Strain-Induced Nematic Phase Separation in Polymer Melts and Gels

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ABSTRACT: Recent experiments strongly suggest the existence of nematic-like short-range orientational interactions in polymer melts and networks. In this paper we study a mean-field model which includes a Maier-Saupe interaction between monomers of polymer chains in a melt or a polymer network and find that external strain can induce phase separation in a mixture of chemically identical species which differ only in molecular weight. This mechanism for phase separation results from an exchange of mixing entropy, lost upon separating the small chains from the longer chains, for nematic free energy, gained by orienting the longer chains. The essential point is that the external strain field acts directly only on the longer chains. A detailed analysis of the spinodal condition, which incorporates elastic strain and orientational degrees of freedom, reveals that the interplay between strain and orientational fluctuations induces anisotropic spinodal decomposition in a blend under uniaxial strain: the peak in the accompanying structure factor lies either along or perpendicular to the axis of strain, depending on material parameters.

I. Introduction

Orientational, or *nematic*, interactions in polymer networks and melts have attracted attention for years.[3-17] DiMarzio[3] and later Tanaka and Allen[4] studied the packing entropy of a lattice comprising chains of freely jointed bonds, to model an affinely deformed rubber network. More recently, Deloche,[5] Jarry and Monnerie,[8] and Doi *et al.*[10,11] included an energetic Maier-Saupe nematic interaction between monomers, analogous to that postulated for thermotropic liquid crystals.[18] Orientational effects have also been considered for semiflexible chains of various chain architectures and flexibilities.[12,13,19,20] An understanding of the effects of orientational interactions in melts and gels is important for understanding the response to external fields which couple directly to the orientation of the monomers, such as anisotropic flows or stresses or magnetic fields.

In this paper we show explicitly how an applied strain may be modeled as an *external nematic field* applied directly to monomers stretched between cross-links in a network (or entanglement points in a melt, for well-separated time scales). By working with Gaussian chains with a stress applied to their end points and a Maier-Saupe orientational interaction between monomers, we obtain, in a unified manner, Flory's Gaussian elasticity theory, the free energy associated with orientational order, and the coupling between the orientational order and the applied strain. We apply this theory to a model system of a polymer gel with a chemically-identical polymeric solvent. In addition to this model system we believe the discussion embraces bidisperse blends of long, highly entangled host chains and much smaller chains, as long as the relaxation times for the two species are well-separated.

We recover previous results for the stress-strain relation of a gel with orientational interactions,[5] and derive a convenient description of the two-component system, from which we demonstrate an instability to anisotropic phase separation under an applied uniaxial strain. We identify two contributions to this anisotropy: one familiar from classical elasticity theory, which favors fluctuations with wavevectors $\mathbf{k}$ perpendicular to the strain axis $\hat{\mathbf{z}}$, and another from the softening of the shear modulus by orientational fluctuations, which favors fluctuations with $\mathbf{k}$ parallel to $\hat{\mathbf{z}}$. A detailed analysis of the fluctuation spectrum shows that the instability toward phase separation occurs for $\mathbf{k}\|\hat{\mathbf{z}}$; the corresponding experimental signature of this behavior is, for example, a neutron scattering pattern peaked along the $\hat{\mathbf{z}}$ axis ("abnormal butterfly"). ["Normal" and "abnormal" refer to scattering patterns with symmetries characteristic or uncharacteristic of the predictions of classical elasticity theory.] At nematic couplings below that required to induce phase separation (at a given extension) there is a crossover to a regime characterized by "normal butterfly" scattering, where classical elasticity dominates the fluctuation behavior and the peak scattering strength is normal to $\hat{\mathbf{z}}$, and the system is stable with respect to phase separation. An incompatibility between the polymers (non-zero Flory χ parameter) can induce phase separation in this "normal" regime. Finally, the onset of phase separation depends critically on the proximity of an underlying isotropic-nematic (I-N) transition and on the size of the Landau parameters in the orientational free energy expansion. The appearance of phase separation is a specific case of a general phenomenon: the miscibility of two species which respond differently to an applied external field is reduced upon applying the external field. This difference in response effectively induces a repulsion between the two species whereby the species with the stronger response is frustrated by the more weakly-responding element, so much so that phase separation ensues at high fields.

The outline of this paper is as follows. In section II we describe experiments which suggest significant nematic interactions in polymer melts. In section III we present a heuristic mean-field argument which identifies the basic mechanism for strain-induced phase separation. In section IV we outline our microscopic model and the resulting

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Landau theory, and in section V we present the effective elastic theory predicted by this model and briefly discuss the phase behavior. In section VI we incorporate the relation between elastic strain and composition variations and demonstrate an instability to phase separation, with an initial wavevector determined by a competition between strain fluctuations, which favor needle-like domains, and orientation fluctuations, which favor pancake-like domains. There are many interesting questions, which we leave for the future, about the phase separation kinetics and the resulting domain structures. Finally, in section VII we summarize our work.

II. Motivation and Preliminaries

We focus on experiments which measure the anisotropy induced in uniaxially-strained two-component systems. A simple way to test for nematic interactions is to strain either a network or a highly entangled melt (*host*) containing a fraction of relatively short *guest* polymers. The guests initially feel a stress due to the network deformation but quickly relax conformationally via reptation. The existence of short-range orientational (nematic) interactions between the guest monomers and those of the constrained host chains is then manifested in nonzero guest nematic order $Q^g_{\alpha\beta}$, where

$$\mathbf{Q}^g = \frac{1}{N_g n_g}\sum_{i=1}^{N_g n_g}\left\langle \hat{\mathbf{u}}^i\hat{\mathbf{u}}^i - \frac{1}{3}\mathbf{I}\right\rangle \qquad (2.1)$$

Here n_g is the number of guest chains, N_g is the guest monomer number per chain, $\hat{\mathbf{u}}^i$ is the orientation vector of monomer i, and $\mathbf{I}$ is the identity tensor. The host order parameter $\mathbf{Q}^h$ is non-zero even in the absence of nematic interactions, due to the applied stress.

Experiments testing this effect were performed by Deloche *et al.*[5] and Boue *et al.*[21] with free deuterated guest chains dispersed in a network. D-NMR measurements revealed induced nematic order in the guest chains,[5] while neutron scattering on similar samples[21] revealed approximately isotropic guest *conformations*. Hence the guest chains are conformationally relaxed while still possessing orientational order due to interactions with the strained and anisotropic host, providing evidence for short-range orientational interactions in polymers.

More recent experiments by Ylitalo *et al.*[22] probed host and guest order in strained polybutadiene polymer melts by simultaneously measuring the total sample birefringence and the dichroism due to the deuterated guests. These experiments extracted the ratio ϵ of guest to host order, defined by

$$S^g = \epsilon S^h \qquad (2.2)$$

where the scalar order parameter S is defined by

$$\mathbf{Q} = S\left(\hat{\mathbf{z}}\hat{\mathbf{z}} - \frac{1}{3}\mathbf{I}\right) \qquad (2.3)$$

and $\hat{\mathbf{z}}$ is the strain axis. Strains of 30–45% were applied to these samples. We are primarily interested in two significant features of these experiments: (1) For small guest $\epsilon \sim 0.9$, which supports the existence of considerably short-range orientational interactions. (2) The ratio $\epsilon(N_g)$ is roughly constant for $N_g \lesssim N_e$ and decreases dramatically to $\epsilon \sim 0.4$ for $N_g \gtrsim 5N_e$, where N_e is the typical number of monomers between entanglements. This contradicts the expected result that for long enough guest chains the host and guest are indistinguishable and have the same degree of nematic order. This drop occurs in a regime where the time scales of the two species are still well-separated, so that the host–guest approximation still applies. [In the reptation model the relaxation times scale as $\tau \sim N^3$, and in the experiments[22] the largest ratio of guest to host monomer numbers was $N_g/N_h \sim 0.08$.] These features provided the initial motivation for this work.

We make four assumptions to model the effects of strain on these binary blends: (i) We assume the time scales for host and guest relaxation are well-separated, $\tau^g_{rep} \ll \tau^h_{rep}$. Since a melt cannot support strain indefinitely, these experiments cannot be addressed within an equilibrium framework. However, given the assumption of well-separated time scales it is reasonable to expect the small chains to equilibrate for a given configuration of long chains. Hence we treat the longer chains as a network and the smaller chains as a polymeric solvent; while this procedure approximately identifies the onset of phase separation in a melt, it does not address the kinetics of phase separation. Our theory is accurate, of course, for a gel/solvent system. (ii) We assume the cross-link points deform affinely. (iii) We include a Maier–Saupe nematic interaction between all monomers. An orientational interaction can be either energetic, such as a gain in van der Waals energy between parallel monomers, or entropic, such as an anisotropic excluded volume resulting from packing considerations, and a physical system incorporates some combination of the two. Our choice of a Maier–Saupe, or energetic, interaction is primarily for computational convenience. (iv) We model the external stress as applied only to the host chains.

Consider the consequences of an external field directly applied to the host. The guest chains couple indirectly to the strain through their interaction with the host; the reduction in their orientational entropy upon aligning with the host reduces the efficacy of the applied strain. Thus, in a strained gel which is initially isotropic, the host monomers gain free energy by orienting in response to the strain, but not as much as they would gain in the absence of the guests. Phase separation can occur when the free energy gain due to the extra orientation of the host in the absence of guest chains compensates for the free energy cost of segregating the two populations, which comprises the simple demixing entropy and the elastic cost of stretching the host to locally change the composition. The phase-separated state is a dispersion of guest-rich regions with relatively little nematic order in a host with greater nematic order. Hence a signature of this phase separation behavior is a decrease in ϵ.

Let us consider a deformation of the host,

$$r_\alpha = E_{\alpha\beta} r^o_\beta \qquad (2.4)$$

where $\mathbf{r}$ is a position coordinate in the strained system and $\mathbf{r}^o$ is the reference Cartesian coordinate of the unstrained system (note summation convention). For an affine deformation the cross-link end-to-end vectors $\mathbf{R}$ are assumed to transform according to the same deformation $\mathbf{E}$. Thus, the distribution of end-to-end vectors $\{\mathbf{R}\}$ satisfies

$$\langle R_\alpha R_\beta\rangle_E = E_{\alpha\lambda}E_{\beta\rho}\langle R^o_\lambda R^o_\rho\rangle_o \qquad (2.5)$$

$$= \frac{1}{3}N_h b^2 W_{\alpha\beta} \qquad (2.6)$$

where we assume the underformed distribution of end-to-end vectors satisfies $\langle R^o_\alpha R^o_\beta\rangle_o = 1/3 N_h b^2 \delta_{\alpha\beta}$, and we have introduced the strain tensor $W_{\alpha\beta}$,

$$W_{\alpha\beta} = (\mathbf{E}\mathbf{E}^{\mathrm{T}})_{\alpha\beta} = \frac{\partial r_\alpha}{\partial \mathbf{r}^\circ}\cdot\frac{\partial r_\beta}{\partial \mathbf{r}^\circ} \tag{2.7}$$

N_{h} is the number of monomers between cross-links and b is the statistical segment length. The average $\langle\cdot\rangle_E$ is over all end-to-end vectors in the presence of the deformation $\mathbf{E}$, while $\langle\cdot\rangle_0$ is the average in the underformed state. For a uniaxial deformation along $\hat{\mathbf{z}}$,

$$\mathbf{W} = c^2\begin{pmatrix} \lambda^{-1} & 0 & 0 \\ 0 & \lambda^{-1} & 0 \\ 0 & 0 & \lambda^2 \end{pmatrix} \tag{2.8}$$

where λ is the extension ratio and c^3 is the relative volume change of the deformation;

$$c^3 = \frac{1-\phi_0}{1-\phi} = \det \mathbf{E} \tag{2.9}$$

Here ϕ_0 and ϕ are the guest volume fractions before and after the deformation. The traceless part of the deformation tensor, for uniaxial strain, is

$$\mathring{\mathbf{W}} = c^2(\lambda^2 - \lambda^{-1})(\hat{\mathbf{z}}\hat{\mathbf{z}} - {}^1/_3\mathbf{I}) \tag{2.10}$$

This is a measure of the nematic strength of an applied strain. We use the notation $\mathring{\mathbf{E}} \equiv \mathbf{E} - {}^1/_3\mathbf{I}\ \mathrm{Tr}\ \mathbf{E}$ for the traceless part of any tensor $\mathbf{E}$, where $\mathrm{Tr}\ \mathbf{E} = E_{\alpha\alpha}$ is the trace.

To understand the significance of the constraint (2.9), consider a deformation $\mathbf{u}(\mathbf{r}) = \mathbf{r}' - \mathbf{r}$, for which the deformation and strain tensors change according to

$$E'_{\alpha\beta} = E_{\alpha\beta} + E_{\lambda\beta}\frac{\partial u_\alpha}{\partial r_\lambda} \tag{2.11}$$

$$W'_{\alpha\beta} = W_{\alpha\beta} + W_{\alpha\lambda}\nabla_\lambda u_\beta + W_{\beta\lambda}\nabla_\lambda u_\alpha + W_{\lambda\rho}\nabla_\lambda u_\alpha \nabla_\rho u_\beta \tag{2.12}$$

To lowest order in $\mathbf{u}(\mathbf{r})$ the composition variation is (from eq 2.9)

$$\delta(1-\phi) = -(1-\phi)\nabla\cdot\mathbf{u} \tag{2.13}$$

This relation is equivalent to the assumptions that the system is incompressible and the local change in the host volume fraction is given by the volume change of the deformation of the gel cross-link points. The exceptions to this are dangling ends and small scale (compared to the mesh size) loops which need not move affinely. This constraint differs significantly from the coupling envisioned recently by Rabin and Bruinsma[23] in their description of "butterfly" patterns in soft solids. In ref 23 the strain $\mathbf{u}$ and concentration $\delta\phi$ fluctuations are assumed to be *coupled* by a term $C_c\delta\phi\ \nabla\cdot\mathbf{u}$ in the free energy, which applies when $\delta\phi$ is an additional independent conserved order parameter such as the composition of a precipitate in an elastic solid,[24-26] or when the affine deformation hypothesis breaks down. This hypothesis breaks down at a distance smaller than the cross-link distance, which does not affect our discussion below at very small wavevectors. Also, experiments suggest a breakdown of the affine deformation hypothesis at moderate strain ($\lambda \sim 1.5$);[27] we believe that the qualitative nature of our results survives this breakdown.

III. Weiss Mean-Field Theory

In this section we outline a Weiss mean-field theory which indicates the fundamental instability governing phase separation. We will assume chemically-identical host and guest monomers, which respond to their local nematic fields with the same bare susceptibility χ_0. Within mean-field theory the local nematic field H^{loc} due to the surrounding monomers is proportional to the average value of the nematic order:

$$H^{\mathrm{loc}} = w[\phi S^{\mathrm{g}} + (1-\phi)S^{\mathrm{h}}] \tag{3.1}$$

where w governs the strength of the nematic interaction and ϕ is the guest volume fraction. The guest order parameter S^{g} then obeys

$$S^{\mathrm{g}} = \chi_0 H^{\mathrm{loc}} \tag{3.2}$$

In addition to H^{loc}, the host monomers feel an external field H^{ext} because they are being stretched. A reasonable estimate for H^{ext} is the anisotropy in the applied strain, distributed equally among the host monomers between cross-links (a good assumption for moderate strains, $\lambda^2/N_{\mathrm{h}} \ll 1$):

$$H^{\mathrm{ext}} = (\lambda^2 - \lambda^{-1})/N_{\mathrm{h}} \tag{3.3}$$

Hence the host nematic order responds as follows:

$$S^{\mathrm{h}} = \chi_0(H^{\mathrm{ext}} + H^{\mathrm{loc}}) \tag{3.4}$$

The self-consistent set of equations (3.1)–(3.4) determines the induced nematic order as a function of applied strain:

$$S^{\mathrm{g}} = \frac{(\lambda^2 - \lambda^{-1})}{N_{\mathrm{h}}}\frac{\chi_0^{\,2}w(1-\phi)}{1-\chi_0 w} \tag{3.5a}$$

$$S^{\mathrm{h}} = \frac{(\lambda^2 - \lambda^{-1})}{N_{\mathrm{h}}}\frac{\chi_0(1-\chi_0 w\phi)}{1-\chi_0 w} \tag{3.5b}$$

The apparent divergence at $\chi_0 w = 1$ signals a nearby I–N transition. [The actual I–N transition is not at $w = \chi_0^{-1}$ because symmetry dictates a cubic term in the nematic Landau free energy which induces a first-order transition at $w_{\mathrm{IN}} < \chi_0^{-1}$.[28] However, eqs 3.5 are correct for linear response.] For $w = 0$ the guest order vanishes, as expected, and for $w \neq 0$ the guest chains *reduce* the host nematic order. This reduction drives the phase separation. The work done by an applied strain is the gain in nematic free energy per monomer, $\beta\Delta f_{\mathrm{nem}}[\phi] = -(1-\phi)\int_0^{(\lambda^2-\lambda^{-1})/N_{\mathrm{h}}} S^{\mathrm{h}}\, \mathrm{d}H^{\mathrm{ext}}$, and is

$$\beta\Delta f_{\mathrm{nem}}[\phi] = -\frac{1}{2}\frac{(\lambda^2 - \lambda^{-1})^2}{N_{\mathrm{h}}^2}\frac{\chi_0(1-\phi)(1-\chi_0 w\phi)}{1-\chi_0 w} \tag{3.6}$$

(with $\beta^{-1} = k_{\mathrm{B}}T$). Clearly, the gain in free energy is larger where there are fewer guest monomers. To examine the possibility for phase separation to take advantage of this, we add the translational entropy per monomer,

$$\beta f_{\mathrm{mix}}[\phi] = \frac{\phi}{N_{\mathrm{g}}}\ln\phi \tag{3.7}$$

We include only the guest chain mixing entropy because we consider times short with respect to the host chain relaxation times. For small strains the total free energy $\Delta f[\phi] = \Delta f_{\mathrm{nem}}[\phi] + f_{\mathrm{mix}}[\phi]$ is concave as a function of ϕ, and hence a homogeneous state is stable for all ϕ. However, for larger strains (and correspondingly higher nematic free energies) the system is thermodynamically unstable for certain volume fractions. The condition for thermodynamic stability, $\partial^2\Delta f/\partial\phi^2 > 0$, is

$$\frac{1}{N_{\mathrm{g}}\phi} - \frac{(\lambda^2 - \lambda^{-1})^2}{N_{\mathrm{h}}^{\ 2}}\frac{\chi_{\mathrm{o}}^{\ 2}w}{1 - \chi_{\mathrm{o}}w} > 0 \tag{3.8}$$

When this inequality is violated the system is unstable toward phase separation. From this relation we may identify several effects which promote phase separation: (1) increased effective strain $(\lambda^2 - \lambda^{-1})/N_{\mathrm{h}}$, which increases the local nematic field; (2) longer guest chains N_{g}, which reduce the entropy cost for phase separation; (3) more guest chains ϕ; (4) stronger nematic interaction w and bare susceptibility χ_{o}, which implies an underlying isotropic–nematic transition in the melt. Phase separation occurs such that the host excludes guest monomers to gain nematic free energy by aligning with the applied strain, with the result that the guest monomers acquire less nematic order per bond than before phase separation, and the host monomers more. This provides a possible explanation for the curious drop in the ratio $S^{\mathrm{g}}/S^{\mathrm{h}}$ as a function of N_{g} in the experiments of ref 22.

This mean-field argument is heuristic, particularly the approach of treating the strain as an external nematic field coupling directly to the host, but these ideas are supported by a microscopic calculation below. Also, we have so far omitted the host elastic energy which opposes phase separation. This will be included in section VI.

IV. Microscopic Model

We first consider the host and guest polymers to be chemically identical freely-jointed chains with a microscopic Maier–Saupe interaction between monomers. The extension to include incompatibility is straightforward and will be included as needed. The n_{g} free guest chains have N_{g} monomers while, subject to the condition $\tau_{\mathrm{rep}}^{\mathrm{g}} \ll \tau_{\mathrm{rep}}^{\mathrm{h}}$, the host is represented by a gel of n_{h} chains of N_{h} monomers stretching between cross-links. We include a "stress" $\Pi_{\alpha\beta}$ acting as the host chain end points $\mathbf{R}$—i.e. on the cross-link end-to-end vectors—which we ultimately Legendre transform in favor of the desired applied strain $\mathbf{W}$. The partition function is

$$Z[\mathbf{\Pi}, \mathbf{H}^{\mathrm{h}}, \mathbf{H}^{\mathrm{g}}] = \int \mathcal{D}\mathbf{r}^{\mathrm{g}}\, \mathcal{D}\mathbf{r}^{\mathrm{h}}\, \mathcal{D}\mathbf{R} \prod_{i}^{n_{\mathrm{h}}} \delta(\mathbf{R}^i - \sum_{s=1}^{N_{\mathrm{h}}} \mathbf{u}_{i;s}^{\mathrm{h}}) \times \exp\left\{\frac{3}{N_{\mathrm{h}}b^2}\sum_{i=1}^{n_{\mathrm{h}}} \mathbf{R}^i\cdot\mathbf{\Pi}\cdot\mathbf{R}^i\right\} \prod_{i,s}^{n_{\mathrm{g}},N_{\mathrm{g}}} W_{\mathrm{o}}[\mathbf{u}_{i;s}^{\mathrm{g}}] \prod_{i,s}^{n_{\mathrm{h}},N_{\mathrm{h}}} W_{\mathrm{o}}[\mathbf{u}_{i;s}^{\mathrm{h}}] \times \exp\{-\beta\mathcal{H}\} \tag{4.1}$$

Here, $\mathbf{u}_{i;s} = \mathbf{r}_{i;s+1} - \mathbf{r}_{i;s}$ is the bond for monomer s of guest chain i and the measure is over all monomer positions $\mathbf{r}$. The free statistical weight $W_{\mathrm{o}}[\mathbf{u}]$ enforces fixed bond length:

$$W_{\mathrm{o}}[\mathbf{u}] = \frac{1}{4\pi b^2}\delta(|\mathbf{u}| - b) \tag{4.2}$$

The Hamiltonian $\mathcal{H}$, the sum of nematic interactions and field terms,

$$\mathcal{H} = -\frac{1}{2}\rho w_{\mathrm{o}} \int \mathrm{Tr}\, \hat{\mathbf{Q}}^2(\mathbf{r})\, \mathrm{d}^3r - \rho(1 - \phi)\int \mathbf{H}^{\mathrm{g}}{:}\hat{\mathbf{Q}}^{\mathrm{h}}(\mathbf{r})\, \mathrm{d}^3r - \rho\phi\int \mathbf{H}^{\mathrm{h}}{:}\hat{\mathbf{Q}}^{\mathrm{g}}(\mathbf{r})\, \mathrm{d}^3r \tag{4.3}$$

is defined in terms of the nematic operator $\hat{\mathbf{Q}}(\mathbf{r}) = (1 - \phi)\hat{\mathbf{Q}}^{\mathrm{h}}(\mathbf{r}) + \phi\hat{\mathbf{Q}}^{\mathrm{g}}(\mathbf{r})$, where the guest and host order parameters are defined by

$$\rho(1 - \phi)\hat{\mathbf{Q}}^{\mathrm{h}}(\mathbf{r}) = \sum_{i=1}^{n_{\mathrm{h}}}\sum_{s=1}^{N_{\mathrm{h}}} \mathbf{Q}_{i;s}^{\mathrm{h}}\delta(\mathbf{r} - \mathbf{r}_{i;s}^{\mathrm{h}}) \tag{4.4}$$

$$\rho\,\phi\,\hat{\mathbf{Q}}^{\mathrm{g}}(\mathbf{r}) = \sum_{i=1}^{n_{\mathrm{g}}}\sum_{s=1}^{N_{\mathrm{g}}} \mathbf{Q}_{i;s}^{\mathrm{g}}\delta(\mathbf{r} - \mathbf{r}_{i;s}^{\mathrm{g}}) \tag{4.5}$$

$$\mathbf{Q}_{i;s}^{\mathrm{h(g)}} = \hat{\mathbf{u}}_{i;s}^{\mathrm{h(g)}}\,\hat{\mathbf{u}}_{i;s}^{\mathrm{h(g)}} - \frac{1}{3}\mathbf{I} \tag{4.6}$$

[We use the notation $\mathbf{A}{:}\mathbf{B} \equiv A_{\alpha\beta}B_{\beta\alpha} = \mathrm{Tr}\,\mathbf{AB}$.] The total monomer density is $\rho = (n_{\mathrm{h}}N_{\mathrm{h}} + n_{\mathrm{g}}N_{\mathrm{g}})/V$, where v is the volume; $\phi = n_{\mathrm{g}}N_{\mathrm{g}}/(n_{\mathrm{g}}N_{\mathrm{g}} + n_{\mathrm{h}}N_{\mathrm{h}})$ is the guest volume fraction; and $\hat{\mathbf{u}} = \mathbf{u}/|\mathbf{u}|$. The homogeneous external nematic fields $\mathbf{H}^{\mathrm{h}}$ and $\mathbf{H}^{\mathrm{g}}$ are introduced for calculating the Landau free energy density as a function of the average of $\hat{\mathbf{Q}}$. Although we consider $\mathbf{H}_{\mathrm{ext}}^{\mathrm{h}} = \mathbf{H}_{\mathrm{ext}}^{\mathrm{g}} = 0$, the strain $\mathbf{W}$ emerges as an effective external field which acts only on the host.

The free energy is

$$\beta\mathcal{F}[\mathbf{\Pi},\mathbf{H}^{\mathrm{h}},\mathbf{H}^{\mathrm{g}}] = -\ln Z[\mathbf{\Pi},\mathbf{H}^{\mathrm{h}},\mathbf{H}^{\mathrm{g}}] \tag{4.7}$$

and the deformation of the end-to-end vectors between cross-links is (see eq 2.6)

$$\mathbf{W} = -\frac{\delta\mathcal{F}[\mathbf{\Pi},\mathbf{H}^{\mathrm{h}},\mathbf{H}^{\mathrm{g}}]}{\delta\mathbf{\Pi}} \tag{4.8}$$

We choose as orientational order parameters the average host nematic order per host monomer:

$$\mathbf{Q}^{\mathrm{h}} = \langle V^{-1}\int \mathrm{d}^3r\,\hat{\mathbf{Q}}^{\mathrm{h}}\rangle \tag{4.9}$$

which may be calculated by

$$n_{\mathrm{h}}N_{\mathrm{h}}\mathbf{Q}^{\mathrm{h}} = -\frac{\delta\mathcal{F}[\mathbf{\Pi},\mathbf{H}^{\mathrm{h}},\mathbf{H}^{\mathrm{g}}]}{\delta\mathbf{H}^{\mathrm{h}}} \tag{4.10}$$

and similarly for the guests. The thermodynamic potential $\Phi[\mathbf{W},\mathbf{H}^{\mathrm{h}},\mathbf{H}^{\mathrm{g}}]$ is then

$$\Phi[\mathbf{W},\mathbf{H}^{\mathrm{h}},\mathbf{H}^{\mathrm{g}}] = \mathcal{F}[\mathbf{\Pi},\mathbf{H}^{\mathrm{h}},\mathbf{H}^{\mathrm{g}}] + \mathbf{\Pi}{:}\mathbf{W} \tag{4.11}$$

in terms of which $\mathbf{\Pi} = \delta\Phi/\delta\mathbf{W}$. The effective (Landau) potential is given by a further Legendre transform

$$F[\mathbf{W}, \mathbf{Q}^{\mathrm{h}}, \mathbf{Q}^{\mathrm{g}}] = \Phi[\mathbf{W}, \mathbf{H}^{\mathrm{h}}, \mathbf{H}^{\mathrm{g}}] + n_{\mathrm{h}}N_{\mathrm{h}}\mathbf{H}^{\mathrm{h}}{:}\mathbf{Q}^{\mathrm{h}} + n_{\mathrm{g}}N_{\mathrm{g}}\mathbf{H}^{\mathrm{g}}{:}\mathbf{Q}^{\mathrm{g}} \tag{4.12}$$

with $\mathbf{H}^{\mathrm{h}}$ and $\mathbf{H}^{\mathrm{h}}$ given in terms of $\mathbf{Q}^{\mathrm{h}}$ and $\mathbf{Q}^{\mathrm{g}}$ by eq 4.10. In the absence of external nematic fields the equilibrium conditions are found by minimizing $F[\mathbf{W},\mathbf{Q}^{\mathrm{h}},\mathbf{Q}^{\mathrm{g}}] - \mathbf{\Pi}^{\mathrm{ext}}{:}\mathbf{W}$,

$$\frac{\delta F[\mathbf{W}, \mathbf{Q}^{\mathrm{h}}, \mathbf{Q}^{\mathrm{g}}]}{\delta\mathbf{Q}^{\mathrm{h}}} = \frac{\delta F[\mathbf{W}, \mathbf{Q}^{\mathrm{h}}, \mathbf{Q}^{\mathrm{g}}]}{\delta\mathbf{Q}^{\mathrm{g}}} = 0 \tag{4.13a}$$

$$\frac{\delta F[\mathbf{W},\mathbf{Q}^{\mathrm{h}},\mathbf{Q}^{\mathrm{g}}]}{\delta \mathbf{W}} = \boldsymbol{\Pi}^{\mathrm{ext}} \tag{4.13b}$$

where $\boldsymbol{\Pi}^{\mathrm{ext}}$ is the externally applied stress. We will see below how $\boldsymbol{\Pi}^{\mathrm{ext}}$ is related to the physical stress tensor $\sigma_{\alpha\beta}$ in the gel.

At this stage the Landau theory must be calculated perturbatively in the order parameters (see Appendix A). Completing this procedure, we find the following Landau free energy per monomer:

$$f[\mathbf{Q}^{\mathrm{h}},\mathbf{Q}^{\mathrm{g}},\mathbf{W},\phi] = f_{\mathrm{mix}}[\phi] + (1-\phi)f_{\mathrm{N}}^{\mathrm{h}}[\mathbf{Q}^{\mathrm{h}}] + \phi f_{\mathrm{N}}^{\mathrm{g}}[\mathbf{Q}^{\mathrm{g}}] + f_{\mathrm{int}}[\mathbf{Q}^{\mathrm{h}},\mathbf{Q}^{\mathrm{g}},\mathbf{W},\phi] + f_{\mathrm{el}}[\mathbf{W},\phi] \tag{4.14}$$

The entropic contribution from the orientational degrees of freedom is the nematic (N) free energy density,

$$\beta f_{\mathrm{N}}[\mathbf{Q}] = \frac{1}{2}A\,\mathrm{Tr}\,\mathbf{Q}^2 - \frac{1}{3}B\,\mathrm{Tr}\,\mathbf{Q}^3 + \frac{1}{4}C[\mathrm{Tr}\,\mathbf{Q}^2]^2 \tag{4.15}$$

where the Landau coefficients for the guests are

$$A_{\mathrm{g}} = \frac{15}{2} \qquad B_{\mathrm{g}} = \frac{225}{14} \qquad C_{\mathrm{g}} = \frac{8325}{196} \tag{4.16}$$

and the host Landau coefficients are

$$A_{\mathrm{h}} = A_{\mathrm{g}}\left(1 + \frac{3}{5N_{\mathrm{h}}}\right) \qquad B_{\mathrm{h}} = B_{\mathrm{g}}\left(1 + \frac{33}{25N_{\mathrm{h}}}\right) \qquad C_{\mathrm{h}} = C_{\mathrm{g}}\left(1 + \frac{17713}{9435N_{\mathrm{h}}}\right) \tag{4.17}$$

The orientational entropy loss of a $\mathbf{Q}^{\mathrm{h}}$ fluctuation is larger than that of a $\mathbf{Q}^{\mathrm{g}}$ fluctuation because the host end points are constrained to be $\mathbf{W}$ (eq 2.6), while the guest end points are free. [This distinction is only sensible in the gel approximation and does not apply to an equilibrium (unstrained) melt.] The elastic free energy,

$$\beta f_{\mathrm{el}}[\mathbf{W},\phi] = \frac{1-\phi}{2N_{\mathrm{h}}}\left[\mathrm{Tr}\left(\mathbf{W} - \mathbf{I} - \frac{1}{2}\ln \mathbf{W}\right) + \frac{A_{\mathrm{h}}\,\mathrm{Tr}\,\mathring{\mathbf{W}}^2}{25N_{\mathrm{h}}}\right] \tag{4.18}$$

is Flory's classical rubber elasticity theory[29] with a correction (the last term) due to the introduction of the orientational order parameter. In the absence of nematic interactions this correction is canceled upon minimizing $f[\mathbf{Q}^{\mathrm{h}},\mathbf{Q}^{\mathrm{g}},\mathbf{W},\phi]$ with respect to $\mathbf{Q}^{\mathrm{h}}$, to recover Gaussian elasticity. The interaction free energy is the sum of the host orientational interaction with the strain, nematic interactions, and the incompatibility between host and guest chains:

$$\beta f_{\mathrm{int}}[\mathbf{Q}^{\mathrm{h}},\mathbf{Q}^{\mathrm{g}},\mathbf{W},\phi] = -\frac{A_{\mathrm{h}}}{5N_{\mathrm{h}}}(1-\phi)\mathring{\mathbf{W}}:\mathbf{Q}^{\mathrm{h}} - \frac{w}{2}\mathrm{Tr}[(1-\phi)\mathbf{Q}^{\mathrm{h}} + \phi\mathbf{Q}^{\mathrm{g}}]^2 + \chi\phi(1-\phi) \tag{4.19}$$

where $w = \beta w_{\mathrm{o}}$ and χ is the Flory parameter.[30] The total free energy is given by

$$F[\mathbf{Q}^{\mathrm{h}},\mathbf{Q}^{\mathrm{g}},\mathbf{W},\phi] = \rho\int \mathrm{d}^3r\, f[\mathbf{Q}^{\mathrm{h}},\mathbf{Q}^{\mathrm{g}},\mathbf{W},\phi] \tag{4.20}$$

$$= \rho\int \mathrm{d}^3r^{\mathrm{o}}\frac{(1-\phi_{\mathrm{o}})}{(1-\phi)} f[\mathbf{Q}^{\mathrm{h}},\mathbf{Q}^{\mathrm{g}},\mathbf{W},\phi] \tag{4.21}$$

where we have used eq 2.9. Equation 4.21 is convenient for variational calculations.

Equation 4.15 is an expansion to $\mathcal{O}(\mathbf{Q})^4$, and eq 4.19 includes the lowest order coupling between $\mathbf{Q}^{\mathrm{h}}$ and $\mathbf{W}$. Higher order couplings are of the form $\mathbf{Q}^2\mathbf{W}/N_{\mathrm{h}}$, $\mathbf{Q}\mathbf{W}^2/N_{\mathrm{h}}^2$, etc., which, because $\mathbf{Q} \sim N_{\mathrm{h}}^{-1}$ (upon minimizing with respect to $\mathbf{Q}^{\mathrm{h}}$), are of order N_{h}^{-3}. Hence the free energy is correct to $\mathcal{O}(N_{\mathrm{h}}^{-2})$. We retain the higher order terms ($\mathbf{Q}^3$ and $\mathbf{Q}^4$) in eq 4.15 to include nonlinear effects near the isotropic–nematic transition.

The effect of the deformation is as discussed in our heuristic mean-field argument: the effective nematic field per monomer (eq 4.19, first term) is the strain anisotropy reduced by a factor of the mesh size N_{h}, applied only to the host. Note that our results are for arbitrary strain fields, including biaxial deformations. A similar form of strain-orientation coupling was first proposed by de Gennes in the context of a tenuously cross-linked polymer–nematic gel with a weak shear modulus, to discuss the effects of strain on the nematic transition in the gel and the softening of the shear modulus by orientation fluctuations.[31,32] Similar free energies have also been proposed by several other authors[5,8,14,15,20] for gels or networks with orientational interactions and a small molecule (nonnematic) solvent. In particular, the theory of Warner and Wang[20] is a self-consistent theory which reduces to our Landau expansion.

V. Effective Elastic Theory and Phase Behavior

From the free energy we may now compute the stress–strain relation of the gel/solvent system. The stress tensor $\sigma_{\alpha\beta}$ follows from examining the change in free energy under an applied deformation $\mathbf{u}(\mathbf{r}) = \mathbf{r}' - \mathbf{r}$, according to[33]

$$\delta F = \int \mathrm{d}^3r\, \sigma_{\alpha\beta}\nabla_{\alpha}u_{\beta} \tag{5.1}$$

from which $\sigma = 2\mathbf{W}^{\mathrm{T}}\delta\mathcal{F}/\delta\mathbf{W} = 2\mathbf{W}^{\mathrm{T}}\boldsymbol{\Pi}^{\mathrm{ext}}$ and (using eqs 2.13 and 4.21)

$$\frac{\sigma}{\rho k_{\mathrm{B}}T} = \left[f - (1-\phi)\frac{\partial f}{\partial(1-\phi)}\right]\mathbf{I} + \frac{(1-\phi)}{N_{\mathrm{h}}}\mathbf{W}\left[\mathbf{I} - \frac{2A_{\mathrm{h}}}{5}\mathbf{Q}^{\mathrm{h}} + \frac{2A_{\mathrm{h}}}{25N_{\mathrm{h}}}\mathring{\mathbf{W}}\right] \tag{5.2}$$

For weak strains the induced orientational order is, to $\mathcal{O}(N_{\mathrm{h}}^{-1})$,

$$\mathbf{Q}^{\mathrm{h}} = \frac{(A_{\mathrm{g}} - w\phi)}{5(A_{\mathrm{g}} - w)}\frac{\mathring{\mathbf{W}}}{N_{\mathrm{h}}} \tag{5.3a}$$

$$\mathbf{Q}^{\mathrm{g}} = \frac{w(1-\phi)}{5(A_{\mathrm{g}} - w)}\frac{\mathring{\mathbf{W}}}{N_{\mathrm{h}}} \tag{5.3b}$$

and for uniaxial strains the stress anisotropy, $\Delta\sigma \equiv \sigma_{zz} - \sigma_{xx}$, is

$$\frac{\Delta\sigma}{\rho k_{\mathrm{B}}T} = \frac{(1-\phi)c^2(\lambda^2 - \lambda^{-1})}{N_{\mathrm{h}}}\left[1 - \frac{(1-\phi)\chi_{\mathrm{N}}}{2N_{\mathrm{h}}}c^2(2\lambda^2 + \lambda^{-1})\right] \tag{5.4}$$

where χ_{N} is the susceptibility for a pure host system in an external nematic field which couples via $-\mathbf{H}_{\mathrm{ext}}^{\mathrm{h}}:\mathbf{Q}^{\mathrm{h}}$:

$$\chi_{\mathrm{N}} = \frac{w}{5(A_{\mathrm{g}} - w)} \tag{5.5}$$

Note that a nematic interaction allows a larger extension λ for a given stress anisotropy. In other words, a nematic interaction increases the response to an applied shear strain or softens the shear modulus. Similar stress–strain relations have been given by Deloche[5] and Jarry and Monnerie.[8]

We can see this softening in another guise by considering terms quadratic in $\mathbf{Q}^{\mathrm{h}}$ and $\mathbf{Q}^{\mathrm{g}}$. Integrating these orientational degrees of freedom out of the free energy, eq 4.14, leaves the following effective elastic theory for the system:

$$\beta f_{\mathrm{el}}^{\mathrm{eff}}[\mathbf{W},\phi] = \frac{1-\phi}{2N_{\mathrm{h}}}\left[\mathrm{Tr}\left(\mathbf{W} - \mathbf{I} - \frac{1}{2}\ln \mathbf{W}\right) - \frac{\chi_{\mathrm{N}}(1-\phi)A_{\mathrm{g}}}{5N_{\mathrm{h}}}\,\mathrm{Tr}\,\mathring{\mathbf{W}}^2\right] \tag{5.6}$$

For a deformation $\mathbf{u}(\mathbf{r})$ the strain tensor becomes $W_{\alpha\beta} = \delta_{\alpha\beta} + \partial_\alpha u_\beta + \partial_\beta u_\alpha + \nabla u_\alpha \cdot \nabla u_\beta$, and we may expand eq 5.6 to quadratic order in $\mathbf{u}(\mathbf{r})$ to obtain the standard elastic free energy density (in dimensions of energy per volume now, rather than energy per monomer) of an isotropic solid,[33]

$$f_{\mathrm{iso}} = \frac{1}{2}K(\nabla\cdot\mathbf{u})^2 + \frac{1}{4}\mu(\phi)\left(\partial_\alpha u_\beta + \partial_\beta u_\alpha - \frac{2}{3}\delta_{\alpha\beta}\nabla\cdot\mathbf{u}\right)^2 \tag{5.7}$$

with bulk modulus K and shear modulus $\mu(\phi)$:

$$K(\phi) = \rho k_{\mathrm{B}}T\frac{1-\phi}{N_{\mathrm{h}}} \tag{5.8a}$$

$$\mu(\phi) = \rho k_{\mathrm{B}}T\frac{1-\phi}{3N_{\mathrm{h}}}\left[1 - \frac{2\chi_{\mathrm{N}}(1-\phi)A_{\mathrm{g}}}{5N_{\mathrm{h}}}\right] \tag{5.8b}$$

The shear modulus is softened due to nematic interactions and acquires a nontrivial composition dependence. Note that $\partial\mu/\partial(1-\phi)$ can change sign for sufficiently large χ_{N}; this effect is more pronounced when considering small fluctuations $\mathbf{u}(\mathbf{r})$ about an already-strained state. This nonlinearity also softens the bulk modulus K for finite strain, due to the constraint (2.13). These effects are crucial in the results that follow. For $\chi_{\mathrm{N}} = 0$ the bulk and shear moduli are equivalent to those derived by Onuki for a gel, with the identification of $\rho(1-\phi)/N_{\mathrm{h}}$ as the average cross-link density, $\bar{\nu}$ in his notation.[34] For a non-zero uniaxial strain the free energy governing harmonic fluctuations about the resulting state is that of a uniaxial solid, with five elastic constants. The isotropic gel is elastically stable for positive $K(\phi)$ and $\mu(\phi)$, and thermodynamically unstable for $K(\phi) + 4\mu(\phi)/3 = 0$, as discussed in refs 35 and 36.

We may calculate the ratio ϵ for weak strain from eqs 5.3:

$$\epsilon = \frac{w(1-\phi)}{A_{\mathrm{g}} - w\phi} \tag{5.9}$$

which allows one to determine experimentally the ratio w/A_{g}.

A realistic calculation of the phase behavior when the system phase separates under an applied strain is very difficult because of the long-range elastic interactions, and we leave this for future work. Here we restrict ourselves to a few qualitative comments on the phase behavior of this system and concentrate below on the nature of the spinodal instability. We note, however, that Warner and Wang have calculated the phase diagram of an isotropic solvent in a nematic gel in quiescent (unstrained) conditions.[20]

In zero strain the host and guest chains are identical and undergo a first-order isotropic–nematic transition at $w_{\mathrm{IN}}^{\circ} = A - B^2/(27C) = 7.27$, with a discontinuity $\Delta S_{\mathrm{IN}} = B/(3C) = 0.13$. As with a nematic liquid crystal with positive susceptibility in a magnetic field,[37] an applied strain decreases both ΔS_{IN} and w_{IN}, and for sufficiently strong strain the discontinuous transition disappears altogether and the system behaves smoothly as a function of nematic interaction. For larger guest fractions the strain required to suppress the transition is greater, for the strain then couples weakly to the entire system and its effectiveness decreases. Since the field couples directly to the host, the I–N transition occurs at a smaller w for a system richer in host. As discussed in section III, phase separation can occur when nematic effects are strong enough compared to elastic and entropic effects. Depending on the strength of the Landau coefficients this phase separation can occur in the pretransitional or strongly nematic ranges of w. In the case where $A_{\mathrm{h}} \neq A_{\mathrm{g}}$, as appears here, the behavior is complicated by further phase-separation tendencies.

In a melt the stress relaxes on the order of the host reptation time, and any phase separation eventually ceases as the system reverts to a homogeneous unstrained melt; the system cannot reach an equilibrium strained state. In a gel the system coarsens and eventually reaches an equilibrium phase-operated state. Phase separation requires distorting the host chains: stretching them to avoid the pockets rich in guests and compressing them in the guest-poor regions. The increase in elastic free energy, together with the connectivity imposed by the cross-links and the symmetry of the strain, leads to the following effects: (1) phase separation is anisotropic, with the domain shape determined by a competition between orientation and strain fluctuations; (2) while the final equilibrium state in the biphasic region may be two large domains, the presence of long-range elastic interactions may "trap" the system in very long-lived metastable states, as has been seen by Tanaka in the deswelling of conventional gels by rapidly changing the temperature (or solvent quality).[38] We will not address this last point here.

VI. Elastic and Fluctuation Effects

A. Structure Factor. We now incorporate the elastic energy cost of deforming the host chains and calculate the long wavelength limit of the structure factor. Elastic fluctuations are especially important because of the constraint $\delta(1-\phi) = -(1-\phi)\nabla\cdot\mathbf{u}$, through which longitudinal strain fluctuations are equivalent to composition fluctuations. At this point the affine deformation hypothesis is crucial, and we depart from the analysis of Rabin and Bruinsma,[23] who proposed a coupling $C_{\mathrm{c}}\nabla\cdot\mathbf{u}$ in the free energy. As discussed in section II, we believe our results should apply in the long-wavelength limit. We consider harmonic fluctuations about states which minimize the free energy with respect to orientational variations, for a given fixed applied strain $\mathbf{W}$. Strictly speaking, $\mathbf{W}$ is determined by the applied stress through eq 4.13b, and it is possible that a range of strains is prohibited because the elastic modulus is discontinuous at the I–N transition. However, we consider strains $\mathbf{W}$ above that which suppresses the discontinuous I–N transition, so that the stress–strain behavior is continuous.

While one may obtain analytic expressions by assuming a Gaussian form for F ($B = C = 0$), we must include nonlinear corrections to obtain accurate results near the I–N transition. The degrees of freedom are the host and guest fluctuations $\delta\mathbf{Q}^{\mathrm{h}}$ and $\delta\mathbf{Q}^{\mathrm{g}}$; and the strain fluctuations $\nabla\mathbf{u}$, which we separate into transverse strain and composition fluctuations using the constraint $\delta(1-\phi) = -(1-\phi)\nabla\cdot\mathbf{u}$. The relation between $\nabla\cdot\mathbf{u}$ and $\mathbf{W}$ is given by eq 2.12. In general, the fluctuation free energy density is

$$\beta f_{\mathrm{fluc}} = \frac{1}{2}[\delta\sigma{:}\nabla\mathbf{u} + \delta\mathbf{H}^{\mathrm{h}}{:}\delta\mathbf{Q}^{\mathrm{h}} + \delta\mathbf{H}^{\mathrm{g}}{:}\delta\mathbf{Q}^{\mathrm{g}}] \qquad (6.1)$$

where $\mathbf{H}^{\mathrm{h(g)}} = \partial f/\partial\mathbf{Q}^{\mathrm{h(g)}}$, the differentials are given by, for example,

$$\delta\sigma = \frac{\partial\sigma}{\partial\nabla\cdot\mathbf{u}}{:}\nabla\mathbf{u} + \frac{\partial\sigma}{\partial\mathbf{Q}^{\mathrm{h}}}{:}\delta\mathbf{Q}^{\mathrm{h}} + \frac{\partial\sigma}{\partial\mathbf{Q}^{\mathrm{g}}}{:}\delta\mathbf{Q}^{\mathrm{g}} \qquad (6.2)$$

and σ is given by eq 5.2. Upon eliminating all degrees of freedom except for composition fluctuations $\delta\phi(\mathbf{k})$ (see Appendix B), we obtain the effective free energy

$$\Delta f_{\mathrm{eff}}[\delta\phi] = \frac{1}{2}\int\frac{\mathrm{d}^3k}{(2\pi)^3}[S_0^{-1}(\hat{\mathbf{k}}) + C(\mathbf{k})]|\delta\phi(\mathbf{k})|^2 \qquad (6.3)$$

where we have written the inverse structure factor as the sum of a term $C(\mathbf{k})$ which vanishes for $\mathbf{k} = 0$, and the portion that remains in the long-wavelength limit, $S_0^{-1}(\hat{\mathbf{k}})$. The structure factor

$$S(\mathbf{k}) = \langle|\delta\phi(\mathbf{k})|^2\rangle \qquad (6.4)$$

$$= \frac{k_{\mathrm{B}}T}{S_0^{-1}(\hat{\mathbf{k}}) + C(\mathbf{k})} \qquad (6.5)$$

is obtainable from, e.g., neutron scattering from systems containing deuterated guests in a protonated host. The full form of $S_0^{-1}(\hat{\mathbf{k}})$ is given by eq B17 in Appendix B.

Before analyzing this result, we examine $S_0^{-1}(\hat{\mathbf{k}})$ for zero applied strain ($\lambda = 1$, $c = 1$):

$$\beta\rho^{-1}S_0^{-1}(\hat{\mathbf{k}})|_{\lambda=1} = \frac{1}{N_{\mathrm{g}}\phi} + \frac{3}{2N_{\mathrm{h}}(1-\phi)} - \frac{4A_{\mathrm{h}}\chi_{\mathrm{N}}}{5N_{\mathrm{h}}^2} - 2\chi \qquad (6.6)$$

The first term is the contribution from the guest translational entropy, and the second term is the contribution to the bulk modulus from classical rubber elasticity theory.[34] The third term is a contribution from orientation fluctuations: it arises from the composition dependence of the effective shear modulus due to orientational interactions (eq 5.8b). For the experimental values[22] $\phi \simeq 0.2$ and $\epsilon \sim 0.9$, and $w \sim 6.9$ (based on eq 5.9), the ratio of strain to orientation contributions is about $N_{\mathrm{h}}/4.9$, where $N_{\mathrm{h}} \sim 20 - 40$ (recall that N_{h} in the melt corresponds to the entanglement monomer number). Hence, even in the absence of an applied strain the presence of a nearby nematic transition has small, yet noticeable, effects on composition fluctuations.

While the structure factor, eq B17, is quite complicated, we may understand its qualitative behavior by considering weak strain. Upon substituting the linearized values for $\mathbf{Q}^{\mathrm{h}}$ and $\mathbf{Q}^{\mathrm{g}}$ (eqs 5.3) and setting $B = C = 0$, we find

$$\begin{aligned}\beta\rho^{-1}S_0^{-1}(\hat{\mathbf{k}}) = {} & \frac{1}{N_{\mathrm{g}}\phi} + \frac{1 + 2\hat{\mathbf{k}}\cdot\mathbf{W}\cdot\hat{\mathbf{k}}}{2N_{\mathrm{h}}(1-\phi)} - 2\chi - \\ & \frac{3\chi_{\mathrm{N}}}{2N_{\mathrm{h}}^2}\Big[\mathrm{Tr}\,\mathring{\mathbf{W}}^2 + 2\Big\{\hat{\mathbf{k}}\cdot\mathbf{W}^2\cdot\hat{\mathbf{k}} + \frac{1}{3}(\hat{\mathbf{k}}\cdot\mathbf{W}\cdot\hat{\mathbf{k}})^2 + \\ & (\hat{\mathbf{k}}\cdot\mathring{\mathbf{W}}\cdot\hat{\mathbf{k}})(\hat{\mathbf{k}}\cdot\mathbf{W}\cdot\hat{\mathbf{k}})\Big\} - 4\hat{\mathbf{k}}\cdot\mathbf{W}\cdot\mathring{\mathbf{W}}\cdot\hat{\mathbf{k}}\Big]\end{aligned} \qquad (6.7)$$

While this structure factor is qualitatively correct for moderate strains, $\lambda \lesssim 1.5$, the actual phase separation behavior is highly dependent on the parameters B and C.

The first and third terms of eq 6.7 are contributions from the guest entropy and host–guest incompatibility, respectively. The second term is anisotropic and comes from the elastic energy of locally dilating the gel to change the composition.[34] This term favors fluctuations with $\mathbf{k}\perp\hat{\mathbf{z}}$, or "needle-like" composition fluctuations (assuming uniaxial symmetry), producing the so-called "normal butterfly" scattering pattern (Figure 4). This may easily be understood if we think of the gel as a a network of springs. After a uniaxial extension there are more springs per unit area for area elements with normals $\hat{\mathbf{n}}$ parallel to $\hat{\mathbf{z}}$ than for area elements with $\hat{\mathbf{n}}\perp\hat{\mathbf{z}}$. Hence, modulations which stretch the gel farther along $\hat{\mathbf{z}}$ stretch more chains per area than modulations normal to $\hat{\mathbf{z}}$ and cost more energy. Thus the purely elastic contribution to the structure factor is peaked along $\mathbf{k}\perp\hat{\mathbf{z}}$.

The terms in brackets are contributions from the nematic interaction. The first of these is isotropic and vanishes for $\lambda = 1$. This is primarily responsible for phase separation and is the term given by the rough mean-field argument in section III. The next three terms, in braces, arise from host orientation fluctuations and favor "pancakes" over needles. The first two terms do not vanish in zero strain ($\mathbf{W}|_{\lambda=1} = \mathbf{I}$) and arise from the direct coupling of the host order to the strain fluctuations in f_{int} (eq 4.19). The third term vanishes for zero strain ($\mathring{\mathbf{W}}|_{\lambda=1} = \mathbf{0}$) and arises from fluctuations about a state that has some orientational order. The last term in brackets vanishes for zero strain and originates from the entropic cost of orienting the guests. This term favors needles over pancakes; i.e. it opposes the other nematic terms. The sum of the nematic terms favors pancakes, giving rise to the "abnormal" butterfly scattering pattern (Figure 5).

The instability toward phase separation (spinodal) is given by $S_0^{-1}(\hat{\mathbf{k}}) + C(\mathbf{k}) = 0$, while $S_0^{-1}(\hat{\mathbf{k}}) < 0$ signifies a quench into a two-phase region. Since ϕ is conserved, the initial growth of fluctuations upon a quench (quickly applied strain) obeys[39]

$$\partial_t\delta\phi(\mathbf{k}) = -Mk^2[S_0^{-1}(\hat{\mathbf{k}}) + C(\mathbf{k})]\delta\phi(\mathbf{k}) + \mathcal{O}(\delta\phi^2) \qquad (6.8)$$

where M is the mobility. For a quench the system is unstable to phase separation at long wavelengths, with shorter wavelengths stable, and the cutoff is determined by $S_0^{-1}(\hat{\mathbf{k}}) + C(\mathbf{k}) = 0$. As the system coarsens, nonlinear terms in eq 6.8 eventually limit growth at long wavelengths; this is a consequence of the long-range nature of the elastic interactions.

The fastest growing mode for a quench is a long-wavelength composition variation along the direction which maximizes $|S_0^{-1}(\hat{\mathbf{k}})|$. This direction is determined by a competition between needle-like ($\theta = \pi/2$) and pancake-like ($\theta = 0$) fluctuations, driven by, respectively, orientation and elastic fluctuations. Note, however, that behavior at shorter wavelengths is determined by the details of $C(\mathbf{k})$.

B. Scattering and Phase Behavior. We first discuss the possibility of spontaneous phase separation for *zero* applied strain, a phenomenon only relevant for the gel/solvent system. [The isotropic solvent/unstrained nematic gel system has been treated in detail by Wang and Warner.[20]] For $\lambda = 1$ an instability to phase separation occurs for

$$\begin{aligned}&\frac{1}{N_{\mathrm{p}}\phi} + \frac{3}{N_{\mathrm{h}}(1-\phi)} - \\ &\qquad \frac{16w_{\phi}A_{\mathrm{h}}A_{\mathrm{g}}}{75N_{\mathrm{h}}^2(1-\phi)[A_{\mathrm{g}}A_{\mathrm{h}} - w_{\phi}(\phi A_{\mathrm{h}} + (1-\phi)A_{\mathrm{g}})]} \le 0\end{aligned} \qquad (6.9)$$

Table 1. Comparison of Microscopic Theories of the I–N Transition with Experiment[a]

system	a_0	B	C	ΔS	$(1 - T^*/T_{\mathrm{IN}})$
Gaussian chains—this work	7.5	16.1	42.5	0.13	0.030
wormlike chains—semiflexible limit[19]	11.25	36.2	54.4	0.22	0.079
wormlike chains— rigid rod limit[19]	7.5	16.1	19.5	0.28	0.066
small molecules—Maier–Saupe theory[52] [b]	12.3	39.8	35.4	0.37	0.13
experiment: HCN[53]	8.7	0.42	0.39	0.36	0.0019
experiment: 8CB[54]	4.4	0.30	0.25	0.4	0.003
experiment: MBBA[55]	2.89	0.19	0.16	0.4	0.003

[a] This comparison demonstrates how microscopic theories systematically fail to accurately represent experimental data. The Landau coefficients are those for a free energy per molecule of the form $(k_BT)^{-1}f_N[\mathbf{Q}] = {}^1/_2\tilde{A}\ \mathrm{Tr}\ \mathbf{Q}^2 - {}^1/_3B\ \mathrm{Tr}\ \mathbf{Q}^3 + {}^1/_4C[\mathrm{Tr}\ \mathbf{Q}^2]^2$, where $\tilde{A} = a_0(1 - T^*/T)$. For this theory the order parameter discontinuity is $\Delta S = B/(3C)$, where $Q_{\alpha\beta} = S(n_\alpha n_\beta - \delta_{\alpha\beta}/3)$ and $(T_{\mathrm{IN}} - T^*)/T_{\mathrm{IN}} = B^2/(2Ca_0)$. In this language $\tilde{A} = A_h - w$. We quote our theory for $\phi = 0$ and ignore the $1/N_h$ correction to A_h. Experimental Landau coefficients have been normalized by the molecular volume to dimensionless units. The important point is the discrepancy between the theoretical and experimentally determined values for $(1 - T/T_{\mathrm{IN}})$. For the calculations used in the text we have taken $B_g = 0.5$ and $C_g = 0.6$. [b] Here we cite the Landau expansion of the Maier–Saupe free energy at the predicted transition temperature. The exact results from the theory are qualitatively similar: $\Delta S = 0.28$, $(1 - T^*/T_{\mathrm{IN}}) = 0.15$.

which may be rewritten as (using $A_h = A_g(1 + 3/(5N_h))$) On the other hand, the nematic coupling at which the I–N

$$w_\phi \geq A_h\left\{1 + \frac{\phi}{5N_h}\left[\frac{3N_h(1-\phi) + N_g(8-5\phi) - 2\chi\phi(1-\phi)N_gN_h}{N_h(1-\phi) + 3N_g\phi - 6\chi\phi(1-\phi)N_gN_h}\right]\right\}^{-1} \tag{6.10}$$

transition occurs is bounded by

$$A_g - \frac{B_g^{\,2}}{27C_g} \leq w_{\mathrm{IN}} \leq A_h - \frac{B_h^{\,2}}{27C_h} \tag{6.11}$$

Hence, $w_{\mathrm{IN}} < A_h$ and $w_\phi < A_h$. If $w_{\mathrm{IN}} < w_\phi$, then spontaneous phase separation may only occur in the nematic regime. For the Landau coefficients we have derived we find $w_{\mathrm{IN}} \ll w_\phi$ for all ϕ and for $N_h < 1000$, and hence phase separation in the *absence* of strain can only occur well inside the nematic region of the phase diagram. Thus extremely strong strains are required to induce phase separation in a system which is isotropic in an unstrained state, and in all likelihood our analysis breaks down at such large strains. If, however, the shift $A - w_{\mathrm{IN}}$ induced by the cubic term B at the first-order I–N transition is much smaller, one may reach a regime where $w_\phi \simeq w_{\mathrm{IN}}$. In such cases we may expect strain-induced phase separation in a system which is isotropic in the relaxed state. There is reason to believe that the shift $A - w_{\mathrm{IN}}$ may actually be much smaller: previous studies of the I–N transition based on the Maier–Saupe theory, upon which our discussion is based, are known to greatly overestimate the quantity $A - w_{\mathrm{IN}}$, by a factor of order 40 (see Table 1). This translates, in our model, into an equivalent overestimate of the Landau coefficients. If we adjust B and C accordingly, w_{IN} increases and makes tenable the possibility of having $w_\phi \simeq w_{\mathrm{IN}}$, hence increasing the likelihood of strain-induced phase separation in a system which is isotropic in the unstrained state. The calculations performed in the rest of the paper correct for this characteristic discrepancy between theory and experiment. [This issue has been raised recently by Sheng and Tao, who have shown how to account for this inconsistency by generalizing the Maier–Saupe theory to account for the density change at the transition.[40]]

We now examine the instability to strain-induced phase separation, with the inclusion of elastic effects. We have chosen values for the Landau coefficients B and C ($B/A = 1/15$, $C/A = 2/25$), characteristic of a realistic I–N transition ($\Delta S = 0.27$, $(T_{\mathrm{IN}} - T^{\mathrm{ast}})/T_{\mathrm{IN}} = 0.0015$). We find that the spinodal occurs for $\hat{\mathbf{k}} \| \hat{\mathbf{z}}$, corresponding to layering with normals along the strain direction. Figure 1 shows the spinodal curves at various extension ratios ($\lambda = 1.3 - 2.1$) for $N_h = 20$ and $N_g = 300$, and Figure 2 shows the spinodal curves for $\lambda = 1.5$ and $N_g = 100 - 500$. In the latter case the spinodal curves saturate at large N_g, as the entropic cost of demixing vanishes. For these parameters phase separation occurs in a system which is isotropic in the unstrained state ($w_{\mathrm{IN}} \simeq 7.5$).

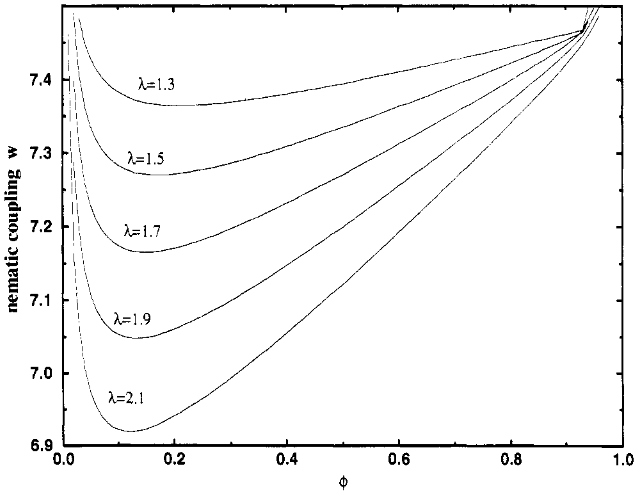

Figure 1. Spinodal curves for $N_h = 20$, $N_g = 300$, and $\lambda = 1.3$, 1.5, 1.7, 1.9, 2.1.

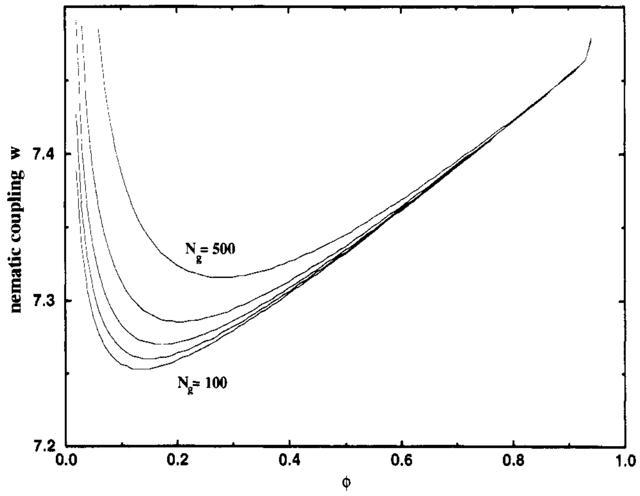

Figure 2. Spinodal curves for $\lambda = 20$, $N_g = 300$, and $N_h = 100$, 200, 300, 400, 500.

Figure 3 displays the crossover behavior from weak nematic couplings where the fluctuation spectrum is dominated by strain fluctuations, preferring needle-like fluctuations to strong nematic couplings near the spinodal where the fluctuation spectrum is pancake-like, reflecting

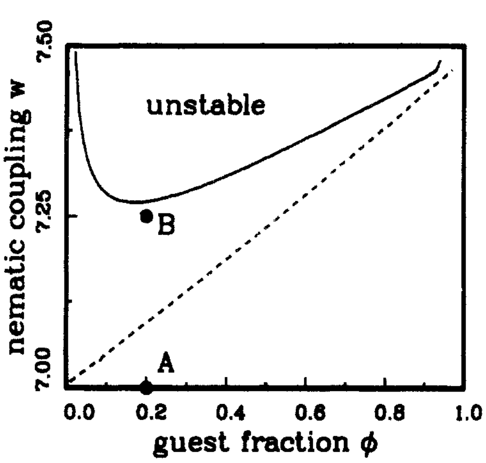

Figure 3. Spinodal curve for $\hat{\mathbf{k}}\|\hat{\mathbf{z}}$, $\lambda = 1.5$, $N_h = 20$, $N_g = 300$. The dashed line denotes the crossover between scattering dominated by orientational fluctuations (abnormal butterflies) at high w and scattering dominated by elastic fluctuations (normal butterflies). Scattering behavior at A is shown in Figure 4, while that at B is shown in Figure 5. The equilibrium isotropic–nematic transition occurs at $w_{\rm IN} = 7.49$.

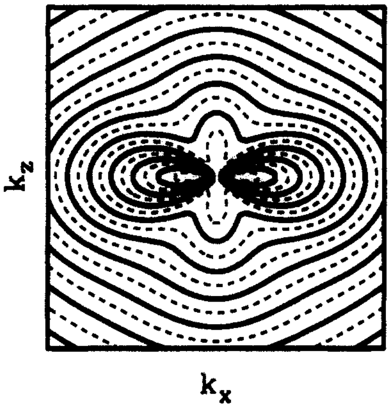

Figure 4. Normal butterfly scattering pattern for $\lambda = 1.5$, $w = 6.8$, $N_h = 20$, $N_g = 300$, $\phi = 0.2$. Point A in Figure 3.

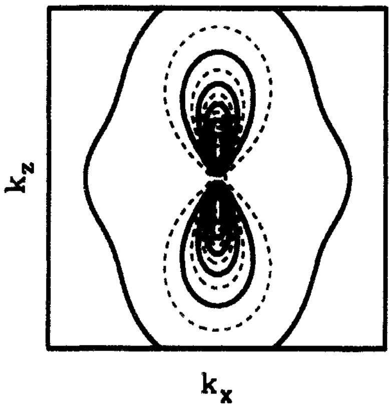

Figure 5. Abnormal butterfly scattering pattern for $\lambda = 1.5$, $w = 7.3$, $N_h = 20$, $N_g = 300$, $\phi = 0.2$. Point B in Figure 3.

the incipient phase-separation behavior. Figures 4 and 5 show the structure factor in these two regimes, displaying the characteristic normal and abnormal butterfly patterns. For these plots we have used the large-$\mathbf{k}$ structure factor $C(\mathbf{k}) = (k^2(1-\phi) + \mathbf{k}\cdot\mathbf{W}\cdot\mathbf{k}\phi)/(18\phi(1-\phi))$, which is slightly anisotropic in the "normal" direction.[41] We leave for the future a full calculation of the details of the structure factor at larger wavevectors. The structure factor in the nematic regime is strikingly similar to that observed in several recent experiments on strained networks and melts.[42,43]

These calculations are for $\chi = 0$; for a non-zero Flory incompatibility χ the value at which phase separation occurs is reduced. This raises an interesting distinction between the gel and the blend. A gel remains homogeneous at a much larger χ than does a melt of very long polymers, of size $N_{\rm mon} \gg N_g > N_h$ (recall again that N_h is the entanglement length in the melt, or strand length in the gel), because the entropic cost opposing phase separation in the melt, $(1-\phi)\log(1-\phi)/N_{\rm mon}$, is replaced in the gel by the much larger elastic cost, $\sim 1/N_h$. Hence we may only consider a very small χ ($\sim 1/N_g$) in the melt before the *unstrained* system is unstable to phase separation, while the gel is stable against phase separation for a larger χ ($\sim 1/N_h$). The effect of increasing χ on the strained state is therefore much different for the two cases. In a homogeneous melt χ is overwhelmed by the elastic effects on short time scales and undergoes "transient spinodal decomposition" into abnormal butterflies. In contrast, in a gel we may have a relatively large χ, and hence an applied strain can induce phase separation at a considerably lower w_ϕ. In fact, one can in principle induce phase separation in a gel in the regime where scattering is dominated by elastic fluctuations: i.e. the spinodal instability occurs for $\mathbf{k} \perp \hat{\mathbf{z}}$, to needles rather than pancakes. We emphasize that our discussion is limited to the initial instability, while later growth is dominated by nonlinear effects and should be quite interesting.

Finally, we mention the implications of these results for the experiments of ref 22. Polybutadiene has entanglement monomer number $N_e \sim 35$, and experiments were carried out at guest volume fractions $\phi \simeq 0.2$, with extension ratios of $\lambda \sim 30$–45%.[22] The experimental values for the ratio $\epsilon = S^g/S^h$ lay within (error bars) $\epsilon \in (0.78$–$0.98)$, hence placing w within (from eq 5.9) $w \in (6.12$–$7.4)$. A decrease in ϵ came as the guest molecular weight was increased above $N_g/N_e \sim 5$. Our calculations showed an instability to phase separation at the limits of these values: $N_e = 35$, $N_g = 300$, $\lambda = 1.5$, $w_{\rm IN} \simeq 7.4$, and for a choice of Landau coefficients which, though somewhat arbitrary, was guided by historical comparisons of theoretical and experimental studies of the I–N transition in low molecular weight liquid crystals. Hence the application of our theory to these particular experiments is suggestive, while by no means conclusive. Further tests to resolve the relevance of nematic interactions to this particular system include verifying whether or not there is an appreciable χ parameter between the protonated and deuterated butadiene chains and whether or not phase separation could have occurred in the systems with longer guests even *before* the application of strain; testing for the morphology of any phase separation that might appear under strain by, for example, neutron scattering, as has been performed by several other groups;[42,44,45] or examining the qualitative behavior of the system as solvent is added. Finally, we mention a related recent study. Liu and Fredrickson[46] have developed a theory for phase separation in blends of polymers with different flexibilities from which, by comparison with experiments of Bates *et al.*,[47] they predict nematic couplings in the range ${}^{15}/_{4}l_p^{-1} < w < {}^{15}/_{2}l_p^{-1}$, where l_p is the persistence length in units of the statistical segment length: for our discussion $l_p = 1$.

VII. Discussion and Conclusions

We have investigated the phase properties of strain applied to a polymer network containing a polymeric solvent, in which both network and solvent monomers interact via a Maier–Saupe-like nematic interaction. The analysis also applies to a melt where the time scales between the host and guest polymers are sufficiently well-separated that we may ignore the stress relaxation of the melt.

To lowest order a uniaxial strain acts as an external nematic field applied directly to the host monomers, while guest monomers interact indirectly with the external field through their orientational interaction with the host. Thus, the host and guest monomers respond differently to the applied strain and consequently are susceptible to phase separation. This simple linear coupling of strain to the nematic order parameter $\mathbf{Q}$ only strictly holds for a small $\mathbf{Q}$ Landau expansion, and for N_h monomers between network cross-links and strains λ such that $\lambda^2/N_h \lesssim 1$.

Strain fluctuations have important effects on the instability toward phase separation, due to the constraint relating the guest volume fraction ϕ to the strain $\nabla\mathbf{u}$; $\delta\phi = (1 - \phi)\nabla\cdot\mathbf{u}$. This relation is valid at wavelengths long compared to the network mesh size, and we assume the cross-link positions deform affinely. We find an anisotropic spinodal, with the dominant wavevector direction determined by a competition between the fluctuations described by classical elasticity theory, and the interactions of the strain field with nematic fluctuations, which tend to soften the shear modulus. For systems with a zero Flory parameter χ, nematic fluctuations dominate at the spinodal and the instability is toward layers modulated along the strain axis. This modulation comprises related variations in the composition, nematic order, and effective elastic moduli: in the guest-rich regions there are weaker elastic moduli and less orientational order, and the converse is true in the host-rich regions. The characteristic scattering pattern is of the "abnormal butterfly" type. For a given strain there is a crossover at a lower nematic coupling to a regime where the homogeneous state is dominated by elastic fluctuations, with a characteristic "normal butterfly" scattering pattern, and for a gel, a nonzero incompatibility χ between the network and solvent can actually lead to a spinodal in this "normal" regime.

We have performed our stability analysis at zero wavevector and thus cannot address the late stages of phase separation, particularly the kinetics or domain morphology. In the melt these late stages do not exist, of course, because any applied strain eventually relaxes. In a gel the equilibrium phase-separated state is determined by a competition between elastic strain and nematic interface energies, and is presumably a collection of anisotropic domains. The detailed morphology is determined by the nonlinearities in the theory, which we have not addressed. We also note that the nature of critical points in nonlinear elastic theories has been addressed by Golubović and Lubensky,[36] who predicted that strain fluctuations suppress true critical behavior in favor of a first-order transition, with apparent mean-field critical behavior.

Finally, we place this mechanism for producing the "abnormal butterfly" pattern in the context of several recent closely related theories. These may be grouped into theories which consider either (1) composition-dependent elastic moduli,[23,34] or (2) inhomogeneous elastic moduli, in terms of either heterogeneities in the cross-link distribution[44,45] or, equivalently, inhomogeneous coarse-grained elastic moduli.[48,49] The onset of phase separation is a mechanism for introducing inhomogeneities into the system aside from inhomogeneous cross-linking, and the presence of smaller solvent chains which do not couple directly to the strain introduces composition-dependent elastic moduli into the system; hence our description is consistent with these other theories and may be thought of as particular specific microscopic derivation of the macroscopic elastic moduli of a polymer gel. In particular, we have shown how nematic interactions can soften the shear modulus of the system and that the nonlinear elastic theory which describes a gel network hence makes use of this softening to enhance the "abnormal" butterfly pattern of composition fluctuations.

Appendix A: Derivation of the Landau Theory

Here we derive the Landau mean-field theory used in the main text. We first replace the operators $\hat{\mathbf{Q}}^h$ and $\hat{\mathbf{Q}}^g$ in the Maier–Saupe interaction by their mean values $\mathbf{Q}^h$ and $\mathbf{Q}^g$, hence approximating the Hamiltonian by

$$\frac{\mathcal{H}}{N_{tot}} = -\frac{1}{2}w_o \operatorname{Tr}[(1-\phi)\mathbf{Q}^h + \phi\mathbf{Q}^g]^2 - V^{-1}\int d^3r\, [(1-\phi)\mathbf{H}^h_{sc}:\hat{\mathbf{Q}}^h + \phi\mathbf{H}^g_{sc}:\hat{\mathbf{Q}}^g] \quad (A1)$$

We then demand self-consistency through eq 4.10.

The Landau free energy is determined by Legendre transforms from the self-consistent fields to the order parameters, and from the end-to-end vector stress $\boldsymbol{\Pi}$ to the end-to-end vector deformation $\mathbf{W}$. The remaining task is to calculate $\mathcal{F}[\Pi,\mathbf{H}^h,\mathbf{H}^g]$. After the nonlinear fluctuations in $\delta\hat{\mathbf{Q}}$ are ignored, the host and guest configuration integrals decouple from each other, and the mean-field partition function (4.1) becomes a product of single chain partition functions multiplied by an overall factor which accounts for the nematic interaction:

$$Z[\boldsymbol{\Pi},\mathbf{H}^h,\mathbf{H}^g] = (Z_1^h[\boldsymbol{\Pi},\mathbf{H}^g])^{n_g} \exp\left\{\frac{1}{2}N_{tot}w \operatorname{Tr}[(1-\phi)\mathbf{Q}^h + \phi\mathbf{Q}^g]^2\right\} \quad (A2)$$

The single chain partition function for a chain in a nematic field $\mathbf{H}$ with a force Π applied to the chain end points,

$$Z_1^h[\boldsymbol{\Pi},\mathbf{H}] = \int d^3R\, \mathcal{D}r^h \exp\left\{\frac{3}{N_h b^2}\mathbf{R}\cdot\boldsymbol{\Pi}\cdot\mathbf{R}\right\}\prod_{s=1}^{N_h} W_o[\mathbf{u}^h(s)] \times \delta(\mathbf{R} - \sum_{s=1}^{N_h}\mathbf{u}^h(s)) \exp\{\beta\rho(1-\phi)\int d^3r\, \mathbf{H}:\hat{\mathbf{Q}}^h\} \quad (A3)$$

may be rewritten as

$$Z_1^h[\boldsymbol{\Pi},\mathbf{H}] = \int d^3R \exp\left\{\frac{3}{N_h b^2}\mathbf{R}\cdot\boldsymbol{\Pi}\cdot\mathbf{R}\right\}\psi[\mathbf{R};\mathbf{H},N_h] \quad (A4)$$

where

$$\psi[\mathbf{R};\mathbf{H},N_h] = \int d^3k\, e^{i\mathbf{k}\cdot\mathbf{R}}\left[\int\frac{d\hat{\nu}}{4\pi}e^{\hat{\nu}\cdot\mathring{\mathbf{H}}\cdot\hat{\nu} + i\hat{\nu}\cdot\mathbf{k}}\right]^{N_b} \quad (A5)$$

is proportional to the propagator for a walk of N_h steps with end-to-end distance $\mathbf{R}$, in the presence of a nematic field $\mathbf{H}$. Note that only the traceless part of $\mathbf{H}$ appears. Here $\hat{\nu}$ is a unit bond orientation vector. Now we assume N_h is large enough so that we may truncate the integral in the brackets at quadratic order in $\mathbf{k}$[50] and expand this expression to quadratic order in the nematic field $\mathbf{H}$. After some algebra we obtain

$$\psi[\mathbf{R};\mathbf{H},N_h] \simeq I_0^{N_b}(\mathbf{H})[\det \mathbf{M}^{-1}(\mathbf{H})]^{-1/2} \times \exp\left\{-\frac{3}{2N_h b^2}\mathbf{R}\cdot\mathbf{M}(\mathbf{H})\cdot\mathbf{R}\right\} \quad (A6)$$

where

$$I_0^{N_h}(\mathbf{H}) = 1 + \frac{1}{15}\operatorname{Tr}\mathring{\mathbf{H}}^2 + \frac{4}{315}\operatorname{Tr}\mathring{\mathbf{H}}^3 + \frac{1}{630}(\operatorname{Tr}\mathring{\mathbf{H}}^2)^2 + \mathcal{O}(\mathbf{H}^5) \quad (A7)$$

and the Gaussian walk has been modified according to the following matrix:

$$\mathbf{M}^{-1}(\mathbf{H}) = \left[1 - \frac{4}{105}\,\mathrm{Tr}\,\mathring{\mathbf{H}}^2\right]\mathbf{I} + \frac{2}{5}\mathring{\mathbf{H}}\left[1 - \frac{23}{945}\,\mathrm{Tr}\,\mathring{\mathbf{H}}^2\right] + \frac{4}{35}\mathring{\mathbf{H}}^2 + \mathcal{O}(\mathbf{H}^4) \quad \text{(A8)}$$

The corrections to the Gaussian walk lead to the $\mathcal{O}(N_h^{-1})$ corrections to the host Landau coefficients (eqs 4.17). The free energy $\mathcal{F}_1{}^h = -k_BT \ln Z_1^h$, of the single host chain is now

$$\beta\mathcal{F}_1^h[\mathbf{\Pi},\mathbf{H}] = -N_h \ln I_0(\mathbf{H}) + \frac{1}{2}\,\mathrm{Tr}\ln\,[\mathbf{M}(\mathbf{H}) - 2\Pi] - \frac{1}{2}\,\mathrm{Tr}\ln\,\mathbf{M}(\mathbf{H}) \quad \text{(A9)}$$

where we have discarded constant terms. Upon performing a Legendre transform from $\mathbf{\Pi}$ to $\mathbf{W}$ via eqs 4.8–4.11, we find the thermodynamic potential for a single host chain,

$$\Phi_1^h[\mathbf{W},\mathbf{H}] = -N_h \ln I_0(\mathbf{H}) - \frac{1}{2}\,\mathrm{Tr}\ln\mathbf{W} + \frac{1}{2}\,\mathrm{Tr}[\mathbf{WM}(\mathbf{H}) - \mathbf{I}] - \frac{1}{2}\,\mathrm{Tr}\ln\mathbf{M}(\mathbf{H}) \quad \text{(A10)}$$

The final Legendre transform from $\mathbf{H}^h$ to $\mathbf{Q}$ via eqs 4.10 and 4.11 yields the single chain host free energy,

$$F_1^h[\mathbf{Q}^h,\mathbf{W}] = N_h f_N[\mathbf{Q}^h] + \frac{1}{2}[\mathrm{Tr}(\mathbf{W} - \mathbf{I}) - \log\det\mathbf{W}] - \frac{1}{5}A_h\mathring{\mathbf{W}}:\mathbf{Q}^h + \frac{1}{50}A_h\,\mathrm{Tr}\,\mathring{\mathbf{W}}^2/N_h \quad \text{(A11)}$$

In this expansion we have kept terms to $\mathcal{O}(N_h^{-2})$, because $\mathbf{Q} \sim 1/N_h$ after minimizing, and we assume strains $\mathbf{W}$ of order 1. Performing the same procedure for the guest chains, without the field $\mathbf{\Pi}$, yields the simpler single-chain free energy: $\mathcal{F}_1^g[\mathbf{Q}^g] = N_g f_N[\mathbf{Q}^g]$.

Up to this point we have only considered the conformational degrees of freedom. To account for the entire free energy change, we must include the constraint that the n_h chains are connected by cross-links (gel) or entanglement points (melt) into a network.[29] This connectivity may be accommodated, within mean-field theory, by multiplying the partition function by the probability $\mathcal{P}[n_h] \sim (\nu/V)^{2n_h/z}$, where $2n_h$ is the number of chain ends, z is the coordination number (we take $z = 4$), ν is the volume of a cross-link, and ν/V is the a priori probability of a cross-link occurring. The contribution to the free energy from this constraint is then $F_{\text{net}} = -k_BT \ln \mathcal{P}$. This contribution changes under deformations which do not preserve volume, yielding[29,51]

$$\beta\Delta F_{\text{net}} = \frac{1}{4}n_h\,\mathrm{Tr}\ln\mathbf{W} \quad \text{(A12)}$$

Combining the single-chain free energies for n_h host chains and n_g guest chains, the contribution due to nematic interactions (i.e. the last term in eq A2), and the connectivity correction ΔF_{net}, we obtain the total deformation free energy:

$$F[\mathbf{W},\mathbf{Q}^h,\mathbf{Q}^g,\phi] = n_hF_1^h[\mathbf{Q}^h,\mathbf{W}] + n_gN_gf_N[\mathbf{Q}^g] - \frac{1}{2}N_{\text{tot}}w\,\mathrm{Tr}[(1-\phi)\mathbf{Q}^h + \phi\mathbf{Q}^g]^2 + \Delta F_{\text{net}} \quad \text{(A13)}$$

The free energy density quoted in the text, eq 4.14, follows upon normalizing F by the total monomer number $N_{\text{tot}} = n_hN_h + n_gN_g$.

Appendix B: Calculation of the Structure Factor

In this appendix we outline the reduction of the fluctuation free energy to an effective free energy governing composition fluctuations. The fluctuating quantities are host and guest orientation $\mathbf{Q}^h$ and $\mathbf{Q}^g$, and the strain field, $\nabla_\alpha u_\beta$. Throughout this appendix we use the incompressibility relations $\delta\phi = (1-\phi)\nabla\cdot\mathbf{u}$ and $\delta\phi(\mathbf{k}) = (1-\phi)i\mathbf{k}\cdot\mathbf{u}(\mathbf{k})$. We begin by expanding using eq 6.1 about states which minimize the free energy, eq 4.14, according to eqs 4.13a and 4.13b. Since the order parameters are of order $1/N_h$ we parametrize the orientational order by

$$\mathbf{Q}^h = \frac{\tilde{S}_h}{N_h}\mathrm{e}_1 \quad \text{(B1)}$$

and similarly for the guest, where we use the following basis of orthonormal traceless-symmetric tensors:

$$\mathbf{e}_1 = \sqrt{3/2}\left(\hat{\mathbf{z}}\hat{\mathbf{z}} - \frac{1}{3}\mathbf{I}\right) \quad \text{(B2a)}$$

$$\mathbf{e}_2 = \sqrt{1/2}(\hat{\mathbf{x}}\hat{\mathbf{x}} - \hat{\mathbf{y}}\hat{\mathbf{y}}) \quad \text{(B2b)}$$

$$\mathbf{e}_3 = \sqrt{1/2}(\hat{\mathbf{z}}\hat{\mathbf{x}} - \hat{\mathbf{x}}\hat{\mathbf{z}}) \quad \text{(B2c)}$$

$$\mathbf{e}_4 = \sqrt{1/2}(\hat{\mathbf{z}}\hat{\mathbf{y}} - \hat{\mathbf{y}}\hat{\mathbf{z}}) \quad \text{(B2d)}$$

$$\mathbf{e}_5 = \sqrt{1/2}(\hat{\mathbf{x}}\hat{\mathbf{y}} + \hat{\mathbf{y}}\hat{\mathbf{x}}) \quad \text{(B2e)}$$

which satisfy $\mathbf{e}_a:\mathbf{e}_b = \delta_{ab}$. The fluctuation free energy in the presence of $\mathbf{W}$, $\mathbf{Q}^h$, and $\mathbf{Q}^g$ is (expanding eq 4.14 according to eq 6.1)

$$\begin{aligned}\beta f_{\text{fluc}}[\nabla_\alpha u_\beta,\delta\mathbf{Q}^h,\delta\mathbf{Q}^g] = {}& \frac{1}{2}\phi[\alpha_g\,\mathrm{Tr}(\delta\mathbf{Q}^g)^2 - \beta_g\,\mathrm{Tr}\,(\delta\mathbf{Q}^g)^2\mathrm{e}_1 + \\ & \gamma_g(\mathrm{Tr}\,\mathbf{Q}^g\mathbf{e}_1)^2] + \frac{1}{2}(1-\phi)[\alpha_h\,\mathrm{Tr}(\delta\mathbf{Q}^h)^2 - \beta_h\,\mathrm{Tr}\,(\delta\mathbf{Q}^h)^2\mathrm{e}_1 + \\ & \gamma_h(\mathrm{Tr}\,\mathbf{Q}^g\mathrm{e}_1)^2] - w\phi(1-\phi)\delta\mathbf{Q}^h:\delta\mathbf{Q}^g - \\ & \frac{2A_h(1-\phi)}{15N_h}\mathrm{Tr}(\delta\mathbf{Q}^h\cdot\mathbf{W}\cdot\nabla\mathbf{u}) + \frac{1}{2}\left[\frac{1}{N_g\phi} - \frac{w(\tilde{S}_h - \tilde{S}_g)^2}{N_h{}^2} + \right. \\ & \left.\frac{1}{2N_h(1-\phi)} - 2\chi\right]\delta\phi^2 + \frac{w(\tilde{S}_h - \tilde{S}_g)}{N_h}\mathbf{e}_1:[\phi\delta\mathbf{Q}^g + (1 - \\ & \phi)\delta\mathbf{Q}^h]\delta\phi + \frac{(1-\phi)}{2N_h}W_{\alpha\beta}[\nabla_\alpha\mathbf{u}\cdot\nabla u_\beta + \nabla_\alpha\mathbf{u}\cdot\nabla_\beta\mathbf{u} - \\ & \nabla_\alpha u_\beta\nabla\cdot\mathbf{u}] + \frac{A_h(1-\phi)\tilde{S}_h(1-\phi)}{5N_h}[(\mathrm{e}_1\mathbf{W}):\nabla\mathbf{u}(\nabla\cdot\mathbf{u}) - \\ & W_{\lambda\beta}\mathbf{e}_1:\nabla_\lambda\mathbf{u}\nabla_\beta\mathbf{u} - (\mathbf{e}_1\mathbf{W})_{\alpha\beta}\nabla_\beta\mathbf{u}\cdot\nabla u_\alpha] + \\ & \frac{2A_h(1-\phi)}{25N_h{}^2}[2(\mathbf{W}\cdot\nabla\mathbf{u}):\mathbf{P}:(\mathbf{W}\cdot\nabla\mathbf{u}) + (\mathring{\mathbf{W}}\mathbf{W})_{\alpha\beta}\nabla\cdot u_\alpha\nabla_\beta\mathbf{u} + \\ & \mathring{W}_{\lambda\rho}W_{\alpha\beta}\nabla_\alpha u_\lambda\nabla_\beta u_\rho - (\mathring{\mathbf{W}}\mathbf{W})_{\alpha\beta}\nabla_\beta u_\alpha\nabla\cdot\mathbf{u}] \quad \text{(B3)}\end{aligned}$$

In obtaining this we have used the relation $\partial W_{\alpha\beta}/\partial(\nabla_\lambda u_\rho) = W_{\alpha\lambda}\delta_{\beta\rho} + W_{\beta\lambda}\delta_{\alpha\rho}$, which follows from eq 2.12. $P_{\sigma\beta\mu\rho} = {}^1/_2(\delta_{\sigma\mu}\delta_{\beta\rho} + \delta_{\beta\mu}\delta_{\sigma\rho} - {}^2/_3\delta_{\sigma\beta}\delta_{\mu\rho})$ is the projector onto traceless-symmetric tensors. We have defined coefficients

$$\alpha_h = A_h - w(1-\phi) + C\tilde{S}_h{}^2/N_h{}^2 \quad \text{(B4a)}$$

$$\beta_h = 2B_h\tilde{S}_h/N_h \quad \text{(B4b)}$$

$$\gamma_h = 2C_h\tilde{S}_h{}^2/N_h{}^2 \quad \text{(B4c)}$$

$$\alpha_g = A_g - w\phi + C\tilde{S}_g{}^2/N_h{}^2 \quad \text{(B4d)}$$

$$\beta_g = 2B_g\tilde{S}_g/N_h \quad \text{(B4e)}$$

$$\gamma_g = 2C_g\tilde{S}_g{}^2/N_h{}^2 \qquad \text{(B4f)}$$

It is now straightforward to integrate out the orientation fluctuations $\delta\mathbf{Q}^h$ and $\delta\mathbf{Q}^9$ to obtain the free energy governing strain and composition fluctuations. To perform these Gaussian integrals, we project the order parameter onto the basis $\{\mathbf{e}_a\}$ and perform the integration over the amplitudes of the independent modes $\{\eta\}$. For example, terms involving $\mathbf{Q}^g$, which appear in the form

$$\Delta F_g = \frac{1}{2}Q^g_{\alpha\beta}M_{\alpha\beta\lambda\rho}Q^g_{\lambda\rho} + \mathbf{Q}^g{:}\mathbf{V} \qquad \text{(B5)}$$

may be written as

$$\Delta F_g = \frac{1}{2}\eta_a{}^g(K^g)_{ab}{}^{-1}\eta_b{}^g + \eta_a{}^g v_a \qquad \text{(B6)}$$

where

$$\mathbf{Q}^g = \eta_a{}^g\mathbf{e}_a \qquad \text{(B7)}$$

$$M_{\alpha\beta\lambda\rho} = (\mathbf{e}_a)_{\alpha\beta}(K^g)^{-1}_{ab}(\mathbf{e}_b)_{\lambda\rho} \qquad \text{(B8)}$$

$$\eta^g_a = \mathbf{e}_a{:}\mathbf{Q}^g \qquad \text{(B9)}$$

$$(K^g)^{-1}_{ab} = \mathbf{e}_a{:}\mathbf{M}{:}\mathbf{e}_b \qquad \text{(B10)}$$

and similarly for $\mathbf{V}$. (We sum over repeated Latin indices $a, b = 1, ..., 5$.) For the case at hand a direct calculation shows that

$$(K^g)_{ab}{}^{-1} = \alpha_g\delta_{ab} - \beta_g\,\mathrm{Tr}(\mathbf{e}_a\mathbf{e}_1\mathbf{e}_b) + \gamma_g\delta_{a1}\delta_{b1} \qquad \text{(B11)}$$

$$v_a = w\phi(1-\phi)[\nabla\cdot\mathbf{u}\delta_{a1}(\tilde{S}_g - \tilde{S}_h)/N_h + \eta^h_a] \qquad \text{(B12)}$$

The Gaussian integral over the independent degrees of freedom $\{\eta^g_a\}$ may then be performed immediately. We perform the integral over the host degrees of freedom in an analogous manner, introducing

$$(K^h)_{ab}{}^{-1} = \alpha_h\delta_{ab} - \beta_h\,\mathrm{Tr}(\mathbf{e}_a\mathbf{e}_1\mathbf{e}_b) + \gamma_h\delta_{a1}\delta_{b1} - w^2\phi(1-\phi)K^g_{ab} \qquad \text{(B13)}$$

Explicit calculation shows that $\mathrm{Tr}(\mathbf{e}_a\mathbf{e}_1\mathbf{e}_b) = \mathrm{diag}(1,-1,{}^1/_2,{}^1/_2,-1)/\sqrt{6}$ is a diagonal matrix in the indices $a, b = 1, 5$; and hence so are $\mathbf{K}^g$ and $\mathbf{K}^h$. We finally arrive at the following effective free energy in terms of strain and composition fluctuations:

$$\beta f_{\mathrm{fluc}} = \frac{1}{2}\Bigg[\frac{1}{N_g\phi} - \frac{w(\tilde{S}_h - \tilde{S}_g)^2}{N_h{}^2} + \frac{1}{2N_h(1-\phi)} - 2\chi - \frac{w^2(\tilde{S}_h - \tilde{S}_g)^2}{N_h{}^2}[1 + \phi K^g_{11} + (1-\phi)K^h_{11}(1 + w\phi K^g_{11})^2]\Bigg]\delta\phi^2 - \frac{4A_h{}^2\boldsymbol{\xi}\cdot\mathbf{K}^h\cdot\boldsymbol{\xi}}{25N_h{}^2(1-\phi)} + \frac{4A_h w(\tilde{S}_h - \tilde{S}_g)}{5N_h{}^2}\xi_1 K^h_{11}[1 + w\phi K^g_{11}]\delta\phi + \frac{(1-\phi)}{2N_h}W_{\alpha\beta}[\nabla_\alpha\mathbf{u}\cdot\nabla u_\beta + \nabla_\alpha\mathbf{u}\cdot\nabla_\beta\mathbf{u} - \nabla_\alpha u_\beta\nabla\cdot\mathbf{u}] + \frac{A_h(1-\phi)\tilde{S}_h(1-\phi)}{5N_h}[(\mathbf{e}_1\mathbf{W}){:}\nabla\mathbf{u}(\nabla\cdot\mathbf{u}) - W_{\lambda\beta}\mathbf{e}_1{:}\nabla_\lambda\mathbf{u}\nabla_\beta\mathbf{u} - (\mathbf{e}_1\mathbf{W})_{\alpha\beta}\nabla_\beta\mathbf{u}\cdot\nabla u_\alpha] + \frac{2A_h(1-\phi)}{25N_h{}^2}[2(\mathbf{W}\cdot\nabla\mathbf{u}){:}\mathbf{P}{:}(\mathbf{W}\cdot\nabla\mathbf{u}) + (\mathring{\mathbf{W}}\mathbf{W})_{\alpha\beta}\nabla\cdot u_\alpha\nabla_\beta\mathbf{u} + \mathring{W}_{\lambda\rho}W_{\alpha\beta}\nabla_\alpha u_\lambda\nabla_\beta u_\rho - (\mathring{\mathbf{W}}\mathbf{W})_{\alpha\beta}\nabla_\beta u_\alpha\nabla\cdot\mathbf{u}] \qquad \text{(B14)}$$

Here we have introduced $\xi_a = (1-\phi)\,\mathrm{Tr}[\mathbf{e}_\alpha\mathbf{W}(\nabla\mathbf{u})]$.

We now transform to Fourier space and make the simplifying approximation of keeping terms only to order $1/N_h{}^2$. This enables us to replace $\nabla_\alpha u_\beta$ above by $i\hat{k}_\alpha\hat{k}_\beta\delta\phi(\mathbf{k})/(1-\phi)$ and drop the transverse strain degrees of freedom, because an explicit integration over the transverse strain degrees of freedom introduces terms of order $1/N_h{}^3$ or smaller. We then have

$$\xi_a = \hat{\mathbf{k}}\cdot\mathbf{e}_a\mathbf{W}\cdot\hat{\mathbf{k}} \qquad \text{(B15)}$$

and, for uniaxial strain,

$$\xi_1 = \frac{1}{\sqrt{6}}[\cos^2\theta(2\lambda^2 + \lambda^{-1}) - \lambda^{-1}] \qquad \text{(B16a)}$$

$$\xi_2 = \frac{1}{\sqrt{2}}\lambda^{-1}\sin^2\theta \qquad \text{(B16b)}$$

$$\xi_3 = \frac{1}{\sqrt{2}}(\lambda^2 + \lambda^{-1}) \qquad \text{(B16c)}$$

$$\xi_4 = \xi_5 = 0 \qquad \text{(B16d)}$$

Performing this substitution yields the free energy in the text, eq 6.3, with the following wavevector-dependent contribution to the structure factor, $S_0{}^{-1}(\hat{\mathbf{k}})$, given to order $1/N_h{}^2$ by

$$\beta\rho^{-1}S_0{}^{-1}(\hat{\mathbf{k}}) = \frac{1}{N_g\phi} + \frac{1 + 2J_1(\hat{\mathbf{k}})}{2N_h(1-\phi)} + \frac{2A_g}{25N_h{}^2(1-\phi)}\Big[J_2(\hat{\mathbf{k}}) + \frac{1}{3}J_1{}^2(\hat{\mathbf{k}}) + I_0(\hat{\mathbf{k}})J_1(\hat{\mathbf{k}})\Big] - \frac{2}{3}w^2(S_h - S_g)^2[1 + \phi K^g_{11} + (1-\phi)K^h_{11}(1 + w\phi K^g_{11})^2] - \frac{2A_gS_hJ_1(\hat{\mathbf{k}})(3\cos^2\theta - 1)}{15N_h(1-\phi)} - \frac{4A_g{}^2\boldsymbol{\xi}(\hat{\mathbf{k}})\cdot\mathbf{K}^h\cdot\boldsymbol{\xi}(\hat{\mathbf{k}})}{25N_h{}^2(1-\phi)} + \frac{4A_gw\sqrt{\frac{2}{3}}(S_h - S_g)}{5N_h}\xi_1(\hat{\mathbf{k}})K^h_{11}[1 + w\phi K^g_{11}] - 2\chi \qquad \text{(B17)}$$

This is one of the primary results of this work. We have renormalized the order parameters to

$$\mathbf{Q}^h = S_h\left(\hat{\mathbf{z}}\hat{\mathbf{z}} - \frac{1}{3}\mathbf{I}\right) \qquad \text{(B18)}$$

and similarly for the guest, where S_g and S_h satisfy the equilibrium conditions (4.13a) and are of order $1/N_h$ ($S^h = (3/2)^{1/2}\tilde{S}^h/N_h$, $S^g = (3/2)^{1/2}\tilde{S}^g/N_h$). In this expression we have defined several angular functions which, for uniaxial volume-preserving ($c = 1$) strain take the forms ($\hat{\mathbf{k}}\cdot\hat{\mathbf{z}} = \cos\theta$)

$$I_0(\hat{\mathbf{k}}) = \hat{\mathbf{k}}\cdot\mathring{\mathbf{W}}\cdot\hat{\mathbf{k}} = \frac{1}{3}(\lambda^2 - \lambda^{-1})(3\cos^2\theta - 1) \qquad \text{(B19a)}$$

$$J_1(\hat{\mathbf{k}}) = \hat{\mathbf{k}}\cdot\mathbf{W}\cdot\hat{\mathbf{k}} = (\lambda^2 - \lambda^{-1})\cos^2\theta + \lambda^{-1} \qquad \text{(B19b)}$$

$$J_2(\hat{\mathbf{k}}) = \hat{\mathbf{k}}\cdot\mathbf{W}^2\cdot\hat{\mathbf{k}} = (\lambda^4 - \lambda^{-2})\cos^2\theta + \lambda^{-2} \qquad \text{(B19c)}$$

$I_0(\hat{\mathbf{k}})$ vanishes and $J_1(\hat{\mathbf{k}})$ and $J_2(\hat{\mathbf{k}})$ become unity for zero strain ($\lambda = 1$).

References and Notes

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