Phase Separation Kinetics of Rod/Coil Mixtures

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ABSTRACT: Equations of motion are presented that describe the kinetics of phase separation of mixtures of rods and coils into an isotropic phase rich in coils and a nematic phase rich in rods. The equations were derived using dynamical mean field theory and contain only a few pure-component parameters, such as the self-diffusion coefficients and molecular weights of the rods and coils. In such a system, both composition and orientation density evolve with time in a coupled fashion, so the presence of orientational order has a pronounced effect on the domain morphology at all but the latest stages of phase separation. The formalism presented here will provide insights into the control of domain morphology and properties of bicontinuous polymeric structures produced by quenching spinodal decomposition processes.

I. Introduction

Mixtures of liquid crystalline molecules with flexible engineering polymers have attracted widespread interest because of their potential applications. Polymer-dispersed liquid crystals and polymer-stabilized liquid crystals have been used in electro-optic applications such as liquid displays and light shutters.[1,2] On the other hand, blends of flexible polymers with "high-performance" polymers, such as liquid crystalline polymers (LCP's) or stiff conjugated (electrically conducting) polymers, have unique properties imparted by the high-performance polymers, such as high tensile strength or electrical conductivity.[3,4] Because high-performance polymers are often quite costly, there is an incentive to develop blends with relatively small amounts of the high-performance additive. For example, conducting polymer blends have been prepared where less than 3% of surfactant-stabilized polyaniline is dispersed in a fibrillar network that macroscopically spans a poly(methyl methacrylate) (PMMA) matrix.[5] Thin films of this material have been used as electrodes in plastic light-emitting diodes.

In spite of the considerable promise of high-performance blends and small-molecule liquid crystal/polymer mixtures, surprisingly little theoretical work has been done to elucidate the factors that control their morphology. This is difficult because these blends are almost never homogeneous dispersions; rather, they are composites of domains of different phases. For example, the blends tend to separate into an isotropic phase rich in the flexible polymer, coexisting with a nematic phase rich in the rodlike component.[6,7] In true equilibrium, these phases would separate completely. Therefore, in most cases the domain morphology of a blend depends on the nonequilibrium process of phase separation and is often preserved by quenching the slowly phase-separating system below a glass or freezing transition. Our aim in the present paper is to develop a theoretical framework capable of describing the kinetics of phase separation in blends of rodlike molecules with flexible coils. The rods could be either short, to model liquid crystals, or long, to model liquid crystalline polymers. While thermotropic LCP's are generally semiflexible rather than perfectly rigid, a rodlike description is at least suggestive of their dynamical behavior. Moreover, we note that conjugated polymers can be quite stiff due to electronic delocalization; indeed, surfactant-stabilized polyaniline is known to exhibit nematic order in solution.[8] Thus, we will also model conjugated polymers as long rods.

It is known experimentally that the kinetics of phase separation in rod/coil mixtures can lead to very different morphologies than are found in flexible polymer blends. For example, in the case of polyaniline in PMMA[5] mentioned above, the rodlike component can form fibrillar domains that connect into a continuous network even at relatively low volume fractions.[9] From a theoretical point of view, the main difference is the presence of orientational order in one of the emerging phases. As the system phase separates into an isotropic phase rich in coils and a nematic phase rich in rods, both composition and orientational densities evolve as a function of position and time and must be tracked in order to completely specify the morphological state. Thus, there are two order parameter fields in the problem. This should be contrasted with the more commonly studied case of a blend of two flexible homopolymers, where only a single composition field, namely the volume fraction of one component, needs to be tracked with time. The volume fraction of the other component can then be deduced using the condition of incompressibility.

Our approach is to use dynamical mean field theory to derive equations of motion for the local composition and local orientational density. The equations of motion contain transport coefficients (i.e. Onsager coefficients) multiplying thermodynamic forces that can be expressed as derivatives of an appropriate free energy functional. Dynamical mean field theory (essentially the dynamical random phase approximation) enables us to express the Onsager coefficients in terms of single-macromolecule quantities, such as the translational diffusion coefficient of the coil and the rotational diffusion coefficient of the rod. The final ingredient in the equations of motion is a nonlocal, nonlinear free energy functional that has already been calculated in terms of both order param-

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eters for the general case of a mixture of two wormlike polymers with arbitrary bending rigidities.[10] The rod/coil blend considered here is a special case of the mixtures examined in ref 10.

To our knowledge, there have only been two previous calculations aimed at understanding the kinetics of phase separation in isotropic/nematic mixtures. Shimada et al.[11] considered the special case of a rod/solvent mixture. Their calculation was restricted to the linear regime, where only small deviations are present in the composition and orientation from the homogeneous, isotropic state. In contrast, our equations are applicable to a broad class of rigid/flexible mixtures and can be carried into the nonlinear regime, where they provide a basis for numerical solutions.[12] Lansac et al.[13] have also described the phase separation kinetics using two coupled equations of motion, but they neglect cross terms that originate from generalized currents in composition and orientation due to nonlocal forces. We believe that these neglected terms must be restored in order to achieve a realistic dynamical model of phase separation kinetics in rigid/flexible blends.

Our strategy for deducing the equations of motion for the composition and orientational densities is as follows. We begin by calculating the linear response functions for a hypothetical noninteracting mixture of rods and coils in section II. We then use dynamical mean field theory to express the response functions of the interacting system in terms of those for the noninteracting system in section III. The next step is to extract the Onsager coefficients from the response functions in section IV; note that the Onsager coefficients are therefore derived assuming linear response. We present our resulting equations of motion and discuss their physical significance in section V. Finally, in section VI, we apply the equations of motion to examine the early stage (linearized) spinodal decomposition of a system quenched from a mixed isotropic state into a region of coexistence between an isotropic phase rich in coils and a nematic phase rich in rods.

II. Response Functions of Noninteracting Rods and Coils

Our first step toward computing Onsager coefficients is to derive a set of linear response functions. We start by calculating response functions for a hypothetical solution of noninteracting rods (species A) at average volume fraction ϕ_A in an external potential and for a solution of noninteracting coils at volume fraction ϕ_B in an external potential. These noninteracting response functions will then be combined in section III, using dynamical mean field theory to obtain the response functions for an interacting mixture of rods and coils at volume fractions ϕ_A and $\phi_B = 1 - \phi_A$, respectively. Both the rods and coils are assumed to consist of cylindrical segments of length a_0, diameter $d_0 = a_0\sqrt{4/\pi}$, and volume $v_0 = a_0{}^3$. It will prove convenient in the following to scale all lengths by a_0; hence, we subsequently work in units for which $a_0 = v_0 = 1$. The rods are taken to be N_A segments long, and the coils are N_B segments long. Each segment of a coil has an orientation that is uncorrelated with the orientations of all other segments (freely jointed model). Our ultimate aim is to deduce equations of motion for the two collective order parameters at relatively long times, when the intrachain coordinates have attained local equilibrium, but the composition and orientational densities have not yet reached their equilibrium values. Because we are interested in the long-time response, it is convenient to work with Fourier–Laplace transforms and focus on the response to a low-frequency perturbing potential.

The two order parameters of interest in the present paper are a nematic orientation density of rodlike segments, $S^{ij}(\vec{r},t)$, defined microscopically for a single rod by

$$S^{ij}(\vec{r},t) \equiv \int_0^{N_A} \mathrm{d}s\ \delta(\vec{r} - \vec{R}(s,t))\left(u_i(t)\ u_j(t) - \frac{1}{3}\delta_{ij}\right) \tag{1}$$

and the A-species (rodlike) segment number density, $\phi_A(\vec{r},t)$, defined by

$$\phi_A(\vec{r},t) \equiv \int_0^{N_A} \mathrm{d}s\ \delta(\vec{r} - \vec{R}(s,t)) \tag{2}$$

In the above expressions, s indexes the segments along a rod and $\vec{R}(s,t)$ denotes the position of the sth segment at time t. The quantity $\vec{u}(t)$ is a unit vector indicating the rod orientation at time t. We employ lower case italic subscripts and superscripts to denote elements of vectors and tensors in a fixed Cartesian laboratory frame; repeated indices imply summation (Einstein convention). An expression identical in form to eq 2 can be written for the number density of the flexible coil species B, $\phi_B(\vec{r},t)$. Finally, we note that since we work in units where $a_0 = v_0 = 1$, $\phi_A(\vec{r},t)$ and $\phi_B(\vec{r},t)$ can be interpreted as volume fractions.

Next, we introduce Fourier–Laplace transforms, defined for example for the case of the orientation density by

$$S^{ij}(\vec{q},\omega) = \int_0^{\infty} \mathrm{d}t \int \mathrm{d}\vec{r}\ e^{i\vec{q}\cdot\vec{r}+i\omega t} S^{ij}(\vec{r},t) \tag{3}$$

Similar expressions can be written for the transforms of the two microscopic volume fractions $\phi_A(\vec{r},t)$ and $\phi_B(\vec{r},t)$. We now consider the linear dynamical response of the coil species B in a hypothetical state in which the B coils are noninteracting, both with each other and with the rods, but are present at the average mixture volume fraction ϕ_B. A weak external chemical potential field (conjugate to B) with wavevector $\vec{q}$ and frequency ω, $h_\phi^B(\vec{q},\omega)$, gives rise to a small change in the ensemble-averaged volume fraction of coils $\phi_B(\vec{q},\omega)$:

$$\phi_B(\vec{q},\omega) = \chi_{\phi,\phi}^B(\vec{q},\omega)\ h_\phi^B(\vec{q},\omega) \tag{4}$$

where $\chi_{\phi,\phi}^B(\vec{q},\omega)$ is the linear response function of the noninteracting system. Since we are only interested in the low-frequency response (times longer than the longest internal Rouse or reptation time), we assume that the dynamics of a noninteracting chain can be represented by a single center-of-mass diffusion coefficient, D_B. For the solution of noninteracting coils, the resulting response function is then[14,15]

$$\chi_{\phi,\phi}^B(\vec{q},\omega) = \frac{q^2 D_B S_B(\vec{q})}{-i\omega + D_B q^2} \tag{5}$$

where $S_B(\vec{q}) = \phi_B N_B g(q^2 R_g^2) \approx \phi_B N_B$ and is the static structure factor, ϕ_B is the average volume fraction of coils, N_B is the degree of polymerization of the coils, R_g is the radius of gyration of the coils, and $g(x)$ is the Debye function.[16] This expression is accurate for wavevectors that are small compared to the inverse radius of gyration of the chain and at time scales that are long compared to the relaxation times of the internal Rouse or reptation modes.

For a solution of rods, the calculation of the noninteracting response functions is considerably more complex. There are four important response functions to be obtained, corresponding to the response of ϕ_A and S^{ij} to an external potential $h_\phi(\vec{q},\omega)$ conjugate to the volume fraction of rods and to an external potential $h_S^{ij}(\vec{q},\omega)$ that is conjugate to the orientation density $S^{ij}(\vec{q},\omega)$ of the rods. In order to calculate the response of the rods to these potentials, we use the Doi equation[11,16] for the distribution function $f(\vec{r},\vec{u},t)$. This distribution function represents the probability density of finding any rod in the noninteracting solution oriented along $\vec{u}$, with its center of mass at $\vec{r}$ at time t. The distribution function is normalized such that $\int \mathrm{d}\vec{u} \int \mathrm{d}\vec{r}\, f = n_{\mathrm{rods}}$, where n_{rods} is the number of rods in the system. The Doi equation is an equation of motion for f in an external field $h(\vec{r},\vec{u},t)$ that acts on a rod with orientation $\vec{u}$ at position $\vec{r}$:

$$\frac{\partial f}{\partial t} = \frac{\partial}{\partial \vec{r}}\cdot[D_{\|}\vec{u}\vec{u} + D_{\perp}(I - \vec{u}\vec{u})]\cdot\left[\frac{\partial f}{\partial \vec{r}} + f\frac{\partial h}{\partial \vec{r}}\right] + D_{\mathrm{r}} R\cdot[Rf + fRh] \quad (6)$$

where I is the second rank identity matrix, $D_{\|}$ and $D_{\perp}$ are the parallel and perpendicular components of the translational diffusion coefficient tensor, D_{r} is the rotational diffusion coefficient, and R is the rotational operator $R = \vec{u} \times \partial/\partial\vec{u}$. The operator R^2 is perhaps more familiar as the Laplacian on the unit sphere. The expectation values of the volume fraction $\phi \equiv \phi_A$ and orientation density order parameters can be expressed as linear functionals of the distribution function:

$$\phi(\vec{r},t) = \int \mathrm{d}\vec{u} \int \mathrm{d}\vec{r}\,' \int_0^{N_A} \mathrm{d}s\, \delta\left(\vec{r} - \left[\vec{r}\,' + \left(s - \frac{1}{2}N_A\right)\vec{u}\right]\right) f(\vec{r}\,',\vec{u},t)$$

$$S^{ij}(\vec{r},t) = \int \mathrm{d}\vec{u} \int \mathrm{d}\vec{r}\,' \int_0^{N_A} \mathrm{d}s\, \delta\left(\vec{r} - \left[\vec{r}\,' + \left(s - \frac{1}{2}N_A\right)\vec{u}\right]\right)\left(u_i u_j - \frac{1}{3}\delta_{ij}\right) f(\vec{r}\,',\vec{u},t) \quad (7)$$

In Fourier space, these order parameters are

$$\phi(\vec{q},t) = N_A \int \mathrm{d}\vec{u}\, j_0\left(\frac{1}{2}N_A \vec{q}\cdot\vec{u}\right) f(\vec{q},\vec{u},t)$$

$$S^{ij}(\vec{q},t) = N_A \int \mathrm{d}\vec{u}\, j_0\left(\frac{1}{2}N_A \vec{q}\cdot\vec{u}\right)\left(u_i u_j - \frac{1}{3}\delta_{ij}\right) f(\vec{q},\vec{u},t) \quad (8)$$

where $j_0(x) = \sin x/x$. Next, we apply external fields h_ϕ and h_S^{ij} conjugate to ϕ and S^{ij}. The resulting external potential is

$$\begin{aligned} V(\vec{q},t) &= V_\phi(\vec{q},t) + V_S^{ij}(\vec{q},t) \\ &= -h_\phi(\vec{q},t)\,\phi(-\vec{q},t) - h_S^{ij}(\vec{q},t)\, S^{ij}(-\vec{q},t), \end{aligned} \quad (9)$$

so the equivalent external field acting on a *rod* at $\vec{r}$ with orientation $\vec{u}$ at time t is

$$h(\vec{r}\,',\vec{u},t) = N_A \int \frac{\mathrm{d}\vec{q}}{(2\pi)^3} e^{-i\vec{q}\cdot\vec{r}\,'} j_0\left(\frac{1}{2}N_A \vec{q}\cdot\vec{u}\right)\left[h_\phi(\vec{q},t) + h_S^{ij}(\vec{q},t)\left(u_i u_j - \frac{1}{3}\delta_{ij}\right)\right] \quad (10)$$

This is the external field that appears in eq 6. We note that the above expression is a nonlocal relation between h and h_ϕ, h_S, arising from the fact that the fields h_ϕ and h_S act on all monomers of a rod, even those at a distance away from the center of mass.

With the effective external field (eq 10) in hand, we can now use eq 6 to calculate the response of the solution to the weak external fields h_ϕ and h_S. We linearize the distribution function f around its isotropic value: $f_0(\vec{r},\vec{u},t) = \phi/4\pi N_A$, where ϕ/N_A is the average number density of rods. We then Fourier–Laplace transform the Doi equation to work with $f(\vec{q},\vec{u},\omega)$. By forming appropriate moments of $f(\vec{q},\vec{u},\omega)$ (see eq 8), the expectation values of the first order changes in the order parameters ϕ and S^{ij} can be calculated from eq 6. Finally, we expand the $\vec{u}$ dependence of the distribution function in spherical harmonics and truncate at $l = 2$. The resulting responses of ϕ and S^{ij} to an external field h_ϕ can be expressed as

$$\phi(\vec{q},\omega) = \chi_{\phi\phi}^{A}(\vec{q},\omega)\, h_\phi(\vec{q},\omega)$$

$$S^{ij}(\vec{q},\omega) = \chi_{S\phi}(\vec{q},\omega) U^{ij} h_\phi(\vec{q},\omega) \quad (11)$$

while the response to an external field h_S^{ij} in the low wavevector, low frequency limit is of the form

$$\phi(\vec{q},\omega) = \chi_{\phi S}(\vec{q},\omega) U^{kl} h_S^{kl}(\vec{q},\omega)$$

$$S^{ij}(\vec{q},\omega) = \sum_{n=0}^{2} \chi_{SS}^{(n)}(\vec{q},\omega) T_n^{ijkl} h_S^{kl}(\vec{q},\omega) \quad (12)$$

where there is an implied summation over repeated Cartesian indices. The tensors U^{ij} and T^{ijkl} are defined in the Appendix. In the low frequency limit, the response functions have the form

$$\chi_{\phi\phi}^{A}(\vec{q},\omega) = \frac{\tilde{\chi}_{\phi\phi}^{A}(\vec{q})}{-i\omega + \omega_{\phi\phi}^{A}}$$

$$\chi_{\phi S}(\vec{q},\omega) = \frac{\tilde{\chi}_{\phi S}(\vec{q})}{-i\omega + \omega_{\phi S}}$$

$$\chi_{S\phi}(\vec{q},\omega) = \chi_{\phi S}(\vec{q},\omega)$$

$$\chi_{SS}^{(n)}(\vec{q},\omega) = \frac{\tilde{\chi}_{SS}^{(n)}(\vec{q})}{-i\omega + \omega_{SS}^{(n)}} \quad (13)$$

where, to order q^2 (except for $\tilde{\chi}_{\phi S}$, which we compute to the lowest nonvanishing order),

$$\tilde{\chi}_{\phi\phi}^{A}(\vec{q}) = \phi_A N_A D_t q^2$$

$$\omega_{\phi\phi}^{A} = D_t q^2$$

$$\tilde{\chi}_{\phi S}(\vec{q}) = -\phi_A \frac{D_r D_t}{540\Delta D} q^4 N_A{}^4$$

$$\omega_{\phi S} = \frac{D_r D_t}{2\Delta D} q^2 N_A{}^2$$

$$\tilde{\chi}_{SS}^{(0)} = \frac{\phi_A}{5} D_r\left[1 + q^2\left(-\frac{11}{252}N_A{}^2 + \frac{2}{63}\frac{\Delta D}{D_r} - \frac{2}{135}\frac{(\Delta D)^2}{D_r D_t} + \frac{1}{6}\frac{D_t}{D_r} - \frac{1}{135}\frac{N_A{}^2}{D_t} - \frac{1}{1080}\frac{D_r N_A{}^4}{D_t}\right)\right]$$

$$\omega_{SS}^{(0)} = 6D_r\left[1 + q^2\left(\frac{2}{63}\frac{\Delta D}{D_r} - \frac{2}{135}\frac{(\Delta D)^2}{D_r D_t} + \frac{1}{6}\frac{D_t}{D_r} - \frac{1}{135}\frac{N_A{}^2}{D_t} - \frac{1}{1080}\frac{D_r N_A{}^4}{D_t}\right)\right]$$

$$\tilde{\chi}_{SS}^{(1)} = \frac{\phi_A}{5} D_r \left[1 + q^2 \left(-\frac{1}{28} {N_A}^2 + \frac{1}{63} \frac{\Delta D}{D_r} + \frac{1}{6} \frac{D_t}{D_r} \right) \right]$$

$$\omega_{SS}^{(1)} = 6 D_r \left[1 + q^2 \left(\frac{1}{63} \frac{\Delta D}{D_r} + \frac{1}{6} \frac{D_t}{D_r} \right) \right]$$

$$\tilde{\chi}_{SS}^{(2)} = \frac{\phi_A}{5} D_r \left[1 + q^2 \left(-\frac{1}{84} {N_A}^2 - \frac{2}{63} \frac{\Delta D}{D_r} + \frac{1}{6} \frac{D_t}{D_r} \right) \right]$$

$$\omega_{SS}^{(2)} = 6 D_r \left[1 + q^2 \left(-\frac{2}{63} \frac{\Delta D}{D_r} + \frac{1}{6} \frac{D_t}{D_r} \right) \right] \qquad (14)$$

In the above equations, we have introduced the notations

$$D_t = \frac{1}{3} D_{\parallel} + \frac{2}{3} D_{\perp}$$

$$\Delta D = D_{\parallel} - D_{\perp} \qquad (15)$$

III. Response Functions of an Interacting Mixture of Rods and Coils

To calculate the response functions of the interacting mixture from the response functions of a noninteracting solution of rods and of coils, we use a type of mean field theory. The specific approach is known as the dynamical random phase approximation (RPA) and has been applied to a variety of problems in polymer physics.[17] Other than direct chemical interactions between monomers of the rod and coil species (described by a Flory interaction parameter χ_F), we include anisotropic interactions between the rodlike segments (described by a Maier–Saupe parameter w) and a total chemical potential field μ to enforce incompressibility of the two-component blend. According to linear response theory, the following expressions define the response functions of an interacting, incompressible system (denoted by overbars):

$$\phi_A(\vec{q},\omega) = \bar{\chi}_{\phi\phi}(\vec{q},\omega)\ h_{\phi}(\vec{q},\omega) + \bar{\chi}_{\phi S}(\vec{q},\omega) U^{ij} h_S^{ij}(\vec{q},\omega)$$

$$S^{ij}(\vec{q},\omega) = \bar{\chi}_{\phi S}(\vec{q},\omega) U^{ij} h_{\phi}(\vec{q},\omega) + \sum_{n=0}^{2} \bar{\chi}_{SS}^{(n)}(\vec{q},\omega) T_n^{ijkl} h_S^{kl}(\vec{q},\omega) \qquad (16)$$

Within dynamical RPA, we can also express the response in terms of the noninteracting response functions and effective external fields that include the three types of interactions:

$$\phi_A(\vec{q},\omega) = \chi_{\phi\phi}^{A}(\vec{q},\omega)\ h_{A\phi}^{eff}(\vec{q},\omega) + \chi_{\phi S}(\vec{q},\omega) U^{ij} h_S^{eff\ ij}(\vec{q},\omega)$$

$$\phi_B(\vec{q},\omega) = \chi_{\phi\phi}^{B}(\vec{q},\omega)\ h_{B\phi}^{eff}(\vec{q},\omega)$$

$$S^{ij}(\vec{q},\omega) = \chi_{\phi S}(\vec{q},\omega) U^{ij} h_{A\phi}^{eff}(\vec{q},\omega) + \sum_{n=0}^{2} \chi_{SS}^{(n)}(\vec{q},\omega) T_n^{ijkl} h_S^{\mathrm{eff}\ kl}(\vec{q},\omega) \qquad (17)$$

where the effective fields such as $h_{A\phi}^{eff}$ contain contributions from direct isotropic and anisotropic interactions and from a potential $\mu(\vec{q},\omega)$ that enforces the incompressibility constraint. Incorporating the isotropic interaction χ_F between monomers on the rods and monomers on the coils, dynamical RPA leads to

$$h_{A\phi}^{eff} = h_{A\phi} + \mu - \chi_F \phi_B$$

$$h_{B\phi}^{eff} = h_{B\phi} + \mu - \chi_F \phi_A \qquad (18)$$

Similarly, if we assume that there is an anisotropic interaction (Maier–Saupe parameter), w, that acts to align rodlike segments, then dynamical RPA yields

$$h_S^{eff\ ij} = h_S^{ij} + w S^{ij} \qquad (19)$$

By enforcing the incompressibility condition

$$\phi_A(\vec{q},\omega) + \phi_B(\vec{q},\omega) = 0 \quad \text{for } q \neq 0 \qquad (20)$$

it is possible to solve for the chemical potential $\mu(\vec{q},\omega)$. This result can then be substituted back into eq 17 and then rewritten in the form of eq 16 to obtain the response functions for the fully interacting mixture. The field h_{ϕ} denotes the exchange potential field $h_{A\phi} - h_{B\phi}$ and naturally arises once the incompressibility constraint has been imposed. The final expressions for the response functions are

$$\bar{\chi}_{\phi\phi} = \frac{\hat{\chi}_{\phi\phi}}{1 - 2\chi_F \hat{\chi}_{\phi\phi}}$$

$$\bar{\chi}_{\phi S} = \frac{\hat{\chi}_{\phi S}}{(1 - 2\chi_F \hat{\chi}_{\phi\phi})(1 - w\hat{\chi}_{SS}^{(0)})}$$

$$\bar{\chi}_{SS}^{(n)} = \frac{\hat{\chi}_{SS}^{(n)}}{1 - w\hat{\chi}_{SS}^{(n)}} \qquad (21)$$

where

$$\hat{\chi}_{\phi\phi} = \frac{\chi_{\phi\phi}^{A} \chi_{\phi\phi}^{B}}{\chi_{\phi\phi}^{A} + \chi_{\phi\phi}^{B}}$$

$$\hat{\chi}_{\phi S} = \frac{\chi_{\phi S} \chi_{\phi\phi}^{B}}{\chi_{\phi\phi}^{A} + \chi_{\phi\phi}^{B}}$$

$$\hat{\chi}_{SS}^{(0)} = \chi_{SS}^{(0)} - \frac{(\chi_{\phi S})^2}{\chi_{\phi\phi}^{A} + \chi_{\phi\phi}^{B}}$$

$$\hat{\chi}_{SS}^{(1)} = \chi_{SS}^{(1)}$$

$$\hat{\chi}_{SS}^{(2)} = \chi_{SS}^{(2)} \qquad (22)$$

The functions $\hat{\chi}_{\phi\phi}$, $\hat{\chi}_{\phi S}$, and $\hat{\chi}_{SS}$ are the response functions for an incompressible mixture of otherwise *noninteracting* rods and coils, while the functions $\bar{\chi}_{\phi\phi}$, $\bar{\chi}_{\phi S}$, and $\bar{\chi}_{SS}$ are the response functions for an incompressible mixture of *interacting* rods and coils. Note that the barred functions are equivalent to the hatted functions when the interaction parameters χ_F and w are set to zero.

IV. Onsager Coefficients

Given the response functions of the interacting mixture, it is straightforward to calculate the Onsager coefficients.[14,18] From the forms of the tensors U^{ij} and T^{ijkl} (see the Appendix), it is evident that the composition order parameter $\phi(\vec{q},\omega)$ is only coupled to one component of the orientational order parameter, namely $S^{zz}(\vec{q},\omega)$, where for convenience we have taken $\hat{\mathbf{z}} \parallel \hat{\mathbf{q}}$. Equation 16 can be expressed in matrix form:

$$\begin{pmatrix} \phi \\ S^{zz} \end{pmatrix} = \begin{pmatrix} \bar{\chi}_{\phi\phi} & \bar{\chi}_{\phi S} \\ 2\bar{\chi}_{\phi S} & (^4/_3)\bar{\chi}_{SS}^{(0)} \end{pmatrix} \begin{pmatrix} h_{\phi} \\ U^{ij} h_S^{ij} \end{pmatrix} \qquad (23)$$

or equivalently in the shorthand

$$\vec{\phi} = \overleftrightarrow{\chi} \cdot \vec{h} \qquad (24)$$

The factor of 2 in the 21 position of the matrix comes from the factor $U^{zz} = 2$ (see eq 16). Similarly, the factor of $^4/_3$ in the 22 position of the matrix comes from the relation $T_0^{zzij} = (^4/_3)U^{ij}$ (see the Appendix).

The other four independent components of $\overleftrightarrow{S}$ are decoupled from one another:

$$S^{xz} = 2\chi_{SS}^{(1)}(h_S^{xz} + h_S^{zx})$$

$$S^{yz} = 2\chi_{SS}^{(1)}(h_S^{yz} + h_S^{zy})$$

$$S^{xy} = 2\chi_{SS}^{(2)}(h_S^{xy} + h_S^{yx})$$

$$S^{xx} - S^{yy} = 4\chi_{SS}^{(2)}(h_S^{xx} - h_S^{yy}) \tag{25}$$

To extract the Onsager coefficients, we start with the canonical form of the equations of motion and recast them in the form of eq 24. The equations of motion for a mixture in external fields h_ϕ and h_S are assumed to be of the form

$$\frac{\partial\phi(\vec{q},t)}{\partial t} = \tilde{\Gamma}_{\phi\phi}\frac{\delta\Omega}{\delta\phi(-\vec{q},t)} + \tilde{\Gamma}_{\phi S}U^{ij}\frac{\delta\Omega}{\delta S^{ij}(-\vec{q},t)}$$

$$\frac{\partial S^{ij}(\vec{q},t)}{\partial t} = \tilde{\Gamma}_{\phi S}U^{ij}\frac{\delta\Omega}{\delta\phi(-\vec{q},t)} - \sum_{n=0}^{2}\tilde{\Gamma}_{SS}^{(n)}T_n^{ijkl}\frac{\delta\Omega}{\delta S^{kl}(-\vec{q},t)} \tag{26}$$

where the thermodynamic potential $\Omega[\phi,\overleftrightarrow{S}]$ is the sum of the free energy in the absence of h_ϕ and h_S, $F[\phi,\overleftrightarrow{S}]$, with the energy contributed by the two fields:

$$\Omega[\phi,\overleftrightarrow{S}] = F[\phi,\overleftrightarrow{S}] - V^{-1}\sum_{\vec{q}}[h(\vec{q},t)\phi(-\vec{q},t) + h_S^{ij}(\vec{q},t)S^{ij}(-\vec{q},t)] \tag{27}$$

In the above, V denotes the system volume and the $\tilde{\Gamma}$ variables denote Onsager kinetic coefficients. We shall be primarily concerned with the low-frequency response of the two order parameters, so we will evaluate the Onsager coefficients only in the $\omega \to 0$ limit. In order to compare eq 26 to the result of linear response theory, eqs 24 and 25, we must linearize the derivatives of the free energy $F[\phi,\overleftrightarrow{S}]$ that appear in eq 26. This corresponds to the retaining only quadratic terms in the free energy functional. From eq 26 it thus follows that the Laplace-transformed, linearized equations of motion are[18]

$$-i\omega\vec{\phi} = \overleftrightarrow{\Gamma}\cdot[\overleftrightarrow{M}\cdot\vec{\phi} - \vec{h}] \tag{28}$$

where $\overleftrightarrow{M}$ is the matrix of second derivatives formed from $F[\phi,\overleftrightarrow{S}]$. Solving for $\vec{\phi}$ in terms of $\vec{h}$, we find

$$\vec{\phi} = (i\omega + \overleftrightarrow{\Gamma}\cdot\overleftrightarrow{M})^{-1}\cdot\overleftrightarrow{\Gamma}\cdot\vec{h} \tag{29}$$

Comparing eq 29 to eq 24, it follows that

$$(i\omega + \overleftrightarrow{\Gamma}\cdot\overleftrightarrow{M})^{-1}\cdot\overleftrightarrow{\Gamma} = \overleftrightarrow{\chi} \tag{30}$$

or, solving for $\overleftrightarrow{\Gamma}$,

$$\overleftrightarrow{\Gamma} = i\omega\overleftrightarrow{\chi}\cdot(1 - \overleftrightarrow{M}\cdot\overleftrightarrow{\chi})^{-1} \tag{31}$$

In the present linearized theory, i.e. taking F to be a quadratic form, $\overleftrightarrow{M}$ is equal to the inverse of the structure factor tensor $\overleftrightarrow{\Sigma}$:

$$\overleftrightarrow{M} = (\overleftrightarrow{\Sigma})^{-1} = \begin{pmatrix} \Sigma_{\phi\phi} & \Sigma_{\phi S} \\ 2\Sigma_{\phi S} & ^4/_3\Sigma_{SS}^{(0)} \end{pmatrix}^{-1} \tag{32}$$

In addition, the structure factor tensor $\overleftrightarrow{\Sigma}(\vec{q})$ is related to the zero-frequency limit of the response function tensor, e.g.

$$\Sigma_{\phi\phi}(\vec{q}) = \lim_{\omega\to 0}\bar{\chi}_{\phi\phi}(\vec{q},\omega) \tag{33}$$

with similar expressions for $\Sigma_{\phi S}(\vec{q})$ and $\Sigma_{SS}^{(n)}(\vec{q})$. In the low frequency limit, the response functions can be expressed in the form

$$\bar{\chi}_{\phi\phi}(\vec{q},\omega) = \Sigma_{\phi\phi}(\vec{q})(1 + i\omega/\omega_{\phi\phi}) \tag{34}$$

with similar formulae for the other response functions. Separating the part of the response function tensor with a linear dependence on ω yields

$$\overleftrightarrow{\chi}(\vec{q},\omega) = \overleftrightarrow{\Sigma}(\vec{q}) + i\omega\overleftrightarrow{Y}(\vec{q}) \tag{35}$$

where

$$\overleftrightarrow{Y} = \begin{pmatrix} \Sigma_{\phi\phi}/\omega_{\phi\phi} & \Sigma_{\phi S}/\omega_{\phi S} \\ 2\Sigma_{\phi S}/\omega_{\phi S} & ^4/_3\Sigma_{SS}^{(0)}/\omega_{SS} \end{pmatrix} \tag{36}$$

Next, if we substitute eqs 32–35 into eq 31, the following result is obtained

$$\overleftrightarrow{\Gamma} = -\overleftrightarrow{\chi}\cdot(\overleftrightarrow{\Sigma}^{-1}\cdot\overleftrightarrow{Y})^{-1} \tag{37}$$

However, we are really only concerned with the low-frequency limit of this expression in order to obtain frequency-independent Onsager coefficients. Thus,

$$\overleftrightarrow{\Gamma} = -\overleftrightarrow{\Sigma}\cdot\overleftrightarrow{Y}^{-1}\cdot\overleftrightarrow{\Sigma} \tag{38}$$

This is the final expression used to evaluate the Onsager coefficients $\tilde{\Gamma}_{\phi\phi}$, $\tilde{\Gamma}_{\phi S}$, and $\tilde{\Gamma}_{SS}^{(0)}$.

We must still solve for the remaining two Onsager coefficients $\tilde{\Gamma}_{SS}^{(1)}$ and $\tilde{\Gamma}_{SS}^{(2)}$ appearing in eq 26. This is straightforward because the other four components of the orientation density, namely S^{xz}, S^{yz}, S^{xy}, and $S^{xx} - S^{yy}$, are not coupled to each other or to ϕ or S^{zz}. We find

$$\tilde{\Gamma}_{SS}^{(1)} = -\Sigma_{SS}^{(1)}\omega_{SS}^{(1)}$$

$$\tilde{\Gamma}_{SS}^{(2)} = -\Sigma_{SS}^{(2)}\omega_{SS}^{(2)} \tag{39}$$

These are of the same form as eq 38, but because the components are uncoupled, the 2 × 2 matrices in eq 38 are replaced by 1 × 1 matrices.

V. Results and Discussion

The results for the Onsager coefficients derived in the last section can be expressed in terms of the single-coil or rod diffusion coefficients. Our final expressions for the equations of motion are

$$\frac{\partial\phi(\vec{q},t)}{\partial t} = -q^2\Gamma_{\phi\phi}\frac{\delta F}{\delta\phi(-\vec{q},t)} - q^2\Gamma_{\phi S}U^{ij}\frac{\delta F}{\delta S^{ij}(-\vec{q},t)}$$

$$\frac{\partial S^{ij}(\vec{q},t)}{\partial t} = -q^2\Gamma_{\phi S}U^{ij}\frac{\delta F}{\delta\phi(-\vec{q},t)} - \sum_{n=0}^{2}\Gamma_{SS}(1 + q^2{R_n}^2)T_n^{ijkl}\frac{\delta F}{\delta S^{kl}(-\vec{q},t)} \tag{40}$$

where

$$\Gamma_{\phi\phi} = \frac{\phi(1-\phi)N_\mathrm{A}N_\mathrm{B}D_\mathrm{t}D_\mathrm{c}}{\phi N_\mathrm{A}D_\mathrm{t} + (1-\phi)N_\mathrm{B}D_\mathrm{c}}$$

$$\Gamma_{\phi S} = \frac{1}{270}\frac{\phi(1-\phi)N_\mathrm{A}N_\mathrm{B}}{\phi N_\mathrm{A} + (1-\phi)N_\mathrm{B}}\left\{{N_\mathrm{A}}^2D_\mathrm{r} + \frac{D_{\phi\phi}}{D_\mathrm{t}}[2\Delta D - {N_\mathrm{A}}^2D_\mathrm{r}]\right\}$$

$$\Gamma_{SS} = \frac{1}{5}\phi N_{\mathrm{A}} D_{\mathrm{r}}$$

$$R_0{}^2 = -\frac{11}{252}N_{\mathrm{A}}{}^2 + \frac{2}{63}\frac{\Delta D}{D_{\mathrm{r}}} + \frac{1}{6}\frac{D_{\mathrm{t}}}{D_{\mathrm{r}}} - \frac{2}{135}\frac{(\Delta D)^2}{D_{\mathrm{r}}D_{\mathrm{t}}} - \frac{1}{135}\frac{\Delta D}{D_{\mathrm{t}}}N_{\mathrm{A}}{}^2 - \frac{1}{1080}\frac{D_{\mathrm{r}}N_{\mathrm{A}}{}^4}{D_{\mathrm{t}}}$$

$$R_1{}^2 = -\frac{1}{28}N_{\mathrm{A}}{}^2 + \frac{1}{63}\frac{\Delta D}{D_{\mathrm{r}}} + \frac{1}{6}\frac{D_{\mathrm{t}}}{D_{\mathrm{r}}}$$

$$R_2{}^2 = -\frac{1}{84}N_{\mathrm{A}}{}^2 - \frac{2}{63}\frac{\Delta D}{D_{\mathrm{r}}} + \frac{1}{6}\frac{D_{\mathrm{t}}}{D_{\mathrm{r}}} \qquad (41)$$

The diffusion constants D_{t} and ΔD are given in eq 15 and

$$D_{\phi\phi} = \frac{[\phi N_{\mathrm{A}} + (1-\phi)N_{\mathrm{B}}]D_{\mathrm{t}}D_{\mathrm{B}}}{\phi N_{\mathrm{A}}D_{\mathrm{t}} + (1-\phi)N_{\mathrm{B}}D_{\mathrm{B}}} \qquad (42)$$

The free energy functional F was computed in ref 10; a quadratic form for the special case of rod–coil mixtures is given in eq 44 below.

As mentioned in the previous section, the matrices $\overleftrightarrow{U}$ and $\overleftrightarrow{T}$ act to couple the appropriate components of $\overleftrightarrow{S}$ to ϕ and to each other. For example, $\overleftrightarrow{U}$ is a symmetric second rank tensor that allows ϕ to couple only to the projection of $\overleftrightarrow{S}$ in the $\hat{\mathbf{q}}\hat{\mathbf{q}}$ direction. (Recall that we have defined $\hat{\mathbf{z}} \parallel \hat{\mathbf{q}}$.) From eq 40, we see that the form of $\overleftrightarrow{T}_0$ guarantees that $\partial S^{zz}/\partial t$ depends only on

$$\frac{\delta F}{\delta S^{zz}} - \frac{1}{3}\left[\frac{\delta F}{\delta S^{xx}} + \frac{\delta F}{\delta S^{yy}} + \frac{\delta F}{\delta S^{zz}}\right]$$

Similarly, $\overleftrightarrow{T}_1$ guarantees that $\partial S^{xz}/\partial t$ depends only on $\delta F/\partial S^{xz}$ and that the equations for $\partial S^{xz}/\partial t$ and $\partial S^{yz}/\partial t$ are identical upon interchange of x and y. This symmetry arises from invariance with respect to rotations around the z-axis. The roles of $\overleftrightarrow{U}$ and $\overleftrightarrow{T}$ will be further clarified by the linearized analysis of phase separation presented in section VI.

The equations of motion can also be expressed in real space. For the purpose of illustration, we shall omit the terms involving the coefficients R_n, which involve higher order gradients. The remaining terms yield

$$\frac{\partial\phi(\vec{r},t)}{\partial t} = \Gamma_{\phi\phi}\nabla^2\frac{\delta F}{\delta\phi(\vec{r},t)} + 3\Gamma_{\phi S}\left(\nabla_i\nabla_j - \frac{1}{3}\delta_{ij}\nabla^2\right)\frac{\delta F}{\delta S^{ij}(\vec{r},t)}$$

$$\frac{\partial S^{ij}(\vec{q},t)}{\partial t} = 3\Gamma_{\phi S}\left(\nabla_i\nabla_j - \frac{1}{3}\delta_{ij}\nabla^2\right)\frac{\delta F}{\delta\phi(\vec{r},t)} - \left(2\delta_{ik}\delta_{jl} + 2\delta_{il}\delta_{jk} - \frac{4}{3}\delta_{ij}\delta_{kl}\right)\Gamma_{SS}\frac{\delta F}{\delta S^{kl}(\vec{r},t)} \qquad (43)$$

The term involving $\Gamma_{\phi\phi}$ in eq 40 contains a prefactor of $-q^2$ (in the real-space version in eq 43, the prefactor is ∇^2). This is because the order parameter ϕ is conserved. Note, however, that the terms involving Γ_{SS} in eq 40 do not contain a prefactor of q^2; this is because the overall degree of orientational order is not a conserved variable. It is important to note that the magnitude of Γ_{SS} depends on the rotational diffusion constant, D_{r}, as shown in eq 41. Orientational order is not conserved because it can change both locally and globally due to rotational diffusion. If, however, we set $D_{\mathrm{r}} = 0$, then the coefficient $\Gamma_{SS}(1+q^2R_n{}^2)$ is proportional to q^2 with a coefficient $\Gamma_{SS}R_n{}^2$ that depends on the translational diffusion coefficients, $D_{\parallel}$ and $D_{\perp}$, but not on D_{r}. Thus, if rotational diffusion is suppressed, the orientational density $\overleftrightarrow{S}$ can change only by rods undergoing translational diffusion. In that limit, $\overleftrightarrow{S}$ becomes a conserved quantity, with a decay rate proportional to q^2. Note that for rods in the semidilute regime[16] (a typical situation of interest), we expect $D_{\mathrm{r}} \sim 1/N_{\mathrm{A}}{}^5$. Thus, for long rods, rotational diffusion in the semidilute regime is extremely slow, and $\Gamma_{SS} \ll \Gamma_{SS}q^2R_n{}^2$ for $q > 1/N_{\mathrm{A}}{}^2$. In this situation, the relaxation is dominated by translational diffusion in the direction along the rods, $D_{\parallel} \sim 1/N_{\mathrm{A}}$. Overall, these considerations clarify why it is important to keep the terms $q^2R_n{}^2$ in the equations of motion, even though they appear to be higher order corrections.

The cross terms involving $\Gamma_{\phi S}$ in eqs 40–43 deserve comment, because they are not commonly included. Indeed, Lansac et al.[13] have considered phase separation into coexisting isotropic and nematic phases without the cross terms. Although the terms appear with a coefficient q^2 in eq 40, this is not because of any conservation law. Rather, the origin of the q^2 term is the nonlocality inherent in the shape of the rods. A force at $\vec{r}$ can give rise to a current in ϕ or $\overleftrightarrow{S}$ at $\vec{r}'$, if $|\vec{r} - \vec{r}'|$ is less than the rod length. Nonlocal contributions to kinetic coefficients are commonplace in polymer systems, since polymers are extended objects. The effect of nonlocality in $\Gamma_{\phi\phi}$ on spinodal decomposition in polymer blends has been studied extensively.[19-21] The difference in the present case of $\Gamma_{\phi S}$ is that the nonlocal term is the leading term in the gradient expansion of the Onsager coefficient. This is because $\partial\phi/\partial t$ is a scalar and $\delta F/\delta\overleftrightarrow{S}$ is a tensor. Thus, $\delta F/\delta\overleftrightarrow{S}$ can appear in the equation for $\partial\phi/\partial t$ only if it is contracted with another second rank tensor. The only local second rank tensor that can be constructed is the isotropic tensor δ_{ij}, because there is no other local direction in the problem. However, if we now use the reciprocity relation and apply the same tensor δ_{ij} to $\delta F/\delta\phi$ in the dynamical equation for $\overleftrightarrow{S}$, we find that this tensor does not preserve the traceless property of $\overleftrightarrow{S}$. If we consider *nonlocal* terms, however, the gradient operator $\vec{\nabla}$ defines a direction that can be used to construct the dyadic tensor $\nabla_i\nabla_j$, and this leads to a second rank tensor $\nabla_i\nabla_j - {}^1/_3\nabla^2\delta_{ij}$ that preserves the tracelessness of $\overleftrightarrow{S}$. Equivalently, the vector $\vec{q}$ defines a direction in the q-space version of the equations (eq 40).

Next, we consider the term involving Γ_{SS} in eq 43. This term is purely local, but both $\partial\overleftrightarrow{S}/\partial t$ and $\delta F/\delta\overleftrightarrow{S}$ are second rank tensors. This local term is allowed because the coefficient $(2\delta_{ik}\delta_{jl} + 2\delta_{il}\delta_{jk} - {}^4/_3\delta_{ij}\delta_{kl})$ is an isotropic fourth rank tensor and therefore does not require a local direction. This tensor also preserves the traceless property of $\overleftrightarrow{S}$.

Finally, note that we have neglected nonlocality in $\Gamma_{\phi\phi}$. While this can be important in describing the dynamics of short wavelength concentration modes, nonlocality becomes much less important as the relevant wavelengths exceed the size of individual rods or coils. Thus, we have dropped the q-dependence of $\Gamma_{\phi\phi}$ in the same spirit as the calculation of the free energy functional,[10] which was based on a gradient expansion. Given the form of the response functions in section III, it is actually straightforward to include the complete q-dependence of $\Gamma_{\phi\phi}$. However, it is difficult to calculate the complete q-dependence of the other Onsager coefficients, $\Gamma_{\phi S}$ and Γ_{SS}, so we have restricted our calculation to a gradient expansion in all of the Onsager coefficients.

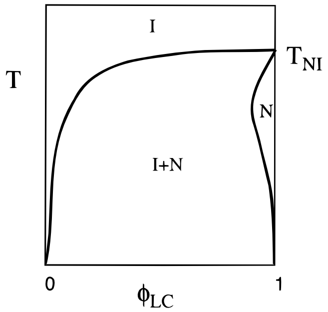

Figure 1. A possible phase diagram for a mixture of a liquid crystal with a flexible polymer. We have plotted temperature, T, as a function of the volume fraction of liquid crystal, ϕ_{LC}. Above the isotropic−nematic transition temperature for the pure liquid crystal (labeled T_{NI}), the two components mix. Below T_{NI}, the components separate into an isotropic phase rich in polymer coexisting with a nematic phase rich in liquid crystal.

VI. Linearized Analysis of Spinodal Decomposition

In order to illustrate the role of the tensors $\overleftrightarrow{U}$ and $\overleftrightarrow{T}$ in the equations of motion (eq 40), we have performed a linearized analysis of the phase separation kinetics following a quench from a stable state to an unstable state.[22] We take the stable state to be a mixed, isotropic state with ϕ constant and $\overleftrightarrow{S} = 0$ and consider a quench into a coexistence region consisting of an isotropic phase rich in coils and a nematic phase rich in rods. A schematic phase diagram is shown in Figure 1. Phase diagrams of this type were obtained by Holyst and Schick[23] for rod/coil mixtures. The expression for the bulk free energy that is minimized to produce the phase diagram shown in Figure 1 consists of the Flory−Huggins free energy for the composition order parameter added to a Landau−deGennes free energy for the orientational order parameter.[23] In contrast to previous formulations,[24] the coefficients in the Landau−deGennes expansion are not free parameters; they depend on composition and have been calculated from microscopic models of coils and rods in terms of the molecular weights. We note that despite the approximations inherent in using a Landau−deGennes expansion to describe the first-order isotropic/nematic transition, the free energy expressions yield phase diagrams in good qualitative agreement with experiments.[25] Finally, nonlocal square-gradient terms in the free energy have also been calculated[10] from microscopic models. The free energy functional consists of both the bulk free energy and square-gradient terms. Since we are only interested in a linearized analysis here, it suffices to retain only the quadratic terms in the free energy functional. Thus, the free energy (in units of k_BT) has the form[23,10]

$$F = \frac{1}{2V}\sum_{\vec{q}}[(A + M_0q^2)|\phi(\vec{q})|^2 + (B + L_1q^2)S^{ij}(\vec{q})S^{ij}(-\vec{q}) + L_2q_iq_jS^{ik}(\vec{q})S^{jk}(-\vec{q}) - 2L_0q_iq_j\phi(\vec{q})S^{ij}(-\vec{q})] \quad (44)$$

where the coefficients are

$$A(\phi) = \frac{1}{N_A\phi} + \frac{1}{N_B(1-\phi)} - 2\chi_F$$

$$B(\phi) = \frac{15}{2}\frac{1}{\phi N_A} - w$$

$$M_0(\phi) = \frac{1}{36}\left[\frac{N_A}{\phi} + \frac{4}{1-\phi}\right]$$

$$L_0(\phi) = \frac{1}{12}\frac{N_A}{\phi}$$

$$L_1(\phi) = \frac{5}{56}\frac{N_A}{\phi}$$

$$L_2(\phi) = \frac{5}{14}\frac{N_A}{\phi} \quad (45)$$

and we remind the reader that N_A is the number of segments in the rod and N_B is the number of segments in the coil. Also, we recall that the Flory chi parameter, χ_F, measures the strength of isotropic interactions and the Maier−Saupe parameter, w, measures the strength of anisotropic interactions. Both parameters generally increase as the temperature is lowered. For the present investigation, we choose the initial (before the quench) values of χ_F and w such that the parameters A and B are both positive, indicating stability of a single, homogeneous, isotropic phase. The final (after the quench) value of χ_F is also chosen so that A is positive. This ensures that the system is stable to isotropic/isotropic phase separation. On the other hand, we choose the after-quench value of w such that *the coefficient B is negative*. This ensures that the system is unstable to isotropic/nematic phase separation. While other cases could be examined, e.g. both A and B negative, it is our experience that the present situation is easily realized experimentally.[25]

We now consider the response of the system to a fluctuation $\phi(\vec{q})$. Since the system is isotropic to begin with, the response must be independent of the direction $\hat{\mathbf{q}}$. We are therefore free to choose $\hat{\mathbf{z}} \parallel \hat{\mathbf{q}}$. In order to obtain the equation of motion, we must first calculate the functional derivatives $\delta F/\delta\phi(-\vec{q},t)$ and $\delta F/\delta S^{ij}(-\vec{q},t)$ (see eq 40). We find

$$\frac{\delta F}{\delta\phi(-\vec{q},t)} = (A + M_0q^2)\phi(\vec{q},t) - L_0q^2S^{zz}(\vec{q},t)$$

$$\frac{\delta F}{\delta S^{zz}(-\vec{q},t)} = -L_0q^2\phi(\vec{q},t) + (B + L_1q^2 + L_2q^2)S^{zz}(\vec{q},t)$$

$$\frac{\delta F}{\delta S^{xx}(-\vec{q},t)} = (B + L_1q^2)S^{xx}(\vec{q},t)$$

$$\frac{\delta F}{\delta S^{xy}(-\vec{q},t)} = (B + L_1q^2)S^{xy}(\vec{q},t)$$

$$\frac{\delta F}{\delta S^{xz}(-\vec{q},t)} = (B + L_1q^2 + {}^1\!/_2L_2q^2)S^{xz}(\vec{q},t) \quad (46)$$

The remaining derivatives can be obtained by using $x \leftrightarrow y$ symmetry. In the following, we will drop the arguments $(\vec{q},t)$ on ϕ and $\overleftrightarrow{S}$.

Next, we consider the combination $U^{ij}(\delta F/\delta S^{ij})$ that appears in the first equation in eq 40. From the Appendix, $U^{ij} = 3(\delta_{iz}\delta_{jz} - {}^1\!/_3\delta_{ij})$. Combining this with the derivatives listed in eq 46 leads to

$$U^{ij}\frac{\delta F}{\delta S^{ij}} = -2L_0q^2\phi + 3[B + (L_1 + {}^2\!/_3L_2)q^2]S^{zz} \quad (47)$$

Note that the tensor $\overleftrightarrow{U}$ ensures that only S^{zz} appears in this equation. The equation of motion for ϕ is thus given by

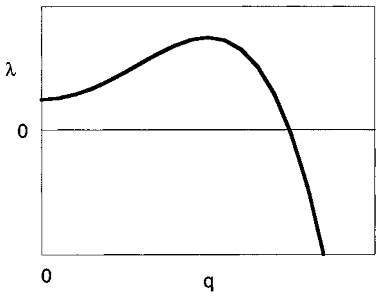

Figure 2. Sketch of the dispersion relation for a component of the orientational density $\overleftrightarrow{S}$ that does not couple to the composition order parameter ϕ. The components S^{xz}, S^{yz}, S^{xy}, and $S^{xx} - S^{yy}$ all have dispersion relations that are qualitatively similar. Note that the growth rate λ is nonzero at $q = 0$; this is because $\overleftrightarrow{S}$ is not a conserved order parameter.

$$\frac{\partial\phi}{\partial t} = -q^2\Gamma_{\phi\phi}[(A + M_0q^2)\phi - L_0q^2S^{zz}] - q^2\Gamma_{\phi S}[-2L_0q^2\phi + 3[B + (L_1 + {}^2/_3L_2)q^2]S^{zz}] \quad (48)$$

Next, we consider the equation of motion for S^{zz} in eq 40. There are two contributions. The first depends on $U^{zz}(\delta F/\delta\phi)$, where $U^{zz} = 2$. The second contribution depends on $\Sigma_{n=0}^{2}\Gamma_{SS}(1 + q^2R_n^{\ 2})T_n^{zzkl}(\delta F/\delta S^{kl})$. But according to the definitions in the Appendix, $T_n^{zzkl} = 0$ except for $n = 0$, and $T_0^{zzkl} = 4(\delta_{kz}\delta_{lz} - {}^1/_3\delta_{kl}) = {}^4/_3U^{kl}$. As a result, we find

$$\frac{\partial S^{zz}}{\partial t} = -2q^2\Gamma_{\phi S}[(A + M_0q^2)\phi - L_0q^2S^{zz}] - \frac{4}{3}\Gamma_{SS}(1 + q^2R_0^{\ 2})[-2L_0q^2\phi + 3[B + (L_1 + {}^2/_3L_2)q^2]S^{zz}] \quad (49)$$

Similarly,

$$\frac{\partial S^{xz}}{\partial t} = -4\Gamma_{SS}(1 + q^2R_1^{\ 2})(B + L_1q^2 + {}^1/_2L_2q^2)S^{xz}$$

$$\frac{\partial S^{yz}}{\partial t} = -4\Gamma_{SS}(1 + q^2R_1^{\ 2})(B + L_1q^2 + {}^1/_2L_2q^2)S^{yz}$$

$$\frac{\partial}{\partial t}(S^{xx} - S^{yy}) = -4\Gamma_{SS}(1 + q^2R_2^{\ 2})(B + L_1q^2)(S^{xx} - S^{yy})$$

$$\frac{\partial S^{xy}}{\partial t} = -4\Gamma_{SS}(1 + q^2R_2^{\ 2})(B + L_1q^2)S^{xy} \quad (50)$$

To carry out a linear analysis of spinodal decomposition,[22] we assume that $\phi(\vec{q},t) = \phi(\vec{q})e^{\lambda t}$ and $\overleftrightarrow{S}(\vec{q},t) = \overleftrightarrow{S}(\vec{q})e^{\lambda t}$ and solve for λ in terms of q. From eq 50, it is clear that S^{xz} and S^{yz} have the same dispersion relation. For the case of interest, where $B < 0$, there is a band of unstable modes, as shown schematically in Figure 2. The fastest growing mode is

$$\lambda_{xz}^{max} = 4\Gamma_{SS}|B| + \Gamma_{SS}\frac{(|B|R_1^{\ 2} - L_1 - {}^1/_2L_2)^2}{R_1^{\ 2}(L_1 + {}^1/_2L_2)}$$

$$q_{\max}^{\ \ 2} = \frac{(|B|R_1^{\ 2} - L_1 - {}^1/_2L_2)}{2R_1^{\ 2}(L_1 + {}^1/_2L_2)} \quad (51)$$

Note that λ is nonzero when $q = 0$; this is allowed because $\overleftrightarrow{S}$ is not conserved.

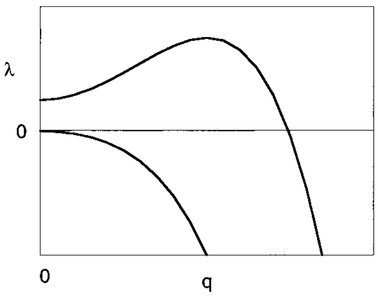

Figure 3. Sketch of the dispersion relation for the two mixed modes involving ϕ and S^{zz}. The unstable mode is a pure S^{zz} mode at $q = 0$, so its growth rate does not vanish there. The stable mode is a pure ϕ mode at $q = 0$, so its growth rate is zero at $q = 0$.

Similarly, $S^{xx} - S^{yy}$ and S^{xy} have the same dispersion relation, again of the form sketched in Figure 2. In this case, the fastest growing mode is

$$\lambda_{xy}^{max} = 4\Gamma_{SS}|B| + \Gamma_{SS}\frac{(|B|R^{22} - L_1)^2}{R_2^{\ 2}L_1}$$

$$q_{\max}^{\ \ 2} = \frac{|B|R_2^{\ 2} - L_1}{2R_2^{\ 2}L_1} \quad (52)$$

Finally, the modes for ϕ and S^{zz} are coupled. We can write the equations of motion, eqs 48 and 49, in matrix form

$$\lambda\begin{pmatrix}\phi \\ S^{zz}\end{pmatrix} = \begin{pmatrix}a_{11} & a_{12} \\ a_{21} & a_{22}\end{pmatrix}\begin{pmatrix}\phi \\ S_{zz}\end{pmatrix} \quad (53)$$

where the matrix elements a_{ij} can be extracted from eqs 48 and 49. When this matrix is diagonalized, we find two mixed modes, the forms of which are sketched in Figure 3. One of the modes is always stable and the other is unstable for a band of wavevectors. Note that the stable mode is a pure ϕ mode at $q = 0$, so it satisfies $\lambda = 0$ at $q = 0$. The fastest growing mode is

$$\lambda_{\phi S}^{max} = 4\Gamma_{SS}|B| + \frac{\Gamma_{SS}(|B|R_0^{\ 2} - L_1 - {}^2/_3L_2)^2}{R_0^{\ 2}(L_1 + {}^2/_3L_2) + {}^3/_8A\dfrac{\Gamma_{\phi S}^{\ \ 2}}{\Gamma_{SS}^{\ \ 2}} - L_0\dfrac{\Gamma_{\phi S}}{\Gamma_{SS}}}$$

$$q_{\max}^{\ \ 2} = \frac{1}{2}\,\frac{|B|R_0^{\ 2} - L_1 - {}^2/_3L_2}{R_0^{\ 2}(L_1 + {}^2/_3L_2) + {}^3/_8A\dfrac{\Gamma_{\phi S}^{\ \ 2}}{\Gamma_{SS}^{\ \ 2}} - L_0\dfrac{\Gamma_{\phi S}}{\Gamma_{SS}}} \quad (54)$$

In order to determine which of the three unstable modes grows the fastest, we must assess the relative magnitudes of the single-particle diffusion coefficients. According to Doi and Edwards,[16] the rod diffusion coefficients in the semidilute regime satisfy certain scalings with the rod length N_A. We set all the prefactors in the scaling relationships to be unity and use

$$D_{\|} = \frac{1}{2N_A}$$

$$D_{\perp} = 0$$

$$D_r = \frac{3}{N_A^{\ 5}}$$

$$D_B = \frac{1}{6N_B} \quad (55)$$

These diffusion coefficients are expressed in units of

k_BT/ζ, where ζ is a segmental friction coefficient. With the above scalings, the maximum growth rates of the three different modes for $N_A \gg 1$ are given by

$$\lambda_{\phi S}^{max} \approx 1018.5 \frac{|B|^2}{A(1-\phi)^2}$$

$$\lambda_{xy}^{max} \approx 0.15|B|^2 \phi {N_A}^3$$

$$\lambda_{xz}^{max} \approx 0.08|B|^2 \phi {N_A}^3 \tag{56}$$

Hence, for sufficiently large long rods (N_A on the order of 10 or larger), the growth rate is fastest for the modes S^{xy} and $S^{xx} - S^{yy}$. For sufficiently short rods, however, the growth rate is fastest for the coupled $\phi - S^{zz}$ mode. In other words, for long rods, the growth rate is fastest when the average rod orientation is perpendicular to the wavevector q, or equivalently, parallel to the developing interfaces. For short rods, however, the growth rate is fastest when the average rod orientation is parallel to q, or perpendicular to the developing interfaces. The latter is a purely kinetic effect, since the free energy functional used here biases the rods to be oriented parallel to the interface.[26] We note, however, that our equations of motion are most reliable when both the rods and the polymers are long. In particular, the free energy does not include chemical end effects; i.e., the end and middle monomers are assumed to have the same interactions. Such end effects can be significant for short rods. One manifestation of this neglect of chemical end effects is the failure of the free energy to yield homeotropic alignment of short rods at surfaces; our free energy always prefers parallel alignment of rods to surfaces.

In the limiting case where the rods are long and the coils are extremely short, our analysis describes phase separation kinetics of rod/solvent mixtures. Such systems were studied by Shimada et al.[11] in the linear regime. Shimada et al. derived coupled equations of motion for the number density of rods and the orientational density of rods, while we have derived equations of motion for the number density of rod segments or, equivalently, the local volume fraction of the rodlike component and the orientational density of rod segments. Moreover, they considered only excluded volume interactions between hard rods, while we allow for arbitrary isotropic and anisotropic interaction parameters (χ and w). As a result, they only find an instability toward phase−phase separation into an isotropic phase rich in solvent coexisting with a nematic phase rich in rods. Our more general formulation also allows for an instability into an isotropic phase rich in solvent coexisting with an isotropic phase rich in rods. These differences preclude an exact comparison between the two theories, but the general forms of the equations and qualitative predictions are the same.

In summary, we have used dynamic mean field theory to derive the equations of motion for a system with two coupled order parameters, namely composition and orientation. Our framework can be used to study a host of problems involving phase separation, ranging from small-molecule liquid crystal/flexible polymer mixtures to liquid crystalline polymer/solvent mixtures. In addition, our approach will clarify the role of orientational order in determining domain morphology. Because of the presence of orientational order, the composition pattern that results from spinodal decomposition can be quite different from the ordinary isotropic case (for example, a binary blend of two flexible polymers). We have performed a linear analysis of the simplest case of phase separation into coexisting orientationally ordered and disordered phases, but more complex analyses, following our equations to later stages of the phase separation process, are straightforward to carry out. Nevertheless, we have seen that even our simple analysis yields insight into the role of molecular ordering on the nonequilibrium process of phase separation.

VII. Appendix. The Tensors $\overleftrightarrow{U}$ and $\overleftrightarrow{T}$

The tensors $\overleftrightarrow{U}$ and $\overleftrightarrow{T}$ enforce the symmetry properties of $\overleftrightarrow{S}$. They guarantee that $\overleftrightarrow{S}$ remains a traceless, symmetric tensor as it evolves with time. In addition, they ensure that ϕ only couples to the projection of $\overleftrightarrow{S}$ in the $\hat{\mathbf{q}}\hat{\mathbf{q}}$ direction. In order to define the tensors, it is convenient to set $\hat{\mathbf{q}} \parallel \hat{\mathbf{z}}$. The tensor $\overleftrightarrow{U}$ is then

$$U^{ij} = 3(\delta_{iz}\delta_{jz} - {}^1\!/_3\delta_{ij}) \tag{57}$$

Similarly, the tensor $\overleftrightarrow{T}_0$ is

$$T_0^{ijkl} = 6(\delta_{iz}\delta_{jz} - {}^1\!/_3\delta_{ij})(\delta_{kz}\delta_{lz} - {}^1\!/_3\delta_{kl}) \tag{58}$$

Note that $U^{zz} = 2$ and $T_0^{zzkl} = 4(\delta_{kz}\delta_{lz} - {}^1\!/_3\delta_{kl}) = {}^4\!/_3U^{kl}$.

The other two tensors $\overleftrightarrow{T}_1$ and $\overleftrightarrow{T}_2$ are more conveniently expressed in terms of their nonzero matrix elements. In particular, the nonzero elements of $\overleftrightarrow{T}_1$ are

$$T_1^{ijkl} = 2 \quad \text{for } (ijkl) = \begin{pmatrix} 1313 \\ 1331 \\ 2323 \\ 2332 \\ 3113 \\ 3131 \\ 3223 \\ 3232 \end{pmatrix} \tag{59}$$

Similarly, the nonzero elements of $\overleftrightarrow{T}_2$ are

$$T_2^{ijkl} = -2 \quad \text{for } (ijkl) = \begin{pmatrix} 1122 \\ 2211 \end{pmatrix}$$

$$T_2^{ijkl} = 2 \quad \text{for } (ijkl) = \begin{pmatrix} 1111 \\ 1212 \\ 1221 \\ 2112 \\ 2121 \\ 2222 \end{pmatrix} \tag{60}$$

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