Piezoelectricity in Cholesteric Liquid Crystalline Structures

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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, with $\hat{\mathbf{n}}$ perpendicular to the helical axis. This picture is obtained from a Ginzburg-Landau functional using a uniaxial 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) for every layer locally. In a coarse grained description, averaged over many pitch lengths, the symmetry is D_∞, with the helical axis as preferred direction. 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 there be a longitudinal piezoelectric effect.

Recently, in a series of very thorough investigations[2−4] the existence of a longitudinal piezoelectric effect has been demonstrated experimentally in some elastomeric cholesteric liquid crystals. A sufficient amount of static compression gives rise to a cholesteric monodomain with the helical axis parallel to the axis of the cylinders. Increasing compression a static voltage parallel to the helical axis occurs (longitudinal piezoelectric effect). It has been demonstrated that both, flexoelectric effects due to the presence of deformations of the director field as well as electrostrictive effects are absent. This has been confirmed by the measurement of the inverse piezoelectric effect[3].

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 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[5,6] in certain low molecular weight cholesteric liquid crystals, which, again, is not compatible with the D_2 symmetry. In this communication we will discuss, which unconventional structures are possible and where they can occur using symmetry and Ginzburg-Landau type arguments.

2. Conic Structures in Low Molecular Weight Systems

We will show that even for uniaxial nematics, if chiralized, 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 parameter $Q_{ij} = S(n_i n_j - \frac{1}{3}\delta_{ij})$ 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 $\nabla\nabla Q\nabla Q$, 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 $\Theta_n = const.$. 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[7], 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 or tilted with respect to the plane perpendicular to the helix axis depending on some Ginzburg-Landau parameters. In the former case ($\hat{\mathbf{m}} \perp \hat{\mathbf{p}}$) 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) 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[5] 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. $\hat{\mathbf{n}} \cdot \hat{\mathbf{n}}^{(2)} \neq 0, 1$. It is assumed 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. 5) or a helix. Adopting this scenario we will show that the cholesteric state can then support a longitudinal piezoelectric effect.

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

$$\hat{n}_i = \delta_{ix} \cos q_0 z + \delta_{iy} \sin q_0 z$$
$$\hat{n}_i^{(2)} = \delta_{ix}(\cos q_0 z \cos\theta - \sin q_0 z \cos\psi \sin\theta)$$
$$+ \delta_{iy}(\sin q_0 z \cos\theta + \cos q_0 z \cos\psi \sin\theta) + \delta_{iz} \sin\psi \sin\theta \qquad (3.1)$$

where $\cos\theta = \hat{\mathbf{n}} \cdot \hat{\mathbf{n}}^{(2)}$ is fixed and related to the molecular geometry. 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, e.g. $\psi = 0$ means $\hat{\mathbf{n}}^{(2)} \perp \hat{\mathbf{p}}$ (where $\hat{\mathbf{p}}$ 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.(3.1) and assuming that θ and ψ are spatially homogeneous, the free energy density reduces to

$$f = \alpha T + (\beta + \gamma \cos^2\psi)T^2 + O(T^3) \qquad (3.2)$$

from which the equilibrium structure is obtained by minimization with respect to T and ψ. The coefficients α, β and γ are still functions of the angle θ 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) $\psi = \psi_0 \neq 0, \pi/2$. The first one 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 third 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.(3.2) are important (i.e. T is not small), while the structures i) and ii) are possible also for small T.

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. Here we will deal with additional chiral equilibrium structures and their symmetries.

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[8]. 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. Chiralizing such a weakly biaxial nematic system there are at least two possibilities: Either the averaged angle between the individual side-chain and the local backbone segment is fixed and preserved upon chiralizing (fixed cone cholesterics or FCC), or the conformational anisotropy of the backbone is more or less unaffected by the formation of the helix in the side-chain system (conformational biaxial cholesterics or CBC). In the latter case the preferred direction of the backbone conformation and the helical axis generally do not coincide, while in the former case 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. sec. 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. 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. The polar axis changes sign periodically when going along the helix axis, thus describing antiferroelectricity. 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 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. 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, as is obtained by minimizing the gradient free energy density. 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. This 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 biaxiality 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, $\hat{\mathbf{m}}^{(0)} \equiv (\hat{\mathbf{n}}\times\hat{\mathbf{l}})/\mid\hat{\mathbf{n}}\times\hat{\mathbf{l}}\mid$, 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 $\hat{\mathbf{m}}\cdot\hat{\mathbf{l}} \neq 0$). Describing the tilted biaxiality perturbatively by an order parameter $M_{ij} \equiv M(\hat{m}_i\hat{m}_j - \hat{m}_i^{(0)}\hat{m}_j^{(0)})$ the appropriate Ginzburg-Landau free energy (density) is minimized with respect to both, the tilt order parameter M as well as the tilt angle of $\hat{\mathbf{m}}$, generally resulting in a non-zero M and a non-zero tilt angle. 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).

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.

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.

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