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Spinodal Decompositions Driven by Orientation Fluctuations

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We study early stages of spinodal decomposition (SD) in polymer/liquid crystal mixtures by solving linearized time-dependent Landau-Ginzburg equations for concentration (conserved order parameter) and orientation (nonconserved order parameter). We calculate structure factors for concentration and for orientation, depending on a quench temperature and concentration. We find a new SD process driven by instability of the orientational order parameter.

Keywords: Spinodal decomposition; Lyotropic systems; landau-Ginzburg equations; structure factors; orientational fluctuations; concentration fluctuations

1. INTRODUCTION

In Lyotropic liquid crystalline systems, a biphasic region between an isotropic and a nematic phase appears, depending on temperature

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and concentration. When such a system is thermally quenched from a stable isotropic phase into an unstable part of the biphasic region, fluctuations of concentration and of orientation take place and isotropic or nematic droplets appear with time. The instability of these systems is driven by the competition between phase separation and nematic ordering.

In this paper, we study early stages of spinodal decomposition (SD) in liquid crystal-polymer mixtures [1-9] by solving linearized time-dependent Landau-Ginzburg equations for concentration (conserved order parameter) and orientation (nonconserved order parameter)[10-16]. We calculate structure factors for concentration and for orientation. The aim of this paper is to study the early stages of the SD. Depending on the concentration of liquid crystal, we find two types of SD.

2. PHASE DIAGRAMS OF POLYMER-LUQUID CRYSTAL MIXTURES

In this section we introduce the free energy to describe the static phase diagrams of polymer/liquid crystal mixtures[1-9]. We here use for simplicity the Landau expansion form for nematic free energy[9,17]. The dimensionless equilibrium free energy density $f(\phi, S)$ of polymer/liquid crystal mixtures is given by

$$\begin{aligned} f(\phi,S) &= \frac{1-\phi}{n_p}\ln(1-\phi)+\frac{\phi}{n_l}\ln\phi+\chi\phi(1-\phi) \\ &\quad +\nu\phi^2\left[\frac{1}{2}\left(1-\frac{\eta}{3}\right)S^2-\frac{\eta}{9}S^3+\frac{\eta}{6}S^4\right], \end{aligned} \tag{1}$$

where ϕ is the volume fraction of the liquid crystals and S is the 'scalar' orientational order parameter of the liquid crystals discussed further below, n_p is the number of segments on the polymer, n_l is axis ratio of the liquid crystal molecule, and $\eta \equiv n_l\nu\phi$. The value $\chi(\equiv U_0/k_BT)$ is the Flory-Huggins interaction parameter related to isotropic inter-

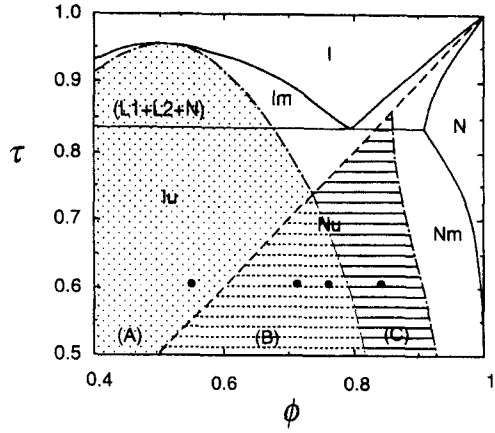

FIGURE 1: Phase diagram of a polymer/liquid crystal mixture with $n_p = n_l = 2$ and $\nu/\chi = 1.4$. The solid curve refers to the binodal and the dotted line shows the first-order NIT line. The dash-dotted line shows the spinodal. Closed circles indicate temperature quenches from the stable isotropic phase into the isotropic unstable (Iu; A) and nematic unstable (Nu;B, C) regions.

actions between unlike molecular species[18] and $\nu(\equiv U_a/k_BT)$ parameterizes the orientation-dependent (Maier-Saupe) interactions between the liquid crystals[19]. The typical phase diagram on the temperature-concentration plane is shown in Fig. 1 which is calculated with $n_p = n_l = 2$ and $\nu/\chi = 1.4$. The reduced temperature $\tau(\equiv T/T^{\circ}_{NI})$ is normalized by the nematic-isotropic transition (NIT) temperature T°_{NI} of the pure liquid crystal. The solid curve refers to the binodal and the dotted line shows the first-order NIT line. The dash-dotted line shows the spinodal. Note that the origin is suppressed on the ϕ-axis. When $\tau = 0.831$, we have a triple point where two isotropic liquid phases $(L_1 + L_2)$ and a nematic phase (N) can si-

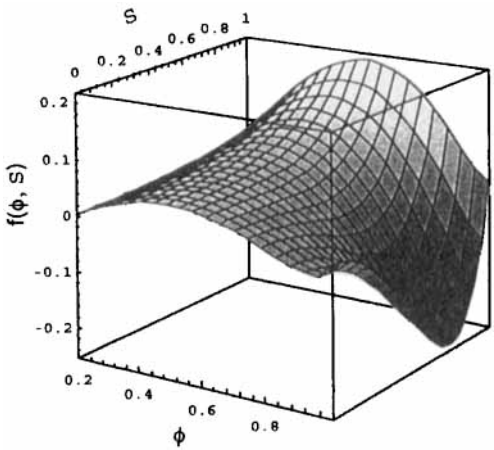

FIGURE 2: Free energy as a function of ϕ and S at $\tau = 0.6$.

multaneously coexist. Below the triple point, we have the two-phase coexistence between an isotropic and a nematic phase. Such phase diagram are observed in the mixtures of n-tetracosane and nematic liquid crystal (PAA)[3]. In the biphasic region between the nematic and the isotropic phases, we have two different metastable regions: an isotropic metastable (Im) and a nematic metastable (Nm), and two unstable regions: an isotropic unstable (Iu; A) and a nematic unstable (Nu; B, C). The region (A), lying below the isotropic spinodal curve and above the NIT line, corresponds to the system which is initially unstable with respect to concentration fluctuations, but metastable to orientational ordering. The region (B), between the isotropic spinodal curve and the NIT line, is initially unstable to both concentration and orientational ordering. The region (C) between the isotropic spinodal curve and the nematic spinodal curve shows the system which is initially unstable with respect to orientational ordering, but metastable to concentration fluctuations. Thus if we thermally quench from an isotropic phase ($S = 0$) to these different regions, we can expect the

variety of the SD processes even in the early stages. For example, Figure 2 shows the free energy (1) as a function of ϕ and S for $\tau = 0.6$. The three regions are on the curve with $S = 0$, immediately after we quench to $\tau = 0.6$. In the next section we consider the phase separation dynamics for two order parameters.

3. KINETIC EQUATIONS

The kinetic equations of motion for concentration ϕ and for orientational order parameter S_{ij} (traceless symmetric tensor) are given by

$$\frac{\partial \phi(r,t)}{\partial t} = \Gamma_\phi \nabla^2 \Big(\frac{\delta F}{\delta \phi}\Big), \tag{2}$$

$$\frac{\partial S_{ij}(r,t)}{\partial t} = -\Gamma_S \Big(\frac{\delta F}{\delta S_{ij}} + \Lambda(r,t)\delta_{ij}\Big), \tag{3}$$

where the transport coefficients Γ_ϕ and Γ_S are taken as constant. The Lagrange multiplier Λ in Eq.(3) will be chosen to ensure conservation of the trace of S_{ij}. The total free energy (F) can be expressed in terms of a local bulk free energy density $f(\phi, S_{ij})$, the gradients of the two order parameters, and the coupling term between two order parameters[14, 15]:

$$\begin{aligned} F(\phi, S_{ij}) &= \int dr \Big[f(\phi, S_{ij}) + \frac{K_0}{2}(\nabla\phi)^2 + L_0 \partial_i \phi \partial_j S_{ij} \\ &\quad + \frac{L_1}{2}(\partial_k S_{ij})^2 + \frac{L_2}{2}\partial_i S_{ik} \partial_j S_{jk} \Big]. \end{aligned} \tag{4}$$

By using the linearized analysis of Eqs. (2) and (3), we can calculate the structure factors for concentration and for orientational order parameter[20].

4. STRUCTURE FACTORS

Figure 3(a) and (b) show the temporal evolution of the compositional structure factor S_ϕ and of the orientational structure factor S_S,

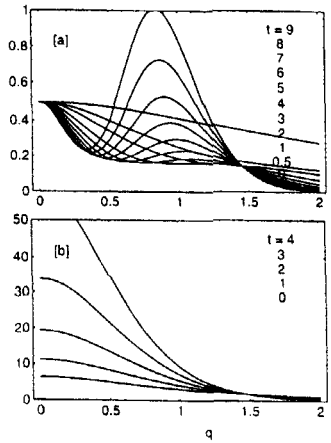

FIGURE 3: Temporal evolution of the compositional structure factor (a) S_ϕ and of the orientational structure factor (b) S_S, for the temperature quench into a nematic unstable region (C).

respectively, for the temperature quench from an isotropic state into a nematic unstable region (C) ($\tau = 0.6, \phi = 0.85$), where the system is initially unstable with respect to orientational order parameter ($f_{SS} < 0$) and metastable with respect to concentration ($f_{\phi\phi} > 0$)[9]. In the very early stages, the concentration fluctuation becomes weak with time because $f_{\phi\phi} > 0$. However the orientational fluctuations grow exponentially with time because $f_{SS} < 0$. Further increasing time, a peak in S_ϕ appears and shifts to the lower values of the wave number. There is no longer the time stage in which the peak position in S_ϕ is invariant, which was predicted by Cahn's linearized theory for isotropic SD in the early stages. The instability of the orientational ordering initially induces the SD and the concentration fluctuation is induced by the coupling between the two order parameters.

In conclusion, we find two distinct growth mechanism in the SD. One

is the concentration fluctuation-induced SD in an isotropic unstable region. In this case the behavior of the SD follows Cahn's linearized theory which means no shift in the compositional structure factor is observed in the early stage. The other growth mechanism is the SD which is driven by the instability with respect to orientational order in the nematic unstable region. In this case, the peak position in the compositional structure factor shifts to lower values of the wave number with time. There is no longer the time stage predicted by the Cahn linearized theory. On increasing the concentration of the liquid crystals, the behavior of the SD is changed from the concentration fluctuation- to orientation fluctuation-induced SD. The droplet growth, or coarsening process, is advanced by the instability of the orientational ordering.

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