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Interference of phase separation and gelation: A zeroth-order kinetic model

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We propose a Ginzburg-Landau-type model to describe the kinetics of mixtures undergoing a sol-gel transition (nonconserved order parameter) simultaneously with phase separation (conserved order parameter). We compute the temporal development of the structure factor and determine the wave vector $q_{\max}$ at which the structure factor is maximal. We find that after a certain time t_f, $q_{\max}$ saturates at a final value q_f, and we calculate the temperature dependence of both t_f and q_f. The predictions of this zeroth-order model agree remarkably well with recent kinetic measurements in gelatin-water-methanol mixtures.

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During the process of phase separation in polymeric systems, the morphology of a system changes continuously [1]. Recent interest has focused on controlling the morphology of the final product by arresting the phase-separation process at some intermediate stage [2–5], leaving the system in a state of microphase separation. One way of achieving this is by coupling the process of phase separation to a thermoreversible "physical" gelation occurring in the same temperature range. Such microphase separated gels have been observed in synthetic linear polymers [6–9], as well as in gelatin [4,5] and solutions of multiblock copolymers [10]. For example, phase separation of certain linear polymers in solution may induce strong associations in the form of cross-links or microcrystals between parts of the polymer chains, forming a thermoreversible, physical gel. Conversely, the onset of gelation could arrest the phase-separating system producing microphase-separated polymer-poor domains in a gel matrix. The equilibrium aspects of this phenomenon have been modeled in terms of correlated-percolation models [11] and as tricritical phenomena [3]. Here, we address the question of how the kinetics of gelation "interfere" with the kinetics of phase separation. We develop a zeroth-order model that couples the kinetics of physical gelation to a phase-separation process, and find surprisingly good agreement with recent experiments [5].

(i) *Phase separation without gelation* is described in mean-field approximation by the normalized Ginzburg-Landau free energy [1(a),12]

$$f_\psi = \frac{1}{2}|\nabla\psi|^2 - \epsilon\frac{\psi^2}{2} + \frac{\psi^4}{4}, \tag{1a}$$

where $\epsilon \equiv (T_c - T)/T_c$ is the reduced temperature, T_c the critical temperature, and ψ the order parameter—related to the local polymer concentration ϕ by $\phi = (\psi + 1)/2$. Figure 1 shows the coexistence and spinodal lines associated with f_ψ.

The evolution of the (conserved) concentration is described by the Cahn-Hilliard equation [1(a)]

$$\frac{\partial\psi}{\partial t} = \nabla\cdot M_\psi\nabla\frac{\delta f_\psi}{\delta\psi} = -\nabla\cdot M_\psi\nabla(\nabla^2\psi + \epsilon\psi - \psi^3). \tag{1b}$$

Here M_ψ is the mobility, which in conventional treatments is assumed to be constant [1].

(ii) *The sol-gel transition without phase separation* can be described by [13]

$$f_c = -g\frac{c^2}{2} + \frac{c^3}{3}. \tag{2a}$$

Here $c = c(T,\phi)$ denotes the gel concentration, i.e., the fraction of polymers belonging to the infinite gel network

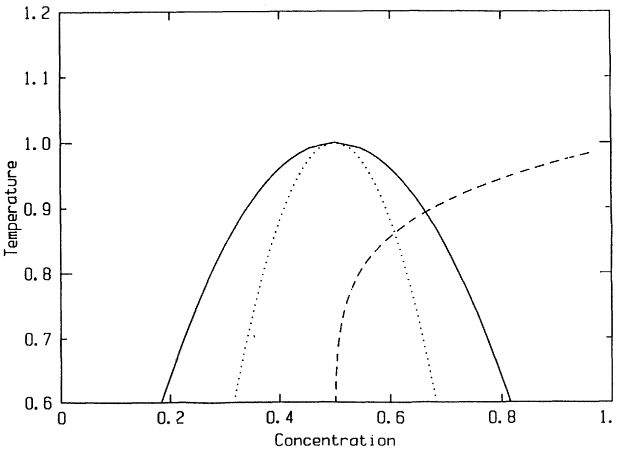

FIG. 1. The temperature-concentration phase diagram showing the coexistence curve (——), the spinodal (···), and the sol-gel transition line (- - -) for the system described in the text.

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and $g \equiv g(T, \phi)$ is a parameter that controls the position of the sol-gel line in the phase diagram of the system; $g < 0$ corresponds to the sol phase, $g > 0$ to the gel phase. We model the gelation kinetics by using the dynamical equation for the local gel concentration $c(r)$, a "nonconserved order parameter" [1(a)],

$$\frac{\partial c}{\partial t} = -M_c \frac{\delta f_c}{\delta c} = M_c(gc - c^2). \tag{2b}$$

The gelation mobility M_c fixes the time scale of the gelation process.

(iii) *The "coupling" of phase separation and gelation* is accomplished by making M_ψ a function of c and g a function of ϕ. Thus the evolution of c becomes dependent on ϕ and at equilibrium $c = g(T, \phi)$. In the presence of gelation the viscosity increases dramatically [5], so that locally regions whose viscosity is much higher than the solution viscosity can be considered to belong to the gel phase. Thus we expect a substantial decrease in the polymer mobility M_ψ in those regions where the gel concentration c becomes nonzero. Thus, M_ψ must be a fast-decaying function of c; here we use

$$M_\psi(c) = \exp(-c/c_0), \tag{3}$$

where $c_0 \ll 1$ [14]. Thus, when $c \gg c_0$, the polymer concentration ψ does not change any more [15].

Since our model couples the dynamical equations of a conserved order parameter with that of a nonconserved order parameter it is a realization of model *C* in the Hohenberg-Halperin classification [16]. The added feature of our model is that the mobility M_ψ varies both temporally and spatially. In order to calculate $g(\phi)$, we focus on thermoreversible gels where cross-links are formed due to noncovalent interactions [6–9,17] involving only a fraction p of the monomers in the polymer which are in the proper configuration to form cross-links. Accordingly, we define the sol-gel transition temperature by the condition $p\phi = \phi^*$, where $p\phi$ is the concentration of cross-links and ϕ^* is the critical concentration necessary to form a macroscopic gel. Since the sol-gel transition corresponds to $g = 0$, in Eq. (2b), we define $g(\phi)$ by $g(\phi) \equiv (p\phi - \phi^*)/(1 - \phi^*)$. Here the denominator is chosen to normalize g to 1 when $p = 1$ and $\phi = 1$. The temperature dependence of p determines the sol-gel line; we assume that $p = \exp(\Delta F/kT)/[1 + \exp(\Delta F/kT)]$.

In order to study the interference of the kinetics of gelation and the kinetics of phase separation following a quench from the stable to the unstable region, we numerically integrate [1(c)] Eqs. (1b) and (2b) on a square lattice of size 128×128 using a parallel computer (Connection Machine CM-2). No noise is added to the equations, except in the initial conditions for $\psi(r, t = 0)$ to initiate the phase separation from the unstable fixed point ($\psi = 0, c = 0$); $\phi^* = 0.5$, $\Delta F = 10kT - kT \ln 24\,000$ [18]. The sol-gel line is shown in Fig. 1. For determining the two mobilities we choose $c_0 = 0.01$ and $M_c = 0.02$. Using these parameters, we calculate the time evolution of the spherically averaged structure factor $S(q, t)$ [1] as a function of wave vector q at selected times, and averaged over 50 realizations to diminish effects due to initial conditions; our results for $T = 0.77T_c$ are shown in Fig. 2(a).

For comparison, Fig. 2(b) shows the corresponding calculation of the structure factor for phase separation without gelation ($M_\psi \equiv 1$). The striking difference between the late-time behavior of the two cases is readily apparent in Figs. 2(c) and 2(d). We see an initial time-independent value of $q_{\max}$ (the value of q corresponding to the maximum $S_{\max}$ in S) and an exponential growth of $S_{\max}$ [characteristic of linear Cahn-Hilliard theory without noise [1(a)]], followed by a decrease of $q_{\max}$ and a slow growth of $S_{\max}$ when the nonlinearity in (1b) becomes significant. In the case of phase separation with

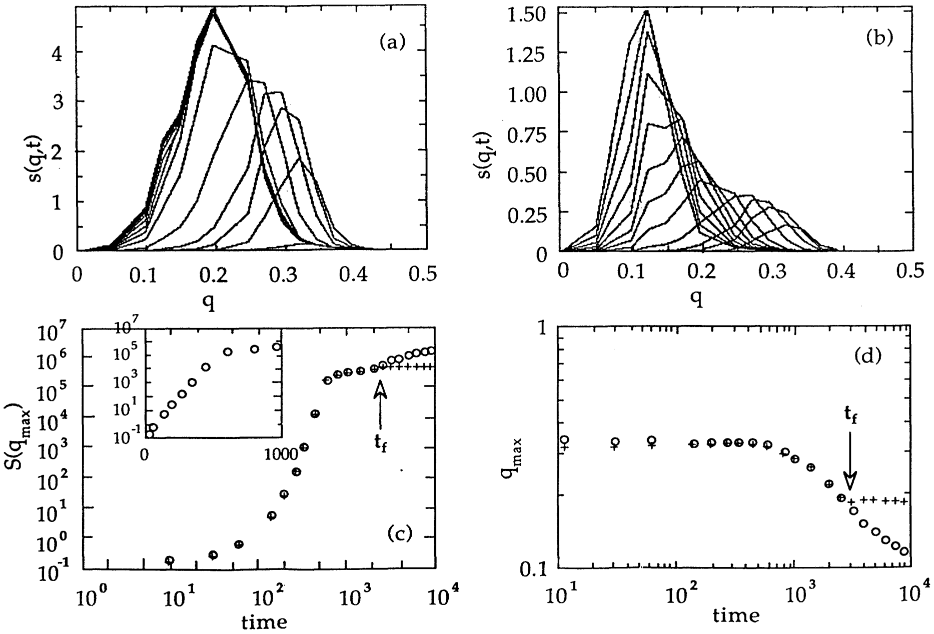

FIG. 2. Structure factors $S(q, t)$ obtained at $T = 0.77T_c$. The structure-factor values should be multiplied by 10^5 for part (a) and 10^6 for part (b), but are otherwise in arbitrary units. The unit for q is inverse lattice spacing. Since the results are for a 128×128 lattice, the smallest $q = 2\pi/128 = 0.049$. From right to left the times are $t = 600$, 800, 1000, 1400, 2000, 2600, 3000, 4000, 5000, 6200, 7600, 9000. The unit of time is determined by the mobility, which is equal to 1 initially. (a) With gelation. (b) Without gelation ($M_\psi \equiv 1$). (c) log-log plot and semilog plot (inset) of $S_{\max}$ vs time t; with gelation (+) and without gelation (○). (d) log-log plot of $q_{\max}$ vs time t; with gelation (+) and without gelation (○).

gelation, Figs. 2(c) and 2(d) show that at a certain time $t_f = t_f(T)$, neither $S_{\max}$ nor $q_{\max}$ changes further.

We find [Fig. 3(a)] that the value of $q_{\max}$ observed in the initial stages decreases with increasing temperature, as expected from the increase of the correlation length on approaching the spinodal. Moreover, for deeper quenches, the decrease of $q_{\max}$ begins at an earlier time t_n, due to the faster onset of nonlinearity [19]. We find that for higher temperatures, t_f increases [Fig. 3(b)] and correspondingly $q_{\max}$ decreases before saturating at $q = q_f$ [Fig. 3(c)]. We understand this observation in terms of our finding that the phase-separation process produces domains which grow to some finite size, but then get pinned as the polymer-rich phase reaches the sol-gel line and the gelation process starts. The smaller is the temperature, the closer is the system to the sol-gel line (Fig. 1) and, therefore, the earlier in time is the onset of gelation—so the larger is q_f (Fig. 3).

Figure 3 also compares our results with recent experiments on a gelatin-water-methanol mixture [5]. The experimental data clearly show that at late times $q_{\max}$ saturates at a final value q_f at a well-defined time t_f. Moreover, for increasing temperature, t_f increases, and q_f decreases [20], suggesting that in these experiments by the time gelation occurs the phase-separation process is well into the nonlinear regime.

We next address the question of the sensitivity of our conclusions to the two parameters c_0 and M_c. We found that $S(q,t)$ and its temperature dependence are insensitive to both parameters provided they are not too large. Changing c_0 or M_c only affects the actual values of t_f and q_f; for larger c_0 and smaller M_c, t_f increases and q_f decreases. For $c_0 = 0.02$ and $M_c > 0.1$, gelation becomes so fast that phase separation is stopped before any significant coarsening of the morphology occurs [t_f is comparable to t_n—Fig. 3(a)]. The detailed forms of the spinodal and the sol-gel lines do not affect the overall behavior.

In summary, we have proposed a zeroth-order kinetic model for describing the influence of gelation on the kinetics of phase separation that couples the appropriate differential equations—one for the phase separation (conserved), and one for the gelation process (nonconserved). The coupling is introduced by allowing the mobility to depend upon the gel concentration, and the sol-gel transition temperature to depend on the polymer concentration [21]. As a consequence the mobility varies with time. The process of spinodal decomposition leads to the formation of a spanning network of polymer-rich regions where the polymer concentration is higher than the gelation threshold. The phase-separation process thus promotes the gelation process even when the average polymer concentration is lower than ϕ^*, which might explain the formation of gels in linear polymer solutions upon quenching into the unstable region of the polymer-solvent phase diagram [6–9,23]. Our model captures the essential physics: the phase-separation process produces domains which grow to some finite size and then get "pinned" due to gelation, which manifests itself as a crossover in the structure factor from a *time-dependent* to a *time-independent* behavior. Approaching the sol-gel transition line, this crossover moves toward smaller times and larger values of q_f—in agreement with recent experiments.

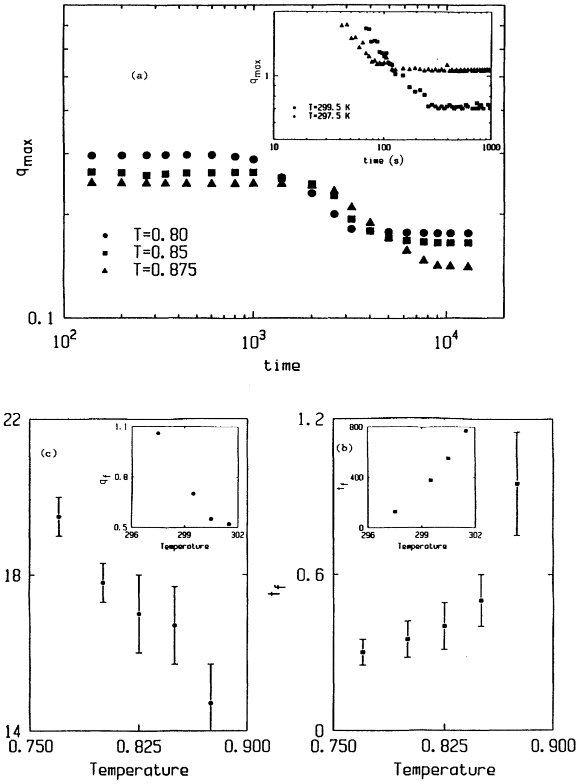

FIG. 3. (a) Time dependence of $q_{\max}$ for three different temperatures, $T = 0.80$, $T = 0.85$, and $T = 0.875$. (b) Temperature dependence of the gelation time t_f. (c) Temperature dependence of the final value q_f of $q_{\max}$. These quantities are obtained solving numerically the model described in the text. The values for t_f are plotted in units of 10^4. The data in the insets are adapted from experiments [5] on gelatin. The data clearly show that at late times $q_{\max}$ saturates at a well-defined time t_f. For increasing temperature, t_f increases [inset of (b)] and q_f decreases [inset of (c)] implying that by the time gelation occurs, the phase separation process is well into the nonlinear regime. The experiments do not show the initial growth at constant $q_{\max}$, which is characteristic of linear Cahn-Hilliard theory without thermal noise [22].

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[15] The total free energy of the system is now given by $f_{\text{tot}} = f_c + f_\psi$. Thus the evolution of ψ should be controlled by $\delta f_{\text{tot}}/\delta\psi$. This adds an extra term $(\delta f_c/\delta\psi)$ in Eq. (1b), which modifies the equilibrium solution compared to the case where no gelation is observed. We neglect such a term because we are interested only in the metastable states produced by the freezing of the mobility. In our model, such a term would indeed become significant only for $c \gg c_0$, i.e., when $M_\psi(c)$ is practically zero.

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