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Mechanic and electromechanic effects in biaxially stretched liquid crystal elastomers

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The effect of combined electromechanic force fields in nematic side chain liquid crystal elastomers will be analyzed. A biaxially stretched plate in the x- and y-directions under an electric field applied in the perpendicular direction to the plate will be considered. A neo-Hookean model is chosen, which implies Gaussian behaviour. Results are obtained for both a soft and semisoft case showing the effect of the electric field on the rotation of the director and the free energy density function. © *2013 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4790154]

When a slab of a nematic side chain liquid crystal elastomer (NSCLCE) is uniaxially stretched perpendicularly to the initial direction of the director, this one tends to rotate. Then, the soft elasticity phenomenon appears.[1] It gives rise in the stress-strain curve to a plateau with zero slope, which indicates zero shear modulus; in this zone, no energy cost exists. In contrast, in the case of random copolymers or materials showing either anisotropy or compositional fluctuations, the soft behaviour is lost. In this case, only a part of the free energy of deformation of the conventional elastomers is needed to perform the complete rotation of the director and then the so-called semi-softness behaviour appears. In the zone corresponding to the rotation of the director, the stress-strain curve exhibits no zero slope but a positive one.

In contrast, the biaxially stretched slab case has not received a parallel attention. This is probably due to the inherent technical difficulties to apply two pair of equal stretches to the elastomer. However, the analysis of biaxial stretching slabs of nematic liquid crystals still leads to interesting results. Moreover, the effect of an electric field applied perpendicular to the two stretched direction can also reveal interesting facts.

In the present study, a neo-Hookean model is chosen, which implies: (a) Gaussian behaviour and (b) the system has been oriented before the crosslinking step is done.[2] To give account of the non linear elastic behaviour of the NSCLCE, a neoclassical model has been proposed and expressed in terms of the so-called Trace formula by Bladon, Terentjev, and Warner[1] to represent the free energy of deformation. The model can be conveniently modified for the case of semi-soft behaviour.

Of course, the aforementioned option is not the only possible one. For example, Brand *et al.*[3] proposed a nonlinear macroscopic model, which is in fact an extension of an early idea by de Gennes[4] and which captures the essential facts experimentally observed.[5]

Having these premises in mind, slabs of NSCLCE equibiaxially stretched in the x- and y-directions are analyzed in the four following situations: no electric field applied for the (a) soft elastic case and (b) semisoft case, and an applied electric field perpendicular to the two stretching directions for (c) soft elastic case and (d) semisoft case. It is assumed that the material has been previously prepared in such a way that the director was aligned in a direction perpendicular to the slab and parallel to the electric field if applied, that is, along to the z-axis (Figure 1). In this way, the electric field should enter in energetic competition with the mechanical force field represented by the two pairs of biaxial deformations.

For our purposes, it is noteworthy that the clamps, through which the stretch is imposed to the sample, impede shear strain in their proximity. Then, concomitantly with the soft or semisoft modes of deformation, a microstructure in the form of stripe domains is developed as the usual way of deformation of these materials.[5,6] This reveals a compromise between the soft or semisoft deformation and the constraining boundary conditions. From a structural point of view, the appearance of stripe domains corresponds to a like-smectic phase mechanically induced from the nematic one. The theoretical aspects of this problem have been addressed by DeSimone *et al.*[7–9] via a process of quasiconvexification of the free energy of deformation by using variational techniques associated to phase transitions in crystalline solids. In any case, it should be taken into account that the appearance of shears and striping structures should be a general phenomenon, which is not necessarily an indication of semisoft elasticity.

Let us assume the following expression for the mechanical free energy of a neo-Hookean anisotropic liquid crystal nematic elastomer:[10]

$$F_m = \frac{\mu}{2}\left(\mathrm{tr}\mathbf{B_e} + \alpha\,\mathrm{tr}(\mathbf{C}\mathbf{I_0^{-1}})\right), \tag{1}$$

where μ is an elastic coefficient, tr represent the trace, $\mathbf{B} = \mathbf{F}\mathbf{F}^\mathbf{T}$ and $\mathbf{C} = \mathbf{F}^\mathbf{T}\mathbf{F}$ are, respectively, the left and right Cauchy-Green tensors, where $\mathbf{F}$ is the deformation gradient, $\mathbf{B_e} = \mathbf{l}^{-1/2}\mathbf{F}\mathbf{F}^\mathbf{T}\mathbf{l}^{-1/2}$, $\mathbf{l_0} = \mathbf{l}(\mathbf{n_0})$, where $\mathbf{n_0}$ is the initial mesogens alignment, $\mathbf{l} = a^{2/3}\mathbf{n}\otimes\mathbf{n} + a^{-1/3}(\mathbf{I} - \mathbf{n}\otimes\mathbf{n})$, where $\mathbf{n}$ is the direction of the mesogens after alignment, a is the ratio of effective step lengths, and α gives account of the

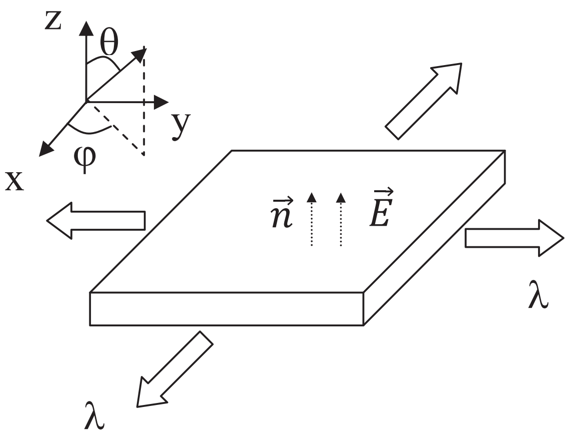

FIG. 1. Equibiaxially stretched plate samples in the x- and y-directions under an electric field in the z-direction.

anisotropy of the samples thus introducing semisoftness. The tensor $\mathbf{n}\otimes\mathbf{n}$ describes the liquid crystal order and is directly related to the de Gennes order tensor $\mathbf{Q}$. Equation (1) has been previously proposed by DeSimone *et al.*[11] The first term on the right hand side of Eq. (1) is a modified version of the trace formula of Warner and Terentjev[1] after an affine change of reference configuration to take into account the orientation in the material (see the details in Ref. 11). The second term on the right hand side of Eq. (1) is the contribution due to the semisoft behaviour.

Accordingly, in the case of a slab subjected to biaxially stretches along the x and y axes by equal elongation ratios, the deformation gradient $\mathbf{F}$ should take, in principle, the following form:

$$\begin{pmatrix} \lambda a^{-1/6} & 0 & 0 \\ 0 & \lambda a^{-1/6} & 0 \\ 0 & 0 & \lambda^{-2}a^{1/3} \end{pmatrix}, \tag{2}$$

where, as required by the incompressibility condition, $\det\mathbf{F}=1$.

Substitution of Eq. (2) in Eq. (1) should provide the expression for the mechanical free energy. However, for uniaxial stretching experiments in sheets of nematic elastomers held between two rigid clamps, the resulting expression for the free energy is not convex for $a\neq 1$. This means that uniform configurations may have higher energy than complex patterns with the same average deformation.[7,8] As a consequence, energetically optimal fine phase structures are predicted that realize the quasiconvexification of the rough energy landscape. This fact accounts for the stripe domains observed[5] in the fine structure of the material. From a formal point of view, this imposes the appearance of a shear term $\mathbf{F}_{(13)}$ in the deformation gradient, where a bracketed subindex indicates a component of the $\mathbf{F}$ tensor.

In biaxial experiments, this scheme should be modified and an additional term $\mathbf{F}_{(23)}$ should appear. Moreover, recent experiments[6] in thin films of a soft nematic gel confined between two horizontal plates impose the appearance of shear terms $\mathbf{F}_{(12)}$ or $\mathbf{F}_{(13)}$. The new deformation gradient can be resolved in, at least, four deformation gradients satisfying certain kinematic compatibility conditions.[9] The preceding scheme has been recently applied to the biaxially stretched sheets of neo-Hookean liquid crystal elastomers.[10] A possible resulting deformation gradient decomposition leads to

$$\mathbf{F}=\frac{1}{4}[\mathbf{F_{11}}+\mathbf{F_{12}}+\mathbf{F_{21}}+\mathbf{F_{22}}]=\frac{1}{4}\left[\begin{matrix}\begin{pmatrix} \lambda a^{-1/6} & 0 & \gamma a^{1/3} \\ \gamma' a^{1/3} & \lambda a^{-1/6} & \delta a^{1/3} \\ 0 & 0 & \lambda^{-2}a^{1/3}\end{pmatrix}+\begin{pmatrix} \lambda a^{-1/6} & 0 & -\gamma a^{1/3} \\ \gamma' a^{1/3} & \lambda a^{-1/6} & -\delta a^{1/3} \\ 0 & 0 & \lambda^{-2}a^{1/3}\end{pmatrix}+ \\ +\begin{pmatrix} \lambda a^{-1/6} & 0 & -\gamma a^{1/3} \\ -\gamma' a^{1/3} & \lambda a^{-1/6} & \delta a^{1/3} \\ 0 & 0 & \lambda^{-2}a^{1/3}\end{pmatrix}+\begin{pmatrix} \lambda a^{-1/6} & 0 & \gamma a^{1/3} \\ -\gamma' a^{1/3} & \lambda a^{-1/6} & -\delta a^{1/3} \\ 0 & 0 & \lambda^{-2}a^{1/3}\end{pmatrix}\end{matrix}\right]. \tag{3}$$

Note that if a no zero term appears in the position 12 of some of the matrices of the previous decomposition, the incompressibility condition is not preserved. Then, according to the Eqs. (1) and (3), the mechanical free energy results

$$F_m=\frac{\mu}{2}\left\{\begin{matrix} (\lambda^2+\gamma^2 a)\left(1+(a^{-1}-1)\sin^2\theta\cos^2\varphi\right)+ \\ +\left(\lambda^2+(\gamma'^2+\delta^2)a\right)\left(1+(a^{-1}-1)\sin^2\theta\sin^2\varphi\right)+ \\ +\lambda^{-4}a\left(1+(a^{-1}-1)\cos^2\theta\right)+2(\delta\gamma a+\gamma'\lambda a^{1/2})(a^{-1}-1)\sin^2\theta\sin\varphi\cos\varphi+ \\ +2\lambda^{-2}a(a^{-1}-1)\sin\theta\cos\theta(\gamma\cos\varphi+\delta\sin\varphi)+\alpha(2\lambda^2+\lambda^{-4}+\gamma^2+\delta^2+\gamma'^2 a)\end{matrix}\right\}. \tag{4}$$

In the calculation of the free energy, the following normalized orientations of the nematic director are used for, respectively, each one of the four matrices in Eq. (3)

$$\begin{aligned}\mathbf{n_{11}}&=(\cos\varphi\sin\theta,\sin\varphi\sin\theta,\cos\theta),\mathbf{n_{12}}=(-\cos\varphi\sin\theta,-\sin\varphi\sin\theta,\cos\theta),\\ \mathbf{n_{21}}&=(-\cos\varphi\sin\theta,\sin\varphi\sin\theta,\cos\theta),\mathbf{n_{22}}=(\cos\varphi\sin\theta,-\sin\varphi\sin\theta,\cos\theta).\end{aligned} \tag{5}$$

In Eq. (5), θ and φ are, respectively, the rotation and meridian angles.

For an electric field directed along the z-axis, the electrical free energy can be written as

$$F_{el} = -\frac{1}{2}\varepsilon_0\left(\varepsilon_\perp E^2 + \varepsilon_a(\mathbf{E}\cdot\mathbf{n})^2\right), \tag{6}$$

where as usual ε_0 is the permittivity of the evacuated space, $\varepsilon_\perp$ the permittivity of the isotropic sample, and $\varepsilon_a = \varepsilon_\parallel - \varepsilon_\perp$ the dielectric anisotropy.

For the present sample configuration and on account that the term $-\frac{1}{2}\varepsilon_0 E^2$ is independent of the orientation of $\mathbf{n}$ and consequently can be omitted, one has

$$F_{el} = -\frac{1}{2}\varepsilon_0\varepsilon_a E^2\cos^2\theta. \tag{7}$$

The total free energy is obtained by adding Eqs. (4) and (7).

After applying the equilibrium conditions, $F_\theta = F_\varphi = F_{\gamma'} = F_{\delta'} = F_\gamma = F_\delta = 0$, where the sub-index indicate derivation with respect to the corresponding variable, the following set of equations are obtained:

$$\begin{aligned}&(\lambda^2+\gamma^2 a)\sin 2\theta\cos^2\varphi + \left(\lambda^2 + (\delta^2+\gamma'^2)a\right)\\&\times\sin 2\theta\sin^2\varphi - \lambda^{-4}a\sin 2\theta + 2(\delta\gamma a + \lambda\gamma' a^{1/2})\\&\times\sin 2\theta\sin\varphi\cos\varphi + 2\lambda^{-2}a\cos 2\theta(\gamma\cos\varphi + \delta\sin\varphi)\\&+\frac{1}{\mu(a^{-1}-1)}\varepsilon_0\varepsilon_a E^2\sin 2\theta = 0,\end{aligned} \tag{8a}$$

$$\begin{aligned}&-(\lambda^2+\gamma^2 a)\sin^2\theta\sin 2\varphi + \left(\lambda^2+(\delta^2+\gamma'^2)a\right)\\&\times\sin^2\theta\sin 2\varphi + 2(\delta\gamma a + \lambda\gamma' a^{1/2})\sin^2\theta\cos 2\varphi\\&+\lambda^{-2}a\sin 2\theta(-\gamma\sin\varphi + \delta\cos\varphi) = 0,\end{aligned} \tag{8b}$$

$$\begin{aligned}&2\gamma' a\left(1+(a^{-1}-1)\sin^2\theta\sin^2\varphi\right)\\&+2\lambda a^{1/2}(a^{-1}-1)\sin^2\theta\sin\varphi\cos\varphi + 2\alpha\gamma' a = 0,\end{aligned} \tag{8c}$$

$$\begin{aligned}&2\gamma a\left(1+(a^{-1}-1)\sin^2\theta\cos^2\varphi\right)\\&+2\delta a(a^{-1}-1)\sin^2\theta\sin\varphi\cos\varphi\\&+2\lambda^{-2}a(a^{-1}-1)\sin\theta\cos\theta\cos\varphi + 2\alpha\gamma = 0,\end{aligned} \tag{8d}$$

$$\begin{aligned}&2\delta a\left(1+(a^{-1}-1)\sin^2\theta\sin^2\varphi\right)\\&+2\gamma a(a^{-1}-1)\sin^2\theta\sin\varphi\cos\varphi\\&+2\lambda^{-2}a(a^{-1}-1)\sin\theta\cos\theta\sin\varphi + 2\alpha\delta = 0.\end{aligned} \tag{8e}$$

For the present purposes instead of solving the preceding set of equations, it is more convenient to examine the behaviour of these equations in the limit values of the rotation angle θ.

Consequently, one has

$$\begin{aligned}&\text{from Eq. (8a)},\ \theta=0 \leftrightarrow \delta=\gamma=0,\\&\text{from Eq. (8b)},\ \theta=0 \leftrightarrow \delta=\gamma, \varphi=\pi/4, \gamma'=0,\\&\text{from Eq. (8c)},\ \theta=0 \leftrightarrow \gamma'=0, \gamma=0\ or\ \delta=0,\\&\text{from Eq. (8d)},\ \theta=0 \leftrightarrow \gamma=0, \delta=0\ or\ \gamma'=0,\\&\text{from Eq. (8e)},\ \theta=0 \leftrightarrow \delta=0, \gamma=0\ or\ \gamma'=0.\end{aligned} \tag{9}$$

Moreover from Eq. (8b), $\theta = 0$ is a solution of such equation.

$$\text{From Eq. (8a)},\ \theta=\pi/2 \leftrightarrow \delta=\gamma=0, \tag{10}$$

$$\text{from Eq. (8b)},\ \theta=\pi/2,\ \delta=\gamma=0 \rightarrow \gamma' = -\frac{2\lambda a^{-1/2}}{\tan 2\varphi}, \tag{11}$$

$$\begin{aligned}&\text{from Eq. (8c)},\ \theta=\pi/2,\\&\delta=\gamma=0 \rightarrow \gamma' = -\frac{\lambda a^{-1/2}(a^{-1}-1)\sin 2\varphi}{2\left(1+(a^{-1}-1)\sin^2\varphi\right)+2\alpha}.\end{aligned} \tag{12}$$

Equalizing the right hand side of the Eqs. (11) and (12), one obtains

$$\tan^4\varphi = \frac{a(1+\alpha)}{(1+\alpha a)}. \tag{13}$$

For example, if one takes $a = 2$ and $\alpha = 0.2$, then $\varphi = 48.848^\circ$, whereas in the soft case, $\alpha = 0$ and $\varphi = 49.94^\circ$, in agreement with the result obtained in Ref. 10.

Solving the system of Eqs. (8), one obtains

$$\begin{aligned}&\lambda^6\left[\frac{1+\alpha}{(1+\alpha)+(a^{-1}-1)\sin^2\theta}\right]^{1/2} + \frac{\varepsilon_0\varepsilon_a E^2\lambda^4}{\mu(a^{-1}-1)}\\&-\frac{(1+\alpha a^{-1})(1+\alpha)}{[(1+\alpha a^{-1})+(a^{-1}-1)\sin^2\theta]^2} = 0.\end{aligned} \tag{14}$$

In the soft case with electric field, $E \neq 0$ and $\alpha = 0$,

$$\begin{aligned}&\lambda^6\left[\frac{1}{1+(a^{-1}-1)\sin^2\theta}\right]^{1/2} + \frac{\varepsilon_0\varepsilon_a E^2\lambda^4}{\mu(a^{-1}-1)}\\&-\frac{1}{[1+(a^{-1}-1)\sin^2\theta]^2} = 0.\end{aligned} \tag{15}$$

In absence of electric field, $E = 0$, one has

$$\lambda^6 - \frac{(1+\alpha a^{-1})(1+\alpha)^{1/2}\left((1+\alpha)+(a^{-1}-1)\sin^2\theta\right)^{1/2}}{[(1+\alpha a^{-1})+(a^{-1}-1)\sin^2\theta]^2} = 0. \tag{16}$$

In the soft case without electric field,

$$\lambda^6 - \frac{1}{[1+(a^{-1}-1)\sin^2\theta]^{3/2}} = 0. \tag{17}$$

For the former value of a together with $\varepsilon_a = 50, \mu = 10^6$Pa, $E = 2\cdot 10^7$V/m, and on account that $\varepsilon_0 = 8.854\cdot 10^{-12}$F/m, one obtains, for each one of the four cases under consideration, the limiting values for θ as shown in the Table I.

TABLE I. Limit values of λ during director rotation (from $\theta = 0$ to $\theta = \pi/2$) for both the soft and semisoft case with and without applied electric field (E = 0 V/m and E = $2\cdot 10^7$ V/m).

	E = 0 V/m		E = $2\cdot 10^7$ V/m	
	$\theta = 0$	$\theta = \pi/2$	$\theta = 0$	$\theta = \pi/2$
Soft ($\alpha = 0$)	$\lambda = 1$	$\lambda = 1.189$	$\lambda = 1.064$	$\lambda = 1.226$
Semisoft ($\alpha = 0.2$)	$\lambda = 1.014$	$\lambda = 1.187$	$\lambda = 1.078$	$\lambda = 1.227$

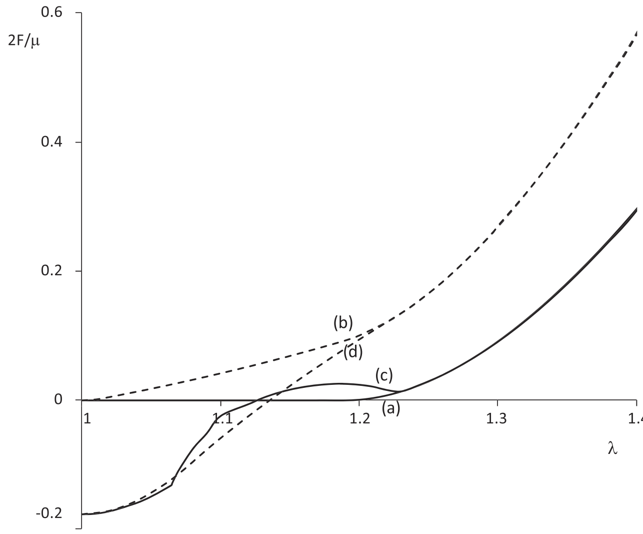

FIG. 2. Free energy representation for (a) soft case with E = 0 V/m, (b) semi soft case with E = 0 V/m, (c) soft case with $E = 2 \cdot 10^7$ V/m, (d) semi soft case with $E = 2 \cdot 10^7$ V/m. ($\alpha = 0.2$ for the semi soft case, a = 2, $\mu = 10^6$ Pa, for both soft and semisoft cases it has been considered $\gamma' > 0$).

The results corresponding to the soft case in absence of electric field (see, Ref. 10) are recovered. The results of Table I indicate that the semisoft behaviour decreases the interval of stretching ratio for which the director is rotating with and without the presence of the electric field. Moreover, as expected, the application of the electric field tends to increase the values of the stretching ratios λ for which the rotation of the director starts and is finished.

The free energies of the system for the soft and semi-soft cases and in absence and presence of electric field as a function of the stretching ratio λ are shown in the Figure 2. More theoretical as well as experimental work should be done in order to enlarge these conclusions for more general cases.

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