

Viscoelastic effects in early stage phase separation in polymeric systems

Akira Onuki and Takashi Taniguchi
Department of Physics, Kyoto University, Kyoto 606, Japan

(Received 7 November 1996; accepted 24 December 1996)

We examine how viscoelasticity affects early stage spinodal decomposition in polymer solutions and blends when fluctuations of the stress and the composition are coupled in dynamics. The coupling is increased with increasing asymmetry between the two components. We introduce a long viscoelastic length ξ_{ve} within which the stress relaxation governs the composition relaxation. It can be of the order of the tube length in the reptation theory in strongly asymmetric polymer blends. For shallow quenching phase separation proceeds on time scales slower than the stress relaxation time τ and the kinetic coefficient depends on the wave number q as q^{-2} for $q\xi_{ve} > 1$. On the other hand, for deep quenching phase separation takes place as in gels on time scales faster than τ . We describe the crossover between these two cases by assuming a single stress relaxation time. © 1997 American Institute of Physics. [S0021-9606(97)50113-9]

I. INTRODUCTION

Recently a great number of phase separation experiments have been performed on polymer solutions¹ and blends,^{2,3} where phase separation occurs on much slower time scales and much longer spatial scales than in usual fluids with low molecular weights. Theories⁴⁻¹¹ predicted that, if we are interested in processes on spatial scales longer than the gyration radius, characteristic features of spinodal decomposition remain the same as those derived from simple dynamic models for usual fluids. However, some experiments have revealed unusual effects presumably ascribable to viscoelasticity peculiar to polymers. In an asymmetric blend of PVME/d-PS, Schwahn *et al.*¹² found that the Onsager kinetic coefficient $L(q)$ observed in early stage spinodal decomposition strongly depends on the wave number q as $L(q)/L(0) \sim q^{-2}$ for $q \gtrsim R_0^{-1}$ with $R_0 = 1070\text{\AA}$. This value of R_0 was five to seven times larger than the gyration radius R_g , while Pincus⁵ predicted the same q dependence but with $R_0 = R_g$ for symmetric ($N_1 = N_2$) polymer blends by examining one chain motion in a tube in the reptation theory. In a more symmetric blend of d-PS/PS Muller *et al.*¹³ still obtained $R_0/R_g \sim 2$. In these blends they also observed non-exponential relaxation of the dynamic structure factor in one phase states, suggesting significant viscoelastic effects on the composition relaxation in the systems. Similar observation of $R_0/R_g \sim 2$ was also made for a blend of d-PB/PB by Jinnai *et al.*¹⁴ We believe that this effect stems from collective diffusion among the two components which takes place to achieve viscoelastic stress balance.¹⁵ The range of this correlated motion extends over a long viscoelastic length ξ_{ve} and should be identified with the observed R_0 in $L(q)$.^{16,17} Such motion indicates the presence of a dynamical coupling between stress and diffusion. Although its relevance to various effects has begun to be recognized rather recently, it is now established that it causes shear-induced phase separation in polymer solutions,¹⁸⁻²⁵ nonexponential decay in dynamic scattering near equilibrium,^{15,16,26} and polymer migration towards the center in a capillary flow.¹⁵

The aims of this paper are first to explain the effects of

the dynamical coupling in early stage phase separation to explain the above experiments and second to propose more systematic experiments to detect viscoelastic effects unique to polymer solutions and asymmetric blends. We shall see that such asymmetry in blends arises from differences in the chain lengths and the monomer friction coefficients of the two polymers. This paper extends results of a short previous paper in this direction by one of the present authors.¹⁶

We also mention formation of sponge-like network structures composed of thin polymer-rich regions in late stage spinodal decomposition of deeply quenched polymer solutions. It has been studied particularly in detail by Tanaka,²⁷ while such patterns were already reported by Aubert and by Song and Torkelson.¹ Tanaka subsequently observed the same network formation in a polymer blend in which one phase is close to its glass transition.²⁸ Therefore, the network formation is a general aspect of binary mixtures where the two components have very different viscoelastic properties. Analytic theory on such highly nonlinear effects is very difficult, so we have recently performed computer simulations as reported in another paper.²⁹ There, we have reproduced the pattern by solving a viscoelastic time-dependent Ginzburg-Landau model which takes account of the dynamical coupling.

The organization of this paper is as follows. In Section II we show that the dynamical coupling is generally present when the network stress acts on the two components asymmetrically or the stress division is asymmetric. In Section III we linearize the dynamic model and examine its implications, where we introduce the viscoelastic length ξ_{ve} and also discuss the dynamic structure factor in the presence of viscoelasticity. In Section IV we examine the growth of the composition fluctuations in unstable temperature regions in polymer solutions and blends when the composition and the stress are coupled.

II. DYNAMICAL COUPLING BETWEEN STRESS AND DIFFUSION

We consider two component viscoelastic fluids where the stress relaxation time τ is very long and a large stress is

produced even against small deformations. It will be called the network stress even when it arises from entanglement with finite lifetimes. If the time scale of deformations is shorter than τ , the system behaves as a soft elastic body. On the other hand, if it is slower than τ , we have a highly viscous fluid. It is then of great importance how the stress can influence spatial inhomogeneities of the composition in various situations.

A. Two-fluid dynamics

To illustrate the concept of the dynamical coupling, let us consider a simple two fluid model of a very viscous two component system.^{15,16,21–25,30} The mass densities, ρ_1 and ρ_2 , of the two components are convected by their velocities, \mathbf{v}_1 and \mathbf{v}_2 , as

$$\frac{\partial}{\partial t} \rho_K = -\nabla \cdot (\rho_K \mathbf{v}_K), \quad (2.1)$$

where $K=1,2$. The total density $\rho = \rho_1 + \rho_2$ obeys the usual continuity equation,

$$\frac{\partial}{\partial t} \rho = -\nabla \cdot (\rho \mathbf{v}), \quad (2.2)$$

where the average velocity \mathbf{v} is defined by

$$\mathbf{v} = \rho^{-1} (\rho_1 \mathbf{v}_1 + \rho_2 \mathbf{v}_2). \quad (2.3)$$

The equations of motion for the two components are

$$\rho_1 \frac{\partial}{\partial t} \mathbf{v}_1 = -\rho_1 \nabla \mu_1 - \zeta (\mathbf{v}_1 - \mathbf{v}_2) + \mathbf{F}_1, \quad (2.4)$$

$$\rho_2 \frac{\partial}{\partial t} \mathbf{v}_2 = -\rho_2 \nabla \mu_2 - \zeta (\mathbf{v}_2 - \mathbf{v}_1) + \mathbf{F}_2. \quad (2.5)$$

Here we consider only very slow motion and neglect temperature inhomogeneities. The μ_1 and μ_2 are appropriately defined chemical potentials and ζ is the friction coefficient between the two components. The \mathbf{F}_1 and \mathbf{F}_2 are the force densities arising from the network stress and the background viscosity. Their sum is related to the divergence of the total stress tensor $\vec{\Pi}_t$ and appears in the equation for the momentum density $\rho \mathbf{v} = \rho_1 \mathbf{v}_1 + \rho_2 \mathbf{v}_2$ as

$$\rho \frac{\partial}{\partial t} \mathbf{v} = -\nabla \vec{\Pi}_t = -(\rho_1 \nabla \mu_1 + \rho_2 \nabla \mu_2) + (\mathbf{F}_1 + \mathbf{F}_2). \quad (2.6)$$

If we assume that the network stress $\vec{\sigma}$ is dominant over the stress due to the background viscosity, we have

$$\mathbf{F}_1 + \mathbf{F}_2 \cong \nabla \cdot \vec{\sigma}. \quad (2.7)$$

Note that the contribution of the network to $\vec{\Pi}_t$ is $-\vec{\sigma}$ with the minus sign in our notation. From (2.4) and (2.5) the relative velocity $\mathbf{w} = \mathbf{v}_1 - \mathbf{v}_2$ is governed by

$$\frac{\partial}{\partial t} \mathbf{w} = -\nabla (\mu_1 - \mu_2) - \zeta \left(\frac{1}{\rho_1} + \frac{1}{\rho_2} \right) \mathbf{w} + \frac{1}{\rho_1} \mathbf{F}_1 - \frac{1}{\rho_2} \mathbf{F}_2. \quad (2.8)$$

If we are interested in slow motion whose characteristic frequencies are much slower than $\zeta(1/\rho_1 + 1/\rho_2)$, we may set $\partial \mathbf{w} / \partial t = \mathbf{0}$ in (2.8) to obtain

$$\mathbf{w} = (\rho_1 \rho_2 / \zeta \rho) \left[-\nabla (\mu_1 - \mu_2) + \frac{1}{\rho_1} \mathbf{F}_1 - \frac{1}{\rho_2} \mathbf{F}_2 \right]. \quad (2.9)$$

Now we need to know how the network stress is divided between the two components. We may consider three cases. As the simplest case, when the two components are nearly the same, we have a trivial stress division,

$$\mathbf{F}_K = (\rho_K / \rho) \nabla \cdot \vec{\sigma}. \quad (2.10)$$

In this case we find the usual relation $\mathbf{w} \propto -\nabla (\mu_1 - \mu_2)$ valid for fluid binary mixtures with low molecular weights.

B. Polymer solutions and gels

In polymer solutions and gels, the network, which is either transient or permanent, gives rise to large stress acting directly on polymer chains, so that it follows a one-sided stress division,

$$\mathbf{F}_1 \cong \nabla \cdot \vec{\sigma}, \quad \mathbf{F}_2 \cong \mathbf{0}, \quad (2.11)$$

where the solvent viscosity is neglected. Here the subscript 1 denotes the quantities of polymer and the subscript 2 denotes those of solvent. The relative velocity \mathbf{w} becomes

$$\mathbf{w} \cong -(\rho_2 / \zeta \rho) [\rho_1 \nabla (\mu_1 - \mu_2) - \nabla \cdot \vec{\sigma}]. \quad (2.12)$$

We find that imbalance of the network stress ($\nabla \cdot \vec{\sigma} \neq \mathbf{0}$) leads to relative motion between polymer and solvent. This form of \mathbf{w} was originally proposed by Tanaka *et al.*³¹ for polymer gels, where the network is permanent and the coupling is rather obvious, to analyze dynamic light scattering. Recently Helfand and Fredrickson²¹ used the above form for \mathbf{w} for polymer solutions to predict shear-induced composition fluctuations above the coexistence curve. Wittmann and Fredrickson³² afterwards presented a formal theory using the projection operator method to claim that the dynamical coupling arises even on the basis of the Rouse dynamics without entanglement.

C. Polymer blends

For entangled polymer blends consisting of two kinds of polymer chains, an intermediate division¹⁵ has been proposed in the reptation scheme,^{33,34}

$$\mathbf{F}_1 = \alpha_1 \nabla \cdot \vec{\sigma}, \quad \mathbf{F}_2 = \alpha_2 \nabla \cdot \vec{\sigma}, \quad (2.13)$$

where $\alpha_1 + \alpha_2 = 1$. We introduce a dynamical asymmetry parameter α by

$$\alpha = \rho (\alpha_1 / \rho_1 - \alpha_2 / \rho_2), \quad (2.14)$$

in terms of which (2.9) becomes

$$\mathbf{w} = -(\rho_1 \rho_2 / \zeta \rho^2) [\rho \nabla (\mu_1 - \mu_2) - \alpha \nabla \cdot \vec{\sigma}]. \quad (2.15)$$

For simplicity we are assuming that the two polymers have the same monomer size b and the same monomer number N_e between two consecutive entanglement points and that they obey reptation dynamics moving in common tubes with

diameters of order $N_e^{1/2}b$.³⁴ Using the polymerization indices N_1 and N_2 and the volume fractions ϕ_1 and ϕ_2 , α may be expressed as

$$\alpha = (N_1\zeta_{01} - N_2\zeta_{02}) / (\phi_1 N_1\zeta_{01} + \phi_2 N_2\zeta_{02}). \quad (2.16)$$

Here ζ_{01} and ζ_{02} are the friction constants of the monomers of the two polymers and can generally be different in our theory even if the common values of b and N_e are assumed. So the dynamical coupling can arise even for $N_1 \cong N_2$. In particular, the trivial stress division (2.10) or $\alpha = 0$ follows for $N_1\zeta_{01} = N_2\zeta_{02}$, while the one-sided division (2.11) or the limit of polymer solutions follows for $N_1\zeta_{01} \gg N_2\zeta_{02}$ and $N_1\zeta_{01}\phi_1 \gg N_2\zeta_{02}\phi_2$. In addition, the reptation theory leads to the expression of the friction coefficient ζ in (2.4) and (2.5),

$$\frac{1}{\zeta} = N_e \left(\frac{1}{\phi_1 N_1 \zeta_{01}} + \frac{1}{\phi_2 N_2 \zeta_{02}} \right). \quad (2.17)$$

We note that (2.15) and (2.17) yield the well-established expression for the mutual diffusion coefficient^{11,35-37}

$$\begin{aligned} D_m &= \zeta^{-1} (\phi_1 \phi_2)^2 (\partial^2 f / \partial \phi_1^2) \\ &= (\phi_2 N_1 D_1 + \phi_1 N_2 D_2) (\phi_2 / N_1 + \phi_1 / N_2 - \phi_1 \phi_2 \chi) \end{aligned} \quad (2.18)$$

between two entangled polymers, where f is the free energy density. On the second line we have used the Flory-Huggins free energy,³³ χ being the interaction parameter, and $D_1 \propto N_e / N_1^2 \zeta_{01}$ and $D_2 \propto N_e / N_2^2 \zeta_{02}$ are the diffusion constants of single chains obeying reptation dynamics.³⁴ In our theory D_m is the diffusion constant governing only large scale composition fluctuations with wavelengths larger than a viscoelastic length ξ_{ve} to be introduced below in (3.15) or (4.17). Namely, the diffusion description is not valid on spatial scales shorter than ξ_{ve} .

Although ζ_{01} and ζ_{02} are assumed to be the same in Ref. 15 for simplicity, we will even have $\zeta_{01} \gg \zeta_{02}$ if the first component is close to its glass transition (where ζ should sensitively depend on ϕ as a ϕ -dependent glass transition temperature is approached³⁸). In such a case, the one-sided stress division (2.11) or $\alpha \cong 1/\phi$ will hold unless the first component is dilute. As another situation, if only the first component is entangled and the second component is not entangled, the one-sided stress division $\alpha \cong 1/\phi_1$ follows and the friction constant ζ is determined by the second component as $\zeta \cong \phi_2 \zeta_{02}$ if both ϕ_1 and ϕ_2 are not very small.

D. Tube velocity

We then introduce a tube velocity \mathbf{v}_T as in Ref. 15 by

$$\mathbf{v}_T = \mathbf{v} + \phi(1 - \phi)\alpha\mathbf{w}, \quad (2.19)$$

which is an average velocity of the entanglement structure. It is equal to the polymer velocity for polymer solutions. This concept was first introduced by Brochard.³⁷ The network stress is determined by the gradient tensor of \mathbf{v}_T . For example, for motions slower than the stress relaxation time τ , the network stress is expressed as¹⁵

$$\sigma_{ij} = \eta(\phi) \left[\frac{\partial}{\partial x_j} v_{Ti} + \frac{\partial}{\partial x_i} v_{Tj} - \frac{2}{3} \delta_{ij} \nabla \cdot \mathbf{v}_T \right], \quad (2.20)$$

where $\eta(\phi)$ is the viscosity of the mixture dependent on ϕ . Note that $\nabla \cdot \mathbf{v}_T$ is nonvanishing when diffusion is taking place. In fact, for small deviations we have

$$\nabla \cdot \mathbf{v}_T \cong \alpha \phi (1 - \phi) \nabla \cdot \mathbf{w} \cong -\alpha \frac{\partial}{\partial t} \delta \phi. \quad (2.21)$$

It is not trivial what velocity appears in the constitutive relation (2.20). For polymer solutions Doi³⁰ first stated that the polymer velocity \mathbf{v}_p should appear.

III. COUPLED EQUATIONS OF COMPOSITION AND STRESS

A. Linearized dynamic equations

For simplicity we assume that the mass densities of the pure components are the same and the fluid is incompressible. Then the mass composition ρ_1/ρ and the volume fraction ϕ of the first component coincide. For the average velocity $\mathbf{v} = \phi \mathbf{v}_1 + (1 - \phi) \mathbf{v}_2$ we may assume the incompressibility condition $\nabla \cdot \mathbf{v} = 0$. Because ϕ is convected by $\mathbf{v}_1 = \mathbf{v} + (1 - \phi)\mathbf{w}$, we obtain

$$\begin{aligned} \frac{\partial}{\partial t} \phi + \mathbf{v} \cdot \nabla \phi &= -\nabla \cdot (\phi(1 - \phi)\mathbf{w}) \\ &= \nabla \cdot L [\nabla (\delta F / \delta \phi) - \alpha \nabla \cdot \vec{\sigma}], \end{aligned} \quad (3.1)$$

where

$$L = \phi^2 (1 - \phi)^2 / \zeta \quad (3.2)$$

is the kinetic coefficient and $\rho(\mu_1 - \mu_2)$ is replaced by $\delta F / \delta \phi$, F being the free energy functional, in the Ginzburg-Landau scheme. We then assume that small deviations are produced in a homogeneous state without macroscopic flow. To linear order the Fourier component of the deviation $\delta \phi$ obeys

$$\frac{\partial}{\partial t} \phi_q = -\Gamma_q \phi_q - L \alpha Z_q, \quad (3.3)$$

where

$$\Gamma_q = L q^2 (r_0 + C q^2) \quad (3.4)$$

is the decay rate in the absence of the viscoelastic coupling, Z_q is the Fourier transformation of

$$Z = \nabla \cdot \nabla \cdot \vec{\sigma} \quad (3.5)$$

and we have set

$$\delta F / \delta \phi = (r_0 - C \nabla^2) \delta \phi. \quad (3.6)$$

The stress is determined by the tube velocity \mathbf{v}_T . To make the simplest theory we assume that the network stress is traceless,

$$\sum_j \sigma_{jj} = 0, \quad (3.7)$$

and obeys³⁹

$$\frac{\partial}{\partial t} \sigma_{ij} + (\mathbf{v}_T \cdot \nabla) \sigma_{ij} = G(\phi) \left[\frac{\partial}{\partial x_j} v_{Ti} + \frac{\partial}{\partial x_i} v_{Tj} - \frac{2}{3} \delta_{ij} \nabla \cdot \mathbf{v}_T \right] - \frac{1}{\tau(\phi)} \sigma_{ij}. \quad (3.8)$$

Here $G(\phi)$ is the shear modulus and $\tau(\phi)$ is the relaxation time of shear stress assumed to be very long and strongly dependent on ϕ . However, the assumption (3.7) is problematic because the diagonal part $\sigma_d = \sum_j \sigma_{jj}/3$ will also relax slowly with a long relaxation time τ_ℓ in general. Our treatment is allowable for $\tau \gg \tau_\ell$. We note that generalization to take account of such a slow relaxation of σ_d can be important in many systems such as gels and fluids near glass transition, so it is a problem in the future. Now by linearizing our simplified equation (3.8) and using (2.21) we obtain

$$\frac{\partial}{\partial t} Z_q = -\tau^{-1} Z_q + \frac{4}{3} G \alpha q^2 \frac{\partial}{\partial t} \phi_q \quad (3.9)$$

for small deviations around a homogeneous state.

To show the physical meaning of (3.8), let us consider a weak, homogeneous, and stationary flow, for which (3.8) is solved to give (2.20) with the Newtonian viscosity

$$\eta = G\tau. \quad (3.10)$$

More generally, in weak, homogeneous, and oscillatory shear flow, the frequency-dependent complex viscosity is obtained as

$$\eta^*(\omega) = \eta / (1 + i\omega\tau), \quad (3.11)$$

which is the well-known formula for the Maxwell model.³⁹ For rapid motions, on the other hand, our system behaves as a gel and

$$\sigma_{ij} \cong G \left[\frac{\partial}{\partial x_j} u_{Ti} + \frac{\partial}{\partial x_i} u_{Tj} - \frac{2}{3} \delta_{ij} \nabla \cdot \mathbf{u}_T \right], \quad (3.12)$$

where \mathbf{u}_T is the time integral of \mathbf{v}_T and has the meaning of the displacement of the network.

Now we have the coupled equations for ϕ_q and Z_q . If (3.9) is integrated and $Z_q(t)$ is removed, we obtain a dynamic equation of $\phi_q(t)$ in a time-convolution form,

$$\frac{\partial}{\partial t} \phi_q(t) = -\Gamma_q \phi_q(t) - \frac{4}{3} \alpha^2 L G q^2 \int_0^t dt' \times \exp[-(t-t')/\tau] \frac{\partial}{\partial t'} \phi_q(t'), \quad (3.13)$$

where we have assumed $Z_q(0) = 0$ for simplicity. This equation is of the same form as that proposed by Binder *et al.*⁴⁰ They assumed that the chemical potential of the composition depends linearly on a slowly relaxing, scalar variable. Their equations are different from ours in nonlinear regimes. Jäckle and Pieroth examined in more detail the dynamics for general coupling between the order parameter and a slow scalar variable.⁴¹

B. Viscoelastic length and gel-like behavior

Obviously there are two limiting cases. When the time scale of ϕ_q is slower than τ , we may set $\partial Z_q(t)/\partial t = 0$ in (3.9) or $\partial \phi_q(t')/\partial t' = \partial \phi_q(t)/\partial t$ in (3.13). The resultant effect is very simple,^{15,16} the kinetic coefficient is modified as

$$L_{\text{eff}}(q) = L / (1 + \xi_{\text{ve}}^2 q^2), \quad (3.14)$$

where ξ_{ve} is a viscoelastic length defined by

$$\xi_{\text{ve}} = \left(\frac{4}{3} \alpha^2 \eta L \right)^{1/2}. \quad (3.15)$$

The effective decay rate of $\phi_q(t)$ is then

$$\Gamma_{\text{eff}}(q) = (L_{\text{eff}}(q)/L) \Gamma_q = L q^2 (r_0 + C q^2) / (1 + \xi_{\text{ve}}^2 q^2). \quad (3.16)$$

This change of the kinetic coefficient follows even for general stress relaxation if τ is taken to be the longest relaxation time. We shall see that ξ_{ve} is very long in the presence of entanglement as will be shown explicitly in (4.15) and (4.17) below. As a result, there can be a sizable wave number region in which $\xi_{\text{ve}}^{-1} \ll q \ll \xi^{-1} = (|r_0|/C)^{1/2}$, where ξ is the thermal correlation length for $r_0 > 0$. There, the stress relaxation decelerates the composition relaxation as

$$\Gamma_{\text{eff}}(q) \cong L r_0 / \xi_{\text{ve}}^2 \cong r_0 \left/ \left(\frac{4}{3} \alpha^2 \eta \right) \right. \sim \Gamma_\xi \xi^2 / \xi_{\text{ve}}^2, \quad (3.17)$$

where $\Gamma_\xi = LC\xi^{-4}$ is the composition decay rate at $q \sim \xi^{-1}$ in the absence of the dynamic coupling. Here we should not forget to require $|\Gamma_{\text{eff}}(q)| \ll 1/\tau$ as the self-consistency condition. So we introduce a parameter ϵ by

$$\epsilon = |r_0| \left/ \left(\frac{4}{3} \alpha^2 G \right) \right. . \quad (3.18)$$

If $\epsilon \ll 1$, the above condition is satisfied in the wide region $q \ll \alpha(G/C)^{1/2} (\sim \epsilon^{-1/2} \xi^{-1})$ surely resulting in (3.17). However, if $\epsilon \gg 1$, it is satisfied only for very long wavelengths $q \ll (L\tau|r_0|)^{-1/2} (\sim \epsilon^{-1/2} \xi_{\text{ve}}^{-1})$, where $L_{\text{eff}}(q) \cong L$ and (3.17) holds in no region of q .

In the opposite limit $\tau \gg 1/\Gamma_q$, the system behaves as a gel and the composition decay rate is given by

$$\Gamma_{\text{gel}}(q) = \Gamma_q + \tau^{-1} \xi_{\text{ve}}^2 q^2 = L q^2 \left(r_0 + \frac{4}{3} \alpha^2 G + C q^2 \right). \quad (3.19)$$

This was first proposed by Tanaka *et al.*³¹ for polymer gels in which $r_0 = K_{\text{os}}/\phi^2$ and $\alpha = 1/\phi$, K_{os} being the osmotic modulus. They measured the diffusion constant of gels,

$$D_{\text{gel}} = (K_{\text{os}} + 4G/3)/\zeta, \quad (3.20)$$

by dynamic light scattering. From this expression we can easily conclude that spinodal decomposition, which takes place for $r_0 < 0$, should proceed on time scales longer than τ if $r_0 + \frac{4}{3} \alpha^2 G > 0$ (or $\epsilon < 1$). This aspect will be discussed in Section IV.

C. Dynamic scattering

General solutions of (3.3) and (3.9) are expressed as

$$\delta\phi(t) = A_1 \exp(-\Omega_1 t) + A_2 \exp(-\Omega_2 t), \quad (3.21)$$

where Ω_1 and Ω_2 are the roots of

$$\Omega^2 - \left(\frac{1}{\tau} + \Gamma_q + \frac{4}{3} \alpha^2 GLq^2 \right) \Omega + \frac{1}{\tau} \Gamma_q = 0 \quad (3.22)$$

and A_1 and A_2 are constants determined from $\delta\phi(0)$ and $\delta Z(0)$. We notice that the coupling between the two variables becomes weak leading to $\Omega \cong \Gamma_q, 1/\tau$ at long wavelengths, $q\xi_{ve} < 1$, where ξ_{ve} is defined by (3.15).

We may further add thermal random source terms on the right hand sides of (3.3) and (3.9). By imposing the fluctuation-dissipation relations, we may calculate the time correlation function for the composition fluctuations in one-phase states ($r_0 > 0$) in the incompressible limit,

$$S_q(t) = \langle \phi_q(t) \phi_q(0)^* \rangle. \quad (3.23)$$

In our model its Laplace transformation is expressed as¹⁵

$$\int_0^\infty dt e^{-i\omega t} S_q(t) = S_q(0) [1 + \xi_{ve}^2 q^2 \eta^*(\omega)/\eta] / \times [i\omega(1 + \xi_{ve}^2 q^2 \eta^*(\omega)/\eta) + \Gamma_q], \quad (3.24)$$

where $\eta^*(\omega)$ is the frequency-dependent complex viscosity given by (3.9) and η is the zero-frequency viscosity given by (3.10). As a result $S_q(t)$ decays with the two relaxation rates, Ω_1 and Ω_2 , as⁴²⁻⁴⁵

$$S_q(t)/S_q(0) = \chi_1 \exp(-\Omega_1 t) + \chi_2 \exp(-\Omega_2 t), \quad (3.25)$$

where $\chi_1 + \chi_2 = 1$. This form of the dynamic structure factor was first proposed by Brochard and de Gennes⁴² as an interpolation formula between gels and solutions. Their theory is consistent with the one-sided stress division (2.11). We note that the decay is single-exponential for $\alpha = 0$ (without the dynamical coupling). In particular, if $\Gamma_q \gg 1/\tau$ (which is frequently the case in dynamic light scattering experiments), some calculations yield

$$\Omega_1 \cong \Gamma_{gel}(q), \quad \Omega_2 \cong \Gamma_q / (\tau \Gamma_q + \xi_{ve}^2 q^2) = \Gamma_q / \tau \Gamma_{gel}(q), \quad (3.26)$$

where $\Gamma_{gel}(q)$ is defined by (3.19) and

$$\chi_2 \cong \xi_{ve}^2 q^2 / (\tau \Gamma_q + \xi_{ve}^2 q^2) = 1 / [\epsilon(1 + \xi^2 q^2) + 1]. \quad (3.27)$$

We furthermore assume $q \ll \xi^{-1}$ to find

$$\Omega_1 \cong D_{gel} q^2, \quad \Omega_2 \cong \epsilon / (1 + \epsilon) \tau, \quad \chi_2 \cong 1 / (1 + \epsilon), \quad (3.28)$$

where D_{gel} is defined by (3.20). We note that Ω_2 becomes independent of q as $q \rightarrow 0$, but its limiting value is smaller than $1/\tau$ by $\epsilon/(1 + \epsilon)$. When $S_q(t)$ exhibits a double-exponential decay, the above formulae should be checked in comparison with rheological data of η and τ . Nonvanishing of ϵ indicates the presence of the dynamical coupling. Furthermore, if r_0 may be estimated (using the Flory-Huggins theory, for example), α is obtained from (3.18).

More generally, (3.24) can be used for any stress relaxation with multiple relaxation times, where $\eta^*(\omega)$ is taken to be a general frequency-dependent complex shear viscosity. This generalization is crucial in explaining dynamic light scattering at the sol-gel transition,^{46,47} where $\eta^*(\omega) \propto (i\omega)^{-\beta}$ with $\beta \sim 0.6$ and $S_q(t)$ decays algebraically as $t^{-1+\beta}$ ¹⁵ as observed in Refs. 46 and 47.

IV. SPINODAL DECOMPOSITION

When the temperature coefficient r_0 (or the osmotic modulus K_{os} in polymer solutions) is negative, one phase states become unstable and spinodal decomposition takes place even in the presence of viscoelasticity. This is because (3.22) gives a negative solution Ω_1 for $r_0 < 0$ at long wavelengths. Its absolute value $|\Omega_1|$ is the linear growth rate of the fluctuations in the early stage spinodal decomposition. For polymer blends we introduce the Flory-Huggins free energy,³³

$$f = \frac{k_B T}{v_0} \left[\frac{1}{N_1} \phi \ln \phi + \frac{1}{N_2} (1 - \phi) \ln(1 - \phi) + \chi \phi(1 - \phi) + \frac{1}{2} C |\nabla \phi|^2 \right], \quad (4.1)$$

where v_0 is the volume occupied by one monomer and χ is the so-called interaction parameter dependent on the temperature T . In the gradient term the coefficient C may be determined using the random phase approximation³³ as

$$C = \frac{1}{18} (k_B T / v_0) b^2 / \phi(1 - \phi), \quad (4.2)$$

where b is the monomer size. Then the parameter r_0 in (3.6) is expressed as

$$r_0 = (k_B T / v_0) \left(\frac{1}{N_1 \phi} + \frac{1}{N_2 (1 - \phi)} - \chi \right). \quad (4.3)$$

The polymer solution case is obtained by setting $N_1 = N$ and $N_2 = 1$.

We assume that the coupling strength α is not small. Then we introduce a length ℓ by

$$\ell^{-2} = 4G\alpha^2/3C. \quad (4.4)$$

For $r_0 < 0$ the parameter ϵ defined by (3.18) becomes

$$\epsilon = -r_0 / \left(\frac{4}{3} \alpha^2 G \right) = \xi^{-2} \ell^2, \quad (4.5)$$

which represents the depth of quenching. The length $\xi = (|r_0|/C)^{-1/2}$ is the range of the thermal fluctuations. The peak wave number in the structure factor in spinodal decomposition is given by $\xi^{-1}/2^{1/2}$ in the early stage in the absence of viscoelasticity. As a characteristic frequency of the composition relaxation on the scale of ℓ , we introduce

$$\Gamma_\ell = LC\ell^{-4}. \quad (4.6)$$

The stress relaxation rate $1/\tau$ and the growth rate $|\Omega_1|$ will be scaled by Γ_ℓ as

$$\gamma = 1/(\Gamma_\ell \tau), \quad R = |\Omega_1|/\Gamma_\ell. \quad (4.7)$$

From the definition of ℓ , (4.4), we notice

$$\xi_{ve}^2/\ell^2 = 1/\gamma \quad \text{or} \quad \xi_{ve} = \gamma^{-1/2}\ell. \quad (4.8)$$

We will assume $\gamma \ll 1$ or equivalently $\xi_{ve} \gg \ell$. The equation for $R = |\Omega_1|/\Gamma_\ell$ is obtained by rescaling (3.22) as

$$R^2 + [\gamma + (1 - \epsilon)x + x^2]R = \gamma(\epsilon - x)x, \quad (4.9)$$

where

$$x = (q\ell)^2 < \epsilon. \quad (4.10)$$

The upper limit of x is required to ensure the existence of a positive R .

A. Polymer solutions

First we limit ourselves to semidilute polymer solutions,³³ where

$$\phi \ll 1, \quad \phi/\phi_c \gg 1, \quad (4.11)$$

$\phi_c = N^{-1/2}$ being the critical volume fraction. The Flory–Huggins free energy is simplified as

$$f = (k_B T/v_0) \left[\frac{1}{N} \phi \ln \phi + \left(\frac{1}{2} - \chi \right) \phi^2 + \frac{1}{6} \phi^3 \right]. \quad (4.12)$$

The parameter r_0 is related to the osmotic modulus K_{os} by

$$K_{os} = \phi^2 r_0 = (k_B T/v_0) \phi^2 \left[\phi + (1 - 2\chi) + \frac{1}{N\phi} \right]. \quad (4.13)$$

The spinodal curve $K_{os} = 0$ is given by $K_{os} = 0$, which is $2\chi - 1 \cong \phi$ for $\phi \gg \phi_c$. The friction coefficient ζ is of the following order

$$\zeta \sim 6\pi\eta_0 b^{-2} \phi^2, \quad (4.14)$$

where η_0 is the solvent viscosity. Furthermore, because $\alpha = 1/\phi$, the viscoelastic length is estimated as

$$\xi_{ve} \sim \xi_b (\eta/\eta_0)^{1/2}, \quad (4.15)$$

which is much longer than the blob size $\xi_b \sim b/\phi$ in semidilute theta solvents. For semidilute solutions with good solvent this length was first introduced by de Gennes and Brochard⁴⁸ by $\xi_{ve} = (D_{co}\tau)^{1/2}$, where $D_{co} \sim k_B T/6\pi\eta_0\xi$ is the cooperative diffusion constant, ξ being the correlation length (\sim the blob size). Their definition indicates that the diffusion is faster than the stress relaxation on spatial scales shorter than ξ_{ve} . Milner⁵ noticed importance of this length in the problem of shear-induced phase separation. On the other hand, the length ℓ is given by $\ell = (4C/3G)^{1/2}\phi$. If we assume the simple scaling result $G \propto \phi^3$, we find that ℓ is on the order of $\sim b/\phi$. However, some authors claimed that G depends on ϕ somewhat differently as $G \propto \phi^2$ in Ref. 42 or $G \propto \phi^{7/3}$.⁴⁹ The depth of the quenching is represented by the ratio of the osmotic modulus to the shear modulus as

$$\epsilon = -3K_{os}/4G. \quad (4.16)$$

It is known that K_{os}/G is of order 1 in theta solvents above the coexistence curve, whereas it is much smaller than 1 in good solvents.⁵⁰

B. Polymer blends

As shown in Ref. 15 the viscoelastic length ξ_{ve} defined by (3.15) can be at most on the order of the tube length in the reptation theory. In fact, if use is made of (2.16), (2.17), and (3.2), we obtain

$$\xi_{ve}^2 = \frac{4}{3} (\phi_1 \phi_2)^2 \left(\frac{N_1 \zeta_{01} - N_2 \zeta_{02}}{\phi_1 N_1 \zeta_{01} + \phi_2 N_2 \zeta_{02}} \right)^2 \times \left(\frac{N_e}{\phi_1 N_1 \zeta_{01}} + \frac{N_e}{\phi_2 N_2 \zeta_{02}} \right) \eta, \quad (4.17)$$

where $\phi_1 = \phi$ and $\phi_2 = 1 - \phi$. In particular, if the first component is much more viscous (due to larger values of the polymerization index or the friction coefficient) than the second component and is not dilute, we may have $\phi_1 N_1 \zeta_{01} \gg \phi_2 N_2 \zeta_{02}$ and $\eta \sim \zeta_{01} \phi b^2 N_1^3 / N_e^2$. The latter is the reptation expression for the viscosity. In this case it follows the one-sided stress division, so $\alpha \sim 1/\phi$, $\xi_{ve} \sim b N_1 / N_e^{1/2}$ (\sim the tube length), and $G \sim (k_B T/v_0) \phi / N_e$. The length ℓ defined by (4.4) becomes of the order of the tube diameter $N_e^{1/2} b$. Thus $\xi_{ve} \sim \ell N_1 / N_e \sim R_g (N_1 / N_e)^{1/2}$, R_g being the gyration radius of the first component. In these estimates we have assumed the reptation result $\eta \propto N_1^3$, whereas $\xi_{ve} \propto N_1^{1.2}$ follows if the experimental result $\eta \propto N_1^{3.4}$ is used.¹⁷

C. Three regimes of quenching

We examine (4.9) and seek the maximum R_m of R at $x = x_m$ as a function of x . The peak wave number and the maximum growth rate in the original units are expressed as

$$q_m = x_m^{1/2} / \ell = (x_m / \epsilon)^{1/2} / \xi, \quad \Gamma_m = \Gamma_\ell R_m, \quad (4.18)$$

respectively. In Fig. 1 we show R as a function of x for several ϵ at $\gamma = 1/\Gamma_\ell \tau = 10^{-3}$. We can see that R is much suppressed for $\epsilon \leq 1$ as compared to the usual form $R = (\epsilon - x)x$ for $\gamma = \infty$ or without the dynamical coupling. We display R_m in Fig. 2 and x_m in Fig. 3 as functions of $1/\gamma$ and ϵ . For $1/\gamma \gg 1$ and $\epsilon \leq 1$ they are much smaller than in the case $\gamma \geq 1$. In Fig. 2 the curve determined by $R_m = \gamma$ (or $\Gamma_m = 1/\tau$) is written on the surface of R_m . The growth rate exceeds the stress relaxation rate or $R_m > \gamma$ only in the gel region given by $\gamma \ll 1$ and $\epsilon \geq 1$ as will be discussed below. In the following we give analytic results for three typical cases.

1. Shallow quenching

Figure 4 shows how R is decreased from the usual form $R = (\epsilon - x)x$ as $1/\gamma$ is increased. To understand this behavior let us assume $\epsilon \ll 1$, under which (4.9) gives

$$R \cong (\epsilon - x)x / (1 + x/\gamma), \quad (4.19)$$

in agreement with (3.16). For very shallow quenching $\epsilon \ll \gamma$ the viscoelastic effect can be neglected, so that the peak position is $x_m \cong \epsilon/2$ and the maximum of R is $R_m \cong \epsilon^2/4$ as in the usual case. However, for $\gamma \ll \epsilon \ll 1$, the x -dependence in the denominator of (4.19) is crucial and

$$x_m \cong (\gamma\epsilon)^{1/2}, \quad R_m \cong \gamma\epsilon, \quad (4.20)$$

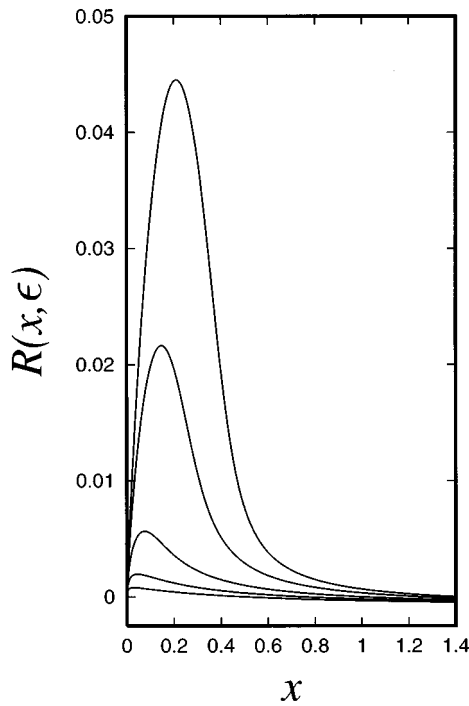


FIG. 1. The dimensionless growth rate $R(x, \epsilon)$ versus $x = (q\ell)^2$ for several quench depths, $\epsilon=0.5, 0.75, 1.0, 1.25, 1.4$, from below at $\gamma=10^{-3}$. Here the length ℓ is defined by (4.4) and ϵ by (4.5), while $1/\gamma$ is the dimensionless stress relaxation time.

from which the peak wave number and the maximum growth rate are obtained as

$$q_m \cong \epsilon^{1/4} / (\xi_{ve}\ell)^{1/2} = (\xi_{ve}\xi)^{-1/2}, \quad \Gamma_m \cong \epsilon/\tau, \quad (4.21)$$

respectively, in the original units. The growth rate is much smaller than $1/\tau$. Remarkably, the peak wave number and the maximum growth rate are reduced by $(\gamma/\epsilon)^{1/4}$ and γ/ϵ , respectively, for $\epsilon \gg \gamma$ due to the viscoelastic effect.

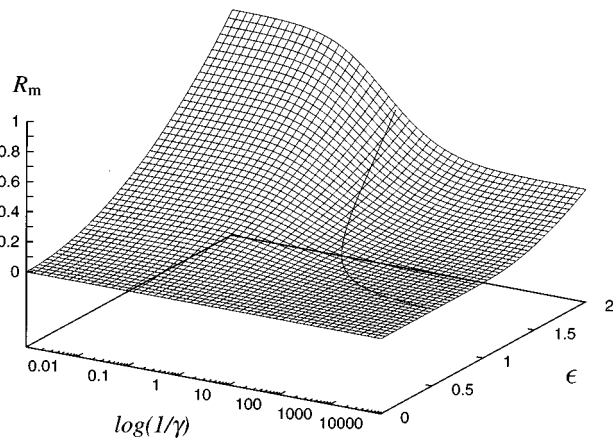


FIG. 2. The maximum growth rate R_m as a function of $1/\gamma$ and ϵ . For $1/\gamma \ll 1$ the usual form $R_m \cong \epsilon^2/4$ without the dynamic coupling is obtained, while the gel form $R_m \cong (\epsilon-1)^2/4$ follows for $1/\gamma \gg 1$.

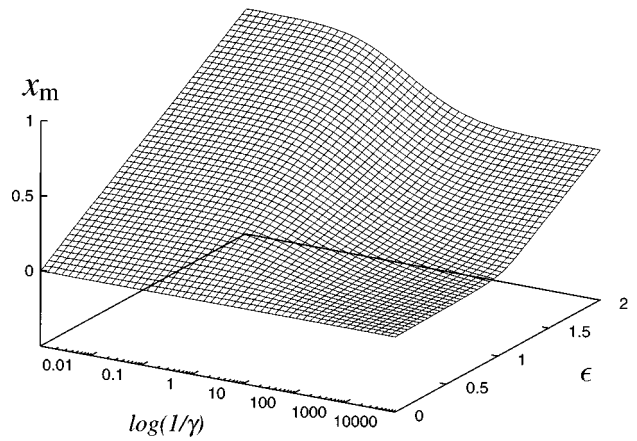


FIG. 3. The square $x_m = (q_m\ell)^2$ of the dimensionless peak wave number $q_m\ell$ as a function of $1/\gamma$ and ϵ . A crossover can be seen from the usual behavior $x_m \cong \epsilon/2$ to the gel behavior $x_m \cong (\epsilon-1)/2$ as $1/\gamma$ is increased.

In this shallow quenching case the kinetic coefficient in the diffusive equation for $\delta\phi$ may be interpreted to be modified as

$$L_{\text{eff}}(q) = L/(1+x/\gamma) = L/(1+q^2\xi_{ve}^2) \quad (4.22)$$

as already discussed in (3.14). This q -dependence is very large in highly entangled cases. Interestingly, the viscoelastic effect can be strong even when the growth is much slower than τ .

2. Intermediate quenching

When ϵ is smaller than 1 and satisfies $1-\epsilon \gg \gamma^{1/3}$ and $\epsilon \gg \gamma$, we shall see

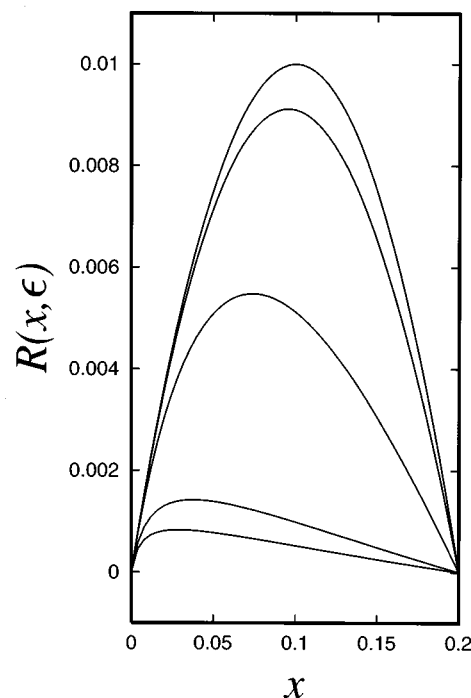


FIG. 4. $R(x, \epsilon)$ at $\epsilon=0.2$ for $\gamma=5 \times 10^{-3}, 10^{-2}, 10^{-1}, 1, \infty$ from below.

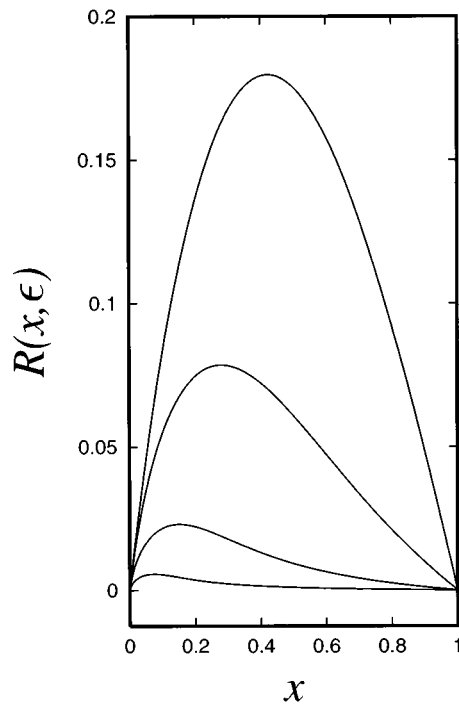


FIG. 5. $R(x, \epsilon)$ at $\epsilon=1$ for $\gamma = 10^{-3}, 10^{-2}, 10^{-1}, 1$ from below.

$$x_m \cong [\gamma \epsilon / (1 - \epsilon)]^{1/2}, \quad R_m \cong \gamma \epsilon / (1 - \epsilon), \quad (4.23)$$

in the Appendix. Notice that (4.19) is a special case of (4.23). Therefore, in the original units we have

$$q_m = [\epsilon / (1 - \epsilon)]^{1/4} (\xi_{ve} \ell)^{-1/2}, \quad \Gamma_m = \epsilon / (1 - \epsilon) \tau. \quad (4.24)$$

The x_m and R_m increase as ϵ approaches to 1. Particularly for $|1 - \epsilon| \ll \gamma^{1/3}$, we may set $\epsilon=1$ in solving (4.9) to obtain $x_m \cong \gamma^{1/3}$ and $R_m \cong \gamma^{2/3}$. Thus, we find at $\epsilon=1$

$$q_m \cong \xi_{ve}^{-1/3} \ell^{-2/3}, \quad \Gamma_m \cong \tau^{-2/3} \Gamma^{1/3}. \quad (4.25)$$

In Fig. 5 we display R versus x at $\epsilon=1$ for various γ .

3. Deep quenching

As will be shown in the Appendix, when ϵ slightly exceeds 1 or $\epsilon - 1 \gg \gamma^{1/3}$ more precisely, the system undergoes spinodal decomposition as a gel in the early stage, where in accord with (3.19) we obtain

$$R \cong (\epsilon - 1 - x)x. \quad (4.26)$$

Therefore $x_m \cong (\epsilon - 1)/2$ and $R_m \cong (\epsilon - 1)^2/4$, so that

$$q_m \cong [(\epsilon - 1)/2]^{1/2} \ell, \quad \Gamma_m \cong [(\epsilon - 1)/2]^2 \Gamma \ell. \quad (4.27)$$

We may consider only the growth in the region $x < \epsilon - 1$ because the growth in the region $\epsilon - 1 < x < \epsilon$ is very small and negligible for $\gamma \ll 1$. We notice that Γ_m soon exceeds $1/\tau$ for $\epsilon - 1 > 2\gamma^{1/2}$. In systems with very long τ , therefore, the spinodal point, which is $\epsilon=0$ as long as $\tau < \infty$, will appear to be shifted to the gel spinodal point $\epsilon=1$ attained in the limit $\tau = \infty$.⁵¹ Figure 6 shows R versus x for various ϵ at $1/\gamma = 10^3$. We can see that the growth rate increases abruptly

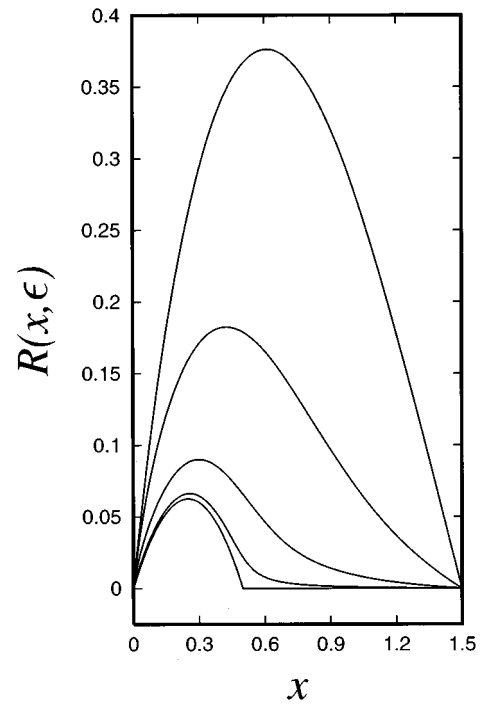


FIG. 6. $R(x, \epsilon)$ at $\epsilon=1.5$ for $\gamma=0, 10^{-3}, 10^{-2}, 10^{-1}, 1$ from below. The curve of $\gamma=0$ represents the gel limit.

in the region $x \leq \epsilon - 1$ once we are in the gel regime $\epsilon - 1 > \gamma^{1/3}$. Of course in very late stages ($t \gg \tau$) the system should behave as a fluid, whereas in gels phase separation is stopped or frozen at a particular stage. We here remark that spinodal decomposition in gels has not yet attracted enough attention.^{51,52} We may also mention analogous phase separation behavior in solid binary alloys with elastic misfits,⁵³ where softer regions are more easily deformed anisotropically than harder regions.

V. SUMMARY AND REMARKS

The results of Sections II and III are in essence contained in Refs. 15 and 16. We stress that the parameter α representing the strength of the dynamical coupling arises from the asymmetry in the friction coefficients and the polymerization indices as in (2.16) for blends. Muller *et al.*¹³ used a blend in which the two polymers have nearly the same polymerization indices, but they seem to have different friction coefficients giving rise to the dynamical coupling. More systematic experiments are very desirable on asymmetric blends, for example, blends in which one component is close to its glass transition as in Ref. 28. The results of Section IV are obtained by straightforward calculations on the basis of the equations in Section III. We have found that early stage behavior in spinodal decomposition sensitively depends on the dimensionless quench depth ϵ defined by (4.5). To perform experiments in which ϵ is controlled and nucleation is avoided, it is desirable to choose a blend near its critical point which is asymmetric and highly viscoelastic.

The viscoelastic effects in late stage phase separation processes are also of great interest as exemplified in Refs. 27 and 28. Numerical simulations are useful to gain insights in this direction.²⁹

In this paper we have neglected nucleation expected in the metastable temperature and composition region. The droplet growth should be strongly slowed down by viscoelasticity if the droplet radius R is smaller than the viscoelastic length ξ_{ve} .⁵⁴ The effect cannot be neglected in particular when the critical radius R_c is smaller than ξ_{ve} . Such effects will be examined in future work.

Note added: We would like to thank the referee for bringing to our attention a very recent paper treating early stage spinodal decomposition in viscoelastic fluids by Kumaran and Fredrickson.⁵⁵ It starts with dynamic equations for the composition, the stress field, and the velocity field. However, they are very different from ours; in particular, the dynamic coupling term ($\propto \nabla \cdot \vec{\sigma}$) in (2.12) or (2.15) is neglected, thus leading to different predictions.

APPENDIX

From (4.9) the dimensionless growth rate R is obtained in the form,

$$R = \sqrt{F_1(x)^2 + \gamma(\epsilon - x)x} - F_1(x) \\ = \gamma(\epsilon - x)x / [\sqrt{F_1(x)^2 + \gamma(\epsilon - x)x} + F_1(x)] \quad (\text{A1})$$

with

$$F_1(x) = \frac{1}{2}(\gamma - \delta x + x^2), \quad (\text{A2})$$

where ϵ , γ , and x are defined in Section IV and $\delta = \epsilon - 1$. By setting $dR/dx = 0$ we obtain the equation for $x = x_m$,

$$(\epsilon - 2x) \left[2(\gamma - \delta x + x^2) \left(x - \frac{\delta}{2} \right) + \gamma(\epsilon - 2x) \right] \\ = 4 \left(x - \frac{\delta}{2} \right)^2 (\epsilon - x)x. \quad (\text{A3})$$

Further we assume $x \ll \epsilon$ and replace $\epsilon - 2x$ and $\epsilon - x$ by ϵ to obtain

$$x^3 - \frac{\delta}{2}x^2 - \gamma x + (\delta - 1)\gamma = 0. \quad (\text{A4})$$

First, for $\delta = 0$ ($\epsilon = 1$), (A4) is solved to give

$$x = \gamma^{1/3} + \frac{1}{3}\gamma^{2/3} + \dots, \quad (\text{A5})$$

which leads to (4.25). We can check that the relation $x \cong \gamma^{1/3}$ holds for $|\delta| \ll \gamma^{1/3}$. Second, if $\delta \gg \gamma^{1/3}$, the last two terms of (A4) are small and

$$x \cong \delta/2. \quad (\text{A6})$$

In this case we may set $\gamma = 0$ in (A1) and obtain (4.26) from $F_1(x) < 0$ in the region $x < \delta$. Third, if $\delta < 0$ and $|\delta| \gg \gamma^{1/3}$, we may assume $x \propto \gamma^{1/2}$ in (A4) to obtain (4.23). In estimating the maximum R_m we use the first line of (A1) for the gel

case $\delta \gg \gamma^{1/3}$ and the second line for the other cases. In (3.14) or (4.22) the effective kinetic coefficient in the shallow quench case is shown. Generally, it is obtained from the second line of (A1) in the form,

$$L_{\text{eff}}(q) = L\gamma / [\sqrt{F_1(x)^2 + \gamma(\epsilon - x)x} + F_1(x)] \quad (\text{A7})$$

which reduces to (4.22) for $\epsilon \ll 1$, $\gamma \ll 1$, and $x \ll 1$.

¹ As experiments on polymer solutions see, e.g., S. Nojima, K. Shiroshita, and T. Nose, *Polym. J.* **14**, 289 (1982); J. H. Aubert, *Macromolecules* **23**, 1446 (1990); J. Lal and R. Bansil, *ibid.* **24**, 290 (1991); N. Kuwahara and K. Kubota, *Phys. Rev. A* **45**, 7385 (1992); S. W. Song and M. Torkelson, *Macromolecules* **27**, 6390 (1994).

² As experiments on polymer blends see, e.g., H. Snyder and P. Meakin, *J. Chem. Phys.* **79**, 5588 (1983); F. S. Bates and P. Wilzius, *ibid.* **91**, 3258 (1989).

³ T. Hashimoto, in *Materials Science and Technology*, edited by E. L. Thomas (VCH, Weinheim, 1993), Vol. 12, p. 251.

⁴ P. G. de Gennes, *J. Chem. Phys.* **72**, 4756 (1980).

⁵ P. Pincus, *J. Chem. Phys.* **75**, 1996 (1981).

⁶ K. Binder, *J. Chem. Phys.* **79**, 6387 (1983).

⁷ A. Onuki, *J. Chem. Phys.* **85**, 1122 (1986).

⁸ K. Kawasaki and K. Sekimoto, *Macromolecules* **22**, 3063 (1989).

⁹ A. Ziya Akcasu, *Macromolecules* **22**, 3682 (1989).

¹⁰ K. Binder, in *Materials Science and Technology*, edited by P. Haasen (VCH, Weinheim, 1991), Vol. 5, p. 405.

¹¹ K. Binder, *Adv. Polym. Sci.* **112**, 181 (1994).

¹² D. Schwahn, S. Janssen, and T. Springer, *J. Chem. Phys.* **97**, 8775 (1992).

¹³ G. Müller, D. Schwahn, H. Eckerlebe, J. Rieger, and T. Springer, *J. Chem. Phys.* **104**, 5826 (1996).

¹⁴ H. Jinnai, H. Hasegawa, T. Hashimoto, and C. C. Han, *J. Chem. Phys.* **99**, 4845 (1993).

¹⁵ M. Doi and A. Onuki, *J. Phys. II France* **2**, 1631 (1992).

¹⁶ A. Onuki, *J. Non-Cryst. Solids* **172–174**, 1151 (1994).

¹⁷ K. Kawasaki and T. Koga, *Physica A* **201**, 115 (1993).

¹⁸ X. L. Wu, D. J. Pine, and P. K. Dixon, *Phys. Rev. Lett.* **66**, 2408 (1991).

¹⁹ T. Hashimoto and K. Fujioka, *J. Phys. Soc. Jpn.* **60**, 356 (1991); T. Hashimoto and T. Kume, *ibid.* **61**, 1839 (1992).

²⁰ W. van Egmond, D. E. Werner, and G. Fuller, *J. Chem. Phys.* **96**, 7742 (1992).

²¹ E. Helfand and H. Fredrickson, *Phys. Rev. Lett.* **62**, 2468 (1989).

²² A. Onuki, *J. Phys. Soc. Jpn.* **59**, 3472 (1990).

²³ S. T. Milner, *Phys. Rev. E* **48**, 3874 (1993).

²⁴ H. Ji and E. Helfand, *Macromolecules* **28**, 3869 (1995).

²⁵ A. Onuki, R. Yamamoto and T. Taniguchi, *J. Phys. II France* (to be published).

²⁶ P. K. Dixon, D. J. Pine, and X. L. Wu, *Phys. Rev. Lett.* **68**, 2239 (1992).

²⁷ H. Tanaka, *Phys. Rev. Lett.* **71**, 3158 (1993); *J. Chem. Phys.* **100**, 5253 (1994).

²⁸ H. Tanaka, *Phys. Rev. Lett.* **76**, 787 (1996).

²⁹ T. Taniguchi and A. Onuki, *Phys. Rev. Lett.* **77**, 4910 (1996).

³⁰ M. Doi, in *Dynamics and Patterns in Complex Fluids*, edited by A. Onuki and K. Kawasaki (Springer, Berlin, 1990), p. 100.

³¹ T. Tanaka, L. O. Hocker, and G. B. Benedik, *J. Chem. Phys.* **59**, 5151 (1973).

³² H. P. Wittmann and G. H. Fredrickson, *J. Phys. I France* **4**, 1791 (1994).

³³ P. G. de Gennes, *Scaling Concepts in Polymer Physics*, 2nd ed. (Cornell University, Ithaca, 1985).

³⁴ M. Doi and S. F. Edwards, *The Theory of Polymer Dynamics* (Oxford, New York, 1986).

³⁵ E. J. Kramer, P. F. Green, and C. J. Palmstrom, *Polymer* **25**, 473 (1984).

³⁶ H. Silescu, *Makrom. Chem. Rapid Commun.* **5**, 519 (1984).

³⁷ F. Brochard, *Molecular Conformation and Dynamics of Macromolecules in Condensed Systems*, edited by M. Nagasawa (Elsevier, New York, 1988), p. 249.

³⁸ M. G. Brereton, E. W. Fischer, G. Fytas, and U. Murschall, *J. Chem. Phys.* **86**, 5174 (1987).

³⁹ R. G. Larson, *Constitutive Equations for Polymer Melts and Solutions* (Butterworths, Boston, 1986).

⁴⁰ K. Binder, H. L. Frish, and J. Jäckle, *J. Chem. Phys.* **85**, 1505 (1986).

⁴¹ J. Jäckle and M. Pieroth, *Z. Phys. B* **72**, 25 (1988); in *Structure, Relax-*

- ation, and *Physical Aging of Glassy Polymers*, edited by R. J. Roe and J. M. O'Reilly (Materials Research Society, Pittsburgh, 1991), p. 49.
- ⁴²F. Brochard and P. G. de Gennes, *Macromolecules* **10**, 1157 (1977); F. Brochard, *J. Phys. (Paris)* **44**, 39 (1983).
- ⁴³M. Adam and M. Delsanti, *Macromolecules* **18**, 1760 (1985).
- ⁴⁴S. -J. Chen and G. C. Berry, *Polymer* **31**, 793 (1990).
- ⁴⁵N. Nemoto, A. Koike, and K. Osaki, *Macromolecules* **29**, 1445 (1996).
- ⁴⁶J. E. Martin and J. P. Wilcoxon, *Phys. Rev. Lett.* **61**, 373 (1988).
- ⁴⁷M. Adam, M. Delsanti, J. P. Munich, and D. Durand, *Phys. Rev. Lett.* **61**, 706 (1988).
- ⁴⁸F. Brochard and P. G. de Gennes, *Physicochem. Hydrodyn.* **4**, 313 (1983).
- ⁴⁹R. H. Colby and M. Rubinstein, *Macromolecules* **23**, 2753 (1990).
- ⁵⁰M. Adam and M. Delsanti, *J. Phys. (Paris)* **44**, 1185 (1983); **45**, 1513 (1984); M. Adam, *J. Non-Cryst. Solids* **131–133**, 773 (1991).
- ⁵¹In gels, when the bulk osmotic modulus K_{os} is negative but $K_{os} + G/3 > 0$, only a single macroscopic mode becomes unstable against homogeneous volume changes without enhancement of small scale fluctuations. For $K_{os} + G/3 < 0$ surface modes become unstable resulting in corrugations of the gel–solvent interface. For $K_{os} + 4G/3 < 0$ usual spinodal decomposition occurs in the bulk region. We obtained this conclusion neglecting heterogeneities of the crosslinkages, which may affect the nature of the transition, however. On such aspects, see, A. Onuki, *Advances in Polymer Science*, edited by K. Dusek (Springer, Berlin, 1993), Vol. 109, p. 63.
- ⁵²K. Sekimoto, N. Suematsu, and K. Kawasaki, *Phys. Rev. A* **39**, 4912 (1989).
- ⁵³A. Onuki and H. Nishimori, *Phys. Rev. B* **43**, 13649 (1991).
- ⁵⁴A. Onuki, *J. Phys. II France* **2**, 1505 (1992).
- ⁵⁵V. Kumaran and G. H. Fredrickson, *J. Chem. Phys.* **105**, 8304 (1996).