

A Non-Local Model for Liquid Crystal Elastomers

R. Ennis¹, L. C. Malacarne^{1,2}, P. Palffy-Muhoray¹ and M. Shelley³,

¹*Liquid Crystal Institute, Kent State University, 44242 Kent, OH - USA*

²*Universidade Estadual de Maringá, 87020-900 Maringá, Paraná - Brazil*

³*Courant Institute of Mathematical Sciences, New York University, New York, NY - USA*

We have developed a fully non-local model to describe the behavior of nematic liquid crystal elastomers. The free energy, incorporating both elastic and nematic contributions, is a function of the material displacement vector and the orientational order parameter tensor. The free energy cost of spatial variations of these order parameters is taken into account through non-local interactions rather than through the use of gradient expansions. We also give an expression for the Rayleigh dissipation function. The equations of motion, for displacement and orientational order, are obtained from the free energy and the dissipation function by the use of a Lagrangian approach. We examine the free energy and the equations of motion in the limit of long wavelength and small amplitude variations of displacement and orientational order parameter. We compare our results with those in the literature. If the scalar order parameter is held fixed, we recover the usual viscoelastic theory.

Liquid crystal elastomers (LCEs), first proposed by de Gennes[1] and synthesized by Finkelmann[2], are solid orientationally ordered rubbers. They consist of weakly cross-linked liquid crystal polymers with orientationally ordered side- or main-chain mesogenic units. The salient feature of LCEs is the coupling between mechanical deformation and orientational order.[3]. As a result of this coupling, these materials can exhibit exceptionally large responses to external stimuli, suggesting a variety of potential applications. These range from artificial muscles[4] to mechanically tunable photonic band gap materials[5] and bifocal contact lenses [6].

Much of the experimental and theoretical work on LCEs has been carried out during the past decade. Equilibrium properties are relatively well understood, but dynamic phenomena have not yet been thoroughly characterized. Since these often involve large deformations and complex viscoelastic behavior, they are incompletely understood. In nematic LCEs, both scalar order parameter and director orientation are coupled to the mechanical deformation. At temperatures far from the nematic-isotropic transition, strain induced changes of the scalar order parameter are typically small, and frequently assumed to be spatially uniform[7]. However, some of the most interesting aspects of nematic elastomers, such as changes in shape due to excitations, are associated with non-uniform changes in the order parameter tensor, e.g. Ref. [8, 9].

We present a non-local continuum description of nematic LCEs. Our fundamental variables are the displacement vector of cross-links and the orientational order parameter tensor. Since gradient expansions of the free energy can lead to ill-posedness of the problem of its minimization [10], we use a non-local formalism, where the effects of spatial variations of the displacement and order parameter on the free energy are taken into account via the fully non-local interactions. We also propose a Rayleigh dissipation function, which is local due to the short range of the dissipative interactions. Using a Lagrangian approach, we obtain the equations of motion for the material displacement and the orientational order parameter. Finally, we examine the free energy and the equations of motion in the limit of long wavelength and small amplitude variations of displacement and orientational order parameter, and compare our results with those existing in the literature.

I. FREE ENERGY

A. The elastic free energy

The elastic part of the free energy of either an isotropic or a liquid crystal elastomer in a continuum description can be written in terms of non-local interactions between connected cross-links. In our formalism,

$$F_{\text{el}} = \frac{1}{2} \int \rho_o P_o(\mathbf{r}, \mathbf{r}') g(\mathbf{r} + \mathbf{R}, \mathbf{r}' + \mathbf{R}') d^3\mathbf{r} d^3\mathbf{r}' \quad (1)$$

where ρ_o is the cross-link density, P_o is the probability-density for finding the ends of a polymer chain at \mathbf{r} and \mathbf{r}' in the undeformed sample, and g is the interaction kernel. $\mathbf{R}(\mathbf{r})$ denotes the displacement of a material point from its original position \mathbf{r} in the undistorted sample, and the vector $\mathbf{X} = \mathbf{r} + \mathbf{R}$ is the Eulerian, while \mathbf{r} is the Lagrangian coordinate. The integrals are taken over the sample volume. In an isotropic system, the probability density of finding

the ends of a polymer chain of length \mathcal{L} at \mathbf{r} and \mathbf{r}' is given by

$$P_{\text{iso}}(\mathbf{r}, \mathbf{r}') = \left(\frac{3}{2\pi\mathcal{L}a} \right)^{3/2} \exp \left(-\frac{3(r_\alpha - r'_\alpha)\mathbb{L}_{\alpha\beta}^{-1}(r_\beta - r'_\beta)}{2\mathcal{L}a} \right) \quad (2)$$

where a is the persistence- or step length, and \mathbb{L}_o^{-1} is the dimensionless inverse step-length tensor. Since the system is isotropic, \mathbb{L}_o^{-1} is just the identity.

In the anisotropic LCE system, following Warner and Terentjev [3], we take

$$P_o(\mathbf{r}, \mathbf{r}') = \left(\frac{3}{2\pi\mathcal{L}a} \right)^{3/2} \frac{1}{(\det \mathbf{L}_o)^{1/2}} \exp \left(-\frac{3(r_\alpha - r'_\alpha)L_{\alpha\beta}^{-1}(r_\beta - r'_\beta)}{2\mathcal{L}a} \right) \quad (3)$$

where $L_{\alpha\beta}$ is the effective dimensionless step length tensor in the undeformed sample, and \mathbf{L}_o appears in the denominator as a result of normalization. The interaction kernel is the free energy of a Gaussian coil, given by

$$g(\mathbf{r} + \mathbf{R}, \mathbf{r}' + \mathbf{R}') = -kT \ln P(\mathbf{r} + \mathbf{R}, \mathbf{r}' + \mathbf{R}') \quad (4)$$

where k is Boltzmann's constant, T is the temperature and $P(\mathbf{r}, \mathbf{r}')$ is the probability density for the coil-ends, given by

$$P(\mathbf{r}, \mathbf{r}') = \left(\frac{3}{2\pi\mathcal{L}a} \right)^{3/2} \frac{1}{(\det \mathbf{L})^{1/2}} \exp \left(-\frac{3(r_\alpha - r'_\alpha)L_{\alpha\beta}^{-1}(r_\beta - r'_\beta)}{2\mathcal{L}a} \right) \quad (5)$$

where $L_{\alpha\beta}$ is the effective dimensionless step length tensor in the deformed sample. In general, $L_{\alpha\beta}$ depends on the degree of orientational order, and hence on the order parameter tensor. The free energy then takes the form

$$F_{\text{el}}^c = \frac{1}{2}kT \int \rho_o P_o(\mathbf{r}, \mathbf{r}') \times \left[\frac{3}{2\mathcal{L}a}(r'_\alpha + R'_\alpha - r_\alpha - R_\alpha)L_{\alpha\beta}^{-1}(r'_\beta + R'_\beta - r_\beta - R_\beta) + \frac{1}{2} \ln \det \mathbf{L} \right] d^3\mathbf{r} d^3\mathbf{r}' \quad (6)$$

omitting an additive constant. By writing the free energy as $F = \int \mathcal{F} d^3\mathbf{r}$, we have, explicitly for the elastic free energy density,

$$\mathcal{F}_{\text{el}}^c(\mathbf{r}) = \frac{1}{2}kT\rho_o \left(\frac{3}{2\pi\mathcal{L}a} \right)^{3/2} \int \frac{1}{(\det \mathbf{L}_o)^{1/2}} \exp \left(-\frac{3(r_\alpha - r'_\alpha)L_{\alpha\beta}^{-1}(r_\beta - r'_\beta)}{2\mathcal{L}a} \right) \times \left[\frac{3}{2\mathcal{L}a}(r'_\alpha + R'_\alpha - r_\alpha - R_\alpha)L_{\alpha\beta}^{-1}(r'_\beta + R'_\beta - r_\beta - R_\beta) + \frac{1}{2} \ln \det \mathbf{L} \right] d^3\mathbf{r}' \quad (7)$$

1. Compressibility

The expression for the elastic free energy above describes the entropic contributions associated with changing the distance between the end points of polymer chains. It does not describe Van der Waals or steric interactions responsible for the condensed phase of the system and for determining bulk compressibility. Experimentally, it is found that most rubbers and liquid crystal elastomers are nearly volume conserving. Rather than constructing a more detailed free energy, capable of producing an equation of state for the system, we therefore propose two approaches for enforcing volume conservation. Volume conservation requires that, to lowest order,

$$\frac{\partial R_\alpha}{\partial r_\alpha} = 0 \quad (8)$$

The first approach to enforce this is include in the free energy density the term

$$\frac{1}{2}\mathcal{B}\left(\frac{\partial R_\alpha}{\partial r_\alpha}\right)^2 \quad (9)$$

which penalizes volume change. The quantity \mathcal{B} corresponds to the bulk modulus and approaches infinity in the limit that the elastomer becomes incompressible. Alternately, one may include a potential energy density function $P(\mathbf{R})$

in the free energy which is determined by the requirement that Eq. (8) remain satisfied. P may be regarded as an internal pressure. Both approaches accomplish the desired result, here we choose the first, and write for the elastic contribution to the free energy density

$$\mathcal{F}_{\text{el}}(\mathbf{r}) = \frac{1}{2}kT\rho_o \left(\frac{3}{2\pi\mathcal{L}a}\right)^{3/2} \int \left\{ \frac{1}{(\det \mathbf{L}_o)^{1/2}} \exp\left(-\frac{3(r_\alpha - r'_\alpha)L_{o\alpha\beta}^{-1}(r_\beta - r'_\beta)}{2\mathcal{L}a}\right) \times \left[\frac{3}{2\mathcal{L}a}(r'_\alpha + R'_\alpha - r_\alpha - R_\alpha)L_{\alpha\beta}^{-1}(r'_\beta + R'_\beta - r_\beta - R_\beta) + \ln \det \mathbf{L} \right] + \frac{1}{2}\mathcal{B}\left(\frac{\partial R_\alpha}{\partial r_\alpha}\right)^2 \right\} d^3\mathbf{r}' \quad (10)$$

B. The nematic free energy

The free energy associated with liquid crystalline order of the mesogenic constituents of the elastomer can be written in terms of the non-local dispersion interactions using an inhomogeneous mean field approach. We assume the mesogens are effectively cylindrically symmetric, with the symmetry axis along the unit vector $\hat{\mathbf{I}}$. The orientation of the mesogen is specified by the symmetric, traceless tensor

$$\sigma_{\alpha\beta} \equiv \frac{1}{2}(3l_\alpha l_\beta - \delta_{\alpha\beta}) \quad (11)$$

where l_α is the α^{th} cartesian component of $\hat{\mathbf{I}}$ and $\delta_{\alpha\beta}$ the Kroenecker delta. This description occurs naturally when considering anisotropic dispersion forces [11] and retains the inversion symmetry of the nematic phase [12]. The orientational order parameter $Q_{\alpha\beta}$ is

$$Q_{\alpha\beta} \equiv \langle \sigma_{\alpha\beta} \rangle \quad (12)$$

where the square brackets $\langle \dots \rangle$ denote ensemble average. $Q_{\alpha\beta}$ is real, symmetric and traceless; it can be written as

$$\mathbf{Q} = -\frac{1}{2}(S - P)\hat{\mathbf{L}}\hat{\mathbf{L}} - \frac{1}{2}(S + P)\hat{\mathbf{M}}\hat{\mathbf{M}} + S\hat{\mathbf{N}}\hat{\mathbf{N}} \quad (13)$$

where the eigenvector $\hat{\mathbf{N}}$ associated with the largest eigenvalue S is the nematic director;

$$S = \langle \frac{1}{2}(3(\hat{\mathbf{I}} \cdot \hat{\mathbf{N}})^2 - 1) \rangle \quad (14)$$

and

$$P = \langle \frac{3}{2}((\hat{\mathbf{I}} \cdot \hat{\mathbf{L}})^2 - (\hat{\mathbf{I}} \cdot \hat{\mathbf{M}})^2) \rangle \quad (15)$$

are the uniaxial and biaxial scalar order parameters. To retain conventional notation, we write the nematic director $\hat{\mathbf{N}} = \hat{\mathbf{n}}$. The biaxial order parameter P can be significant in strongly deformed systems.

The interaction energy of two mesogens located at $\mathbf{X} = \mathbf{r} + \mathbf{R}$ and $\mathbf{X}' = \mathbf{r}' + \mathbf{R}'$ due to London-Van der Waals dispersion interactions is of the form

$$\mathcal{E}_{12} = -C \frac{J_{\alpha\beta\gamma\delta}(\mathbf{X} - \mathbf{X}') (\delta_{\alpha\beta} + \alpha_a \sigma_{\alpha\beta}(\mathbf{X})) (\delta_{\gamma\delta} + \alpha_a \sigma_{\gamma\delta}(\mathbf{X}'))}{|\mathbf{X} - \mathbf{X}'|^6} \quad (16)$$

where C is the interaction strength, and α_a is the relative polarizability anisotropy of the mesogen, given by

$$\alpha_a = \frac{2(\alpha_{\parallel} - \alpha_{\perp})}{(2\alpha_{\perp} + \alpha_{\parallel})} \quad (17)$$

where α_{\parallel} and α_{\perp} are the polarizabilities parallel and perpendicular to $\hat{\mathbf{I}}$. The directional coupling tensor $J_{\alpha\beta\gamma\rho}$ is

$$J_{\alpha\beta\gamma\delta}(\mathbf{X} - \mathbf{X}') \equiv (3\frac{Z_\alpha Z_\gamma}{Z^2} - \delta_{\alpha\gamma})(3\frac{Z_\beta Z_\delta}{Z^2} - \delta_{\beta\delta}) \quad (18)$$

where Z_α is a component of the vector $\mathbf{Z} = \mathbf{X}' - \mathbf{X}$. In the mean field approximation, at constant mesogen density ρ_m , the single particle pseudopotential for a particle with orientation $\sigma_{\alpha\beta}$ in the bulk becomes [11]

$$\begin{aligned} \mathcal{E}(\mathbf{X}, \sigma_{\alpha\beta}) = & -\rho_m U_o(\mathbf{X}) \\ & -\rho_m \sigma_{\alpha\beta}(\mathbf{X}) U_{\alpha\beta}(\mathbf{X}) - \frac{3}{2} \rho_m \alpha_a C \int_{|\mathbf{X}-\mathbf{X}'|>d} \frac{(Q_{\alpha\beta}(\mathbf{X}') - Q_{\alpha\beta}(\mathbf{X})) Z_\alpha Z_\beta}{|\mathbf{X} - \mathbf{X}'|^8} d^3 \mathbf{X}' \\ & -\rho_m (\sigma_{\alpha\beta}(\mathbf{X}) - \frac{1}{2} Q_{\alpha\beta}(\mathbf{X})) Q_{\gamma\delta}(\mathbf{X}) U_{\alpha\beta\gamma\delta}(\mathbf{X}) \\ & -\frac{1}{2} \rho_m \alpha_a^2 C Q_{\alpha\beta}(\mathbf{X}) \int_{|\mathbf{X}-\mathbf{X}'|>d} J_{\alpha\beta\gamma\delta}(\hat{\mathbf{Z}}) \frac{(Q_{\gamma\delta}(\mathbf{X}') - Q_{\gamma\delta}(\mathbf{X}))}{|\mathbf{X} - \mathbf{X}'|^6} d^3 \mathbf{X}' \end{aligned} \quad (19)$$

where $d = d(\mathbf{Q}(\mathbf{X}), \mathbf{Q}(\mathbf{X}'))$ is the distance of closest approach, and

$$U_o(\mathbf{X}) \equiv 3C \int_{|\mathbf{X}-\mathbf{X}'|>d} \frac{1}{|\mathbf{X} - \mathbf{X}'|^6} d^3 \mathbf{X}' \quad (20)$$

$$U_{\alpha\beta}(\mathbf{X}) \equiv 3\alpha_a C \int_{|\mathbf{X}-\mathbf{X}'|>d} \frac{Z_\alpha Z_\beta}{|\mathbf{X} - \mathbf{X}'|^8} d^3 \mathbf{X}'$$

$$U_{\alpha\beta\gamma\delta}(\mathbf{X}) \equiv \alpha_a^2 C \int_{|\mathbf{X}-\mathbf{X}'|>d} \frac{J_{\alpha\beta\gamma\delta}(\hat{\mathbf{Z}})}{|\mathbf{X} - \mathbf{X}'|^6} d^3 \mathbf{X}'. \quad (21)$$

The distance of closest approach d for anisometric mesogens is a function of the relative orientation, and hence, on the average, a function of the the nematic order parameter $Q_{\alpha\beta}$. It is well known that that these steric interactions are required for the correct description of the nematic phase, including its deformations [13][14]. The nematic free energy density at \mathbf{X} is given, to within an additive constant, by

$$\mathcal{F}_{\text{nem}}(\mathbf{X}) = -\rho_m kT \ln \int \exp\left(-\frac{\mathcal{E}(\mathbf{X}, \sigma_{\alpha\beta})}{kT}\right) d^2 \hat{\mathbf{i}} \quad (22)$$

For continuous deformations, \mathbf{X} is a single valued function of \mathbf{r} , and the free energy density can be expressed in terms of Lagrangian coordinates. Assuming incompressibility, $\int \mathcal{F}(\mathbf{r}) d^3 \mathbf{r} = \int \mathcal{F}(\mathbf{X}) d^3 \mathbf{X}$, and the nematic free energy density is given, explicitly, by

$$\mathcal{F}_{\text{nem}}(\mathbf{r}) = \rho_m \mathcal{E}_1(\mathbf{r}) - \rho_m kT \ln \int \exp\left(-\frac{\mathcal{E}_2(\mathbf{r}, \sigma_{\alpha\beta})}{kT}\right) d^2 \hat{\mathbf{i}} + \rho_m \mathcal{E}_{\text{non-local}}(\mathbf{r}) \quad (23)$$

where the single particle pseudopotential, as function of Lagrangian coordinates, is $\mathcal{E}(\mathbf{r}, \sigma_{\alpha\beta}) = \mathcal{E}_1(\mathbf{r}) + \mathcal{E}_2(\mathbf{r}, \sigma_{\alpha\beta}) + \mathcal{E}_{\text{non-local}}(\mathbf{r})$ and

$$\mathcal{E}_1(\mathbf{r}) \equiv -\rho_m U_o(\mathbf{r}) + \frac{1}{2} \rho_m U_{\alpha\beta\gamma\delta}(\mathbf{r}) Q_{\alpha\beta}(\mathbf{r}) Q_{\gamma\delta}(\mathbf{r}) \quad (24)$$

$$\mathcal{E}_2(\mathbf{r}, \sigma_{\alpha\beta}) \equiv -\rho_m \sigma_{\alpha\beta}(\mathbf{r}) U_{\alpha\beta}(\mathbf{r}) - \rho_m U_{\alpha\beta\gamma\delta}(\mathbf{r}) \sigma_{\alpha\beta}(\mathbf{r}) Q_{\gamma\delta}(\mathbf{r}) \quad (25)$$

$$\begin{aligned} \mathcal{E}_{\text{non-local}}(\mathbf{r}) \equiv & -\frac{3}{2} \rho_m \alpha_a C \int_{|\mathbf{Z}|>d} \frac{(Q_{\alpha\beta}(\mathbf{r}') - Q_{\alpha\beta}(\mathbf{r})) Z_\alpha Z_\beta}{|\mathbf{Z}(\mathbf{r}, \mathbf{r}')|^8} d^3 \mathbf{r}' \\ & -\frac{1}{2} \rho_m \alpha_a^2 C \int_{|\mathbf{Z}|>d} J_{\alpha\beta\gamma\delta}(\hat{\mathbf{Z}}) \frac{Q_{\alpha\beta}(\mathbf{r}) (Q_{\gamma\delta}(\mathbf{r}') - Q_{\gamma\delta}(\mathbf{r}))}{|\mathbf{Z}(\mathbf{r}, \mathbf{r}')|^6} d^3 \mathbf{r}' \end{aligned} \quad (26)$$

where $\mathbf{Z}(\mathbf{r}, \mathbf{r}') = \mathbf{X}' - \mathbf{X} = \mathbf{r}' + \mathbf{R}'(\mathbf{r}) - \mathbf{r} - \mathbf{R}(\mathbf{r}')$ as before.

For simplicity, it may be assumed that the dependence of the distance of closest approach d does not depend on nematic order. In this case, the nematic free energy density simplifies to give

$$\begin{aligned} \mathcal{F}_{\text{nem}}(\mathbf{r}) = & \frac{1}{2} \rho_m^2 U Q_{\alpha\beta}^2(\mathbf{r}) - \rho_m kT \ln \int \exp\left(\frac{\rho_m U}{kT} \sigma_{\alpha\beta}(\mathbf{r}) Q_{\alpha\beta}(\mathbf{r})\right) d^2 \hat{\mathbf{i}} \\ & + \frac{1}{2} \rho_m U \int_{|\mathbf{Z}|>d} J_{\alpha\beta\gamma\delta}(\hat{\mathbf{Z}}) \frac{Q_{\alpha\beta}(\mathbf{r}) (Q_{\gamma\delta}(\mathbf{r}) - Q_{\gamma\delta}(\mathbf{r}'))}{|\mathbf{Z}(\mathbf{r}, \mathbf{r}')|^6} d^3 \mathbf{r}' \end{aligned} \quad (27)$$

where

$$U = \frac{4\pi}{5} \frac{\alpha_a^2 C}{d^3} \quad (28)$$

and we have neglected the constant term

$$-\rho_m^2 U_o = -\rho_m^2 \frac{4\pi C}{d^3} \quad (29)$$

The first two terms in Eq. (27) constitute the tensor version of the local Maier-Saupe free energy, while the non-local third term describes the free energy cost of inhomogeneities in the order parameter field [11]. The two contributions, Eqs. (10) and (23) or (27), give

$$\mathcal{F}(\mathbf{r}) = \mathcal{F}_{\text{el}}(\mathbf{r}) + \mathcal{F}_{\text{nem}}(\mathbf{r}) \quad (30)$$

the total free energy density for the elastomer.

II. EQUATIONS OF MOTION

The dynamical equations can be obtained from the generalized Lagrange's equations. Two scalar functions must be specified, the Lagrangian

$$\mathcal{L} = \int (\mathcal{E}_{\text{kin}} - \mathcal{F}) d^3\mathbf{r} \quad (31)$$

where \mathcal{E}_{kin} is the kinetic energy density, and $\mathcal{F} = \mathcal{F}_{\text{el}} + \mathcal{F}_{\text{nem}}$ is the free energy density, and the Rayleigh dissipation function \mathcal{R} . We ignore contributions from the nematic order parameter to the kinetic energy, and so have

$$\mathcal{E}_{\text{kin}}(\mathbf{r}) = \frac{1}{2} \rho \dot{\mathbf{R}}^2(\mathbf{r}) \quad (32)$$

where ρ is the mass density.

We write the local Rayleigh dissipation density function as an expansion in terms of $\dot{Q}_{\alpha\beta}$ and the velocity gradient, $\nabla_{\alpha}^e \dot{R}_{\beta}$, and have, to lowest order,

$$\mathcal{R} = T\dot{\mathcal{S}} = \frac{1}{2} \nu_{\alpha\beta\gamma\delta}^{(2)} \dot{Q}_{\alpha\beta} \dot{Q}_{\gamma\delta} + \nu_{\alpha\beta\gamma\delta}^{(3)} (\nabla_{\beta}^e \dot{R}_{\alpha}) \dot{Q}_{\gamma\delta} + \frac{1}{2} \nu_{\alpha\beta\gamma\delta}^{(4)} (\nabla_{\beta}^e \dot{R}_{\alpha}) (\nabla_{\delta}^e \dot{R}_{\gamma}) \quad (33)$$

where the spatial derivatives are with respect to Eulerian coordinates. We assume that terms that depend on the gradient of the order parameter tensor, $\nabla_{\kappa}^e \dot{Q}_{\alpha\beta}$, are small compared to the other terms present, and are ignored. The viscous coefficients $\nu_{\alpha\beta\gamma\delta}$ are constructed from δ_{ij} and Q_{ij}^0 with the appropriate symmetry. As is usually done in nematodynamics, we choose these coefficients with the same tensorial structure as the free energy density. The equations of motion are obtained by solving

$$\int \left[\frac{d}{dt} \frac{\partial \mathcal{E}_{\text{kin}}}{\partial \dot{R}_{\kappa}} + \frac{\delta \mathcal{F}}{\delta R_{\kappa}} + \frac{\delta \mathcal{R}}{\delta \dot{R}_{\kappa}} \right] d^3\mathbf{r} = 0 \quad (34)$$

or, on integrating the last term by parts,

$$\int \left[\frac{d}{dt} \frac{\partial \mathcal{E}_{\text{kin}}}{\partial \dot{R}_{\kappa}} + \frac{\delta \mathcal{F}}{\delta R_{\kappa}} - \nabla_{\gamma}^e \frac{\partial \mathcal{R}}{\partial \nabla_{\gamma}^e \dot{R}_{\kappa}} \right] d^3\mathbf{r} = 0 \quad (35)$$

and

$$\int \left[\frac{\delta \mathcal{F}}{\delta Q_{\alpha\beta}} + \frac{\delta \mathcal{R}}{\delta \dot{Q}_{\alpha\beta}} \right] d^3\mathbf{r} = 0 \quad (36)$$

Evaluating derivatives gives the equations of motion for the material points

$$\rho \ddot{R}_{\alpha} = -\frac{\delta \mathcal{F}}{\delta R_{\alpha}} + \nu_{\alpha\beta\gamma\delta}^{(3)} \nabla_{\beta}^e \dot{Q}_{\gamma\delta} + \nu_{\alpha\beta\gamma\delta}^{(4)} (\nabla_{\beta}^e \nabla_{\delta}^e \dot{R}_{\gamma}) \quad (37)$$

and for the nematic order parameter

$$\nu_{\alpha\beta\sigma\xi}^{(2)} \dot{Q}_{\sigma\xi} = -\frac{\delta \mathcal{F}}{\delta Q_{\alpha\beta}} - \nu_{\sigma\xi\alpha\beta}^{(3)} (\nabla_{\xi}^e \dot{R}_{\sigma}) \quad (38)$$

The equations of motion Eq. (37) and (38), together with the free energy densities Eqs. (10) and (23) or (27) are our main results. They form the basis for our subsequent studies of deformations in nematic elastomers.

III. SMALL AMPLITUDE - LONG WAVELENGTH APPROXIMATION

A. Free energy

1. The elastic free energy

The free energy in our model is

$$\mathcal{F}(\mathbf{r}) = \mathcal{F}_{\text{el}}(\mathbf{r}) + \mathcal{F}_{\text{nem}}(\mathbf{r}) \quad (39)$$

where $\mathcal{F}_{\text{el}}(\mathbf{r})$ and $\mathcal{F}_{\text{nem}}(\mathbf{r})$ are given by Eqs. (10) and (23) in terms of the length tensor $L_{\alpha\beta}(\mathbf{Q})$ and the distance of closest approach $d(\mathbf{Q}(\mathbf{X}), \mathbf{Q}(\mathbf{X}'))$. This is the free energy density in its most general, non-local form. We now consider approximations to this free energy density to examine its behavior and to make contact with existing results in the literature.

First, we assume that the nematic order parameter $Q_{\alpha\beta}$ in the deformed system differs only slightly from the order parameter $Q_{\alpha\beta}^0$ in the undeformed system, and write

$$Q_{\alpha\beta}(\mathbf{r}) = Q_{\alpha\beta}^0(\mathbf{r}) + \Delta_{\alpha\beta}(\mathbf{r}) \quad (40)$$

where $\Delta_{\alpha\beta}$ is small compared to unity. We shall refer to $\Delta_{\alpha\beta}$ as the displacement of the order parameter from its value $Q_{\alpha\beta}^0(\mathbf{r})$ in the undeformed system. Second, we assume that the wavelengths of deformations are long compared to the relevant interaction lengths a and $\sqrt{\mathcal{L}a}$, and that the integrand can be adequately approximated by a gradient expansion to second order. The displacement $\Delta_{\alpha\beta}(\mathbf{r}')$ of the nematic order parameter at location \mathbf{r}' can then be expressed in terms of its value at \mathbf{r}

$$\Delta_{\alpha\beta}(\mathbf{r}') = \Delta_{\alpha\beta}(\mathbf{r}) + \Delta_{\alpha\beta,\gamma}(\mathbf{r})z_\gamma + \frac{1}{2}\Delta_{\alpha\beta,\gamma\rho}(\mathbf{r})z_\gamma z_\rho + \dots, \quad (41)$$

where $z_\alpha \equiv r'_\alpha - r_\alpha$ is the distance in Lagrangian coordinates, and the comma denotes differentiation so that $f_{\alpha,\beta} \equiv \partial f_\alpha / \partial x_\beta$. The displacement $\mathbf{R}'(\mathbf{r}')$ can be similarly expanded in terms of its value at \mathbf{r} to give

$$R'_\alpha(\mathbf{r}') = R_\alpha(\mathbf{r}) + R_{\alpha,\gamma}(\mathbf{r})z_\gamma + \frac{1}{2}R_{\alpha,\gamma\rho}(\mathbf{r})z_\gamma z_\rho + \dots \quad (42)$$

We expand the free energy density to second order in Δ and R , with the highest order terms Δ^2, R^2 and $R\Delta$, respectively and permit at most two gradients in the expression. It is straightforward to carry out the expansion. We define $\varepsilon_{\alpha\beta} \equiv R_{\alpha,\beta}$, $\bar{Q}_{\alpha\beta} \equiv \frac{1}{2}(Q_{\alpha\beta}(\mathbf{r}) + Q_{\alpha\beta}(\mathbf{r}'))$, assume that $L_{\alpha\beta} = L_{\alpha\beta}(\mathbf{Q})$ and take $Q_{\alpha\beta}$ to be spatially uniform. The elastic part of the free energy density is then given by

$$\mathcal{F}_{\text{el}}(\mathbf{r}) = \frac{1}{2}\mu_{\alpha\beta\gamma\rho}^{(2,\text{el})}\Delta_{\alpha\beta}(\mathbf{r})\Delta_{\gamma\rho}(\mathbf{r}) + \mu_{\alpha\beta\gamma\rho}^{(3)}\varepsilon_{\alpha\beta}\Delta_{\gamma\rho} + \frac{1}{2}\mu_{\alpha\beta\gamma\rho}^{(4)}\varepsilon_{\alpha\beta}\varepsilon_{\gamma\rho} + \frac{1}{2}\mathcal{K}_{\alpha\beta\kappa\gamma\rho\tau}^{(\text{el})}\Delta_{\alpha\beta,\kappa}\Delta_{\gamma\rho,\tau} \quad (43)$$

where the coefficients are

$$\mu_{\alpha\beta\gamma\rho}^{(2,\text{el})} = \mu \left(\frac{3}{2\mathcal{L}a} \frac{\partial^2 L_{\sigma\xi}^{-1}}{\partial \bar{Q}_{\alpha\beta} \partial \bar{Q}_{\gamma\rho}} \Big|_{\bar{Q}=Q^0} \langle z_\sigma z_\xi \rangle + \frac{1}{2} \frac{\partial^2 \ln \det \mathbf{L}}{\partial \bar{Q}_{\alpha\beta} \partial \bar{Q}_{\gamma\rho}} \Big|_{\bar{Q}=Q^0} \right) \quad (44)$$

$$\mu_{\alpha\beta\gamma\rho}^{(3)} = \mu \left(\frac{3}{\mathcal{L}a} \frac{\partial L_{\alpha\sigma}^{-1}}{\partial \bar{Q}_{\gamma\rho}} \Big|_{\bar{Q}=Q^0} \langle z_\sigma z_\beta \rangle \right) \quad (45)$$

$$\mu_{\alpha\beta\gamma\rho}^{(4)} = \mu \left(\frac{3}{\mathcal{L}a} L_{\sigma\alpha\gamma}^{-1} \langle z_\beta z_\rho \rangle \right) \quad (46)$$

and

$$\mathcal{K}_{\alpha\beta\kappa\gamma\rho\tau}^{(\text{el})} = -\frac{\mu}{4} \left(\frac{3}{\mathcal{L}a} \frac{1}{2} \frac{\partial^2 L_{\sigma\xi}^{-1}}{\partial \bar{Q}_{\alpha\beta} \partial \bar{Q}_{\gamma\rho}} \Big|_{\bar{Q}=Q^0} \langle z_\sigma z_\xi z_\kappa z_\tau \rangle + \frac{1}{2} \frac{\partial^2 \ln \det \mathbf{L}}{\partial \bar{Q}_{\alpha\beta} \partial \bar{Q}_{\gamma\rho}} \Big|_{\bar{Q}=Q^0} \langle z_\kappa z_\tau \rangle \right) \quad (47)$$

where

$$\langle z_\alpha \dots z_\beta \rangle \equiv \int P_o(\mathbf{z}) z_\alpha \dots z_\beta d^3\mathbf{z} \quad (48)$$

and

$$\mu \equiv \frac{1}{2} kT \rho_o \left(\frac{3}{2\pi \mathcal{L} a} \right)^{3/2} \quad (49)$$

We have omitted an additive constant, and have ignored surface terms that arise in transforming second gradient to squared first gradients terms, such as $-\mathcal{K}_{\alpha\beta\gamma\lambda\mu\nu} \Delta_{\alpha\beta} \Delta_{\gamma\lambda, \mu\nu} = \mathcal{K}_{\alpha\beta\gamma\lambda\mu\nu} \Delta_{\alpha\beta, \nu} \Delta_{\gamma\lambda, \nu} + \text{surface term}$. Incompressibility requires that $\varepsilon_{\alpha\alpha} \equiv 0$. It is straightforward to show that, sufficiently far from any surface,

$$\langle z_\alpha z_\beta \rangle = \frac{1}{3} L_{o\alpha\beta} \mathcal{L} a \quad (50)$$

Next, we assume a simple dependence of the step length tensor on the nematic order parameter

$$L_{\alpha\beta} = \delta_{\alpha\beta} + b \overline{Q}_{\alpha\beta} \quad (51)$$

where b is the dimensionless step-length anisotropy. \mathbf{L}^{-1} and $\det \mathbf{L}$ can be evaluated at once using the Cayley-Hamilton theorem which gives

$$\mathbf{L}^{-1} = \frac{\mathbf{L}^2 - \mathbf{L} \text{tr} \mathbf{L} + \frac{1}{2} \left((\text{tr} \mathbf{L})^2 - \text{tr} (\mathbf{L}^2) \right) \mathbf{I}}{-\frac{1}{2} \text{tr} (\mathbf{L}^2) \text{tr} \mathbf{L} + \frac{1}{3} \text{tr} (\mathbf{L}^3) + \frac{1}{6} (\text{tr} \mathbf{L})^3} \quad (52)$$

and

$$\det \mathbf{L} = \frac{1}{3} \text{tr} (\mathbf{L}^3) + \frac{1}{6} (\text{tr} \mathbf{L})^3 - \frac{1}{2} \text{tr} (\mathbf{L}^2) \text{tr} \mathbf{L} \quad (53)$$

where $\text{tr} \mathbf{L} \equiv L_{\alpha\alpha}$ is the trace of \mathbf{L} and \mathbf{I} is the identity.

The term $\mu_{\alpha\beta\gamma\rho}^{(4)} \varepsilon_{\alpha\beta} \varepsilon_{\gamma\rho}$ has the expected form of the elastic energy of an anisotropic solid; in our model, the anisotropy arises through the nematic order parameter \mathbf{Q}^0 of the undeformed sample. The coefficient $\mathcal{K}_{\alpha\beta\kappa\gamma\rho\tau}^{(el)}$ has a complex structure, but if it is evaluated for the case of vanishing order parameter in the undeformed sample with $\mathbf{Q}_o = 0$, the simpler form

$$\frac{1}{2} \mathcal{K}_{\alpha\beta\kappa\gamma\rho\tau}^{(el)} \Delta_{\alpha\beta, \kappa} \Delta_{\gamma\rho, \tau} = \frac{1}{2} \mathcal{C}_1 \Delta_{\alpha\beta, \gamma} \Delta_{\alpha\beta, \gamma} + \frac{1}{2} \mathcal{C}_2 \Delta_{\alpha\beta, \beta} \Delta_{\alpha\gamma, \gamma} + \frac{1}{2} \mathcal{C}_3 \Delta_{\alpha\beta, \gamma} \Delta_{\alpha\gamma, \beta} \quad (54)$$

is obtained, with $\mathcal{C}_2 = \mathcal{C}_3 = 2\mathcal{C}_1 = -\frac{1}{12} \mu \mathcal{L} a b^2$. Although it originates in the elastic part of the free energy, the expression in Eq. (54) has the same form as the phenomenological free energy density of a deformed nematic in the tensor representation

$$\mathcal{F}_{\text{deGennes}}^{(\text{nem})} = \frac{1}{2} L_1 \Delta_{\alpha\beta, \gamma} \Delta_{\alpha\beta, \gamma} + \frac{1}{2} L'_2 \Delta_{\alpha\beta, \beta} \Delta_{\alpha\gamma, \gamma} + \frac{1}{2} L'_3 \Delta_{\alpha\beta, \gamma} \Delta_{\alpha\gamma, \beta} \quad (55)$$

The last two terms differ only by a surface term which does not enter the dynamical equations in the bulk, and we write

$$\mathcal{F}_{\text{deGennes}}^{(\text{nem})} = \frac{1}{2} L_1 \Delta_{\alpha\beta, \gamma} \Delta_{\alpha\beta, \gamma} + \frac{1}{2} L_2 \Delta_{\alpha\beta, \beta} \Delta_{\alpha\gamma, \gamma} (+\text{surface term}), \quad (56)$$

with $L_2 \equiv L'_2 + L'_3$. A stability analysis by de Gennes [13], who introduced Eq. (56), shows that a positive definite free energy density requires

$$L_1 > 0 \text{ and } L_2 > -3L_1/2 \quad (57)$$

but not $L_2 > 0$. However, in Eq. (54) the coefficient \mathcal{C}_1 is negative; the free energy density would therefore not be positive definite without the contribution from the nematic part of the free energy density.

2. The nematic free energy

We expand the nematic part of the free energy density in Eq. (23) similarly, and obtain

$$\mathcal{F}_{\text{nem}} = \frac{1}{2}\mu_{\alpha\beta\gamma\rho}^{(2,\text{nem})}\Delta_{\alpha\beta}\Delta_{\gamma\rho} + \frac{1}{2}\mathcal{K}_{\alpha\beta\kappa\gamma\rho\tau}^{(\text{nem})}\Delta_{\alpha\beta,\kappa}\Delta_{\gamma\rho,\tau}. \quad (58)$$

Terms containing $\varepsilon_{\alpha\beta}$ are of higher order in wavenumber and do not appear. The coefficients $\mu_{\alpha\beta\gamma\rho}^{(2,\text{nem})}$ and $\mathcal{K}_{\alpha\beta\kappa\gamma\rho\tau}^{(\text{nem})}$ are functions of \mathbf{Q}_0 ; they can be determined for any particular choice of the distance of closest approach d . For example, if d does not depend on nematic order, the nematic free energy density is given by Eq. (27), and it follows that

$$\mu_{\alpha\beta\gamma\rho}^{(2,\text{nem})}\Delta_{\alpha\beta}\Delta_{\gamma\rho} = A\Delta_{\alpha\beta}\Delta_{\beta\alpha} \quad (59)$$

and

$$\mathcal{K}_{\alpha\beta\kappa\gamma\rho\tau}^{(\text{nem})}\Delta_{\alpha\beta,\kappa}\Delta_{\gamma\rho,\tau} = B\left(\frac{11}{14}\Delta_{\alpha\beta,\gamma}\Delta_{\alpha\beta,\gamma} - \frac{12}{14}\Delta_{\alpha\beta,\beta}\Delta_{\alpha\gamma,\gamma}\right) \quad (60)$$

where A and B are positive constants [11].

The total free energy density for the nematic elastomer, expanded to second order, is

$$\begin{aligned} \mathcal{F} = & \frac{1}{2}\mu_{\alpha\beta\gamma\rho}^{(2)}\Delta_{\alpha\beta}\Delta_{\gamma\rho} + \mu_{\alpha\beta\gamma\rho}^{(3)}\varepsilon_{\alpha\beta}\Delta_{\gamma\rho} + \frac{1}{2}\mu_{\alpha\beta\gamma\rho}^{(4)}\varepsilon_{\alpha\beta}\varepsilon_{\gamma\rho} \\ & + \frac{1}{2}\mathcal{K}_{\alpha\beta\kappa\gamma\rho\tau}\Delta_{\alpha\beta,\kappa}\Delta_{\gamma\rho,\tau} + \frac{1}{2}\mathcal{B}(\varepsilon_{\alpha\alpha})^2 + \frac{1}{2}\mathcal{C}(\Delta_{\alpha\alpha})^2 \end{aligned} \quad (61)$$

where $\mu_{\alpha\beta\gamma\rho}^{(2)} \equiv \mu_{\alpha\beta\gamma\rho}^{(2,\text{el})} + \mu_{\alpha\beta\gamma\rho}^{(2,\text{nem})}$ and $\mathcal{K}_{\alpha\beta\kappa\gamma\rho\tau} \equiv \mathcal{K}_{\alpha\beta\kappa\gamma\rho\tau}^{(\text{el})} + \mathcal{K}_{\alpha\beta\kappa\gamma\rho\tau}^{(\text{nem})}$. The quantities \mathcal{B} and \mathcal{C} may be regarded as Lagrange multipliers enforcing the constraints of constant volume and traceless nematic order parameter. Conditions (57) must hold for Eq. (61).

Eq. (61) shows that the presence of the cross-linked elastomer matrix changes the nematic-isotropic transition temperature and contributes to the elastic constants L_1 and L_2 of the nematic. A change in the transition temperature due to contributions from the elastomer has been pointed out in Ref. [15], where only a scalar nematic order parameter was considered.

In our second order gradient approximation, we have omitted surface terms. It is well known that surface terms that arise from transforming second gradient terms to squared first gradient terms can lead to a free energy that is unbounded from below, and to an ill-posed minimization problem [10]. This can be avoided by using the fully non-local free energy to obtain the dynamical equations, and only then perform the gradient expansion [11].

A result similar to Eq. (54) is obtained when the scalar order parameter S is assumed to be constant, as in Ref. [16].

3. Limiting cases

If the reference state is isotropic, on enforcing incompressibility, we have for the uniform contribution of the elastic free energy

$$\mathcal{F}_{\text{el}}^{\text{un}} = \frac{\mu}{4}(b\Delta_{\gamma\rho} - 2\varepsilon_{\gamma\rho}^{\text{S}})^2, \quad (62)$$

omitting a surface term. This leads to a soft (spontaneous) deformation when $\varepsilon_{\gamma\rho}^{\text{S}} = \frac{1}{2}b\Delta_{\gamma\rho}$, where $\varepsilon_{\gamma\rho}^{\text{S}}$ is the symmetric part of the deformation tensor $\varepsilon_{\gamma\rho}$.

It is straight forward to show that Eq. (43) contains the usual continuum elastic free energy density [3] in terms of the nematic director. We again take the scalar order parameter S to be constant, and keeping terms in Eq. (43) to second order in the director displacement $\delta\hat{\mathbf{n}}$ gives

$$\Delta_{\alpha\beta} = \frac{3}{2}S^0(n_{\alpha}^0\delta n_{\beta} + n_{\beta}\delta n_{\alpha} + \delta n_{\alpha}\delta n_{\beta}). \quad (63)$$

We arrive at the usual free energy by considering terms in Eq. (43) to second order in the director displacement, $\delta\hat{\mathbf{n}}$, and enforcing $\Delta_{\alpha\alpha} = 0$.

B. Equations of motion

The general equations of motion are given, in terms of the dissipation and the non-local free energy, in Eqs. (37) and (38). We now consider approximations to these to examine the behavior of the system and to make contact with existing results in the literature. As before, we assume that the wavelengths of deformations are long compared to the relevant interaction lengths a and $\sqrt{\mathcal{L}a}$, and that the displacement of the order parameter is much smaller than unity. We also assume here that the displacement R is small compared to r , and we therefore do not distinguish between gradients in the Euler and Lagrangian coordinates. The equations of motion (37) and (38) become

$$\rho \ddot{R}_\alpha = \frac{\partial}{\partial x_\beta} \left[\frac{\partial \mathcal{F}}{\partial R_{\alpha,\beta}} + \nu_{\alpha\beta\gamma\lambda}^{(3)} \dot{\Delta}_{\gamma\lambda} + \nu_{\alpha\beta\gamma\lambda}^{(4)} \dot{R}_{\gamma,\lambda} \right] \quad (64)$$

and

$$\nu_{\alpha\beta\gamma\lambda}^{(2)} \dot{\Delta}_{\gamma\lambda} = -\frac{\partial \mathcal{F}}{\partial \Delta_{\alpha\beta}} + \frac{\partial}{\partial x_\gamma} \frac{\partial \mathcal{F}}{\partial \Delta_{\alpha\beta,\gamma}} - \nu_{\gamma\lambda\alpha\beta}^{(3)} \dot{R}_{\gamma,\lambda} \quad (65)$$

with \mathcal{F} given by Eq. (61). We assume the viscous coefficients $\nu_{\alpha\beta\gamma\lambda}^{(k)}$ to be proportional to the coupling tensors $\mu_{\alpha\beta\gamma\lambda}^{(k)}$ in Eq. (61), as is commonly done in nematodynamics. These can be written in terms of S^0 and $\hat{\mathbf{n}}^0$, the scalar nematic order parameter and director in the undeformed sample, as shown in the Appendix.

1. Spatially uniform scalar nematic order parameter

For the case of constant scalar nematic order parameter, we write the order parameter displacement as

$$\Delta_{\alpha\beta} = \frac{3}{2} S^0 (n_\alpha^0 \delta n_\beta + n_\beta^0 \delta n_\alpha + \delta n_\alpha \delta n_\beta) \quad (66)$$

since $\Delta_{\alpha\alpha} = 0$ and $n_\alpha n_\alpha = 1$. From the expressions for the viscosity tensors in the Appendix, obtain the viscous stress

$$\sigma'_{\gamma\rho} = \frac{\partial \mathcal{R}}{\partial \dot{\varepsilon}_{\rho\gamma}} = \nu_1 n_\gamma^0 n_\rho^0 (n_\alpha^0 \dot{\varepsilon}_{\alpha\beta}^S n_\beta^0) + \nu_2 n_\gamma^0 N_\rho + \nu_3 N_\gamma n_\rho^0 + \nu_4 \dot{\varepsilon}_{\rho\gamma}^S + \nu_5 n_\gamma^0 \dot{\varepsilon}_{\rho\alpha}^S n_\alpha^0 + \nu_6 n_\alpha^0 \dot{\varepsilon}_{\alpha\gamma}^S n_\rho^0 \quad (67)$$

and viscous director field

$$g'_\gamma = -\frac{\partial \mathcal{R}}{\partial \delta \dot{n}_\gamma} = \lambda_1 N_\gamma + \lambda_2 n_\alpha^0 \dot{\varepsilon}_{\alpha\gamma}^S \quad (68)$$

where $N_\gamma \equiv (\delta \dot{n}_\gamma - \dot{\varepsilon}_{\gamma\alpha}^A n_\alpha^0)$, and $\varepsilon_{\alpha\beta}^S$ and $\varepsilon_{\alpha\beta}^A$ are the symmetric and anti-symmetric parts of $\varepsilon_{\alpha\beta}$. The viscous stress is in the Ericksen-Leslie form [17], and the coefficients are given by $\nu_1 = -\nu(r-1)^2/r$, $\nu_2 = \nu(1-r)$, $\nu_3 = \nu(1-r)/r$, $\nu_4 = 2\nu$, $\nu_5 = \nu(r-1)$, and $\nu_6 = \nu(1-r)/r$. The parameter $r \equiv l_{\parallel}/l_{\perp}$ is a measure of the anisotropy of the polymer chain. The coefficients obey the Parodi relations, $\nu_2 + \nu_3 = \nu_6 - \nu_5$, $\lambda_1 = \nu_2 - \nu_3$ and $\lambda_2 = \nu_5 - \nu_6$. The dissipation function is positive definite [17] because for $\nu > 0$ the following inequalities are satisfied: $\nu_4 \geq 0$, $2\nu_4 + \nu_5 + \nu_6 \geq 0$, $2\nu_1 + 3\nu_4 + 2\nu_5 + 2\nu_6 \geq 0$ and $-4\lambda_1(2\nu_4 + \nu_5 + \nu_6) \geq (\nu_2 + \nu_3 - \lambda_2)^2$.

2. Small \mathbf{Q}^0

We next consider the case when the nematic order parameter \mathbf{Q}^0 in the undeformed sample is small, and expand to second order in \mathbf{Q}^0 and Δ . The viscosity coefficients become

$$\nu_{\alpha\beta\sigma\xi}^{(2)} = \frac{\nu}{2} (\delta_{\alpha\xi} \delta_{\sigma\beta} + \delta_{\alpha\sigma} \delta_{\beta\xi}) \quad (69)$$

$$\nu_{\alpha\beta\gamma\rho}^{(3)} = -\frac{\nu}{2} (\delta_{\alpha\gamma} \delta_{\beta\rho} + \delta_{\beta\gamma} \delta_{\alpha\rho}) + \nu (Q_{\alpha\gamma}^0 \delta_{\beta\rho} + \delta_{\beta\gamma} Q_{\alpha\rho}^0) \quad (70)$$

which gives the dynamical equation for the nematic order parameter

$$\dot{\Delta}_{\alpha\beta} = -\frac{1}{\nu} \left[\frac{\partial \mathcal{F}}{\partial \Delta_{\alpha\beta}} - \nabla_{\kappa} \frac{\partial \mathcal{F}}{\partial \nabla_{\kappa} \Delta_{\alpha\beta}} \right] + \dot{\varepsilon}_{\alpha\beta}^S + [\dot{\varepsilon}_{\alpha l}^A Q_{\kappa\beta}^0 - Q_{\alpha\kappa}^0 \dot{\varepsilon}_{l\beta}^A] - [Q_{\alpha\kappa}^0 \dot{\varepsilon}_{\kappa\beta}^S + \dot{\varepsilon}_{\alpha\kappa}^S Q_{\kappa\beta}^0] \quad (71)$$

This is in agreement with the results of Olmsted and Goldbart [18] for pure nematics, except for the last term in Eq. (71), which they did not explicitly give since they regarded it as a higher order reactive term. This type of term, and higher order terms in \mathbf{Q}^0 , appears in a nonlinear expansion in their formalism. A similar result in pure nematic theory is obtained using the Poisson-bracket approach by Stark and Lubensky [19] and by Pleiner *et al.* [20] in a polymeric system.

3. Spatially uniform strain

Finally, we consider the case when a uniform strain is applied to the sample, and the nematic tensor order parameter is spatially uniform. The equilibrium configuration can be obtained from the stationary solution of Eq.(65), $\partial \mathcal{F} / \partial \Delta_{\alpha\beta} = 0$, which gives

$$\mu_{\alpha\beta\gamma\rho}^{(2)} \Delta_{\gamma\rho} + \mu_{\gamma\rho\alpha\beta}^{(3)} \varepsilon_{\gamma\rho} = 0 \quad (72)$$

where $\Delta_{\alpha\alpha} = 0$. This expression, together with the explicit expressions for the coefficients, shows how the order parameter tensor responds to applied strain. If the strain is along the initial director direction, a change in the scalar order parameter results. Strain applied perpendicular to the director leads to biaxiality, but in this small deformation approximation the director remains constant. Shearing the sample gives rise to off-diagonal terms in order parameter tensor, implying director rotation.

IV. SUMMARY

In this paper, we propose a non-local continuum model to describe the dynamics of non-uniform deformations in nematic elastomers in terms of the material displacement vector and the nematic order parameter tensor. We have derived expressions for the non-local free energy including contributions from both elastic and nematic interactions. Our formalism for elastic interactions is based on the work of Warner and Terentjev[3]. We have obtained equations of motion for the material displacement and the order parameter from the free energy and the Rayleigh dissipation function via a Lagrangian formalism. The equations of motion are expected to be valid in the case of large and inhomogeneous deformations and strains.

We have examined the behavior in the limit of long-wavelength and small amplitude variations of displacement and orientational order parameter. In this limit, the predictions of our model are in agreement with existing results in the literature. To facilitate the comparison, we have carried out a gradient expansion of the free energy density instead of the dynamical equations in the long-wavelength limit, and ignored surface contributions when converting second gradient to squared gradient terms. Incorporating these surface terms would lead to an ill-posed minimization problem[10][11]. The formally correct approach is to first derive the dynamical equations in fully non-local form, as we have done, and only then take the long-wavelength limit[11]. More detailed work, including numerical simulations, is currently under way.

Acknowledgments

Support for this work was provided by the National Science Foundation (NSF) and the Brazilian National Research Council (CNPq).

V. APPENDIX

The viscous coefficients $\nu_{\alpha\beta\gamma\lambda}^{(k)}$ are be proportional to the coupling tensors $\mu_{\alpha\beta\gamma\lambda}^{(k)}$ in Eq. (61). These can be written in terms of S^0 and $\hat{\mathbf{n}}^0$, the scalar nematic order parameter and director in the undeformed sample. They become, to

second order in \mathbf{Q}_o , assuming $L_{ij} = \delta_{ij} + bQ_o$ and ignoring terms which do not contribute,

$$\begin{aligned} \mu_{\alpha\beta\gamma\lambda}^{(2,e1)} = & \alpha^{(2)} (\delta_{\alpha\gamma}\delta_{\beta\lambda} + \delta_{\alpha\lambda}\delta_{\beta\gamma}) + \beta^{(2)} (\delta_{\alpha\gamma}n_{\beta}^0n_{\lambda}^0 + \delta_{\beta\gamma}n_{\alpha}^0n_{\lambda}^0 + \delta_{\alpha\lambda}n_{\beta}^0n_{\gamma}^0 + \delta_{\beta\lambda}n_{\alpha}^0n_{\gamma}^0) \\ & + \gamma^{(2)}n_{\alpha}^0n_{\beta}^0n_{\gamma}^0n_{\lambda}^0, \end{aligned} \quad (73)$$

$$\mu_{\alpha\beta\gamma\lambda}^{(3)} = \alpha^{(3)} (\delta_{\alpha\gamma}\delta_{\beta\lambda} + \delta_{\alpha\lambda}\delta_{\beta\gamma}) + \beta^{(3)} (n_{\alpha}^0n_{\gamma}^0\delta_{\beta\lambda} + n_{\alpha}^0n_{\lambda}^0\delta_{\beta\gamma}) + \gamma^{(3)} (\delta_{\alpha\beta} - n_{\alpha}^0n_{\beta}^0) \delta_{\gamma\lambda} \quad (74)$$

$$\begin{aligned} \mu_{\alpha\beta\gamma\lambda}^{(4)} = & \mu \left(\delta_{\alpha\gamma}\delta_{\beta\lambda} + \left(\frac{l_{\perp}}{l_{\parallel}} - 1 \right) n_{\alpha}^0n_{\gamma}^0\delta_{\beta\lambda} + \left(\frac{l_{\parallel}}{l_{\perp}} - 1 \right) n_{\beta}^0n_{\lambda}^0\delta_{\alpha\gamma} \right) \\ & + \mu \left(\frac{l_{\perp}}{l_{\parallel}} - 1 \right) \left(\frac{l_{\parallel}}{l_{\perp}} - 1 \right) n_{\alpha}^0n_{\beta}^0n_{\gamma}^0n_{\lambda}^0 \end{aligned} \quad (75)$$

where we define

$$l_{\parallel} \equiv 1 + bS^0 \quad (76)$$

$$l_{\perp} \equiv 1 - bS^0/2 \quad (77)$$

and the scalar coefficients in Eqs. (73) and (74) are given by

$$\alpha^{(2)} \equiv \frac{\mu}{\det \mathbf{L}_o} \frac{b^2 (1 + bS^0)}{4} = \frac{\mu b^2}{4} \frac{1}{l_{\perp}^2} \quad (78)$$

$$\beta^{(2)} \equiv -\frac{\mu}{\det \mathbf{L}_o} \frac{3}{8} b^3 S^0 = \frac{\mu b^2}{4} \left(\frac{1}{l_{\perp} l_{\parallel}} - \frac{1}{l_{\perp}^2} \right) \quad (79)$$

$$\gamma^{(2)} \equiv \frac{\mu}{\det \mathbf{L}_o} \frac{9}{8} b^2 \frac{(bS^0)^2}{1 + bS^0} = \frac{\mu b^2}{2} \left(\frac{1}{l_{\perp}} - \frac{1}{l_{\parallel}} \right)^2 \quad (80)$$

$$\alpha^{(3)} \equiv \frac{\mu}{\det \mathbf{L}_o} \left(-\frac{b}{2} - b \frac{bS^0}{4} + b \frac{(bS^0)^2}{4} \right) = -\frac{\mu b}{2l_{\perp}} \quad (81)$$

$$\beta^{(3)} \equiv \frac{\mu}{\det \mathbf{L}_o} \frac{3}{4} b^2 S^0 \left(1 - \frac{bS^0}{2} \right) = \frac{\mu b}{2} \left(\frac{1}{l_{\perp}} - \frac{1}{l_{\parallel}} \right) \quad (82)$$

The corresponding viscosity tensors are given by replacing μ with $\nu \equiv c\mu$ in the above equations, where c is a constant.

-
- [1] P. G. de Gennes, *CR ACAD SCI II B* **281**, 101-103 (1975).
 [2] H. Finkelmann, H. Kock, and G. Rehage, *Macromol. Rapid Comm.* **2**, 371 (1981).
 [3] M. Warner and E. M. Terentjev, *Liquid Crystal Elastomers* (Clarendon Press, Oxford, 2003).
 [4] P. G. de Gennes, C. R. Acad. Sci., Paris, **324**, 343-348 (1997); D. K. Shenoy, D. L. Thomsen III, A. Srinivasan, P. Keller, and B. R. Ratna, *Sensor Actuator A* **96**, 184-188 (2002).
 [5] H. Finkelmann, s. T. Kim, A. Munoz, P. Palfy-Muhoray and B. Taheri, *Adv. Mater.* **13** 1069-1072 (2001).
 [6] H. Finkelmann et al., Patent No. 99/25788.
 [7] P. Bladon, M. Warner, and E. M. Terentjev, *Macromolecules* **27**, 7067-7075 (1994).
 [8] M. Camacho-Lopez, H. Finkelmann, P. Palfy-Muhoray, and M. Shelley, *Nat. Mater.* **3**, 307-310 (2004).
 [9] Y. Yu, M. Nakano, Tomiki Ikeda, *Nature* **425**, 145 (2003).
 [10] C. Oldano, G. Barbero, *Phys. Lett.* **110**, 213 (1985).
 [11] R. Ennis, *Ph. D. Dissertation*, Chemical Physics, Kent State University (2004).
 [12] P. G. de Gennes and J. Prost, *The Physics of Liquid Crystals* 2nd ed. (Oxford University Press, Oxford, 1993).
 [13] P. G. de Gennes, *Mol. Cryst. Liq. Cryst.*, **12**, 193-214, (1971).
 [14] G. Marrucci and F. Greco, *Mol. Cryst. Liq. Cryst.*, **206**, 17-30, (1991).
 [15] M. Warner and K. P. Gelling, *J. Chem. Phys.* **88**, 4008-4013 (1988).
 [16] E. M. Terentjev, M. Warner and G. C. Verney, *J. Phys. II*, **6**, 1049 (1996).
 [17] See for example; S. Chandrasekhar, *Liquid Crystals*, (Cambridge University Press, Cambridge, 1992).
 [18] P. D. Olmsted and P. Goldbart, *Phys. Rev. A* **41**, 457845-81 (1990).
 [19] H. Stark and T. C. Lubensky, *Phys. Rev. E* **67**, 061709 (2003).
 [20] H. Pleiner, M. Liu, H. R. Brand, *Rheol. Acta* **41**, 375-382 (2002).