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Nematic elastomers: From a microscopic model to macroscopic elasticity theory

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A Landau theory is constructed for the gelation transition in cross-linked polymer systems possessing spontaneous nematic ordering, based on symmetry principles and the concept of an order parameter for the amorphous solid state. This theory is substantiated with help of a simple microscopic model of cross-linked dimers. Minimization of the Landau free energy in the presence of nematic order yields the neoclassical theory of the elasticity of nematic elastomers and, in the isotropic limit, the classical theory of isotropic elasticity. These phenomenological theories of elasticity are thereby derived from a microscopic model, and it is furthermore demonstrated that they are universal mean-field descriptions of the elasticity for all chemical gels and vulcanized media.

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I. INTRODUCTION

The classical theory of rubber elasticity [1] has been remarkably successful in describing the behavior of elastomeric systems in which there is no long-ranged nematic order. A blend of phenomenology and molecular-level reasoning, it is based on a few simple assumptions and bears great predictive and descriptive power. It models rubbery materials (i.e., elastomers) as incompressible networks of entropic Gaussian polymer chains and, further, assumes that the cross-links (i.e., the junctions of the polymer network) are fixed in space (for any given macroscopic deformation) but nevertheless deform affinely under macroscopic deformation. The classical theory gives their elastic free-energy density f as

$$f=\frac{\mu}{2}\mathrm{Tr}\,\mathbf{\Lambda}^T\mathbf{\Lambda}, \tag{1.1}$$

for a spatially uniform deformation $\mathbf{r}\rightarrow\mathbf{\Lambda}\cdot\mathbf{r}$ that conserves the volume (i.e., obeys $\det\mathbf{\Lambda}=1$). For most rubbery materials the assumption of volume conservation (i.e., incompressibility) is well satisfied. The shear modulus μ is given by $n_c k_B T$, where T is the temperature and k_B is Boltzmann's constant. (Henceforth, we choose units in which $k_B T$ is unity.) The parameter n_c is usually referred to as "the density of effective chains in the network." The classical theory [i.e., Eq. (1.1) and the associated arguments supporting it] explains many essential features of rubbery materials, such as their stress-strain curves (at least for deformations that are not too large), and the striking temperature dependence of their shear moduli, as well as their strain-induced birefringence (i.e., the stress-optical effect).

There are several important issues left unresolved by the classical theory. First, for a given cross-link density, "the effective chain density," is not calculated within the theory. A correct theoretical understanding of this issue is an important mission of the percolation-vulcanization theory [2–4]. Second, in the intermediate range of strains there is a universal and significant downward deviation of the experimental stress-strain curve, compared with the theoretical prediction of the classical theory. This deviation has traditionally been attributed to entanglement effects [5–7]. However, it has recently been pointed out [8] that the classical theory has an important internal inconsistency, in that it ignores the entropy associated with thermal fluctuations of the positions of the cross-linkers. It was further shown [8] that the entropy associated with these fluctuations is comparable to the entropy of polymer chains that is included by the classical theory, and that this entropy depends sensitively on the macroscopic deformation. The inclusion of this missing entropy leads to a qualitatively and quantitatively better fit to the stress-strain relation. Entanglement effects are known to play an important role in the dynamical properties of polymer solutions and melts. Nevertheless, we believe that their importance (or relevance) to the static properties of rubbery materials needs to be critically reexamined. A resolution of this issue may be achieved via the comparison of materials possessing various levels of entanglement.

Recently, an elegant anisotropic generalization of the classical model [9,10], known as the neoclassical model, was constructed to describe the highly unusual elasticity of nematically ordered elastomers, i.e., rubbery materials having (spontaneously) broken rotational symmetry, and has done so with considerable success. According to the neoclassical model, in the presence of nematic order the elastic free energy of a nematic elastomer under a volume-conserving deformation $\mathbf{\Lambda}$ is given by

$$f=\frac{\mu}{2}\mathrm{Tr}\,\mathbf{l}_0\mathbf{\Lambda}^T\mathbf{l}^{-1}\mathbf{\Lambda}, \tag{1.2}$$

where $\mathbf{l}_0$ and $\mathbf{l}$ are the (in general, anisotropic) step-length tensors in the initial (i.e., $\mathbf{\Lambda}=\mathbf{I}$) and the deformed (i.e., $\mathbf{\Lambda}\neq\mathbf{I}$) states that characterize the conformations of the polymer chains. The step-length tensors $\mathbf{l}_0$ and $\mathbf{l}$ have the symmetry of the nematic order parameters, viz. Q^0 in the initial state and Q in the deformed state, respectively. A remarkable feature of Eq. (1.2) is that in the nematic phase, for which $\mathbf{l}_0$ and $\mathbf{l}$ are both anisotropic and differ only by a rotation, there exists a continuous manifold of deformations that cost zero elastic free energy [11–14]. This so-called soft elasticity has not been observed in experiment [15,16]. Several explanations have been invoked to account for the discrepancy between the predictions of the neoclassical theory and the experimental findings. Nematic elastomers usually condense into a multidomain structure, unless an external field is applied, thus introducing an external anisotropy, in particular, if the sample is cross-linked in the stretched state [17]. Alternatively, approximations of the neoclassical theory, e.g., the assumption of affine deformations, could be responsible for the observed "nonsoft" elasticity. The effects of thermal and quenched fluctuations on the soft modes of the neoclassical theory are the focus of intensive study [14,18,19]. For recent reviews, see Refs. [9,10,14,20,21].

In a classic paper, Deam and Edward [2] initiated a fully statistical-mechanical approach to the study of rubber elasticity that incorporates both thermal fluctuations and quenched disorder along with repulsive interactions. This replica-based approach has been explored in detail [3] and has been applied to a variety of microscopic models. The long-length-scale physics was shown to be universal, applying to gels as well as vulcanized matter. Consequently, the associated Landau theory [22] provides the natural framework for a discussion of the long-length-scale physics of elastomers, especially in the vicinity of the gelation-vulcanization critical point.

The aim of the present work is to establish the connection between the statistical-mechanical approach and the neoclassical elasticity of nematic elastomers at the level of mean-field theory. As we shall work at the level of coarse-grained effective field-theory descriptions, with the original polymer degrees of freedom having been completely integrated out, the issue of entanglement does not concern us. For the sake of simplicity, our focus will be on incompressible systems, although our approach can readily be extended to allow for compressibility. We begin our task in Sec. II by generalizing the Landau theory for the gelation-vulcanization transition to allow for systems that have spontaneous nematic order. Our construction makes use only of the transformation properties of the order parameters for random solidification and nematic ordering, and the symmetry properties of the free energy, and hence should apply completely generally to nematic elastomers. In Sec. III we study the statistical mechanics of a microscopic model of cross-linked dimers coupled via Maier-Saupe interactions, and use it to derive the Landau theory discussed in Sec. II. We return to the Landau theory in Sec. IV to show that the neoclassical theory of the elasticity of nematic elastomers, Eq. (1.2), emerges via the stationary point of the Landau free energy. As one would expect, we recover the classical theory of rubber elasticity, Eq. (1.1), in the limit of isotropic states.

II. LANDAU THEORY OF NEMATIC ELASTOMERS

We begin with the real-space version of the order parameter field $\Omega(\hat{x})$ for the replica field theory of vulcanization [4] in d dimensions, which is a function of the $(1+n)$-fold replicated d vectors $\hat{x}=(\mathbf{x}^0,\ldots,\mathbf{x}^n)$. Its expectation value is given by

$$\langle\Omega(\hat{x})\rangle=\langle\Omega(\mathbf{x}^0,\ldots,\mathbf{x}^n)\rangle=\sum_{j=1}^{N}\langle\prod_{\alpha=0}^{n}\delta(\mathbf{x}^\alpha-\mathbf{c}_j^\alpha)\rangle_{1+n}-\frac{N}{V_0V^n}. \tag{2.1}$$

Here, $\mathbf{c}_j^\alpha$ (with $\alpha=0,1,\ldots,n$) are the $1+n$ replicas of the position d vectors of the N particles (indexed by $j=1,\ldots,N$) that comprise the system. Of these, $\mathbf{c}_j^0$ describes the position of the jth particle right before cross-linking (i.e., in the preparation state), and $\{\mathbf{c}_j^1,\ldots,\mathbf{c}_j^n\}$ (n-fold replicated) describes its positions in a state after cross-linking (i.e., in the measurement state). V_0 is the volume of the system in the preparation state, and V is its volume in the measurement state (which may in principle differ from V_0). The angle brackets $\langle\cdots\rangle_{1+n}$ denote an average over the replicated positions of the monomers $\mathbf{c}_j^\alpha$. One can readily see that the first term in Eq. (2.1) gives the joint probability density that a particle is found at $\mathbf{x}^0$ at the time of cross-linking and that the same particle is later found at $\{\mathbf{x}^1,\ldots,\mathbf{x}^n\}$, respectively, in n independent measurements performed at widely separated times after cross-linking [23], averaged over the N particles constituting the system. In the liquid state, all particles are delocalized, and therefore this joint probability density is independent of the positions $\{\mathbf{x}^0,\mathbf{x}^1,\ldots,\mathbf{x}^n\}$, and is simply given by the constant N/V_0V^n. The order parameter therefore vanishes in the liquid state. In the gel state, however, a nonzero fraction of the particles belong to the infinite cluster and are localized: Their positions after cross-linking are now strongly correlated with their positions right before cross-linking. As we shall discuss in much more detail in Sec. IV, this correlation, as well as the fraction of particles that have gelled, is captured by the nonvanishing value exhibited by the order parameter, Eq. (2.1), in the gel phase.

The order-parameter expectation value in the one-replica sector is given by

$$\delta\rho^\alpha(\mathbf{x}^\alpha)\equiv\langle\Omega^\alpha(\mathbf{x}^\alpha)\rangle=\int\langle\Omega(\hat{x})\rangle\prod_{\beta(\neq\alpha)}d\mathbf{x}^\beta=\sum_{j=1}^{N}\langle\delta(\mathbf{x}^\alpha-\mathbf{c}_j^\alpha)\rangle_{1+n}-\frac{N}{\mathcal{V}^\alpha} \tag{2.2}$$

for $\alpha=0,\ldots,n$, where $\mathcal{V}^\alpha\equiv(V_0,V,\ldots,V)$. Defined this way, it is clear that $\delta\rho^0(\mathbf{x}^0)$ is the density fluctuation in the preparation ensemble, i.e., in the liquid state, whereas $\delta\rho^\alpha(\mathbf{x}^\alpha)$ (for $\alpha=1,\ldots,n$) are the density fluctuations in the measurement ensemble, i.e., after cross-linking. In the following, we shall treat the component of the order parameter Ω that lies in the one-replica sector (i.e., $\delta\rho^\alpha$) explicitly, so that Ω now has components only in the higher-replica sector.

The Landau free energy for vulcanization and/or gelation for isotropic systems is given by

$$F_V[\Omega] = \int d\hat{x}\left(\frac{K_0}{2}(\nabla_0\Omega)^2 + \frac{K}{2}\sum_{\alpha=1}^{n}(\nabla_\alpha\Omega)^2 + \frac{r}{2}\Omega^2 - \frac{v}{3!}\Omega^3\right) + \frac{B_0}{2}\int d\mathbf{x}^0\,\delta\rho^0(\mathbf{x}^0)^2 + \frac{B}{2}\sum_{\alpha=1}^{n}\int d\mathbf{x}^\alpha\,\delta\rho^\alpha(\mathbf{x}^\alpha)^2, \tag{2.3}$$

where $\nabla^\alpha \equiv \partial/\partial\mathbf{x}^\alpha$ (for $\alpha=0,\ldots,n$). The parameter r triggers the transition to the solid state when it becomes negative (i.e., when the density of cross-links exceeds some critical value). B_0 and K_0 are, respectively, the inverse susceptibility for density fluctuations and the chain stretchability, both in the preparation ensemble, and B and K are the corresponding quantities in the measurement ensemble [4]. A larger value of K (or K_0) corresponds to floppier polymer chains that are easier to stretch.

In the original version of this Landau theory for vulcanization and/or gelation [22], the one-replica-sector (i.e., density) fluctuations $\delta\rho^\alpha(\mathbf{x}^\alpha)$ were simply excluded, which corresponds to the incompressible limit $B_0=B=\infty$, i.e., the repulsive interactions were taken to be infinitely strong, so that the particle density could not fluctuate at all. To avoid unnecessary complications our focus here will similarly be on incompressible systems although, as mentioned above, our approach can readily be extended to allow for compressibility. Furthermore, it was originally assumed that the parameters K_0 and K are equal to one another. However, it should be noted that neither K_0 and K, nor B_0 and B, need to be identical, as they describe systems at two potentially differing states, one right before the cross-linking and the other after the cross-linking.

We note that the order-parameter field $\Omega(\hat{x})$, Eq. (2.1), of this Landau theory is a single-particle quantity (albeit replicated). The original polymer degrees of freedom are integrated out in deriving the Landau theory, and consequently the issue of topological entanglement becomes irrelevant in this theory. The inclusion of entanglement effects in the original theory would simply lead to a quantitative modification of the parameters in the Landau theory, Eq. (2.3), not an invalidation of the theory itself.

A variety of rubbery solids in which there are mesogenic chemical groups can display nematic order [10], which is characterized by a symmetric, traceless order-parameter field $Q=\{Q_{ab}\}$, irrespectively of the underlying microscopic constitution of the system. The simplest way to incorporate the possibility of nematic ordering into our Landau theory is to couple the gel order-parameter field Ω to replicas of the symmetric traceless tensor fields, i.e., $Q^\alpha(\mathbf{x}^\alpha)$ (with $\alpha=0,1,\ldots,n$). Of these fields, Q^0 describes nematic order in the preparation ensemble, whereas the Q^α (for $\alpha=1,\ldots,n$) describe nematic order in the (n-fold replicated) measurement ensemble. The resulting free energy must be invariant under the simultaneous rotation of Q^α and the spatial position vectors $\mathbf{x}^\alpha$, independently for each replica α. The lowest-order coupling between Ω and a uniform nematic order-parameter field allowed by symmetry is

$$F_{VN} = \int d\hat{x}\left(\frac{\eta_0}{2}Q^0_{ab}\nabla^0_a\Omega\nabla^0_b\Omega + \frac{\eta}{2}\sum_{\alpha=1}^{n}Q^\alpha_{ab}\nabla^\alpha_a\Omega\nabla^\alpha_b\Omega\right), \tag{2.4}$$

where ∇^α_a indicates a derivative with respect to the ath Cartesian component of the αth replicated position vector. The signs of the coupling constants η_0 and η depend on details of the chemical structure of the nematic entities under consideration. An example will be given in the next section, where we compute the coupling constants for a particular model: Cross-linked dimers. As is well known, the gradient term in the Landau free energy for a magnetic system reflects the underlying coupling between spatially proximate spins. In the setting of vulcanized systems the gradient term reflects the coupling between constituents due to crosslinks, mediated by spatially extended, stretchable entities such as polymer chains. Nematic order confers anisotropy on this coupling, as manifested by the anisotropy acquired by the effective step-length tensor that we shall see in Sec. IV.

Other terms are allowed by symmetry as well, such as

$$\int d\hat{x}\,\Omega(\hat{x})(\nabla^\alpha_a\nabla^\alpha_b Q^\alpha_{ab})(\nabla^\beta_c\nabla^\beta_d Q^\beta_{cd}), \tag{2.5a}$$

$$\int d\hat{x}\,\Omega(\hat{x})^2\nabla^\alpha_a\nabla^\alpha_b Q^\alpha_{ab}, \tag{2.5b}$$

which are of the same (or lower) order in Ω as those kept in Eq. (2.4). However, these terms vanish for conditions of uniform nematic order, and therefore they can be ignored in our discussion of macroscopic elasticity at the mean-field level. Even restricting ourselves to uniform nematic order, there will be additional terms of higher order in Q in Eq. (2.4). We ignore these terms here, even though the magnitude of the nematic order parameter is not necessarily small. However, our main results will not be affected by these terms. In particular, the symmetry of the step-length tensor is captured correctly, and only its magnitude will be affected by these higher order terms.

The total free energy

$$F[\Omega,Q] = F_V[\Omega] + F_N[Q] + F_{VN}[\Omega,Q] \tag{2.6}$$

also contains a part, F_N, that depends only on the replicated nematic order parameter $\{Q^0,Q^1,\ldots,Q^n\}$ and accounts for the interactions between neighboring (anisotropic) particles that favor nematic order. In the next section, we shall give F_N explicitly (3.8) for a particular microscopic model—cross-linked dimers.

The above Landau free energy is completely general, as it is based on symmetry and length-scale arguments. However, it is useful to substantiate it with help of a microscopic model. This will be done in the following section, in which we consider the simplest model of a nematic elastomer: A system of cross-linked dimers. As we shall see, the microscopic model gives rise to precisely the above free energy, with the additional benefit of yielding explicit expressions of the expansion coefficients in terms of the parameters of the microscopic model. After rederiving the Landau theory, in

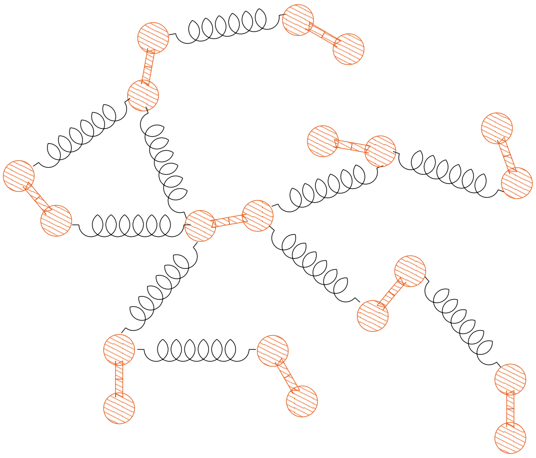

FIG. 1. (Color online) Model of dimers cross-linked by harmonic springs.

Sec. IV we work out its implications for the elasticity of nematic elastomers. Thereby, we derive the previously phenomenological neoclassical theory from a microscopic model.

III. MICROSOPIC MODEL

A simple microscopic model for a nematic elastomer consists of N rigid dimers that interact with one another via a Maier-Saupe type of interaction. Dimer j consists of two particles having d-dimensional position vectors $\mathbf{c}_{j,1}$ and $\mathbf{c}_{j,2}$. The relative separation of the two particles is fixed to be l, and the orientation of the dimer is specified by the unit vector

$$\mathbf{n}_j = \frac{\mathbf{c}_{j,1}-\mathbf{c}_{j,2}}{|\mathbf{c}_{j,1}-\mathbf{c}_{j,2}|}. \tag{3.1}$$

Parallel or antiparallel alignment of the dimers is energetically favored, as described by the following interaction potential:

$$H_{\text{nem}} = -\frac{1}{2}\sum_{i,j=1}^{N} J_{i,j}[(\mathbf{n}_i\cdot\mathbf{n}_j)^2 - d^{-1}]. \tag{3.2}$$

Here, $J_{i,j}$ specifies the strength and range of the interaction.

The system of N dimers is cross-linked via Hookean springs (see Fig. 1). We randomly choose M pairs of particles $\mathcal{C}=\{i_e,s_e;j_e,t_e\}_{e=1}^{M}$, with the first (i_e) and third (j_e) indices indicating which dimers $(1,\ldots,N)$ are linked by cross-link e $(=1,\ldots,M)$ and the second (s_e) and fourth (t_e) indices indicating which of the particles (1 or 2) in the dimers are connected by the cross-links. Each cross-linked pair is connected via a Hookean spring of typical extent b,

$$H_{\text{xlink}} = \frac{1}{2b^2}\sum_{e=1}^{M} |\mathbf{c}_{i_e,s_e} - \mathbf{c}_{j_e,t_e}|^2. \tag{3.3}$$

All particles are taken to repel one another at short distances, as described by the excluded-volume interaction

$$H_{\text{ev}} = \frac{\lambda}{2}\sum_{i,j=1}^{N}\sum_{s,t=1,2}\delta(\mathbf{c}_{i,s}-\mathbf{c}_{j,t}). \tag{3.4}$$

We shall focus on the situation in which the excluded-volume parameter λ is very large, so that the density fluctuations are fully suppressed. The total Hamiltonian is thus given by $H=H_{\text{nem}}+H_{\text{xlink}}+H_{\text{ev}}$, and we aim to address the randomly constrained partition function

$$Z(\mathcal{C}) = \int \prod_{i,s} d\mathbf{c}_{i,s} e^{-H} \prod_{j=1}^{N} \delta(|\mathbf{c}_{j,1}-\mathbf{c}_{j,2}|-l) \tag{3.5}$$

associated with the configuration $\mathcal{C}$ of quenched disorder (i.e., the random cross-linking).

The above model is able to account for both the gelation transition, which is controlled by the number of cross-links M, and the nematic ordering transition, which is controlled by the strength of the Maier-Saupe coupling $J_{i,j}$ relative to the temperature. (Recall that we are using units in which $k_{\text{B}}T=1$.) As these parameters can be varied independently, the system shows a rich phase diagram exhibiting nematic and isotropic sol and gel phases [24]. Here, we concentrate on a nematic gel phase in order to investigate the elasticity of the anisotropic gel.

The distribution of quenched disorder is taken to be of the Deam-Edwards type:

$$P(\mathcal{C}) \propto \frac{1}{M!}\left(\frac{V}{2N}\frac{\mu^2}{(2\pi b^2)^{d/2}}\right)^{M} Z(\mathcal{C}), \tag{3.6}$$

and the average of the logarithm of the partition function is achieved with the help of replicas (see the appendixes for details). The resulting free energy per dimer, $f\equiv F/N$, can be decomposed into three terms: One accounting for the gelation transition, one for the nematic ordering, and a coupling term,

$$f[\Omega,Q] = f_V[\Omega] + f_N[Q] + f_{VN}[\Omega,Q]. \tag{3.7}$$

The first of these terms is given via Eq. (2.3) but with particular values for the parameters $r=1-\mu^2$, $v=1/6$, and $K_0=K=(\frac{1}{6}l^2+b^2)/2$. Moreover, since we are considering incompressible systems all terms in the free energy associated with density fluctuations are suppressed.

The nematic free energy f_N has the standard form [25]. We assume that the interaction $J_{i,j}=J(\mathbf{c}_i-\mathbf{c}_j)$ depends only on the distance between the dimer centers of mass $\mathbf{c}_j=(\mathbf{c}_{j,1}+\mathbf{c}_{j,2})/2$. The corresponding Fourier-transformed function $J(\mathbf{k})$ is expected to be monotonically decreasing, giving rise to spatially uniform nematic order at sufficiently low temperatures. We denote by $J_0^{\alpha}\equiv J^{\alpha}(\mathbf{k}=\mathbf{0})$ the maximum coupling constant, and we allow for the possibility that the cross-linking and measurements of the anisotropic elasticity are done at different temperatures. Mathematically, this is achieved by allowing the possibility of there being two distinct coupling constants, one for replica $\alpha=0$ (i.e., for the preparation ensemble) and one for replicas $\alpha=1,2,\ldots,n$ (i.e., for the measurement ensemble).

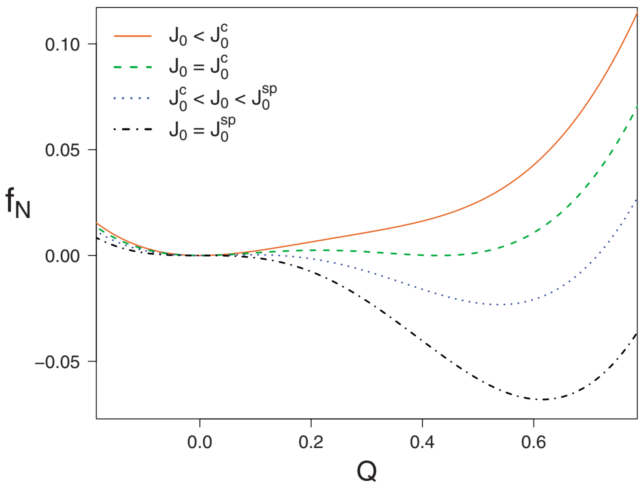

FIG. 2. (Color online) Nematic free energy as a function of Q for various values of the coupling constant associated with the Maier-Saupe interaction. The transition point is denoted by J_0^c, whereas J_0^{sp} indicates the limit of local stability of the isotropic phase.

In this paper, we treat the nematic order within mean-field theory only, and make the following Ansatz for the order parameter of a uniform, uniaxial nematic state: $Q^\alpha_{a,b}(\mathbf{k}=\mathbf{0}) = Q^\alpha(n_a n_b - d^{-1}\delta_{a,b})$. When substituted into the free energy, this yields a first-order transition, as expected. The nematic part of the free energy f_N decomposes into a sum over uncoupled replicas: $f_N = \Sigma_{\alpha=0}^n f_N^\alpha$, with

$$f_N^\alpha = \frac{J_0^\alpha}{3} Q^\alpha(Q^\alpha + 1) - \ln\left(\int_0^1 dy \, \exp(J_0^\alpha Q^\alpha y^2)\right). \tag{3.8}$$

The above free energy is shown in Fig. 2. It displays a discontinuous transition from an isotropic to a nematic phase at $J_0^c = 6.812$, at which the order parameter jumps from zero to the nonzero value $Q = 0.429$.

The terms in the free energy that couple the nematic and gel order parameters are, to lowest order, given by

$$Nf_{VN} = \int d\hat{x}\Big(\sum_{\alpha=0}^n \eta^\alpha Q^\alpha_{ab}(\nabla^\alpha_a\Omega)(\nabla^\alpha_b\Omega) + \sum_{\alpha=0}^n g_1^\alpha \Omega^2(\nabla^\alpha_a\nabla^\alpha_b Q^\alpha_{ab}) + \sum_{\alpha,\beta=0}^n g_2^{\alpha,\beta}\Omega(\nabla^\alpha_a\nabla^\alpha_b Q^\alpha_{ab})(\nabla^\beta_c\nabla^\beta_d Q^\beta_{cd})\Big). \tag{3.9}$$

The coupling constants are determined by the strength of the Maier-Saupe interaction J_0^α, the cross-link concentration μ^2, and the length of the rods l,

$$\eta^\alpha \sim g_1^\alpha \sim J_0^\alpha l^2 \mu^4 \quad \text{and} \quad g_2^{\alpha,\beta} \sim J_0^\alpha J_0^\beta l^4 \mu^2.$$

(Their precise values are given in the appendix.) The first term in Eq. (3.9) is precisely of the form given in Eq. (2.4). The second and third terms involve spatial derivatives of the nematic order parameter $\nabla_a\nabla_b Q_{a,b}$, and these vanish in the saddle-point approximation. Hence, in the mean-field approximation, if we assume Q^α to be constant in space, the microscopic model yields the Landau free energy given in Sec. II.

IV. ISOTROPIC AND ANISOTROPIC RUBBER ELASTICITY

We shall only consider the case of uniform nematic ordering deep in the nematic phase, and hence we may neglect the feedback of the Ω ordering on the nematic order. We therefore assume $\{Q^0, Q, \ldots, Q\}$ to be constants, characterizing the uniform nematic order in the preparation and measurement states, respectively. Additionally, it will be understood that B_0 and B have values that are positive and very large, consistent with the assumption that the system is incompressible. This appropriately guarantees that the saddle-point value of Ω vanishes in the one-replica sector. Accordingly, we require that $V_0 = V$. By varying the total free energy over the vulcanization-gelation order parameter Ω, we arrive at the saddle-point equation

$$K_0 l^0_{ab}\nabla^0_a\nabla^0_b\bar{\Omega} + K\sum_{\alpha=1}^n l_{ab}\nabla^\alpha_a\nabla^\alpha_b\bar{\Omega} = r\bar{\Omega} - \frac{v}{2}\bar{\Omega}^2, \tag{4.1}$$

in which summations over repeated Cartesian indices are, as usual, implied. The tensors $\mathbf{l}_0$ and $\mathbf{l}$ in this formula are shorthand for

$$l^0_{ab} \equiv \delta_{ab} + \frac{\eta_0}{K_0} Q^0_{ab} \quad \text{and} \quad l_{ab} \equiv \delta_{ab} + \frac{\eta}{K} Q_{ab}. \tag{4.2}$$

As we shall see below, they are in fact the (dimensionless) effective step-length tensors of the initial and deformed states that appear in the neoclassical elastic free energy, Eq. (1.2).

The saddle-point equation (4.1) should be solved under the constraint of the vanishing of $\bar{\Omega}$ in the one-replica sector. Let us first consider the following simple Ansatz [26]:

$$\bar{\Omega}(\hat{x}) = q\int d\mathbf{z}\left\{\int d\tau \frac{p(\tau)}{\mathcal{N}(\tau)} \exp\left[-\frac{\tau}{2}\left(\mathbf{y}^0\cdot\mathbf{l}_0^{-1}\cdot\mathbf{y}^0 + \sum_{\alpha=1}^n \mathbf{y}^\alpha\cdot\mathbf{l}^{-1}\cdot\mathbf{y}^\alpha\right)\right] - \frac{1}{V_0^{1+n}}\right\}, \tag{4.3a}$$

$$\mathbf{y}^0 \equiv \mathbf{x}^0 - \mathbf{z}, \quad \mathbf{y}^\alpha \equiv \mathbf{x}^\alpha - \mathbf{z},$$
$$\mathcal{N}(\tau) \equiv (\pi/\tau)^{(1+n)d/2}(\det \mathbf{l}_0)^{1/2}(\det \mathbf{l})^{n/2}, \tag{4.3b}$$

where the d-dimensional vector $\mathbf{z}$ is integrated over the volume of the (preparation) system V_0. Evidently, if both the preparation state and the measurement state are isotropic (i.e., $Q^0 = Q = 0$ and $\mathbf{l}_0 = \mathbf{l} = \mathbf{I}$), the above saddle-point Ansatz reduces to the form appropriate to isotropic gelled systems [3], with $p(\tau)$ being the distribution of inverse square localization lengths. The interpretation of the saddle point (4.3) is as follows. A certain fraction q of the particles belong to the infinite cluster (i.e., the gel fraction) and are localized in space. In the preparation ensemble (i.e., replica 0) each localized particle fluctuates around the point $\mathbf{z}$ subject to the Gaussian variance matrix $\tau^{-1}\mathbf{l}_0$, and in the measurement ensemble (i.e., replicas 1 to n) fluctuates around the same point $\mathbf{z}$ but with variance matrix $\tau^{-1}\mathbf{l}$. The state described by this saddle point corresponds to a nematic elastomer that has not been subjected to an elastic deformation. From Eqs. (4.2) it

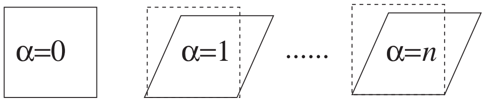

FIG. 3. A macroscopic uniform deformation, imposed after cross-linking, changes affinely the average positions of particles in the measurement state (i.e., the measurement replicas $\alpha=1,\ldots,n$), with respect to their positions in the preparation state (i.e., preparation replica $\alpha=0$).

is straightforward to see that the role of a nonvanishing nematic order is to confer spatial anisotropy on the position fluctuations of the localized particles. Finally, a continuous distribution $p(\tau)$ of (inverse square) localization scales τ reflects the fact that in a typical realization of quenched disorder, the localization length fluctuates from place to place in the sample, i.e., elastomers are spatially heterogeneous.

In the gel phase (i.e., $r<0$), we find that the Ansatz Eq. (4.3) does indeed solve Eq. (4.1), provided that

$$q = 2|r| \tag{4.4a}$$

and that $p(\tau)$ satisfies the following integro-differential equation:

$$\frac{\tau^2}{2}p'(\tau) = \left(\frac{|r|}{4v} - \tau\right)p(\tau) - \frac{|r|}{4v}\int_0^\tau p(\tau')p(\tau-\tau')d\tau'. \tag{4.4b}$$

Equations (4.4a) and (4.4b) are identical to those found for the isotropic case [3], up to trivial rescaling of parameters.

We now come to the main point of the present paper: Obtaining the elastic free energy of performing uniform, volume-preserving deformations of isotropic and nematic random solids. To do this, we shall impose a volume preserving, but otherwise arbitrary, homogeneous deformation of the boundary of the system after cross-linking, which is characterized by the deformation gradient tensor $\mathbf{\Lambda}$ (the determinant of which is unity). We proceed by hypothesizing the following geometrical modification [27] of the original saddle-point solution (4.3):

$$\mathbf{y}^\alpha = \mathbf{x}^\alpha - \mathbf{z} \to \begin{cases} \mathbf{x}^0 - \mathbf{z} & (\alpha=0), \\ \mathbf{x}^\alpha - \mathbf{\Lambda}\cdot\mathbf{z} & (\alpha\neq 0). \end{cases} \tag{4.5}$$

By substituting this modified Ansatz into Eq. (4.1), we find that it is indeed a solution, provided q and $p(\tau)$ are, respectively, given by Eqs. (4.4a) and (4.4b) (in the limit $n\to 0$).

We now argue that this new saddle point, $\bar{\Omega}_{\mathbf{\Lambda}}$ [given by Eq. (4.3) with the replacement Eq. (4.5)] describes a uniformly deformed nematic elastomer: In the preparation replica a localized particle continues to exhibit Gaussian fluctuations around the position $\mathbf{z}$, with an unchanged variance matrix $\tau^{-1}\mathbf{l}_0$; however, in the measurement replicas it fluctuates around the new position $\mathbf{\Lambda}\cdot\mathbf{z}$ (i.e., the deformation of the old position) but in a manner controlled by the same variance matrix $\tau^{-1}\mathbf{l}$ as in the undeformed state. Hence, the average positions of the particle before and after cross-linking are related to one another by the linear transformation $\mathbf{\Lambda}$, as illustrated in Fig. 3. This is precisely a macroscopic uniform deformation. Also, it now becomes clear that even though the average positions of particles are deformed by $\mathbf{\Lambda}$, the fluctuations around the average positions are independent of deformation [29]. This result is, however, an artifact of our mean-field approximation, and is not expected to hold for a real heterogeneous amorphous solid, in which there are order-parameter fluctuations.

We now calculate the elastic free-energy density of nematic elastomers $f_{\mathrm{el}}(\mathbf{\Lambda})$ at the mean-field level. To do this, we insert the deformed saddle point (4.3), modified according to Eqs. (4.5), into the total free-energy density (2.6), and subtract the value corresponding to the undeformed (i.e., $\mathbf{\Lambda}=\mathbf{I}$ and $Q^0=Q$) saddle point. Then, dividing appropriately by nV (recall that there are n replicas of the measurement ensemble) and taking the replica limit (i.e., $n\to 0$), we find the elastic free-energy density of an incompressible nematic elastomer,

$$f_{\mathrm{el}}(\mathbf{\Lambda}) = \lim_{n\to 0}\frac{1}{nV}(F[\bar{\Omega}_{\mathbf{\Lambda}}] - F[\bar{\Omega}]) = \frac{\mu}{2}\mathrm{Tr}\,\mathbf{l}_0\mathbf{\Lambda}^T\mathbf{l}^{-1}\mathbf{\Lambda} - \frac{\mu}{2}d, \tag{4.6a}$$

where

$$\mu \equiv \frac{4}{3}\frac{K_0}{K}\frac{|r|^3}{v^2}. \tag{4.6b}$$

Equation (4.6a) coincides with the free-energy density of the neoclassical theory of nematic elastomers, Eq. (1.2), up to a trivial additive constant. If $Q^0=Q=0$ then, by Eqs. (4.2), we have $\mathbf{l}_0=\mathbf{l}=\mathbf{I}$, and our result trivially reduces to the classical theory of isotropic rubber elasticity, Eq. (1.1). Finally, the scaling of the shear modulus as $|r|^3$ is a mean-field result which has been derived via other methods [28,30]. We emphasize that Eqs. (4.6a) are derived from the Landau theory of gelation, generalized to include nematic ordering. This Landau theory provides the effective field theory for the long-length-scale physics of gelation. Consequently, it is independent of short-distance details, and thus provides a universal mean-field description for the elasticity of all forms of vulcanized matter near the vulcanization point, provided that the corresponding transition is described by the Landau theory. This observation explains, in part, the tremendous success of the classical theory of rubber elasticity, Eq. (1.1), and its anisotropic generalization, the neoclassical theory, Eq. (1.2).

V. CONCLUSIONS AND OUTLOOK

We have extended the Landau theory for isotropic elastomers to the setting of nematic ordering, focusing on incompressible systems. Symmetry and length-scale principles dictate the coupling between the order parameters for amorphous solidification and for nematic ordering. The neoclassical theory of nematic elastomers was thus shown to be derivable from the saddle-point approximation of the resulting Landau theory. Our approach can readily be extended to allow for compressibility.

In addition, a simple microscopic model of nematic elastomers was introduced. In it, rigid dimers with a Maier-

Saupe interaction are randomly cross-linked, giving rise to a gel phase exhibiting nematic ordering. This microscopic model was shown to reproduce the Landau theory, generalized to nonuniform nematic ordering. Thereby, the macroscopic elasticity of nematic elastomers is connected to a microscopic, statistical-mechanical model.

What is perhaps most valuable about our approach is that it provides a platform for the systematic study of quenched spatial fluctuations in various forms of vulcanized matter. Until recently, there has been very little quantitative or phenomenological modeling of fluctuations such as these [31], although a heuristic discussion can be found in Ref. [32]. As a first step in this direction, we have analyzed the fluctuations of the elastic constants and the random residual stress for isotropic elastomers [33]. In the context of nematic elastomers it is of particular interest to understand whether or not the well-known soft mode of nematic elastomers [11–14] survives in the presence of nonaffine deformations. More generally, the interplay of nematic distortions and internal as well as externally applied stresses is of great interest. The present work constitutes a starting point for such studies.

ACKNOWLEDGMENTS

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APPENDIX A: AVERAGING OVER CROSS-LINK CONFIGURATIONS USING REPLICAS

In this appendix we present elements of our analysis of the microscopic model. The first step is to eliminate the quenched disorder, so as to obtain the disorder average, denoted by F, of the free energy. This is achieved with the help of replicas,

$$-F=[\ln Z_M(\mathcal{C})]=\lim_{n\to 0} n^{-1}\{[Z_M(\mathcal{C})^n]-1\}. \qquad \text{(A1)}$$

Here, $[\cdots]$ denotes the disorder average, i.e., the average over all cross-link configurations, weighted by the Deam-Edwards distribution (3.6). As this distribution is proportional to the randomly constrained partition function itself, we can write $[Z_M(\mathcal{C})^n]=\mathcal{Z}_{n+1}/\mathcal{Z}_1$. The disorder average can be worked out explicitly, by analogy with the case of flexible chains [3] or hard rods, and yields

$$\mathcal{Z}_{n+1}=\left\langle \exp\left(\frac{\mu^2 V}{2N}\sum_{i,j=1}^{N}\sum_{s,t=1}^{2} e^{-\Sigma_{\alpha=0}^{n}(\mathbf{c}_{i,s}^{\alpha}-\mathbf{c}_{j,t}^{\alpha})^2/2b^2}\right)\right\rangle_{n+1}^{H_0}.$$

The thermal average, denoted by $\langle\cdots\rangle$, is taken with the Boltzmann weight $\exp(-H_0)$, where $H_0\equiv H_{\text{ev}}+H_{\text{nem}}$ is the Hamiltonian of the uncross-linked melt. The subscript $n+1$ refers to the $(n+1)$-fold replication of the system. The normalization of the disorder distribution is given by $\mathcal{Z}_1=\lim_{n\to 0}\mathcal{Z}_{n+1}$, so that the disorder-averaged free energy follows from

$$-F=\lim_{n\to 0}\frac{\mathcal{Z}_{n+1}-\mathcal{Z}_1}{n\mathcal{Z}_1}. \qquad \text{(A2)}$$

APPENDIX B: DECOUPLING AND COLLECTIVE FIELDS

The next step in the analysis is the decoupling of the different (replicated) dimers in the Maier-Saupe interaction, as well as in the interactions arising from cross-linking. To decouple the interactions due to cross-linking, we note that the exponent in $\mathcal{Z}_{n+1}$ can be written as a quadratic form

$$\mathcal{Z}_{n+1}=\left\langle \exp\left(\frac{2N\mu^2}{V^n}\sum_{\hat{k}} u_{\hat{k}}|\rho_{\hat{k}}|^2\right)\right\rangle_{n+1}^{H_0} \qquad \text{(B1)}$$

by introducing the $n+1$-fold replicated density

$$\rho_{\hat{k}}\equiv\frac{1}{2N}\sum_{i=1}^{N}\sum_{s=1}^{2} e^{i\hat{k}\hat{c}_{i,s}}. \qquad \text{(B2)}$$

The sum over replicated wave vectors $\Sigma_{\hat{k}}$ runs over all vectors $\hat{k}$ with $k_\mu^\alpha\in\frac{2\pi}{V^{1/d}}\mathbb{Z}$ for $\mu=1,\ldots,d$ and $\alpha=0,\ldots,n$. The coefficient $u_{\hat{k}}$ is simply the Fourier transform of the cross-link constraint. For harmonic springs it is explicitly given by

$$u_{\hat{k}}=\prod_{\alpha=0}^{n}\int d\mathbf{x}e^{-i\mathbf{k}^{\alpha}\cdot\mathbf{x}}e^{-|\mathbf{x}|^2/2b^2}=(2\pi b^2)^{d(n+1)/2}e^{-\hat{k}^2b^2/2},$$

where the limit $V\to\mathbb{R}^d$ has been taken.

The sum over replicated wave vectors $\Sigma_{\hat{k}}$ in Eq. (B1), is decomposed into the 0-replica sector ($\hat{k}=\hat{0}$), the one-replica sector [$\hat{k}$ nonzero in only one replica, i.e., $\hat{k}=(\mathbf{0},\ldots,\mathbf{k},\ldots,\mathbf{0})=\mathbf{k}\hat{e}^{\alpha}$], and the higher-replica sector, abbreviated as HRS. The 0-replica sector is trivial because $\rho_{\hat{0}}=2N$ and does not fluctuate. The one-replica sector of the collective coordinate,

$$\rho_{\mathbf{k}}^{\alpha}=\frac{1}{2N}\sum_{i=1}^{N}\sum_{s=1}^{2} e^{i\mathbf{k}\cdot\mathbf{c}_{i,s}^{\alpha}}, \qquad \text{(B3)}$$

accounts for fluctuations in the density. The excluded-volume interaction is quadratic in the density, i.e.,

$$e^{-\Sigma_{\alpha=0}^{n}H_{\text{ev}}^{\alpha}}=\exp\left(-\frac{2N^2}{V}\sum_{\alpha=0}^{n}\sum_{\mathbf{k}}\lambda^{\alpha}|\rho_{\mathbf{k}}^{\alpha}|^2\right), \qquad \text{(B4)}$$

and can be combined with the one-replica sector of Eq. (B1) to obtain the following representation of the partition function:

$$\mathcal{Z}_{n+1}\sim\left\langle \exp\left(-N\sum_{\alpha=0}^{n}\sum_{\mathbf{k}}{}'\tilde{\lambda}_{\mathbf{k}}^{\alpha}|\rho_{\mathbf{k}}^{\alpha}|^2+N\tilde{\mu}^2\sum_{\hat{k}\in\text{HRS}}u_{\hat{k}}|\rho_{\hat{k}}|^2\right)\right\rangle_{n+1}^{\text{nem}}.$$

Here, $\Sigma_{\mathbf{k}}'$ denotes a sum over all $\mathbf{k}$'s, excluding $\mathbf{k}=0$. The average is taken with respect to the Boltzmann weight $\exp(-H_{\text{nem}})$, and $\tilde{\mu}^2\equiv 4\mu^2/V^n$ and

$$\tilde{\lambda}_{\mathbf{k}}^{\alpha}\equiv 4N\lambda^{\alpha}/V-\tilde{\mu}^2u_{\mathbf{k}\hat{e}^{\alpha}}.$$

The last step is to rewrite the Maier-Saupe interaction as a quadratic form by introducing the nematic order parameter, which is a symmetric, traceless tensor,

$$U^{\alpha}_{ab}(\mathbf{k}) = \frac{1}{N}\sum_{i=1}^{N} e^{i\mathbf{k}\cdot\mathbf{c}_i^{\alpha}}(n^{\alpha}_{ia}n^{\alpha}_{ib} - d^{-1}\delta_{a,b}). \tag{B5}$$

Here, we denote by $\mathbf{c}_i \equiv (\mathbf{c}_{i,1}+\mathbf{c}_{i,2})/2$ the center of mass of dimer i and assume that the interaction $J_{i,j}$ in Eq. (3.2) depends only on the distance between the centers of mass of the two interacting dimers,

$$J^{\alpha}_{i,j} = \frac{V}{N}J^{\alpha}(\mathbf{c}^{\alpha}_i - \mathbf{c}^{\alpha}_j). \tag{B6}$$

With these definitions the orientational interaction can be represented as a quadratic form,

$$\exp\left(-\sum_{\alpha=0}^{n} H^{\alpha}_{\mathrm{nem}}\right) = \exp\left(\frac{N}{2}\sum_{\alpha=0}^{n}\sum_{\mathbf{k}} J^{\alpha}(\mathbf{k})|U^{\alpha}_{ab}(\mathbf{k})|^2\right),$$

with $J^{\alpha}(\mathbf{k})$ being the Fourier transform of $J^{\alpha}(\mathbf{c}^{\alpha}_i - \mathbf{c}^{\alpha}_j)$, and summation convention being adopted for repeated Cartesian indices.

It is now straightforward to decouple the different (replicated) dimers by suitable Hubbard-Stratonovich transformations, by introducing collective fields for the density $\Omega^{\alpha}_{\mathbf{k}}$, the gel order parameter $\Omega_{\hat{k}}$, and the nematic order parameter $Q^{\alpha}_{ab}(\mathbf{k})$. [When introducing the collective fields, care must be taken of the symmetries of the collective fields, $\Omega_{-\hat{k}} \equiv \Omega^{*}_{\hat{k}}$, $\Omega^{\alpha}_{-\mathbf{k}} \equiv (\Omega^{\alpha}_{\mathbf{k}})^{*}$, and $Q^{\alpha}_{ab}(-\mathbf{k}) \equiv Q^{\alpha}_{ab}(\mathbf{k})^{*}$, which require us to constrain the fields to half-spaces. However, in the resulting expressions the fields can be continued to the full space of arguments.] The partition function $\mathcal{Z}_{n+1}$ is then represented as a functional integral over these collective fields,

$$\mathcal{Z}_{n+1} \sim \int \mathcal{D}\Omega\mathcal{D}Q \exp[-Nf_{n+1}\{\Omega_{\hat{k}},\Omega^{\alpha}_{\mathbf{k}},Q^{\alpha}_{ab}(\mathbf{k})\}], \tag{B7}$$

with a Landau-Wilson free energy per dimer f_{n+1} given by

$$\begin{aligned} f_{n+1}\{\Omega_{\hat{k}},\Omega^{\alpha}_{\mathbf{k}},Q^{\alpha}_{ab}(\mathbf{k})\} = {} & \frac{\tilde{\mu}^2}{2}\sum_{\hat{k}\in\mathrm{HRS}} u_{\hat{k}}|\Omega_{\hat{k}}|^2 + \frac{1}{2}\sum_{\alpha=0}^{n}\sum_{\mathbf{k}}{}'\tilde{\lambda}^{\alpha}_{\mathbf{k}}|\Omega^{\alpha}_{\mathbf{k}}|^2 \\ & + \frac{1}{2}\sum_{\alpha=0}^{n}\sum_{\mathbf{k}} J^{\alpha}(\mathbf{k})|Q^{\alpha}_{ab}(\mathbf{k})|^2 \\ & - \ln\Bigg\langle \exp\Bigg(\tilde{\mu}^2\sum_{\hat{k}\in\mathrm{HRS}} u_{\hat{k}}\Omega_{\hat{k}}\sum_{s=1}^{2} e^{-i\hat{k}\hat{c}_s} \\ & + i\sum_{\alpha=0}^{n}\sum_{\mathbf{k}}{}'\tilde{\lambda}^{\alpha}_{\mathbf{k}}\Omega^{\alpha}_{\mathbf{k}}\sum_{s=1}^{2} e^{-i\mathbf{k}\cdot\mathbf{c}^{\alpha}_s} \\ & + \sum_{\alpha=0}^{n}\sum_{\mathbf{k}} J^{\alpha}(\mathbf{k})Q^{\alpha}_{ab}(\mathbf{k})e^{-i\mathbf{k}\cdot\mathbf{c}^{\alpha}} \\ & \times(n^{\alpha}_a n^{\alpha}_b - d^{-1}\delta_{a,b})\Bigg)\Bigg\rangle^{\mathrm{dim}}_{n+1}. \end{aligned} \tag{B8}$$

The average $\langle\cdots\rangle^{\mathrm{dim}} = (4\pi l^2 V)^{-1}\int d\mathbf{c}_1 d\mathbf{c}_2\,\delta(|\mathbf{c}_1-\mathbf{c}_2|-l)\cdots$ refers to a single dimer of fixed length l.

APPENDIX C: LANDAU-WILSON FREE ENERGY

We only consider phases that exhibit macroscopic translational invariance. Mathematically, this can be achieved by requiring the excluded-volume interaction to be sufficiently strong that it overcomes the effective attractive interaction due to cross-linking,

$$\tilde{\lambda}^{\alpha}_{\mathbf{k}} = 4N\lambda^{\alpha}/V - \tilde{\mu}^2 u_{\mathbf{k}\hat{e}^{\alpha}} > 0,$$

which ensures stability with respect to macroscopically inhomogeneous states. In fact, to simplify the presentation we shall go further than this by considering systems that are not just stable with respect to macroscopic inhomogeneity but, rather, are strictly incompressible, so that macroscopic density fluctuations are completely suppressed. This is accomplished by taking the excluded-volume parameter λ to be very large. Our reason for doing this is that we are concentrating on the coupling terms between the nematic and gel order parameters, and hence we want to keep the analysis as simple as possible. The free energy, Eq. (B8), then simplifies to

$$\begin{aligned} f_{n+1}\{\Omega_{\hat{k}},Q^{\alpha}_{ab}(\mathbf{k})\} = {} & \frac{\tilde{\mu}^2}{2}\sum_{\hat{k}\in\mathrm{HRS}} u_{\hat{k}}|\Omega_{\hat{k}}|^2 + \sum_{\alpha=0}^{n}\sum_{\mathbf{k}}\frac{J^{\alpha}(\mathbf{k})}{2}|Q^{\alpha}_{ab}(\mathbf{k})|^2 \\ & - \ln\langle\exp[G_1(\Omega)+G_2(Q)]\rangle^{\mathrm{dim}}_{n+1}. \end{aligned}$$

Here, we have introduced the abbreviations

$$G_1(\Omega) \equiv \tilde{\mu}^2\sum_{\hat{k}\in\mathrm{HRS}} u_{\hat{k}}\Omega_{\hat{k}}\sum_{s=1,2} e^{-i\hat{k}\hat{c}_s},$$

$$G_2(Q) \equiv \sum_{\alpha=0}^{n}\sum_{\mathbf{k}} J^{\alpha}(\mathbf{k})Q^{\alpha}_{ab}(\mathbf{k})e^{-i\mathbf{k}\cdot\mathbf{c}^{\alpha}}\left(n^{\alpha}_a n^{\alpha}_b - \frac{1}{3}\delta_{a,b}\right), \tag{C1}$$

and specialized to three spatial dimensions (i.e., $d=3$).

If the nematic order parameter vanishes, the above free energy reduces to a special case of the universal gelation transition free energy discussed, e.g., in Ref. [22]. If the gel order parameter vanishes, the free energy has only the nematic contribution. Within mean-field theory, we only consider uniform nematic order and, furthermore, assume a uniaxial state, for which $Q^{\alpha}_{ab}(\mathbf{0}) = Q^{\alpha}(t_a t_b - \delta_{a,b}/3)$. Here, $\mathbf{t}$ denotes the unit vector along the preferred axis of the nematic state. With this Ansatz, the free energy is of the standard mean-field type, given in Eq. (3.8),

$$\begin{aligned} f_N\{Q^{\alpha}_{ab}(\mathbf{0})\} = {} & \frac{1}{2}\sum_{\alpha=0}^{n} J^{\alpha}_0 Q^{\alpha}_{ab}(\mathbf{0})^2 \\ & - \ln\left\langle \exp\left[\sum_{\alpha=0}^{n} J^{\alpha}_0 Q^{\alpha}_{ab}(\mathbf{0})\left(n^{\alpha}_a n^{\alpha}_b - \frac{1}{3}\delta_{a,b}\right)\right]\right\rangle^{\mathrm{dim}}_{n+1}. \end{aligned}$$

We have, furthermore, assumed that the interaction $J_{i,j}$ falls off monotonically with distance, so that the Fourier transform $J(\mathbf{k})$ is maximal for $\mathbf{k}=\mathbf{0}$, $J_0 \equiv J(\mathbf{0}) \geq J(\mathbf{k})$ for all $\mathbf{k}$.

The interesting terms are the ones that couple the nematic and gel order parameters. At cubic order in Ω and Q (i.e., ΩQQ or $\Omega\Omega Q$) there are two such terms:

$$\langle G_1(\Omega)G_2(Q)^2\rangle_{n+1}^{\mathrm{dim}} = \tilde{\mu}^2 \sum_{\alpha,\beta=0}^{n} \sum_{\mathbf{p},\mathbf{q}} \sum_{\hat{k}\in\mathrm{HRS}} u_{\hat{k}} J^\alpha(\mathbf{p}) J^\beta(\mathbf{q}) \Omega_{\hat{k}} Q^\alpha_{ab}(\mathbf{p}) Q^\beta_{cd}(\mathbf{q}) \times \sum_{s=1}^{2} \left\langle e^{-i(\mathbf{p}\cdot\mathbf{c}^\alpha + \mathbf{q}\cdot\mathbf{c}^\beta + \hat{k}\hat{c}_s)} \left(n^\alpha_a n^\alpha_b - \frac{1}{3}\delta_{a,b} \right) \times \left(n^\beta_c n^\beta_d - \frac{1}{3}\delta_{c,d} \right) \right\rangle_{n+1}^{\mathrm{dim}}, \tag{C2a}$$

$$\langle G_1(\Omega)^2 G_2(Q)\rangle_{n+1}^{\mathrm{dim}} = \tilde{\mu}^4 \sum_{\alpha=0}^{n} \sum_{\mathbf{q}} \sum_{\hat{k},\hat{p}\in\mathrm{HRS}} u_{\hat{k}} u_{\hat{p}} J^\alpha(\mathbf{q}) \Omega_{\hat{k}} \Omega_{\hat{p}} Q^\alpha_{ab}(\mathbf{q}) \times \sum_{s,s'=1}^{2} \left\langle e^{-i(\hat{k}\hat{c}_s + \hat{p}\hat{c}_{s'} + \mathbf{q}\cdot\mathbf{c}^\alpha)} \left(n^\alpha_a n^\alpha_b - \frac{1}{3}\delta_{a,b} \right) \right\rangle_{n+1}^{\mathrm{dim}}. \tag{C2b}$$

To proceed further with the computation of these two cubic terms we need to compute the single-dimer correlations.

APPENDIX D: SINGLE-DIMER CORRELATIONS

The simplest such correlation is of the form

$$\langle e^{-i\Sigma_{\nu=1}^{m} \mathbf{k}_\nu \cdot \mathbf{c}_{s_\nu}} \rangle_1^{\mathrm{dim}} = \frac{\sin(l|\tilde{\mathbf{k}}|)}{l|\tilde{\mathbf{k}}|} \delta_{\Sigma_{\nu=1}^{m}\mathbf{k}_\nu, 0}. \tag{D1}$$

with $\tilde{\mathbf{k}} = \Sigma_{\nu=1}^{m} \delta_{s_\nu,2} \mathbf{k}_\nu$. We also need the correlation

$$\left\langle \left(n_a n_b - \frac{1}{3}\delta_{a,b} \right) e^{-i[\mathbf{k}\cdot\mathbf{c}_s + \mathbf{p}\cdot(\mathbf{c}_1+\mathbf{c}_2)/2]} \right\rangle_1^{\mathrm{dim}} = g(l|\mathbf{p}|/2) \left(\frac{p_a p_b}{p^2} - \frac{1}{3}\delta_{a,b} \right) \delta_{\mathbf{k}+\mathbf{p},0}, \tag{D2}$$

in which the function $g(a)$ is given by

$$g(a) \equiv \left(\frac{1}{a} - \frac{3}{a^3} \right) \sin(a) + \frac{3}{a^2}\cos(a) \overset{a\to 0}{\longrightarrow} \frac{a^2}{10}. \tag{D3}$$

With help of these correlations we can evaluate the expression in Eq. (C2a). First, we note that there is no contribution for $\alpha=\beta$, as this implies a $\hat{k}$ lying in the one-replica sector, where Ω vanishes. Thus, we arrive at

$$\langle G_1(\Omega)G_2(Q)^2\rangle_{n+1}^{\mathrm{dim}} = \tilde{\mu}^2 \sum_{\alpha\neq\beta} \sum_{\mathbf{k},\mathbf{p}} J^\alpha(\mathbf{k}) J^\beta(\mathbf{p}) \left(\frac{k_a k_b}{|\mathbf{k}|^2} - \frac{1}{3}\delta_{a,b} \right) Q^\alpha_{ab}(\mathbf{k}) \times \left(\frac{p_c p_d}{|\mathbf{p}|^2} - \frac{1}{3}\delta_{c,d} \right) Q^\beta_{cd}(\mathbf{p}) u_{\mathbf{k}\hat{e}^\alpha + \mathbf{p}\hat{e}^\beta} \Omega_{-\mathbf{k}\hat{e}^\alpha - \mathbf{p}\hat{e}^\beta} g(l|\mathbf{k}|/2) \times g(l|\mathbf{p}|/2). \tag{D4}$$

In the long-wavelength limit the above expression further simplifies to

$$\langle G_1(\Omega)G_2(Q)^2\rangle_{n+1}^{\mathrm{dim}} \sim \frac{\tilde{\mu}^2}{800} \sum_{\alpha\neq\beta} \sum_{\mathbf{k},\mathbf{p}} u_{\hat{0}} J^\alpha_0 J^\beta_0 \Omega_{-\mathbf{k}\hat{e}^\alpha - \mathbf{p}\hat{e}^\beta} k_a k_b Q^\alpha_{ab}(\mathbf{k}) p_c p_d Q^\beta_{cd}(\mathbf{p}). \tag{D5}$$

Similarly, the expression in Eq. (C2) is computed to be

$$\langle G_1(\Omega)^2 G_2(Q)\rangle_{n+1}^{\mathrm{dim}} = \frac{\tilde{\mu}^4}{2} \sum_{\alpha=0}^{n} \sum_{\hat{k}\in\mathrm{HRS}} \sum_{\mathbf{q}} u_{\hat{k}} u_{\hat{k}+\mathbf{q}\hat{e}^\alpha} J^\alpha(\mathbf{q}) \Bigg[g(l|\mathbf{q}|/2) \times \left(\frac{q_a q_b}{\mathbf{q}^2} - \frac{1}{3}\delta_{a,b} \right) + \prod_{\beta(\neq\alpha)} \frac{\sin(l|\mathbf{k}^\beta|)}{l|\mathbf{k}^\beta|} g(l|\mathbf{k}^\alpha + \mathbf{q}/2|) \times \left(\frac{(k^\alpha + q/2)_a (k^\alpha + q/2)_b}{|\mathbf{k}^\alpha + \mathbf{q}/2|^2} - \frac{1}{3}\delta_{a,b} \right) \Bigg] \Omega_{\hat{k}} \Omega_{-\hat{k}-\mathbf{q}\hat{e}^\alpha} Q^\alpha_{ab}(\mathbf{q}). \tag{D6}$$

In the limit of long wavelength the expression simplifies to

$$\langle G_1(\Omega)^2 G_2(Q)\rangle_{n+1}^{\mathrm{dim}} = \frac{\tilde{\mu}^4 l^2}{5} \sum_{\alpha=0}^{n} \sum_{\hat{k}\in\mathrm{HRS}} \sum_{\mathbf{q}} u_{\hat{0}} u_{\hat{0}} J^\alpha_0 [q_a q_b + (k^\alpha + q/2)_a (k^\alpha + q/2)_b] \times \Omega_{\hat{k}} \Omega_{-\hat{k}-\mathbf{q}\hat{e}^\alpha} Q^\alpha_{ab}(\mathbf{q}). \tag{D7}$$

Rewriting Eqs. (D7) in real space, one recovers the coupling terms given in Eq. (3.9).

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