# Spinodal decomposition in gels

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We construct a Ginzburg-Landau model for gels undergoing spinodal decomposition in terms of the polymer volume fraction and a deformation tensor. We numerically demonstrate that the domain growth is extremely slowed down in late stages, where the surface tension force, which drives the coarsening in usual fluids, is cancelled by the elastic force. The patterns closely resemble those observed in highly viscoelastic, asymmetric binary mixtures. [S1063-651X(99)50202-X]

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Gels are network systems composed of cross-linked polymers and can swell enormously in solvent [1]. Such soft elastic systems exhibit interesting phase transition behavior as the solvent quality becomes poor [2]. In particular, Tanaka *et al.* presented a theory of dynamic light scattering [3] and observed critical slowing down of the polymer density fluctuations [4]. After Dušek and Patterson's prediction [5], a discontinuous volume phase transition in gels has been observed [6,7]. Here a macroscopic shape change of gels takes place with absorption or desorption of solvent through the interface between the gel and the surrounding solvent. Hence such shape changes are extremely time-consuming unless the gel size is very small. In experiments it is often the case that, when a swollen gel is suddenly brought into an unstable temperature region, it instantly turns opaque without any appreciable volume change [8]. This means that gels undergo spinodal decomposition with enhancement of small scale fluctuations and that the resultant two-phase structure is eventually pinned due to elasticity arising from the cross-linkage. In a closely related effect, experiments have shown that domain structures in phase-separating polymers can be pinned if cross-links are introduced by gelation [9], chemical cross-linking reaction [10], or photo-cross-linking [11]. In addition, use of linearly polarized light to induce photo-cross-linking has produced lamellar domain structures, probably due to anisotropic network formation [12].

Unfortunately, there have been few theoretical investigations into these problems. In a first paper, Sekimoto *et al.* demonstrated that a steady spongelike domain structure is produced by elastic pinning [13] in a two-dimensional microscopic network system. They also found elongation of domains under uniaxial compression. It is worth noting that these features are very analogous to elastic effects in solid binary alloys [14].

In this paper we formulate a simple time-dependent Ginzburg-Landau model for neutral gels and use it to (numerically) study spinodal decomposition. We impose periodic boundary conditions in solving the equations, so we assume that the total volume is fixed and there are no macroscopic shape changes. Thus, our results apply in the interior region far from the gel-solvent interface or when the gel surface is fixed to a solid boundary wall.

Let the Cartesian coordinates of a deformed gel be denoted by $\mathbf{x}=(x_1,x_2,x_3)$ and those of the initial homogeneous gel by $\mathbf{x}_0=(x_{01},x_{02},x_{03})$. Then the local deformation is represented by the deformation tensor $\{\Gamma_{ij}\}=\{\partial x_i/\partial x_{0j}\}$ [15]. The network (polymer) volume fraction is related to the determinant of the tensor,

$$\phi=\phi_0/\mathrm{Det}\{\Gamma_{ij}\}, \tag{1}$$

where $\phi_0$ is the initial volume fraction. The total free energy $F=F_\phi+F_{el}$ consists of two parts [16–18],

$$F_\phi=k_BT\int d\mathbf{x}\left[f(\phi,T)+\frac{1}{2}C|\nabla\phi|^2\right], \tag{2}$$

$$F_{el}=\frac{1}{2}k_BT\int d\mathbf{x}\nu_0\frac{\phi}{\phi_0}\sum_i W_{ii}. \tag{3}$$

Here $f(\phi,T)$ depends on $\phi$ and the temperature $T$, $\nu_0$ is the cross-link density in the initial state, and

$$W_{ij}=\sum_\ell \Gamma_{i\ell}\Gamma_{j\ell}. \tag{4}$$

The free energy has been expressed in the Euler representation or in the deformed space. The origin of the elastic part of the free energy is as follows. Flory [1] assumed that if a homogeneous isotropic rubber or gel with a cubic shape is deformed into a rectangular shape, the elastic free energy needed is of the form $\Delta F_{el}=\frac{1}{2}k_BT\nu_0V_0[\Sigma_i\alpha_i^2-3-2B\log(\alpha_1\alpha_2\alpha_3)]$, where $V_0$ is the initial volume, $B$ is a constant, and $\alpha_i$ are the elongation ratios in the three principal axes, so $\phi=\phi_0/(\alpha_1\alpha_2\alpha_3)$. Obviously, the term proportional to $\Sigma_i\alpha_i^2$ becomes $F_{el}$ in Eq. (3) for slowly varying $\Gamma_{ij}$, because the volume element $d\mathbf{x}$ in the deformed gel and $d\mathbf{x}_0$ in the initial gel are related by $d\mathbf{x}_0=d\mathbf{x}\phi/\phi_0$ from Eq. (1). In Eqs. (2) and (3) $F$ is written as a functional of $\phi$ and $\Gamma_{ij}$. In a similar viscoelastic model for polymer solutions [19,20], where entanglements are transient, $\phi$ and $\Gamma_{ij}$ can be treated as independent variables. However, in our present gel model, $\phi$ and $\Gamma_{ij}$ are related by Eq. (1), because the network is assumed to be permanent.

We may calculate the stress tensor $\vec{\vec{\Pi}} = \{\Pi_{ij}\}$ by superposing an infinitesimal additional displacement $\delta\mathbf{x}$ onto $\mathbf{x}$ and expressing the free energy change as [15]

$$\delta F = -\int d\mathbf{x} \sum_{ij} \Pi_{ij} \frac{\partial}{\partial x_j} \delta x_i. \tag{5}$$

Here $\delta\Gamma_{ij} = \partial \delta x_i / \partial x_{0j}$, $\partial \delta x_i / \partial x_j = \Sigma_\ell \Gamma^{\ell j} \delta\Gamma_{i\ell}$, where $\{\Gamma^{ji}\} = \{\partial x_{0j} / \partial x_i\}$ is the inverse matrix of $\{\Gamma_{ij}\}$. The incremental change of $\phi$ is given by $\delta\phi = -\phi \Sigma_i \partial \delta x_i / \partial x_i$. Then, $\vec{\vec{\Pi}}$ consists of two terms [16]. The first term is determined by $F_\phi$ as

$$\Pi_{\phi ij} = k_B T \left[ P_1 \delta_{ij} + C \frac{\partial \phi}{\partial x_i} \frac{\partial \phi}{\partial x_j} \right], \tag{6}$$

where $P_1 = \phi \partial f / \partial \phi - f - \mathbf{\nabla} \cdot (C \phi \mathbf{\nabla}\phi)/2 - \phi C \nabla^2 \phi/2$. This is of the same form as the stress tensor for fluid binary mixtures. The second term is the elastic part,

$$\sigma_{ij} = k_B T \nu_0 (\phi/\phi_0) W_{ij}. \tag{7}$$

The resultant force density acting on the network is

$$-\mathbf{\nabla} \cdot \vec{\vec{\Pi}} = -\phi \mathbf{\nabla} \frac{\delta}{\delta\phi} F_\phi + \mathbf{\nabla} \cdot \vec{\vec{\sigma}}. \tag{8}$$

Here $F_\phi$ is regarded as a functional of $\phi$ and $\mathbf{\nabla} = \partial/\partial\mathbf{x}$ represents taking the space derivative in the Euler representation. As stated above, $F$ can also be treated as a functional of $\mathbf{x}$ in the Lagrange representation; then Eq. (5) leads to $(\delta F/\delta\mathbf{x})_{\mathbf{x}_0} = (\phi_0/\phi)\mathbf{\nabla} \cdot \vec{\vec{\Pi}}$.

Next we discuss dynamics. In gels swollen by solvent, the network motion is highly damped by the friction with the solvent, so the network velocity with respect to the solvent velocity is given by [3,17]

$$\mathbf{v} = -\zeta^{-1} \mathbf{\nabla} \cdot \vec{\vec{\Pi}} + \mathbf{f}_R. \tag{9}$$

Here, $\zeta$ is the friction coefficient between the network and the solvent, and $\mathbf{f}_R$ is the Gaussian and Markovian noise. In the semidilute condition we have $\zeta \sim 6\pi \eta_s \xi^{-2}$, where $\eta_s$ is the solvent viscosity and $\xi$ is a characteristic correlation length ($\propto \phi^{-1}$ in theta solvent). In the Lagrange picture, Eq. (9) may be regarded as a Langevin equation,

$$\mathbf{v} = \left( \frac{\partial \mathbf{x}}{\partial t} \right)_{\mathbf{x}_0} = -\zeta^{-1} \frac{\phi}{\phi_0} \left( \frac{\delta F}{\delta\mathbf{x}} \right)_{\mathbf{x}_0} + \mathbf{f}_R. \tag{10}$$

The fluctuation-dissipation theorem in the Lagrange representation is written as

$$\langle f_{Ri}(\mathbf{x}_0, t) f_{Rj}(\mathbf{x}_0', t') \rangle$$

$$= 2 k_B T \zeta^{-1} (\phi/\phi_0) \delta(\mathbf{x}_0 - \mathbf{x}_0') \delta(t-t') \delta_{ij},$$

where $(\phi/\phi_0)\delta(\mathbf{x}_0 - \mathbf{x}_0')$ is replaced by $\delta(\mathbf{x}-\mathbf{x}')$ in the Euler representation.

The Lagrange time-derivative $(\partial/\partial t)_{\mathbf{x}_0}$ and the Euler time-derivative $\partial/\partial t \equiv (\partial/\partial t)_{\mathbf{x}}$ are related by $(\partial/\partial t)_{\mathbf{x}_0} = \partial/\partial t$

$+ \mathbf{v} \cdot \mathbf{\nabla}$. Further using the relation $(\partial\Gamma_{ij}/\partial t)_{\mathbf{x}_0} = \partial v_i/\partial x_{0j}$ $= \Sigma_\ell (\partial x_\ell/\partial x_{0j})(\partial v_i/\partial x_\ell)$, we obtain the equation for $\{\Gamma_{ij}\}$,

$$\left( \frac{\partial}{\partial t} + \mathbf{v} \cdot \mathbf{\nabla} \right) \Gamma_{ij} - \sum_\ell D_{i\ell} \Gamma_{\ell j} = 0. \tag{11}$$

Here, $D_{ij} = \partial v_i/\partial x_j$ is the velocity gradient tensor. The symmetric tensor $\{W_{ij}\}$ in Eq. (4) is governed by

$$\left( \frac{\partial}{\partial t} + \mathbf{v} \cdot \mathbf{\nabla} \right) W_{ij} - \sum_\ell (D_{i\ell} W_{\ell j} + W_{i\ell} D_{j\ell}) = 0, \tag{12}$$

where the left-hand side is called the upper convective time derivative of tensor variables in the literature [21]. If the network is transient as in polymer solutions, there should be a damping term on the right-hand side of Eq. (12). It is usually taken to be $-(W_{ij} - \langle W_{ij} \rangle)/\tau$ in the simplest approximation with a single relaxation time $\tau$, where $\langle W_{ij} \rangle \propto \delta_{ij}$ is the equilibrium average [21,20].

The continuity equation for $\phi$ follows from Eq. (1) as

$$\frac{\partial}{\partial t} \phi = -\mathbf{\nabla} \cdot (\phi \mathbf{v}) = \mathbf{\nabla} \cdot L \left( \mathbf{\nabla} \frac{\delta F_\phi}{\delta\phi} - \frac{1}{\phi} \mathbf{\nabla} \cdot \vec{\vec{\sigma}} \right) + \theta_R, \tag{13}$$

where $L = \phi^2/\zeta$ is the kinetic coefficient and $\theta_R = -\mathbf{\nabla} \cdot (\phi \mathbf{f}_R)$ is the random force characterized by $\langle \theta_R(\mathbf{x}, t) \theta_R(\mathbf{x}', t') \rangle = 2 k_B T \mathbf{\nabla} \cdot \mathbf{\nabla}' L \delta(\mathbf{x}-\mathbf{x}') \delta(t-t')$. The linearized version of Eq. (13) was first used to analyze dynamic light scattering from gels [3]. Here, diffusion of the polymer is caused by the chemical potential gradient $\mathbf{\nabla}(\delta F_\phi/\delta\phi)$ and the elastic force density $\mathbf{\nabla} \cdot \vec{\vec{\sigma}}$. This means that there is a dynamical coupling between diffusion and stress [22]. Note that the same dynamic equation has been used for polymer solutions, where the coupling gives rise to a variety of dynamical effects such as nonexponential relaxation in dynamic light scattering [22] and shear-induced phase separation [23,20].

We consider the stability of a homogeneous, uniaxially deformed gel against small network deformation for general spatial dimensionality $d$. We assume $x_i = \alpha_i x_{0i} + u_i$, where $\alpha_1 = \alpha_\parallel$ and $\alpha_i = \alpha_\perp$ for $i \geq 2$. From Eq. (9), the linearized dynamic equation for the small displacement $\mathbf{u}$ can readily been obtained in the Fourier space. In particular, the longitudinal part or the density deviation evolves exponentially in time with the decay rate,

$$\Gamma_{\mathbf{q}} = \frac{k_B T}{\zeta} \left[ \phi^2 (f'' + C q^2) q^2 + \nu_0 \frac{\phi}{\phi_0} \sum_i \alpha_i^2 q_i^2 \right], \tag{14}$$

where $f'' = \partial^2 f/\partial\phi^2$. Here, the average volume fraction $\phi_0/(\alpha_\perp^{d-1} \alpha_\parallel)$ is simply written as $\phi$. Note that $\Gamma_{\mathbf{q}}$ depends on the direction of $\mathbf{q}$. (i) In the isotropic case the corresponding elastic free energy is of the standard form [24] in the long wavelength limit with the bulk and shear moduli being expressed as $K = k_B T[\phi^2 f'' - (1-2/d)\nu_0(\phi/\phi_0)^{1-2/d}]$ and $G = k_B T \nu_0 (\phi/\phi_0)^{1-2/d}$, respectively. The system is linearly stable for $k_B T(\phi^2 f'' + \nu_0 \alpha^{-1+2/d}) = K + (2-2/d)G \geq 0$, whereas spinodal decomposition occurs for $K + (2-2/d)G < 0$ [25]. (ii) If the system is uniaxially expanded or if $\alpha_1$
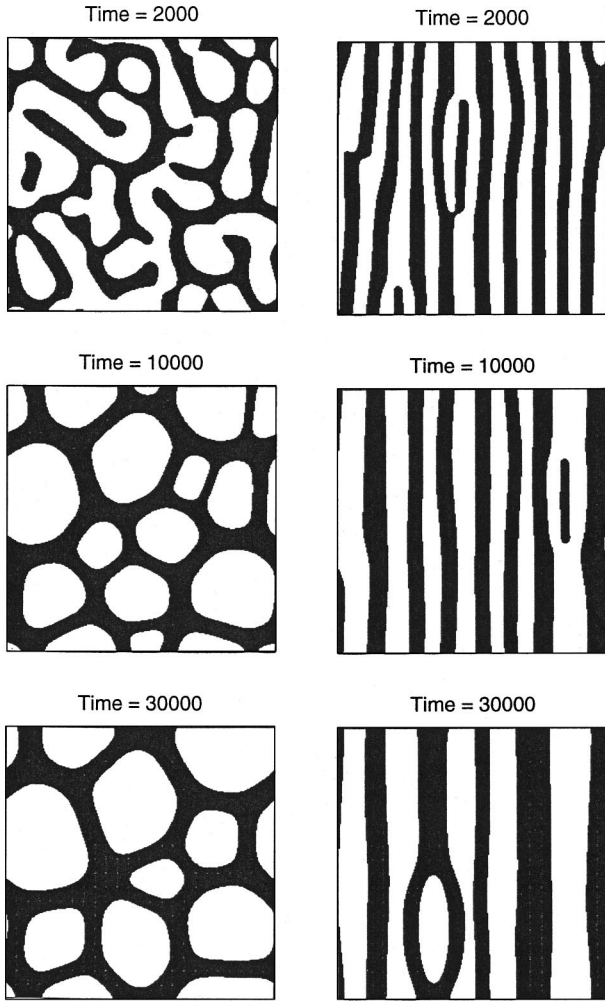
FIG. 1. Temporal evolution of domain structures in our dynamical model for phase separation in gels. The three frames on the left correspond to the isotropic case with $\nu_0^* = 0.3$, and those on the right correspond to the uniaxial case with $\nu_0^* = 0.1$. Polymer-rich regions are marked in black, whereas solvent-rich regions are not marked. Note that the saturation values of the order parameter are asymmetric, being higher in the polymer-rich phase.

$=\alpha_\parallel$ is largest, the thermal fluctuations are uniaxially suppressed in the stretched direction. Hence spinodal decomposition occurs in the perpendicular directions for $f'' + \nu_0(\phi/\phi_0)\alpha_\perp^2 < 0$. We expect the formation of cylindrical domains in three dimensions. (iii) For uniaxial compression, where $\alpha_\perp$ is smallest, the thermal fluctuations become uniaxially enhanced in the stretched direction, resulting in platelike domains.

We now present representative numerical results in the two-dimensional case. For simplicity, we assume that the free energy density $f$ is written in terms of $\psi \equiv 2\phi/\phi_0 - 1$ as $f = a(-b\psi^2/2 + \psi^4/4)$ where $a, b$ are positive constants and the friction constant $\zeta$ is proportional to $\phi^2$ as $\zeta = \zeta_0(\phi/\phi_0)^2$. By measuring space and time in units of $\ell = (C\phi_0^2/8a)^{1/2}$ and $t_0 = C\zeta_0\phi_0^2/(32 k_B T a^2)$, Eq. (13) is rewritten as $\partial\psi/\partial t = -\mathbf{\nabla}\cdot\mathbf{J}$ with

$$\mathbf{J} = \mathbf{\nabla}[(b - \psi^2 + 2\mathbf{\nabla}^2)\psi] + \nu_0^*(1+\psi)^{-1}\mathbf{\nabla}\cdot\overset{\leftrightarrow}{Z}, \quad (15)$$

where $\mathbf{J} = (1+\psi)\mathbf{v}$, $\overset{\leftrightarrow}{Z} = (\phi/\phi_0)\overset{\leftrightarrow}{W}$, and $\nu_0^* = \nu_0/a$ is the dimensionless cross-link density. The random force term is neglected here. From Eqs. (1) and (4), we have $Z_{xx}Z_{yy} - Z_{xy}^2 = 1$, so it is convenient to introduce $M$ by $Z_{xx} = (1 + Z_{xy}^2)^{1/2}e^M$ and $Z_{yy} = (1 + Z_{xy}^2)^{1/2}e^{-M}$. From Eq. (12) we obtain

$$\left(\frac{\partial}{\partial t} + \mathbf{v}\cdot\mathbf{\nabla}\right)M = D_{xx} - D_{yy} + \left(\frac{D_{xy}}{Z_{xx}} - \frac{D_{yx}}{Z_{yy}}\right)Z_{xy},$$

$$\left(\frac{\partial}{\partial t} + \mathbf{v}\cdot\mathbf{\nabla}\right)Z_{xy} = D_{xy}Z_{yy} + D_{yx}Z_{xx}. \quad (16)$$

We integrated Eqs. (15) and (16) for $\psi$, $M$, and $Z_{xy}$ using a simple Euler-discretization scheme on an $N^2$ lattice (with $N = 256$) for $b = 0.8$ and $\langle\psi\rangle = 0$. Our scheme used isotropic Laplacians and partial derivatives, and the mesh sizes were $\Delta x = 1$ and $\Delta t = 0.05$. The initial condition was specified in terms of the undeformed coordinates $\mathbf{x}_0 = (x_0, y_0)$ as $\alpha_\parallel x_0 + f_x = n(\Delta x)$ and $\alpha_\perp y_0 + f_y = m(\Delta x)$ at each lattice point, $(n,m) = (\Delta x)^{-1}\mathbf{x}$, $(n,m = 1,\ldots,N)$. The variables $f_x$ and $f_y$ were random numbers given independently at each lattice point. The parameter $\lambda \equiv (\alpha_\parallel/\alpha_\perp)^{1/2}$ measures the degree of uniaxial extension.

Figure 1 shows typical network domain structures in an isotropic case, with $\lambda = 1$ and $\nu_0^* = 0.3$, and in a uniaxial case, with $\lambda = \sqrt{2}$ and $\nu_0^* = 0.1$. The domain structures for the isotropic case closely resemble patterns observed in deeply quenched polymer solutions and asymmetric polymer blends [26,27]. This is as expected because the viscoelastic coupling in Eq. (13) ($\propto \mathbf{\nabla}\cdot\overset{\leftrightarrow}{\sigma}$) is important in these systems. On the other hand, in the uniaxial case, we can see the formation of

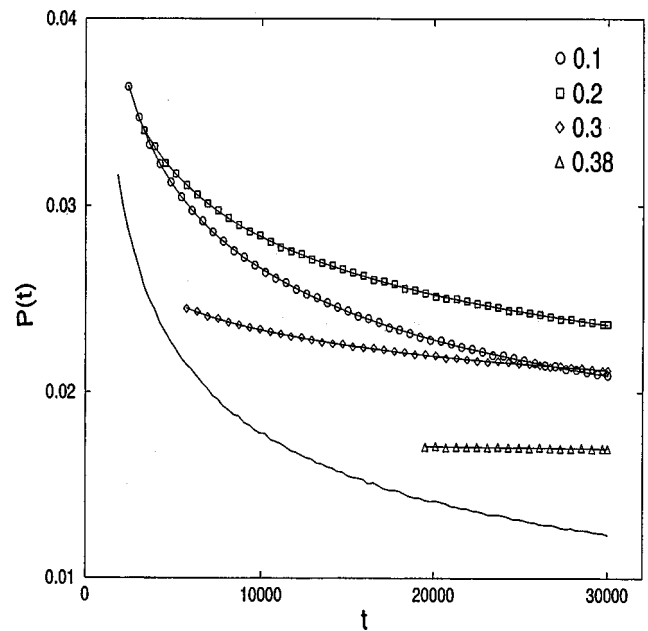

FIG. 2. Time dependence of the perimeter density $P(t)$ for $\nu_0^* = 0.1$, 0.2, 0.3, and 0.38, denoted by the symbols indicated. For comparison, we also plot (as a solid line) $P(t)$ vs $t$ for the case without elastic effects ($\nu_0^* = 0$), which obeys the Lifshitz-Slyozov law $P(t) \sim t^{-\alpha}$ with $\alpha = 1/3$. For the other curves, $\alpha \simeq 0.24$, 0.17, 0.09, and 0.02 for $\nu_0^* = 0.1$, 0.2, 0.3, and 0.38, respectively.

lamellar structures. In Fig. 2 we plot the perimeter density $P(t)(=$ # of broken bonds$/N^2)$ vs $t$ in the isotropic case, each curve being an average over 40 independent runs. Because $P(t)$ measures the inverse length scale of the domains, Fig. 2 demonstrates extreme slowing down of the domain growth. This is consistent with the experiments [8–12] and the simulation [13].

In Fig. 2, the $P(t)$ curves are well approximated by power-law fits ($\sim t^{-\alpha}$) with the growth exponents consistent with $\alpha = \frac{1}{3}(1 - 2\nu_0^*/b)$ in the range of our computation time ($t < 3 \times 10^4$). There is no theory for such late stage behavior, which delicately depends on various factors such as the form of the elastic free energy and the space dimensionality. We should also point out that $\psi$ takes a long time to saturate to the local equilibrium values in the two phases as $\nu^*$ is increased. We defined the saturation time $\tau_s$ such that the average of $\psi$ in the solvent-rich regions ($\psi < 0$) reaches $-0.8b^{1/2}$ at $t = \tau_s$. Then we obtained $\tau_s \sim (b - 2\nu^*)^{-1}$, where $b = 2\nu^*$ is the spinodal point as can be seen from the long wavelength behavior of Eq. (14). Figure 2 only plots data for $t > \tau_s$, so the range of data is smallest for $\nu_0^* = 0.38$.

Let us conclude with the following remarks.

(i) We are currently studying the effects of heterogeneities of the network structure, which act as quenched disorder. These are known to drastically affect the scattering amplitude, even in disordered states—particularly in uniaxial gels [17,28–31]. One of our results (not presented here) shows that heterogeneities strongly amplify the growth of initial fluctuations.

(ii) It is known that the scattering amplitude has a maximum at an intermediate wave number in the presence of ions [28–30]. It is of great interest to understand how charges alter the phase separation behavior when an ionized gel is quenched into an unstable region. This problem constitutes a future direction for our study of spinodal decomposition in gels.

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