Morphogenesis in nematic liquid crystal/polymer materials*

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Abstract

Materials used in such optical devices as flat panel displays often consist of liquid crystal droplets dispersed in a polymer matrix. Because the behavior of the devices depends on the size, shape, and distribution of these droplets, understanding pattern formation in these materials is crucial for optimal processing. The droplets can be formed in a number of ways, all of which combine the processes of phase separation and orientational ordering. The fact that these two processes are coupled makes this problem both theoretically and computationally challenging.

Materials composed of liquid crystal-rich droplets dispersed in a polymer-rich matrix are currently used in many optical devices, including new flat panel displays and light shutters. The droplets are usually formed via polymerization-induced, solvent evaporation-induced, or temperature-induced phase separation, all of which combine the processes of spinodal decomposition and orientational ordering. Understanding the pattern formation and eventual droplet formation in these materials is crucial because the behavior of the devices depends on the size, shape, and distribution of these droplets. The coupling between spinodal decomposition and ordering makes this problem in morphogenesis both theoretically and computationally rich and challenging. In this extended abstract, we present a set of coupled equations of motion for the concentration field and the orientational order parameter of a model polymer/liquid crystal blend, based on a theoretical framework developed recently by Liu and Fredrickson [1,2] for a blend of worm-like polymers of arbitrary rigidity. We outline efforts to simulate the

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equations of motion focusing on the effect of isotropic–nematic ordering of the liquid crystals on the kinetics and morphology of spinodal decomposition that occurs following a temperature quench. This work is the result of on-going collaboration between researchers at and affiliated with the Center for Theoretical and Computational Materials Science at NIST and researchers at the Center for Advanced Liquid Crystalline Polymer Materials at Kent State University. More information on this project may be obtained at our web site [3].

Spinodal decomposition of two flexible polymers may be modeled by a time-dependent Cahn–Hilliard equation of motion for a conserved scalar concentration field (order parameter) with the Flory–Huggins–DeGennes free energy functional [4]. Nematic ordering of a single-component liquid crystal or rigid-rod polymer may be modeled by a time-dependent Ginzburg–Landau equation of motion for a non-conserved tensor director field (order parameter) with a Landau–DeGennes free energy functional [5]. To model a blend of flexible and rigid-rod polymers undergoing both spinodal decomposition and isotropic–nematic ordering, the concentration field and director field order parameters, which are strongly coupled to each other, must be tracked simultaneously. To do so, we follow the theoretical development of Liu and Fredrickson [1,2] and combine the two approaches typically used to model the individual processes into the following set of coupled equations of motion:

$$\frac{\partial \phi}{\partial t} = \Gamma_{\phi\phi} \partial_i \partial_i \frac{\delta F}{\delta \phi} + d\Gamma_{\phi S} \left(\partial_k \partial_l - \frac{1}{d} \delta_{kl} \partial_i \partial_i \right) \frac{\delta F}{\delta S_{kl}}, \tag{1}$$

$$\frac{\partial S_{ij}}{\partial t} = \left(\delta_{ik}\delta_{jl} - \frac{1}{d}\delta_{ij}\delta_{kl} \right)$$
$$\times \left[d\Gamma_{\phi S} \partial_k \partial_l \frac{\delta F}{\delta \phi} - (d+1)\Gamma_{SS}(1 - R_0^2 \nabla^2) \frac{\delta F}{\delta S_{kl}} \right]. \tag{2}$$

Here d is the spatial dimension, ϕ is the local concentration density of liquid crystal (and by incompressibility $1 - \phi$ is the local concentration density of polymer), and $S_{ij} \equiv \phi Q_{ij}$ denotes the ijth component of the tensor orientational density, where Q_{ij} is the usual orientational order parameter of a single-component liquid crystal [6]. The transport coefficients $\Gamma_{\phi\phi}$, $\Gamma_{\phi S}$, and Γ_{SS} depend on ϕ, and using dynamical mean field theory may be expressed in terms of single particle quantities, such as the translational and rotational diffusion coefficients [2]. The last term in Eq. (2) has been simplified from a more complicated tensorial integral equation expression. The free energy functional is given by

$$F = \frac{\phi}{N_A} \log \phi + \frac{1-\phi}{N_B} \log(1-\phi) + \chi\phi(1-\phi)$$
$$+ \frac{1}{2}(B(\phi) - W)S_{ij}S_{ji} - \frac{1}{3}C(\phi)S_{ij}S_{jk}S_{ki} + \frac{1}{4}D(\phi)S_{ij}S_{ji}S_{lk}S_{lk}$$
$$+ \frac{1}{2}M_0(\phi)(\nabla\phi)^2$$

$$+ L_0(\phi) \partial_i \phi \partial_j S_{ij}$$
$$+ \tfrac{1}{2} L_1(\phi)(\partial_k S_{ij})^2 + \tfrac{1}{2} L_2(\phi) \partial_i S_{ik} \partial_j S_{jk} , \qquad (3)$$

where the coefficient of each term in the last three lines of Eq. (3) depends non-trivially on ϕ, and on quantities such as the chain lengths and Kuhn lengths. The first line in Eq. (3) is the usual Flory–Huggins bulk free energy for a polymer blend. The second line is the usual Landau–DeGennes bulk free energy for a single-component nematic liquid crystal, in terms of orientational density S rather than the usual Q. W is the Maier–Saupe parameter, which measures the strength of the anisotropic interactions. The third line describes the energy cost of gradients in the local liquid crystal density, while the sixth line describes the usual orientational elasticity of splay, twist and bend. The fifth line couples gradients in the local concentration and orientation, and has the effect of aligning the rods with the interface between liquid crystal-rich and polymer-rich domains. It is important to note that the coefficients in these expressions have been calculated explicitly [1], and unlike those for small molecule systems are not unknown parameters.

We take $\chi = a/T + \chi_o$ and $W = b/T + W_o$, where a, b, W_o and χ_o are adjustable parameters. A typical phase diagram for our liquid crystal/polymer blend is shown in Fig. 1. Note the existence of both a second-order critical point and an isotropic-nematic transition temperature. There is a kink in the spinodal at a concentration ϕ_{ord}, above which the liquid crystal develops nematic order. To the left of the kink, the spinodal is identical to that of a non-ordered blend. The shape of the phase diagram, and the relative positions of T_c, T_{ord}, and T_{NI}, may be modified by tuning N_A, N_B, a, b, W_o and χ_o.

Model C in the Hohenberg–Halperin classification scheme is the phase-field model that most closely resembles the LCP model presented above. However, the LCP model differs from the usual version of Model C due to the tensorial nature of the second order parameter, and due to the presence of the cross terms (the terms multiplying $\Gamma_{\phi S}$) [7]. The cross terms in Eqs. (1) and (2) arise from nonlocal contributions to the currents. Such contributions are expected in polymer and rod-like systems where the objects are spatially extended, but not in the small molecule systems to which Model C has been primarily applied. The inclusion of these terms greatly increases the computational complexity of the problem, but is necessary from both a physical and mathematical point of view [8].

To solve the discretized versions of the coupled equations of motion we employ both first order Euler and fourth-order Runge–Kutta numerical integration schemes. These methods have proven enormously successful in previous studies of the simpler Cahn–Hilliard and TDGL equations for both conserved and non-conserved scalar order parameters. While both approaches appear to be successful in achieving both accuracy and stability for extremely shallow quenches in the LCP system, more sophisticated routines are necessary for deeper quenches when ordering of the director field at the domain interfaces is strong. For these cases we have implemented a semi-implicit Crank–Nicholson algorithm using sparse matrix methods.
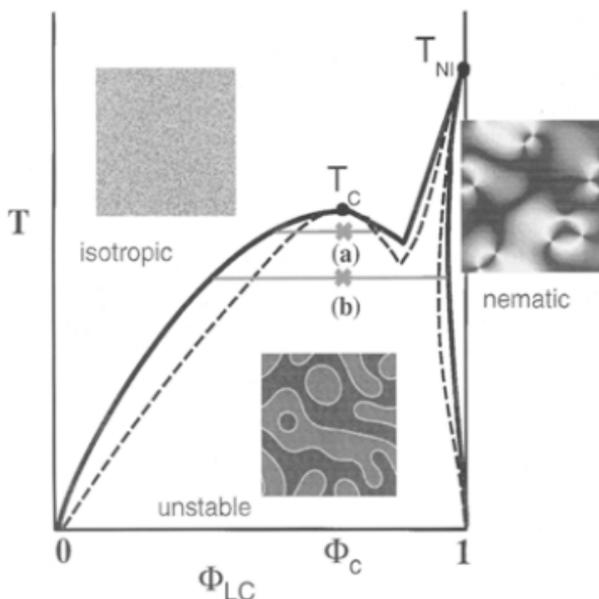
Fig. 1. Schematic phase diagram for a polymer/liquid crystal blend. ϕ is the local bulk concentration of liquid crystal, and T is the temperature. The thick, solid line is the coexistence curve, and the dashed line is the spinodal. See text for discussion of relevant features. The inset shows the concentration field of the stable, isotropic state, the concentration field of the unstable, phase-separating state in the absence of LC ordering, and the orientational order of the pure nematic state as viewed between crossed polarizers.

For simplicity, we consider a thin film in which both the concentration field and the director field are confined to two dimensions. The equations become

$$\frac{\partial \phi}{\partial t} = \Gamma_{\phi\phi} \nabla^2 \frac{\delta F}{\delta \phi} + \Gamma_{\phi S} \left[(\partial_x^2 - \partial_y^2) \left(\frac{\delta F}{\delta S_{xx}} - \frac{\delta F}{\delta S_{yy}} \right) + 4 \partial_x \partial_y \frac{\delta F}{\delta S_{xy}} \right], \tag{4}$$

$$\frac{\partial S_{xx}}{\partial t} = \Gamma_{\phi S}(\partial_x^2 - \partial_y^2) \frac{\delta F}{\delta \phi} - \frac{3}{2} \Gamma_{SS} \left(1 - R_0^2 \nabla^2 \right) \left(\frac{\delta F}{\delta S_{xx}} - \frac{\delta F}{\delta S_{yy}} \right), \tag{5}$$

$$\frac{\partial S_{xy}}{\partial t} = 2\Gamma_{\phi S}\partial_x \partial_y \frac{\delta F}{\delta \phi} - 3\Gamma_{SS}(1 - R_0^2 \nabla^2) \frac{\delta F}{\delta S_{xy}}. \tag{6}$$

For a system consisting of short rods ($N_A = 10$) and long chains ($N_B = 100$), we perform temperature quenches from the isotropic, one-phase region to the two-phase region characterized by coexistence of a polymer-rich, isotropic phase and a liquid-crystal rich, nematic phase.

Here we compare two cases: (a) a very shallow quench where the final concentration of the liquid-crystal-rich phase is not high enough to induce nematic order in that

phase, and (b) a deeper quench where the concentration of the liquid crystal rich phase becomes greater than that required for nematic ordering. In the latter case, spinodal decomposition occurs first upon lowering the temperature, and nematic ordering occurs while the system is still in the intermediate stages of phase separation.

When the system undergoes a very shallow quench (point (a) in Fig. 1) the morphology apparently evolves in a manner typical of other systems undergoing ordinary spinodal decomposition [4]. We are investigating the effect of the anisotropic nature of the diffusion of the liquid crystals on the scaling behavior. In a deeper quench (point (b) in Fig. 1), the local concentration density in the liquid-crystal-rich phase eventually surpasses a value of ϕ given by $B(\phi_{ord}) = W$. At this point, the director field becomes nonzero in those regions where $\phi \geqslant \phi_{ord}$, and nematic ordering begins. Early observations show the elongation of domains due to the ordering, as well as the migration of defects to the domain interface. Both of these features are observed in experiments.

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