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Continuum theory of ferroelectric smectic C* elastomers

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Abstract. — The continuum free energy is derived for a crosslinked network of smectic C and chiral smectic C* liquid crystal polymers under small strain and orientational distortions. The coupling between elastic strain, the smectic C order parameter and the polarization (induced or spontaneous in C* phase) is examined and several new orientational and polarizational effects are predicted. Using group representation theory we obtain all relevant invariants, describing the coupling terms in the free energy. It is shown, on the other hand, that some effects in conventional smectic C liquid crystals, for example the bistability and switching in ferroelectric C*, no longer exist in corresponding elastomers. Possible experimental configurations to observe some of the predicted effects are briefly discussed.

1. Introduction.

Liquid crystalline elastomers have recently attracted much theoretical and experimental attention. Crosslinking of polymer chains creates a rubber with the corresponding translational elasticity. When such crosslinking is performed in an anisotropic state, then memory of such a state becomes frozen in because the topology of networking points distribution is fixed. A variety of new material properties is generated [1-3]. These properties stem from the coupling between mechanical fields, easily created and controlled in rubbers, and the anisotropic phase structure of liquid crystals. A considerable amount of work has been done on nematic elastomers, including preliminary phenomenological models [4, 5], experiments [6-8] and detailed molecular theories [9-11].

Smectic elastomers represent a very different system from the mechanical point of view because they have two characteristic length scales, the smectic layer spacing and the (typically much larger) networking point separation. Layers represent a more rigid component of the system and they may be rotated or otherwise distorted by deformations of the polymer network. Physically the main coupling between layers and the network is the penalty for their relative translation. Let \( U(r) \) be the network displacement vector and \( u(r) \) the local displacement of layers along their normal \( \hat{z} \). Then the coupling \( \sim kT(N_x/R^2_0)(u - U_x)^2 \) penalizes an attempt to translate the periodic smectic lattice relative to the underlying network, with \( N_x \) the crosslink-
ing density and \( R_0 \) the radius of gyration of the network strand, \( R_0^2 \sim N_z^{-1} \). It is important to emphasize that the local coupling \((u - U_i)^2\) generates the coupling between layer distortions and certain components of a uniform strain \((\lambda_{zz} - \frac{\partial u}{\partial x})^2\), \((\lambda_{zz} - \frac{\partial u}{\partial x})^2\) and \((\lambda_{xy} - \frac{\partial u}{\partial y})^2\), where \(\lambda_{ij} = \partial U_i/\partial x_j\), with coefficients proportional to the square of the sample size. This effectively locks uniform smectic distortions affinely with the strain \(\lambda\). However, the smectic variable \(u(r)\) determines the phase of a density wave at wavenumber \(q_0\), an inverse layer spacing, while \(U(r)\) measures displacements near zero wavenumber. Therefore \(U_x\) and \(u\) are independent variables and do not count the same displacement twice. Together with an affine part, \(u(r)\) may contain independent, short-wavelength layer deformations that keep the network (crosslinking points distribution) and the sample shape undistorted at large. We therefore consider two distortion fields — of the network and of the layer system, realizing that a significant part of the layer deformation \(u\) is rigidly determined by the network deformation \(U_x\) on large length scales, \(u = U_x + u_1\). Thus \(u_1\) is the fluctuating part of \(u\). Recently we have presented the continuum theory of smectic A and chiral smectic A* rubbers [12], based on group representation theory, predicting several new mechanical and piezoelectric effects generated by coupling between \(\lambda\) and \(\nabla u_1\). This paper reports the results of a similar analysis of the smectic C and chiral smectic C* elastomers (for convenience further on we shall drop the subscript 1 at the smectic field \(u_1\)).

Smectic C is a special phase among all the variety of liquid crystals. Since the discovery of the ferroelectric behaviour of the chiral C* smectic by Meyer et al. [13] this class of materials has attracted great industrial and scientific interest. Most important properties, however, require well-oriented samples, often with an untwisted helicoidal structure. This orientation is achieved in conventional C* materials by surface alignment, electric or magnetic fields or by shear flow. These techniques often fail for liquid crystal polymers due to their high viscosity. Crosslinked networks of such polymers offer a wide prospects of constructing various orientations and polarizational states in the smectic C* phase by mechanical fields [3, 8, 14]. As in the cases of nematic and smectic A rubbers, the network strain tensor \(\lambda_{ij}\) plays a vital role. The infinitesimal strain \(\lambda_{ij}\) is defined as \(\Lambda_{ij} - \delta_{ij}\) where the Cauchy strain tensor \(\Lambda_{ij}\) determines the sample shape [9-11]. This paper uses group representation theory to deduce the complete set of invariant terms in the free energy of smectic C and C* elastomers, involving translational and orientational variables and the polarization. In addition to the standard smectic, electrical and rubber elastic parts to the free energy, we have new terms unique to smectic C elastomers associated with new couplings made possible. In the end of this paper we briefly discuss some possibilities of experimental observations of these couplings including spontaneous and electrically driven distortions.

Let us note here that liquid crystalline elastomers (as all rubbers) can withstand very large translational deformations and the general theory should not be limited to infinitesimal displacement gradients, as would be the case in conventional elastic solids. On the level of a continuum model, however, it is much simpler and more illustrative to restrict ourselves only to the case of small deformations. This case retains all essential symmetry properties and many predictions can be readily made simply by writing the continuum free energy of deformation.

This paper is organized as follows. Next section gives a general discussion of smectic C and C* phases and sets the ground for the subsequent detailed analysis. In section 3 we describe the continuum model of smectic and network coupling deep in the C* phase, using the properties of its point symmetry group \(C_2\) (in all cases we separate chiral and non-chiral contributions, which will survive in the corresponding centrosymmetric smectic C elastomer). Section 4 gives the similar analysis, but near the A-C phase transition, where the tilt angle (related to smectic C order parameter) is small and one can obtain simplified equations using
the properties of more symmetric A phase. Section 5 considers two (out of many) examples of particular effects that are predicted by this continuum theory: spontaneous shape change of the sample at the A-C phase transition and switching by external electric field. The reader not wishing to follow the group theoretic arguments of this paper will find all the allowed coupling terms stated and discussed and should simply skip the group representation analysis. For instance, at the beginning of section 3 the character of rotations is discussed geometrically and then, in equations (6-9) the couplings are discussed in groups. The appendix interprets geometrically less obvious terms in equations (8) and (9). The coupling contributions to the free energy density are summarized in (10). Likewise in section 4, equation (13) yields the allowed terms, they are discussed geometrically in (14-17). The examples discussed in section 5 and appendix give further geometrical feel for our results (as does Ref. [12] on smectic A elastomers).

2. Ferroelectric smectic C* elastomer.

Smectic C liquid crystals have a one-dimensional density modulation (layers) with the optical axis (director \( \mathbf{n} \)) tilted with respect to the layer normal. This represents a significant difference in comparison with the smectic A phase, where the optical axis direction \( \mathbf{n} \) is locked to the local layer normal and is not an independent continuum variable. Smectic A has the point symmetry group \( D_{\infty h} \) (or non-centrosymmetric \( D_{\infty} \) for chiral smectic A* material). Smectic C has an additional degree of freedom — an azimuthal rotation of the tilted director around the layer normal, which is a Goldstone mode at the transition from the A-phase (from which smectic C typically appears). The C-phase has a two-component order parameter \( \xi \), representing the coupling between the wave vector of the density modulation, \( \mathbf{k} \| \mathbf{n}_0 \) and the director deviation, \( \delta \mathbf{n} \), from the \( \hat{z} \) axis of the underlying smectic A. Assuming that the layer structure and the nematic order do not change significantly during this transition, the two component order parameter may be written as \( \xi \sim [\mathbf{n}_0 \times \delta \mathbf{n}] : \)

\[
\xi_z = -n_x n_y, \quad \xi_y = n_z n_x
\]

and is a vector in the layer plane, perpendicular to \( \delta \mathbf{n} \) (see Fig. 1 and [15] for details of the A-C phase transition). The point group of the resulting smectic C phase is \( C_{2h} \) and that of the chiral smectic C* phase is \( C_2 \).

It should be noted that an attempt to create a continuum model of chiral smectic C* rubbers has been made previously [16]. That work, however, appears unsatisfactory for two important reasons: (i) the polar unit vector \( \hat{p} \) (not to be mixed with our notation \( \mathbf{p} \) for a local polarization axis!) along the axis of a helicoidal structure is chosen as a variable in the free energy density (coarse grain approximation). This violates the point symmetry of the phase. (ii) Following the old arguments of de Gennes [4] only the relative rotation of the network and of the smectic c-director is accounted for, while we now know that anisotropic rubbers have much more subtle, both symmetric and antisymmetric elasticity [11, 12, 17]. As a result of (i), theory [16] obtains some non-existent effects, for example terms like \( \mathbf{p} (\mathbf{p} \cdot \mathbf{E}) \nabla \phi \) (Eqs. (1),(4) of [16]) predict a polarization along the helix axis on changing the helix pitch... Other effects in [16] are known to have different interpretation (for example, standard flexoelectricity). In addition, the model [16] is not applicable to any uniform (i.e. non-helical) structure. As a result of (ii) that model fails to describe effects of symmetric shear strains of the network and related piezoelectric effects (we shall argue below that these effects may be stronger than relative rotations). Therefore we have to consider the task of deriving a continuum theory of smectic C and C* elastomers in its full scope here, heavily referring to a similar analysis and detailed discussion of smectic A system [12].
We shall develop the continuum description of smectic C* (or C) elastomers from two different positions: deep inside the smectic C phase and at small order parameter, in this case utilizing the properties of the A-C transition. Far from this transition, when the magnitude of the order parameter $|\xi|$ is not vanishingly small and the helical twisting is prevented by some means, the properties of the material under infinitesimal deformations are not different from those in conventional monoclinic crystals and are well-described in various textbooks [18]. For example, such “unwound” smectic C* has a standard piezoelectric effect, $\gamma_{ijk} P_{i} \lambda_{jk}^{S}$, with eight independent coefficients $\gamma$ (the superscript S denotes that only the symmetric part of $\lambda_{ij}$ is taken into consideration, $\lambda_{ij}^{S} = \frac{1}{2}[\lambda_{ij} + \lambda_{ji}]$). Of these eight invariants, four contribute to the change $P$ in spontaneous polarization $P_{s}$ (assume that $P_{s}$ points along the $\tilde{y}$ axis in the Fig. 1):

$$\begin{align*}
P_{y} \lambda_{yy}, & P_{y} \lambda_{zz}, & P_{y} \lambda_{xz} & \text{and} & P_{y} \lambda_{xz}^{S}.
\end{align*}$$

(2)

The other four independent components of this piezoeffect are induced in two perpendicular directions:

$$\begin{align*}
P_{z} \lambda_{yz}, & P_{z} \lambda_{xy} & \text{and} & P_{z} \lambda_{yz}^{S}, & P_{z} \lambda_{xy}^{S}.
\end{align*}$$

(3)

Note, that even in the helically twisted material, the piezoelectric polarization induced in the $\tilde{z}$ direction — along the helix axis (layer normal) by the symmetric shear deformation is not vanishing after averaging. This effect is similar to the piezoelectricity along the helical axis in cholesteric elastomers [17] and is absent in conventional liquid crystals.

When the smectic C* order parameter $|\xi|$ becomes small near the phase transition to the A*-phase at increasing temperature, the eight independent piezoeffect coefficients corresponding to terms in equations (2) and (3) can be expanded in powers of $|\xi|$. Comparison with the corresponding piezoeffect in smectic A [12], $\tilde{\nu}_{0}(P_{z} \lambda_{yz}^{S} - P_{y} \lambda_{xz}^{S})$, tells that six of these coefficients vanish at $|\xi| \rightarrow 0$, while the coefficients of $P_{y} \lambda_{yz}^{S}$ and $P_{z} \lambda_{xz}^{S}$ become equal and of the opposite sign.

Analysis of representations of the group $C_2$ (and of its centrosymmetric counterpart $C_{2h}$) gives expansions of relevant contributions to the free energy in terms of irreducible representations, see table II below for trivial representations $\Gamma_{0}$. Clearly the number of independent terms in each category is very high, which is a natural consequence of the very low symmetry
of the phase. There is a total of 144 invariants arising from the cross couplings of $P$ and $\lambda_{ij}$ with orientational deformations of the smectic $C^*$. In most realistic cases of smectic $C$ phase, however, it is not necessary to take all of these invariants into account. In the example above we have seen that only one out of eight combinations $\sim P\lambda$ was relevant at small order parameter $|\xi| \ll 1$ where one is tending to the case of smectic $A^*$ elastomers. One can expect similar reduction for other terms as well. The reason is that, typically, the smectic C order parameter is proportional to the tilt angle of the optical axis and is small in a wide region of phase existence. In this case some of the invariants under the $C_2$ (or $C_{2h}$) group operations, which are proportional to higher powers of $|\xi|$ can be neglected. The remaining major effects can be discovered using the properties of the more symmetric group $D_{\infty}$ (or $D_{\infty h}$) appropriate to smectic $A^*$ (or A) and the order parameter $\xi$ which grows as we evolve from the corresponding A-phase. It is done in the fashion, similar to the Landau description of the 2nd order phase transitions when invariants in the low-symmetry phase, containing the given power of the order parameter, are found as trivial representations in the high-symmetry phase of the free energy contributions, containing the physical quantity that is the order parameter in that given power. For instance the two component order parameter $\xi$ of smectic C transforms according to the irreducible representation $\Gamma_1$ of the group $D_\infty$ (or $D_{\infty h}$) of smectic A. Likewise the wave vector of the density modulation $k|n_0$ transforms as $\Gamma_1^{(D_\infty)}$ and the director deviation, $\delta n$, from the $\hat{z}$ axis in smectic C transforms as $\Gamma_1^{(D_\infty)}$. Taking combinations and powers of these and other quantities we must, within $D_\infty$, identify the resulting invariants of the C phase.

This analysis using smectic A as a basis is meaningful, of course, only so long as it is possible to expand in powers of the order parameter, i.e. near 2nd order transitions – which happens to be the case for the smectic C phase. Such analysis for the liquid smectic $C^*$ (or C) phase is presented, for example, in [15, 19]. In elastomers we have to examine additional effects, imposed by translational deformations. In the limit of small tilt angle $\theta$ of the director, the free energy density is much simpler to analyse, using smectic A as a basis. At the same time such an analysis retains all essential symmetry properties and effects of the smectic $C^*$ phase. We shall examine this limit in more detail in section 4.

3. Free energy of deformations ($C_2$).

Note, first of all, that all effects described in [12] for smectic A* (or A) elastomers remain valid below the transition into the corresponding C phase, with the difference that they become split into many independent invariants in the low symmetry phase, see for instance the piezoelectric terms above. In this section we shall use the full low symmetry $C_2$, first recalling the underlying liquid smectic $C^*$ free energy [19] in the absence of crosslinking, and then giving the form of the rubber elastic free energy (at small deformations) for an elastomer with $C_2$ symmetry.

The monoclinic chiral group $C_2$ of two-fold rotation about the axis $\xi$ is cyclic (i.e. abelian) and has only one-dimensional irreducible representations (see Tab. I): trivial $\Gamma_0$, which corresponds to a vector component along the principal axis direction (which is thus also the direction of polarization, $p$, in the layer plane), and $\Gamma_1$, which changes sign under 180° rotation about this axis and corresponds to a vector component in the plane including the layer normal $\mathbf{E}$ and the director tilt $\delta n$, figure 1.

Any vector transforms as $V = \Gamma_0 \oplus 2\Gamma_1$ under this group's operations. Hence the chiral smectic $C^*$ phase has an equilibrium polarization $P_0$ in the layer plane, which corresponds to a trivial component $\Gamma_0$ in the vector representation and is perpendicular to the director (in contrast, the non-chiral group $C_{2h}$ has only a scalar trivial representation and, therefore, regular smectic C is non-polar and uniform in equilibrium). Normally the bulk polarization is
Table I. — Characters of irreducible representations of the group $C_2$ with operations: unity - 1 and rotation by 180° around the $\hat{z}$ axis in the layer plane - $c_2$.

<table>
<thead>
<tr>
<th>$C_2$</th>
<th>$\hat{1}$</th>
<th>$c_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma_0$</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$\Gamma_1$</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>$V$</td>
<td>3</td>
<td>-1</td>
</tr>
<tr>
<td>$V \otimes V$</td>
<td>9</td>
<td>1</td>
</tr>
</tbody>
</table>

Table II. — Expansions of terms containing $\lambda, \Omega, \xi$ and $P$ in the free energy density in terms of irreducible representations of the group $C_2$.

| | $\lambda^S$ | $[V \otimes V]$ | $4\Gamma_0 \oplus 2\Gamma_1$ |
| | $\lambda^A$ | $\{V \otimes V\}$ | $\Gamma_0 \oplus 2\Gamma_1$ |
| | $(\lambda^S)^2$ | $[[V^2]^2]$ | $13\Gamma_0 \oplus 8\Gamma_1$ |
| $\lambda^S \Omega$ | $[V \otimes V] \otimes V$ | $8\Gamma_0 \oplus 10\Gamma_1$ |
| $\lambda^S \nabla \Omega$ | $[V \otimes V] \otimes V \otimes V$ | $28\Gamma_0 \oplus 26\Gamma_1$ |
| $\lambda^S \Omega$ | $V \otimes [V \otimes V] \otimes V$ | $28\Gamma_0 \oplus 26\Gamma_1$ |
| $P \lambda^S \nabla \Omega$ | $V \otimes [V \otimes V] \otimes V$ | $80\Gamma_0 \oplus 82\Gamma_1$ |

not observable due to the twisting in the smectic $C^*$ phase: at the phase transition from the $A^*$ phase ($D_\infty \Gamma_1 \subset C_2$ group transformation) the Lifshits invariant, $[\xi_z(\partial \xi_y/\partial z) - \xi_y(\partial \xi_z/\partial z)] \sim \theta^2(\partial \phi/\partial z)$, induces an equilibrium twist of this polarization when moving along the layer normal direction $\hat{z}$.

A convenient variable to describe deformations in the $C$ phase is the rotation vector with three components: layer distortions $\Omega_x = \partial u/\partial y, \Omega_y = -\partial u/\partial x$ and azimuthal rotation of the director $\Omega_z \equiv \phi$, where $\hat{z}$ is chosen as an equilibrium layer normal and $u(\mathbf{r})$ is the local displacement of layers along $\hat{z}$. Thus $\Omega_z \rightarrow \Gamma_1$ represents the azimuthal rotation of the director in the layer plane. By choosing $\hat{z}$ along $\mathbf{n}_\perp \equiv c$ we can identify $\Omega_x \equiv \Omega_c \rightarrow \Gamma_1$ and $\Omega_y \equiv \Omega_p \rightarrow \Gamma_0$ (Tab. I). The smectic $C$ elastic free energy can be then derived (see [19, 20]) by looking for the trivial representations contained in the term proportional to $(\nabla \Omega)^2$, since this free energy cannot depend on the angles of uniform rotation themselves. There are certain constraints on layer deformations, following from the definition of $\Omega$: $\partial \Omega_x/\partial z = \partial \Omega_y/\partial z = 0, \partial \Omega_z/\partial x = -\partial \Omega_y/\partial y$. Taking into account these constraints one has only the following relevant irreducible representations $\nabla \Omega \equiv \dot{V} \otimes \dot{V} \rightarrow 3\Gamma_0 \oplus 3\Gamma_1$ (in a brief appendix we discuss how these constraints reduce the number of invariants). Therefore, $(\nabla \Omega)^2 \rightarrow 12\Gamma_0 \oplus ...$. Adding the layer compression term and grouping those combinations that transform into each other by integration by parts we can write the smectic $C$ energy of deformations (see [19])

$$\frac{1}{2} B \left(\frac{\partial u}{\partial z}\right)^2 + A_{12} \left(\frac{\partial^2 u}{\partial \rho^2}\right)^2 + A_{21} \left(\frac{\partial^2 u}{\partial c^2}\right)^2 + A \left(\frac{\partial^2 u}{\partial \rho \partial c}\right)^2 +$$
\[ C_1 \left( \frac{\partial^2 u}{\partial c^2} \right) \frac{\partial \phi}{\partial p} + C_2 \left( \frac{\partial^2 u}{\partial p^2} \right) \frac{\partial \phi}{\partial p} + C_0 \left( \frac{\partial^2 u}{\partial p \partial c} \right) \frac{\partial \phi}{\partial z} + \]

\[ B_1 \left( \frac{\partial \phi}{\partial c^2} \right)^2 + B_2 \left( \frac{\partial \phi}{\partial p^2} \right)^2 + B_3 \left( \frac{\partial \phi}{\partial z^2} \right)^2 + B_{13} \frac{\partial \phi}{\partial c} \frac{\partial \phi}{\partial z} \]  

(4)

where we have returned to the original concept of layer displacement field \( u(r) \) and azimuthal rotation angle \( \phi(r) \) (in this section the order parameter is assumed to be of the order of unity). Cartesian coordinates \( \vec{c} \) and \( \vec{p} \) correspond to the usual \( \vec{x} \) and \( \vec{y} \) axes, chosen along the director projection \( \vec{n}_\perp = \vec{c} \) and the local polarization \( \vec{p} \) (see Fig. 1). Equation (4) contains only non-chiral terms and is the same in smectic C and C* phases.

As shown in the Table II, \( (\alpha^S)^2 \rightarrow 13\Gamma_0 \oplus 8\Gamma_1 \) and hence there are thirteen independent linear rubber elastic moduli, corresponding to the following terms in the free energy \( F_{rub} = \frac{1}{2} Q_{ijkl} \lambda^S_{ij} \lambda^S_{kl} : \)

\[ (\lambda_{zz})^2, (\lambda_{zc})^2, (\lambda_{cc})^2, (\lambda_{pp})^2, (\lambda_{cp})^2, (\lambda_{zp})^2, \]

\[ \lambda_{zz}\lambda^S_{cc}, \lambda_{zz}\lambda^S_{cc}, \lambda_{zz}\lambda^S_{pp}, \lambda_{zz}\lambda^S_{cp}, \lambda_{zp}\lambda^S_{pp}, \lambda_{zp}\lambda^S_{cc}, \lambda_{zp}\lambda^S_{cp}, \lambda_{zp}\lambda^S_{zp} \]  

(5)

where subscripts \( c \) and \( p \) correspond, as in equation (4), to the directions in the layer plane along \( \vec{n}_\perp \) and the local spontaneous polarization \( P_s \), respectively. In most cases the constraint of the rubber incompressibility is present (see the discussion in [12]). This condition reads \( \text{Det}[\Lambda_{ij}] = 1 \), which fixes the trace of the small deformation tensor \( \lambda_{ij} \), \( \text{Tr}[\lambda_{ij}] \rightarrow 0 \). As a result of this constraint the number of independent terms \( \sim \lambda^2 \) in the elastic energy of incompressible rubber is twelve. At the same time the apparent number of linear rubber elastic invariants is only nine, because the incompressibility constraint eliminates all terms in (5) containing \( \lambda_{zz} \) by grouping their moduli in linear combinations. It is interesting to compare invariants (5) with the corresponding rubber elastic energy in the smectic A elastomer [12], which has only three apparent invariant terms (see also the next section).

A new feature in smectic C elastomers is, of course, the coupling between deformations of the network, \( \lambda_{ij} \), and deformations of the smectic C structure, \( \nabla \Omega \). As we have discussed in the Introduction, uniform layer rotations \( \Omega_p \) and \( \Omega_c \) are rigidly locked to the network strain components \( \lambda_{zc} \) and \( \lambda_{zp} \) by the constraint on relative displacements \( |u - U_z|^2 \). Nonuniform layer rotation, represented by \( \nabla \Omega \), may be determined by small non-affine smectic distortions and produces independent effects (the same, incidentally, applies to the component \( \Omega_e = \phi \), which is a purely orientational field). Considering only infinitesimal symmetric strains, \( \alpha^S \rightarrow 4\Gamma_0 \oplus 2\Gamma_1 \), and relevant components of \( \nabla \Omega \rightarrow 3\Gamma_0 \oplus 3\Gamma_1 \) we obtain eighteen independent invariant terms in the coupling free energy, corresponding to all possible products arising from:

\[ 4\Gamma_0^{(\lambda)} \otimes 3\Gamma_0^{(\nabla \Omega)} \rightarrow [\lambda_{zz} + \lambda_{cc} + \lambda_{pp} + \lambda^S_{zz}] \times \left[ \frac{\partial^2 u}{\partial p \partial c} + \frac{\partial \phi}{\partial z} \right] \]  

(6)

and

\[ 2\Gamma_1^{(\lambda)} \otimes 3\Gamma_1^{(\nabla \Omega)} \rightarrow [\lambda^S_{cp} + \lambda^S_{zp}] \times \left[ \frac{\partial^2 u}{\partial p^2} + \frac{\partial \phi}{\partial c} \right] \]

with a different coefficient for each product that arises (the incompressibility constraint, \( \lambda_{zz} \approx -\lambda_{cc} - \lambda_{pp} \), makes the apparent number of independent invariants fifteen). We discuss (6) in more detail in the appendix. It is important to note that all these terms are chiral and
are absent in centrosymmetric smectic C, where the only linear coupling between smectic and rubber distortion fields is related to the uniform layer compression $\gamma \equiv (\partial u/\partial z)$:

$$
\lambda_{zz} \frac{\partial u}{\partial c}; \quad \lambda_{cc} \frac{\partial u}{\partial c}; \quad \lambda_{pp} \frac{\partial u}{\partial c}; \quad \lambda_{zc} \frac{\partial u}{\partial c} \quad (7)
$$

[these terms are present, of course, in the chiral material too in addition to (6); the first term here does not survive in an incompressible system].

There are independent effects describing the coupling between the strain and the relative layer rotations, $\Omega_c$ and $\Omega_p$. This phenomenon represents the penalty for deviations from affine deformation pattern and are similar to those in smectic A elastomers (see the discussion in Introduction and in [12]),

$$
\lambda^{S}_{cp} \frac{\partial u}{\partial c}; \quad \lambda^{S}_{zp} \frac{\partial u}{\partial p} \quad (8)
$$

(as usual, the term containing $\lambda_{zz}$ is effectively eliminated in an incompressible system). It is interesting that, unlike in the smectic A case, layer rotation can be generated not only by shear deformations, but also by extensions and compressions, given by diagonal elements of $\lambda_{ij}$. Finally, there is a coupling between shear deformations and the relative azimuthal rotation of the director, $\Omega_z \equiv \phi$, unique to these tilted smectic elastomers

$$
\lambda_{cp}^{S} \phi; \quad \lambda_{zp}^{S} \phi. \quad (9)
$$

The character of these terms and the geometrical reason for the absence of $\lambda_{zc}^{S} \phi$, for example, is discussed in the appendix, as is the coupling of $\lambda^{A}$ to $\phi$.

Summarizing the discussion in this section we should write symbolically linear cross terms in the total free energy of deformations in a smectic C* elastomer :

$$
F_d = m_{ijkl} \lambda^{S}_{ij} \nabla_k \Omega_l + b_{ij} \lambda^{S}_{ij} \gamma + l_{ijk} \lambda^{S}_{ij} \Omega_k. \quad (10)
$$

Here the corresponding terms describe: strain-curvature coupling (6) with 17 independent coefficients $m_{ijkl}$, strain-layer compression coupling (7) with 4 coefficients $b_{ij}$, strain-rotation coupling (8),(9) with 8 coefficients $l_{ijk}$. The coupling between the antisymmetric part of shear strain and the azimuthal rotation of the director in the layer plane is briefly discussed in the appendix. It has to be emphasized once again that only non-affine layer rotations, $\nabla u$, as mentioned in the introduction, are relevant for this free energy: uniform gradients of $u$ are rigidly locked with the corresponding components of strain in a macroscopic network.

Evidently the total number of invariant terms in the free energy of smectic C (C*) elastomer is already very high and will become even higher when considering polarizational effects, see table II. It is difficult to separate the major, most significant effects. It is worth, therefore, examining the case of relatively small order parameter $|\xi| \ll 1$. We shall examine this limit in more detail in the next section when dealing with the $P\lambda^S \xi$ and $P\lambda^S \nabla \xi$ terms since the 108 invariants provided within $C_2$ symmetry by $P\lambda^S \Omega$ and $P\lambda^S \nabla \Omega$ effects are clearly unmanageable.

4. Expansion at small tilt angles ($D_\infty$).

At $|\xi| \to 0$ we arrive at the case of smectic A (or chiral smectic A*) elastomer [12]. We take the liberty to re-write here the relevant parts of the coupling elastic free energy, depending on
$\Delta$ and non-affine part $\nabla u_1$ (we remind that the subscript 1 is common for all entries of $u$ and is dropped for convenience). We address the reader to that paper for all details and discussion.

$$F_A \approx \frac{1}{2} b_0 u^2 + b_2 \left( \lambda^S_{zz} \frac{\partial u}{\partial x} + \lambda^S_{yz} \frac{\partial u}{\partial y} \right)$$
$$+ \tilde{\kappa}_{12} \left[ (\lambda^S_{zz} - \lambda^S_{yy}) \frac{\partial^2 u}{\partial x \partial y} - \lambda^S_{xy} \left( \frac{\partial^2 u}{\partial x^2} - \frac{\partial^2 u}{\partial y^2} \right) \right]$$
$$+ \tilde{\nu}_0 (P_x \lambda^S_{yz} - P_y \lambda^S_{xz}) + \tilde{\nu} (P_x \lambda^S_{yz} - P_y \lambda^S_{xz}) \frac{\partial u}{\partial z} + \tilde{\nu}' \lambda_{zz} \left( P_x \frac{\partial u}{\partial y} - P_y \frac{\partial u}{\partial x} \right)$$

(11)

where tildes mark the chiral terms which are absent in centrosymmetric materials. The constraint on relative displacements ($u = U_x + u_1(r)$, see the discussion in Introduction) essentially eliminated several terms in (11) and transformed relative rotation coupling into $\lambda^S \nabla_1 u_1$. Instead one arrives at the effective mass for the field $u_1(r)$ and the nonlinear contribution, similar to that for the Helfrich-Hurault effect [19].

At infinitesimal deformations the rubber elasticity part of the free energy, corresponding to the uniaxial symmetry of smectic A is

$$\frac{1}{2} Q_1 (\lambda_{zz} + \lambda_{yy})^2 + \frac{1}{2} Q_{12} (\lambda^S_{zz})^2 + \frac{1}{2} Q_{22} (\lambda^S_{yz})^2 + \frac{1}{2} Q_{22} (\lambda^S_{xz})^2 + \lambda^2_{yy}$$

(12)

[compare with (5) for the system deep in the smectic C phase]. Three rather than five coefficients $Q_i$ [12] are required for this uniaxial system because of the incompressibility constraint demanded for rubber.

We remind the reader that in the limit $|\xi| \ll 1$ the analysis is to be carried out in the smectic $A^*$ reference state with the symmetry $D_{\infty}$ (or $D_{\infty h}$ in centrosymmetric materials), regarding all smectic C effects as perturbations. These additional phenomena are associated with the addition of an extra vector into the problem, namely the smectic C order parameter $\xi$, a vector in the layer plane and hence associated with the representation $\Gamma_1$ of the group $D_{\infty}$, see table III. Let us consider, for simplicity, only uniform or helically twisted (along $\tilde{z}$) configurations (so that $\nabla \Rightarrow \partial/\partial z \rightarrow \Gamma_2$). Then, for infinitesimal deformations (i.e. discarding all $\lambda^A_{\frac{\Delta}{z}}$ components for the reasons already discussed in Sect. 2) we have the following relevant representations (see [12] for illustration of the algebra of these representations):

$$\lambda^S_{ij} \xi_k \rightarrow \Gamma_0 \oplus \Gamma_x \oplus 3 \Gamma_1 \oplus \{\text{higher rank tensors}\}$$
$$\lambda^S_{ij} \nabla_z \xi_l \rightarrow \Gamma_0 \oplus \Gamma_x \oplus 3 \Gamma_1 \oplus \{\text{higher rank tensors}\}$$
$$\lambda^S_{ij} \xi_k \xi_l \rightarrow 3 \Gamma_0 \oplus \{\text{higher rank tensors}\}$$
$$P_k \lambda^S_{ij} \xi_l \rightarrow 4 \Gamma_0 \oplus \{\text{higher rank tensors}\}$$
$$P_k \lambda^S_{ij} \nabla_z \xi_m \rightarrow 4 \Gamma_0 \oplus \{\text{higher rank tensors}\}$$

(13)

and the single combination with the structure $\tilde{\nu}_0 \Delta^S P$ was included in equation (11) above. Corresponding terms, containing also $(\partial u/\partial z) \rightarrow \Gamma_0$, can be written for every invariant in (13). Such terms, however, represent a higher order effect with the same symmetry and may often be neglected.

We now look at the thirteen invariants generated by (13). The translational deformation acts to alter the state of smectic $C^*$ order mainly via the first two contributions in (13):

$$\alpha_0 [\xi_x \lambda^S_{yz} - \xi_y \lambda^S_{xz}]$$
$$\alpha_1 \left( \frac{\partial \xi_x}{\partial z} \lambda^S_{yz} + \frac{\partial \xi_y}{\partial z} \lambda^S_{xz} \right)$$

(14)
Table III. — Irreducible representations and characters for the group \( D_{\infty} \) with operations: unity - \( \tilde{1} \), infinite rotation around the \( \tilde{z} \) axis - \( C_{\phi} \) and rotation by 180° around the axis in the layer plane - \( u_{2} \).

<table>
<thead>
<tr>
<th>( D_{\infty} )</th>
<th>( \tilde{1} )</th>
<th>( C_{\phi} )</th>
<th>( u_{2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Gamma_{0} )</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>( \Gamma_{z} )</td>
<td>1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>( \Gamma_{1} )</td>
<td>2</td>
<td>( 2 \cos \phi )</td>
<td>0</td>
</tr>
<tr>
<td>( \Gamma_{n} )</td>
<td>2</td>
<td>( 2 \cos n\phi )</td>
<td>0</td>
</tr>
<tr>
<td>( V )</td>
<td>3</td>
<td>1 + 2 ( \cos \phi )</td>
<td>-1</td>
</tr>
</tbody>
</table>

These two terms are what the 8 and 28 invariants of \( \lambda^{8}\Omega \) and \( \lambda^{8}\nabla\Omega \) under \( C_{2} \) (see Tab. II) degenerate into when approaching the A-C transition. The term with \( \tilde{c}_{1} \) is chiral and can be found only in C* elastomers (here and below we will designate chiral coefficients with tilde). The first term in (14) represents a "mechanoclinic effect", similar to the electroclinic effect in smectic A* by Garoff and Meyer [21]. In this case spontaneous shear deformations appear with the onset of smectic C order (a non-chiral effect) or, alternatively, one can create such order and all related phenomena by shearing the smectic A rubber along the direction of the layer normal \( \tilde{z} \).

Invariants second-order in \(|\xi|\) take the form:

\[
\alpha_{22}[\xi_{z}^{2}\lambda_{zz} + 2\xi_{z}\xi_{y}\lambda_{zy}^{S} + \xi_{y}^{2}\lambda_{yy}], \quad \alpha_{11}[\xi_{z}^{2}\lambda_{zz}] \{ \alpha_{00}[\xi_{z}^{2}\text{Tr}[\lambda]] \} \quad (15)
\]

(the condition of incompressibility, \( \text{Det}[\lambda] = 1 \), transforms into \( \text{Tr}[\lambda] \rightarrow 0 \), effectively eliminating the last term). These terms represent another component of the mechanoclinic effect discussed above. There are spontaneous extensions and shear in the layer plane in the smectic C elastomer, but these deformations are proportional to the square of the order parameter \(|\xi|\) and are therefore small.

Of the four invariant (\( \Gamma_{0} \)) terms, describing the mixed piezoelectric effect, \( \sim P\lambda\xi \) in (13), three correspond to the polarization in the layer plane (along \( P_{z} \) for diagonal elements of \( \lambda \) and perpendicular to \( P_{z} \) for the in-plane shear deformation) and one (\( \tilde{\nu}_{11} \)) to the polarization along the layer normal:

\[
\tilde{\nu}_{22}[P_{z} (\xi_{z}\lambda_{zz} + \xi_{y}\lambda_{zy}^{S}) + P_{y} (\xi_{z}\lambda_{zy}^{S} + \xi_{y}\lambda_{yy})], \quad \tilde{\nu}_{12}(P_{z}\xi_{z} + P_{y}\xi_{y})\lambda_{zz}, \quad \tilde{\nu}_{11}P_{z} (\xi_{z}\lambda_{zz} + \xi_{y}\lambda_{yy})
\]

\[
\{ \tilde{\nu}_{02}(P_{z}\xi_{z} + P_{y}\xi_{y})\text{Tr}[\lambda] \} \quad (16)
\]

(the last term is effectively eliminated in an incompressible system). All these invariants are chiral and are present only in the smectic C* material. They represent a new uniform piezoelectric effect, arising after the transition into the smectic C* phase due to the additional symmetry breaking, represented by its order parameter \( \xi \).

When there is a helical twisting in the smectic C* elastomer, \( \xi = \xi(z) \), an imposed deformation generates the mixed piezoelectric—flexoelectric effect. Four corresponding non-chiral invariants of \( P\lambda\nabla\xi \) in (13) take the explicit form:

\[
\nu_{22} \left[ P_{z} \left( \frac{\partial \xi_{z}}{\partial z} \lambda_{zy}^{S} - \frac{\partial \xi_{y}}{\partial z} \lambda_{zz} \right) + P_{y} \left( \frac{\partial \xi_{z}}{\partial z} \lambda_{zy}^{S} - \frac{\partial \xi_{y}}{\partial z} \lambda_{zy}^{S} \right) \right],
\]
\[ \nu_{12} \left( P_z \frac{\partial \xi_y}{\partial z} - P_y \frac{\partial \xi_z}{\partial z} \right) \lambda_{zz}, \quad \nu_{11} P_z \left( \frac{\partial \xi_x}{\partial z} \lambda_y^S - \frac{\partial \xi_y}{\partial z} \lambda_z^S \right) \]
\[ \left\{ \nu_{02} \left( P_x \frac{\partial \xi_y}{\partial z} - P_y \frac{\partial \xi_x}{\partial z} \right) \text{Tr}[\lambda] \right\} \]

(17)

(where, as usual, the last term is absent in an incompressible system).

In order to bring these expressions closer to a more familiar notation, let us call \( \theta \) the tilt angle of the director with respect to the layer normal and \( \phi \) the angle of its azimuthal rotation in the plane. Then \( \xi_x = -\frac{1}{2} \sin 2\theta \sin \phi \) and \( \xi_y = \frac{1}{2} \sin 2\theta \cos \phi \) (we may always assume that \( \theta \ll 1 \)). A uniform helix corresponds to \( \phi = qz \). Substitution of this convention into the equations (14-17) shows that the second term in (14) is just the first one, multiplied by \( q \). Similarly — all independent invariants in (17) are the ones in (16) with a factor \( q \) (in the corresponding non-chiral smectic C the equilibrium wave number \( q = 0 \), leaving only the invariants (14) — first term, (15) and (17) in the free energy). On the other hand, unless we consider non-uniform deformations, the main effects of coupling in chiral smectic C\(^*\) elastomers are simply the first term in equation (14) and the piezoelectric terms (16), with coefficients, dependent on the wave vector \( q \) of the helical twisting (if any) in the material.

5. Implementations of the theory.

In the two preceding sections we have outlined several new effects in smectic elastomers and their chiral C\(^*\) modifications. Obviously there are many possible experimental situations where these effects may be observed or utilized, the scope of this paper does not allow us to explore all of them. Here we shall illustrate the present continuum theory of smectic rubbers on just two examples — the phase transition behaviour and the effect of an external electric field.

5.1 Spontaneous Deformations Below A-C Phase Transition. — Liquid crystalline elastomers are unique systems where the simultaneous coupling of a translational deformation field, orientational distortions and polarization takes place. We have seen in the section 3 that when a system with sufficiently low symmetry is considered, the resulting continuum free energy may be quite complicated. Let us consider the simplified geometry of a smectic A elastomer with all layers undistorted and perpendicular to the \( \hat{z} \) axis. The second order A-C phase transition in conventional liquid crystals is described in [15] in detail, here we shall find main effects that are due to the underlying elastomer network. The free energy density of such a simplified uniform system is

\[ F = \frac{1}{2} a \theta^2 + \frac{1}{4} c \theta^4 - \bar{\mu}_p \theta (P_x \sin \phi - P_y \cos \phi) - \alpha_0 \theta (\lambda_y^S \sin \phi + \lambda_z^S \cos \phi) + \bar{\nu}_0 (P_x \lambda_y^S - P_y \lambda_z^S) + \frac{1}{2} Q_{12} [(\lambda_z^S)^2 + (\lambda_y^S)^2] + \frac{1}{2 \chi_\perp} (P_x^2 + P_y^2) \]

(18)

where we have taken \( \xi_x \approx -\theta \sin \phi \) and \( \xi_y \approx \theta \cos \phi \), see figure 1; the coefficient \( a \) is temperature dependent, \( a = a_0(T - T_c) \). Equation (18) contains only the main terms, which are second order in the smectic C order parameter \( |\xi| = \theta \).

Straightforward minimization with respect to the unconstrained fields \( \lambda \) and \( P \) leads to the renormalization of apparent material constants: \( \bar{\mu}_p' = \bar{\mu}_p - \alpha_0 \bar{\nu}_0 / Q_{12} \), \( \alpha'_0 = \alpha_0 - \chi_\perp \bar{\mu}_p \bar{\nu}_0 \); \( \chi'_\perp = \chi_\perp \left[ 1 - \chi_\perp \bar{\nu}_0^2 / Q_{12} \right]^{-1} \) and \( Q'_{12} = Q_{12} - \chi_\perp \bar{\nu}_0^2 \). A second order phase transition will take place at a lower temperature in comparison with the corresponding uncrosslinked polymer smectic: \( a' = a - \alpha'_0 / Q_{12} - \chi'_\perp \bar{\mu}_p' \). And, finally, there are spontaneous deformation and
polarization (in chiral system) induced by the arising smectic C order:

$$\lambda_{xx}^{S} = \frac{\alpha_{0}'}{Q_{12}} \theta \cos \phi \ , \quad \lambda_{yy}^{S} = \frac{\alpha_{0}'}{Q_{12}} \theta \sin \phi$$

$$P_{z} = \chi_{1}^{\perp} \mu^{\perp} \theta \sin \phi \ , \quad P_{y} = -\chi_{1}^{\perp} \mu^{\perp} \theta \cos \phi$$

(19)

while the optimized free energy is independent on the azimuthal angle $\phi$, $F = \frac{1}{2} \alpha' \theta^{2} + \frac{1}{4} \theta^{4}$, i.e. the Goldstone mode is preserved in such mechanically unconstrained smectic C elastomer.

Equations (19) show that spontaneous polarization $P_{s}$ is created in the layer plane perpendicular to the tilted director orientation (i.e. $P_{s}||\xi$, as expected from the symmetry arguments). There is a spontaneous shear deformation in the plane containing the layer normal and the current optical axis of the material, see figure 1. Both these fields are linearly proportional to the order parameter near the transition. Similar procedure of minimization with respect to other components of the deformation tensor [using expressions (15) and (16)] gives these deformations, also based on the $\hat{z} - n$ plane, as a second order effect:

$$\lambda_{xy}^{S} = \frac{1}{2Q_{22}} (\alpha_{22} - \tilde{\nu}_{22} \tilde{\mu}^{\perp} \chi_{1}^{\perp}) \theta^{2} \sin 2\phi$$

$$\frac{1}{2} [\lambda_{xx} - \lambda_{yy}] = \frac{1}{2Q_{22}} (\alpha_{22} \cos 2\phi + \tilde{\nu}_{22} \tilde{\mu}^{\perp} \chi_{1}^{\perp}) \theta^{2}$$

$$\frac{1}{2} [\lambda_{xx} + \lambda_{yy}] = \frac{1}{2(Q_{1} + 2Q_{22})} [\alpha_{11} - \alpha_{22} - (\tilde{\nu}_{12} - \tilde{\nu}_{22}) \tilde{\mu}^{\perp} \chi_{1}^{\perp}] \theta^{2}.$$  

(20)

The spontaneous shape change (19) and (20) should be clearly seen on experiment. One of the obvious applications of such effect is the control of the A-C transition point by external stresses, which introduce mechanical constraints on the sample (in the limiting case of sample with totally clamped shape the transition will not take place at all). Application of some stresses may break the rotational symmetry of smectic A in the layer plane and therefore eliminate the Goldstone mode — degeneracy with respect to azimuthal angle $\phi$.

We have considered here a mechanically unconstrained sample. In chiral material the resulting smectic C* phase will also be helically twisted [15] around the layer normal with the wave number, similarly renormalized due to the coupling with the network. Accordingly the spontaneous shape change of the sample will take a curious helical form, resembling a screw thread, albeit modified by the complexities of induced torsional deformations. We do not pursue this here. The inverse experiment is also interesting: the unwinding of an unconstrained smectic C* elastomer by the application of electric field.

5.2 SWITCHING BY ELECTRIC FIELD. — One of the features of the ferroelectric smectic C* phase of conventional liquid crystals, most important for applications, is the property of bistability with respect to the azimuthal switching of its polarization (see [22], for example). In infinite samples there is no energy difference, or a barrier between the two configurations in figure 2 with polarization up and down respectively. The same is true for some bounded geometries, the main example is SSFLC (surface stabilized ferroelectric liquid crystal) alignment [22]. Hence the switching between these two states (by an external electric field, for example) is controlled only by viscous forces associated with the corresponding bulk reorientation.

When the orientational order is frozen into the topology of a polymer network, this situation may change. In a mechanically unconstrained sample the free energy does not depend on the azimuthal angle $\phi$ and thus the polarization (and the optical axis with it) will be rotated by an applied electric field with only viscous resistance. We predict that this will generate
a remarkable experimental effect: the current sample shape will change in electric field so that the plane of the spontaneous shear (19) will rotate around layer normal as well. Surface anchoring of the director may lead to non-uniform configurations as rotation proceeds thereby giving a resistance. This however should be small, characteristic of that encountered in non crosslinked systems.

Another physical situation occurs when the sample is mechanically constrained. Let us consider the alignment of figure 2 where the displacements along the $\hat{y}$ axis is prohibited (by mechanical clamps, for example). This eliminates the components of deformation tensor: $\lambda_{yy} = 0$, $\lambda_{xy} = 0$, $\lambda_{yz} = 0$. The azimuthal position of the director is described by the orientation of the order parameter $\xi$. Any attempt to rotate this vector, by application of external torque, generates the corresponding deformation of the network, which is now made to remember its initial conformation. For the same reasons one should expect a dramatic decrease in the portion of a dielectric susceptibility $\chi$ of constrained liquid crystalline elastomers, which is determined by reorientation of permanent molecular dipoles.

Substituting above constraints into the free energy with the electric field term $-E_x P_x - E_y P_y$ we obtain the following results.

i) In the standard switching geometry, $E = E_y$, the relevant part of the free energy is

$$F = \text{Cte} - \frac{1}{2} Q_{12} \lambda_0^2 \cos^2 \phi + E P_s \cos \phi$$

where $\lambda_0 = (\alpha_0/Q_{12}) \theta$ and $P_s = \chi_1 \mu_0 \theta$ are the magnitudes of spontaneous shear deformation and polarization respectively. This corresponds to a threshold transition between the two states with $\phi = 0$ (polarization up in Fig. 2) and $\phi = \pi$ (polarization down). The material does not respond to an applied electric field until $E = E^* = Q_{12} \lambda_0^2 / P_s$ when it is forced into the state with the opposite polarization and relative deformation $\lambda_{xz} = -2 \lambda_0$ (with respect to the initial shape). The threshold field $E^*$ is not large as in the case of electric field effects in nematic elastomers [23, 24], but scales rather as $E^* \sim \theta$. The threshold field and the corresponding jump in mechanical state should be easily accessible to experiment.

ii) Consider the field $E = E_x$, that is applied perpendicular to the spontaneous polarization, figure 2. In this case the relevant part of the free energy is

$$F = \text{Cte} - \frac{1}{2} Q_{12} \lambda_0^2 \cos^2 \phi - E P_s \sin \phi.$$

There is thus a linear change in the azimuthal orientation of polarization in the layer plane (and of the optical axis of the sample), $\sin \phi = E P_s / (Q_{12} \lambda_0^2)$. The electric field rotates the
polarization until at \( E = E^* \) their orientations coincide (the same process takes place, in fact, for all orientations of \( \mathbf{E} \) in the layer plane). Let us note once again that the magnitude of this characteristic field, \( E^* \), should be linear in the smectic C order parameter \( \theta \) and in the crosslinking point density, \( N_z \), of the rubber:

\[
E^* = \frac{(\alpha_0^l)^2}{Q_{12}} \frac{\theta}{\chi_{\perp} \tilde{\mu}_p^l (1 - \chi_{\perp} \tilde{\mu}_0^l / Q_{12})}
\]

where we expect that both \( \alpha_0 \) and \( Q_{12} \) are proportional to \( N_z \).

6. Conclusions.

This paper gives a systematic group-theoretical analysis of the continuum free energy of basic liquid crystalline monodomain smectic elastomers. A variety of new macroscopic effects is generated by the interaction between the orientational (liquid crystalline) and translational (network) degrees of freedom in these unusual materials. Noncentrosymmetric (chiral) systems exhibit rich piezoelectric effects in response to both types of deformations. Many of the predicted effects are easily observable on experiment and some of them have been already reported in recent years.

The continuum description of this paper is essentially restricted to a case of infinitesimal translational deformations of a network, although in reality elastomers can withstand a very large strain. Only in section 2 a few relevant terms in the free energy of smectic A elastomer, proportional to the antisymmetric part of the strain tensor, are presented to illustrate some additional effects, relevant at higher values of \( \lambda \). It is important to emphasize, that in the general case this antisymmetric part \( \lambda^A \) is not directly related to a uniform body rotation of a sample and does contribute to a free energy at higher orders in \( \lambda \). This asymmetric elasticity of liquid crystalline elastomers is, however, a small effect at infinitesimal deformations — which is consistent with the microscopic interpretation of the couple-stress elasticity in solids. Let us note also, that phenomenological modelling of elastic effects at \( \lambda \sim 1 \) is virtually senseless and a consistent molecular theory, similar to [10, 11] for nematic elastomers, is needed in this case.

Another restriction, also imposed in order to reduce the number of considered effects and make the remaining results more clear, is the condition of the material incompressibility, \( \det[\Lambda] = 1 \). This is not a necessary condition in highly swollen elastomers — which is often the case in experiment. Allowing network compressibility would bring up additional, presumably observable, mechanical and polarizational effects, albeit at longer time scales associated with solvent exchange.

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Appendix.

Geometric considerations.

Much of the group theoretical analysis in this paper, especially that in the section 4, is familiar from the smectic C literature, but the application to strain \( \Lambda \) is new. We accordingly give some
background to expressions used in the text. In (iii) and (iv) we concentrate on geometrical interpretation of relative rotation coupling terms introduced in section 3.

(i) \( \nabla \Omega \rightarrow 3\Gamma_0 \oplus 3\Gamma_1 \) under the operations of the point group \( C_2 \). Both representations of \( \nabla \) and \( \Omega \) have the character of a vector \( V \) and one would expect from table I that \( \nabla \Omega \rightarrow V \otimes V = 5\Gamma_0 \oplus 4\Gamma_1 \). However, writing \( \nabla \Omega \) in full:

\[
\left( \frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z} \right) (\Omega_x, \Omega_y, \Omega_z) \equiv \left( \Gamma_{11}^V, \Gamma_{01}^V, \Gamma_{12}^V \right) \otimes \left( \Gamma_{11}^\Omega, \Gamma_{01}^\Omega, \Gamma_{11}^\Omega \right)
\]  

(24)

(taking the axis \( \bar{z} \) in the layer plane along the direction of polarization, the principal direction of \( C_2 \)), we see that certain combinations are eliminated. For instance \( \frac{\partial}{\partial z} \Omega_x \rightarrow \Gamma_1 \) is removed as \( \frac{\partial}{\partial z} \Omega_y \rightarrow \Gamma_0 \) and one of \( \frac{\partial}{\partial y} \Omega_x = -\frac{\partial}{\partial x} \Omega_y \rightarrow \Gamma_0 \) (in the latter, to avoid double counting).

(ii) \( \lambda \) and expressions involving \( \lambda^S \) are represented as \( 4\Gamma_1 \oplus 2\Gamma_2 \). Recall that under the operations of \( C_2 \) directions \( \bar{z}, \bar{c} \) transform as \( \Gamma_1 \) and the axis \( \vec{p} \rightarrow \Gamma_0 \). Diagonal elements \( \lambda_{pp}, \lambda_{zz} \) and \( \lambda_{cc} \) transform like \( \Gamma_0 \) (the latter two correspond to the operation \( \Gamma_1 \otimes \Gamma_1 \rightarrow (-1)^2 = 1 \)). Both directions of \( \lambda_{cc} \) are likewise \( \Gamma_1 \) and hence this is overall \( \Gamma_1 \). In contrast \( \lambda_{zp} \) and \( \lambda_{cp} \) involve \( \Gamma_1 \) and \( \Gamma_0 \) and are overall \( \Gamma_1 \). This structure is explicitly shown in (6). The chirality of these terms can be demonstrated from the odd number of coordinate directions involved. e.g.

in \( \lambda_{zz} \frac{\partial^2 u}{\partial p \partial c} \), which gives a sign change on inversion.

(iii) Equation (9), terms like \( \lambda \phi \): the nematic director (optical axis) is situated in the plane of \( \bar{z} \) and \( \bar{c} \). Imagine a cube of rubber with \( \bar{z}, \bar{c} \) and \( \vec{p} \) as three orthogonal edges. Shear deformations \( \lambda_{zp}^S \) and \( \lambda_{cp}^S \) extend cube diagonals that then lead to a rotation relative to \( n \) of the matrix. Terms in (9) can be thought of as cross terms in expressions like \( (\lambda_{zp}^S - \phi)^2 \) which penalize relative rotation of \( n \) and the matrix. In contrast \( \lambda_{zc}^S \) induces a rotation of \( n \) in the \( \bar{z} - \bar{c} \) plane, inducing therefore a change in the tilt angle \( \theta \), but not an azimuthal rotation \( \phi \). Hence the term \( \lambda_{zc}^S \phi \) is absent in (9) as it leads to an altogether different rotation about the axis \( \vec{p} \) (such a term, containing \( \Omega_p \), already exists in (8): \( \lambda_{zc}^S \frac{\partial u}{\partial c} \)). The group theoretical argument is quite straightforward, though less revealing than the geometrical one: \( \lambda_{zc} \rightarrow V_2 \otimes V_c = \Gamma_1 \otimes \Gamma_1 = \Gamma_0 \) but the azimuthal rotation angle \( \phi \equiv \Omega_z \rightarrow \Gamma_1 \) whereupon \( \lambda_{zc} \phi \rightarrow \Gamma_0 \otimes \Gamma_1 = \Gamma_1 \), that is, not an invariant under the group \( C_2 \).

(iv) Combinations with antisymmetric parts of strain \( \sim \lambda^A \Omega \), not addressed in the main text: such terms can be understood by example. \( \lambda_{cp}^A \) represents the rotation of a rubber matrix about \( \bar{c} \) and \( \frac{\partial u}{\partial \vec{p}} \) is a layer rotation about \( \bar{c} \). Inspection of figure 1 shows that \( \frac{\partial u}{\partial \vec{p}} \), a rotation about the \( \bar{c} \) axis, in effect also generates a rotation of the optical axis \( n \) about \( \bar{z} \). Hence there must be a coupling term \( \lambda_{cp}^A \frac{\partial u}{\partial \vec{c}} \) penalizing the rotation relative to that of the matrix. In contrast the same matrix rotation about \( \bar{z} \) (\( \lambda_{cp}^A \)) does not couple with \( \frac{\partial u}{\partial c} \) because, again, \( \frac{\partial u}{\partial c} \) rotates \( n \) about the axis \( \vec{p} \perp n \), not giving any azimuthal rotation in the plane. The coupling \( \lambda_{cp}^A \phi \) is entirely straightforward, deriving from the relative rotation about \( \bar{z} \), \( (\lambda_{cp}^A - \phi)^2 \). The coupling \( \lambda_{cp}^A \phi \) stems from the matrix rotation about \( \bar{c} \), which has an effect of rotating the tilted
director about $\tilde{z}$. The absence of analogous $\lambda^{\delta}_{zc} \frac{\partial u}{\partial c}$ and $\lambda^{\delta}_{zp} \frac{\partial u}{\partial p}$ is rather complicated. They are ruled out by the relative translation coupling $(u - U_z)^2$, which leads only to terms $\lambda^{\delta}_{zc} \frac{\partial u_1}{\partial c}$ and $\lambda^{\delta}_{zp} \frac{\partial u_1}{\partial p}$ already given in (8).

References