Piezoelectricity of chiral nematic elastomers

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Abstract. A molecular model of freely jointed chains of chiral monomers is developed to describe the piezoelectric effect in chiral nematic elastomers. The model, an extension of the neo-classical theory of nematic polymer networks, takes into account a chiral biasing of molecular alignment under shear which leads to induced polarisation if the monomers contain a transverse dipole moment. The resulting theory is fully non-linear in elastic deformations, in the spirit of ordinary rubber elasticity. The expansion to the highest order in small strains gives the three linear piezoelectric coefficients predicted by phenomenological models.

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1 Introduction

Liquid crystalline elastomers and gels – rubbery polymer networks with a spontaneously broken orientational symmetry – exhibit a number of unique physical effects and have been a subject of extensive study in recent years. Many different systems have been synthesised: side-chain nematic and smectic polysiloxanes and polyacrylates, as well as several main-chain nematic and smectic polymers, all crosslinked by a variety of methods. The review [1] gives a summary of this activity, together with theoretical concepts rationalising the observed physical properties. Most of the characteristic effects in liquid crystalline elastomers and gels are based on the coupling between their high rubber-elasticity and their orientational order, reflected in the shape anisotropy of polymer strands in the network. Resulting mechanical and optical properties become rich in non-linear behaviour, instabilities and spectacular anomalies.

A natural extension of this research is into polarisational properties of liquid crystalline elastomers. By analogy with their "parent" ordinary liquid crystals, one might expect interesting and potentially useful effects involving electric polarisation and external fields. In particular, chiral (non-centrosymmetric) materials have been known to exhibit important properties, such as a non-linear optical response and piezoelectricity. Indeed, after the theoretical prediction [2], piezoelectricity has been found in cholesteric side-chain elastomers [3,4] and in polydomain elastomers combining main-chain and side-chain mesogenic groups [5]. Curiously, although it has been later pointed out [6,7] that the original theoretical model [2] is incorrect, the physical effect of polarisation induced by

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mechanical deformation has been undeniable. Assuming that the cholesteric order (with its equilibrium helical texture being further altered by an external strain) is too complex for a clean separation of this new effect, a continuum theory [6] has been developed for an untwisted texture of cholesteric elastomer, a so-called "chiral nematic" state with a uniform director alignment. The resulting prediction for the linear piezoelectric polarisation takes the form

$$\mathbf{P} = \gamma_1\big[\hat{\mathbf{n}} \times (\underline{\underline{\varepsilon}} \cdot \hat{\mathbf{n}})\big] + \gamma_2\hat{\mathbf{n}}(\boldsymbol{\omega} \cdot \hat{\mathbf{n}}) + \gamma_3\boldsymbol{\omega} \ , \qquad (1)$$

where $\gamma_{1,2,3}$ are the phenomenological piezoelectric coefficients. Here $\mathbf{P}$ is the electric polarisation, $\hat{\mathbf{n}}$ the nematic director, $\varepsilon_{ij} = \frac{1}{2}\left[\partial_i u_j + \partial_j u_i\right]$ the symmetric elastic strain and $\boldsymbol{\omega} = \frac{1}{2}\mathrm{curl}\,\boldsymbol{u}$ the effective rotation vector corresponding to the antisymmetric part of strain. The last two terms in (1) describe the response to antisymmetric deformations applied to a uniaxial chiral material (note that the constant γ_3 would not vanish even in the isotropic phase). However, the non-trivial antisymmetric strain in isotropic bodies is at least cubic in deformation and these two terms do not describe the true linear piezoelectricity. This is not to say that their effect cannot be detected: elastomers and gels are capable of very large deformations where the mechanically non-linear piezoelectricity would generate a polarisation response, for instance at multiple frequencies of an oscillating mechanical input. Another aspect of antisymmetric deformations in nematic elastomers is the effect of relative rotation, the difference between the local rotation of an elastic matrix $\boldsymbol{\omega}$ and that of the director. In fact, only the difference $(\boldsymbol{\omega} - [\hat{\mathbf{n}} \times \delta\hat{\mathbf{n}}])$ is a valid independent elastic variable and one may expect it to produce a piezoelectric response due to the γ_2, γ_3 terms.
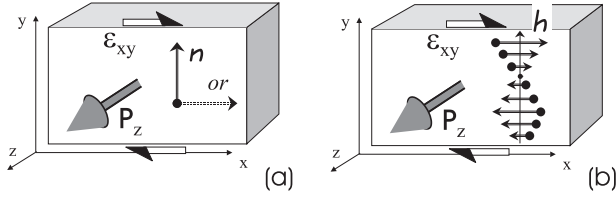
Fig. 1. A schematic representation of vectors and deformations in the first term of equations (1) and (2): (a) A chiral material with the uniform director along $\hat{x}$ or $\hat{y}$, symmetrically sheared in the $\hat{x}\hat{y}$ plane, generates a piezoelectric polarisation along the $\hat{z}$ axis. (b) A corresponding response of helically twisted cholesterics: when the shear is applied in the plane that includes the helical axis $\hat{\mathbf{h}}$, the polarisation is induced in the perpendicular direction.

Still, the most interesting is the first term (γ_1) in equation (1), which describes a linear piezoelectric polarisation induced in the direction perpendicular to a symmetric shear deformation in the plane that includes the (uniform) director $\hat{\mathbf{n}}$, see Figure 1a. Although not new from the symmetry point of view, such an effect has not been unambiguously identified in rubbery polymer materials. However, the model [6] has been erroneously extended into twisted cholesteric textures. The corrected version [7], which used the adequate coarse-graining of the sufficiently tight cholesteric helix, resulted in a similar expression for polarisation (in a slightly altered notation)

$$\mathbf{P} = \tilde{\gamma}_1\left[\hat{\mathbf{h}} \times (\underline{\underline{\boldsymbol{\varepsilon}}} \cdot \hat{\mathbf{h}})\right] + \tilde{\gamma}_2\hat{\mathbf{h}}(\boldsymbol{\omega} \cdot \hat{\mathbf{h}}) + \tilde{\gamma}_3\boldsymbol{\omega} \ . \qquad (2)$$

Here the unit pseudo-vector $\hat{\mathbf{h}}$ is the helix axis. These three terms correspond to a combination of entries in the original piezoeffect (1): $\tilde{\gamma}_1 \Rightarrow \gamma_1$, $\tilde{\gamma}_2 \Rightarrow -\gamma_2$, $\tilde{\gamma}_3 \Rightarrow (\gamma_2 + \gamma_3)$. However, the authors of [7] only considered an ordinary (non-chiral, microscopically centrosymmetric) flexoelectric effect as the mechanism for polarisation induced by deformations of a cholesteric helix. Since the flexoelectric effect depends on gradients of the director, their coefficients $\tilde{\gamma}_{1,2,3}$ were necessarily proportional to q_o, the wave number of cholesteric helix. The first term $\tilde{\gamma}_1$ describes the response to a symmetric shear deformation, which has been specifically examined in a subsequent experimental work [8]. However, it can hardly be clear what sort of complex internal deformation is occuring inside a helically twisted texture which is being sheared across the helix axis, Figure 1b. Therefore, even the conclusions about the magnitude of the observed effect may be unreliable. From both theoretical and experimental points of view it is important to return to the original picture of a uniform chiral-nematic texture and examine its unambiguous piezoelectric response to an appropriate set of uniform shear deformations.

All the existing theoretical models have the same deficiency: being essentially phenomenological, they cannot shed any light on the real microscopic processes that cause a mechanically induced disbalance of molecular dipoles, which produces the macroscopic piezoelectric polarisation. Also, they are confined to linear deformations, whereas the

experience of nematic rubber elasticity [1] has shown that most interesting and important effects take place in the regime of high (rubber) elasticity. This paper attempts to address this question and examine a simplest molecular model of freely-jointed chiral polymer chains, its conformation change under the elastic strain in the network and the resulting macroscopic piezoelectric effect. We thus derive a full non-linear expression for such polarisation, which takes a qualitative form

$$\mathbf{P} \simeq n_s \, d \, Q \, \Delta \, \left(\hat{\mathbf{n}} \cdot \underline{\underline{\boldsymbol{\lambda}}}\right) \cdot \left[\underline{\underline{\boldsymbol{\lambda}}}^T \times \hat{\mathbf{n}}\right], \qquad (3)$$

where $\hat{\mathbf{n}}$ is the nematic director and the deformation is described by the general (non-symmetric) Cauchy strain tensor $\underline{\underline{\boldsymbol{\lambda}}}$. The full expression (18) derived below includes the difference in orientations of director $\hat{\mathbf{n}}$ before and after the deformation, which may occur at large strains. Important factors of crosslinking density n_s, the nematic order parameter Q, the molecular dipole d and Δ, the dimensionless measure of the molecular chirality, determine the magnitude of this polarisation. On expansion to the linear order in small deformations ($\varepsilon = \lambda - 1$) we recover all three terms in equation (1) and determine the phenomenological piezoelectric coefficients $\gamma_{1,2,3}$. In particular, the important linear coefficient γ_1 is found as $\gamma_1 \simeq n_s d Q \Delta$, which gives a crude estimate $\gamma_1 \sim 10^{-4} - 10^{-5} \, \mathrm{C/m^2}$ for some typical values of elastomer parameters. This, combined with the low value of the elastic modulus ($\mu \sim 10^5 \mathrm{J/m^3}$), makes the equilibrium piezoelectricity in rubbers a very attractive effect for many applications. The main result of this paper, the fully non-linear piezoelectric polarisation, is given in Section 4; Section 5 describes the limit of linear elastic response deriving the equation (1). In the Conclusions we return to the experiment [8] and analyse its findings assuming they were due to a real piezoelectric effect as described in this paper.

2 Coupling of chirality and deformations

Before proceeding with statistical-mechanical calculations, we shall first discuss qualitative reasons for the mechanically induced disbalance of dipoles of chiral molecules. Molecular chirality has been discussed extensively in the past [9] and was the direct cause of several physical effects, such as the ferroelectricity in smectic C* [10]. For a molecule (chain monomer in our case) to be chiral one should be able to identify a dimensionless pseudoscalar parameter such as $(\hat{\mathbf{d}} \cdot [\hat{\mathbf{u}} \times \hat{\mathbf{v}}]) = \sin\Theta\cos\Psi$ in Figure 2. We shall see below that when such monomers are connected into a chain and one examines the orientational biasing induced by stretching such chains, the relevant mechanical parameter is $\Delta = (b/a)(\hat{\mathbf{d}} \cdot [\hat{\mathbf{u}} \times \hat{\mathbf{v}}])$, i.e. it also involves the geometric aspect ratio of a monomer.

Now let us consider a simple case when all three vectors are perpendicular, $\hat{\mathbf{u}} \perp \hat{\mathbf{v}} \perp \hat{\mathbf{d}}$, so that we consider only the transverse molecular dipole and the measure of the molecular chirality is now the length of the perpendicular spur (essentially, the $b\sin\Theta$ in Fig. 2), in comparison with the main mesogenic monomer length a. Let such
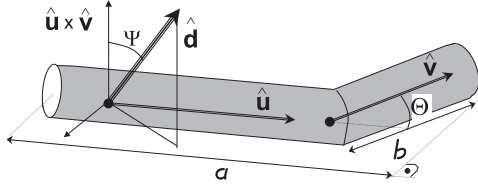
Fig. 2. A sketch of the chiral mesogenic molecule. The long molecular axis $\hat{\mathbf{u}}$ is the direction that couples to the nematic mean field. The steric dipole can be parametrised by another unit vector, $\hat{\mathbf{v}}$, not parallel to the principal axis. The molecule possesses an electric dipole in the direction $\hat{\mathbf{d}}$, non-coplanar with the pair of $\hat{\mathbf{u}}$-$\hat{\mathbf{v}}$.

monomers be connected into polymer chains, which are aligned with their main axes $\hat{\mathbf{u}}$ along the nematic director, see Figure 3a. Because the nematic order is uniaxial and quadrupolar, there is no preference in any particular orientation of $\hat{\mathbf{v}}$ (along the spur) or $\hat{\mathbf{d}}$, represented by dots and crosses, in or out of the page in Figure 3a. Suppose all such chains are crosslinked into the network so that a shear deformation, as in Figure 3b, causes a corresponding chain stretching at an angle to the nematic director. Asymmetric monomers are now forced to accommodate the deformation and they can do it by aligning the *monomer* end-to-end vector $a\,\hat{\mathbf{u}} + b\,\hat{\mathbf{v}}$ along the diagonal in Figure 3b. If at the same time they are kept aligned with their long axes $\hat{\mathbf{u}}$ along the nematic director, the orientation of vectors $\hat{\mathbf{v}}$ becomes biased. This is a purely geometric argument having nothing to do with chirality. However, if the monomers are chiral with transverse dipole moments as in Figure 3, the orientation of these moments becomes biased as well, *i.e.* there is a net polarisation induced in the direction perpendicular to the plane of $\hat{\mathbf{n}}$ and the shear. A counterside of this argument is that if the director is allowed to rotate freely, according to the imposed strain, there would be no biasing and no polarisation. A regime when nematic elastomer is allowed unrestricted director rotation under strain is called "soft deformation" (see [1] for detail). We shall indeed find in the explicit calculation below that all soft elastic deformations result in the zero piezoelectric response.

This picture serves to convince oneself that a chiral rubbery network stretched in the direction oblique to $\hat{\mathbf{n}}$ can generate a polarisation in the direction perpendicular to both the extension and the nematic director – as in fact shown in Figure 1a. We should expect that the degree of biasing is proportional to the monomer aspect ratio (b/a) and to the transverse component of molecular dipole, *i.e.* to the chiral parameter Δ. In the body of this paper we shall explicitly calculate the effect expressed pictorially in Figure 3. We use the freely jointed chain model, ignoring many possibly important effects of monomer interactions and correlations along the chain. However, being the first molecular-statistical model of chiral elastomers, this model has a benefit of extreme conceptual simplicity. We hope its results will help to identify the relevant parameters and properties of true piezoelectric effect in rubbers.
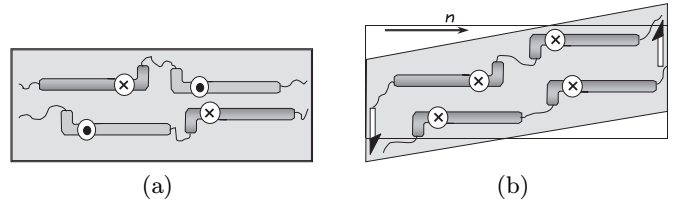

Fig. 3. When an imposed shear stretches the chains of L-shaped monomers, preserving the nematic alignment $\hat{\mathbf{n}}$, their conformation becomes biased [from (a) to (b)]. When the monomers are chiral, *i.e.* there is a consistent sign in the parameter Δ, the transverse molecular dipoles align preferentially (crosses show dipoles into the page). This sketch is analogous to the famous image of ferroelectric smectic C*, by Meyer, with molecules represented as "fish" with dipole moments pointing out of their eyes [11].

3 Statistics of freely jointed chains

Ignoring the monomer pair interactions and taking into account the nematic order *via* the mean-field potential, the only relevant macroscopic variable for a polymer chain is its end-to-end distance $\mathbf{R}$. The chain free energy is purely entropic and is determined by the statistical weight of N connected monomers under the constraint of fixed $\mathbf{R} = \sum_{s=1}^{N} \left(a\,\hat{\mathbf{u}}_s + b\,\hat{\mathbf{v}}_s \right)$. Note the appearance of the perpendicular vector $\hat{\mathbf{v}}$ with the small $(b \ll a)$ length of the spur for each monomer, as in Figure 3a. Since we are interested in polarisational effects, another constraint has to be taken into account: the total dipole moment of a chain is $\mathbf{p} = \sum_{s=1}^{N} \mathbf{d}_s \equiv \sum_{s=1}^{N} \left(d_\parallel \hat{\mathbf{u}}_s + d_\perp \hat{\mathbf{v}}_s + d_t [\hat{\mathbf{u}} \times \hat{\mathbf{v}}] \right)$. The qualitative discussion above (and, in fact, the explicit calculation) confirms that the only relevant component of molecular dipole is the transverse d_t, the projection of $\mathbf{d}_s$ on the direction perpendicular to both $\hat{\mathbf{u}}$ and $\hat{\mathbf{v}}$.

We now write the statistical weight of a freely jointed chain with N monomers:

$$W[\mathbf{R}, \mathbf{p}] = \int \mathcal{D}\hat{\mathbf{u}}\mathcal{D}\hat{\mathbf{v}}\, \delta\left(\mathbf{R} - \sum_{s=1}^{N} \left[a\,\hat{\mathbf{u}}_s + b\,\hat{\mathbf{v}}_s \right] \right) \quad (4)$$

$$\cdot \delta\left(\mathbf{p} - \sum_{s=1}^{N} d_t [\hat{\mathbf{u}}_s \times \hat{\mathbf{v}}_s] \right) \prod_s f[\hat{\mathbf{u}}_s],$$

where the probablity distribution $f[\hat{\mathbf{u}}]$ is determined by the nematic mean field potential, $f \sim \exp\left[J(\hat{\mathbf{u}} \cdot \hat{\mathbf{n}})^2 \right]$. The integrals over the unit vectors $\hat{\mathbf{u}}_s$ and $\hat{\mathbf{v}}_s$ are further constrained by the condition that $\hat{\mathbf{u}}_s \perp \hat{\mathbf{v}}_s$ at each monomer. As usual, we shall not require the explicit form of this probability, but simply use the uniaxial average results, such as

$$\langle \hat{u}_s^\alpha \hat{u}_s^\beta \rangle = \frac{1}{3}(1 - Q)\delta_{\alpha\beta} + Q n_\alpha n_\beta \ \equiv \frac{1}{3a}\ell_{\alpha\beta}, \quad (5)$$

where the anisotropic chain step-length tensor is introduced in the last equation. This tensor describes the equilibrium anisotropic shape of nematic polymers *via*

the average end-to-end distance: $\langle R^\alpha R^\beta \rangle = \frac{1}{3}aN\ell_{\alpha\beta}$; $\ell_{\alpha\beta} = \ell_\perp \delta_{\alpha\beta} + [\ell_\parallel - \ell_\perp]n_\alpha n_\beta$.

The evaluation of statistical weight $W[R,P]$ is fairly straightforward and is usually done by exponentiating the delta-functional constraints:

$$W[\mathbf{R},\mathbf{P}] = \int d\boldsymbol{\psi} d\boldsymbol{\phi} \, e^{i\boldsymbol{\psi}\cdot\mathbf{R}+i\boldsymbol{\phi}\cdot\mathbf{P}} \int \prod_s d\hat{\mathbf{u}}_s d\hat{\mathbf{v}}_s \, f[\hat{\mathbf{u}}_s]$$
$$\times \, e^{-i\sum_s (a\,\boldsymbol{\psi}\cdot\hat{\mathbf{u}}_s + b\,\boldsymbol{\psi}\cdot\hat{\mathbf{v}}_s + d_t\boldsymbol{\phi}\cdot[\hat{\mathbf{u}}_s\times\hat{\mathbf{v}}_s])}. \quad (6)$$

Expanding the exponential in power series, one is looking for appropriate pairings of variables $\hat{\mathbf{u}}$ and $\hat{\mathbf{v}}$ which produce the nonzero results after averaging. One such combination comes from the second-order term

$$-\frac{1}{2}a^2 \sum_{s,t} \langle \hat{u}_s^\alpha \hat{u}_t^\beta \rangle \psi_\alpha \psi_\beta, \quad (7)$$

another from the analogous second-order term

$$-\frac{1}{2}b^2 \sum_{s,t} \langle \hat{v}_s^\alpha \hat{v}_t^\beta \rangle \psi_\alpha \psi_\beta, \quad (8)$$

the third – from another square, but this time involving the auxilliary field to the dipole moment

$$-\frac{1}{2}d_t^2 \sum_{s,t} \langle [\hat{\mathbf{u}}_s \times \hat{\mathbf{v}}_s]^\alpha [\hat{\mathbf{u}}_t \times \hat{\mathbf{v}}_t]^\beta \rangle \phi_\alpha \phi_\beta \quad (9)$$

and the most important new contribution arises from the third-order cross term

$$i\,abd_t \sum_{s,t,w} \langle \hat{u}_s^\alpha \hat{v}_t^\beta [\hat{\mathbf{u}}_w \times \hat{\mathbf{v}}_w]^\gamma \rangle \psi_\alpha \psi_\beta \phi_\gamma. \quad (10)$$

One can easily check that higher powers of this series produce much smaller results, due to the increasing power of $1/N$. The first of the four relevant contributions, equation (7), is the main source of chain configurational entropy and produces the anisotropic Gaussian distribution $W[R]$. The second equation (8) generates a small correction to this Gaussian: on averaging the perpendicular vectors we obtain $\langle \hat{v}^\alpha \hat{v}^\beta \rangle = \frac{1}{2}(\delta_{\alpha\beta} - \hat{u}^\alpha \hat{u}^\beta)$, the perpendicular projection operator, which generates another even-order in $\hat{\mathbf{u}}$ term analogous to (7) but with the small prefactor $(b/a)^2$. The third equation (9), which also requires a use of the projection operator, results in the contribution to the entropic free energy proportional to the anisotropic dielectric susceptibility term $\sim \frac{1}{2\chi}P^2$. The evaluation of equation (10) requires a delicate analysis of products of mutually perpendicular vectors and results in the compact expression $\frac{1}{2}iNabd_tQ(\hat{\mathbf{n}}\cdot\boldsymbol{\psi})(\hat{\mathbf{n}}\cdot[\boldsymbol{\psi}\times\boldsymbol{\phi}])$.

The next step is the evaluation of integrals over auxilliary fields by the steepest descent method. Equation (6) transforms into

$$W = \int d\boldsymbol{\psi} d\boldsymbol{\phi} \, e^{\{i\boldsymbol{\psi}\cdot\mathbf{R}-\frac{1}{6}aN\boldsymbol{\psi}\underline{\underline{\ell}}\boldsymbol{\psi}\}} e^{\{i\boldsymbol{\phi}\cdot\mathbf{p}-\frac{1}{6}N\boldsymbol{\phi}\underline{\underline{\kappa}}\boldsymbol{\phi}\}} \quad (11)$$
$$\times \left(1 + \frac{1}{6}iNbd_t \, \tilde{\ell}_{\alpha\beta} \, \epsilon_{\beta\gamma\delta} \, \psi_\alpha \psi_\gamma \phi_\delta\right),$$

where the parameters of Gaussian exponential terms are given by the uniaxial matrices

$$\tilde{\ell}_{\alpha\beta} = \tilde{\ell}_\perp \delta_{\alpha\beta} + [\tilde{\ell}_\parallel - \tilde{\ell}_\perp]n_\alpha n_\beta \quad (12)$$

$$\kappa_{\alpha\beta} = \frac{1}{2}d_t^2 \left[(2+Q)\delta_{\alpha\beta} - 3Q\,n_\alpha b_\beta\right] \quad (13)$$

with

$$\tilde{\ell}_\perp = a\left[1 - Q + \frac{1}{2}(b/a)^2[2+Q]\right]$$
$$\tilde{\ell}_\parallel = a\left[1 + 2Q + (b/a)^2[1-Q]\right].$$

We shall often find it appropriate to neglect the small and qualitatively irrelevant $\left(\frac{b}{a}\right)^2$ corrections to $\tilde{\ell}$ and use the "old" step lengths $\ell_\parallel$ and $\ell_\perp$ instead, with their ratio $r = \ell_\parallel/\ell_\perp$ being the only essential parameter defining the nematic rubber elasticity. By analogy, one can examine the ratio of parameters $\kappa_\parallel/\kappa_\perp$ and find that $\kappa_\parallel/\kappa_\perp = 2/(1+r)$, perhaps not surprisingly decreasing with increasing prolate anisotropy r.

The integrals in equation (11) are evaluated at the saddle points

$$\boldsymbol{\psi}^* = i\frac{3}{aN}\underline{\underline{\ell}}^{-1}\cdot\mathbf{R} + ... \; ; \quad \boldsymbol{\phi}^* \approx i\frac{3}{N}\underline{\underline{\kappa}}^{-1}\cdot\mathbf{p} + ... \quad (14)$$

There are small corrections to these saddle points which, however, can be shown [12] not to contribute to the final free energy at leading order. Equally, the normalisation of the statistical weight W only contributes to an irrelevant renormalisation of dielectric susceptibility.

The resulting optimal statistical weight is Gaussian in both end-to-end distance and dipole moment, with a small chiral correction $\sim \mathbf{R}\,\mathbf{R}\,\mathbf{p}$. At this stage it is convenient to transform from the dipole moment to the polarisation $\mathbf{P}$, an intensive variable. Assuming we have a polymer melt, not a solution, the polarisation $\mathbf{P}$ is given by the total dipole moment per unit volume, $\mathbf{P} = \mathbf{p}/(Nv_o)$, with v_o the monomer volume. The resulting (entropic) free energy of a chosen chain, $F_c[R,P] = -k_BT\ln W$, takes the form

$$\frac{F_c}{k_BT} \approx \frac{3}{2aN}\left(\mathbf{R}\cdot\underline{\underline{\ell}}^{-1}\cdot\mathbf{R}\right) + \frac{3Nv_o^2}{2}\left(\mathbf{P}\cdot\underline{\underline{\kappa}}^{-1}\cdot\mathbf{P}\right) \quad (15)$$
$$- \frac{9v_o}{2N}\frac{b}{a^2}d_t\left(\underline{\underline{\kappa}}^{-1}\cdot\underline{\underline{\epsilon}}\cdot\underline{\underline{\ell}}^{-1}\right)\mathbf{R}\,\mathbf{R}\,\mathbf{P},$$

where we have ignored the normalisation terms, which do not depend on either $\mathbf{R}$ or $\mathbf{P}$, and higher order terms such as R^4 or R^2P^2.

The entropic free energy of a freely jointed chain of chiral mesogenic monomers with transverse dipole moments, equation (15), has all the features one might expect. In the lowest, Gaussian approximation it behaves as a Hookean spring in response to stretching its ends ($F \sim R^2$) and it has a dielectric susceptibility part $F \sim \frac{1}{2\chi}P^2$, both effects appropriately uniaxial in the nematic phase. The chiral coupling between the chain stretching and its net dipole moment, which has a qualitative form $F \sim (\hat{\mathbf{n}}R)(\hat{\mathbf{n}}[R \times P])$, is a novelty: it expresses the effect depicted in Figure 3b and is the basic source of piezoelectricity in chiral anisotropic rubbers.

4 Quenched average for a deformed network

Classical rubber elasticity theory finds the free energy of a network strand connecting two crosslinks, a distance $\mathbf{R}$ apart. In our case this is given by equation (15). The initial distribution of strands by lengths and orientations of their end-to-end vectors established at the network formation is topologically frozen for the rest of the network life. Such a rubbery network resists deformations because connected crosslinking points, that we consider to move affinely with (in geometrical proportion to) the body, change their separation to $\mathbf{R}' = \underline{\underline{\lambda}} \cdot \mathbf{R}$ and thereby lower the configurational freedom of the connecting chain. The entropy then falls and the free energy rises. Finding the total free energy increase means the quenched averaging of the deformed-chain free energy with the statistical weight $W[R_0]$ at network formation.

Performing the quenched average with the Gaussian distribution $W[R_0]$ is straightforward, even in the uniaxial nematic case and with the addition of new terms with polarisation. The average rubber-elastic free energy, per network strand of N monomers is, therefore, $F_s = \langle F_c \left[\underline{\underline{\lambda}} \mathbf{R}_0, \mathbf{P} \right] \rangle_{W[R_0]}$. Multiplying F_s by the number of network strands per unit volume, n_s which is proportional to the crosslinking density of the elastomer $[n_s \simeq (N v_o)^{-1}]$, we obtain the free energy density of a piezoelectric rubber:

$$f = \frac{1}{2} n_s k_B T \mathsf{Tr} \left(\underline{\underline{\ell}}^{-1} \underline{\underline{\lambda}} \, \underline{\underline{\ell}}_0 \underline{\underline{\lambda}}^T \right) + \frac{1}{2} \, \mathbf{P} \, \underline{\underline{\chi}}^{-1} \mathbf{P} \qquad (16)$$
$$+ \frac{3}{2} n_s k_B T \, v_o \, \frac{b d_t}{a} \, \left(\underline{\underline{\ell}}^{-1} \underline{\underline{\lambda}} \, \underline{\underline{\ell}}_0 \underline{\underline{\lambda}}^T \right)_{ij} \epsilon_{ijk} \, \kappa_{kl}^{-1} P_l$$

where we used the average $\langle R_0^\alpha R_0^\beta \rangle = \frac{1}{3} a N \ell_0^{\alpha\beta}$, which depends on the nematic director orientation $\hat{\mathbf{n}}_0$ at network formation. The first term is the neo-classical nematic rubber-elastic energy [1]. The second, dielectric term defines the entropic part of relevant (transverse) susceptibility $\underline{\underline{\chi}} = \frac{1}{3k_B T v_o} \underline{\underline{\kappa}}$,

$$\chi_{\alpha\beta} = \frac{d_t^2}{6 k_B T v_o} \left[(2+Q)\delta_{\alpha\beta} - 3Q \, n_\alpha b_\beta \right]. \qquad (17)$$

Interestingly, the new chiral coupling between the elastic strains and the induced polarisation (the full non-linear piezoelectricity) in equation (16) is reduced to a compact form, which shows that the polarisation is determined by the antisymmetric part of exactly the same combination of strains and orientations that enters into the nematic rubber elasticity. The equilibrium value of this induced polarisation is, after minimisation of the free energy density,

$$P_k = -\frac{1}{2} n_s \left(\frac{b d_t}{a} \right) \epsilon_{kij} \left(\underline{\underline{\ell}}^{-1} \underline{\underline{\lambda}} \, \underline{\underline{\ell}}_0 \, \underline{\underline{\lambda}}^T \right)_{ij}. \qquad (18)$$

This represents the full non-linear piezoelectric polarisation induced by elastic strains in a chiral nematic elastomer or gel network. It is a local expression, in which the initial uniform orientation of the nematic director $\hat{\mathbf{n}}_0$ (a principal axis of $\underline{\underline{\ell}}_0$) can be rotated by the strains to the new orientation $\hat{\mathbf{n}}$ (represented by $\underline{\underline{\ell}}$). It is quite obvious that in the isotropic phase this expression gives zero, because when both $\underline{\underline{\ell}}$ and $\underline{\underline{\ell}}_0$ are unit matrices one obtains $P_k \sim \epsilon_{kij} (\underline{\underline{\lambda}} \, \underline{\underline{\lambda}}^T)_{ij}$, a vanishing product of symmetric and antisymmetric matrices.

The main strength of neo-classical theory of rubber elasticity [1] is that it does not depend on any specific model of polymer chain forming the network. Apart from the standard rubber energy scale, given by the shear modulus $\mu = n_s k_B T$, everything else depends only on the dimensionless ratio $r = \ell_\parallel / \ell_\perp$ of backbone chain step lengths – a quantity that can be independently measured. The richness of nematic rubber elasticity stems from the uniaxial symmetry and the mobility of director $\hat{\mathbf{n}}$, the principal axis of matrices $\underline{\underline{\ell}}$, i.e. in the fact that $\underline{\underline{\ell}}$ after deformation can be different from $\underline{\underline{\ell}}_0$ before ($\hat{\mathbf{n}} \neq \hat{\mathbf{n}}_0$).

The piezoelectric polarisation (18) exhibits a similar universality. The only additional parameter it depends on is $(b d_t / a)$. If we recall that d_t is the projection of molecular dipole moment $\mathbf{d}$ on the direction $[\hat{\mathbf{u}} \times \hat{\mathbf{v}}]$, this parameter can be re-written as $|d|\Delta$, where the dimensionless quantity Δ is the relevant measure of molecular chirality and mechanical bias of each monomer. It can be determined independently, theoretically or experimentally (see [9], for instance). We then conclude that the piezoelectric polarisation of chiral nematic elastomers depends linearly on the crosslinking density n_s, molecular dipole d and the pseudo-scalar measure of chirality Δ. The dependence on nematic order parameter Q is different for different strain geometries.

5 Linear piezoelectricity at small deformations

Equation (18) for the piezoelectric effect in a chiral nematic elastomer contains all the relevant features of this phenomenon. One should expect a great variety of new physical effects at large deformations. However, one of our purposes here was to derive the first consistent microscopic model for the linear piezoelectricity, equation (1), and in particular the coefficient γ_1.

The limit of small (linear) deformations is determined by two conditions. First, one writes the Cauchy strain tensor as $\lambda_{ij} = \delta_{ij} + \varepsilon_{ij}$, where the (non-symmetric) deformation tensor $\underline{\underline{\varepsilon}}$ is assumed small. Secondly, we need to disallow independent director rotation during this deformation (because the difference between $\hat{\mathbf{n}}$ and $\hat{\mathbf{n}}_0$ is itself proportional to at least the first power of ε), so that the step length tensors $\underline{\underline{\ell}}$ and $\underline{\underline{\ell}}_0$ are identical. We then obtain, after expansion to linear order,

$$\epsilon_{kij} \left(\underline{\underline{\ell}}^{-1} \underline{\underline{\lambda}} \, \underline{\underline{\ell}} \, \underline{\underline{\lambda}}^T \right)_{ij} = -\frac{r-1}{r} \epsilon_{kij} \left(n_i n_l \varepsilon_{lj} + r \, n_i n_l \varepsilon_{lj}^T \right).$$

After replacing the deformation tensor by the sum of its symmetric and antisymmetric parts, $\varepsilon_{kl} = \varepsilon_{kl}^S + \epsilon_{ikl}\omega_i$, and some straightforward algebra one obtains the linear

piezoelectric polarisation

$$\mathbf{P} \approx -\frac{1}{2}n_s \left(\frac{bd_t}{a}\right)\frac{r-1}{r} \tag{19}$$
$$\cdot\left[(r+1)\left[\hat{\mathbf{n}}\times\underline{\underline{\varepsilon}}^S\cdot\hat{\mathbf{n}}\right] - (r-1)\left[\hat{\mathbf{n}}\times[\boldsymbol{\omega}\times\hat{\mathbf{n}}]\right]\right].$$

The anisotropy of polymer chains can also be expressed by the backbone order parameter Q (proportional to the main nematic order, but often much smaller as in side-chain mesogenic polymers), see equation (12). At small Q we have $(r-1)\approx 3Q$ and the three linear piezoelectric coefficients of equation (1) take the form

$$\gamma_1 = -\frac{1}{2}n_s\left(\frac{bd_t}{a}\right)\frac{r^2-1}{r} \simeq -3n_s\left(\frac{bd_t}{a}\right)Q\;; \tag{20}$$

$$\gamma_2 = -\gamma_3 = -\frac{1}{2}n_s\left(\frac{bd_t}{a}\right)\frac{(r-1)^2}{r} \simeq -\frac{9}{2}n_s\left(\frac{bd_t}{a}\right)Q^2.$$

Let us remember that in deriving the linear piezoelectric polarisation (19) we assumed that the nematic director is immobile in the first approximation. This is the reason the linear antisymmetric strains $\underline{\underline{\varepsilon}}^A = \underline{\underline{\varepsilon}}\cdot\boldsymbol{\omega}$ find their way into the effect: the normally physically relevant relative rotation between the elastic network and the nematic director reduces to $\boldsymbol{\omega}$ at constant $\hat{\mathbf{n}}$. A notable fact is that none of the three coefficients survives in the isotropic phase, at $Q = 0$. This should not be surprising because the physical meaning and the relevance of ω in the absence of nematic order changes. An adequate molecular theory of piezoelectric response of an isotropic chiral rubber requires a much more detailed model and will be the subject of a separate work.

6 Conclusion

This paper describes an ultimately simple molecular model that combines the chirality of monomers with their uniaxial alignment in the nematic phase and their connectivity into polymer strands of a rubbery network. The geometric concept of shear-induced disbalance of transverse molecular dipoles is summarised in Figure 3. The calculations that follow produce the fully non-linear piezoelectric polarisation in response to (possibly large) deformations of nematic rubber. In analysing Figure 3 one should not put any specific relevance into the main-chain arrangement of mesogenic units. The picture serves to make clear the symmetries and geometric preconditions involved in the effect. A majority of liquid crystalline elastomers and gels produced so far are, in fact, of side chain mesogenic polymers which are also well-described by the neo-classical theory of nematic rubber elasticity. Without any loss of generality one can devise a sketch for a chiral side-chain mesogenic monomer, with mechanical asymmetry and perpendicular dipole d_t, see for instance Figure 4. Chaining such monomers together and applying a shear strain as in Figure 3b would result in the coherent biasing of transverse dipoles. On the level of present model the only dif-
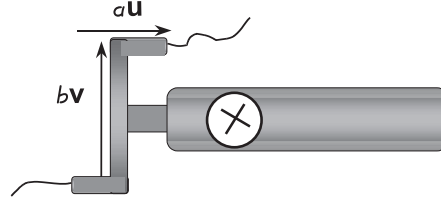

Fig. 4. An example of chiral mesogenic side-group monomer with transverse dipole moment into the page. The parameter Δ is the same as in the main text but, possibly, of a different magnitude due to a different meaning of b/a. Note that oblate and prolate polymer backbone is achieved in this model by having b/a greater or less than one.

ference between main and side-chain polymers is in the magnitude of the chain anisotropy $r = \ell_\parallel/\ell_\perp$: it has been reported $r \geq 1.5$ in different side-chain polymers (which means that the induced backbone anisotropy is not very large, $Q \sim 0.2$, say), but neutron scattering shows it may be a very large quantity in a main-chain nematic polymer, $r \simeq 10{-}70$ [13].

Another common practice is to induce chirality by diluting the polymer (or swelling the gel network) in a chiral solvent. Our simple model applies to this case equally well, with a slightly altered meaning of parameter Δ. Naturally non-chiral monomers do not possess a dipole $d_t = d[\hat{\mathbf{u}}\times\hat{\mathbf{v}}]$ and, therefore, the mechanical deformation cannot produce a polarisation. However, in a local field created by chiral solvent the monomers would acquire an induced chirality, due to the molecular polarisability (see [14], for instance). This solvent-induced chirality can be viewed as an induced d_t. Its value has to be determined by the analysis of polymer and solvent polarisabilities, but the theory of piezoelectric effect presented here remains fully applicable.

The main piezoelectric coefficient in equation (18) can be expressed as $\gamma \simeq n_s d\Delta$, times an appropriate power of the backbone order parameter Q, see (20). In making quantitative predictions we should recall that the crosslinking density n_s is also a factor in the rubber modulus, so the one can estimate it as $n_s \sim 10^{25}$ m^{-3} (at room temperature and for the typical modulus $\mu \sim 10^5$ J/m^3). Let us take the molecular dipole $d \sim 1e\cdot 1$ Å $\sim 10^{-29}$ C m, which may turn out to be a significant underestimate. Let us also take $Q \sim 0.5$ because clearly this does not affect the overall estimate significantly (unless $Q = 0$ or a very strongly anisotropic main-chain polymer is considered). The rest depends on the scalar dimensionless parameter of molecular chirality $\Delta \sim (b/a)\sin\Theta\cos\Psi$ in Figure 2. Let us, for the sake of argument, take $Q\Delta \sim 0.1$ although in a real system this may turn out to be either much smaller, or *vice versa* – closer to or even greater than unity. We then arrive at a very crude estimate $\gamma \sim 10^{-5}$ C/m^2.

In the experimental study [8] the setup was exactly that of Figure 1b with a simple shear applied across the cell of thickness $L_y = 20~\mu$m (along $\hat{\mathbf{y}}$ direction, $\varepsilon = u_y/L_y$) and the voltage was measured between

the plates of a large parallel capacitor with $C = 20$ nF. The charge was created between the z-faces of the cell of dimensions $L_x = L_z \approx 10$ mm. We have explained in the Introduction that the physical mechanisms behind the polarisation induced by highly nonuniform deformations of cholesteric helix [8] are ambiguous (in particular, there should be a large contribution from ordinary flexoelectric effect). However, let us estimate the slope of the experimentally measured voltage $vs.$ displacement, assuming the polarisation was induced by the real piezoelectric effect described here. The total charge induced on the chosen faces of the sample is $q = P_z(L_x L_y) = \gamma \varepsilon L_x L_y$. The voltage is then $V = q/C = (\gamma L_x/C)\, u_y$. Taking the above estimate of piezocoefficient γ, the slope of the $V(u)$ plot should be ~ 5 V/m. This is remarkably close to the experimental value one extracts from Figure 3 of [8]. Before rejoicing, however, let us remember that many factors could influence both theoretical and experimental result (not the least, the response at a high frequency may be very different from the equilibrium results of this paper).

Notwithstanding these uncertainties, we have raised the unusual possibility of a polarisation response in rubber, an amorphous material with high internal mobility and low modulus, capable of very large deformations.

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