now one has - due to the lower symmetry - a larger number of piezoelectric moduli.

In conclusion we can state that locally C_1 symmetric cholesteric structures (or locally C_2 symmetric ones with the symmetry axis parallel to the helical axis) supporting a longitudinal piezoelectric effect, can occur in low molecular weight systems as well as in polymeric and elastomeric systems, but it is much more likely to find them in the latter cases. For the systems, where experimentally a longitudinal piezoelectric effect has been demonstrated, further investigations are necessary to reveal the detailed structure of their cholesteric state.

Acknowledgements

Appendix 1:

In this Appendix we give a Ginzburg-Landau description of the helix formation at a first order isotropic to cholesteric phase transition in low molecular weight systems. The uniaxial orientational order S is not infinitesimally small and is assumed to be given by the homogeneous part of the Ginzburg-Landau free energy. The gradient part of this free energy (density), which governs the spatial structure of the state, is expanded up to cubic

order in $Q_{ij} = S(\hat{n}_i \hat{n}_j - (1/3)\delta_{ij})$ reading

$$f = a\,Q_{ij}\epsilon_{ikl}\nabla_k Q_{lj} + c_1(\nabla_j Q_{ij})(\nabla_l Q_{il}) + c_2(\nabla_j Q_{ik})(\nabla_j Q_{ik})$$

$$+ (b_1\,\delta_{jl}\delta_{pq} + b_2\,\delta_{jp}\delta_{lq})\epsilon_{mik}(\nabla_m\nabla_j Q_{il})(\nabla_p Q_{kq}) + d\,Q_{kl}Q_{jl}\epsilon_{pik}\nabla_p Q_{ij}$$

$$+ e_1 Q_{kl}(\nabla_j Q_{ik})(\nabla_j Q_{il}) + e_2 Q_{il}(\nabla_j Q_{ij})(\nabla_k Q_{lk})$$

$$+ f^{(1)}_{jlpqrs}\,\epsilon_{ikm}(\nabla_m Q_{kj})(\nabla_l Q_{ip})(\nabla_q Q_{rs}) + f^{(2)}_{jlpqrs}\,\epsilon_{ikm}(\nabla_m Q_{jl})(\nabla_p Q_{iq})(\nabla_r Q_{ks})$$

$$+ g_{ijklmpqrs}Q_{ij}(\nabla_k Q_{lm})(\nabla_p\nabla_q Q_{rs}) + O(S^4, q_0^4)$$

$$(A.1)$$

With the conic helical ansatz

$$n_i(\mathbf{r}) = (\hat{a}_i\cos[q_0\hat{\mathbf{p}}\cdot\mathbf{r}] + \hat{b}_i\sin[q_0\hat{\mathbf{p}}\cdot\mathbf{r}])\cos\Theta_n + (\hat{\mathbf{a}}\times\hat{\mathbf{b}})_i\sin\Theta_n \qquad (A.2)$$

eq.(A.1) reduces to

$$f = \cos^2\Theta_n\left(q_0 C + \frac{1}{2}q_0^2[D_1 + D_2\cos^2\Theta_n] + \frac{1}{3}q_0^3[B_1 + B_2\cos^2\Theta_n + B_3\cos^4\Theta_n]\right)$$

$$(A.3)$$

where the coefficients C, B_ν and D_ν follow from the parameters and tensors a to g of eq. (A.1). Minimizing with respect to the helical wavelength q_0 and the tilt angle Θ_n then leads to two possible equilibrium states with either $\Theta_n = 0$, the untilted simple screw structure, or $\Theta_n \neq 0$, the tilted (conic) structure. The latter can exist only, if the coefficients in eq.(A.3) fulfil certain complicated conditions. In particular, for small q_0, the conic structure does not exist.

In the untilted case [2] as well as in the conic case the helix introduces a small biaxiality, i.e. a preferred direction, $\hat{\mathbf{m}}$, in the plane perpendicular to $\hat{\mathbf{n}}$. With a biaxial order parameter $B_{ij} \equiv Q_{ij} + M_{ij}$ with $M_{ij} \equiv M(\hat{m}_i\hat{m}_j - (1/3)\delta_{ij})$, where the biaxial order M vanishes as q_0^2 and Q_{ij} is assumed to be given by the procedure outlined above, the Ginzburg-Landau expansion leads to a free energy (density) for M_{ij} and its gradients of

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the form of eq.(3.1), when t_{ij} is replaced by M_{ij} there. In terms of $\hat{\mathbf{m}}$ and $\hat{\mathbf{n}}$ this equation has the form

$$f_m = F_1 \hat{\mathbf{m}} \cdot curl\hat{\mathbf{m}} + F_2 \hat{n}_i (\hat{\mathbf{n}} \times \hat{\mathbf{m}}) \cdot \vec{\nabla} \hat{m}_i + F_3 \hat{m}_i (\hat{\mathbf{m}} \times \hat{\mathbf{n}}) \cdot \vec{\nabla} \hat{n}_i + \frac{1}{2} G_1 (div\hat{\mathbf{m}})^2$$
$$+ \frac{1}{2} G_2 (\hat{\mathbf{m}} \cdot curl\hat{\mathbf{m}})^2 + \frac{1}{2} G_3 (\hat{\mathbf{m}} \times curl\hat{\mathbf{m}})^2 + \frac{1}{2} G_4 (\hat{\mathbf{n}} \cdot curl\hat{\mathbf{m}})^2 \qquad (A.4)$$
$$+ \frac{1}{2} G_5 (\hat{\mathbf{n}} \times curl\hat{\mathbf{m}})^2 + \frac{1}{2} G_6 (\hat{\mathbf{m}} \cdot curl\hat{\mathbf{n}})^2 + \frac{1}{2} G_7 (\hat{\mathbf{m}} \times curl\hat{\mathbf{n}})^2$$

With the general ansatz

$$m_i(\mathbf{r}) = \hat{a}_i (\sin[q_0 \hat{\mathbf{p}} \cdot \mathbf{r}] \sin \psi - \cos[q_0 \hat{\mathbf{p}} \cdot \mathbf{r}] \sin \Theta_n \cos \psi)$$
$$\qquad (A.5)$$
$$- \hat{b}_i (\cos[q_0 \hat{\mathbf{p}} \cdot \mathbf{r}] \sin \psi + \sin[q_0 \hat{\mathbf{p}} \cdot \mathbf{r}] \sin \Theta_n \cos \psi) + (\hat{\mathbf{a}} \times \hat{\mathbf{b}})_i \cos \Theta_n \cos \psi$$

and eq. (A.2) this reduces to

$$f_m(\psi) = \alpha' + \beta' \cos^2 \psi + \gamma' \cos^4 \psi \qquad (A.6)$$

from which one can in principle obtain an equilibrium solution with nonvanishing tilt angle of $\hat{\mathbf{m}}$, $\sin \Theta_m \equiv \cos \Theta_n \cos \psi \neq 0$ (Fig.1). There is C_1 symmetry and a polar axis (along the helical axis) defined by

$$q_0 \epsilon_{ijk} (\hat{\mathbf{n}} \cdot \vec{\nabla}) \hat{n}_i (\hat{\mathbf{m}} \cdot \vec{\nabla}) \hat{m}_j = -q_0^3 \hat{p}_k \sin \Theta_n \sin \Theta_m \sin \Theta_{n \times m} \qquad (A.7)$$

if the tilt angles Θ_n and Θ_m are non-zero and if $\hat{\mathbf{n}}$ and $\hat{\mathbf{m}}$ are not coplanar with $\hat{\mathbf{p}}$ (in the coplanar case $\Theta_n = \pi/2 - \Theta_m$ and $\hat{\mathbf{n}} \times \hat{\mathbf{m}}$ is untilted, since $\sin \Theta_{n \times m} \equiv (\cos^2 \Theta_n - \sin^2 \Theta_m)^{1/2} = 0$). However, due to the smallness of the biaxial order M, all the terms contributing to γ' in eq. (A.6) may generally be neglected in the case discussed here leading to the untilted $\hat{\mathbf{m}}$ – structure, only.

Appendix 2: Hydrodynamic Description

In the bulk of this manuscript we have discussed the conditions for the appearance of cholesteric structures with a polar axis parallel to the helical axis (C_∞ symmetry globally).

Naturallly the question arises how the macroscopic and hydrodynamic properties of such a phase differ from those of conventional cholesteric structures (D_∞ symmetry globally). We will concentrate in the following on global properties exclusively, i.e. on length scales large compared to the pitch for which a 'coarse-grained' [16] hydrodynamic description applies. Such an analysis has been given by Lubensky [17] for nonpolar cholesterics. We modified this description by incorporating into the hydrodynamic equations reversible dynamic terms [18-24] that exist only for the various types of polar cholesteric phases considered here. These polar terms (including in particular the material tensor g_{ij} or its anisotropic part g_a) provide an additional coupling between the stress tensor and the molecular field of the director. Since they are of higher order in the gradients than the non-polar coupling terms, they do not play a significant role, generally, and it seems to be hard to distinguish experimentally a conventional from an unconventional cholesteric structure by their presence or absence. Another subtle polar effect (a dissipative dynamic coupling between the stress tensor and a temperature gradient as well as an electric field) was mentioned in the App. of Ref. [25].

Static polar coupling effects, such as (longitudinal) piezoelectricity and pyroelectricity, were discussed by the authors for both, low molecular weight liquid crystals [24-26] and liquid crystalline elastomers [15, 27]. These effects exist only in the polar structures discussed in this paper and are absent in the conventional cholesteric structures. Of course, to determine directly whether the systems studied in refs. [5-7] belong to the class of polar cholesterics, it would be highly desirable to measure a P - E hysteresis loop in order to find out the precise electric properties of the ground state of these cholesteric liquid crystalline elastomers. Clearly the same type of experiment is also necessary for the low molecular weight systems investigated in refs. [8, 9].

Figure Captions:

Fig.1: Two orthogonal directions $\hat{\mathbf{n}}$, $\hat{\mathbf{m}}$, both spiraling about the helical axis $\hat{\mathbf{p}}$ and both tilted out of the plane perpendicular to $\hat{\mathbf{p}}$ by the angle Θ_n and Θ_m, respectively. The structure has locally C_1 symmetry (except for $\hat{\mathbf{n}}$, $\hat{\mathbf{m}}$, and $\hat{\mathbf{p}}$ being coplanar).

Fig.2: Two oblique directions $\hat{\mathbf{n}}$, $\hat{\mathbf{n}}^{(2)}$ ($\Theta \neq 0, \pi/2$) spiraling about the helix axis $\hat{\mathbf{p}}$, where i) both are untilted, ii) they are coplanar with $\hat{\mathbf{p}}$, and iii) $\hat{\mathbf{n}}^{(2)}$ is tilted and not coplanar (general case). The symmetry of the structures is locally C_2 with the polar axis parallel (case i) or perpendicular (case ii) to $\hat{\mathbf{p}}$, while case iii) corresponds to C_1 symmetry locally.

Fig.3: The direction $\hat{\mathbf{n}}$ spirals about the helical axis $\hat{\mathbf{p}}$ and is perpendicular to $\hat{\mathbf{p}}$ (simple screw structure); the direction $\hat{\mathbf{l}}$ of the backbone conformational anisotropy is i) oblique or ii) perpendicular to $\hat{\mathbf{p}}$. The local symmetry is C_1 (case i) or C_2 (case ii) with the symmetry axis parallel to $\hat{\mathbf{p}}$ (except for the planes, where $\hat{\mathbf{p}}$, $\hat{\mathbf{n}}$, and $\hat{\mathbf{l}}$ are coplanar).

Fig.4: The direction $\hat{\mathbf{n}}$ spirals about the helical axis $\hat{\mathbf{p}}$ including a fixed angle $\psi_0(\psi_0 \neq 0, \pi/2)$ with the helical axis $\hat{\mathbf{p}}$. The average preferred direction $\hat{\mathbf{l}}$ of the backbone is parallel to the helical axis $\hat{\mathbf{p}}$.

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