Phenomenological description of semi-soft nematic elastomers

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Nematic elastomers are new materials that have many remarkable properties. In this article, we study how nonlinear elasticity of semi-soft nematic elastomers can be described phenomenologically. We start with a theory based on strain tensor only, and then continue to develop a phenomenological description with the liquid crystal order tensor included explicitly. Such a description has the virtue of being able to treat the strain tensor and the liquid crystal order tensor equally and thus making the complicated symmetries of nematic elastomers easier to understand.

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1. Introduction

Liquid crystalline elastomers (LCEs) are a new type of matter. In the past few decades, studies of them have thrived[1] because of their many potential applications in industry, such as temperature-controlled actuators, artificial muscles,[2,3] tunable lasers,[4] and optical data storage.[5] LCEs are formed by cross-linking liquid crystalline polymers. Thus, LCEs possess not only the optical and electric properties of liquid crystals but also the elastic properties of rubbers: they can maintain their shapes and have the ability to return to their original configurations when deformed. For this reason, LCEs are sometimes also called solid liquid crystals. Mesogens in LCEs exhibit the same order as they exhibit in uncross-linked systems, and there are nematic, smectic, cholesteric, and other elastomers. In this article, we will focus on nematic elastomers (NEs).

Coupling between liquid crystalline mesogens and the polymer network of an NE causes the elastomer to change its shape as liquid crystalline order develops. For instance, when the mesogens undergo a transition from the isotropic phase to the nematic phase, the elastomer will spontaneously elongate along one direction and shrink along perpendicular directions. On the other hand, liquid crystalline ordering also changes with the polymer network conformation. If the shape of an NE is changed by applied external stress, the optical properties of mesogens also change. It is this coupling between polymer networks and liquid crystalline ordering that makes NEs highly responsive to external stimuli (including heat, light, electric field, etc.) and hence a good candidate for many applications in industry.

The coupling between the mesogens and the polymer network also gives NEs many unique properties, among which the most remarkable are the so-called soft elasticity[6,7] and semi-soft elasticity. Soft elasticity refers to elastic deformations that cost no energy. In particular, if we pull a soft nematic elastomer along a direction perpendicular to its anisotropy direction, there is no resisting stress until a critical value of strain is reached, that is, there exists a zero-stress plateau. However, to obtain soft elasticity, we need the polymers forming an elastomer to be cross-linked in the isotropic state.[8] Given that mono-domain samples are usually created by a second cross-linking in a nematic state, this zero-stress plateau is usually not seen in experiments. Instead, the height of plateaus in the measured stress–strain curves is of a small value.[9] Systems exhibiting nonzero-stress plateaus are called semi-soft elastomers.[10]

The molecular theory of NEs was proposed by Warner and Terentjev and has been quite successful in explaining experimental results.[1] Phenomenological description of NEs was first developed by de Gennes *et al.*[11] and then by Lubensky *et al.*[12] In this article, we will adopt a different approach to develop a new phenomenological description that can show the symmetry properties of semi-soft NEs more clearly and handle the nonlinear elasticity more constantly.

This article is organized as follows. We start in Section 2 with a brief review of elastic theories — we introduce the strain tensor and how the elastic energy of a normal elastic medium can be constructed from the strain tensor. In Section 3, we construct for NEs a phenomenological elastic energy based on the strain tensor only; in Section 4, we construct a phenomenological theory with both the strain tensor and the nematic order tensor included. A short summary is presented in Section 5.

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2. Strain and elastic energy

An elastic medium is described by a reference configuration, which is referred to as a reference space, with mass points at positions $\boldsymbol{x}$. Upon distortion of the medium, points $\boldsymbol{x}$ are mapped to points

$$R(\boldsymbol{x}) = \boldsymbol{x} + \boldsymbol{u}(\boldsymbol{x}) \tag{1}$$

in a new configuration (referred to as a target space, where $\boldsymbol{u}$ is the displacement variable). Elastic distortions on scales much larger than the distance between crosslinks can be described by the Cauchy deformation tensor $\underline{\underline{\lambda}}$,

$$\lambda_{ij} = \frac{\partial R_i}{\partial x_j} \equiv \partial_j R_i = \delta_{ij} + \eta_{ij}, \tag{2}$$

where

$$\eta_{ij} = \partial_j u_i \tag{3}$$

is the displacement gradient tensor. The change of the distance between two nearby points is then

$$\mathrm{d}R^2 - \mathrm{d}x^2 = 2u_{ij}\mathrm{d}x_i\mathrm{d}x_j, \tag{4}$$

where

$$\begin{aligned} u_{ij} &= \frac{1}{2}\left(\lambda_{ki}\lambda_{kj} - \delta_{ij}\right) \ \text{ or } \ \underline{\underline{u}} = \frac{1}{2}\left(\underline{\underline{\lambda}}^{\mathrm{T}}\underline{\underline{\lambda}} - \underline{\underline{\delta}}\right) \\ &= \frac{1}{2}\left(\partial_j u_i + \partial_i u_j + \partial_i u_k \partial_j u_k\right) = \frac{1}{2}\left(\eta_{ij} + \eta_{ji} + \eta_{ki}\eta_{kj}\right). \end{aligned} \tag{5}$$

u_{ij}, which is symmetric by construction, is the familiar Green strain tensor.[13] Under rotations of the reference space, $\boldsymbol{x} \to \underline{\underline{O}}_{\mathrm{R}}\boldsymbol{x}$, where $\underline{\underline{O}}_{\mathrm{R}}$ is a rotation matrix; while under rotations in the target space, $\boldsymbol{R} \to \underline{\underline{O}}_{\mathrm{T}}\boldsymbol{R}$, where $\underline{\underline{O}}_{\mathrm{T}}$ is also a rotation matrix. Thus $\underline{\underline{\lambda}} \to \underline{\underline{O}}_{\mathrm{T}}\underline{\underline{\lambda}}\underline{\underline{O}}_{\mathrm{R}}^{\mathrm{T}}$ and

$$\underline{\underline{u}} \to \frac{1}{2}\left(\underline{\underline{O}}_{\mathrm{R}}\underline{\underline{\lambda}}^{\mathrm{T}}\underline{\underline{O}}_{\mathrm{T}}^{\mathrm{T}}\underline{\underline{O}}_{\mathrm{T}}\underline{\underline{\lambda}}\underline{\underline{O}}_{\mathrm{R}}^{\mathrm{T}} - \underline{\underline{\delta}}\right) = \underline{\underline{O}}_{\mathrm{R}}u\underline{\underline{O}}_{\mathrm{R}}^{\mathrm{T}}$$

is invariant under rotations of the target space and transforms like a rank-2 tensor under rotations of the reference space.

The free energy density f (energy per unit volume of the reference space) can be written either as a function of $\underline{\underline{\lambda}}$, $f\left(\underline{\underline{\lambda}}\right)$, or as a function of $\underline{\underline{u}}$, $f\left(\underline{\underline{u}}\right)$. However, in the absence of external stress, it is usually expressed as a function of $\underline{\underline{u}}$ because $\underline{\underline{u}}$ is invariant under rotations of the target space as is the energy density. The explicit form of f in terms of $\underline{\underline{u}}$ can be written down phenomenologically if we know the symmetry properties of a system. For example, for isotropic systems (like glasses and rubbers), the elastic energy of a distorted state is also invariant under rotations of the reference space. Thus, to the harmonic order of $\underline{\underline{u}}$, the free energy density of an isotropic system is

$$f\left(\underline{\underline{u}}\right) = \frac{1}{2}B\left(\mathrm{Tr}\underline{\underline{u}}\right)^2 + \mu\mathrm{Tr}\underline{\underline{u}}^2, \tag{6}$$

where B and μ are, respectively, the compression and shear modulus, given that $\left(\mathrm{Tr}\underline{\underline{u}}\right)^2$ and $\mathrm{Tr}\left(\underline{\underline{u}}\right)^2$ are the only two second-order rotationally invariant quantities that can be constructed from $\underline{\underline{u}}$. The linear terms in $\underline{\underline{u}}$ should not be included here since we have assumed that the reference state is an equilibrium state. For a uniaxial system with anisotropy axis along the z axis, we have

$$\begin{aligned} f = {} & \frac{1}{2}C_1 u_{zz}^2 + C_2 u_{zz}\left(u_{xx} + u_{yy}\right) + \frac{1}{2}C_3\left(u_{xx} + u_{yy}\right)^2 \\ & + C_4\left(u_{xx}^2 + u_{yy}^2 + 2u_{xy}^2\right) + C_5\left(u_{xz}^2 + u_{yz}^2\right), \end{aligned} \tag{7}$$

which is invariant under rotations in the xy plane in the reference space. The phenomenological elastic energies of crystals depend on their point-group symmetry.

The initial reference state represented by points $\boldsymbol{x}$ may become unstable under some circumstances, and thus the system will jump into a new equilibrium state represented by points $\boldsymbol{x}'$. To explore the elasticity of this new state, we may either use strains and stresses measured relative to the original reference state or use strains and stresses relative to the new equilibrium state. These two approaches are equivalent to each other. We will show below the relations between these two sets of variables.

If we assume mass points in the new equilibrium reference state are related to those in the original reference state via an initial Cauchy deformation tensor $\underline{\underline{\lambda}}^0$, namely,

$$\boldsymbol{x}'_i = \lambda^0_{ij}\boldsymbol{x}_j, \tag{8}$$

then we have

$$\lambda_{ij} = \lambda'_{ik}\lambda^0_{kj}, \tag{9}$$

where $\lambda_{ij} = \partial R_i/\partial x_j$ is the deformation tensor relative to the original reference space and $\lambda'_{ij} = \partial R_i/\partial x'_j$ is the deformation tensor relative to the new reference space. The deviation of strain tensor $\underline{\underline{u}}$ from its new equilibrium value $\underline{\underline{u}}_0$ is thus

$$\delta\underline{\underline{u}} = \underline{\underline{u}} - \underline{\underline{u}}_0 = \frac{1}{2}\left(\underline{\underline{\lambda}}^{\mathrm{T}}\underline{\underline{\lambda}} - \underline{\underline{\lambda}}^{0\mathrm{T}}\underline{\underline{\lambda}}^0\right) = \underline{\underline{\lambda}}^{0\mathrm{T}}\underline{\underline{u}'}\underline{\underline{\lambda}}^0, \tag{10}$$

where

$$\underline{\underline{u}'} = \frac{1}{2}\left(\underline{\underline{\lambda}}'^{\mathrm{T}}\underline{\underline{\lambda}}' - \underline{\underline{\delta}}\right)$$

is the strain tensor relative to the new reference space.

3. Strain-only theory

A complete elastic energy density of nematic elastomers, which will be presented in the next section, should include both the strain tensor and the nematic order tensor since nematic elastomers have both the rubber-like elastic properties and the orientational properties of nematics. However, if we are only interested in their mechanical properties, the nematic tensor can be integrated out and we thus have an effective strain-only energy density, which up to the fourth order in $\underline{\underline{u}}$ can be expressed as

$$f\left(\underline{\underline{u}}\right) = \frac{1}{2}B\left[\mathrm{Tr}\underline{\underline{u}} - (E/B)\,\mathrm{Tr}\underline{\underline{u}}_{\mathrm{t}}^2\right]^2$$

$$+\mu \mathrm{Tr}\underline{\underline{u}}_{\mathrm{t}}^2 - C\mathrm{Tr}\underline{\underline{u}}_{\mathrm{t}}^3 + D\left(\mathrm{Tr}\underline{\underline{u}}_{\mathrm{t}}^2\right)^2 - h\mathrm{Tr}\boldsymbol{n}_0\boldsymbol{n}_0\underline{\underline{u}}_{\mathrm{t}}, \quad (11)$$

where

$$\underline{\underline{u}}_{\mathrm{t}} = \underline{\underline{u}} - \frac{1}{3}\underline{\underline{\delta}}\mathrm{Tr}\underline{\underline{u}} \quad (12)$$

is the symmetric traceless part of $\underline{\underline{u}}$, B and μ are respectively the bulk and effective shear modulus. $\underline{\underline{u}}$ is measured relative to the equilibrium state of $\mu = \infty$ or the equilibrium state at infinitely large temperature. (At finite temperature, this reference state is not an equilibrium state because of the existence of the linear term.) This energy density is rotationally invariant in the target space as is $\underline{\underline{u}}$, but it is not in the reference space. The linear term, $-h\mathrm{Tr}\boldsymbol{n}_0\boldsymbol{n}_0\underline{\underline{u}}_{\mathrm{t}}$, is added to reflect the locked-in anisotropy introduced during the second cross-linking procedure of producing mono-domain nematic elastomers. The vector $\boldsymbol{n}_0$ represents the anisotropy direction at the time of the second cross-linking. Higher-order symmetry-breaking terms have been ignored because the linear term captures the important physics of a uniaxial system.

The effective shear modulus μ is now a function of temperature T. It decreases as temperature decreases. If h= 0, there is a phase transition from the isotropic state, which is also the reference space of the strain tensor, to a nematic state when μ gets smaller than a critical value. In this case ($h = 0$), the energy is also rotationally invariant in the reference space, which means a nematic state (state A) characterized by $\underline{\underline{u}}^0$ is degenerate to another nematic state (state B) characterized by

$$\underline{\underline{O}}_{\mathrm{R}} \cdot \underline{\underline{u}}^0 \cdot \underline{\underline{O}}_{\mathrm{R}}^{\mathrm{T}}, \quad (13)$$

where $\underline{\underline{O}}_{\mathrm{R}}$ is any rotation matrix in the reference space. More specifically, as shown in Fig. 1, if $\underline{\underline{u}}^0$ is a uniaxial extension along the z axis

$$\underline{\underline{u}}^0 = \begin{pmatrix} u_\perp^0 & & \\ & u_\perp^0 & \\ & & u_\parallel^0 \end{pmatrix}, \quad (14)$$

and $\underline{\underline{O}}_{\mathrm{R}}$ represents rotation by θ about the y axis,

$$\underline{\underline{O}}_{\mathrm{R}} = \begin{pmatrix} \cos\theta & 0 & \sin\theta \\ 0 & 1 & 0 \\ -\sin\theta & 0 & \cos\theta \end{pmatrix}, \quad (15)$$

then state B can be characterized by the following strain tensor measured relative to state A,

$$\begin{aligned} \underline{\underline{u}}' &= \left(\underline{\underline{\lambda}}^{0\mathrm{T}}\right)^{-1}\left(\underline{\underline{O}}_{\mathrm{R}}\underline{\underline{u}}^0\underline{\underline{O}}_{\mathrm{R}}^{\mathrm{T}} - \underline{\underline{u}}^0\right)\left(\underline{\underline{\lambda}}^0\right)^{-1} \\ &= \frac{1}{4}(r_{\mathrm{a}}-1)\begin{pmatrix} 1-\cos 2\theta & 0 & r_{\mathrm{a}}^{-1/2}\sin 2\theta \\ 0 & 0 & 0 \\ r_{\mathrm{a}}^{-1/2}\sin 2\theta & 0 & -r_{\mathrm{a}}^{-1}(1-\cos 2\theta) \end{pmatrix}, \end{aligned} \quad (16)$$

where $\underline{\underline{\lambda}}^0$ is the deformation tensor corresponding to $\underline{\underline{u}}^0$ with $\lambda_\perp^0 = \sqrt{1+2u_\perp^0}$ and $\lambda_\parallel^0 = \sqrt{1+2u_\parallel^0}$, and

$$r_{\mathrm{a}} = \frac{\lambda_\parallel^{02}}{\lambda_\perp^{02}} \quad (17)$$

is the anisotropy ratio. Note that $u'_{xx} > 0$ and $u'_{xz} \neq 0$, implying that state B has been stretched along the x axis and sheared relative to state A. Since states A and B are degenerate with each other, this stretch and shear cost no energy. Thus we can easily explain the vanishing of the C_5 defined in Eq. (7) for a soft nematic elastomer and the appearance of the zero-stress plateau in the soft stress–strain curve.

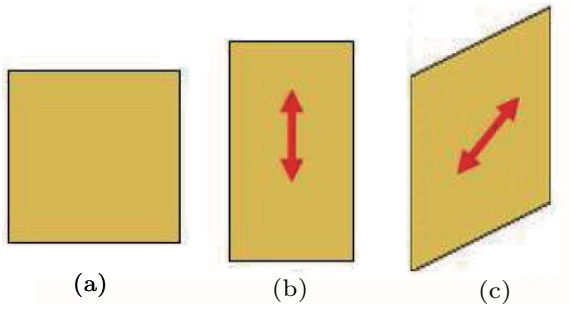


Fig. 1. (color online) Schematic representation of the soft elasticity: (a) the isotropic state, (b) state A, (c) state B, where the arrows represent anisotropy directions.

Our goal is to determine the energy of elastic distortions relative to the equilibrium state. To this end, it is useful to introduce a complete set of five orthonormal symmetric traceless matrices I_{ij}^α satisfying $I_{ij}^\alpha I_{ij}^\beta = \delta^{\alpha\beta}$

$$\underline{\underline{I}}^0 = \sqrt{\frac{2}{3}}\begin{pmatrix} -1/2 & 0 & 0 \\ 0 & -1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad (18a)$$

$$\underline{\underline{I}}^1 = \sqrt{\frac{1}{2}}\begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \quad (18b)$$

$$\underline{\underline{I}}^2 = \sqrt{\frac{1}{2}}\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \quad (18c)$$

$$\underline{\underline{I}}^3 = \sqrt{\frac{1}{2}}\begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix}, \quad (18d)$$

$$\underline{\underline{I}}^4 = \sqrt{\frac{1}{2}}\begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}. \quad (18e)$$

Any symmetric traceless tensor, $\underline{\underline{m}}$, can be expressed as a linear combination of these five matrices:

$$\underline{\underline{m}} = \sum_{\alpha=0}^{4} m_\alpha \underline{\underline{I}}^\alpha,$$

with $m_\alpha = \mathrm{Tr}\underline{\underline{m}}\underline{\underline{I}}^\alpha$. Thus, we have

$$m_0 = \sqrt{\frac{2}{3}}\left[m_{zz} - \frac{1}{2}(m_{xx}+m_{yy})\right], \quad (19a)$$

$$m_1 = \sqrt{\frac{1}{2}}(m_{xx}-m_{yy}), \quad (19b)$$

$$m_2 = \sqrt{2}m_{xy}, \quad (19c)$$

$$m_3 = \sqrt{2}m_{xz}, \tag{19d}$$

$$m_4 = \sqrt{2}m_{yz}. \tag{19e}$$

The free energy given in Eq. (11) can then be expressed in terms of $u_{t\alpha}$'s introduced in Eqs. (19a)–(19e) because $\underline{\underline{u}}_t$ is also symmetric and traceless. If $\boldsymbol{n}_0$ aligns along the z axis, we have

$$\begin{aligned} f = {} & \frac{1}{2}B\Big[u_5 - (E/B)\sum_{\alpha=0}^{4} u_{t\alpha}^2\Big]^2 + \mu\sum_{\alpha=0}^{4} u_{t\alpha}^2 + D\Big(\sum_{\alpha=0}^{4} u_{t\alpha}^2\Big)^2 \\ & - C\left[\frac{1}{2}\sqrt{\frac{2}{3}}u_{t0}^3 - \sqrt{\frac{3}{2}}u_{t0}\left(u_{t1}^2 + u_{t2}^2\right) + \frac{1}{2}\sqrt{\frac{3}{2}}u_{t0}\left(u_{t3}^2 + u_{t4}^2\right)\right] \\ & - \frac{1}{2\sqrt{2}}C\Big[3u_{t1}\left(u_{t2}^2 - u_{t3}^2\right) + 6u_{t2}u_{t3}u_{t4}\Big] \\ & - \sqrt{\frac{2}{3}}hu_{t0}, \end{aligned} \tag{20}$$

where $u_5 = \mathrm{Tr}\,\underline{\underline{u}}$. The equilibrium state of this energy is a uniaxial phase with $u_{t1} = u_{t2} = u_{t3} = u_{t4} = 0$, $\mathrm{Tr}\,\underline{\underline{u}} = (E/B)u_{t0}^2$, and u_{t0} is determined by the following equation,

$$2\mu u_{t0} + 4Du_{t0}^3 - \sqrt{\frac{3}{2}}Cu_{t0}^2 = \sqrt{\frac{2}{3}}h. \tag{21}$$

The deformation tensor of the equilibrium state is then

$$\underline{\underline{\lambda}}_0 = \begin{pmatrix} \lambda_{0\perp} & & \\ & \lambda_{0\perp} & \\ & & \lambda_{0\parallel} \end{pmatrix}, \tag{22}$$

where

$$\lambda_{0\perp} = \sqrt{1 - \sqrt{\frac{2}{3}}u_{t0} + \frac{2}{3}\frac{E}{B}u_{t0}^2}, \tag{23}$$

$$\lambda_{0\parallel} = \sqrt{1 + 2\sqrt{\frac{2}{3}}u_{t0} + \frac{2}{3}\frac{E}{B}u_{t0}^2}. \tag{24}$$

Expanding Eq. (20) to the second order in deviations $\delta u_{t\alpha}$ yields

$$\begin{aligned} \delta f = {} & \frac{1}{2}B\left[\delta u_5 - 2(E/B)u_{t0}^0\delta u_{t0}\right]^2 \\ & + \frac{1}{2}A_1\delta u_{t0}^2 + \frac{1}{2}A_2\left(\delta u_{t1}^2 + \delta u_{t2}^2\right) \\ & + \frac{1}{2}A_3\left(\delta u_{t3}^2 + \delta u_{t4}^2\right), \end{aligned} \tag{25}$$

where

$$\begin{aligned} A_1 &= 2\left(\mu + 6Du_{t0}^{02} - \sqrt{\frac{3}{2}}Cu_{t0}^0\right), \\ A_2 &= 2\left(\mu + 2Du_{t0}^{02} + \sqrt{\frac{3}{2}}Cu_{t0}^0\right), \\ A_3 &= \sqrt{\frac{3}{2}}\frac{h}{u_{t0}^0}, \end{aligned} \tag{26}$$

and u_{t0}^0 is given by Eq. (21). Using Eqs. (19a)–(19e) and converting the strain variables into those relative to the equilibrium state [see Eq. (10)], we obtain the elastic free energy for a uniaxial system,

$$\begin{aligned} \delta f = {} & \frac{1}{2}C_1u_{zz}'^2 + C_2u_{zz}'\left(u_{xx}' + u_{yy}'\right) + \frac{1}{2}C_3\left(u_{xx}' + u_{yy}'\right)^2 \\ & + C_4\left(u_{xx}'^2 + u_{yy}'^2 + 2u_{xy}'^2\right) + C_5\left(u_{xz}'^2 + u_{yz}'^2\right), \end{aligned} \tag{27}$$

where

$$\begin{aligned} C_1 &= \lambda_{0\parallel}^4\left(B + \frac{2}{3}A_1 - 4\sqrt{\frac{2}{3}}Eu_{t0}^0 + \frac{8}{3}\frac{E^2}{B}u_{t0}^{02}\right), \\ C_2 &= \lambda_{0\parallel}^2\lambda_{0\perp}^2\left(B - \frac{1}{3}A_1 - \sqrt{\frac{2}{3}}Eu_{t0}^0 - \frac{4}{3}\frac{E^2}{B}u_{t0}^{02}\right), \\ C_3 &= \lambda_{0\perp}^4\left(B - \frac{1}{3}A_2 + \frac{1}{6}A_1 + 3\sqrt{\frac{2}{3}}Eu_{t0}^0 + \frac{2}{3}\frac{E^2}{B}u_{t0}^{02}\right), \\ C_4 &= \frac{1}{2}\lambda_{0\perp}^4A_2, \\ C_5 &= \lambda_{0\parallel}^2\lambda_{0\perp}^2A_3 = \lambda_{0\parallel}^2\lambda_{0\perp}^2\sqrt{\frac{2}{3}}\frac{1}{u_{t0}^0}h. \end{aligned} \tag{28}$$

Thus the shear modulus C_5 vanishes when $h \to 0$, in the absence of the symmetry-breaking term $-h\mathrm{Tr}\,\boldsymbol{n}_0\boldsymbol{n}_0\underline{\underline{u}}_t$, the system is soft and it does not resist shears in planes containing the anisotropy axis. Note, if higher-order terms are included in Eq. (11), the values of the C_i's change accordingly, because of the contribution from those higher-order terms.

4. Theory with strain and order tensor

In this section, we develop a phenomenological theory for semi-soft nematic elastomers with both the strain tensor and the nematic order tensor included. The explicit inclusion of the orientational degrees of freedom enables us to investigate not only the mechanical but also the optical and electric properties of nematic elastomers.

In such a theory, we need to combine the strain tensor $\underline{\underline{u}}$ with the nematic order tensor $\underline{\underline{Q}}$. As shown in Section 2, $\underline{\underline{u}}$ is invariant under rotations of the target space and transforms as a tensor under rotations of the reference space. However, $\underline{\underline{Q}}$ is a tensor defined in the target space: it transforms as a tensor under rotations of the target space, and rotations of the reference space have no effect on it. Thus, to combine $\underline{\underline{u}}$ and $\underline{\underline{Q}}$, it is necessary to convert $\underline{\underline{Q}}$ to a tensor possessing the same rotational properties as $\underline{\underline{u}}$. For this purpose, we introduce an orthogonal unimodular conversion tensor,[14]

$$\underline{\underline{O}}_C = \underline{\underline{\lambda}}\left(\underline{\underline{\lambda}}^{\mathrm{T}}\underline{\underline{\lambda}}\right)^{-1/2}, \tag{29}$$

which converts a target-space vector, ν, to a reference-space vector, $\overline{\nu}$, via

$$\overline{\nu} = \underline{\underline{O}}_C^{\mathrm{T}} \cdot \nu, \tag{30}$$

and converts a target-space tensor, $\underline{t}$, to a reference-space tensor, $\underline{\bar{t}}$, via

$$\underline{\bar{t}} = \underline{\underline{O}}_C^{\mathrm{T}} \cdot \underline{t} \cdot \underline{\underline{O}}_C. \tag{31}$$

Thus, if $\boldsymbol{n}$ is the nematic director in the target space, then $\overline{\boldsymbol{n}} = \underline{\underline{O}}_C^{\mathrm{T}} \cdot \boldsymbol{n}$ is a reference space vector, which transforms under rotations in the reference space $\underline{\underline{O}}_{\mathrm{R}}$ and is invariant under rotations in the target space $\underline{\underline{O}}_{\mathrm{T}}$. The rotational properties of $\overline{\boldsymbol{n}}$ can be easily proven: with any given $\underline{\underline{O}}_{\mathrm{R}}$ and $\underline{\underline{O}}_{\mathrm{T}}$, $\underline{\underline{\lambda}} \to \underline{\underline{O}}_{\mathrm{T}} \underline{\underline{\lambda}} \underline{\underline{O}}_{\mathrm{R}}^{\mathrm{T}}$, $\boldsymbol{n} \to \underline{\underline{O}}_{\mathrm{T}} \boldsymbol{n}$, thus,

$$\begin{aligned}
\overline{\boldsymbol{n}} &= \left(\underline{\underline{\lambda}}^{\mathrm{T}} \underline{\underline{\lambda}}\right)^{-1/2} \underline{\underline{\lambda}}^{\mathrm{T}} \boldsymbol{n} \\
&\to \left(\underline{\underline{O}}_{\mathrm{R}} \underline{\underline{\lambda}}^{\mathrm{T}} \underline{\underline{O}}_{\mathrm{T}}^{\mathrm{T}} \underline{\underline{O}}_{\mathrm{T}} \underline{\underline{\lambda}} \underline{\underline{O}}_{\mathrm{R}}^{\mathrm{T}}\right)^{-1/2} \underline{\underline{O}}_{\mathrm{R}} \underline{\underline{\lambda}}^{\mathrm{T}} \underline{\underline{O}}_{\mathrm{T}}^{\mathrm{T}} \underline{\underline{O}}_{\mathrm{T}} \boldsymbol{n} \\
&= \left(\underline{\underline{O}}_{\mathrm{R}} \underline{\underline{\lambda}}^{\mathrm{T}} \underline{\underline{\lambda}} \underline{\underline{O}}_{\mathrm{R}}^{\mathrm{T}}\right)^{-1/2} \underline{\underline{O}}_{\mathrm{R}} \underline{\underline{\lambda}}^{\mathrm{T}} \boldsymbol{n} \\
&= \underline{\underline{O}}_{\mathrm{R}} \left(\underline{\underline{\lambda}}^{\mathrm{T}} \underline{\underline{\lambda}}\right)^{-1/2} \underline{\underline{O}}_{\mathrm{R}}^{\mathrm{T}} \underline{\underline{O}}_{\mathrm{R}} \underline{\underline{\lambda}}^{\mathrm{T}} \boldsymbol{n} \\
&= \underline{\underline{O}}_{\mathrm{R}} \left(\underline{\underline{\lambda}}^{\mathrm{T}} \underline{\underline{\lambda}}\right)^{-1/2} \underline{\underline{\lambda}}^{\mathrm{T}} \boldsymbol{n} \\
&= \underline{\underline{O}}_{\mathrm{R}} \overline{\boldsymbol{n}}. \qquad (32)
\end{aligned}$$

Similarly, we can show $\underline{\underline{\overline{Q}}} = \underline{\underline{O}}_C^{\mathrm{T}} \cdot \underline{\underline{Q}} \cdot \underline{\underline{O}}_C$ is a reference-space tensor. Note that according to the matrix polar decomposition theorem any nonsingular square matrix can be expressed as the product of a rotation matrix and a symmetric matrix. For the deformation tensor $\underline{\underline{\lambda}}$, $\underline{\underline{\lambda}} = \underline{\underline{O}}_C \cdot \left(\underline{\underline{\lambda}}^{\mathrm{T}} \underline{\underline{\lambda}}\right)^{1/2}$ with $\underline{\underline{O}}_C$ being the rotation part. Because $\det \underline{\underline{O}}_C = 1$, the length of a vector or the magnitude of a tensor does not change after the conversion from the target space to the reference space. Therefore, $\overline{\boldsymbol{n}} = \underline{\underline{O}}_C^{\mathrm{T}} \cdot \boldsymbol{n}$ is still a unit vector, which represents the nematic director defined in the body frame, and its direction represents the relative rotation of the nematic director with respect to the elastic body; and $\underline{\underline{\overline{Q}}} = \underline{\underline{O}}_C^{\mathrm{T}} \cdot \underline{\underline{Q}} \cdot \underline{\underline{O}}_C$ is now the order tensor defined in the body frame.

We can then use $\underline{\underline{u}}$ and $\underline{\underline{\overline{Q}}}$ to construct a phenomenological theory including both the strain tensor and the orientational order tensor. A generic model free-energy density for such a theory should include three parts: the elastic part f_{el}, the orientational-order part f_Q, and the coupling term f_C between the strain tensor and the order tensor,

$$f = f_{\mathrm{el}} + f_Q + f_C. \qquad (33)$$

We can choose the Landau–de Gennes form for f_Q

$$\begin{aligned}
f_Q &= \frac{1}{2} r_Q \mathrm{Tr} \underline{\underline{Q}}^2 - \omega_3 \mathrm{Tr} \underline{\underline{Q}}^3 + \omega_4 \left(\mathrm{Tr} \underline{\underline{Q}}^2\right)^2 \\
&= \frac{1}{2} r_Q \mathrm{Tr} \underline{\underline{\overline{Q}}}^2 - \omega_3 \mathrm{Tr} \underline{\underline{\overline{Q}}}^3 + \omega_4 \left(\mathrm{Tr} \underline{\underline{\overline{Q}}}^2\right)^2, \qquad (34)
\end{aligned}$$

where r_Q is a function of temperature and goes to infinity as temperature goes to infinity; and, to the harmonic order of $\underline{\underline{u}}$ and $\underline{\underline{\overline{Q}}}$, we have

$$\begin{aligned}
f_{\mathrm{el}} + f_C = &\frac{1}{2} B \left(\mathrm{Tr} \underline{\underline{u}}\right)^2 + \mu \mathrm{Tr} \underline{\underline{u}}_t^2 - s \mathrm{Tr} \underline{\underline{u}} \mathrm{Tr} \underline{\underline{\overline{Q}}}^2 \\
&- 2t \mathrm{Tr} \underline{\underline{u}}_t \underline{\underline{\overline{Q}}} - h \mathrm{Tr} \underline{\underline{\overline{Q}}} \underline{\underline{Q}}_C, \qquad (35)
\end{aligned}$$

where $\underline{\underline{u}}_{\mathrm{t}} = \underline{\underline{u}} - (1/3) \underline{\underline{\delta}} \mathrm{Tr} \underline{\underline{u}}$ is the traceless part of $\underline{\underline{u}}$ and $\underline{\underline{u}}$ is measured relative to the equilibrium state of infinitely large temperature. $\underline{\underline{Q}}_C = S_C \left(\boldsymbol{n}_0 \boldsymbol{n}_0 - (1/3) \underline{\underline{\delta}}\right)$ is the nematic order tensor at the time of the second cross-linking, at the time of the second cross-linking, which does not change under rotations of the target space. The linear symmetry-breaking term represents the locked-in anisotropy introduced during the second cross-linking in a nematic phase. If $\underline{\underline{Q}}_C = 0$, the free energy density is invariant under rotations in the reference space and under simultaneous rotations of $\boldsymbol{R}$ and $\underline{\underline{Q}}$ in the target space. The reason why we did not include $\mathrm{Tr} \underline{\underline{u}}_{\mathrm{t}} \underline{\underline{Q}}_C$ in the linear symmetry breaking term is that the free energy should have an isotropic form if $\underline{\underline{\overline{Q}}} \to 0$. As in the strain-only theory, we have also ignored the higher-order symmetry breaking terms since the linear term can serve our purpose very well.

To calculate the equilibrium state, we recast the above free energy into a slightly different form,

$$\begin{aligned}
f &= f_{\mathrm{el}} + f_C + f_Q \\
&= \frac{1}{2} B \left[\mathrm{Tr} \underline{\underline{u}} - (s/B) \mathrm{Tr} \underline{\underline{\overline{Q}}}^2\right]^2 + \mu \mathrm{Tr} \left[\underline{\underline{u}}_{\mathrm{t}} - (t/\mu) \underline{\underline{\overline{Q}}}\right]^2 \\
&\quad - h \mathrm{Tr} \underline{\underline{\overline{Q}}} \underline{\underline{Q}}_C + \frac{1}{2} r'_Q \mathrm{Tr} \underline{\underline{\overline{Q}}}^2 - \omega_3 \mathrm{Tr} \underline{\underline{\overline{Q}}}^3 + \omega'_4 \left(\mathrm{Tr} \underline{\underline{\overline{Q}}}^2\right)^2, \qquad (36)
\end{aligned}$$

where $r'_Q = r_Q - 2t^2/\mu$ and $\omega'_4 = \omega_4 - s^2/(2B)$. Thus, in equilibrium, we have

$$\begin{aligned}
&\mathrm{Tr} \underline{\underline{u}}^0 = \frac{s}{B} \mathrm{Tr} \underline{\underline{\overline{Q}}}^{02}, \\
&\underline{\underline{u}}_t^0 = \frac{t}{\mu} \underline{\underline{\overline{Q}}}^0, \\
&\underline{\underline{\overline{Q}}}^0 = S_0 \left(\boldsymbol{n}_0 \boldsymbol{n}_0 - \frac{1}{3} \underline{\underline{\delta}}\right), \qquad (37)
\end{aligned}$$

with S_0 determined by

$$r'_Q S_0 - \omega_3 S_0^2 + \frac{8}{3} \omega'_4 S_0^3 = h S_C, \qquad (38)$$

where S_C is the order parameter of the nematic state at the time of the second cross-linking.

To calculate the free energy of deviations from this equilibrium state, we express $\underline{\underline{u}}_{\mathrm{t}}$ and $\underline{\underline{\overline{Q}}}$ as

$$\begin{aligned}
\underline{\underline{u}}_{\mathrm{t}} &= \sum_{\alpha=0}^{4} u_{\mathrm{t}\alpha} \underline{\underline{I}}^{\alpha}, \\
\underline{\underline{\overline{Q}}} &= \sum_{\alpha=0}^{4} \overline{Q}_{\alpha} \underline{\underline{I}}^{\alpha},
\end{aligned}$$

where $\underline{\underline{I}}^{\alpha}$'s are the complete set of five orthonormal symmetric traceless matrices introduced in Eqs. (18a)–(18b) in the previous section. The relations between $u_{t\alpha}$ (or $\overline{Q}_{\alpha}$) and u_{tij} (or $\overline{Q}_{ij}$) are given in Eqs. (19a)–(19e). In equilibrium, the only nonzero components are $\overline{Q}_0^0 = \sqrt{2/3} S_0$ and $u_{\mathrm{t}0}^0 = (t/\mu)\sqrt{2/3} S_0$. We also define $u_5 = \mathrm{Tr} \underline{\underline{u}}$, with the equilibrium value $u_5^0 = \mathrm{Tr} \underline{\underline{u}}^0 = (s/B) u_{\mathrm{t}0}^{02}$. We can then expand the f

given in Eq. (36) to the harmonic order of $\delta\overline{Q}_\alpha\left(=\overline{Q}_\alpha-\overline{Q}^0_\alpha\right)$, $\delta u_{t\alpha}\left(=u_{t\alpha}-u^0_{t\alpha}\right)$, and $\delta u_5\left(=u_5-u^0_5\right)$,

$$\begin{aligned}\delta f=&\frac{1}{2}B\left[\delta u_5-2\frac{s}{B}\overline{Q}^0_0\delta\overline{Q}_0\right]^2+\mu\sum_{\alpha=0}^{4}\left[\delta\mu_{t\alpha}-(t/\mu)\,\delta\overline{Q}_\alpha\right]^2\\&+\frac{1}{2}A_1\left(\delta\overline{Q}_0\right)^2+\frac{1}{2}A_2\left(\delta\overline{Q}_1^2+\delta\overline{Q}_2^2\right)\\&+\frac{1}{2}A_3\left(\delta\overline{Q}_3^2+\delta\overline{Q}_4^2\right),\end{aligned}\tag{39}$$

where

$$\begin{aligned}A_1&=r'_Q+12\omega'_4\overline{Q}_0^{02}-\sqrt{6}\omega_3\overline{Q}^0_0,\\A_2&=r'_Q+4\omega'_4\overline{Q}_0^{02}+\sqrt{6}\omega_3\overline{Q}^0_0,\\A_3&=h\frac{S_C}{S_0}.\end{aligned}\tag{40}$$

Integrating out the longitudinal mode $\delta\overline{Q}_0$ and biaxial modes $\delta\overline{Q}_1$ and $\delta\overline{Q}_2$ yields

$$\begin{aligned}\delta f=&\frac{1}{2}B_1\delta u_5^2+\mu_2\left(\delta u_{t1}^2+\delta u_{t2}^2\right)+\mu_0\delta u_{t0}^2-\gamma\delta u_{t0}\delta u_5\\&+\mu\sum_{a=3}^{4}\left[\delta u_{t\alpha}-(t/\mu)\,\delta\overline{Q}_\alpha\right]^2+\frac{1}{2}A_3\left(\delta\overline{Q}_3^2+\delta\overline{Q}_4^2\right),\end{aligned}\tag{41}$$

where

$$\begin{aligned}B_1&=B-\frac{16s^2S_0^2}{9A'},\quad \mu_0=\mu-\frac{4t^2}{3A'},\\\mu_2&=\frac{\mu A_2}{A_2+2t^2/\mu},\quad \gamma=-4\left(\frac{2}{3}\right)^{3/2}\frac{stS_0}{A'},\end{aligned}$$

where

$$A'=A_1+\frac{9s^2}{4B}S_0^2+\frac{3t^2}{\mu}.$$

Using the relation between $u_{t\alpha}$ (or $\bar{Q}_\alpha$) and $u_{tij}(\bar{Q}_{ij})$ and that $\delta u_5=\delta u_{xx}+\delta u_{yy}+\delta u_{zz}$, we obtain

$$\begin{aligned}\delta f=&\frac{1}{2}\overline{B}_1\delta u_{zz}^2+\overline{B}_2\delta u_{zz}\left(\delta u_{xx}+\delta u_{yy}\right)+\frac{1}{2}\overline{B}_3\left(\delta u_{xx}+\delta u_{yy}\right)^2\\&+\mu_2\left(\delta u_{xx}^2+\delta u_{yy}^2+2u_{xy}^2\right)\\&+2\mu\left\{\left[u_{xz}-(t/\mu)\,\overline{Q}_{xz}\right]^2+\left[u_{yz}-(t/\mu)\,\overline{Q}_{yz}\right]^2\right\}\\&+A_3\left(\overline{Q}_{xz}^2+\overline{Q}_{yz}^2\right),\end{aligned}\tag{42}$$

where

$$\begin{aligned}\overline{B}_1&=B_1+\frac{4}{3}\mu_0-2\sqrt{\frac{2}{3}}\gamma,\\\overline{B}_2&=B_1-\frac{2}{3}\mu_0-\frac{1}{2}\sqrt{\frac{2}{3}}\gamma,\\\overline{B}_3&=B_1-\mu_2+\frac{1}{3}\mu_0+\sqrt{\frac{2}{3}}\gamma,\end{aligned}$$

and $\boldsymbol{n}_0$ is assumed to align along the z axis. If the system is cross-linked in an isotropic state, $A_3=0$ and because $\overline{Q}_{xz}\left(\overline{Q}_{yz}\right)$ can relax to eliminate the contribution from $u_{xz}\left(u_{yz}\right)$, there is thus no energy cost arising from shears u_{xz} and u_{yz}.

The strain variables used in Eq. (42) are measured relative to the original reference state, namely the equilibrium state of infinitely large temperature. We need to convert them to the strain variables measured relative to the new equilibrium state,

$$\underline{\underline{u}}'=\left(\underline{\underline{\lambda}}^{0T}\right)^{-1}\delta\underline{\underline{u}}\left(\underline{\underline{\lambda}}^{0}\right)^{-1},\tag{43}$$

where $\underline{\underline{\lambda}}_0$ is the deformation tensor describing the new equilibrium state with

$$\lambda_{0\perp}=\sqrt{1-\sqrt{\frac{2}{3}}u_{t0}+\frac{2}{3}\frac{s}{B}\left(\frac{\mu}{t}u_{t0}\right)^2},\tag{44}$$

$$\lambda_{0\parallel}=\sqrt{1+2\sqrt{\frac{2}{3}}u_{t0}+\frac{2}{3}\frac{s}{B}\left(\frac{\mu}{t}u_{t0}\right)^2}.\tag{45}$$

Since we are interested in the energy cost of rotating the director away from its initial direction, it is thus necessary to determine the relation between $\overline{Q}_{xz}\left(\overline{Q}_{yz}\right)$ and $\delta\boldsymbol{n}=\boldsymbol{n}-\boldsymbol{n}_0$, where $\boldsymbol{n}$ is the director in the target space. For small deformations and rotations, we have

$$\overline{Q}_{az}=S_0\delta\overline{n}_{\rm a}=S_0\left(\delta\boldsymbol{n}_{\rm a}-\eta'^{A}_{az}-\frac{\lambda_{0\parallel}-\lambda_{0\perp}}{\lambda_{0\parallel}+\lambda_{0\perp}}\eta'^{S}_{az}\right),\tag{46}$$

where $a=x$ or y and

$$\eta'^{A}_{az}=\frac{1}{2}\left(\frac{\partial u'_a}{\partial x'_z}-\frac{\partial u'_z}{\partial x'_a}\right)$$

and

$$\eta'^{S}_{az}=\frac{1}{2}\left(\frac{\partial u'_a}{\partial x'_z}+\frac{\partial u'_z}{\partial x'_a}\right)$$

are, respectively, the antisymmetric and symmetric part of the displacement gradient tensor measured in the new equilibrium state. Using Eq. (43) and Eq. (46), we then obtain

$$\begin{aligned}\delta f=&\frac{1}{2}C_1\eta'^2_{zz}+C_2\eta'_{zz}\left(\eta'_{xx}+\eta'_{yy}\right)+\frac{1}{2}C_3\left(\eta'_{xx}+\eta'_{yy}\right)^2\\&+C_4\left(\eta'^2_{xx}+\eta'^2_{yy}+2\eta'^{S2}_{xy}\right)\\&+C_5\sum_{a=x,y}\left[\eta'^{S}_{az}-\beta_1\left(\delta\boldsymbol{n}_{\rm a}-\eta'^{A}_{az}\right)\right]^2\\&+C_6\sum_{a=x,y}\left[\left(\delta\boldsymbol{n}_a-\eta'^{A}_{az}\right)-\beta_2\eta'^{S}_{az}\right]^2,\end{aligned}\tag{47}$$

where

$$\beta_1=\frac{\lambda_{0\parallel}^2-\lambda_{0\perp}^2}{\lambda_{0\parallel}^2+\lambda_{0\perp}^2}=\frac{r_a-1}{r_a+1},\tag{48}$$

$$\beta_2=\frac{\lambda_{0\parallel}-\lambda_{0\perp}}{\lambda_{0\parallel}+\lambda_{0\perp}},\tag{49}$$

and

$$\begin{aligned}C_1&=\lambda_{0\parallel}^4\overline{B}_1,\quad C_2=\lambda_{0\parallel}^2\lambda_{0\perp}^2\overline{B}_2,\\C_3&=\lambda_{0\perp}^4\overline{B}_3,\quad C_4=\lambda_{0\perp}^4\mu_2,\\C_5&=\frac{1}{2}\left(\lambda_{0\parallel}^2+\lambda_{0\perp}^2\right)^2\mu,\quad C_6=A_3S_0^2,\end{aligned}$$

and the approximation that

$$u'_{ij} \approx \eta'^{S}_{ij} = \frac{1}{2}\left(\frac{\partial u'_i}{\partial x'_j} + \frac{\partial u'_j}{\partial x'_i}\right)$$

has been used. As in the strain-only theory, the exact values of the C_i's in the above equation may change if higher order terms are included in Eq. (35).

5. Conclusion

We have developed a phenomenological description for semi-soft nematic elastomers. Particular care has been paid to distinguish the complicated symmetries associated with two different spaces — the reference and target spaces (i.e., the states before and after deformation). Based on the strain tensor, the phenomenological description presented in this paper is particularly suitable for cases where rotational symmetries resulting from the nonlinearity of elasticity are important.[15–19] How the elastic and coupling constants in this description can be related to microscopic theories will be explored in future.

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