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INTRINSICALLY BIAXIAL SYSTEMS: A VARIATIONAL THEORY FOR ELASTOMERS

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Abstract Elastomeric networks of polymer liquid crystals are a classical example of "solid liquid crystals". They are organized in aggregates of ellipsoidal shape, which can be represented by a symmetric tensor field $\boldsymbol{L}$, which is closely related to the nematic order parameter $\boldsymbol{Q}$. We describe a continuum theory, which takes into account both the mechanical forces and the nematic properties of the system.

Keywords Elastomers, deformations, nematic ordering.

INTRODUCTION

The long-chain molecules of some polymeric liquid crystals are able to organize themselves in semiflexible nematic networks, whose shape depends on both the mechanical stresses applied on the system and the orientational degree of order of their nematic cores[1].

Warner, Gelling, and Vilgis[2] first succeeded in obtaining a Landau-de Gennes free energy density fit to describe this "solid liquid crystal". Blandon, Terentjev and Warner[3,4,5] formalized the theory by introducing a positive symmetric tensor $\boldsymbol{L}$ able to describe the microscopic properties of the elastomeric network: the eigenvalues of $\boldsymbol{L}$ represent the mean distance between molecular cores in the direction of their correspondent eigenvectors, so that we can imagine our system as composed by deformable ellipsoids, whose principal directions and semiaxis lengths respectively coincide with the eigenvectors and eigenvalues of $\boldsymbol{L}$.

The order parameter $\boldsymbol{L}$, that henceforth will be referred to as the *shape tensor*, determines also the nematic properties of the system. The distribution of the chains in the networks drives the orientation of the nematic cores of the molecules, and the nematic order tensor $\boldsymbol{Q}$ is related to $\boldsymbol{L}$ by $\boldsymbol{Q}(\boldsymbol{L}) = \boldsymbol{L}/\operatorname{tr}\boldsymbol{L} - \frac{1}{3}\boldsymbol{I}$. Furthermore, if we call $\mu_1 \geq \mu_2 \geq \mu_3$ the eigenvalues of $\boldsymbol{L}$, the nematic *degree of orientation* of $\boldsymbol{Q}$ can be written as:

$$s(\boldsymbol{L}) = \frac{\mu_1\mu_3 - \mu_2^2}{\mu_2 \operatorname{tr}\boldsymbol{L}} \, .$$

The degree of orientation is positive or negative as to whether the shape tensor $\boldsymbol{L}$ is prolate or oblate; as in usual nematics, it takes values in the interval $(-\frac{1}{2}, 1)$. The limiting values $s = -\frac{1}{2}$ and $s = 1$ can be approached only when two of the eigenvalues of the shape tensor coincide and the ratio μ_1/μ_3 tends to 0: in that case, s tends to 1 if μ_2 is equal to μ_3, while it approaches the value $-\frac{1}{2}$ if μ_2 is equal to μ_1.

The equilibrium distribution of the elastomer can be determined by minimizing the free energy functional

$$\mathcal{F}[\boldsymbol{\Lambda}, \boldsymbol{L}] := \int_{\mathcal{V}} \left(\sigma_{\text{el}}(\boldsymbol{\Lambda}, \nabla \boldsymbol{L}) + \sigma(\boldsymbol{\Lambda}, \boldsymbol{L})\right) \mathrm{d}v,$$

where $\mathcal{V}$ is the volume occupied by the material. The macroscopic deformation tensor $\boldsymbol{\Lambda}$ can be either considered as an external parameter, if we are able to fix from outside the mechanical properties of the system, or as a variable itself, in the case of *soft deformations*[4]. We will describe elsewhere[6] the properties of the minimizers of $\mathcal{F}$ with the simple choice $\sigma_{\text{el}} = \kappa|\nabla \boldsymbol{L}|^2$, but here we focus our attention on the homogeneous equilibrium distributions of $\mathcal{F}$, that is on the minimizers of the internal potential σ.

Let us denote by $\boldsymbol{L}_0$ the equilibrium shape of the microscopic networks when no distortion is applied on the system: $\boldsymbol{L}_0$ may still depend on the temperature and the electric and magnetic fields acting on the elastomer; it can be uniaxial or biaxial, and it is related to the microscopic degree of symmetry of the material.

When we apply a deformation $\boldsymbol{\Lambda}$ (with $\det \boldsymbol{\Lambda} = 1$ since the shear modulus is much smaller than the modulus for volume change), the new equilibrium shape $\boldsymbol{L}$ is the minimizer of the potential

$$\sigma(\boldsymbol{L}) := \sigma_{\text{m}}(\boldsymbol{L}) + \sigma_{\text{uni}}(\boldsymbol{L}), \tag{1}$$

with

$$\sigma_{\text{m}}(\boldsymbol{L}) := \frac{kT}{2}\left[\operatorname{tr}\left(\boldsymbol{\Lambda}\boldsymbol{L}_0\boldsymbol{\Lambda}^t\boldsymbol{L}^{-1}\right) - \log\frac{\det \boldsymbol{L}_0}{\det \boldsymbol{L}}\right], \tag{2}$$

and

$$\sigma_{\text{uni}}(\boldsymbol{L}) := a\ \operatorname{tr}\boldsymbol{Q}(\boldsymbol{L})^2 - b\ \operatorname{tr}\boldsymbol{Q}(\boldsymbol{L})^3 + c\ \operatorname{tr}\boldsymbol{Q}(\boldsymbol{L})^4, \text{ with } b, c > 0; \tag{3}$$

as in usual nematic liquid crystals, σ_{uni} pushes towards a uniaxial state either isotropic (if $a \geq 0$) or nematic (if $a < 0$).

The potential σ_{m} takes into account the mechanical interactions exerted within the microscopic networks that make up the elastomers[3]: its minimization brings information about the changes the distortion $\boldsymbol{\Lambda}$ induces on the microscopic shapes of the elastomeric networks. On the other hand, σ_{uni} introduces the interaction among different ellipsoids, so that the value of $\boldsymbol{L}$ minimizing the whole σ is the shape tensor that can be associated to the local distribution of the elastomeric ellipsoids, more than to the shape of every single component.

In the next section we deal only with σ_{m} proving that, for every assigned $\boldsymbol{L}_0$ and $\boldsymbol{\Lambda}$, the potential (2) has a unique minimum; finally, we study σ under the physical assumption that σ_{uni} strongly forbids the onset of biaxial mesoscopic distributions.

MECHANICAL POTENTIAL: MICROSCOPIC SHAPES

In this section we confine our attention to the potential σ_m that determines the microscopic shapes of the elastomeric ellipsoids.

Equilibrium microscopic shapes

Our first result is the following: for every given couple of tensors $\boldsymbol{L}_0$ and $\boldsymbol{\Lambda}$, the potential σ_m, defined in (2), has the unique stationary tensor

$$\boldsymbol{L} = \boldsymbol{L}_{eq} := \boldsymbol{\Lambda}\boldsymbol{L}_0\boldsymbol{\Lambda}^t. \tag{4}$$

To prove this result, we define

$$\boldsymbol{L}_\epsilon := \boldsymbol{L} + \epsilon\,\boldsymbol{U},$$

and we compute the first-order expansion of $\sigma_m(\boldsymbol{L}_\epsilon)$ in powers of ϵ: the stationarity condition for σ_m is then obtained by imposing that the first-order term is the expansion has to be null.

We start by noting that σ_m can be written as

$$\sigma_m(\boldsymbol{L}) = \frac{kT}{2}\left[\operatorname{tr}\left(\boldsymbol{L}_{eq}\boldsymbol{L}^{-1}\right) - \log\frac{\det \boldsymbol{L}_{eq}}{\det \boldsymbol{L}}\right], \tag{5}$$

since $\det\boldsymbol{\Lambda} = 1$ implies $\det \boldsymbol{L}_0 = \det \boldsymbol{L}_{eq}$.

Considering that

$$\boldsymbol{L}_\epsilon^{-1} = \left[\boldsymbol{L}\left(\boldsymbol{I} + \epsilon\,\boldsymbol{L}^{-1}\boldsymbol{U}\right)\right]^{-1} = \left(\boldsymbol{I} - \epsilon\,\boldsymbol{L}^{-1}\boldsymbol{U}\right)\boldsymbol{L}^{-1} + o(\epsilon)$$

$$= \boldsymbol{L}^{-1} - \epsilon\,\boldsymbol{L}^{-1}\boldsymbol{U}\boldsymbol{L}^{-1} + o(\epsilon),$$

$$\det \boldsymbol{L}_\epsilon = \det \boldsymbol{L}\,\det\left(\boldsymbol{I} + \epsilon\,\boldsymbol{L}^{-1}\boldsymbol{U}\right) = \det \boldsymbol{L}\left(1 + \epsilon\operatorname{tr}(\boldsymbol{L}^{-1}\boldsymbol{U}) + o(\epsilon)\right),$$

and

$$\log\det \boldsymbol{L}_\epsilon = \log\det \boldsymbol{L} + \epsilon\operatorname{tr}(\boldsymbol{L}^{-1}\boldsymbol{U}) + o(\epsilon),$$

we have:

$$\sigma_m(\boldsymbol{L}_\epsilon) = \operatorname{tr}(\boldsymbol{L}_{eq}\boldsymbol{L}_\epsilon) + \log\det \boldsymbol{L}_\epsilon - \log\det \boldsymbol{L}_{eq}$$

$$= \sigma_m(\boldsymbol{L}) + \epsilon\left[-\operatorname{tr}\left(\boldsymbol{L}_{eq}\boldsymbol{L}^{-1}\boldsymbol{U}\boldsymbol{L}^{-1}\right) + \operatorname{tr}\left(\boldsymbol{L}^{-1}\boldsymbol{U}\right)\right] + o(\epsilon)$$

$$= \sigma_m(\boldsymbol{L}) + \epsilon\left[\operatorname{tr}\left(\left(\boldsymbol{L}^{-1}\boldsymbol{U}\right)\left(\boldsymbol{I} - \boldsymbol{L}^{-1}\boldsymbol{L}_{eq}\right)\right)\right] + o(\epsilon)$$

$$= \sigma_m(\boldsymbol{L}) + \epsilon\left[\boldsymbol{U}^t \cdot \left(\boldsymbol{I} - \boldsymbol{L}^{-1}\boldsymbol{L}_{eq}\right)\boldsymbol{L}^{-1}\right] + o(\epsilon).$$

The stationarity condition for σ_m then reads

$$\boldsymbol{U}^t \cdot \left(\boldsymbol{I} - \boldsymbol{L}^{-1}\boldsymbol{L}_{eq}\right)\boldsymbol{L}^{-1} = 0 \text{ for all admissible tensors } \boldsymbol{U}. \tag{6}$$

Now, the tensor $\boldsymbol{L}_\epsilon$ has to be symmetric, as $\boldsymbol{L}$, $\boldsymbol{L}_0$, and $\boldsymbol{L}_{eq}$ already are. This implies that the perturbation tensor $\boldsymbol{U}$ is also to be taken symmetric. Equation (6) becomes then

$$\boldsymbol{U} \cdot \left(\boldsymbol{I} - \boldsymbol{L}^{-1}\boldsymbol{L}_{\text{eq}}\right)\boldsymbol{L}^{-1} = 0 \text{ for all symmetric tensors } \boldsymbol{U},$$

implying that the tensor

$$\boldsymbol{W} := \left(\boldsymbol{I} - \boldsymbol{L}^{-1}\boldsymbol{L}_{\text{eq}}\right)\boldsymbol{L}^{-1}$$

has to be skew. Nevertheless, it is easy to verify that $\boldsymbol{W}$ is symmetric by construction, so that $\boldsymbol{W}$ is forced to be equal to $\mathbf{0}$. Finally, since $\boldsymbol{L}$ is invertible, we obtain:

$$\boldsymbol{I} - \boldsymbol{L}^{-1}\boldsymbol{L}_{\text{eq}} = \mathbf{0}$$

or

$$\boldsymbol{L} = \boldsymbol{L}_{\text{eq}}.$$

Stability of the equilibrium shape

To determine the stability of the equilibrium distribution $\boldsymbol{L} = \boldsymbol{L}_{\text{eq}}$ found above, we have to obtain the second-order expansion of $\sigma_{\text{m}}(\boldsymbol{L}_\epsilon)$ in powers of ϵ and to study the sign of the coefficient of ϵ^2 in that power series.

With the same techniques used above it is possible to prove that

$$\boldsymbol{L}_\epsilon^{-1} = \boldsymbol{L}^{-1} - \epsilon\, \boldsymbol{L}^{-1}\boldsymbol{U}\boldsymbol{L}^{-1} + \epsilon^2\boldsymbol{L}^{-1}\boldsymbol{U}\boldsymbol{L}^{-1}\boldsymbol{U}\boldsymbol{L}^{-1} + o(\epsilon^2),$$

and

$$\log\det \boldsymbol{L}_\epsilon = \log\det \boldsymbol{L} + \epsilon\,\text{tr}(\boldsymbol{L}^{-1}\boldsymbol{U}) + \epsilon^2\left[\text{II}_{L^{-1}U} - \frac{1}{2}\left(\text{tr}(\boldsymbol{L}^{-1}\boldsymbol{U})\right)^2\right] + o(\epsilon^2),$$

where II_A denotes the second invariant of the tensor $\boldsymbol{A}$:

$$\text{II}_A := a_{11}a_{22} + a_{22}a_{33} + a_{33}a_{11} - a_{12}a_{21} - a_{13}a_{31} - a_{23}a_{32} \quad \text{if}$$

$$\boldsymbol{A} = \sum_{i,j=1}^{3} a_{ij}\; \boldsymbol{e}_i \otimes \boldsymbol{e}_j.$$

Considering these expansions, the fact that $\sigma_{\text{m}}(\boldsymbol{L}_{\text{eq}}) = \frac{3}{2}\,kT$, and the equilibrium condition (6), we obtain:

$$\begin{aligned}\sigma_{\text{m}}(\boldsymbol{L}_{\text{eq}} + \epsilon\,\boldsymbol{U}) - \frac{3}{2}\,kT &= \epsilon^2\left[\text{tr}\,\boldsymbol{V}^2 + \text{II}_V - \frac{1}{2}\left(\text{tr}\,\boldsymbol{V}\right)^2\right] + o(\epsilon^2) \\ &= \frac{\epsilon^2}{2}\,\text{tr}\,\boldsymbol{V}^2 + o(\epsilon^2) = \frac{\epsilon^2}{4}\left(\left|\boldsymbol{V}\right|^2 + \left|\boldsymbol{V}^t\right|^2\right) + o(\epsilon^2),\end{aligned} \tag{7}$$

where we have used the tensor $\boldsymbol{V} := \boldsymbol{L}_{\text{eq}}^{-1}\boldsymbol{U}$. Note that $\boldsymbol{V}$ can fail to be symmetric, even if $\boldsymbol{L}_{\text{eq}}$ and $\boldsymbol{U}$ are so, but nevertheless the coefficient multiplying ϵ^2 in the expansion of $\sigma_{\text{m}}(\boldsymbol{L}_{\text{eq}} + \epsilon\,\boldsymbol{U})$ is always positive.

Equation (7) proves that $\boldsymbol{L} = \boldsymbol{L}_{\text{eq}}$ is always a relative minimum of σ_{m}. Finally, if we consider that σ_{m} is a smooth function that diverges on the boundary of the set $\mathcal{L}$ of all symmetric positive tensors, we easily conclude that $\boldsymbol{L} = \boldsymbol{L}_{\text{eq}}$ is also the absolute minimum of σ_{m}. ∎

NEMATIC INTERACTION: MESOSCOPIC DISTRIBUTIONS

The microscopic networks of a liquid crystal elastomer assume the ellipsoidal shape $\boldsymbol{L}_{\text{eq}}$ as soon as a distortion $\boldsymbol{\Lambda}$ is applied on the material. We remark that $\boldsymbol{L}_{\text{eq}}$ may become biaxial even if both $\boldsymbol{L}_0$ and $\boldsymbol{\Lambda}$ are uniaxial: actually, the combination $\boldsymbol{\Lambda}\boldsymbol{L}_0\boldsymbol{\Lambda}^t$ is biaxial whenever the principal axes of $\boldsymbol{L}_0$ and $\boldsymbol{\Lambda}$ do not coincide.

However, the nematic interaction described by σ_{uni} tends to align all the (eventually biaxial) ellipsoids to construct a uniaxial distribution*. Since the potential σ_{uni} is usually very strong, in this section we will assume that it succeeds in forbidding all biaxial distributions, so that the global minimum of σ will coincide with the minimum of σ_{m} in $\mathcal{L}_U$, the uniaxial part of $\mathcal{L}$.

Let us then write $\boldsymbol{L}$ as

$$\boldsymbol{L} = \alpha \boldsymbol{I} + \beta\, \boldsymbol{u} \otimes \boldsymbol{u},$$

with $\boldsymbol{u} \cdot \boldsymbol{u} = 1$, and $\alpha > 0$, $\alpha + \beta > 0$, since $\boldsymbol{L}$ must be positively defined. The nematic order parameter tensor associated with $\boldsymbol{L}$ is

$$\boldsymbol{Q} = \frac{\beta}{3\alpha + \beta}\left(\boldsymbol{u} \otimes \boldsymbol{u} - \frac{1}{3}\boldsymbol{I}\right)$$

and, in terms of α, β, and $\boldsymbol{u}$, σ_{m} reduces to:

$$\sigma_{\text{m}} = \frac{kT}{2}\left[\frac{1}{\alpha}\,\text{tr}\,\boldsymbol{L}_{\text{eq}} - \frac{\beta}{\alpha(\alpha+\beta)}\,\boldsymbol{L}_{\text{eq}}\boldsymbol{u} \cdot \boldsymbol{u} - \log \frac{\det \boldsymbol{L}_{\text{eq}}}{\alpha^2(\alpha+\beta)}\right].$$

Equilibrium mesoscopic distributions

The derivatives of σ_{m} with respect to the free parameters α, β, and $\boldsymbol{u}$ give:

$$\frac{\partial \sigma_{\text{m}}}{\partial \alpha} = -\frac{\text{tr}\,\boldsymbol{L}_{\text{eq}}}{\alpha^2} + \frac{\beta(2\alpha+\beta)}{\alpha^2(\alpha+\beta)^2}\,\boldsymbol{L}_{\text{eq}}\boldsymbol{u} \cdot \boldsymbol{u} + \frac{3\alpha + 2\beta}{\alpha(\alpha+\beta)}\,;$$

$$\frac{\partial \sigma_{\text{m}}}{\partial \beta} = \frac{1}{\alpha+\beta}\left(1 - \frac{\boldsymbol{L}_{\text{eq}}\boldsymbol{u} \cdot \boldsymbol{u}}{\alpha+\beta}\right);$$

$$\frac{\partial \sigma_{\text{m}}}{\partial \boldsymbol{u}} = -\frac{2\beta}{\alpha(\alpha+\beta)}\,\boldsymbol{L}_{\text{eq}}\boldsymbol{u}\,.$$

These stationarity equations show that there are *four* possible different types of mesoscopic *uniaxial* equilibrium distributions, under the applied distortion $\boldsymbol{\Lambda}$. If

* A uniaxial distribution of biaxial units can be simply obtained by distributing them symmetrically about the director direction

we decompose L_{eq} as $L_{eq} = \sum \mu_i \, e_i \otimes e_i$, with $\mu_1 \geq \mu_2 \geq \mu_3$, these equilibrium solutions can be written as:

(E1) the *isotropic* distribution

$$L_{iso} = \left(\frac{1}{3}\operatorname{tr} L_{eq}\right) I,$$

corresponding to a nematic order tensor $Q_{iso} = 0$;

(E2) the uniaxial distribution with *positive* degree of orientation

$$L_+ = \frac{\mu_2 + \mu_3}{2} I + \left(\mu_1 - \frac{\mu_2 + \mu_3}{2}\right) e_1 \otimes e_1 \ ,$$

corresponding to

$$Q_+ = \frac{1}{\operatorname{tr} L_{eq}} \left(\mu_1 - \frac{\mu_2 + \mu_3}{2}\right) \left(e_1 \otimes e_1 - \frac{1}{3} I\right) \ ;$$

(E3) the uniaxial distribution

$$L_\pm = \frac{\mu_3 + \mu_1}{2} I + \left(\mu_2 - \frac{\mu_3 + \mu_1}{2}\right) e_2 \otimes e_2 \ ,$$

whose degree of orientation has *not a definite sign*:

$$Q_\pm = \frac{1}{\operatorname{tr} L_{eq}} \left(\mu_2 - \frac{\mu_3 + \mu_1}{2}\right) \left(e_2 \otimes e_2 - \frac{1}{3} I\right) \ ;$$

(E4) the uniaxial distribution with *negative* degree of order

$$L_- = \frac{\mu_1 + \mu_2}{2} I + \left(\mu_3 - \frac{\mu_1 + \mu_2}{2}\right) e_3 \otimes e_3 \ ,$$

corresponding to

$$Q_- = \frac{1}{\operatorname{tr} L_{eq}} \left(\mu_3 - \frac{\mu_1 + \mu_2}{2}\right) \left(e_3 \otimes e_3 - \frac{1}{3} I\right) \ .$$

These four equilibrium distributions may degenerate when L_{eq} is uniaxial. In fact, if $\mu_2 = \mu_3 = \mu_1 - 2\,\delta\mu$, the equilibrium distributions become: L_{iso}, L_+, and any distribution of the form

$$L'_- = (\mu_1 - \delta\mu)\, I + \delta\mu \, e_{23} \otimes e_{23} \ ,$$

where $\delta\mu > 0$ and e_{23} is any unit vector in the plane orthogonal to e_1; L'_- corresponds to:

$$Q'_- = -\frac{\delta\mu}{\operatorname{tr} \boldsymbol{L}_{\mathrm{eq}}} \left(\boldsymbol{e}_{23} \otimes \boldsymbol{e}_{23} - \frac{1}{3} \boldsymbol{I} \right) .$$

When, on the contrary, $\mu_1 = \mu_2 = \mu_3 + 2\,\delta\mu$, the equilibrium distributions are: $\boldsymbol{L}_{\mathrm{iso}}$, $\boldsymbol{L}_-$, and any distribution of the form

$$\boldsymbol{L}'_+ = (\mu_3 + \delta\mu)\, \boldsymbol{I} + \delta\mu\, \boldsymbol{e}_{12} \otimes \boldsymbol{e}_{12} ,$$

where, again, $\delta\mu > 0$ and now $\boldsymbol{e}_{12}$ is any unit vector in the plane orthogonal to $\boldsymbol{e}_3$; $\boldsymbol{L}'_+$ corresponds to:

$$Q'_+ = \frac{\delta\mu}{\operatorname{tr} \boldsymbol{L}_{\mathrm{eq}}} \left(\boldsymbol{e}_{12} \otimes \boldsymbol{e}_{12} - \frac{1}{3} \boldsymbol{I} \right) .$$

Finally, when $\mu_1 = \mu_2 = \mu_3$, that is when $\boldsymbol{L}_{\mathrm{eq}}$ is isotropic, the only existing equilibrium distribution is obviously $\boldsymbol{L}_{\mathrm{iso}} = \boldsymbol{L}_{\mathrm{eq}}$, since it is not possible to obtain anisotropic distributions starting from isotropic objects. $\boldsymbol{L}_\pm$ also coincides with $\boldsymbol{L}_{\mathrm{iso}}$ when the intermediate eigenvalue μ_2 is equal to the arithmetic average of μ_1 and μ_3.

Mechanically-induced transitions in nematic elastomers

Now that we have proved that a nematic elastomer subject to a mechanical distortion $\boldsymbol{\Lambda}$ can reach four different equilibrium distributions, we complete our study by identifying the absolute minimum of the potential energy and the possible transitions that may take place by varying the distortion $\boldsymbol{\Lambda}$.

To this aim, we have to introduce again

$$\boldsymbol{L}_\epsilon := \alpha_\epsilon\, \boldsymbol{I} + \beta_\epsilon\, \boldsymbol{u}_\epsilon \otimes \boldsymbol{u}_\epsilon,$$

where

$$\alpha_\epsilon := \alpha + \epsilon\,\alpha_1, \quad \beta_\epsilon := \beta + \epsilon\,\beta_1, \quad \text{and} \quad \boldsymbol{u}_\epsilon := \boldsymbol{u} + \epsilon\,\boldsymbol{u}_1.$$

Long but straightforward calculations yield to the result that the second-order expansion of $\sigma_{\mathrm{m}}(\boldsymbol{L}_\epsilon)$ in powers of ϵ, in the vicinity of an equilibrium distribution, is given by:

$$\begin{aligned} \sigma_{\mathrm{m}}(\boldsymbol{L}_\epsilon) = \sigma_{\mathrm{m}}(\boldsymbol{L}) + \epsilon^2 \Bigg[& \frac{\alpha_1^2}{\alpha^3} \operatorname{tr} \boldsymbol{L}_{\mathrm{eq}} + 2\, \frac{\beta(2\alpha+\beta)\alpha_1 - \alpha^2\beta_1}{\alpha^2(\alpha+\beta)^2}\, \boldsymbol{L}_{\mathrm{eq}}\boldsymbol{u} \cdot \boldsymbol{u}_1 \\ & - \frac{\beta}{\alpha(\alpha+\beta)}\, \boldsymbol{L}_{\mathrm{eq}}\boldsymbol{u}_1 \cdot \boldsymbol{u}_1 + \left(\frac{(\alpha_1+\beta_1)^2}{(\alpha+\beta)^3} - \frac{\alpha_1^2}{\alpha^3} \right) \boldsymbol{L}_{\mathrm{eq}}\boldsymbol{u} \cdot \boldsymbol{u} - \frac{\alpha_1^2}{\alpha^2} - \frac{(\alpha_1+\beta_1)^2}{2(\alpha+\beta)^2} \Bigg] . \end{aligned} \tag{8}$$

The stability of the single equilibrium distributions follows from the study of the sign of the second-order term in (8); the results are the following:

(i) the isotropic distribution $\boldsymbol{L}_{\mathrm{iso}}$ and the uniaxial distribution $\boldsymbol{L}_\pm$ are both saddle-points of σ_{m}, unless $\boldsymbol{L}_{\mathrm{eq}}$ is isotropic itself; in this case, and only in it, all equilibrium distributions coincide, as we have already pointed out;

(ii) the uniaxial distributions $\boldsymbol{L}_+$ and $\boldsymbol{L}_-$ are always relative minima of σ_{m}.

The absolute minimum of σ_{m} depends on the degree of orientation $s(\boldsymbol{L}_{\mathrm{eq}})$ associated with the shape tensor $\boldsymbol{L}_{\mathrm{eq}}$. In fact, it is easy to verify that

$$\sigma_{\rm m}(\boldsymbol{L}_{\bf iso}) = \frac{3kT}{2}\left(1+\frac{1}{3}\log\frac{(\mu_1+\mu_2+\mu_3)^3}{27\,\mu_1\mu_2\mu_3}\right),$$

$$\sigma_{\rm m}(\boldsymbol{L}_+) = \frac{3kT}{2}\left(1+\frac{1}{3}\log\frac{(\mu_2+\mu_3)^2}{4\mu_2\mu_3}\right),$$

$$\sigma_{\rm m}(\boldsymbol{L}_\pm) = \frac{3kT}{2}\left(1+\frac{1}{3}\log\frac{(\mu_1+\mu_3)^2}{4\mu_1\mu_3}\right),$$

$$\sigma_{\rm m}(\boldsymbol{L}_-) = \frac{3kT}{2}\left(1+\frac{1}{3}\log\frac{(\mu_1+\mu_2)^2}{4\mu_1\mu_2}\right).$$

Now, considering that $\mu_1 \geq \mu_2 \geq \mu_3$, we obtain that $\sigma_{\rm m}(\boldsymbol{L}_{\bf iso})$ is always grater than $\sigma_{\rm m}(\boldsymbol{L}_\pm)$, which in turn is greater than both $\sigma_{\rm m}(\boldsymbol{L}_+)$ and $\sigma_{\rm m}(\boldsymbol{L}_-)$. To recognize the absolute minimizer, we have to compare $\sigma_{\rm m}(\boldsymbol{L}_+)$ and $\sigma_{\rm m}(\boldsymbol{L}_-)$: when the degree of orientation associated with the shape tensor $\boldsymbol{L}_{\bf eq}$ is positive, the absolute minimizer of $\sigma_{\rm m}$ is $\boldsymbol{L}_+$, while $\sigma_{\rm m}(\boldsymbol{L}_-)$ is preferred when $s(\boldsymbol{L}_{\bf eq})$ becomes negative.

A first-order transition between a uniaxial distribution with positive degree of orientation and a uniaxial distribution with negative degree of orientation can be then induced in a liquid crystal elastomer by continuously modifying from outside the deformation $\boldsymbol{\Lambda}$ exerted on the system, as we will show in the following concluding example.

We consider an elastomer with an undistorted uniaxial distribution

$$\boldsymbol{L}_0 = \ell_0(\boldsymbol{e}_x\otimes\boldsymbol{e}_x + \boldsymbol{e}_y\otimes\boldsymbol{e}_y) + \alpha\ell_o\,\boldsymbol{e}_z\otimes\boldsymbol{e}_z,$$

with $\alpha > 1$ in order to have a prolate initial distribution. We now apply on this system a distortion $\boldsymbol{\Lambda}$ which squeezes the system in the z-direction, while spreading it in the x-direction:

$$\boldsymbol{\Lambda} = \lambda\,\boldsymbol{e}_x\otimes\boldsymbol{e}_x + \frac{1}{\lambda}\,\boldsymbol{e}_z\otimes\boldsymbol{e}_z,$$

where also λ is taken to be greater than 1.

The microscopic equilibrium shape will then be

$$\boldsymbol{L}_{\bf eq} = \boldsymbol{\Lambda}\boldsymbol{L}_0\boldsymbol{\Lambda}^t = \ell_0\lambda^2\,\boldsymbol{e}_x\otimes\boldsymbol{e}_x + \ell_0\,\boldsymbol{e}_y\otimes\boldsymbol{e}_y + \frac{\alpha\ell_o}{\lambda^2}\,\boldsymbol{e}_z\otimes\boldsymbol{e}_z.$$

If the potential $\sigma_{\rm uni}$ forbids the onset of biaxial equilibrium distributions $\boldsymbol{L}$, as we have supposed throughout this section, the equilibrium distribution will be determined by the degree of orientation of the tensor $\boldsymbol{L}_{\bf eq}$, and will vary with λ as follows:

(i) if $1 \leq \lambda < \alpha^{\frac{1}{6}}$, the elastomer will relax toward a uniaxial distribution with positive degree of orientation and director parallel to $\boldsymbol{e}_z$;

(ii) if $\alpha^{\frac{1}{6}} < \lambda < \alpha^{\frac{1}{3}}$, the uniaxial equilibrium distribution will have a negative degree of orientation and director parallel to $\boldsymbol{e}_y$;

(iii) finally, if $\lambda > \alpha^{\frac{1}{3}}$, the elastomer will again restore a uniaxial distribution with positive degree of orientation, but its director will become parallel to $\boldsymbol{e_x}$.

Two first-order transitions take then place at the critical values $\lambda = \alpha^{\frac{1}{6}}$ and $\lambda = \alpha^{\frac{1}{3}}$.

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