Piezoelectricity of Cholesteric Elastomers

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Abstract

We consider theoretically the properties of piezoelectricity in cholesteric elastomers. We deduce using symmetry considerations the piezoelectric contributions to the free energy in the context of a coarse-grained description of the material. In contrast to previous work we find that compressions or elongations of the material along the pitch axis do not produce a piezoelectric response, in agreement with fundamental symmetry considerations. Rather only suitable shear strains or local rotations produce a polarization. We propose some molecular mechanisms to explain these effects.
Piezoelectric materials are characterized by the appearance of an electric polarization when a suitable mechanical stress is applied [1]. Symmetry considerations require that these materials be non-centrosymmetric, i.e. not invariant under inversion. Chiral liquid crystals such as a cholesteric or smectic C* satisfy this requirement but their fluid nature will not support a static shear. However, chiral liquid crystalline elastomers which consist of a cholesteric liquid crystal homogeneously embedded in a polymer gel can support static stresses, including shear, due to the presence of the underlying gel structure. Thus, they are candidates for the observation of true piezoelectricity in a liquid crystalline system.

In this paper we consider theoretically the nature of piezoelectricity in a cholesteric elastomer. We show that a shearing of the elastomer along the pitch axis causes a piezoelectric response. Local rotations of the elastic medium can also in principle produce a polarization. In contrast to previous work [2, 3], we find that compressions or elongations of the elastomer along the pitch axis cannot produce a polarization. We also propose some molecular arguments to explain the mechanism of piezoelectricity in these materials. Finally we discuss the relationship of our work to previous experimental studies [4, 5].

Our starting point is a hydrodynamic description of cholesterics in terms of a pitch vector due to Lubensky [6]. While it is possible to develop a description in terms of the director, all macroscopic quantities such as the polarization require a coarse-graining, i.e. an averaging of the director field over the pitch length. The description in terms of the pitch vector is already coarse-grained. We demonstrate below that our theory is equivalent to Terentjev’s theory of piezoelectricity [3] which is phrased in terms of the director. However, the coarse-graining built into the pitch vector description is more convenient in determining the elastic strains associated with piezoelectricity. The director \( \mathbf{n} \) in a cholesteric has the following form [6]:

\[
\mathbf{n}(\mathbf{r}) = \mathbf{n}_0 \cos \psi(\mathbf{r}) + \mathbf{p} \times \mathbf{n}_0 \sin \psi(\mathbf{r}),
\]

where \( \mathbf{p} \) is a unit vector along the pitch axis, \( \mathbf{n}_0 \) is a unit vector in the plane perpendicular to \( \mathbf{p} \), and \( \psi \) is the phase angle of the director. The latter quantity may be expressed as \( \psi = \frac{2\pi}{\lambda} \mathbf{p} \cdot \mathbf{r} + \phi \), where \( \lambda \) is the pitch of the helix, and \( \phi \) is a phase factor. We can define a wavevector \( q_0 \) for the helix via the relation, \( q_0 = \frac{2\pi}{\lambda} \). It is important to note that a helix is not a polar object, i.e. it looks the same whether viewed from the top or the bottom. Mathematically speaking this nonpolarity arises from the
existence of twofold axes parallel to \( n \) and \( p \times n \). Because the helix is a nonpolar object, then as Lubensky first noted, \( p \) can be chosen to be either a vector or a pseudovector. The direction of \( p \) along the helical axis is not a physically relevant quantity. If \( p \) is chosen to be a vector (pseudovector) then the phase angle \( \psi \) is a pseudoscalar (scalar). In either case \( q_0 \) is a pseudoscalar. These symmetry considerations must be borne in mind when constructing free energies or hydrodynamic equations, and will ensure that the helix is treated as a nonpolar object. Providing these symmetries are respected, the coarse-grained theory is completely equivalent to the director theory, contrary to recent assertions [3, 7]. The elastic degrees of freedom of the gel are described by a symmetric strain tensor \( u_{ij} = \frac{1}{2} \left( \frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right) \) as well as a rotation pseudovector \( \omega = \frac{1}{2} \nabla \times u \), where \( u \) is the displacement field of the network.

We now use these symmetry considerations to construct the form of the piezoelectric contribution \( F_p \) to the free energy density, i.e. the contribution linear in the applied electric field \( E \) and the strain. We find the following expression:

\[
F_p = \gamma_1 q_0 E_i \epsilon_{ijk} p_j \delta_{kl} u_{ml} + \gamma_2 q_0 E_i p_i p_j \omega_j + \gamma_3 q_0 E_i \delta_{ij} \omega_j
\]

where \( \gamma_{1,2,3} \) are the piezoelectric coefficients, \( \epsilon_{ijk} \) is the antisymmetric pseudotensor, and \( \delta_{ij}^{(tr)} \) is the projection operator transverse to the pitch axis \( p \), defined by: \( \delta_{ij}^{(tr)} \equiv \delta_{ij} - p_i p_j \). Repeated indices are to be summed over. Each of these terms is a scalar irrespective of whether we choose \( p \) to be a vector or pseudovector. The three terms appearing on the right hand side of equation (2) are the only scalars that can be constructed linear in \( E \) and the strain tensor or rotation pseudovector.

The meaning of these terms is as follows. Summing over the indices we see that the term proportional to \( \gamma_1 \) involves a shear in the \( p \) direction, e.g. sliding the planes of the elastomer perpendicular to \( p \) over each other. If \( p \) is parallel to \( \hat{z} \), then a nonzero \( u_{xz} \) strain component will produce a polarization along the \( y \) axis. There are no contributions to equation (2) from compressions or elongations. This result is not surprising because these latter strains will not destroy the two-fold rotation axes perpendicular to \( p \). The terms proportional to \( \gamma_2 \) and \( \gamma_3 \) involve local rotations in planes parallel and perpendicular to \( p \) respectively. We provide an intuitive explanation below for why these rotations can produce a polarization.

Before discussing possible molecular mechanisms for these terms we con-
sider the relationship of our work to previous studies. Brand [2] was the first to study the piezoelectric response of cholesteric elastomers theoretically. He wrote down the following piezoelectric free energy density $F^B_p$:

$$F^B_p = \zeta_{ijk} q_0 E_i u_{jk}$$

where the piezoelectric tensor $\zeta_{ijk}$ has the form

$$\zeta_{ijk} = \zeta_1 p_i p_j p_k + \zeta_2 p_i \delta^{(tr)}_{jk} + \zeta_3 (p_j \delta^{(tr)}_{ik} + p_k \delta^{(tr)}_{ij}).$$

Unfortunately, this free energy density is not a scalar because $p$ appears raised to an odd power. This incorrect form led Brand to the physically erroneous conclusion that an elongation or compression along the pitch axis can induce piezoelectricity. Likewise the cholesteric piezoelectric term $p_i p_j E_i \nabla_j \psi$ introduced by Brand and Pleiner [8] and reproduced in ref. 2, is also not a scalar. While $p$ appears quadratically, the presence of $\psi$ to the first power leaves the parity of this term ambiguous. It will be a scalar if we choose $\psi$ to be a scalar, but it will be a pseudoscalar if we choose $\psi$ to be a pseudoscalar. In ref. 2 Brand also considered rotations of the elastic network relative to the director. His term $(\psi - p_i \omega_i) q_0 p_j E_j$ is a generalization of our $\gamma_2$ term above to the case where the director can rotate uniformly and is not hindered by the elastic network. However, his additional term coupling this relative rotation to the mass density fluctuations is again incorrect on symmetry grounds.

More recently Terentjev [3] constructed free energies for both chiral and nonchiral nematic elastomers solely in terms of the director. In the former case he wrote down the following piezoelectric free energy density:

$$F^T_p = Q_1 \epsilon_{ijk} E_j n_k u_{il} n_l + Q_2 E_i \omega_i + Q_3 E_i n_i \omega_j n_j$$

Terentjev noted that whereas Brand has three terms coupled to the symmetric strain tensor (equation (4) above), he has only one, the term proportional to $Q_1$. Terentjev attributed this discrepancy to Brand’s use of the coarse-grain approximation for cholesterics, i.e. his use of the pitch axis $p$ rather than the director $n$. Terentjev claimed that a coarse-grain description is often misleading. However, we now demonstrate that when equation (5) is coarse-grained properly, Terentjev’s expression becomes identical to our expression, equation (2). Thus, it was Brand’s incorrect implementation of coarse-graining discussed above that was at fault. Furthermore, as we discuss below, our correct coarse-grain theory has some advantage over
Terentjev’s approach when applied to cholesterics. Terentjev coarse-grained equation (5) incorrectly and concluded erroneously that compressions or elongations along the pitch axis can produce piezoelectricity.

The proper coarse-graining of Terentjev’s expression is easily done if we note that using equation (1), the spatial average of the product $n_i n_j$ over a pitch length equals $\delta_{ij}^{(tr)}$. Denoting the result of coarse-graining Terentjev’s expression by $\langle F_T^p \rangle$, we find:

$$\langle F_T^p \rangle = Q_1 E_i \varepsilon_{ijk} \delta_{jl}^{(tr)} u_{kl} + Q_2 E_i \omega_i + Q_3 E_i \delta_{ij}^{(tr)} \omega_j$$

(6)

The term proportional to $Q_1$ is identical in form to our $\gamma_1$ term if we use the identity:

$$u_{kl} = \delta_{km} u_{ml} = (p_k p_m + \delta_{km}^{(tr)}) u_{ml}$$

(7)

When this identity is inserted into the $Q_1$ term, the last term in equation (7) does not contribute to the final sum over indices. Using a similar identity in the term proportional to $Q_2$ we find that equation (6) is identical to our result, equation (2), with the identifications: $\gamma_2 q_0 = Q_2$ and $\gamma_3 q_0 = Q_2 + Q_3$.

Terentjev applied his free energy density, equation (5), to a uniform director pattern, e.g. a thin layer (compared to the pitch length) of cholesteric elastomer perpendicular to $p$. His $Q_1$ term then leads correctly to a polarization along $p$ when the layer is compressed or elongated along that direction. However, he then concluded erroneously that a macroscopic polarization will arise when one looks at the full pitch. In fact the local polarization averages to zero over the pitch length, as we have seen from our $\gamma_1$ term which only involves shear strains. Once the coarse-grained theory is properly constructed as we have done above in equation (2), it is readily apparent that only shear strains are involved, and no errors will creep into the analysis of piezoelectricity for cholesteric systems.

We now offer some physical arguments to explain the origin of the piezoelectric terms in equation (2). The term proportional to $\gamma_1$ involves a shear in the $p$ direction, e.g. a nonzero $u_{xz}$ strain component, if $p$ is parallel to $\hat{z}$. This shear strain distorts the elastic network. For instance, if the network was initially isotropic it becomes anisotropic with elongation parallel to an axis oriented at 45° to $p$ in the $xz$ plane. Likewise, even if the network is initially anisotropic (locally symmetric about $\hat{n}$) its axis of symmetry rotates towards $p$ through an angle proportional to $u_{xz}$. In either case the director everywhere will gain a $z$-component by rotating about the $y$ axis through an angle $\alpha u_{xz}$, where $\alpha$ is a measure of the coupling of the director to the
strain. The value of $\alpha$ will depend on the material structure. For positive $\alpha$ the director will rotate towards the elongation direction, while for negative $\alpha$ it will rotate away. Equation (1) will be replaced by,

$$
n(r) = \hat{x}\cos\psi(r) + \hat{y}\sin\psi(r) + \hat{z}\cos\psi(r)\alpha u_{xz}, \tag{8}
$$

for small values of $u_{xz}$. This director pattern now exhibits splay and bend as well as the cholesteric twist (see Figure 1). The splay-bend pattern produces a polarization $\mathbf{P}$ due to flexoelectricity [9]:

$$
\mathbf{P} = e_s(\nabla \cdot \mathbf{n}) - e_b(\mathbf{n} \times (\nabla \times \mathbf{n})) \tag{9}
$$

where $e_s$ and $e_b$ are the flexoelectric coefficients. Inserting equation (8) into equation (9) and averaging over a pitch length we find,

$$
\langle \mathbf{P} \rangle = \hat{y}q_0\bar{e}\alpha u_{xz} \tag{10}
$$

where $\bar{e}$ is the arithmetic average of $e_s$ and $e_b$. We thus identify $\gamma_1$ with $\alpha\bar{e}$.

The terms proportional to $\gamma_2$ and $\gamma_3$ cannot be understood on the basis of flexoelectricity and require a more novel mechanism. One scenario is based on the symmetry of the cholesteric molecules, combined with the two component nature of the cholesteric elastomer. Because of its chiral symmetry, each cholesteric molecule can be thought of as a miniature propeller blade. A rotation of the medium surrounding a propeller produces a unique displacement of the propeller, just as a rotation of the propeller would produce a displacement of the medium. This relative displacement of two dissimilar components produces a polarization. In the most extreme case, the gel and the cholesteric molecules carry opposite electrical charges, and the polarization arises from the spatial separation of these charges.

Although the local rotation strains of the gel are valid sources of piezoelectricity, it is difficult to produce them by simple uniform distortion of a macroscopic sample. Thus the $\gamma_1$ term will be the most easily observed piezoelectric effect. Another way to produce relative rotations of the gel and cholesteric molecules is to apply a torque to the cholesteric molecules, for instance by using an externally applied magnetic field $\mathbf{H}$, oriented at an oblique angle to $\mathbf{p}$. The director will rotate typically towards $\mathbf{H}$, and polarization will be induced in the $\mathbf{p} \times \mathbf{H}$ direction, by a combination of both the flexoelectric and the local rotation mechanisms. Note that the gel maintains the average direction of $\mathbf{p}$ during this process; it is only the director which rotates.
Finally, we discuss experiments to observe the piezoelectric effect in these materials. Inspired by Brand’s theory [2] of piezoelectricity in cholesteric elastomers, two groups [4, 5] undertook experiments. Following Brand’s predictions, they looked for a voltage to appear between two plates that compressed a cholesteric elastomer sample in a direction parallel to the helix axis. Had this experiment been performed precisely as stated, the symmetry of the cholesteric would have required a null result. However, both groups saw measurable effects, and Meier and Finkelmann [5] reported extensive experiments to characterize these effects, in relation to variation of the temperature and of the sign and magnitude of $q_0$.

What effect was seen in these experiments? In response to a suggestion by one of us (RBM) that the sample might not be perfectly symmetric, Meier and Finkelmann reported that by altering the shape of the meniscus at one end of the cylindrical samples being studied, from negative to positive curvature, they could change the magnitude and even the sign of the measured effect. This suggests that what they were measuring was in fact the shear-induced piezoelectric effect described above, arising from the nonuniformity of deformation that resulted from compressing the curved end of the sample. The precise geometry of this deformation is unknown, so the resulting voltage produced is impossible to predict.

Although a quantitative value of the piezoelectric coefficient cannot be extracted from the reported experiments, some of the qualitative characterization of the piezoelectric effect in Meier and Finkelmann’s work is quite clear. They did demonstrate that the induced voltage is linear in the strain, after an initial deformation that served to align the sample. They also found that the effect is linear in $q_0$, by changing both the handedness and the magnitude of the helix pitch. Both these results agree with our theory.

In a properly designed experiment, a monodomain sample of linear dimensions $dx$, $dy$, and $dz$, with helix axis in the $z$ direction, would be contained between two parallel plates, located at $z = 0$ and $z = dz$. A shear strain $u_{xz}$ would be created by displacing one of the plates relative to the other in the $x$ direction. This would induce a piezoelectric polarization in the $y$ direction, which would be detected by suitably placed electrodes, for instance on the faces of the sample at $y = 0$ and $y = dy$. This would provide a direct measurement of $\gamma_1$. For the inverse effect, a voltage would be applied to the electrodes, to induce a shear deformation that would be detected by a relative displacement of the parallel plates.
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Figure Caption

Fig. 1: The director pattern in a plane cut through the cholesteric helix at an angle to the helix axis. This plane is rotated about the $y$ axis, through an angle $\alpha_{x2}$ relative to the $z = 0$ plane. The director is parallel to this plane, and exhibits a uniform rotation pattern consisting of alternating bands of splay and bend. This produces a flexoelectric polarization in the $y$ direction.
