# Symmetries and elasticity of nematic gels

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A nematic liquid-crystal gel is a macroscopically homogeneous elastic medium with the rotational symmetry of a nematic liquid crystal. In this paper, we develop a general approach to the study of these gels that incorporates all underlying symmetries. After reviewing traditional elasticity and clarifying the role of broken rotational symmetries in both the reference space of points in the undistorted medium and the target space into which these points are mapped, we explore the unusual properties of nematic gels from a number of perspectives. We show how symmetries of nematic gels formed via spontaneous symmetry breaking from an isotropic gel enforce soft elastic response characterized by the vanishing of a shear modulus and the vanishing of stress up to a critical value of strain along certain directions. We also study the phase transition from isotropic to nematic gels. In addition to being fully consistent with approaches to nematic gels based on rubber elasticity, our description has the important advantages of being independent of a microscopic model, of emphasizing and clarifying the role of broken symmetries in determining elastic response, and of permitting easy incorporation of spatial variations, thermal fluctuations, and gel heterogeneity, thereby allowing a full statistical-mechanical treatment of these materials.

## I. INTRODUCTION

The term liquid crystal [1,2] has traditionally been used to describe phases of matter that exhibit anisotropies characteristic of crystals but that under appropriate conditions flow like a liquid. These phases typically have symmetries intermediate between that of a homogeneous isotropic fluid and that of a three-dimensional periodic crystalline solid. Indeed one can provide an almost complete characterization of a liquid-crystalline phase by specifying its symmetry. For example, the nematic phase, which is spatially homogeneous yet optically uniaxial has $D_{\infty h}$ symmetry. The typical phase sequence for a thermotropic liquid crystal on cooling begins with an isotropic fluid and ends with a crystalline solid after passing through nematic, layered smectic-$A$ and smectic-$C$, and possibly hexatic phases.

There is, however, a large variety of materials that have the same macroscopic symmetry as fluids, but that cannot flow: they are macroscopically homogeneous and isotropic elastic media with a nonvanishing shear modulus that provides resistance to shear distortions. We will refer to these materials, which include everything from glasses to elastomers or rubbers [3], as gels [4]. One can imagine phases arising from a reference state of a *gel* (rather than a liquid) with the same macroscopic symmetries as conventional liquid crystals. As we shall discuss more fully below, these phases do, in fact, exist [5–12], and, because they cannot flow, they have mechanical properties and mode structures that differ significantly from those of standard liquid crystals. We will call these phases "liquid-crystal gels" because they are *gels* with the symmetry of conventional (fluid) liquid crystals. In this paper, we will develop a powerful and general formalism to describe nematic gels and use it to explore their remarkable properties. We will focus particularly on nematic gels that form via spontaneous orientational symmetry breaking from an isotropic gel phase. Our formalism can be generalized to treat other liquid-crystalline gel phases.

There are a large number of experimental realizations of liquid-crystal gels. Of particular interest to us are liquid-crystal elastomers [5–8]. These materials, which are formed by weakly cross linking either sidechain [5] or main-chain [9] polymers, combine the enormous extensibility of rubbers with the orientational properties of liquid crystals. They are, therefore, of considerable technological importance. The existence of the rubbery cross-linked network appears to have relatively little effect on liquid-crystalline phase behavior, and the standard thermotropic nematic, cholesteric, smectic-$A$, and smectic-$C$ phases have their elastomeric counterparts [8,13]. The elastic properties of these phases do, however, crucially depend on whether a given liquid-crystalline order was established before or after crosslinking. Liquid-crystal gels can also be prepared in other ways, for example, by polymerization of monomer solutes in a liquid-crystalline solvent [10], or by confining conventional liquid crystal inside a dilute flexible matrix such as aerosil [11,12].

To fully characterize liquid-crystal gel phases, two complementary basic questions must be addressed: (1) What effect does liquid-crystal order have on the gel *elasticity*? (2) How does the rigidity of the underlying gel affect liquid-crystal *order* and its *stability* to fluctuations? Our primary concern in this paper will be with question (1) applied to nematic gels. With regard to question (2), gel elasticity of weakly cross-linked elastomers has relatively little effect on the existence of liquid-crystalline phases. On the other hand, liquid-crystal elastomers appear experimentally to be more strongly ordered than their fluid counterparts. For example, unlike conventional nematics, which have a milky appearance because of strong fluctuations of the local anisotropy
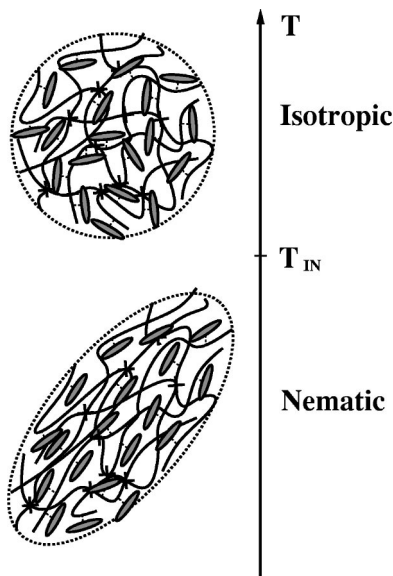
FIG. 1. A cartoon of a liquid-crystal gel undergoing an isotropic-nematic transition, accompanied by a spontaneous uniaxial distortion.

direction, elastomer nematics are clear, indicating suppressed fluctuations and orientational order extending beyond a micron. This property directly and clearly follows from our model of nematic elastomer as well as from an early work [14], and it will be explored in more detail in a future publication [15].

The strong interplay between broken symmetry and the nature of long-wavelength excitations of ordered phases is a major theme of physics [16]. Symmetry principles dictate that ordered thermodynamic phases that break a continuous symmetry have low-energy distortions, or "soft" modes, that are described by an elastic energy depending only on gradients of these Goldstone fields whose spatially uniform increments take the system to symmetry-equivalent states. The form of this elastic free energy is uniquely determined by the properties of the reference phase whose symmetry is broken and by the nature of the broken symmetry itself. Conventional nematic liquid crystals break the rotational isotropy of an isotropic homogeneous liquid, and they are characterized by the Frank elastic free energy [1,2], which is a functional of the Goldstone field **n**, the Frank director specifying the direction of molecular alignment. As illustrated in Fig. 1, nematic phases of liquid-crystal gels that form from an isotropic gel state also spontaneously break rotational isotropy. Their long-wavelength elastic energy, however, differs significantly from the Frank free energy of conventional nematics because the reference gel state (unlike a reference fluid state) has a nonvanishing shear modulus. The elastic distortions of a nematic gel and their coupling to the local anisotropy direction were first considered by de Gennes [6]. Golubović and Lubensky (GL) [17] were the first to consider in detail the unique properties of the elastic energy of a spontaneously formed nematic gel in their study of a model isotropic elastic medium that undergoes a phase transition to a uniaxial state when its shear modulus becomes smaller than a critical value. They found that the Goldstone fields of a

uniaxial gel are displacement fields and that their associated elastic energy is expressed as a function of standard strains of a solid. Normally, the elastic energy of a uniaxial elastic medium is characterized by five independent elastic constants. A nematic gel that forms spontaneously from an isotropic gel is significantly softer than a conventional uniaxial solid: it is characterized by "soft" elasticity in which the elastic constant $C_5$ associated with shears in the plane containing the anisotropy axis vanishes and in which stress vanishes up to critical values of certain shears [18–20].

Many of the properties of nematic elastomers can be explained by an elegant and remarkably simple extension [21] of standard rubber elasticity [22] in which nematic order leads to an anisotropic step-length tensor for random-flight polymer segments between cross-linking points. This "neoclassical" theory of rubber elasticity, which describes a particular realization of an anisotropic gel exhibits "soft" elasticity [14,23] in accord with the general symmetry-based predictions of GL.

In this largely pedagogical paper, we will explore the elastic and orientational properties of nematic gels from a perspective that is an extension of that of Ref. [17] rather that of rubber elasticity [7]. In particular we will describe elastic properties mostly in terms of nonlinear strain tensors familiar from the elastic theory of solids and membranes [24,25] rather than the perhaps more fundamental Cauchy deformation tensor used in rubber elasticity [22] from which the nonlinear strain tensors can be constructed. Strain can be measured relative to any reference state. We will find it useful to measure strain relative to both an isotropic reference state and, as is the most common practice, relative to the equilibrium, strain-free reference state. These states may or may not be the state at the time of preparation that is commonly used as a reference state in the theory of (incompressible) rubbers. Our approach based on nonlinear strains that are invariant under arbitrary rotations of the sample (or, alternatively, as we shall see, the reference state) allows us to keep track of rotational invariances with relative ease. It is particularly well suited, as we will show in a future publication [26], to the treatment of renormalized elasticity arising from the interplay of thermal fluctuations and nonlinear elasticity. The approach is also convenient for the discussion of external-field-induced instabilities of an equilibrium phase. Most importantly, our formalism elucidates the origin of the soft elasticity of nematic gels, making it clear that it arises from general symmetry principles common to any *spontaneously* uniaxially ordered elastic medium and is *not* limited to any specific model of such materials. Our description has the disadvantage compared to the rubber elasticity approach that it does not naturally treat the very large (as much as 400% [27]) extensions that can arise in elastomers.

Though gels in their isotropic state and not under stress are macroscopically isotropic and homogeneous, they are always randomly anisotropic and inhomogeneous at sufficiently short length scales. Consequently, there is a local preferred direction of orientational (and spatial) order that acts as a random orienting (and pinning) field. These quenched fields are also certainly present in anisotropic gels: optical observations in thin films provide direct evidence of their

existence [28,29]. One consequence of such random quenched local fields is that unstretched elastomers cross-linked in the isotropic phase and cooled into the nematic phase exhibit a polydomain orientational structure, which disappears at a polydomain-monodomain transition when a sufficiently large external stress is applied [30]. Such random static fields can easily be incorporated in our formulation of nematic gels. Their study is in principle necessary to understand completely the effect of gel matrix on nematic order [question (2) above]. Such an investigation would parallel a body of work on conventional liquid crystals confined inside the quenched, random, but (nearly) nondeformable environment of rigid gels such as an aerogel [11,31–33]. Experience with these rigid systems indicate that random fields might become qualitatively important at sufficiently long scales. Nevertheless, in this paper, we will completely ignore the effects of random fields and concentrate on properties of anisotropic gels formed from ideal isotropic homogeneous gels. By focusing on gels in which cross links are dense and well percolated, we will also have nothing to say about the nature of the vulcanization transition itself [34].

We will also leave for the future [35] the analysis of "semisoft" nematic elastomers [18,20,36] that are prepared by polymer cross-linking in the nematic phase. These materials are characterized by a small nonvanishing elastic modulus $C_5$ and nonlinear stress-strain curves with a small but nonvanishing stress up to large strains.

This paper is organized as follows. Section II reviews the standard Lagrangian theory of elasticity and establishes notation for sections that follow. It introduces the reference space consisting of points in the undistorted medium and the target space into which these points are mapped. This section emphasizes the *two* distinct rotational invariances of isotropic elastic media, namely invariance with respect to rotation of the deformed sample itself (rotations in the target space) and invariance with respect to rotation of points in the original reference material that map to particular points in the target space (rotations in the reference space). Section II also discusses the standard nonlinear strain tensor, the right Cauchy-Green strain tensor, that is invariant with respect to rotations in the target space and introduces an alternative nonlinear strain tensor, the left Cauchy-Green strain tensor, that is invariant with respect to rotations of the reference space but transforms like rank-2 tensor in the target space. Section III elaborates on the model considered in Ref. [17]. It shows in particular that the elastic energy of the anisotropic gel phase expanded only to harmonic order in the nonlinear strain does not preserve the rotational invariance of the original energy with respect to rotations in the reference space. It also discusses the isotropic-to-anisotropic transition in terms of the alternative strain tensor that preserves rotational invariance in the reference space. Section IV discusses a model with both strain and the symmetric-traceless tensor order parameter $Q_{ij}$ of the nematic state. It shows that the "soft" elasticity of the anisotropic (nematic) state arises because the nematic order parameter can relax strains in the plane containing the anisotropy axis, as first shown by Olmsted [14]. Section IV also derives the elastic energy for nematic glasses deep in the ordered phase, where biaxial fluctua-

tions can be neglected and nematic properties can be described completely by the Frank director. This theory is expressed in terms of generalized nonlinear strains that are functions of strain and relative director orientation and that are invariant with respect to arbitrary simultaneous rotations of the director and mass points. Section V explores the relation between the theory presented here and the neoclassical elastomer theory. Section VI concludes with a discussion of some of the many interesting open problems, such as instabilities of elastomers induced by external perturbations (e.g., electric or magnetic fields) and the effects of thermal fluctuations and quenched local random anisotropy fields, that can conveniently be addressed through our formulation

## II. CLASSICAL LAGRANGIAN ELASTICITY

Classical elasticity [24] provides a phenomenological description of the energy associated with slowly [37] varying distortions of an elastic body from its equilibrium configuration. As discussed in the Introduction, it is a symmetry-restricted theory of the low-energy Goldstone modes associated with spontaneous translational symmetry breaking. In this section, we will review the classical theory of Lagrangian elasticity [38], introducing concepts that will be important for our study of spontaneously uniaxial nematic elastomers.

### A. Strain

The equilibrium unstretched medium occupies a region of a Euclidean 3-space, which we will call the reference space $S_R$. Mass points in this medium are indexed by their vector positions $\mathbf{x} = (x_1, x_2, x_3) \equiv (x, y, z)$ in $S_R$, which are their positions in the unstretched medium. When the medium is distorted, the point originally at $\mathbf{x}$ is mapped to a new point $\mathbf{R}(\mathbf{x}) = (R_1(\mathbf{x}), R_2(\mathbf{x}), R_3(\mathbf{x}))$ in Euclidean space. We will refer to the space of points defined by $\mathbf{R}$ as the target space $S_T$. Since there is no distortion when $\mathbf{R}(\mathbf{x}) = \mathbf{x}$, it is useful to introduce the displacement vector $\mathbf{u}(\mathbf{x})$ that measures the deviation of $\mathbf{R}$ from $\mathbf{x}$,

$$\mathbf{R}(\mathbf{x}) = \mathbf{x} + \mathbf{u}(\mathbf{x}). \tag{2.1}$$

Both $S_R$ and $S_T$ are Euclidean, with distances determined by the unit metric $dx^2 = dx_i dx_i$, and $dR^2 = dR_i dR_i$, where the Einstein summation convention on repeated indices is understood [39]. It is often interesting to consider generalizations of the above picture to a $D$-dimensional reference space and a $d \geq D$ target space; for example, to describe $D$ for two-dimensional tethered membranes fluctuating in $d$ for three-dimensional real space [25]. In this paper, however, we will restrict our attention to $D = d = 3$, leaving discussion of membranes to a future publication [26].

Distortions that vary slowly on a scale set by microscopic lengths of the reference material (interparticle separation in a glass, distance between cross-links in an elastomer, etc.) are described by the Cauchy deformation tensor [39,40]

$$\Lambda_{ij} = \frac{\partial R_i}{\partial x_j} \equiv \partial_j R_i = \delta_{ij} + \eta_{ij}, \tag{2.2}$$

where

$$\eta_{ij} = \partial_j u_i \qquad (2.3)$$

is the displacement gradient tensor. Throughout the paper, we will often use matrix notation in which $\underline{M}$ is the matrix with components $M_{ij}$ and $\underline{M}^T$ is the transpose matrix with components $M_{ji}$.

The energy of the distorted state relative to the undistorted one depends on how much the target space is stretched relative to the reference space, i.e., by how much the distance between two nearby points changes in the mapping from the reference to the target,

$$dR^2 - dx^2 = 2u_{ij}dx_i dx_j, \qquad (2.4)$$

where

$$u_{ij} = \tfrac{1}{2}(\Lambda_{ki}\Lambda_{kj} - \delta_{ij}) \quad \text{or} \quad \underline{u} = \tfrac{1}{2}(\underline{\Lambda}^T\underline{\Lambda} - \underline{\delta})$$

$$= \tfrac{1}{2}(\partial_i u_j + \partial_j u_i + \partial_i u_k \partial_j u_k)$$

$$= \tfrac{1}{2}(\eta_{ij} + \eta_{ji} + \eta_{ki}\eta_{kj}). \qquad (2.5)$$

$u_{ij}$ is the familiar nonlinear Lagrangian strain tensor [24], also called the *right* Cauchy-Green strain tensor or simply the Green strain tensor [40]. It is symmetric by construction. It is also *invariant* (i.e., transforms as a *scalar*) under arbitrary rotations of the *target* space vector **R**, i.e., if $R_i$ is replaced by $R_i' = O_{Tij}R_j$, where $O_{Tij}$ is an arbitrary rotation matrix, $u_{ij}$ does not change. On the other hand, $u_{ij}$ transforms like a rank-2 *tensor* under rotations of the *reference* space, i.e., if $x_i \to x_i' = O_{Rij}^{-1}x_j$, then [41]

$$\underline{u} \to \underline{Q}_R \underline{u} \underline{Q}_R^{-1}. \qquad (2.6)$$

Isotropic solids, e.g., the glasses and gels of interest to us, are (statistically) invariant under arbitrary rotation $\underline{Q}_R$ in the reference space $S_R$. Crystals, on the other hand, have lower symmetry and are invariant only under a point subgroup of all rotations $\underline{Q}_R$.

In contrast, invariance with respect to arbitrary rotations in $S_T$ is a property of *all* elastic media in the absence of external aligning fields, whether they be isotropic, crystalline, or wildly inhomogeneous. Thus, because it, by construction, incorporates the $O_T$ invariance, in most instances, $u_{ij}$ is the strain tensor in terms of which elastic theory is most conveniently formulated. However, here we are interested in systems (gels) that exhibit rotational invariance in the *reference* space, i.e., an $O_R$ invariance of $S_R$, and, therefore, a distinct *left* Cauchy-Green strain tensor,

$$v_{ij} = \tfrac{1}{2}(\Lambda_{ik}\Lambda_{jk} - \delta_{ij}) \quad \text{or} \quad \underline{v} = \tfrac{1}{2}(\underline{\Lambda}\,\underline{\Lambda}^T - \underline{\delta})$$

$$= \tfrac{1}{2}(\partial_i u_j + \partial_j u_i + \partial_k u_i \partial_k u_j)$$

$$= \tfrac{1}{2}(\eta_{ij} + \eta_{ji} + \eta_{ik}\eta_{jk}), \qquad (2.7)$$

is useful [42]. This tensor is invariant under arbitrary rotations $\underline{Q}_R$ in $S_R$, but it transforms like a rank-2 tensor under rotations $\underline{Q}_T$ in $S_T$:

$$\underline{v} \to \underline{Q}_T\underline{v}\ \underline{Q}_T^{-1}. \qquad (2.8)$$

In what follows, we will simply refer to $\underline{u}$ and $\underline{v}$ as right and left strain tensors, respectively.

The left strain tensor $\underline{v}$ can be contracted with other target-space tensors, such as the Maier–Saupe–de Gennes nematic order parameter $Q_{ij}$, or the electric field $E_i$, to form scalar invariants such as $\mathrm{Tr}\underline{v}Q$ or $E_i v_{ij}E_j$. In contrast, the contractions $\mathrm{Tr}\underline{u}Q$ and $E_i u_{ij}E_j$ are *not* scalars since $\underline{u}$ does not transform like a tensor in the same space as the tensors $Q_{ij}$ and $E_iE_j$. In the absence of external aligning fields such as **E** that effectively render the target space anisotropic, the right strain $\underline{u}$ provides a complete description of elastic distortions, even if, as is the case for crystals, the reference space is anisotropic. If $S_R$ is isotropic and there are external fields breaking the isotropy of $S_T$, then $\underline{u}$ cannot provide a similar complete description, but the left strain $\underline{v}$ can. On the other hand, the left strain cannot provide a complete description if the reference space is not isotropic. For example, semisoft elastomers cross-linked in the nematic phase with a director **n**$_0$, which specifies a direction in $S_R$, are invariant under the simultaneous rotations of **n**$_0$ and **x**, **n**$_0 \to \underline{Q}_R^{-1}$**n**$_0$ and **x** $\to \underline{Q}_R^{-1}$**x**, but not under rotations, **x** $\to \underline{Q}_R^{-1}$**x**, of **x** alone. The left strain $\underline{v}$ is a scalar in $S_R$, and it cannot be contracted with the reference space vector **n**$_0$. Thus, it is impossible to construct scalar invariants involving $\underline{v}$ and **n**$_0$ and to construct a free energy in terms of $\underline{v}$ that reflects the anisotropy of $S_R$. If $S_R$ is anisotropic and there are external fields breaking the rotational invariance of $S_T$, then only the deformation tensor $\underline{\Lambda}$ can provide a complete description of the energy of elastic distortions.

### B. Isotropic systems

For most gels, the reference space is macroscopically isotropic and homogeneous, i.e., like an isotropic fluid, it is invariant under **x** $\to$ **T** $+ \underline{Q}_R^{-1}$**x** for arbitrary translations **T** and rotations $\underline{Q}_R$ in $S_R$. Thus, the elastic energy is invariant under **R**(**x**) $\to \underline{Q}_T$**R**(**T** $+ \underline{Q}_R^{-1}$**x**). The invariance under rotations $\underline{Q}_T$ of the target space is easy to understand: different physical orientations of the material (even if arbitrarily distorted) have the same energy. Invariance under $\underline{Q}_R$ is somewhat more subtle though complementary. Figure 2 provides a useful graphic representation of this invariance in two dimensions. Consider a circle of radius $r$ in the reference space consisting of the points **x** $= r(\cos\phi, \sin\phi) \equiv (r,\phi)$. Under distortion, it is mapped onto some closed curve in $S_T$ consisting of points **R**$(\phi)$. Thus, the point $(r, \phi_1)$ in $S_R$ is mapped to the point **R**$_1 =$ **R**$(\phi_1)$ in $S_T$, $(r, \phi_2)$ is mapped to **R**$_2 =$ **R**$(\phi_2)$, and so on. Under a rotation through $\theta$ in $S_R$, $\phi \to \phi + \theta$. Because of the isotropy of the undistorted, reference state, the energy is not changed if the points $(r, \phi - \theta)$ rather than $(r, \phi)$ are mapped to the points **R**$(\phi)$, i.e., if $(r, \phi_1 - \theta)$ is mapped to **R**$_1$, $(r, \phi_2 - \theta)$ to **R**$_2$ and so on.

Care must be taken to incorporate the above symmetries in the free energy density of such homogeneous and isotropic gels. Invariance with respect to translations **T** in $S_R$ is enforced by requiring that the free energy density depend only
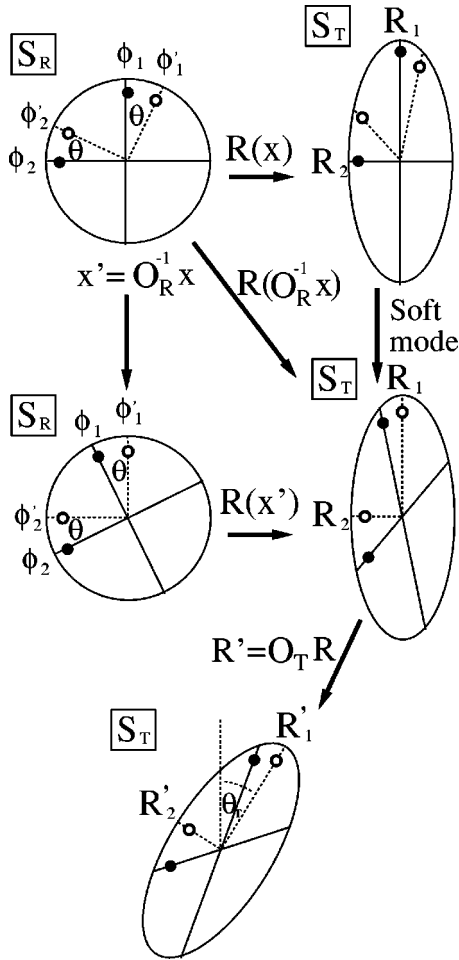
FIG. 2. Schematic representation of mappings from the reference space $S_R$ to the target space $S_T$. The points $\mathbf{x}_1 = (r, \phi_1)$ and $\mathbf{x}_2 = (r, \phi_2)$ in $S_R$ are mapped, respectively, to the points $\mathbf{R}_1$ and $\mathbf{R}_2$ in $S_T$. There is a strain energy $E_S$ associated with this mapping. For isotropic reference spaces, mapping of points in $S_R$, first rotated by $\theta$ inside the reference space (described by a rotation matrix $Q_R^{-1}$) to the same set of points in $S_T$, i.e., mapping points $\mathbf{x}_1' = (r, \phi_1 - \theta)$ and $\mathbf{x}_2' = (r, \phi_2 - \theta)$ to $\mathbf{R}_1$ and $\mathbf{R}_2$ clearly produces the same energy $E_S$ as the unrotated mapping. Subsequent target-space rotation $Q_T$ by $\theta_T$ of the resulting distorted state with points $\mathbf{R}_1$ and $\mathbf{R}_2$ mapped to $\mathbf{R}_1'$ and $\mathbf{R}_2'$ costs no energy. The transformation $\mathbf{R}(\mathbf{x}) \rightarrow Q_T \mathbf{R}(Q_R^{-1} \mathbf{x})$ between energetically-equivalent nematic states is the Goldstone mode responsible for the novel elastic properties of nematic elastomers.

on spatial derivatives of $\mathbf{R}$ with respect to $\mathbf{x}$, i.e., depend only on $\underline{\underline{\Lambda}}$ and possibly higher derivatives of $\mathbf{R}$.

Under rotations in $S_R$ and $S_T$, the Cauchy strain tensor $\Lambda_{ij}$ transforms according to

$$\Lambda_{ij} \rightarrow O_{Tik} \frac{\partial R_k}{\partial x_l'} \frac{\partial x_l'}{\partial x_j} = O_{Tik} \Lambda_{kl} O_{Rlj}^T. \tag{2.9}$$

The free energy density $f$ of an isotropic gel is invariant under *independent* $Q_T$ and $Q_R$ rotations and must satisfy

$$f(\underline{\underline{\Lambda}}) = f(Q_T \underline{\underline{\Lambda}} Q_R^{-1}). \tag{2.10}$$

It must, therefore, be constructed from the scalar invariants $\mathrm{Tr}(\underline{\underline{\Lambda}} \underline{\underline{\Lambda}}^T)^n$ and $\det \underline{\underline{\Lambda}} \underline{\underline{\Lambda}}^T = (\det \Lambda)^2$ [43]. Alternatively, the free energy can be equivalently expressed in terms of $\underline{\underline{u}}$ or $\underline{\underline{v}}$, with the respective invariances

$$f(\underline{\underline{u}}) = f(Q_R \underline{\underline{u}} Q_R^{-1}), \tag{2.11a}$$

$$f(\underline{\underline{v}}) = f(Q_T \underline{\underline{v}} Q_T^{-1}), \tag{2.11b}$$

which are enforced by allowing only fully contracted powers of strain tensors to appear. The energies $f(\underline{\underline{u}})$ and $f(\underline{\underline{v}})$ can be derived from $f(\underline{\underline{\Lambda}})$ using

$$\det \underline{\underline{\Lambda}} \underline{\underline{\Lambda}}^T = \exp \mathrm{Tr} \ln(\underline{\underline{\delta}} + 2\underline{\underline{u}}) = \exp \mathrm{Tr} \ln(\underline{\underline{\delta}} + 2\underline{\underline{v}}),$$

$$\mathrm{Tr}\underline{\underline{u}}^n = \mathrm{Tr}[\tfrac{1}{2}(\underline{\underline{\Lambda}}^T \underline{\underline{\Lambda}} - \underline{\underline{\delta}})]^n = \mathrm{Tr}[\tfrac{1}{2}(\underline{\underline{\Lambda}} \underline{\underline{\Lambda}}^T - \underline{\underline{\delta}})]^n = \mathrm{Tr}\underline{\underline{v}}^n. \tag{2.12}$$

Thus, $f(\underline{\underline{u}})$ and $f(\underline{\underline{v}})$ depend only on $\mathrm{Tr}\underline{\underline{u}}^n = \mathrm{Tr}\underline{\underline{v}}^n$, and $f(\underline{\underline{v}})$ is the *same* function of $\underline{\underline{v}}$ that $f(\underline{\underline{u}})$ is of $\underline{\underline{u}}$. For the discussion of encoding these two $O_R$ and $O_T$ symmetries at the harmonic level in the phonon variable $\mathbf{u}$, see Appendix B.

Although many of the properties of nematic elastomers follow directly from the above invariances, in what follows, it will be useful to have explicit forms for the elastic free energy density. A model free energy in terms nonlinear strain tensor $\underline{\underline{u}}$, up to fourth order in $\underline{\underline{u}}$ is

$$f(\underline{\underline{u}}) = \tfrac{1}{2}\lambda(\mathrm{Tr}\underline{\underline{u}})^2 + \mu \mathrm{Tr}\underline{\underline{u}}^2 - C\mathrm{Tr}\underline{\underline{u}}^3 + D'(\mathrm{Tr}\underline{\underline{u}}^2)^2$$
$$- E'\mathrm{Tr}\underline{\underline{u}}\mathrm{Tr}\underline{\underline{u}}^2. \tag{2.13}$$

As just discussed, this free energy can be expressed equally well in terms of $\underline{\underline{v}}$ merely by replacing $\underline{\underline{u}}$ by $\underline{\underline{v}}$. Invariances with respect to rotations in $S_R$ and $S_T$ are enforced in $f(\underline{\underline{u}})$ in different ways. Symmetry under $Q_T$ is enforced by the construction of the strain tensor $\underline{\underline{u}}$, Eq. (2.5), which, being a scalar in $S_T$, is automatically invariant under $Q_T$. Invariance under $Q_R$ is enforced by only allowing terms in $f(\underline{\underline{u}})$ that transform as a scalar under $Q_R$, i.e., only fully contracted powers of $\underline{\underline{u}}$. In contrast, invariance of $f(\underline{\underline{v}})$ with respect to $Q_R$ is enforced by construction of the strain tensor $\underline{\underline{v}}$ (a scalar in $S_R$), whereas that with respect to $Q_T$ is enforced by only allowing terms in $f(\underline{\underline{v}})$ that transform like a scalar under $Q_T$, i.e., requiring that all the target space indices be contracted.

As usual, the reference state, relative to which $\underline{\underline{u}}$ is defined is taken to be in mechanical equilibrium, guaranteeing that no terms linear in $\underline{\underline{u}}$ appear. The first two terms of $f$ are the standard elastic energy of an isotropic medium with $\lambda$ and $\mu$ the Lamé coefficients [24]. We have included stabilizing nonlinear terms in the strain tensor $\underline{\underline{u}}$ because we will eventually want to consider phase transitions to an anisotropic state induced by a decrease in the shear modulus $\mu$ below a critical value. In the spirit of Landau theory of phase transitions [16], at present, we view $\mu$ as a phenomenological parameter that is allowed to vary and even become negative. As we shall see in more detail in Sec. IV, the origin of a diminishing $\mu$ in liquid-crystal elastomers is the instability of the isotropic state toward the development of nematic liquid-crystal order characterized by the Maier-Saupe order

parameter $Q$. In $f$, we have left out one third-order and three fourth-order terms permitted by symmetry, namely, the ones proportional to $(\text{Tr}\underline{u})^3$, $(\text{Tr}\underline{u})^4$, $(\text{Tr}\underline{u})^2\text{Tr}\underline{u}^2$, and $\text{Tr}\underline{u}\,\text{Tr}\underline{u}^3$, respectively. Though these terms can easily be included, their effect is small for the nearly incompressible systems of most interest to us.

Our primary interest is in the state with *spontaneously* broken rotational symmetry that is produced when $\mu$ falls below a critical value. To describe this state and the transition to it, it is useful to decompose $u_{ij}$ into its scalar (in $S_R$) and symmetric-traceless parts:

$$u_{ij} = \tfrac{1}{3}\delta_{ij}u_{kk} + \tilde{u}_{ij}, \tag{2.14}$$

where

$$\tilde{u}_{ij} = u_{ij} - \tfrac{1}{3}\delta_{ij}u_{kk}. \tag{2.15}$$

Using Eq. (2.14) in Eq. (2.13) and keeping only the lowest-order terms in $\text{Tr}\underline{u}$, we obtain the model free-energy density that we will use in discussions of the anisotropic state and the transition to it,

$$f = \tfrac{1}{2}B[\text{Tr}\underline{u} - (E/B)\text{Tr}\underline{\tilde{u}}^2]^2 + f_1, \tag{2.16}$$

with

$$f_1 = \tfrac{1}{2}A\,\text{Tr}\underline{\tilde{u}}^2 - C\,\text{Tr}\underline{\tilde{u}}^3 + D(\text{Tr}\underline{\tilde{u}}^2)^2, \tag{2.17}$$

where $A = 2\mu$, $B = \lambda + \tfrac{2}{3}\mu$ is the bulk modulus, $E = E' - C$, $D = D' - E^2/(2B)$, and for simplicity we have dropped qualitatively inconsequential cubic and quartic terms in $\text{Tr}\underline{u}$ [44].

### C. Anisotropic systems

Often the reference state is a crystal that is invariant only under operations of some subgroup of $O_3$. In this case, there are additional combinations of the strain tensor that are invariant under the reduced set of symmetry operations of $S_R$, and the elastic energy is in general described, to harmonic order in $u_{ij}$, in terms of a fourth rank elastic-constant tensor $C_{ijkl}$, with $f = \tfrac{1}{2}C_{ijkl}u_{ij}u_{kl}$. We will be particularly interested in uniaxial systems with axis along $\mathbf{n}_0$, for which the general form of the elastic-constant tensor is (but see Sec. III)

$$\begin{aligned}
C_{ijkl} &= C_1 n_{0i}n_{0j}n_{0k}n_{0l} + C_2(n_{0i}n_{0j}\delta_{kl}^{0\perp} + n_{0k}n_{0l}\delta_{ij}^{0\perp}) \\
&\quad + C_3\delta_{ij}^{0\perp}\delta_{kl}^{0\perp} + C_4(\delta_{ik}^{0\perp}\delta_{jl}^{0\perp} + \delta_{il}^{0\perp}\delta_{jk}^{0\perp}) \\
&\quad + \tfrac{1}{2}C_5(\delta_{ik}^{0\perp}n_j^0 n_l^0 + \delta_{il}^{0\perp}n_j^0 n_k^0 \\
&\quad + \delta_{jk}^{0\perp}n_i^0 n_l^0 + \delta_{jl}^{0\perp}n_i^0 n_k^0),
\end{aligned} \tag{2.18}$$

where $\delta_{ij}^{0\perp} = \delta_{ij} - n_{0i}n_{0j}$. The elastic energy in three dimensions with the $z$-axis chosen along $\mathbf{n}_0$ is

$$\begin{aligned}
f_{\text{uni}} &= \tfrac{1}{2}C_1 u_{zz}^2 + C_2 u_{zz}(u_{xx} + u_{yy}) + \tfrac{1}{2}C_3(u_{xx} + u_{yy})^2 \\
&\quad + C_4(u_{xx}^2 + u_{yy}^2 + 2u_{xy}^2) + C_5(u_{xz}^2 + u_{yz}^2). \tag{2.19}
\end{aligned}$$

The strain $u_{ij}$ is still invariant under arbitrary rotation in $S_T$, so $f_{\text{uni}}$ is invariant under these rotations, as it must be. The reduced symmetry of the reference state introduces an asymmetry between the reference and target spaces, and it is no longer so useful to use the alternative strain tensor $\underline{v}$ unless we wish to explicitly discuss coupling between strain and another target-space tensor-field order parameter, such as the Maier-Saupe order parameter for a nematic.

The elastic energy $f_{\text{uni}}$ of Eq. (2.19) is harmonic in the nonlinear strain $u_{ij}$. Higher-order terms in $u_{ij}$ are, of course, permitted and are in fact necessary to preserve full rotational invariance in $S_R$, which is present (but hidden), if the uniaxial asymmetry arises as a result of the *spontaneous* symmetry breaking of an *isotropic* state, as happens in nematic elastomers, introduced in Sec. III.

In semisoft elastomers [18,7], the rotational invariance of the soft-elastomer isotropic state (discussed next) is only weakly broken. Any model describing these systems must introduce anisotropy in such a way that both the isotropic and the anisotropic soft phases are reproduced when the anisotropy is set to zero. The simplest such model can be constructed by adding an anisotropic term

$$f_{\text{anis}} = -h n_{0i}\tilde{u}_{ij}n_{0j}, \tag{2.20}$$

which breaks $O_R$ symmetry, to the free energy of Eq. (2.16). Here $\mathbf{n}_0$ is a vector in $S_R$ that specifies the direction of preferred alignment, and $h$ is a field measuring the anisotropy strength. The properties of this model will be explored in a separate publication [35].

### III. STRAIN-ONLY MODEL OF NEMATIC ELASTOMERS

Under appropriate conditions, for example, for sufficiently small shear modulus $\mu$ in the model free energy of Eq. (2.13), there can be a transition from an isotropic state with $\underline{\Lambda} \sim \underline{\delta}$ to a uniaxial one with two rather than one distinct eigenvalues for $\underline{\Lambda}$. This nematic-gel state is obtained from the isotropic one by stretching or compressing along some arbitrary direction in $S_R$ specified by a unit vector $\mathbf{n}_0$, which without loss of generality we take to be along the $z$ axis. It is characterized by an anisotropic equilibrium right strain tensor $\underline{u}_0$ with principal axis along $\mathbf{n}_0$. The transition to the nematic gel can thus be described completely in terms of the free energy $f(\underline{u})$. Alternatively, the nematic gel can be characterized by an anisotropic equilibrium left strain tensor $\underline{v}_0$ with anisotropy axis along some unit vector $\mathbf{n}_1$ is $S_T$, and the transition to it can be described by $f(\underline{v})$. The nematic gel breaks *both* $O_R$ and $O_T$ symmetry. The description in terms of $\underline{u}$ displays explicitly the broken $O_R$ symmetry and that in terms of $\underline{v}$ the broken $O_T$ symmetry of the nematic gel. The underlying order parameter, however, is the deformation tensor $\underline{\Lambda}$, which exhibits both broken $O_R$ and $O_T$ symmetry in the nematic gel. Even though the nematic gel breaks two symmetries, they are both broken at the same time, and there is only one transition from the isotropic phase to the nematic gel. As discussed in Sec. II B, $f(\underline{u})$ and $f(\underline{v})$ are identical functions of their arguments, and $\underline{u}$ and $\underline{v}$ develop nonzero anisotropic values simultaneously.

Though free energies expressed in terms of the strain $\underline{u}$ and $\underline{v}$ provide complete descriptions of the phase transition to the nematic gel, it is important to remember that the full position function $\mathbf{R}(\mathbf{x})$ or equivalently the displacement $\mathbf{u}(\mathbf{x})$ is needed to describe all configurations of the gel. The tensors $\underline{\Lambda}$, $\underline{u}$, and $\underline{v}$ only provide information about long-wavelength distortions. In nematic gels, the shear modulus for certain shear strains vanishes, and the energy expressed in terms of strains alone is not positive definite. A full statistical mechanical treatment of nematic gels requires the elastic energy appearing in the partition trace to be positive definite, and additional curvature energies depending on the second derivative of $\mathbf{R}(\mathbf{x})$ must be added to it to make it so. This will be discussed in more detail in a separate publication [26].

In this section, we will explore the properties of the spontaneously formed nematic gel described in terms of $\underline{u}$ and $f(\underline{u})$. The description in terms of $\underline{v}$ is essentially equivalent. We will explicitly derive the soft elasticity of nematic gels whereby the strain elastic constant $C_5$ [Eq. (2.19)] vanishes identically [17] and there is zero stress [36] associated with appropriate strains up to a critical value perpendicular and parallel to $\mathbf{n}_0$ as long as other strains [45,46] are allowed to relax to their lowest-energy configurations. Our treatment provides a complete description of nematic gels and transitions to them without any reference to the underlying nematic order. In the next section, we will consider nematic order and its coupling to strain and show that instabilities toward the development of nematic order drive the decrease in the shear modulus discussed in the preceding section.

### A. Description in terms of $u_{ij}$

It is quite clear from the cubic form of the elastic free energy, Eqs. (2.13) and (2.17), that when $\mu$ becomes sufficiently small, for finite $C$, there is a first-order transition from an isotropic to a uniaxially distorted elastic state, which is very similar to the familiar isotropic-to-nematic transition [1,2]. We will consider this transition in more detail in Sec. III C. In this section, we will investigate the resulting anisotropic elastic state, whose properties depend only on the existence of *spontaneously* formed anisotropy and not on any particular model of the isotropic-to-nematic transition.

In the positive (negative) uniaxial state that results from such transition, the elastic material is stretched (compressed) along $\mathbf{n}_0$ in $S_R$ and compressed (stretched) along directions perpendicular to $\mathbf{n}_0$. This anisotropy axis can point in any direction $\mathbf{n}_1$ in $S_T$. For the moment, we will take $\mathbf{n}_1 = \mathbf{n}_0$, i.e., we do not rotate the sample after it has been stretched. In this case, the coordinates of its mass points in $S_T$ are, therefore, described by

$$\mathbf{R}_0(\mathbf{x}) \equiv \mathbf{x}' = \mathbf{x} + \mathbf{u}_0 = \underline{\Lambda}_0 \mathbf{x}, \tag{3.1}$$

where the deformation tensor is spatially uniform and given by

$$\Lambda_{0ij} = \Lambda_{0\perp} \delta_{ij}^{0\perp} + \Lambda_{0\|} n_{0i} n_{0j}, \tag{3.2a}$$

$$= \Lambda_{0\perp} \delta_{ij} + (\Lambda_{0\|} - \Lambda_{0\perp}) n_{0i} n_{0j}, \tag{3.2b}$$

where $\delta_{ij}^{0\perp} = \delta_{ij} - n_{0i} n_{0j}$. The corresponding right equilibrium strain tensor is

$$\underline{u}_0 = \tfrac{1}{2}(\underline{\Lambda}_0^T \underline{\Lambda}_0 - \underline{\delta}). \tag{3.3}$$

The anisotropy of the uniaxial state can be characterized by the anisotropy ratio [47]

$$r = \frac{\Lambda_{0\|}^2}{\Lambda_{0\perp}^2}. \tag{3.4}$$

Since

$$\underline{\Lambda}_0^T \underline{\Lambda}_0 = \Lambda_{0\perp}^2 [\underline{\delta} + (r-1)\mathbf{n}_0 \mathbf{n}_0], \tag{3.5}$$

it is clear that the system is isotropic if $r = 1$ and only anisotropic if $r \neq 1$. Both positive ($r > 1$) and negative ($r < 1$) uniaxial anisotropies are possible, but we will focus mostly on positive uniaxial systems. In incompressible systems, $\det \underline{\Lambda}_0 = \Lambda_{0\|} \Lambda_{0\perp}^2 = 1$, $\Lambda_{0\perp} = \Lambda_{0\|}^{-1/2}$, and $r = \Lambda_{0\|}^3$. Many of the properties of the uniaxial phase depend critically on $r$.

The goal of this section is to explore the elasticity of this spontaneously uniaxially-ordered gel. Distortions in such a system can be described by deviations,

$$\delta\underline{u} = \underline{u} - \underline{u}_0 = \tfrac{1}{2}(\underline{\Lambda}^T \underline{\Lambda} - \underline{\Lambda}_0^T \underline{\Lambda}_0), \tag{3.6}$$

of the strain tensor $\underline{u}$ from its new equilibrium value $\underline{u}_0$, both measured in the coordinates $\mathbf{x}$ of the original isotropic state $S_R$. It is, however, more common and convenient to describe these distortions in terms of displacements $\mathbf{R}'(\mathbf{x}') \equiv \mathbf{R}(\mathbf{x})$ and strains $\underline{u}'(\mathbf{x}')$ expressed as functions of the coordinates $\mathbf{x}' \equiv \mathbf{R}_0(\mathbf{x})$ of the new equilibrium stretched state,

$$\mathbf{R}'(\mathbf{x}') = \mathbf{x}' + \mathbf{u}'(\mathbf{x}') = \mathbf{x} + \mathbf{u}_0 + \delta\mathbf{u}(\mathbf{x}), \tag{3.7a}$$

$$\underline{u}' = \tfrac{1}{2}(\underline{\Lambda}'^T \underline{\Lambda}' - \underline{\delta}) \approx \tfrac{1}{2}(\underline{\eta}' + \underline{\eta}'^T), \tag{3.7b}$$

where $\Lambda'_{ij} = \partial R'_i / \partial x'_j$ and $\eta'_{ij} = \partial u'_i / \partial x'_j$. Since

$$\Lambda_{ij} = \frac{\partial R_i}{\partial x_j} = \frac{\partial R'_i}{\partial x'_k} \frac{\partial x'_k}{\partial x_j} = \Lambda'_{ik} \Lambda_{0kj}, \tag{3.8}$$

the strain deviation $\delta\underline{u}$ is directly proportional to $\underline{u}'$ and therefore proportional to the symmetrized strain ($\underline{\eta}' + \underline{\eta}'^T$)/2 when linearized,

$$\delta\underline{u} = \underline{\Lambda}_0^T \underline{u}' \underline{\Lambda}_0. \tag{3.9}$$

One would normally expect the elastic free energy for strains $\underline{u}'$ about the new uniaxial state to have the form of Eq. (2.19), characterized by five independent elastic constants. However, as discussed in Introduction, the fact that the uniaxial state arose via *spontaneous* symmetry breaking of an isotropic state guarantees that the shear modulus $C_5$ *must* vanish. We now demonstrate this explicitly.

Since the original free energy is invariant under rotations $\underline{Q}_R$ in $S_R$, the anisotropy direction $\mathbf{n}_0$ in $S_R$ is arbitrary, and states characterized by strain $\underline{Q}_R \underline{u}_0 \underline{Q}_R^{-1}$ and $\underline{u}_0$ must have

the same bulk energy. This means that there is no bulk energy cost associated with a strain

$$\underline{u}'(\theta) = (\underline{\Lambda}_0^T)^{-1} (Q_R \underline{u}_0 Q_R^{-1} - \underline{u}_0) \underline{\Lambda}_0^{-1} \qquad (3.10)$$

relative to the uniaxial state characterized by $\underline{u}_0$ since it describes a rotation in $S_R$, and is, therefore, a Goldstone mode of broken $O_R$ symmetry. For rotations through $\theta$ about the $y$ axis,

$$Q_R = \begin{pmatrix} \cos\theta & 0 & \sin\theta \\ 0 & 1 & 0 \\ -\sin\theta & 0 & \cos\theta \end{pmatrix}. \qquad (3.11)$$

Using this $Q_R$ inside Eq. (3.10), we find that $u'_{ij}(\theta)$ is a nontrivial strain even though it describes a pure rotation in $S_R$. Under this rotation, $u'_{ij}(\theta)$ only has components in the $xz$ plane (the plane of rotation $\theta$) that are

$$\underline{u}' = \frac{1}{4}(r-1) \begin{pmatrix} 1-\cos 2\theta & r^{-1/2}\sin 2\theta \\ r^{-1/2}\sin 2\theta & -r^{-1}(1-\cos 2\theta) \end{pmatrix}$$
$$(3.12a)$$

$$\approx \frac{(r-1)}{2\sqrt{r}} \begin{pmatrix} 0 & \theta \\ \theta & 0 \end{pmatrix}, \qquad (3.12b)$$

where $r$ is the anisotropy ratio introduced in Eq. (3.4), and the final form is valid for small $\theta$. Since, as just argued, the elastic free energy must be invariant under rotations in $S_R$, it cannot depend on the rotation angle $\theta$, and, therefore, there must be no energy cost associated with an infinitesimal strain $u'_{xz} = u'_{zx}$. Similarly, invariance with respect to rotations about the $x$ axis implies no energy cost associated with the strain $u'_{yz}$. Thus, the shear elastic modulus $C_5$ must identically vanish in a *spontaneously* uniaxial state, whose *harmonic* elastic energy,

$$f_{\mathrm{uni}}^N = \frac{1}{2} C_1 u'^2_{zz} + C_2 u'_{zz}(u'_{xx} + u'_{yy}) + \frac{1}{2} C_3 (u'_{xx} + u'_{yy})^2$$
$$+ C_4 (u'^2_{xx} + u'^2_{yy} + 2u'^2_{xy}), \qquad (3.13)$$

is characterized by only four elastic constants. The superscript $N$ in $f_{\mathrm{uni}}^N$ is introduced to distinguish it from the standard uniaxial energy $f_{\mathrm{uni}}$ [Eq. (2.19)] with $C_5 \neq 0$. Because $f_{\mathrm{uni}}^N$ contains only quadratic terms in strain $u'_{ij}$ relative to the broken-symmetry uniaxial phase, as in similar systems [48] it is only invariant with respect to *infinitesimal* rotations in $S_R$ and terms nonlinear in $u'_{ij}$ must be incorporated in order to encode the full $O_R$ invariance [15].

There are striking experimental consequences [18–20] of the existence of zero-energy strains $\underline{u}'(\theta)$ given by Eqs. (3.10), (3.12a) for arbitrary $\theta$. Namely, if one of the components of strain $u'_{xz}$, $u'_{xx}$, or $u'_{zz}$ is imposed with the right sign, the other two components can under appropriate boundary conditions adopt values to produce the zero-energy rotational strain of Eq. (3.12a). Under general boundary conditions that prevent access to this zero-energy state, microdomain structures with low-energy rotational strains will form. When

$r > 1$, this relaxation is possible only for positive $u'_{xx}$ (extension perpendicular to the uniaxial direction $\mathbf{n}_0$), negative $u'_{zz}$ (compression along $\mathbf{n}_0$), and either positive or negative $u'_{xz}$. For negative anisotropy systems ($r < 1$), the zero-energy strain relaxation is possible only for negative $u'_{xx}$ and positive $u'_{zz}$.

To illustrate this, consider first a sample with $\mathbf{n}_0$ aligned along the $z$ axis, with $r > 1$. From Eq. (3.12a), it follows that $u'_{xx} = (1/2)(r-1)\sin^2\theta$ is positive for a rotational strain when $r > 1$. Thus, we can only have soft elasticity for extensional strains along $x$, and we take $u'_{xx} > 0$. If no relaxation of strain is allowed, this stretch would cost an energy proportional to $u'^2_{xx}$. If, however, strain relaxation is allowed, strains

$$u'_{zz} = -\frac{1}{r} u'_{xx},$$

$$u'_{xz} = \pm \frac{1}{\sqrt{2r}} \sqrt{u'_{xx}(r-1-2u'_{xx})}, \qquad (3.14)$$

convert the $u'_{xx}$ strain to a zero-energy rotation strain tensor (Goldstone mode) with rotation angle

$$\theta = \sin^{-1} \sqrt{\frac{2u'_{xx}}{r-1}}. \qquad (3.15)$$

Thus, in an ideal system, there is no bulk energy cost associated with strains $0 < u'_{xx} < (r-1)/2$.

The angle $\theta$ specifies the direction of the induced uniaxial equilibrium stretch axis relative to the $z$ axis of a fixed coordinate system in $S_R$. In the current problem, this anisotropy axis is initially along $z$, and it rotates toward the $x$ axis as $u'_{xx}$ is increased until, at the critical strain $u'_{xx} = (r-1)/2$, $\theta = \pi/2$ and the anisotropy axis has been rotated to be along the $x$ axis, as illustrated in Fig. 3. For strains $u'_{xx}$ larger that $(r-1)/2$, the sample will merely stretch along its new anisotropy axis along $x$ with the additional strain $\delta u'_{xx} = u'_{xx} - (r-1)/2$. We can calculate the energy associated with this additional strain from the harmonic free energy of Eq. (3.13) provided we remember that $\delta u'_{xx}$ is measured relative to the original reference system with the anisotropy axis along $z$ rather than $x$, i.e., if we remember to replace $u'_{zz}$ in Eq. (3.13) by $\bar{u}'_{zz} = (\Lambda^2_{0\perp}/\Lambda^2_{0\|}) \delta u'_{xx} = \delta u'_{xx}/r$. $u'_{xx}$ and $u'_{yy}$ should be rescaled as well, but since we minimize over these quantities at fixed $\bar{u}'_{zz}$, we do not have to explicitly consider these rescalings. Performing this minimization, we find

$$\delta f = \begin{cases} 0 & \text{if } \delta u'_{xx} < 0; \\ \frac{1}{2r^2}\left(C_1 - \frac{C_2^2}{2C_4 + 2C_3}\right)(\delta u'_{xx})^2 & \text{if } \delta u'_{xx} > 0. \end{cases}$$
$$(3.16)$$

Consequently, the stress $\partial f / \partial \Lambda'_{xx} = \Lambda'_{xx} \partial f / \partial u'_{xx}$ for an ideal nematic gel is zero for $u'_{xx} < (r-1)/2$ and grows linearly in $\delta u'_{xx}$ for $u'_{xx} > (r-1)/2$ as shown in Fig. 4.
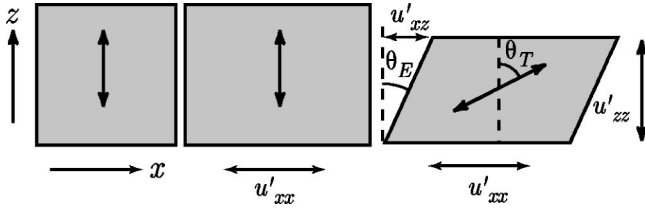
FIG. 3. Schematic representation of the transformations of a rectangular piece of soft nematic gel subjected to a strain perpendicular to its anisotropy axis. If $u'_{zz}$ and $u'_{xz}$ are constrained to be zero, there is no rotation of the anisotropy axis indicated by a double arrow as shown in the middle figure. If these quantities are allowed to relax, the anisotropy axis rotates to produce a state with the same energy as the initial state as shown in the final figure. In the process, the original rectangle is transformed into a parallelogram sheared through an angle $\theta_E$, and its anisotropy axis represented by the double arrow is rotated through an angle $\theta_T$.

The angle $\theta_T$ of rotation of the anisotropy axis in the target space $S_T$ is not the same as the rotation angle $\theta$ in $S_R$. Indeed, since the energy is invariant with respect to rotations in $S_T$, $\theta_T$ would be arbitrary, were it not for boundary conditions. A specific experimental geometry might, for example, demand that there be no change in the $z$ coordinates of mass points as a function of $x'$. This is the situation depicted in Fig. 3. In this case, $\Lambda'_{zx} = 0$, but $\Lambda'_{xz} \neq 0$, and the $xz$ submatrix of $\Lambda'_{ij}$ takes the form

$$\underline{\underline{\Lambda}}' = \begin{pmatrix} \Lambda'_{xx} & \Lambda'_{xz} \\ 0 & \Lambda'_{zz} \end{pmatrix}. \qquad (3.17)$$

This deformation tensor corresponds to a zero-energy rotation in $S_R$ described by a rotation matrix $\underline{\underline{Q}}_R$ [Eq. (3.11)] provided there exists a rotation matrix

$$\underline{\underline{Q}}_T = \begin{pmatrix} \cos\theta_T & \sin\theta_T \\ -\sin\theta_T & \cos\theta_T \end{pmatrix} \qquad (3.18)$$

in the $xz$ plane of $S_T$ such that the strain $\underline{\underline{\Lambda}} = \underline{\underline{\Lambda}}'\underline{\underline{\Lambda}}_0$ relative to the original reference system is $\underline{\underline{Q}}_T\underline{\underline{\Lambda}}_0\underline{\underline{Q}}_R^{-1}$, or

$$\underline{\underline{\Lambda}}' = \underline{\underline{Q}}_T\underline{\underline{\Lambda}}_0\underline{\underline{Q}}_R^{-1}\underline{\underline{\Lambda}}_0^{-1}, \qquad (3.19)$$

an expression that is fully consistent with the form of strain Goldstone mode $\underline{u}'(\theta)$, Eq. (3.12a). A straightforward calculation yields

$$\Lambda'_{zx} = -\cos\theta\sin\theta_T + \sqrt{r}\sin\theta\cos\theta_T, \qquad (3.20)$$

which, upon imposition of the boundary condition of $\Lambda'_{zx} = 0$, Eq. (3.17), gives

$$\sin^2\theta_T = \frac{r\sin^2\theta}{1+(r-1)\sin^2\theta} \qquad (3.21a)$$

$$= \frac{r}{r-1}\left(1 - \frac{1}{\Lambda'^2_{xx}}\right), \qquad (3.21b)$$



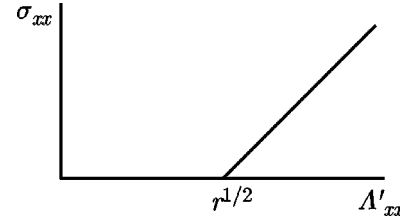FIG. 4. Stress $\sigma_{xx}$ versus strain $\Lambda_{xx}$ for an ideal soft nematic elastomer stretched along a direction perpendicular to the direction of initial alignment. The stress is zero up to a critical strain $\Lambda_{xx} = \sqrt{r}$. Beyond that, the stress initially grows linearly from zero.

where we used $\sin^2\theta = 2u'_{xx}/(r-1)$, Eq. (3.15) and $(\Lambda'_{xx})^2 - 1 = 2u'_{xx}$ to obtain the final form. This is exactly the same result obtained via a direct minimization of the neoclassical rubber energy in the incompressible limit [19].

The angle $\theta_T$ is simply the angle that the uniaxial anisotropy axis makes with the $z$ axis in the target space. This axis is the principal axis of $\underline{\underline{\Lambda}}\underline{\underline{\Lambda}}^T$ (or equivalently of $\underline{\underline{v}}$). A direct calculation of $\underline{\underline{\Lambda}}'\underline{\underline{\Lambda}}_0\underline{\underline{\Lambda}}_0^T\underline{\underline{\Lambda}}'^T$ yields

$$\underline{\underline{\Lambda}}\underline{\underline{\Lambda}}^T = \Lambda_{0\perp}^2\begin{pmatrix} \cos^2\theta_T + r\sin^2\theta_T & (r-1)\sin\theta_T\cos\theta_T \\ (r-1)\sin\theta_T\cos\theta_T & r\cos^2\theta_T + \sin^2\theta_T \end{pmatrix}, \qquad (3.22)$$

which is nothing more than $\underline{\underline{\Lambda}}_0\underline{\underline{\Lambda}}_0^T$ rotated though $\theta_T$ so that the principal axis is along $\mathbf{n}_1 = (\sin\theta_T, \cos\theta_T)$. Under the transformation defined by $\underline{\underline{\Lambda}}'$ of Eq. (3.17), a rectangle will be transformed into a parallelogram with two edges parallel to the $x$ axis and two edges making an angle

$$\theta_E = \tan^{-1}\frac{\Lambda'_{xz}}{\Lambda'_{zz}} = \tan^{-1}\left(\frac{(r-1)\tan\theta_T}{r+\tan^2\theta_T}\right) \qquad (3.23)$$

with the vertical. Both $\theta_E$ and $\theta_T$ are indicated in Fig. 3. Note that the argument of the inverse tangent in the expression for $\theta_E$ rises from zero, reaches a maximum, and then returns to zero as $\theta_T$ passes from zero to $\pi/2$, the maximum angle of rotation of the anisotropy axis. In the process, $\underline{\underline{\Lambda}}$ passes from having extension $\Lambda_{0\|}$ along the $z$ axis and $\Lambda_{0\perp}$ along the $x$ axis to having extension $\Lambda_{0\perp}$ along the $z$ axis and $\Lambda_{0\|}$ along $x$. Thus, the original rectangle is distorted to a parallelogram that first becomes more slanted as strain increases, reaches a maximum slant, and then becomes less slanted until it finally reaches a rectangular form that is precisely the original rectangle rotated by $\pi/2$ before stretching further along the $x$ axis.

It is notable that the expression, Eq. (3.21b), for $\sin\theta_T$ is independent of the detailed form of the elastic energy and that it is characterized only by the level of anisotropy $r$ of the initial uniaxial state and by the deformation $\Lambda'_{xx}$ applied to it. The advantage of our approach is that it makes it clear that the phenomenon of soft response, summarized by Fig. 4, i.e., zero stress for a range of longitudinal strain, applied perpendicular to the uniaxial direction, follows entirely from general symmetry principles of breaking of rotational invariance of the reference state. It is a property of *any* nematic gel

formed spontaneously from an isotropic gel, and is therefore independent of the details of the microscopic model of the gel and the mechanism that drives the uniaxial instability, as confirmed by the generic form for $\theta_T$ in Eq. (3.21b).

There is spectacular experimental evidence [18] for $\theta_T(\Lambda'_{xx})$, Eq. (3.21b). Likewise, experiments confirm the GL prediction of softness (vanishing stress up to a critical value of strain, Fig. 4), in the limit in which the gel is cross-linked in the isotropic phase. In contrast, chemically identical networks cross-linked in the nematic phase exhibit a plateau in the stress-strain curve that approaches zero as the degree of nematic order during cross-linking is decreased. See Ref. [20] for a presentation and discussion of these results.

It is clear that for $r > 1$ an imposed shear strain $u'_{xz}$ or a compressional strain $u'_{zz} < 0$ can be converted to zero-energy rotational strain just as for the case $u'_{xx} > 0$ just considered. The energy of a shear strain is zero for $|u'_{xz}| < (r-1)/(4\sqrt{r})$, and that of a compressional strain is zero for $|u'_{zz}| < (r-1)/(2r)$. While softness with respect to *small* shears below a critical frequency has been observed [49], to our knowledge, our above prediction of softness over a *finite* range of strain for the geometries with imposed $u'_{xz} \neq 0$ or $u'_{zz} < 0$ has not been tested.

The above discussion and the structure of the zero-energy strain $u'_{ij}(\theta)$, Eq. (3.12a), imply that our arguments for soft elasticity go through equally well for the negative uniaxial anisotropy elastomers, $r < 1$, but with reversed signs of the imposed zero-energy strains. Thus, in negative uniaxial elastomers, there is no stress associated with unconstrained *compression* along $x$, $u'_{xx} < 0$ and *extension* along $z$, $u'_{zz} > 0$.

### B. Description in terms of $v_{ij}$

In the discussion just presented, the nematic state and its soft elasticity were described in terms of the right strain tensor $u_{ij}$. As demonstrated in Sec. II B, this state could equally well be described in terms of the left strain tensor $v_{ij}$, which has an equilibrium value

$$\underline{v}_0 = \tfrac{1}{2}(\underline{\Lambda}_0 \underline{\Lambda}_0^T - \underline{\delta}) \tag{3.24}$$

that is identical to $\underline{u}_0$ in the basis defined by $\mathbf{n}_0$. The deviations from the spontaneously anisotropic equilibrium state $\underline{\Lambda}_0$ can be described by

$$\delta\underline{v} = \underline{v} - \underline{v}_0 = \tfrac{1}{2}(\underline{\Lambda}\underline{\Lambda}^T - \underline{\Lambda}_0\underline{\Lambda}_0^T) \tag{3.25}$$

as well as $\delta\underline{u}$. The deviations $\delta\underline{u}$ and $\delta\underline{v}$, however, have different relations to the displacement gradient tensor $\underline{\eta}'$ relative to the anistropic equilibrium state. As we saw in Eq. (3.9), $\delta\underline{u}$ is linearly proportional to $\underline{u}'$ and at linear order depends only on the *symmetrized* part of $\underline{\eta}'$. $\delta\underline{v}$ on the other hand is *not* proportional to $\underline{v}'$ defined by Eq. (2.7) with $\underline{\Lambda}$ replaced by $\underline{\Lambda}'$, and to linear order, it depends on *both* the symmetric and antisymmetric parts of $\underline{\eta}'$. Using Eqs. (3.25) and (2.2), we easily derive

$$\Lambda_{0\perp}^{-2}\delta v_{ij} = \tfrac{1}{2}(\eta'_{ij} + \eta'_{ji} + \eta'_{ik}\eta'_{jk}) + \tfrac{1}{2}(r-1)(n_{0i}n_{0k}\eta'_{jk}$$
$$+ \eta'_{ik}n_{0k}n_{0j} + \eta'_{ik}n_{0k}n_{0l}\eta'_{jl}), \tag{3.26}$$

in terms of $\underline{\eta}'$, with $r$ the previously defined anisotropy ratio [Eq. (3.4]. Using the decomposition

$$\underline{\eta}' = \underline{\eta}'_S + \underline{\eta}'_A \qquad \underline{\eta}'^T = \underline{\eta}'_S - \underline{\eta}'_A, \tag{3.27}$$

where $\eta'_{Sij} = \eta'_{Sji}$ and $\eta'_{Aij} = -\eta'_{Aji}$ are, respectively, the symmetric and antisymmetric parts of $\eta'_{ij}$ and defining a rotation angle

$$\Omega_i = \tfrac{1}{2}\epsilon_{ijk}\frac{\partial u'_k}{\partial x'_j} = \tfrac{1}{2}\epsilon_{ijk}\eta'_{Akj}, \tag{3.28}$$

we obtain

$$\Lambda_{0\perp}^{-2}\delta v_{ij} = \eta'_{Sij} + \tfrac{1}{2}(r-1)[n_{0i}n_{0k}\eta'_{Sjk} + \eta'_{Sik}n_{0k}n_{0j}]$$
$$- \tfrac{1}{2}(r-1)[n_{0i}(\mathbf{n}_0 \times \mathbf{\Omega})_j + (\mathbf{n}_0 \times \mathbf{\Omega})_i n_{0j}] \tag{3.29}$$

to linear order in $\eta'_{ij}$. We thus explicitly demonstrate that $\delta v_{ij}$ is a function of both the symmetric and antisymmetric parts of $\eta'_{ij}$. At first pass, this observation appears to contradict the facts that the linearized form of $\delta u_{ij}$, Eqs. (3.7b) and (3.9), does not depend on $\eta'_{Aij}$, and that the harmonic free energy of the nematic phase must have exactly the same form whether expressed in terms of $\delta u_{ij}$ or $\delta v_{ij}$. The dilemma is resolved by noting that only the soft components of the strain, $\delta v_{xz}$ and $\delta v_{yz}$, depend on $\eta'_{Aij}$, and that, to harmonic order, $f^N_{\text{uni}}(\underline{v})$ is guaranteed by $O_R$ invariance (which leads to vanishing of $C_5$) to be independent of such strains. Consequently, consistent with the expectations, in both $u_{ij}$ and $v_{ij}$ descriptions no antisymmetric part of the deformation tensor $\eta'_{Aij}$ appears.

### C. Isotropic-to-uniaxial transition

In a transition from the isotropic to the uniaxial state, the strain develops a nonvanishing anisotropic component. We can describe this transition equivalently in terms of $\underline{u}$ and $f(\underline{u})$ or in terms of $\underline{v}$ and $f(\underline{v})$. To be concrete, we will use $\underline{u}$-description here. Since the isotropic, volume-changing part of the strain is insensitive to anisotropy, the appropriate order parameter for the transition is the symmetric-traceless component of the strain, $\widetilde{\underline{u}}$ [Eq. (2.15)], which is identical in form to the symmetric-traceless order-parameter tensor $Q_{ij}$ of a nematic liquid-crystalline phase [1,2]. Thus, in mean-field theory, the transition from the isotropic to the uniaxial state is identical to the isotropic-to-nematic transition, whose properties have been exhaustively studied [1,2]. (In Appendix A, we review the formal properties of this transition that are relevant to the current discussion.) To see this in more detail, we can integrate out the "massive" $\text{Tr}\underline{u}$ from $f(\underline{u})$ in Eq. (2.16), to obtain an effective theory in terms of $\widetilde{u}$ alone. This operation yields

$$\text{Tr}\underline{\underline{u}} = \frac{E}{B}\text{Tr}\underline{\underline{\tilde{u}}}^2, \tag{3.30}$$

and the effective free energy reduces to $f - 1(\tilde{u})$ of Eq. (2.17). Because of the presence of a cubic invariant, the free energy $f - 1(\underline{\underline{\tilde{u}}})$ exhibits a first-order transition at $A = A_c = C^2/(12D)$ to a state with

$$\tilde{u}_{ij}^0 = \psi(n_i^0 n_j^0 - \tfrac{1}{3}\delta_{ij}), \tag{3.31}$$

where $\psi$ satisfies the equation of state

$$A - C\psi + \tfrac{8}{3}D\psi^2 = 0. \tag{3.32}$$

The total strain in the distorted state is thus

$$u_{ij}^0 = \tilde{u}_{ij}^0 + \frac{2}{9}\frac{E}{B}\psi^2\delta_{ij}. \tag{3.33}$$

This corresponds to a stretched state with target space positions $\mathbf{R}_0 = \underline{\underline{\Lambda}}_0\mathbf{x}$ characterized by a deformation tensor

$$\underline{\underline{\Lambda}}_0 = \sqrt{1 + 2\underline{\underline{u}}^0} = \begin{pmatrix} \Lambda_{0\perp} & 0 & 0 \\ 0 & \Lambda_{0\perp} & 0 \\ 0 & 0 & \Lambda_{0\|} \end{pmatrix}, \tag{3.34}$$

with

$$\Lambda_{0\perp} = \left(1 + \frac{4}{9}\frac{E}{B}\psi^2 - \frac{2}{3}\psi\right)^{1/2},$$

$$\Lambda_{0\|} = \left(1 + \frac{4}{9}\frac{E}{B}\psi^2 + \frac{4}{3}\psi\right)^{1/2}. \tag{3.35}$$

This form for $\underline{\underline{\Lambda}}_0$ preserves the volume up to order $\psi^2$. The order parameter $\psi$ is a direct measure of the spontaneous stretch anisotropy of the nematic state, with

$$\psi = \tfrac{1}{2}(\Lambda_{0\|}^2 - \Lambda_{0\perp}^2) = \tfrac{1}{2}\Lambda_{0\perp}^2(r - 1), \tag{3.36}$$

where $r$ is defined in Eq. (3.4.

The elastic free energy $f - 1(\underline{\underline{u}})$ can now be expanded in powers of $\delta\underline{\underline{u}} = \underline{\underline{u}} - \underline{\underline{u}}_0$ and reexpressed in terms of $\underline{\underline{u}}'$, defined in Eq. (3.9). Ward identities, imposed by the rotational $O_R$ invariance, guarantee that terms proportional to $(\delta u_{xz})^2$ and $(\delta u_{yz})^2$ vanish. The harmonic elastic energy is, therefore, given by $f_{\text{uni}}^N$ [Eq. (3.13)] with

$$C_1 = \left[B\left(1 - \frac{4E}{3B}\psi\right)^2 - \frac{4}{3}A + \frac{2}{3}C\psi\right]\Lambda_{0\|}^4,$$

$$C_2 = \left[B\left(1 - \frac{4E}{3B}\psi\right)\left(1 + \frac{2E}{3B}\psi\right) + \frac{2}{3}A - \frac{1}{3}C\psi\right]\Lambda_{0\|}^2\Lambda_{0\perp}^2,$$

$$C_3 = \left[B\left(1 + \frac{2E}{3B}\psi\right)^2 - \frac{1}{3}A - \frac{4}{3}C\psi\right]\Lambda_{0\perp}^4,$$

$$C_4 = \frac{3}{2}C\psi\Lambda_{0\perp}^4, \tag{3.37}$$

with $C_5 = 0$, as anticipated in our early discussion of the generic, symmetry-dictated form of the elastic free energy. From Eq. (3.32) we note that $\psi$ has the same sign as $C$, ensuring that $C_4 \sim C\psi$ is always positive.

### D. Biaxial nematic

It is clear from the form of $f_{\text{uni}}^N(\underline{\underline{u}}')$, Eq. (3.13), that if $C_4$ is driven negative [50] the uniaxial state becomes unstable to strains in the $xy$ plane perpendicular to the established uniaxial order, i.e., the uniaxial state becomes unstable relative to a biaxial state with different equilibrium strains in all three directions. A biaxial nematic gel is softer than a unaxial one [51], and, as we will show here, it has no nonvanishing shear modulus in three dimensions. The order parameter for the unaxial-to-biaxial transition is the two-dimensional symmetric-traceless tensor obtained by projecting $\underline{\underline{\tilde{u}}}$ onto the $xy$ plane. Since there are no cubic invariants of a two-dimensional symmetric traceless tensor, the transition from the uniaxial to the biaxial state is generically a continuous transition in the $xy$ universality class.

The biaxial phase is characterized by a Cauchy deformation tensor with three independent components,

$$\underline{\underline{\Lambda}}_0 = \begin{pmatrix} \Lambda_{01} & 0 & 0 \\ 0 & \Lambda_{02} & 0 \\ 0 & 0 & \Lambda_{03} \end{pmatrix}, \tag{3.38}$$

and the corresponding equilibrium strain tensor given by

$$\underline{\underline{u}}_0 = \begin{pmatrix} u_{01} & 0 & 0 \\ 0 & u_{02} & 0 \\ 0 & 0 & u_{03} \end{pmatrix}, \tag{3.39}$$

with $u_{0\alpha} = (\Lambda_{0\alpha}^2 - 1)/2$, $\alpha = 1,2,3$. The additional broken rotational symmetry of the biaxial relative to the uniaxial phase causes more shear elastic moduli to vanish. As in uniaxial gels, strains of the form of Eq. (3.10) [with $\underline{\underline{u}}_0$ given by Eq. (3.39)] that arise from arbitrary three-dimensional rotations $O_R$ in $S_R$ cost no energy. For simplicity, we consider only the most general *infinitesimal* rotation matrix, which can be expressed in terms of rotation angles $\theta_x$, $\theta_y$, and $\theta_z$, respectively about the $x$, $y$, and $z$ axes as

$$O_R = \begin{pmatrix} 1 & -\theta_z & \theta_y \\ \theta_z & 1 & -\theta_x \\ -\theta_y & \theta_x & 1 \end{pmatrix}. \tag{3.40}$$

The symmetric zero-mode strain tensor $\underline{\underline{u}}'$ calculated from this $O_R$ and Eq. (3.10) has components that to linear order in the infinitesimal angles of rotation are $u_{xx}' = u_{yy}' = u_{zz}' = 0$ and

$$u_{xy}' = \Lambda_{01}^{-1}\Lambda_{02}^{-1}(u_{01} - u_{02})\theta_z,$$

$$u'_{xz} = -\Lambda_{01}^{-1}\Lambda_{03}^{-1}(u_{01}-u_{03})\theta_y,$$

$$u'_{yz} = \Lambda_{02}^{-1}\Lambda_{03}^{-1}(u_{02}-u_{03})\theta_x. \qquad (3.41a)$$

Since the underlying $O_R$ invariance demands that there can be no energy cost associated with such zero-mode strains, the elastic energy cannot depend on the shear strains $u'_{xy}$, $u'_{xz}$, or $u'_{yz}$ to harmonic order. The hallmark property of solid that it can support a static shear stress is therefore lost in a spontaneously biaxial solid. The biaxial nematic is an anisotropic tethered fluid [52–54]. The harmonic elastic energy of a biaxial gel, therefore, depends only on the compression/extensional strains $u'_{xx}$, $u'_{yy}$ and $u'_{zz}$ and has the form

$$f_{\text{biax}} = \tfrac{1}{2}\sum B_{\alpha\beta}u'_{\alpha\alpha}u'_{\beta\beta}. \qquad (3.42)$$

There are in general six independent components of $B_{\alpha\beta}$. As in uniaxial gels, there is soft compressional and extensional elasticity in biaxial gels with vanishing stress up to critical values of the strain. We will not treat these properties in detail here.

## IV. NEMATIC GELS: STRAIN AND ORIENTATIONAL ORDER

In this section we extend our formulation of the model of anisotropic gels to include both the elastic and orientational (nematic) degrees of freedom. We first consider a "soft-spin" theory in which orientational order is described by symmetric-traceless nematic order parameter $Q_{ij}$, which has both uniaxial and biaxial components. This theory, which can describe both isotropic and anisotropic phases of gels and the transitions between them, takes explicit account of the coupling between strain and $Q_{ij}$. It can be viewed as a theory in which the familiar isotropic-nematic transition characterized by ordering of $Q_{ij}$ induces elastic distortion. Guided by the underlying rotational symmetry of the nematic gel, we then develop a complementary "hard-spin" model of nematic gels valid deep in the nematically ordered phase. This theory is formulated in terms of the strain and the nematic director **n** alone, with all "massive" modes (e.g., magnitude of the uniaxial order $S$ and biaxial fluctuations) integrated out. A common feature of these complementary models is their invariance with respect to global simultaneous rotations of strain and nematic order. This invariance leads to gaugelike couplings between strain and nematic order, whose harmonic limit reduces to those derived by Olmsted [14] following de Gennes [6]. However, our expression in terms of $v_{ij}$ and **n** for the *globally* invariant energy deep in the nematic phase is new.

### A. Simple model of the *I-N* transition

In the preceding section, we investigated a model in which an isotropic elastic medium undergoes a spontaneous anisotropic distortion triggered by the fall of its shear modulus below a critical value. In liquid-crystal elastomers, the reduction in the shear modulus and the elastic distortion that it leads to are actually driven by the underlying isotropic-

nematic transition of the mesogenic component of the gel, that is, orientational ordering of, e.g., side-chain or main-chain nematogens. It is, therefore, of some interest to develop a model in which the orientational order parameter $Q_{ij}$ explicitly appears.

A generic model free-energy density for such a model of a liquid-crystal gel will consist of an isotropic elastic term $f_{\text{el}}(\underline{u})$, a term $f'_Q(Q)$ for nematic orientational order, and a nematoelastic term $f_C(\underline{v},Q)$ that couples strain to the nematic order parameter $Q_{ij}$:

$$f_{\text{el}-Q} = f_{\text{el}} + f'_Q + f_C. \qquad (4.1)$$

For simplicity, we can take $f_{\text{el}}$ to be the elastic energy $f$ of Eq. (2.13) with only quadratic-order terms in $u_{ij}$ (or, equivalently, $v_{ij}$), and near the *I-N* transition, we can choose the usual Landau–de Gennes form for $f'_Q$:

$$f'_Q = \tfrac{1}{2}r'_Q\text{Tr}\underline{Q}^2 - w_3\text{Tr}\underline{Q}^3 + w'_4(\text{Tr}\underline{Q}^2)^2. \qquad (4.2)$$

Terms in gradients of $Q$ should also be included, but they do not affect the present mean-field discussion, and we will therefore ignore them here. The most general local energy coupling strain to $Q_{ij}$ can be constructed from products of terms invariant under arbitrary rotations in both $S_R$ and $S_T$, whose general form is $\text{Tr}[\underline{v}^{n_1}\underline{Q}^{m_1}\cdots\underline{v}^{n_p}\underline{Q}^{m_p}]$. Note that these terms involve couplings between $v_{ij}$ (rather than $u_{ij}$) and $Q_{ij}$, because $Q_{ij}$ exists in $S_T$, and like $v_{ij}$ transforms like a tensor under rotations in $S_T$ but like a scalar under $O_R$ rotations in $S_R$. To keep our discussion simple, we will for the moment consider a simple form for $f_C$:

$$f_C = -s\text{Tr}\underline{u}\,\text{Tr}\underline{Q}^2 - 2t\text{Tr}\underline{\tilde{v}}\,\underline{Q}, \qquad (4.3)$$

where $\tilde{v}_{ij} = v_{ij} - \tfrac{1}{3}\delta_{ij}v_{kk}$ is the symmetric-traceless part of $v_{ij}$ and where we used the fact that $\text{Tr}\underline{u} = \text{Tr}\underline{v}$. This energy captures the important qualitative features of strain-orientational coupling, namely, that the development of orientational order will drive an anisotropic distortion and a smaller change in volume.

An elastic energy $f_{\text{el}}^u$ that is a function of strain alone can be obtained by integrating $Q$ out of the total free energy of Eq. (4.1). The leading-order correction of this operation to $f_{\text{el}}$ is $-2(t^2/r'_Q)\text{Tr}\tilde{u}^2$. Thus $f_{\text{el}}^u$ has exactly the same form as Eq. (2.13), with $\mu$ replaced by $\mu' = \mu - (2t^2/r'_Q)$. Clearly, $\mu'$ decreases and passes through zero as $r'_Q$ decreases and the *I-N* transition is approached from the isotropic phase. Thus, the decrease in $\mu$ in the models of Sec. III arises from instabilities toward the development of nematic orientational order.

To treat the effects of strain-orientational coupling after the transition to the nematic state occurs, it is useful to recast $f$ in a slightly different form,

$$f_{\text{el}-Q} = \tfrac{1}{2}B[\text{Tr}\underline{u} - (s/B)\text{Tr}\underline{Q}^2]^2 + \mu\text{Tr}[\underline{\tilde{v}} - (t/\mu)\underline{Q}]^2 + f_Q, \qquad (4.4)$$

where

$$f_Q = \tfrac{1}{2} r_Q \mathrm{Tr} \underset{\approx}{Q}^2 - w_3 \mathrm{Tr} \underset{\approx}{Q}^3 + w_4 (\mathrm{Tr} \underset{\approx}{Q}^2)^2 \qquad (4.5)$$

with $r_Q = r_Q' - 2(t^2/\mu)$ and $w_4 = w_4' - (s^2/2B)$. This free energy leads to the equations of state

$$\frac{\partial f}{\partial \mathrm{Tr} \underset{\approx}{u}} = B[\mathrm{Tr} \underset{\approx}{u} - (s/B)\mathrm{Tr} \underset{\approx}{Q}^2] = 0,$$

$$\frac{\partial f}{\partial \tilde{v}_{ij}} = \mu[\tilde{v}_{ij} - (t/\mu)Q_{ij}] = 0, \qquad (4.6)$$

$$\frac{\partial f}{\partial Q_{ij}} = \frac{\partial f_Q}{\partial Q_{ij}} - s[\mathrm{Tr} \underset{\approx}{u} - (s/B)\mathrm{Tr} \underset{\approx}{Q}^2]Q_{ij} - 2t[\tilde{v}_{ij} - (t/\mu)Q_{ij}]$$

$$= 0. \qquad (4.7)$$

The uniaxial solutions to these equations are given by

$$\mathrm{Tr} \underset{\approx}{u}_0 = \frac{s}{B} \mathrm{Tr} \underset{\approx}{Q}_0^2, \qquad (4.8a)$$

$$\tilde{v}_{ij}^0 = \frac{t}{\mu} Q_{ij}^0, \qquad (4.8b)$$

$$Q_{ij}^0 = S(n_{0i}n_{0j} - \tfrac{1}{3}\delta_{ij}), \qquad (4.8c)$$

with $S$ satisfying

$$r_Q S - w_3 S^2 + \tfrac{8}{3} w_4 S^3 = 0. \qquad (4.9)$$

Using these uniaxial solutions Eq. (4.8) in the new stretched state, we find

$$\Lambda_{0\perp}^2 = 1 + \frac{4}{9}\frac{s}{B}S^2 - \frac{2}{3}\frac{t}{\mu}S,$$

$$\Lambda_{0\parallel}^2 = 1 + \frac{4}{9}\frac{s}{B}S^2 + \frac{4}{3}\frac{t}{\mu}S. \qquad (4.10)$$

Note that $\Lambda_{0\parallel}^2 - \Lambda_{0\perp}^2 = 2(t/\mu)S$ is linear in the nematic order parameter $S$.

As discussed in Appendix A, fluctuations away from the equilibrium state are conveniently treated with the introduction of a complete set of five orthonormal symmetric-traceless matrices $I_{ij}^\alpha$ satisfying $I_{ij}^\alpha I_{ji}^\beta = \delta^{\alpha\beta}$ that allow us to expand $Q_{ij}$ and $\tilde{v}_{ij}$ as $Q_{ij} = \Sigma_{\alpha=0}^4 Q_\alpha I_{ij}^\alpha$ and $\tilde{v}_{ij} = \Sigma_{\alpha=0}^4 v_\alpha I_{ij}^\alpha$. Expressions for $Q_\alpha$ and $v_\alpha$ in terms of $Q_{ij}$ and $v_{ij}$, respectively, are given in Eqs. (A2). In particular, $Q_0 = \sqrt{2/3}S$ measures the magnitude of uniaxial order, $Q_1$ and $Q_2$ measure the two independent components of biaxial order, and $Q_3$ and $Q_4$ describe rotations of the direction of uniaxial order. In terms of these variables, we have, to harmonic order in $\delta v_{ij}$ and $\delta Q_{ij}$,

$$\delta f_{el-Q} = \tfrac{1}{2} B[\mathrm{Tr}\delta \underset{\approx}{u} - (4s/3B)S\,\delta S]^2$$

$$+ \mu[\delta v_0 - (t/\mu)\sqrt{2/3}\,\delta S]^2$$

$$+ \mu \sum_{\alpha=1}^4 [v_\alpha - (t/\mu)Q_\alpha]^2$$

$$+ \tfrac{1}{2} A_1 (\delta S)^2 + \tfrac{1}{2} A_2 [Q_1^2 + Q_2^2], \qquad (4.11)$$

where $A_1$ and $A_2$ are given in Eqs. (A6). Rotational invariance of $f_Q$ guarantees that terms $Q_3^2 \sim Q_{xz}^2$ and $Q_4^2 \sim Q_{yz}^2$ do not appear in the nematic state. We can integrate out the "massive" longitudinal mode $\delta S$ and biaxial modes $Q_1$ and $Q_2$ to obtain

$$\delta f_v = \tfrac{1}{2} \bar{B}_1 (\delta v_{zz})^2 + \bar{B}_2 \delta v_{zz} (\delta v_{xx} + \delta v_{yy})$$

$$+ \tfrac{1}{2} \bar{B}_3 (\delta v_{xx} + \delta v_{yy})^2$$

$$+ \bar{B}_4 (\delta v_{xx}^2 + \delta v_{yy}^2 + 2\,\delta v_{xy}^2)$$

$$+ 2\mu([\delta v_{xz} - (t/\mu)Q_{xz}]^2$$

$$+ [\delta v_{yz} - (t/\mu)Q_{yz}]^2), \qquad (4.12)$$

where the coefficients $\bar{B}_a$ are evaluated in Appendix C. This free energy is manifestly invariant under arbitrary rotations in $S_R$ because it is a function of the strain $v_{ij}$ only. However, its invariance in the $S_T$ is restricted to infinitesimal rotations in $O_T$ because we only used the harmonic free energy to integrate over "massive" modes. Because underlying $O_T$ invariance of the nematic state forbids "massive" terms in $Q_{xz}$ and $Q_{yz}$, integration over them also eliminates strains $v_{xz}$ and $v_{yz}$ from the resulting elastic free energy, which, as anticipated takes the form identical to that in Eq. (3.13). Such symmetry-enforced vanishing of an elastic constant (here $C_5$) is mathematically closely related to the well-known Anderson-Higgs mechanism in gauge theories [16].

The terms involving $Q_{xz}$ and $Q_{yz}$ are interesting because they determine the energy cost of rotating the director away from the direction of uniaxial stretch. When we convert to the strain variables of the stretched state using Eq. (3.29) and the expressions, Eq. (4.10), for $\Lambda_{0\perp}$ and $\Lambda_{0\parallel}$ in terms of $S$, we obtain to lowest order in $\delta \mathbf{n} = \mathbf{n} - \mathbf{n}_0$,

$$f_{el}^{v,n} = \tfrac{1}{2} C_1 \eta_{Szz}'^2 + C_2 \eta_{Szz}' (\eta_{Sxx}' + \eta_{Syy}')$$

$$+ \tfrac{1}{2} C_3 (\eta_{Sxx}' + \eta_{Syy}')^2 + C_4 (\eta_{Sxx}'^2 + \eta_{Syy}'^2 + 2\eta_{Sxy}'^2)$$

$$+ \tfrac{1}{2} \mu' \sum_{a=x,y} [\eta_{Saz}' - \beta(\delta n_a - \eta_{Aza}')]^2, \qquad (4.13)$$

where

$$\beta = \frac{(r-1)}{(r+1)} \qquad (4.14)$$

and elastic constants $C_a$ are related to the constants $\bar{B}_a$ via $C_1 = \Lambda_{0\parallel}^4 \bar{B}_1$, $C_2 = \Lambda_{0\parallel}^2 \Lambda_{0\perp}^2 \bar{B}_2$, $C_3 = \Lambda_{0\perp}^4 \bar{B}_3$, $C_4 = \Lambda_{0\perp}^4 \bar{B}_4$, and $\mu' = (r+1)^2 \Lambda_{0\perp}^4 \mu$. The form of this energy is in fact the

most general one, and we will derive it again in the following section after we have derived its nonlinear generalization. It is exactly the form obtained by Olmsted [14] following de Gennes [6] and Warner, Bladon, and Terentjev [23]. It shows clearly how the director can relax locally to $\delta n_a = \eta'_{Aza} + \beta^{-1} \eta_{Saz}$ to eliminate any dependence of the free energy on $\eta'_{Saz}$, i.e., to make $C_5 = 0$. It is worth noting that in the original treatment of de Gennes [6], the coefficients of $(\eta'_{Sza})^2$ ($\mu'$ or $4C_{44}$ in the notation of de Gennes), $\eta'_{Sza}(\delta n_a - \eta'_{Sza})$ ($\beta \mu'$ or $D_2$), and $(\delta n_z - \eta'_{Sza})^2$ ($\beta^2 \mu'$ or $D_1$) were treated as independent coefficients, as indeed they are in a general system cross-linked in the nematic phases. Olmsted [14] derived the relations $D_2/\mu' = 2\beta$ and $D_1/\mu' = \beta^2$ for the rotationally invariant neoclassical model of rubber elasticity. These relations, which are required by rotational invariance, emerge naturally from our treatment.

## B. Theory with strain and director

We have just seen how the development of nematic order characterized by $Q_{ij}$ leads to a stretched nematic elastomer with a soft elasticity. The formulation in terms of $Q_{ij}$ is well suited to a description of the transition from the isotropic to the nematic state. Deep in the nematic phase, the theory that best captures the effects of long-wavelength strains and variations in the direction of nematic order is one expressed in terms of strain and the nematic director **n** only, i.e., one in which fluctuations in $S$ and in the biaxial part of $Q_{ij}$ are integrated out. This theory, like others we have discussed must be invariant under both rotations in $S_R$ and under simultaneous rotations of $v_{ij}$ and **n** in $S_T$.

To construct a fully rotationally invariant theory deep in the nematic phase, it is convenient to introduce a local coordinate system defined by the orthonormal triad $\{\mathbf{e}^1, \mathbf{e}^2, \mathbf{e}^3 \equiv \mathbf{n}\}$ consisting of the local director **n** and two vectors $\mathbf{e}^1$ and $\mathbf{e}^2$ perpendicular to **n**. These vectors satisfy

$$\mathbf{e}^\mu \cdot \mathbf{e}^\nu = \delta^{\mu\nu}, \tag{4.15a}$$

$$\sum_{a=1,2} e_i^a e_j^a = \delta_{ij}^\perp \equiv \delta_{ij} - n_i n_j. \tag{4.15b}$$

In what follows, we will adopt a notation in which Greek indices $\mu$ and $\nu$ will run over 1 to 3, and Roman indices $a$ and $b$ will run from 1 to 2, i.e., over the subspace transverse to **n**. The left strain tensor $\underline{\underline{v}}$ can always be expressed in terms of its components in this basis:

$$v_{ij} = v^{\mu\nu} e_i^\mu e_j^\nu, \tag{4.16a}$$

$$= v_{||} n_i n_j + v_\perp^{ab} e_i^a e_j^b + v_{||\perp}^a (n_i e_j^a + e_i^a n_j), \tag{4.16b}$$

where

$$v^{\mu\nu} = e_i^\mu v_{ij} e_j^\nu, \tag{4.17}$$

and

$$v_{||} = n_i v_{ij} n_j, \tag{4.18a}$$

$$v_{||\perp}^a = n_i v_{ij} e_j^a, \tag{4.18b}$$

$$v_\perp^{ab} = e_i^a v_{ij} e_j^b. \tag{4.18c}$$

The components $v^{\mu\nu}$ are invariant under rotations in $S_R$ because $v_{ij}$ is invariant under $O_R$ by construction. They are also invariant under simultaneous rotations of both **R** and the triad $\{\mathbf{e}^\mu\}$ in $S_T$, i.e., they maintain their same numerical value, under simultaneous rotations of $v_{ij}$ and the basis $\{\mathbf{e}^1, \mathbf{e}^2, \mathbf{n}\}$.

A gel whose anisotropic state forms via spontaneous symmetry breaking from the isotropic phase has no preferred or imposed directions, and the elastic free energy will depend only on $v_{||}$, $v_\perp^{ab}$, and $v_{||\perp}^a$. Furthermore, this free energy cannot depend on the arbitrary choice of the vectors $\mathbf{e}^1$ and $\mathbf{e}^2$ in the plane perpendicular to **n**, and it will be a function only of $v^{\mu\nu}$ in the combinations $v_{||}$, $v_\perp^{aa}$, $v_{||\perp}^a v_{||\perp}^a$, and $v_\perp^{ab} v_\perp^{ab}$. Since linear terms proportional to $v_{||}$ and $v_\perp^{aa}$ are present in the anisotropic phase, it will be characterized by a nonvanishing equilibrium strain $v_0^{\mu\nu}$ with components $v_{0||}$ and $v_{0\perp}^{ab}$. If the equilibrium director is $\mathbf{n}_0$, then such a uniaxially distorted state is characterized by the equilibrium strain

$$v_{0ij} = v_{0||} n_{0i} n_{0j} + v_{0\perp}(\delta_{ij} - n_{0i} n_{0j}),$$

$$\equiv \tfrac{1}{2}[G_{ij}(\mathbf{n}_0) - \delta_{ij}], \tag{4.19}$$

where $v_{0||} = (\Lambda_{0||}^2 - 1)/2$, $v_{0\perp} = (\Lambda_{0\perp}^2 - 1)/2$ and

$$G_{ij}(\mathbf{n}) = \Lambda_{0||}^2 n_i n_j + \Lambda_{0\perp}^2(\delta_{ij} - n_i n_j). \tag{4.20}$$

Away from equilibrium, the free energy can be expanded in the deviations

$$\delta v^{\mu\nu} = v^{\mu\nu} - v_0^{\mu\nu} \tag{4.21}$$

of the strain from its equilibrium value. To harmonic order in these deviations, we have

$$\delta f_w = \tfrac{1}{2} C_1 w_{||}^2 + C_2 w_{||} w_\perp^{aa} + \tfrac{1}{2} C_3 (w_\perp^{aa})^2 + C_4 w_\perp^{ab} w_\perp^{ab} + C_5 w_{||\perp}^a w_{||\perp}^a, \tag{4.22}$$

where the rescaled invariant strains are

$$w_{||} = \Lambda_{0||}^{-2}(v_{||} - v_{0||}),$$

$$w_\perp^{ab} = \Lambda_{0\perp}^{-2}(v_\perp^{ab} - v_{0\perp}^{ab}),$$

$$w_{||\perp}^a = \bar{\Lambda}_0^{-2}(v_{||\perp}^a - v_{0||\perp}^a), \tag{4.23}$$

with $\bar{\Lambda}_0^2 = (\Lambda_{0||}^2 + \Lambda_{0\perp}^2)/2$. Obviously, we could define the $w$ strains above without the prefactors. Our choice was made to produce the simplest linearized energy, e.g., $C_3(w_\perp^{aa})^2 \to C_3(\eta'_{xx} + \eta'_{yy})^2$. Without the $\Lambda_{0\perp}^2$ factor in the definition of $w_\perp^{ab}$, the linearized theory would contain the term $C_3 \Lambda_{0\perp}^{-4}(\eta'_{xx} + \eta'_{yy})^2$ instead. Even though this free energy is only an expansion about a uniaxially distorted equilibrium state, unlike the free energies [Eq. (3.13)] expressed in terms

of strain alone that we considered in Sec. III, it is completely invariant with respect to arbitrary rotations in *both $S_R$ and $S_T$*.

The equilibrium values $v_{0||}$ and $v_{0\perp}^{ab}$ do not depend on the particular direction of **n**. If $\{\mathbf{e}^\mu\} = \{\mathbf{e}_0^\mu\}$, then $v_0^{\mu\nu} = e_{0i}^\mu v_{0ij} e_{0j}^\nu$. Away from equilibrium defined by $\mathbf{n}_0$, $v_{ij} = v_{0ij} + \delta v_{ij}$ where $v_{0ij}$ is given by Eq. (4.19) and $\delta v_{ij}$ by Eq. (3.26). Thus

$$\delta v^{\mu\nu} = (e_i^\mu e_j^\nu - e_{0i}^\mu e_{0j}^\nu) v_{0ij} + e_i^\mu \delta v_{ij} e_j^\nu, \quad (4.24)$$

and we have

$$w_{||} = \Lambda_{0||}^{-2} n_i \delta v_{ij} n_j - \tfrac{1}{2}[1 - (1/r)][1 - (\mathbf{n} \cdot \mathbf{n}_0)^2]$$

$$\approx n_{0i} \eta_{ij}' n_{0j}$$

$$= \eta_{zz}', \quad (4.25a)$$

$$w_\perp^{aa} = \Lambda_{0\perp}^{-2} \delta_{ij}^\perp \delta v_{ij} + \tfrac{1}{2}(r-1)[1 - (\mathbf{n} \cdot \mathbf{n}_0)^2]$$

$$\approx \delta_{ij}^{0\perp} \eta_{ij}'$$

$$= \eta_{xx}' + \eta_{yy}', \quad (4.25b)$$

$$w_{||\perp}^a w_{||\perp}^a = \bar{\Lambda}_0^{-4} n_i n_k \delta_{jl}^{0\perp} \delta v_{ij} \delta v_{kl}$$

$$+ 2\beta \bar{\Lambda}_0^{-2} (\mathbf{n} \cdot \mathbf{n}_0) n_i \delta v_{ij} \delta_{jk}^\perp n_{0k}$$

$$+ \beta^2 (\mathbf{n} \cdot \mathbf{n}_0)^2 [1 - (\mathbf{n} \cdot \mathbf{n}_0)^2]$$

$$\approx \sum_l [\eta_{Szl}' - \beta(\delta n_l - \eta_{Alz}')]^2, \quad (4.25c)$$

$$w_\perp^{ab} w_\perp^{ab} = \Lambda_{0\perp}^{-4} \delta_{ik}^\perp \delta_{jl}^\perp \delta v_{ij}' \delta v_{kl}' + (r-1) n_{0i} n_{0j} \delta_{ik}^\perp \delta_{lj}^\perp \delta v_{kl}$$

$$+ \tfrac{1}{4}(r-1)^2 [1 - (\mathbf{n} \cdot \mathbf{n}_0)^2]$$

$$\approx \delta_{ik}^{0\perp} \delta_{jl}^{0\perp} \eta_{Sij}' \eta_{Skl}'$$

$$= \eta_{xx}'^2 + \eta_{yy}'^2 + 2\eta_{Sxy}'^2, \quad (4.25d)$$

where $\beta$ is defined in Eq. (4.14). The energy $\delta f_w$ is characterized by the five elastic constants $C_a$ and the stretching ratio $r$, which has the same value in every one of the nonlinear strains.

Alternative but equivalent expressions for the strains in Eq. (4.23) are useful and elegant. The components of the equilibrium strains $v_0^{\mu\nu}$ have the same value if the basis $\{\mathbf{e}_0^\mu\}$ is transformed to the basis $\{\mathbf{e}^\mu\}$ provided the director $\mathbf{n}_0$ in $G_{ij}(\mathbf{n}_0)$ [Eq. (4.20)] is transformed to **n**. Thus we have

$$v_0^{\mu\nu} = \tfrac{1}{2}[e_{0i}^\mu G_{ij}(\mathbf{n}_0) e_{0j}^\nu - \delta^{\mu\nu}] = \tfrac{1}{2}[e_i^\mu G_{ij}(\mathbf{n}) e_j^\nu - \delta^{\mu\nu}], \quad (4.26)$$

and from Eqs. (2.7), (3.8), and (4.17)

$$v^{\mu\nu} = \tfrac{1}{2}[e_i^\mu \Lambda_{ij}' G_{jk}(\mathbf{n}_0) \Lambda_{kl}'^T e_l^\nu - \delta^{\mu\nu}]. \quad (4.27)$$

From this we obtain

$$\delta v^{\mu\nu} = e_i^\mu V_{ij} e_j^\nu, \quad (4.28)$$

where

$$\underline{V} = \tfrac{1}{2}[\underline{\Lambda}' \underline{G}(\mathbf{n}_0) \underline{\Lambda}'^T - \underline{G}(\mathbf{n})], \quad (4.29)$$

and finally

$$v_{||} = \Lambda_{0||}^{-2} n_i V_{ij} n_j,$$

$$w_\perp^{aa} = \Lambda_{0\perp}^{-2} \delta_{ij}^\perp V_{ij},$$

$$w_{||\perp}^a w_{||\perp}^a = \bar{\Lambda}_0^{-4} n_i n_k \delta_{jl}^\perp V_{ij} V_{kl},$$

$$w_\perp^{ab} w_\perp^{ab} = \Lambda_{0\perp}^{-4} \delta_{ik}^\perp \delta_{jl}^\perp V_{ij} V_{kl}. \quad (4.30)$$

### C. Cross-linking in the nematic phase

If an elastomer is cross linked in the nematic rather than the isotropic phase, the memory of the anisotropy of the state, with a uniaxial direction $\mathbf{n}_0$, at the time of cross-linking is locked in, and full $O_R$ invariance of $S_R$ is reduced down to $D_{\infty h}$ symmetry. If coupling to nematic order is turned off, the system will be characterized by a uniaxial elastic energy of the form of Eq. (2.19) with five elastic constants in general. (Turning off this coupling is not as unphysical as it may seem. This is precisely what is done in treatments of plastic crystals consisting of anisotropic molecules such as $N_2$.) This part of the elastic energy is a function of $u_{ij}$ and is invariant under rotations in $S_T$. It is also invariant under simultaneous rotations of $\mathbf{n}_0$ and **x** in $S_R$ and under operations on **x** in $D_{\infty h}$ at fixed $\mathbf{n}_0$. Couplings to the nematic order parameter $\underline{Q}$ must be invariant under simultaneous rotations of **R** and $\underline{Q}$ in $S_T$ and under simultaneous rotations of **x** and $\mathbf{n}_0$ in $S_R$. The simplest couplings linear in $\underline{Q}$ are of the form

$$f_C^N = -\text{Tr}\underline{\Lambda} \underline{h} \underline{\Lambda}^T \underline{Q} - 2\beta \text{Tr}\underline{v}\underline{Q}, \quad (4.31)$$

where $h_{ij} = h n_{0i} n_{0j}$ and, as before, $\underline{\Lambda}\underline{\Lambda}^T = \underline{\delta} + 2\underline{v}$. The first term in this energy reduces to $-h n_{0i} Q_{ij} n_{0j}$ and favors alignment of principal axes of $\underline{Q}$ along $\mathbf{n}_0$ in the absence of deformation, when the deformation tensor $\underline{\Lambda}$ is the unit tensor.

The generalization of Eq. (4.22) to systems cross-linked in the nematic phase is fairly complicated. It cannot be expressed in terms of the strain $\delta v_{ij}$ alone; it can only be expressed in terms of the more fundamental nonsymmetrized strains $\eta_{ij}$. However, the major effect of cross-linking in the nematic phase is to to make $\mathbf{n}_0$ a preferred direction with an energy cost to rotate away from that direction, which can be described by the addition of a term $-h(\mathbf{n}_0 \cdot \mathbf{n})^2$ to Eq. (4.22) to lowest order in $\eta_{ij}$ [55].

## V. NEOCLASSICAL THEORY OF ELASTOMERS

So far we have described liquid-crystal gels in terms of nonlinear strains, rotationally invariant in either $S_R$ or in $S_T$, relative to some equilibrium reference state, and we have focused on those properties that result from the spontaneous broken rotational symmetry of the nematic state. We have treated the elastic constants in our model free energy as phenomenological parameters to be determined experimentally. To date, experimental realization of liquid-crystalline elastomers are cross-linked liquid-crystalline polymers. They are

rubbers with orientational degrees of freedom of a liquid crystal, and their elastic properties over a very wide range of strains can be described quantitatively by a generalization of the classic theory of rubber elasticity [21]. This is a semimicroscopic theory in which the origin of shear moduli is the reduction of entropy arising from constraining polymers to pass through cross-linking points. In this section, we will show that this theory, when expressed in terms of nonlinear strains, is equivalent to those discussed in preceding sections of this article.

In the simplest version of the neoclassical theory, polymer segments between cross links are viewed as independent random-coil polymers of length $L$. In the anisotropic environment induced by the nematic order, the effective step lengths parallel and perpendicular to the direction of nematic order are different, and mean-square end-to-end displacement is characterized by an anisotropic step-length tensor,

$$\underline{l} = l \underline{\underline{g}}, \tag{5.1}$$

where $l$ is a length and $\underline{\underline{g}}$ is a unitless tensor, reflecting system anisotropy, whose form will be discussed in different contexts below. The probability that the two ends of a single chain are separated by $\mathbf{R}$ is

$$P(\mathbf{R}) = \left[ \frac{\det \underline{l}^{-1}}{(2\pi L/3)^3} \right] \exp\left( -\frac{3}{2L} R_i l_{ij}^{-1} R_j \right). \tag{5.2}$$

The free energy per chain is $f_{\text{chain}} = -T \ln P(\mathbf{R})$. Now assume that the separation $\mathbf{R}$ was produced by an affine transformation from some initial state with separation $\mathbf{R}_0$ such that $R_i = \Lambda_{rij} R_{0j}$, where $\underline{\underline{\Lambda}}_r$ is the deformation tensor relative to the initial state. (Later we will introduce a new reference state and use the symbol $\underline{\underline{\Lambda}}$ to denote deformations relative to that state.) The free energy per chain of the entire elastomer is then $f_{\text{chain}}(\mathbf{R}_0)$ averaged over all separations $\mathbf{R}_0$ of the initial state, which we assume consists of random-walk chain segments characterized by a step-length tensor $\underline{l}_0 = l_0 \underline{\underline{g}}_0$ and a probability distribution given by Eq. (5.2) with $\underline{l}$ replaced by $\underline{l}_0$. The initial state may be viewed as the state at the time of cross-linking. Thus, if the system is cross-linked in the isotropic state, $\underline{l}_0$ will be an isotropic tensor; if it is cross-linked in the nematic state at some temperature $T$, the degree of anisotropy of $\underline{l}_0$ will reflect the degree of nematic order at that temperature. The free energy density relative to the initial state is thus

$$f_{\text{ch}} = \tfrac{1}{2} n T (\text{Tr} \underline{\underline{\Lambda}}_r \underline{l}_0 \underline{\underline{\Lambda}}_r^T \underline{l}^{-1} - \ln \det \underline{l}_0 \underline{l}^{-1}), \tag{5.3}$$

where $n$ is the volume density of chain segments. This purely entropic free energy, whose ground state is the collapsed state with $\underline{\underline{\Lambda}}_r = 0$, cannot alone provide a complete description of the elastic properties of an elastomer. It must be supplemented with some treatment of the short-range enthalpic forces that prevent collapse to infinite density. Merely imposing the incompressibility constraint, $\det \underline{\underline{\Lambda}}_r = 1$, is sufficient to provide a very good description of dense, nearly incompressible systems. We will take a phenomenological

approach in which there is an energy cost, measured by a compression modulus $B_r$, arising from deviations of $\det \underline{\underline{\Lambda}}_r$ from 1:

$$f_B = \tfrac{1}{2} B_r (\det \underline{\underline{\Lambda}}_r - 1)^2. \tag{5.4}$$

Our complete neoclassical energy density is thus $f = f_{\text{ch}} + f_B$.

An important feature of this model is that it depends on $\underline{\underline{\Lambda}}_r$ only via the combination $\underline{\underline{\Lambda}}_r \underline{\underline{g}}_0 \underline{\underline{\Lambda}}_r^T$ because the determinant of a product of tensors is the product of the determinants. Thus, it is convenient to analyze this model in terms of $\underline{\underline{\Lambda}} = \underline{\underline{\Lambda}}_r \underline{\underline{g}}_0^{1/2}$, the strain tensor relative to the isotropic state obtained by rescaling lengths via $\underline{\underline{g}}_0^{1/2}$ [56]. Our model is thus

$$f = \tfrac{1}{2} n T (l_0/l) \text{Tr} \underline{\underline{\Lambda}} \underline{\underline{\Lambda}}^T \underline{\underline{g}}^{-1} + \tfrac{1}{2} n T \ln \underline{\underline{g}}_0 \underline{\underline{g}}^{-1}$$
$$+ \tfrac{1}{2} B_r [ (\det \underline{\underline{\Lambda}} \underline{\underline{\Lambda}}^T / \det \underline{\underline{g}}_0)^{1/2} - 1 ]^2, \tag{5.5}$$

where $n$ is the volume density of chain segments.

We will now analyze two versions of this model: one appropriate to the description of the $I$-$N$ transition and one appropriate to systems deep in the nematic phase. We begin with the $I$-$N$ transition. In this case, we take

$$\underline{\underline{g}}^{-1} = \underline{\underline{\delta}} - \alpha \underline{\underline{Q}},$$
$$\underline{\underline{g}}_0 = (\underline{\underline{\delta}} - \alpha \underline{\underline{Q}}_0)^{-1}, \tag{5.6}$$

where $\underline{\underline{Q}}_0$ is the value of $\underline{\underline{Q}}$ at the time of cross-linking. We could have taken $\underline{\underline{g}}$ rather than $\underline{\underline{g}}^{-1}$ proportional to $\underline{\underline{Q}}$. Since we are interested in small $\underline{\underline{Q}}$, there is little difference between the two choices. Our goal is to recast $f$ in terms of the left strain tensor $\underline{\underline{v}}$ to obtain a free energy of the form of Eq. (4.1). We begin by finding the equilibrium strain tensor $\underline{\underline{\Lambda}}_0$ when $\underline{\underline{Q}} = 0$. Since there is no anisotropy when $\underline{\underline{Q}} = 0$, we have $\underline{\underline{\Lambda}}_0 = \Lambda_0 \delta_{ij}$. A straightforward minimization of $f$ with respect to $\Lambda_0$ when $\underline{\underline{Q}} = 0$ yields the equation of state

$$n T \Lambda_0^2 + B_r (\gamma_0 - 1) \gamma_0 = 0, \tag{5.7}$$

where $\gamma_0 = (\det \underline{\underline{\Lambda}}_0 \underline{\underline{\Lambda}}_0^T / \det \underline{\underline{g}}_0)^{1/2}$. In the incompressible limit $B_r \to \infty$, this yields $\Lambda_0 = (\det \underline{\underline{g}}_0)^{1/2}$. Setting $\underline{\underline{\Lambda}} \underline{\underline{\Lambda}}^T = \Lambda_0^2 (\underline{\underline{\delta}} + 2\underline{\underline{v}})$ and expanding $f$ in powers of $\underline{\underline{v}}$ using

$$\det^{1/2} [\underline{\underline{\delta}} + 2\underline{\underline{v}}] = \exp[\tfrac{1}{2} \text{Tr} \ln(\underline{\underline{1}} + 2\underline{\underline{v}})]$$
$$= 1 + \text{Tr} \underline{\underline{v}} - [\text{Tr} \underline{\underline{v}}^2 - \tfrac{1}{2} (\text{Tr} \underline{\underline{v}})^2] + \cdots, \tag{5.8}$$

we obtain

$$\delta f = \mu \text{Tr} \underline{\underline{v}}^2 + \tfrac{1}{2} B (\text{Tr} \underline{\underline{v}})^2 - \alpha \mu \text{Tr} \underline{\underline{v}} \underline{\underline{Q}} - \tfrac{1}{2} n T \text{Tr} \ln(\underline{\underline{\delta}} - \alpha \underline{\underline{Q}}) \tag{5.9}$$

to harmonic order in $\underline{\underline{v}}$, where $\mu = n T (l_0/l) \Lambda_0^2$ and $B = B_r \gamma_0^2 - \mu$. This energy is identical to $f_{\text{el}} + f_C$ of Eq. (4.1) plus a part depending on $\underline{\underline{Q}}$ alone, which can be absorbed into $f_Q'$ [Eq. (4.2)]. The strain can be integrated out to yield

$$\delta f = -\tfrac{1}{4}\alpha^2 nT[(l_0/l)\Lambda_0^2 - 1)]\text{Tr}\,\underline{\underline{Q}}^2 + O(Q^4)$$

$$\approx -\frac{1}{4}\alpha^2 nT\left[\left(\frac{l_0}{l}-1\right)-\frac{l_0}{l}\frac{nT}{B}\right.$$

$$\left.+\frac{1}{6}\alpha^2\frac{l_0}{l}\left(1-\frac{nT}{B}\right)\text{Tr}\underline{\underline{Q}}_0^2\right]\text{Tr}\underline{\underline{Q}}^2. \qquad (5.10)$$

The final form of this equation was obtained by solving the equation of state [Eq. (5.7)] for $\Lambda_0$ to lowest order in $nT/B$ and $\alpha^2$. In the incompressible limit ($B=\infty$) when $l_0/l=1$, there is no shift in the coefficient of $\text{Tr}Q^2$ and, thus, no shift in the limit of metastability of the isotropic phase when the system is cross-linked in the isotropic phase, but there is a small shift proportional to $\text{Tr}Q_0^2$ when it is cross-linked in the nematic phase [58]. If the system is compressible, $B\neq\infty$, or if the fundamental step lengths $l_0$ and $l$ are different, then there is a shift in the coefficient of $\text{Tr}Q^2$ even when the system is cross-linked in the isotropic phase.

Deep in the nematic phase, biaxial fluctuations are suppressed. If we assume they are completely frozen out, then the step-length tensor depends only on the director, and we can take

$$l_{ij}^{-1}=l_\perp^{-1}[\delta_{ij}+(r^{-1}-1)n_i n_j] \qquad (5.11)$$

and $l_{0ij}=l_{0\perp}[\delta_{ij}+(r-1)n_{0i}n_{0j}]$, where $r=l_\parallel/l_\perp$. Since $\underline{l}_0$ has been scaled away by the transformation from $\underline{\underline{\Lambda}}_r$ to $\underline{\underline{\Lambda}}$, the equilibrium strain $\underline{\underline{\Lambda}}_0$ for a given **n** will have components parallel and perpendicular to **n** and will have the form of Eq. (3.2b) with $n_{0i}$ replaced by $n_i$. As **n** rotates so does $\underline{\underline{\Lambda}}_0$, but the magnitudes $\Lambda_{0\parallel}$ and $\Lambda_{0\perp}$ do not change. Setting $\delta\underline{v}=0$ and minimizing over $\underline{\underline{\Lambda}}_0$, we find the equations of state

$$nT\frac{l_{0\perp}}{l_\perp}\frac{1}{r}\Lambda_{0\parallel}^2+B_r(\gamma_0-1)\gamma_0=0,$$

$$nT\frac{l_{0\perp}}{l_\perp}\Lambda_{0\perp}^2+B_r(\gamma_0-1)\gamma_0=0. \qquad (5.12)$$

These equations imply $\Lambda_{0\parallel}^2/\Lambda_{0\perp}^2=r=l_\parallel/l_\perp$ for all $B_r$. Using $\det(\underline{\underline{\delta}}+2\underline{v}_0+2\,\delta\underline{v})=\det\underline{\underline{\Lambda}}_0\underline{\underline{\Lambda}}_0^T\det(\underline{\underline{\delta}}+\underline{\underline{\Lambda}}_0^{-1}\delta\underline{v}\,\underline{\underline{\Lambda}}_0^{-1})$ and expanding in $\delta\underline{v}$, we obtain

$$\delta f_w'=\mu(w_\parallel^2+w_\perp^{ab}w_\perp^{ab})+\tfrac{1}{2}B(w_\parallel+w_\perp^{aa})^2+2\mu' w_{\parallel\perp}^a w_{\parallel\perp}^a, \qquad (5.13)$$

where $\mu=nT(l_{0\perp}/l_{0\parallel})\Lambda_{0\perp}^2$, $B=B_r\gamma_0^2-\mu$, and $\mu'=\tfrac{1}{4}\mu(2+r+r^{-1})$. This is identical to Eq. (3.13) with $C_1=B+2\mu$, $C_2=B$, $C_3=B$, $C_4=\mu$ and $C_5=2\mu'$.

The free energy $\delta f_w'$ of Eq. (5.13) has a higher symmetry than the most general free energy $\delta f_w$ of Eq. (4.22): it has only three rather than the five independent elastic constants. As a result, certain distortions will have the same energy in the model that do not have the same energy in the most general model. For example, purely dilational and compressional strains with $\Lambda_{xx}$ and $\Lambda_{zz}$ interchanged will have the same energy in $\delta f_w'$ but not in $\delta f_w$. The simplified form of Eq. (5.13) resulted from our use of Eq. (5.11) for $l_{ij}^{-1}$. In

general, $l_{ij}^{-1}$ depends on the full tensor order parameter $Q_{ij}=S(n_i n_j-\tfrac{1}{3}\delta_{ij})+B_{ij}$ where $B_{ij}$ is the biaxial part of $Q_{ij}$ with components in the plane perpendicular to **n**. Deep in the nematic phase, fluctuations $\delta S$ in the magnitude of $S$ and in $B_{ij}$ are small. The most general form of $l_{ij}^{-1}$ to lowest order in $\delta S$ and $B_{ij}$ is

$$l_{ij}^{-1}=l_\perp^{-1}[\delta_{ij}+(r^{-1}-1)n_i n_j$$

$$+a\,\delta S(n_i n_j-\tfrac{1}{3}\delta_{ij})+bB_{ij}], \qquad (5.14)$$

where $a$ and $b$ are numbers. The nematic energy has contributions $\tfrac{1}{2}A_1(\delta S)^2+\tfrac{1}{2}A_2\text{Tr}\underline{\underline{B}}^2$, where $A_1$ and $A_2$ are given, respectively, within Landau–de Gennes mean-field theory by Eq. (A6), in addition to the Frank free energy. Integrating out $\delta S$ and $B_{ij}$ from the total free energy will yield an elastic energy in $w_\parallel$, $w_\perp^{ab}$, and $w_{\parallel\perp}^a$ with five independent elastic constants, whose calculation we leave to the reader. The relative importance of fluctuations in $\delta S$ and $B_{ij}$ depends, of course, on the ratio of $A_1$ to $A_2$. In the Landau–de Gennes model discussed in Appendix A $A_1/A_2<1$ near the transition from the isotropic to the nematic phase, but $A_1/A_2\gg1$ when $|r_Q|\gg w_3^2/w_4$ deep in the nematic phase. Thus, though both fluctuations are suppressed deep in the nematic phase, fluctuations in $\delta S$ are suppressed more than biaxial fluctuations.

### Crosslinking in the nematic phase

There is no qualitative distinction in the simple neoclassical theory between cross-linking in the nematic and isotropic phases. In both cases, the equilibrium phase exhibits the soft-elasticity characteristic of spontaneous breaking of the rotational symmetry of the isotropic state. Thus, additional physics must be added to the simple neoclassical model to produce the expected memory of the anisotropy of the nematic state at cross-linking and the concomitant destruction of soft elasticity. There are a number of mechanisms that will produce this memory. For the purposes of illustration, we will consider here only a simple model studied by Verwey and Warner [36] in which soft elasticity is destroyed via randomness in the sequence of rigid and flexible units along polymer chain segments. The free energy of this model reduces as expected to the general form discussed in Sec. IV C.

The sequence randomness along the chain causes the coupling parameter $\alpha$ to be a random variable with average $\langle\alpha\rangle$ and variance $\langle(\delta\alpha)^2\rangle$. The chain energy [Eq. (5.3)] must be averaged over $\alpha$, which appears in both $\underline{g}$ and $\underline{g}_0$. This average (ignoring the $\det\underline{l}_0\underline{l}^{-1}$ terms) is

$$\langle f_{\text{ch}}\rangle=\tfrac{1}{2}nT(l_0/l)\text{Tr}\underline{\underline{\Lambda}}_r\langle\underline{g}_0\rangle\underline{\underline{\Lambda}}_r^T\langle g^{-1}\rangle+\delta f_{\text{ch}}, \qquad (5.15)$$

where

$$\delta f_{\text{ch}}=\tfrac{1}{2}(l_0/l)nT\text{Tr}\,[\langle\underline{\underline{\Lambda}}_r\underline{g}_0\underline{\underline{\Lambda}}_r^T g^{-1}\rangle-\underline{\underline{\Lambda}}_r\langle\underline{g}_0\rangle\underline{\underline{\Lambda}}_r^T\langle g^{-1}\rangle]$$

$$\approx -\tfrac{1}{2}nT(l_0/l)\langle(\delta\alpha)^2\rangle\text{Tr}\underline{\underline{\Lambda}}_r\underline{\underline{Q}}_0\underline{\underline{\Lambda}}_r^T\underline{\underline{Q}}. \qquad (5.16)$$

We can now proceed as before. Let $\underline{\underline{\Lambda}}_r=\underline{\underline{\Lambda}}\langle\underline{g}_0\rangle^{-1/2}$ express $\underline{\underline{\Lambda}}$ in terms of $\underline{v}$, and expand in powers in $\underline{\underline{Q}}_0$. The result is

$$\langle f_{\rm ch}\rangle = -(l_0/l)nT\langle\alpha\rangle{\rm Tr}\underline{\underline{v}}\,\underline{\underline{Q}}$$
$$-\tfrac{1}{2}nT\langle(\delta\alpha)^2\rangle{\rm Tr}\underline{\underline{\Lambda}}\langle\underline{\underline{g}}_0\rangle^{-1/2}\underline{\underline{Q}}_0\underline{\underline{\Lambda}}^T\langle\underline{\underline{g}}_0^T\rangle\underline{\underline{Q}}+\cdots.$$

(5.17)

This energy is identical to Eq. (4.31) which we expected on general grounds. In the absence of strain, the second term of this equation tends to align the principal axis of $\underline{\underline{Q}}$ along $\underline{\underline{Q}}_0$.

## VI. CONCLUSIONS AND FUTURE DIRECTIONS

In this mostly pedagogical paper we have formulated a classical elasticity theory of nematic liquid-crystal gels, carefully incorporating all underlying symmetries and emphasizing the distinction between independent target and reference space rotational symmetries. Our formulation leads to a straightforward demonstration of the soft elasticity of nematic-gel phases that form via spontaneous symmetry breaking from an isotropic gel. This soft elasticity is characterized by the symmetry-enforced vanishing of a shear modulus and vanishing stress up to critical values of the appropriately applied strain. These and other predictions that emerge from our formulation are consistent with earlier predictions of the neoclassical liquid-crystal rubber theory [5–8], which had been very successful in explaining many beautiful experiments on liquid-crystal elastomers.

The advantage of our formalism is that it elucidates the origin of the novel soft elasticity of nematic gels, showing that it is dictated by general symmetry principles common to *any spontaneously* uniaxially ordered elastic medium and is *not* limited to any specific model of such materials. Thereby, our analysis also demonstrates a close connection between nematically ordered elastomers to other well-studied "soft" lattices, such as smectics (which by symmetry include cholesterics), columnar phases of fluid liquid crystals, and tensionless membranes, where rotational symmetry (corresponding to an arbitrary choice of smectic layers, columns, and membrane normal orientations) similarly enforces the vanishing of specific elastic moduli. This connection allows us to carry over much of the insight from those systems to gels. For example it seems likely that the buckling instability [57] in smectic liquid crystals under extensional strain parallel to layer normals will provide insight into the stripe instability [19] of a nematic elastomer subjected to extensional strain perpendicular to its anisotropy axis or to the as yet unstudied generalization of this phenomenon to compressional strain parallel to the anisotropy axis.

Our formulation also permits a straightforward incorporation of a variety of important effects such as spatial variations due, e.g., to boundary conditions, ever present thermal fluctuations [59], and local gel heterogeneity [31,32], thereby allowing a full statistical-mechanical treatment of nematic elastomers. Again, experience with smectics [31,32,59], columnar phases [31,32] of conventional liquid crystals, and the flat phase of tensionless elastic membranes [52–54] strongly suggests that the latter two effects will qualitatively modify long scales elastic properties of nematically ordered gels, leading to phenomena such as, for example, anomalous elasticity, negative Poisson ratio, and topological glass order.

A connection of liquid-crystal gels to a large body of work on closely related systems of conventional liquid crystals confined in *rigid* gels, such as the aerogel [11,31,32], naturally leads to an important general question: What role does gel elasticity play in determining the properties and stability of liquid-crystal phases confined inside *flexible* (as opposed to aerogels) heterogeneous gels such as aerosils [11,12]? With the elastic formulation presented here we plan to address this question in a future publication.

Finally, the presented description is also natural for treatment of fluctuating nematic elastomer membranes [26], which constitute a new universality class of membranes, adding to the well-studied classes of fluid, hexatic, and crystalline membranes [25]. In addition to the richness exhibited by those systems, we expect new physics associated with the interplay of the in-plane and undulation nonlinear elasticity, both expected to be important in elastomer membranes [26]. Finally, such in-plane orientationally ordered elastic membranes are novel realizations of anisotropic membranes, predicted to exhibit flat, tubule, and crumpled phases [60], subsequently observed in Monte Carlo simulations [61]. We plan to explore these and other phenomena and realizations of orientationally ordered elastomers in future publications [26].

## APPENDIX A: REVIEW OF NEMATIC ENERGY

In this appendix, we will review standard treatments of the isotropic-to-nematic transition, principally to establish notation. We introduce a complete set of orthonormal symmetric-traceless tensors $I_{ij}^\alpha$ satisfying ${\rm Tr}\underline{\underline{I}}^\alpha\underline{\underline{I}}^\beta=\delta^{\alpha\beta}$:

$$\underline{\underline{I}}^0=\sqrt{\tfrac{2}{3}}\begin{pmatrix}-\tfrac{1}{2}&0&0\\0&-\tfrac{1}{2}&0\\0&0&1\end{pmatrix},\quad \underline{\underline{I}}^1=\frac{1}{\sqrt{2}}\begin{pmatrix}1&0&0\\0&-1&0\\0&0&0\end{pmatrix},$$

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

$$\underline{\underline{I}}^4=\frac{1}{\sqrt{2}}\begin{pmatrix}0&0&0\\0&0&1\\0&1&0\end{pmatrix}.$$

(A1)

Any symmetric-traceless tensor can be expressed as a linear combination of these matrices: $Q_{ij}=\Sigma_{\alpha=0}^4 Q_\alpha I_{ij}^\alpha$, where $Q_\alpha={\rm Tr}\underline{\underline{Q}}\,\underline{\underline{I}}^\alpha$. Thus,

$$Q_0 = \sqrt{\tfrac{2}{3}}\left[Q_{zz} - \frac{1}{2}(Q_{xx} + Q_{yy})\right], \quad Q_1 = \frac{1}{\sqrt{2}}(Q_{xx} - Q_{yy}),$$

$$Q_2 = \sqrt{2}Q_{xy}, \quad Q_3 = \sqrt{2}Q_{xz}, \quad Q_4 = \sqrt{2}Q_{yz}. \quad \text{(A2)}$$

With $\mathbf{n}^0$ along the $z$ axis, $I_{ij}^0 = \sqrt{3/2}[n_i^0 n_j^0 - (1/3)\delta_{ij}]$. In uniaxial nematic phase, $Q_{ij}^0 = S[n_i^0 n_j^0 - (1/3)\delta_{ij}] = Q_0 I_{ij}^0$ and $Q_0 = \sqrt{2/3}S$. The Landau–de Gennes free energy for a nematic is

$$f_Q = \tfrac{1}{2} r_Q \mathrm{Tr}\underline{\underline{Q}}^2 - w_3 \mathrm{Tr}\underline{\underline{Q}}^3 + w_4 (\mathrm{Tr}\underline{\underline{Q}}^2)^2,$$

$$= \tfrac{1}{2} r_Q \sum_\alpha Q_\alpha^2 + w_4 \left(\sum_\alpha Q_\alpha^2\right)^2$$

$$- w_3 [\tfrac{1}{2}\sqrt{\tfrac{2}{3}}Q_0^3 - \sqrt{\tfrac{3}{2}}Q_0(Q_1^2 + Q_2^2) + \tfrac{1}{2}\sqrt{\tfrac{3}{2}}Q_0(Q_3^2 + Q_4^2)]$$

$$- \frac{1}{2\sqrt{2}}w_3 [3Q_1(Q_2^2 - Q_3^2) + 6Q_2 Q_3 Q_4]. \quad \text{(A3)}$$

Minimization with respect to $Q_0$ yields the equation of state

$$r_Q Q_0 + 4w_4 Q_0^3 - \sqrt{\tfrac{3}{2}}w_3 Q_0^2 = 0. \quad \text{(A4)}$$

Then expansion to second order in deviations $\delta Q_\alpha = Q_\alpha - Q_\alpha^0$ yields

$$\delta f = \tfrac{1}{2}A_1(\delta S)^2 + \tfrac{1}{2}A_2(Q_1^2 + Q_2^2), \quad \text{(A5)}$$

where

$$A_1 = \tfrac{2}{3}(r_Q + 8w_4 S^2 - 2w_3 S),$$

$$A_2 = 3w_3 S. \quad \text{(A6)}$$

As anticipated from the underlying rotational invariance, there are no terms proportional to $\delta Q_3^2$ or $\delta Q_4^2$.

## APPENDIX B: LINEARIZED LIMITS OF EULERIAN AND LAGRANGIAN ELASTICITY

It is often the case that a linearized theory of elasticity, in which nonlinear strains are replaced by their linearized limits and only terms to harmonic order in these linearized strains are included in the free energy, provides an adequate description of elastic distortions. It is, therefore, interesting to see how this linearized limit is reached. It turns out that this limit can be taken more cleanly in the Eulerian picture in which the displacement field is a part of the phase of a mass-density wave rather than the Lagrangian picture in which $\mathbf{u}(\mathbf{x})$ is a displacement relative to a reference configuration. For a further discussion of these two pictures of elasticity, see Ref. [16]. Much of our intuition about how to construct a linearized theory comes from the Eulerian picture in which the displacement field is a vector field in space that obeys the usual rules of transformation of vector fields. In this Appendix, we will discuss the linearized limits of Eulerian and Lagrangian elasticities.

### 1. Eulerian elasticity

In Eulerian elasticity, the displacement field $\mathbf{u}(\mathbf{x})$ is a vector field in three space. Like all vector fields that transform under the same group as space itself, $\mathbf{u}$ transforms under a rotation of the whole sample as

$$\mathbf{u}'(\mathbf{x}) = U\mathbf{u}(\mathbf{x})U^{-1} = \underline{Q}\mathbf{u}(\underline{Q}^{-1}\mathbf{x}), \quad \text{(B1)}$$

where $U$ is a rotation operator (e.g., quantum mechanical operator) and $\underline{Q}$ is its associated three-dimensional rotation matrix. Here the prime indicates the value of the field after the rotation operator is applied. To leave the system unchanged, $U$ must be an operation in the point group of the crystal. In the Eulerian picture, $\mathbf{u}(\mathbf{x})$ is a Goldstone field associated with the broken spatial symmetry of a crystal. Thus, strictly speaking, the highest-symmetry point group in three dimensions in the cubic group. To make contact with our discussion of gels, we can, however, imagine a system in which all rotations are in the point group. Since $\mathbf{u}$ is a vector field, $\partial_i u_j$ is a tensor field that satisfies

$$(\partial_i u_j)'(\mathbf{x}) = U\partial_i u_j U^{-1} = O_{ik}\partial_k' u_l(\mathbf{x}')O_{lj}^{-1}, \quad \text{(B2)}$$

where $\mathbf{x}' \equiv \underline{Q}^{-1}\mathbf{x}$, $\partial_i' = \partial/\partial x_i'$, and as before the prime indicates the value of the operator after rotation. Alternatively, we can introduce

$$\eta_{ij} = \partial_j u_i, \quad \text{(B3)}$$

which

$$\underline{\eta}' = \underline{Q}\,\underline{\eta}\,\underline{Q}^{-1}. \quad \text{(B4)}$$

Scalars created from $\underline{\eta}$ or from $\mathbf{u}$ and its derivatives are invariant under $U$. For example,

$$\eta_{ii} = \partial_i u_i, \quad \eta_{ij}\eta_{ji}, \quad \text{(B5)}$$

etc., are scalars under $U$.

The above symmetries and considerations apply to *any* vector field. The displacement field $\mathbf{u}$, however, has additional properties arising from the fact that it is a Goldstone field. In particular, the system is invariant under rotation of the mass-density wave crystal (which is not the same thing as rotating the whole sample). The transformation

$$\mathbf{x} - \mathbf{u}(\mathbf{x}) \rightarrow \underline{Q}[\mathbf{x} - \mathbf{u}(\mathbf{x})] \quad \text{(B6)}$$

rotates the crystal. Thus, the transformation

$$\mathbf{u} \rightarrow \mathbf{u}'(\mathbf{x}) = -\underline{Q}[\mathbf{x} - \mathbf{u}(\mathbf{x})] + \mathbf{x} \quad \text{(B7)}$$

does not change the energy of the system. This implies that the elastic energy will depend only on the Eulerian *symmetrized* strain,

$$u_{ij}^E = \partial_i u_j + \partial_i u_j - \partial_i u_k \partial_j u_k \approx \partial_i u_j + \partial_i u_j, \quad \text{(B8)}$$

$$\approx \partial_i u_j + \partial_i u_j, \quad \text{(B9)}$$

where the final form is its harmonic limit.

Thus, we have two symmetries: (1) symmetries associated with rotation of the whole sample, and (2) rotations of the lattice. Invariance with respect to the first requires that the energy depend only on scalars formed by contracting indices of both gradients and **u**'s. The second invariance requires that the energy be a function only of the nonlinear strain $u_{ij}^E$. The interesting thing is that *both $u_{ij}^E$ and* its linearized form transform like tensors under (1), i.e., under $O$. Thus, contracted tensors of either $\underline{\underline{u}}^E$ or its linearized form are scalars under $O$.

### 2. Lagrangian elasticity

In Lagrangian elasticity, there are as we have discussed two symmetries: (1) rotations $O_T$ in the target space and (2) rotation $O_R$ in the reference space. Under these operations, the displacement vector satisfies

$$\mathbf{R}'(\mathbf{x}) = \underline{\underline{Q}}_T \mathbf{R}(\underline{\underline{Q}}_R^{-1}\mathbf{x}). \tag{B10}$$

Under infinitesimal rotations,

$$O_{Tij} = \delta_{ij} + \epsilon_{ijk}\theta_{Tk}, \tag{B11}$$

$$O_{Rij} = \delta_{ij} + \epsilon_{ijk}\theta_{Rk}, \tag{B12}$$

and

$$\partial_i u_j' = \partial_i' u_j + \epsilon_{ijp}(\theta_{Rp} - \theta_{Tp}) + \epsilon_{ikp}\partial_k' u_j \theta_{Rp} - \epsilon_{kjp}\partial_i' u_k \theta_{Tp}. \tag{B13}$$

The energy is invariant under independent rotations through $\theta_R$ and $\theta_T$. As we have seen, these invariances are guaranteed by making the free energy a function only of the fully contracted $u_{ij}$ or $v_{ij}$ tensors.

Now, let us look at the linearized limit. Under both rotations, we have

$$\partial_i u_j' + \partial_j u_i' = \partial_i' u_j + \partial_j' u_i + (\epsilon_{ikp}\partial_k' u_j + \epsilon_{jkp}\partial_k' u_i)\theta_{Rp}$$
$$- (\epsilon_{kjp}\partial_i' u_k + \epsilon_{kip}\partial_j' u_k)\theta_{Tp}. \tag{B14}$$

Note that to leading order in $u$ and $\theta$, this symmetrized combination is independent of $\theta_R$ and $\theta_T$ as it should be. The terms of order $\theta u$ tell us about the tensorial rotation properties of the system. If $\theta_R = \theta_T = \theta$, then the symmetrized combination $u_{ij}^S = \partial_i u_j + \partial_j u_i$ transforms like a tensor, i.e.,

$$\underline{\underline{u}}'^S = \underline{\underline{Q}}\,\underline{\underline{u}}^S\underline{\underline{Q}}^{-1}. \tag{B15}$$

The linearized strain $\underline{\underline{u}}^S$ does not, however, transform like a tensor under independent rotations $\theta_R$ and $\theta_T$. If, for example, $\theta_R$ is zero, the term proportional to the product $\theta_{Ri}u_k$ in the transformation of $\underline{\underline{u}}^S$ depends on both the symmetric and antisymmetric parts of $\partial_i u_j$. Only the fully nonlinear strains $u_{ij}$ and $v_{ij}$ transform like tensors even to linear order in $\theta_R$ or $\theta_T$. We leave it as an exercise to verify this explicitly. *Thus, we cannot use the linearized tensors to discuss the rotation and tensorial properties of strains in the Lagrangian*

*language.* We can, however, as discussed above, use them fruitfully in the Eulerian language. However, once we have constructed a rotationally invariant Lagrangian energy, we can replace nonlinear strains by linearized ones to discuss harmonic elastic fluctuations.

### APPENDIX C: EVALUATION OF $B_A$

In this appendix, we outline the algebraic steps between Eqs. (4.11) and (4.12). We need to integrate over $\delta S$ and $Q_1$ and $Q_2$. Since these variables appear only to quadratic order, the integration is trivial and yields

$$\delta f_{u-v} = \tfrac{1}{2}B_1(\mathrm{Tr}\delta\underline{\underline{u}})^2 + \mu_2(v_1^2 + v_2^2) + \mu_0\delta v_0^2 - \gamma\delta v_0\mathrm{Tr}\delta\underline{\underline{u}}, \tag{C1}$$

where

$$B_1 = B - \frac{16s^2S^2}{9A'},$$

$$\mu_0 = \mu - \frac{4t^2}{3A'},$$

$$\mu_2 = \frac{\mu A_2}{A_2 + (2t^2/\mu)},$$

$$\gamma = -4\left(\frac{2}{3}\right)^{3/2}\frac{stS}{A'}, \tag{C2}$$

where

$$A' = A_1 + \frac{9s^2}{4B}S^2 + \frac{3t^2}{\mu}. \tag{C3}$$

Setting $\mathrm{Tr}\delta\underline{\underline{u}} = (\delta v_{xx} + \delta v_{yy} + \delta v_{zz})$, replacing $v_0$, $v_1$, and $v_2$ with expressions obtained from Eqs. (A2) (with the tensor $\underline{\underline{Q}}$ replaced by $\delta\underline{\underline{v}}$) and including the $\delta v_\alpha - (t/\mu)\delta Q_\alpha$ with $\alpha = 3,4$ terms in Eq. (4.11), we obtain Eq. (4.12) with

$$\bar{B}_1 = B_1 + \frac{4}{3}\mu_0 - 2\sqrt{\frac{2}{3}}\gamma,$$

$$\bar{B}_2 = B_2 - \frac{2}{3}\mu_0 - \frac{1}{2}\sqrt{\frac{2}{3}}\gamma,$$

$$\bar{B}_3 = B_1 - \mu_2 + \frac{1}{3}\mu_0 + \sqrt{\frac{2}{3}}\gamma,$$

$$\bar{B}_4 = \mu_2. \tag{C4}$$

[1] P.G. de Gennes and J. Prost, *The Physics of Liquid Crystals* (Clarendon Press, Oxford, 1993).

[2] S. Chandrasekhar, *Liquid Crystals* (Cambridge University Press, Cambridge, 1992).

[3] The nature of order in a glass, the glass phase transition, and even the existence of a glass phase in the strictest sense of the word is still a subject of debate and active research. An order parameter for a glass phase, related to the Edwards-Anderson spin-glass order parameter (see, for example, Ref. [34]), can be constructed. Dynamically, the glass transition is associated with ergodicity breaking, and it is quite clear that, at least locally, translational and orientational symmetry is broken in each specific sample. Since each realization of a glass is not invariant even under discrete rotations and translations, a glass breaks more symmetries than a crystal and therefore (in the technical sense of the word) is more ordered than even crystals. However, on long scales, glasses and gels are statistically homogeneous and isotropic, and are statistically as disordered as a simple isotropic liquid. This latter property is what allows liquid-crystal gels to spontaneously break these spatial *statistical* symmetries of isotropic gels.

[4] A gel is a network consisting of polymer segments linked by units that tie three or more segment ends together. An elastomer or rubber is a particular type of gel formed by cross-linking polymers with four functional units that tie four ends of four polymer segments together. See Paul J. Flory, *Principles of Polymer Chemistry* (Cornell University Press, Ithaca, NY, 1969).

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[37] By slow we mean a distortion whose wavelength is much longer than the mesh spacing.

[38] In Lagrangian elasticity, the fundamental variables are displacements of mass points parametrized as positions in a reference material. In Eulerian elasticity, the fundamental variables are phases of mass-density waves as a function of position in space. See Ref. [16], Chap. 6 and App. B.

[39] To more explicitly distinguish the target and reference spaces, one might want to introduce a distinct notation for vectors (and tensors) in the target and reference spaces, e.g., $(\vec{R})_i = R_i$ and $(\mathbf{x})_a = x_a$, with $\vec{R} = x_a \hat{e}_a + \vec{u}(\mathbf{x})$ and $\hat{e}_a$ and orthonormal target space triad with $a \in 1,2,3$. In this notation, the deformation tensor is given by $\Lambda_{ia} = \partial_a R_i$, with the right Green strain tensor $u_{ab} = \frac{1}{2}(\Lambda_{ia}\Lambda_{ib} - \hat{e}_a \cdot \hat{e}_b)$ and the left Green strain tensor $v_{ij} = \frac{1}{2}(\Lambda_{ia}\Lambda_{ja} - e_{ia}e_{ja})$ more explicitly distinguished. This notation also makes it clear that in fact $\Lambda_{ia}$ is *not*, strictly speaking, a rank-2 tensor, but transforms as a direct product of reference and target *vectors*. However, in the current context, where the dimension of the reference and target spaces is the same $d = D = 3$ and $e_{ia} = \delta_{ia}$, this more explicit (but cumbersome) notation is superfluous. In the notation that we employ here, where such (important) distinction is not explicitly made, one can think of the target space as the transformed (deformed) reference space and therefore still the same space. The two

rotational symmetries are then associated with rotational invariance of undeformed and deformed solid.

[40] R.M. Ogden, in *Nonlinear Elasticity: Theory and Applications*, edited by Y.B. Fu and R.W. Ogden (Cambridge University Press, Cambridge, 2001).

[41] We have chosen to set $x_i' = O_{Rij}^{-1} x_j$ rather than $x_i' = O_{Rij} x_j$ so that under simultaneous rotations in $S_R$ and $S_T$, $\mathbf{R}(\mathbf{x}) \rightarrow Q_T \mathbf{R}(Q_R^{-1} \mathbf{x})$. If $Q_R = Q_T$, this transformation looks like the standard transformations of fields that transform under the same group as the spatial points $\mathbf{x}$. See, for example, Michael Peskin and Daniel Schroeder, *An Introduction to Quantum Field Theory* (Perseus Books, Reading, MA, 1995), Chap. 1.

[42] The combinations $\underline{\underline{\Lambda}}^T \underline{\underline{\Lambda}}$ and $\underline{\underline{\Lambda}} \underline{\underline{\Lambda}}^T$ are referred to, respectively, as the right and left Cauchy-Green deformation tensors [40].

[43] In three dimensions, there are, of course, only three independent invariants, which can, for example, be $\mathrm{Tr}\underline{\underline{\Lambda}} \underline{\underline{\Lambda}}^T$, $\mathrm{Tr}(\underline{\underline{\Lambda}} \underline{\underline{\Lambda}}^T)^2$, and $\det \underline{\underline{\Lambda}} \underline{\underline{\Lambda}}^T$ or $\mathrm{Tr}(\underline{\underline{\Lambda}} \underline{\underline{\Lambda}}^T)^3$. All other invariants such as $\mathrm{Tr}(\underline{\underline{\Lambda}} \underline{\underline{\Lambda}}^T)^4$ can be expressed in terms of these three invariants.

[44] The soft-elasticity physics of liquid-crystal gels that we are interested in is contained in $f$. To make contact with incompressible rubber-elasticity models [7], $B \rightarrow \infty$ limit must be taken, restricting the remaining volume nonpreserving degree of freedom $\mathrm{Tr}\underline{\underline{u}}$ to zero.

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[46] In a more microscopic description, the director must also be allowed to relax–see Refs. [23,36,45]. If director and strains are not allowed to relax, the materials are "hard" until an elastic instability is reached [45].

[47] Bladon *et al.* [21] introduced an anisotropy ratio $l_\parallel / l_\perp$ as the ratio of random-flight step lengths of polymers in an elastomer. In equilibrium, this ratio is identical to the one used here.

[48] The simplest example that illustrates this point is an $O(N)$ Heisenberg ferromagnet, with the nonlinear energy functional $H = (|\vec{\phi}|^2 - |\vec{\phi}_0|^2)^2$ clearly reflecting the underlying $O(N)$ symmetry. Expanding the order parameter about the broken symmetry (ferromagnetic) phase with $\vec{\phi} = \vec{\phi}_0 + \vec{\phi}_1$, gives $H = 4(\vec{\phi}_0 \cdot \vec{\phi}_1)^2 + 4(\vec{\phi}_0 \cdot \vec{\phi}_1)|\vec{\phi}_1|^2 + |\vec{\phi}_1|^4$, which to quadratic order in $\vec{\phi}_1$ is clearly only invariant under *infinitesimal* $O(N)$ rotations of $\vec{\phi}$.

[49] S.M. Clarke, A.R. Tajbakhsh, E.M. Terentjev, and M. Warner, Phys. Rev. Lett. **86**, 4044 (2001).

[50] As is clear from Eq. (3.37), within a simple quartic model of $\tilde{\underline{u}}$, Eq. (2.17), valid only close to the isotropic-uniaxial transition (and even then, only if it is weakly first order, so that $\psi$ is small), the elastic constant $C_4$ is strictly positive, precluding a uniaxial-to-biaxial deformation transition. However, a more general free energy density of $\tilde{\underline{u}}$ (e.g., including higher-order nonlinearities in $\tilde{\underline{u}}$) can be shown to lead to $C_4$ that does go negative, thereby triggering the transition to a biaxial distortion.

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[54] P. Le Doussal and L. Radzihovsky, Phys. Rev. Lett. **69**, 1209 (1992).

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[56] This rescaling yields a physical $\mathbf{R}(\mathbf{x})$ if $g_0$ is spatially constant. If, however, $g_0$ varies spatially and has a nonzero curl, as it would for a system cross-linked in a cholesteric state, then this rescaling would not produce a single-valued $\mathbf{R}(\mathbf{x})$. This is the basis of chiral imprinting. See Y. Mao and M. Warner, Phys. Rev. Lett. **84**, 5335 (2000).

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