Early stage spinodal decomposition in viscoelastic fluids

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The effect of viscoelasticity on the early stages of spinodal decomposition is examined. In addition to the concentration and momentum equations for the fluid, the effect of viscoelasticity is included using a linear Maxwell equation for the stress tensor. The growth in the amplitude of the fluctuations depends on the transport coefficient, the viscosity of the fluid, and the relaxation time in the Maxwell model. For simplicity, the nonlinearity due to the quartic term in the expression for the Landau–Ginzburg expression for the free energy is neglected, as are the inertial terms in the momentum conservation equation. The momentum and Maxwell equations are solved exactly to obtain the velocity as a function of concentration, which is then inserted into the concentration equation. There are two types of nonlinearities in the conservation equation—one proportional to the cube of the concentration which leads to a four point vertex, and one proportional to the product of the concentration and the random noise in the stress equation which leads to a three point vertex. In the leading approximation, the renormalization of the transport coefficient due to these vertices is determined using the Hartree approximation, and the renormalization of the noise correlation due to the three point vertex is determined using a one-loop expansion. The renormalized transport coefficient and noise correlation are inserted into the concentration equation to determine the effect of the nonlinearities on the growth of the structure factor. It is found that an increase in the relaxation time tends to increase the rate of growth of the structure factor, and tends to decrease the wave number of the peak in the structure factor. © *1996 American Institute of Physics.* [S0021-9606(96)51040-8]

I. INTRODUCTION

Theories of spinodal decomposition in polymer blends and other heterogeneous polymeric systems, e.g., block copolymers, have been of interest to the polymer science community for some time. Such theories attempt to describe the temporal evolution of compositional order when an initially homogeneous polymer melt is rapidly cooled into an unstable region of the phase diagram. The early studies of de Gennes,[1] Pincus,[2] and Binder[3] analyzed the demixing transition of binary blends of homopolymers. These linearized theories are restricted to the early stages of structural evolution, and are capable of predicting only the wavelength of the most unstable mode. These employ a simple diffusion equation for the concentration field which is similar to those for the early stage spinodal decomposition in simple fluids or metal alloys. However, polymer melts are more complex than simple fluids because they exhibit viscoelastic behavior, and the elasticity of the melt has not been taken into account in previous studies. Moreover, recent experimental evidence indicates that spinodal decomposition in a viscoelastic fluid may be qualitatively different from that in a simple fluid. Tanaka[4] carried out experiments on the phase separation of polystyrene-diethyl malonate mixtures, and observed that the late stage coarsening dynamics is dominated by the viscoelastic effect due to the strong coupling between the stress field and concentration diffusion. Wiltzius and Bates[5] studied the spinodal decomposition in a melt consisting of perdeu-terated and protonated polybutadiene. They observed that the decomposition process could be separated into four stages, and the scaling laws in the intermediate stage is different from that predicted by the current theories for spinodal decomposition in binary fluids. These experiments suggest that viscoelastic stresses could have a significant influence on the spinodal decomposition process. In the present paper we consider the role of viscoelasticity on the early stages of spinodal decomposition.

The earliest theory for the very short time regime of spinodal decomposition is the Cahn–Hilliard–Cook theory,[6–8] which predicts the growth of the structure factor (equal-time pair correlation function of concentration fluctuations) as a function of time. In this approach, a linear stability analysis is applied to the one-phase system to determine the wavelength and the growth rate of the most unstable mode, but this theory cannot predict the coarsening of the fluctuations due to the neglect of nonlinear effects. There have been many theories that attempt to incorporate nonlinear effects in the description of the spinodal decomposition process. The most successful of these was devised by Langer, Baron, and Miller[9] (LBM). Here, the form of the probability distribution function of the concentration is assumed to be the sum of two Gaussian distributions with different means and variances. The closure is achieved by expressing the nth order correlation function $S_n(\mathbf{k},t)$ as the product of the nth moment of the probability distribution

function with the ratio of the structure factor and the variance of the distribution

$$S_n(\mathbf{r},t) = \frac{\langle \psi^n \rangle}{\langle \psi^2 \rangle} S(\mathbf{r},t). \tag{1}$$

Here, $\psi(\mathbf{r},t) = c(\mathbf{r},t) - c_0$ is the departure from the average concentration and the correlation function $S_n(\mathbf{r},t)$ is defined as

$$S_n(\mathbf{r},t) = \langle \psi(\mathbf{x}+\mathbf{r},t)^{n-1}\psi(\mathbf{x},t)\rangle, \tag{2}$$

$S(\mathbf{r},t)$ is used as a shorthand for $S_2(\mathbf{r},t)$. With the above approximation, a closed set of equations is obtained and these equations predict both the coarsening of the structure factor and the formation of a bimodal distribution. The LBM theory was first compared to Monte Carlo simulations of spinodal decomposition in metals based on the kinetic Ising model, and was found to be in good qualitative agreement with the simulations. This theory was extended to binary fluids by Kawasaki and Ohta,[10] who compared their results with the experiments of Goldburg, Shaw, Huang, and Pilant[11] and reported reasonable agreement.

In the present paper, a renormalized perturbation expansion is used to analyze the early stage spinodal decomposition in a viscoelastic fluid. The equations for the fluid are coupled equations of motion for the concentration field, the velocity field, and the stress field. The Langevin equation for the stress field is a novel feature of the present analysis and invokes the time-dependent Maxwell model for a viscoelastic fluid. The momentum equation is coupled to the equation for the stress field due to the dependence of the stress on the gradient of the velocity field. As a first step, we neglect the effect of the quartic nonlinear term in the Landau–Ginzburg free energy and focus instead on the viscoelastic convective couplings. The dynamics of the resulting decomposition process depends on quench depth, fluid viscosity, and the stress relaxation time τ of the Maxwell model. The effect of the nonlinearity due to the quartic term in the free energy is included in the Kawasaki–Ohta theory, so the present results do not coincide with the Kawasaki–Ohta theory in the limit $\tau \to 0$. However, the equations used here coincide with those in the Kawasaki–Ohta theory if the quartic nonlinearities are neglected and τ is set to zero.

The approach adopted in the present paper is different from the LBM theory and more closely resembles the analysis of Grant et al.[12] where a systematic perturbation expansion was employed, and the Gaussian approximation of Langer.[13] However, in those analyzes, the renormalization of the (concentration) transport coefficient was due to the quartic term in the Landau–Ginzburg free energy and this was assumed to be wave number independent. Here, the renormalization is due to the combined action of the convective term in the concentration equation and the elastic term in the Maxwell equation, and the renormalization of the transport coefficient is wave number dependent. In addition, the noise correlation in the stress equation results in a renormalization of the random noise correlation in the concentration equation. Therefore, in the present case, a diagrammatic perturbation analysis is required to determine the renormalization

of both the transport coefficient and the noise correlation. The nonlinearities in the transport equations lead to fourth order vertices, and the renormalizations due to these vertices are calculated using the ''Hartree approximation.'' In the Hartree approximation, the correction to the correlation and response functions due to all bubble diagrams involving the quartic nonlinearity are included, but higher-order loop diagrams and more topologically complex diagrams are not included.[14] This approximation is exact to leading order in the perturbation parameter, but higher order terms contained in the bubble diagrams are also included. In addition, there are cubic vertices that result in the renormalization of the noise correlation in the Langevin equation. This renormalization is calculated using a simple one-loop expansion.

II. ANALYSIS

The basic equations used for analyzing the dynamics of spinodal decomposition in viscoelastic fluids are coupled Langevin equations for the slow variables, which in the present case are the concentration, velocity and stress fields. The equations employed here are similar to the model-H equations[15] that have been used previously for describing the demixing transition in incompressible binary fluids. In the present case, however, it is necessary to write a separate Langevin equation for the stress field, because the dependence of the stress on the velocity field is nonlocal in time due to elastic effects. The conservation equation for the concentration field is

$$\partial_t \psi = -v_\alpha \partial_\alpha \psi + \lambda \partial_\alpha^2 \frac{\delta F}{\delta \psi} + \zeta, \tag{3}$$

where $\psi = \psi(\mathbf{x},t)$ is the concentration field, $v_\alpha = v_\alpha(\mathbf{x},t)$ is the velocity field, $\partial_t \equiv (\partial/\partial t)$, $\partial_\alpha \equiv (\partial/\partial x_\alpha)$, and Greek subscripts are used to denote vectors. The first term on the right is the variation in concentration due to convective transport, the second term is the divergence of the diffusive flux due to gradients in the chemical potential $\delta F/\delta \psi$, and λ is an Onsager transport coefficient describing the rate of collective diffusion. The last term on the right-hand side is the thermal noise required to satisfy the fluctuation–dissipation theorem, whose statistics will be discussed later. The momentum conservation equation states that the transverse component of the divergence of the stress is equal to the applied forces on the system

$$\left[\partial_\beta \sigma_{\alpha\beta} + \partial_\alpha \psi \frac{\delta F}{\delta \psi} \right]_\perp = 0, \tag{4}$$

where $[\cdots]_\perp$ represents the transverse component of the vector (a consequence of the incompressibility constraint). The first term on the left side of the above equation is the divergence of the stress tensor, which includes both viscous and elastic stresses, while the second term is the reciprocal of the convective term in the concentration Eq. (3) and represents the osmotic force density. The inertial terms in the momentum conservation equation have been neglected compared to the viscous and elastic terms. This is a good approximation in most circumstances of practical interest. For example, the

magnitude of the fluctuating velocity V can be obtained by comparing the energy of fluctuations with the thermal energy, i.e., $(\rho V^2 L^3) \sim T$ (L is a characteristic length). This gives $V \sim (T/\rho L^3)^{1/2}$, and the inertial terms can be neglected compared to the viscous ones for $(\mu^2 L/T\rho)^{1/2} \gg 1$ (μ is the shear viscosity). Inserting $\rho = 10^3$ kg/m³ and a lower bound of $\mu = 10^{-3}$ kg/m/s, we find that the inertial terms can be neglected for $L \gg 4 \times 10^{-12}$ m at room temperature. This condition is always satisfied since 10^{-12} m is an atomic length scale.

The equation for the stress tensor is given by the simple linear Maxwell model[16]

$$(\tau \partial_t + 1)\sigma_{\alpha\beta} = \mu(\partial_\alpha v_\beta + \partial_\beta v_\alpha) + \theta_{\alpha\beta}, \quad (5)$$

where τ is a stress relaxation time that can be expressed as the ratio of a shear viscosity μ to a shear modulus G, $\tau = (\mu/G)$. In the above equation, we have neglected the convected derivatives present in the corotational Maxwell model, since these represent higher-order nonlinear contributions to the stress field. The free energy F is given by the usual Landau–Ginzburg expression with additional contributions due to the kinetic energy of the fluid and the elastic strain energy

$$F = \int d\mathbf{x} \left[\frac{K}{2}(\partial_\alpha \psi)^2 - \frac{r}{2}\psi(\mathbf{x},t)^2 + \frac{u}{4}\psi(\mathbf{x},t)^4 \right.$$
$$\left. + \frac{\rho}{2}v_\alpha(\mathbf{x},t)^2 + \frac{1}{4G}\sigma_{\alpha\beta}\sigma_{\beta\alpha} \right], \quad (6)$$

where K and r are positive constants when the system is below the transition temperature. The first three terms in the above equation represent the standard Landau–Ginzburg free energy, the fourth term is the kinetic energy due to the velocity fluctuations, and the last term is the elastic strain energy. By neglecting cubic terms in ψ, we restrict consideration to systems at the critical composition. We also note that r is the parameter proportional to the depth of the quench below the critical temperature.

The analysis is conveniently carried out in Fourier space, where the components of the concentration and velocity fields are

$$\psi(\mathbf{k},t) = \int d\mathbf{x} \exp(ik_\alpha x_\alpha)\psi(\mathbf{x},t),$$
$$\quad (7)$$
$$v_\beta(\mathbf{k},t) = \int d\mathbf{x} \exp(ik_\alpha x_\alpha)v_\beta(\mathbf{x},t).$$

The transformed equations are

$$\partial_t \psi = -\lambda k^2(Kk^2 - r)\psi(\mathbf{k},t) + \zeta(\mathbf{k},t) + \psi(\mathbf{k},0)\delta(t)$$
$$+ i \int_{\mathbf{k}_1} \int_{\mathbf{k}_2} v_\alpha(\mathbf{k}_2,t)k_{1\alpha}\psi(\mathbf{k}_1,t)\delta(\mathbf{k}_1 + \mathbf{k}_2 - \mathbf{k})$$
$$- \lambda u k^2 \int_{\mathbf{k}_1} \int_{\mathbf{k}_2} \int_{\mathbf{k}_3} \psi(\mathbf{k}_1,t)\psi(\mathbf{k}_2,t)\psi(\mathbf{k}_3,t)$$
$$\times \delta(\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3 - \mathbf{k}), \quad (8)$$

$$\mathscr{T}_{\alpha\beta}(\mathbf{k})\left[-ik_\gamma \sigma_{\beta\gamma} - i \int_{\mathbf{k}_1} \int_{\mathbf{k}_2} k_{1\beta}\psi(\mathbf{k}_1,t) \right.$$
$$\left. \times Kk_2^2 \psi(\mathbf{k}_2,t)\delta(\mathbf{k}_1 + \mathbf{k}_2 - \mathbf{k}) \right] = 0, \quad (9)$$

$$(\tau \partial_t + 1)\sigma_{\alpha\beta}(\mathbf{k},t) = -i\mu[k_\alpha v_\beta(\mathbf{k},t) + k_\beta v_\alpha(\mathbf{k},t)]$$
$$+ \theta_{\alpha\beta}(\mathbf{k},t) + \sigma_{\alpha\beta}(\mathbf{k},0)\delta(t), \quad (10)$$

where $\int_{\mathbf{k}} \equiv (2\pi)^{-3}\int d\mathbf{k}$ and $\mathscr{T}_{\alpha\beta}(\mathbf{k}) = \delta_{\alpha\beta} - \hat{k}_\alpha \hat{k}_\beta$ is the transverse projection operator. In the concentration and stress Eqs. (8) and (10), the initial condition has been included as an inhomogeneous term on the right-hand side. Also, in these and all subsequent equations, an implicit factor of $(2\pi)^3$ is absorbed into the definition of each Dirac delta function with wave vector arguments. In going from Eq. (4) to (9), the last term on the left-hand side has been simplified as follows. The terms arising from $(\delta F)/(\delta \psi)$ that are proportional to r and u do not contribute to the momentum equation, because these can be transformed into gradient terms that vanish when contracted with the transverse projection operator. Thus, the only osmotic stress term that survives in the momentum equation is the square gradient term proportional to K.

The random noises ζ and $\theta_{\alpha\beta}$ are assumed to be Gaussian and white with zero mean and the following second moment to satisfy the fluctuation dissipation theorem:

$$\langle \zeta(\mathbf{k},t)\zeta(\mathbf{k}',t) \rangle = 2T\lambda k^2 \delta(\mathbf{k}+\mathbf{k}')\delta(t-t'), \quad (11)$$

$$\langle \theta_{\alpha\beta}(\mathbf{k},t)\theta_{\gamma\xi}(\mathbf{k}',t') \rangle = 2T\mu \delta(\mathbf{k}+\mathbf{k}')\delta(t-t')$$
$$\times (\delta_{\alpha\gamma}\delta_{\beta\xi} + \delta_{\alpha\xi}\delta_{\beta\gamma}). \quad (12)$$

Equation (11) is the standard noise correlation for the concentration equation, but Eq. (12) is novel to the present study, so it is useful to discuss the derivation in some detail. The equation for the stress field can be rewritten as

$$\partial_t \sigma_{\alpha\beta} = -\tau^{-1}\sigma_{\alpha\beta} + G(\partial_\alpha v_\beta + \partial_\beta v_\alpha) + \tau^{-1}\theta_{\alpha\beta}$$
$$= -G\tau^{-1}(\delta_{\alpha\xi}\delta_{\beta\eta} + \delta_{\alpha\eta}\delta_{\beta\xi})\frac{\delta F}{\delta \sigma_{\xi\eta}}$$
$$+ G(\partial_\alpha v_\beta + \partial_\beta v_\alpha) + \tau^{-1}\theta_{\alpha\beta}, \quad (13)$$

where Eq. (6) has been used for the free energy F and $\tau = (\mu/G)$. Since the above equation is now written in canonical form,[15] it is evident that the noise correlation is

$$\tau^{-2}\langle \theta_{\alpha\beta}(\mathbf{k},t)\theta_{\xi\eta}(\mathbf{k}',t') \rangle = 2TG\tau^{-1}\delta(\mathbf{k}+\mathbf{k}')\delta(t-t')$$
$$\times (\delta_{\alpha\xi}\delta_{\beta\eta} + \delta_{\alpha\eta}\delta_{\beta\xi}), \quad (14)$$

which reduces to Eq. (12) because $\tau = (\mu/G)$. It can also be verified that the coupled equations (8), (9), and (10) reduce to the model-H equations for a binary fluid in the limit $\tau \to 0$. In this limit, the equation for the stress tensor can be inserted into the momentum equation to obtain

$$\left[\mu(\partial_\beta^2 v_\alpha + \partial_\alpha \partial_\beta v_\beta) + \xi_\alpha + \partial_\alpha \psi \frac{\delta F}{\delta \psi} \right]_\perp = 0, \quad (15)$$

where the random noise ξ_α is given by $\xi_\alpha = [\partial_\beta \theta_{\alpha\beta}]_\perp$. The correlator for this new random noise [from Eq. (12)] is given by

$$\langle \xi_\alpha(\mathbf{k},t) \xi_\beta(\mathbf{k}',t) \rangle$$

$$= -\langle \mathcal{T}_{\alpha\gamma}(\mathbf{k}) k_\xi \theta_{\gamma\xi} \mathcal{T}_{\beta\eta}(\mathbf{k}') k'_\delta \theta_{\eta\delta}(\mathbf{k}',t') \rangle$$

$$= 2T\mu k^2 \delta(\mathbf{k}+\mathbf{k}') \delta(t-t') . \mathcal{T}_{\alpha\beta}(\mathbf{k}). \qquad (16)$$

The above noise correlation is identical to that used in the model-H equations for binary fluids, indicating that the present formulation is consistent with earlier ones used for binary fluids in the limit $\tau \to 0$.

In the general case of finite stress relaxation time, the momentum and stress equations can be combined and solved to obtain

$$v_\alpha(\mathbf{k},t) = T_{\alpha\beta}(\mathbf{k}) \Bigg\{ -ik_\gamma \theta_{\beta\gamma}(\mathbf{k},t) - i(\tau\partial_t + 1)$$

$$\times \Bigg[\int_{\mathbf{k}_1} \int_{\mathbf{k}_2} k_{1\beta} \psi(\mathbf{k}_1,t) K k_2^2 \psi(\mathbf{k}_2,t)$$

$$\delta(\mathbf{k}_1 + \mathbf{k}_2 - \mathbf{k}) \Bigg] \Bigg\}, \qquad (17)$$
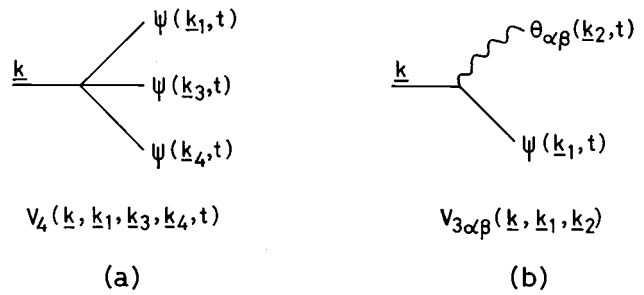
FIG. 1. The four point vertex (a) and three point vertex (b) due to the nonlinear terms in the concentration equation.

where the Oseen tensor $T_{\alpha\beta}(\mathbf{k})$ is

$$T_{\alpha\beta}(\mathbf{k}) = \frac{1}{8\pi\mu} \left(\frac{\delta_{\alpha\beta}}{k^2} - \frac{k_\alpha k_\beta}{k^4} \right). \qquad (18)$$

Subsequently, we scale all wave vectors by $\kappa = (r/K)^{1/2}$, scale all times by $(\lambda\kappa^2 r)^{-1}$, and scale the concentration $\psi(\mathbf{k},t)$ by $(T/\kappa^3 r)^{1/2}$, which is the amplitude of the concentration fluctuations due to thermal effects. The equation for the concentration field now becomes

$$\partial_t \psi(\mathbf{k},t) = -k^2(k^2-1) \psi(\mathbf{k},t) + \zeta(\mathbf{k},t) + \delta(t) \psi(\mathbf{k},0) - \epsilon_d k^2 \int_{\mathbf{k}_1} \int_{\mathbf{k}_2} \int_{\mathbf{k}_3} \psi(\mathbf{k}_1,t) \psi(\mathbf{k}_2,t) \psi(\mathbf{k}_3,t)$$

$$\times \delta(\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3 - \mathbf{k}) + \int_{\mathbf{k}_1} \int_{\mathbf{k}_2} k_{1\alpha} \psi(\mathbf{k}_1,t) \delta(\mathbf{k}_1 + \mathbf{k}_2 - \mathbf{k}) T_{\alpha\beta}(\mathbf{k}_2)$$

$$\times \Bigg\{ \epsilon_c^{1/2} k_{2\gamma} \theta_{\beta\gamma}(\mathbf{k}_2,t) + (\tau\partial_t + 1) \Bigg[\epsilon_c \int_{\mathbf{k}_3} \int_{\mathbf{k}_4} k_{3\beta} \psi(\mathbf{k}_3,t) k_4^2 \psi(\mathbf{k}_4,t) \delta(\mathbf{k}_3 + \mathbf{k}_4 - \mathbf{k}_2) \Bigg] \Bigg\}, \qquad (19)$$

where $\epsilon_d = (uT\kappa^3/r^2)$ is the dimensionless parameter multiplying the nonlinearity arising from the quartic term in the Landau–Ginzburg free energy, and $\epsilon_c = (T\kappa/\lambda\mu r)$ is the parameter that multiplies the convective nonlinearity. In the early stages of spinodal decomposition, the nonlinear terms are small and so ϵ_d and ϵ_c can be treated as small parameters for controlling the perturbation expansion. The dimensionless Oseen tensor is now

$$T_{\alpha\beta}(\mathbf{k}) = \frac{1}{8\pi k^2} \left(\delta_{\alpha\beta} - \frac{k_\alpha k_\beta}{k^2} \right), \qquad (20)$$

and the dimensionless noise correlations are

$$\langle \zeta(\mathbf{k},t) \zeta(\mathbf{k}',t') \rangle = 2k^2 \delta(\mathbf{k}+\mathbf{k}') \delta(t-t'), \qquad (21)$$

$$\langle \theta_{\alpha\beta}(\mathbf{k},t) \theta_{\gamma\xi}(\mathbf{k}',t') \rangle = 2[\delta_{\alpha\xi}\delta_{\beta\gamma} + \delta_{\alpha\gamma}\delta_{\beta\xi}]$$

$$\times \delta(\mathbf{k}+\mathbf{k}') \delta(t-t'). \qquad (22)$$

In the present study, we restrict our attention to the effect of the convective nonlinearity on the spinodal decomposition process (i.e., we set $\epsilon_d = 0$). A diagrammatic perturbation theory is employed in the small parameter ϵ_c. There is a four point vertex and a three point vertex associated with the nonlinear terms shown in Fig. 1. The bare four point vertex function is

$$V_4(\mathbf{k},\mathbf{k}_1,\mathbf{k}_3,\mathbf{k}_4,t) = \epsilon_c k_{1\alpha} T_{\alpha\beta}(\mathbf{k}_2) k_{3\beta} k_4^2 \delta(\mathbf{k}_3 + \mathbf{k}_4 - \mathbf{k}_2)$$

$$\times \delta(\mathbf{k}_1 + \mathbf{k}_2 - \mathbf{k})(\tau\partial_t + 1), \qquad (23)$$

while the three point vertex is

$$V_{3\alpha\beta}(\mathbf{k},\mathbf{k}_1,\mathbf{k}_2) = \epsilon_c^{1/2} k_{1\gamma} T_{\alpha\gamma}(\mathbf{k}_2) k_{2\beta} \delta(\mathbf{k}_1 + \mathbf{k}_2 - \mathbf{k}). \qquad (24)$$

Note that in the three point vertex, we explicitly draw the $\theta_{\alpha\beta}$ correlation line, since this is necessary for calculating the renormalization of the transport coefficient and noise correlation. However, the correlation line for ζ is not explicitly drawn. In Eq. (23), the operator $(\tau\partial_t + 1)$ acts on the product
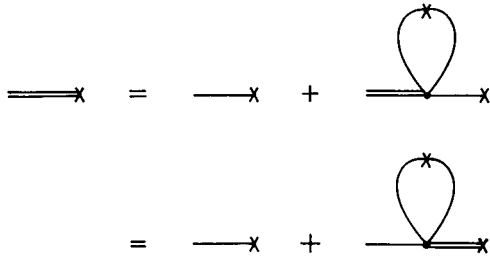
FIG. 2. Dyson equation for the Hartree approximation for the transport coefficient.

FIG. 3. The self-energy due to the four point vertex function which renormalizes the transport coefficient (a), the three point vertex function which renormalizes the transport coefficient (b), and the noise renormalization due to the three point vertex function (c).

of the two legs $\psi(\mathbf{k}_3,t)\psi(\mathbf{k}_4,t)$, and the chain rule is used to calculate the partial derivatives with respect to time.

　　In the present case, the nonlinear terms in the concentration equation result in the renormalization of both the transport coefficient and the noise correlations. The Hartree approximation (Fig. 2) is used to determine the renormalization of the transport coefficient, and the renormalized transport coefficient is given by

$$\Gamma(\mathbf{k},t)t = \Gamma_0(\mathbf{k})t - k^2 \int_0^t dt' \, \Sigma(t'), \tag{25}$$

where Γ_0 is the bare transport coefficient. The details of the approximation are given in the Appendix. The method used here for obtaining the renormalized transport coefficient $\Gamma = \Gamma_0 - k^2\Sigma$ is very similar to the Gaussian approximation of Langer,[13] a simple "mass renormalization". However, the calculations of the self energy in earlier studies were simplified by the fact that the self energy arising from the quartic term in the Landau–Ginzburg free energy is independent of wave vector k and time in the Gaussian approximation, whereas in the present case the self energy depends on k and contains time derivatives.
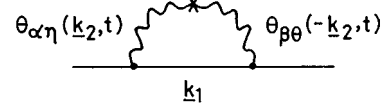
　　The self-energy Σ can be written as a sum of two components $-\Sigma_1$ due to the four point vertex [Fig. 3(a)] and Σ_2 arising from the three point vertex [Fig. 3(b)]. The self energy Σ_1 is given by

$$\Sigma_1(\mathbf{k},t) = \epsilon_c k^{-2} \int_{\mathbf{k}'} [V_4(\mathbf{k},\mathbf{k}',-\mathbf{k}',\mathbf{k},t)$$

$$+ V_4(\mathbf{k},-\mathbf{k}',\mathbf{k}',\mathbf{k},t) + V_4(\mathbf{k},\mathbf{k}',\mathbf{k},-\mathbf{k}',t)$$

$$+ V_4(\mathbf{k},-\mathbf{k}',\mathbf{k},\mathbf{k}',t) + V_4(\mathbf{k},\mathbf{k},\mathbf{k}',-\mathbf{k}',t)$$

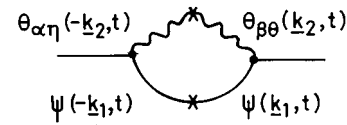$$+ V_4(\mathbf{k},\mathbf{k},-\mathbf{k}',\mathbf{k}',t)][S_0(\mathbf{k}',t)], \tag{26}$$

where $S_0(\mathbf{k}',t) = \langle \psi(\mathbf{k}',t)\psi(-\mathbf{k}',t)\rangle_0$ is the correlation in the concentration field calculated using the linear approximation and neglecting the nonlinear terms in the transport equation. The evaluation of the last two terms in the above integral, proportional to $V_4(\mathbf{k},\mathbf{k},\mathbf{k}',-\mathbf{k}',t)$ and $V_4(\mathbf{k},\mathbf{k},-\mathbf{k}',\mathbf{k}',t)$ is complicated by the fact that they contain the Oseen tensor evaluated at zero wave number $T_{\alpha\beta}(\mathbf{k}'-\mathbf{k}')$, which is infinite. In this case, it is necessary to re-examine the assump-

tions made in simplifying the momentum equation. Previously it was assumed that the inertial term is negligible compared with the viscous term. This assumption is not valid when the wave vector is zero, however, because the viscous term is proportional to k^2. Physically, this is because inertial terms become important when the wavelength of the fluctuations is large. In principle, the equation for the velocity field should be modified to take into account inertial effects. However, a detailed calculation is not necessary, since it can easily be seen that $V_4(\mathbf{k},\mathbf{k},\mathbf{k}',-\mathbf{k}',t)$ and $V_4(\mathbf{k},\mathbf{k},-\mathbf{k}',\mathbf{k}',t)$ are equal in magnitude and opposite in sign for any value of $\mathbf{k}$ and $\mathbf{k}'$, and therefore, the sum of these two contributions vanishes.
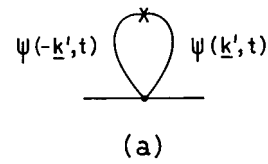
　　Because of the operator $\tau\partial_t + 1$ contained in V_4, the self energy Σ_1 contains a viscous contribution proportional to the bare correlation function $S_0(\mathbf{k},t)$ and an elastic contribution that involves the time derivative of the concentration field. The time derivative $\partial_t\psi(\mathbf{k},t)$ contains two terms:

(i)　　The first proportional to the concentration field $\psi(\mathbf{k}',t)$ and $\psi(\mathbf{k},t)$.

(ii)　　A second due to the random noise and the initial concentration: $\zeta(\mathbf{k},t) + \psi(\mathbf{k},0)\delta(t)$ and $\zeta(\mathbf{k}',t) + \psi(\mathbf{k}',0)c\,\delta(t)$.

The first contribution can be lumped in with the viscous contribution to the self-energy $\Sigma_1(\mathbf{k},t)$, since it just gives an additional contribution proportional to $\tau\Gamma_0(\mathbf{k},t)$ and $\tau\Gamma_0(\mathbf{k}',t)$. These terms can be expressed as
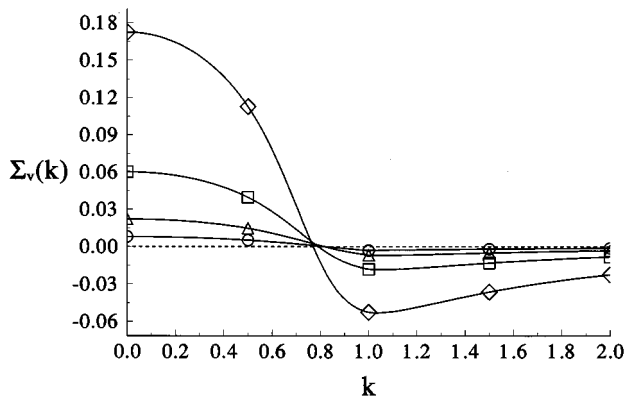
FIG. 4. The self-energy $\Sigma_v(\mathbf{k})$ as a function of k for $\bigcirc$ ($t=2.5$); $\triangle$ ($t=5.0$); $\square$ ($t=7.5$); $\diamond$ ($t=10$).

FIG. 5. The self energy $\Sigma_e(\mathbf{k})$ as a function of k for $\bigcirc$ ($t=2.5$); $\triangle$ ($t=5.0$); $\square$ ($t=7.5$); $\diamond$ ($t=10$).

$$\Sigma_1(\mathbf{k},t)=\epsilon_c k^{-2}\int_{\mathbf{k}'}\{2k_\alpha T_{\alpha\beta}(\mathbf{k}+\mathbf{k}')k_\beta(k'^2-k^2)$$

$$\times[1-\tau\Gamma_0(\mathbf{k}')-\tau\Gamma_0(\mathbf{k})]S_0(\mathbf{k}',t)\}. \qquad (27)$$

The other elastic contribution to the self energy arising from the term $\zeta(\mathbf{k}',t)+\psi(\mathbf{k}',0)\delta(t)$ is

$$\Sigma_1'(\mathbf{k},t)=\epsilon_c k^{-2}\int_{\mathbf{k}'}[2k_\alpha T_{\alpha\beta}(\mathbf{k}+\mathbf{k}')k_\beta(k'^2-k^2)$$

$$\times[\langle\zeta(\mathbf{k}',t)\zeta(-\mathbf{k}',t)\rangle+S_0(\mathbf{k}',0)\delta(t)]. \qquad (28)$$

It can be easily verified that the latter contribution to the self-energy is independent of time, and is not dynamically significant. Therefore, this can be absorbed in the definition of the bare transport coefficient and neglected in the analysis. In addition, there is a contribution arising from the term $\zeta(\mathbf{k},t)+\psi(\mathbf{k},0)\delta(t)$. For $t>0$, this term is proportional to $\zeta(\mathbf{k},t)$, and appears as a renormalization of the correlation of the random noise $\zeta(\mathbf{k},t)$. Therefore, this is coupled with the renormalization of the noise correlation, and is calculated in Eq. (33) later on.

The self-energy contribution from the three point vertex functions is given by the one loop diagram in Fig. 3(b). This evaluates to

$$\Sigma_2(\mathbf{k},t)=\epsilon_c k^{-2}\int_{\mathbf{k}_1}\int_{\mathbf{k}_2}k_{1\alpha}t_{\alpha\gamma}(\mathbf{k}_2)k_{1\beta}T_{\beta\xi}(\mathbf{k}_2)k_{2\eta}$$

$$\times k_{2\theta}\langle\theta_{\alpha\eta}(\mathbf{k}_2,t)\theta_{\beta\theta}(-\mathbf{k}_2,t)\rangle\delta(\mathbf{k}_1+\mathbf{k}_2-\mathbf{k}). \qquad (29)$$

The above contribution to the self-energy provides a constant correction to the transport coefficient, which remains subdominant for all time. Therefore, this contribution can also be lumped in the definition of the bare transport coefficient and does not enter into the analysis. Hence, the only time dependent contribution to the self energy is due to the four point vertex function V_4.

It is necessary to address one further issue before proceeding to evaluate the self-energy, which is the ultraviolet divergence of certain wave vector integrals. In previous stud-
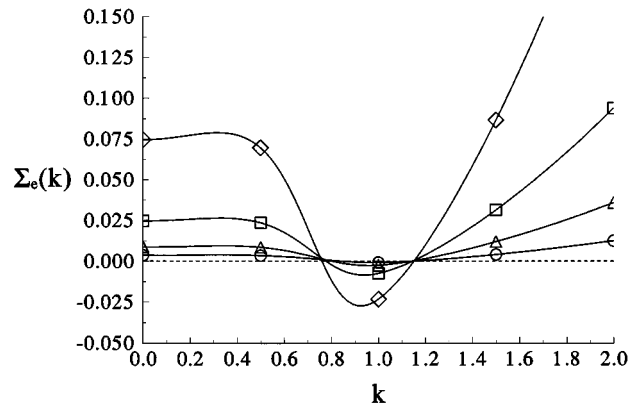
ies, this issue has been resolved by using an upper wave number cutoff. However, here a simpler procedure is employed by recognizing that the divergent contributions to the self-energy are independent of time, and hence, can be absorbed in the definition of the bare transport coefficient. The expression for Σ_1 in Eq. (27) contains the factor

$$S_0(\mathbf{k}',t)=\chi(\mathbf{k}')+\exp(-\Gamma_0 t)[S_0(\mathbf{k}',0)-\chi(\mathbf{k}')], \qquad (30)$$

where $\chi(\mathbf{k}')=(k'^2-1)^{-1}$ and S_0 is the bare correlation function. In the above expression, the last term on the right side gives rise to convergent wave vector integrals, since it is proportional to $\exp[-k^2(k^2-1)t]$ at large k. The divergence of the wave vector integrals is due to the first term on the right, which is independent of time. Therefore, the contribution to the self energy due to this term can be included in the definition of the bare transport coefficient, and can be neglected while evaluating the time dependent corrections to the self-energy. With this redefinition of the transport coefficient, all wave vector integrals in the self-energy are convergent.

The resulting self-energy $\Sigma=\Sigma_1$ can be separated into two components, one due to the viscous and the second due to the elastic contributions to the convective nonlinearity

$$\Sigma(\mathbf{k},t)=\Sigma_v(\mathbf{k},t)+\tau\Sigma_e(\mathbf{k},t). \qquad (31)$$

We have explicitly extracted the linear dependence on τ from the elastic contribution $\Sigma_e(\mathbf{k},t)$. The self-energies $\Sigma_v(\mathbf{k},t)$ and $\Sigma_e(\mathbf{k},t)$ are shown as a function of (dimensionless) k at various (dimensionless) times in Figs. 4 and 5. The self-energy Σ_v has a maximum at $k=0$, and is positive for $k<0.75$. It then decreases to a minimum at $k=1.02$, and increases proportional to k^{-2} in the limit $k\gg1$. This indicates that the convective nonlinearity tends to amplify concentration modes with $k<0.75$, and dampen modes with $k>0.75$. This is in contrast to the nonlinearity due to the quartic term in the free energy, which tends to damp modes at all wave numbers.[12] The self-energy Σ_e is negative in the interval $0.75<k<1.15$ and positive outside this interval, indicating that the modes in the interval $0.75<k<1.18$ are dampened, while all other modes are amplified. The self-energy Σ_e diverges
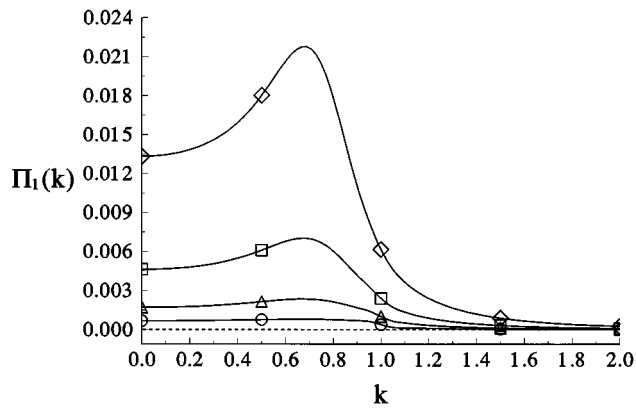
FIG. 6. The renormalization of the noise correlation $\Pi_1(\mathbf{k})$ as a function of k for $\bigcirc$ ($t=2.5$); $\triangle$ ($t=5.0$); $\square$ ($t=7.5$); $\diamond$ ($t=10$).

proportional to k^2 in the limit $k \gg 1$, indicating that modes with higher wave numbers are amplified faster.

In addition to the renormalization of the transport coefficient, the nonlinear terms also produce a renormalization of the concentration noise correlation. This renormalization is caused by the one-loop diagrams shown in Fig. 3(c). It is useful to note that the three point vertex is proportional to $\epsilon_c^{1/2}$, while the four point vertex is proportional to ϵ_c. The renormalization of the noise correlation due to the one-loop diagram involving the three point vertex [which contains the product of two three point vertices, cf. Fig. 3(c)] is of the same order in ϵ_c as the renormalization of the transport coefficient due to a bubble diagrams [which contains one four point vertex, cf. Figs. 3(a) and 3(b)]. However, the renormalization of the noise correlation due a one loop diagram involving the four point vertex is $O(\epsilon_c)$ smaller than that due to the noise correlation, and is neglected in the analysis. The contribution to the self energy of the noise correlation due to the one-loop expansion, $\Pi_1(\mathbf{k},t)$, shown in Fig. 3(c), is
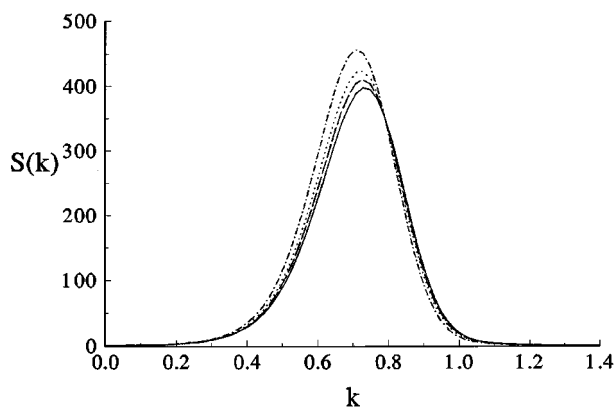

FIG. 7. The structure factor $S(k)$ as a function of k at $t=10$. (solid line) ($\epsilon=0.0$, $\tau=0.0$); (broken line) ($\epsilon=2.0$, $\tau=0.0$); (dotted line) ($\epsilon=2.0$, $\tau=2.0$); (dot-dashed line) ($\epsilon=2.0$, $\tau=5.0$).

$$\Pi_1(\mathbf{k},t) = \epsilon_c k^{-2} \int_{\mathbf{k}_1} \int_{\mathbf{k}_2} k_\alpha T_{\alpha\beta}(\mathbf{k}_2) T_{\beta\gamma}(\mathbf{k}_2) k_\gamma (2k_2^2)$$
$$\times S_0(\mathbf{k}_1,t) \delta(\mathbf{k}_1+\mathbf{k}_2-\mathbf{k}). \qquad (32)$$

In addition to the above, there is an additional contribution to the noise correlation due to the term proportional to $\zeta(\mathbf{k},t)$ which appears due to the time derivative in the elastic nonlinearity [see the discussion just after Eq. (28)]. This is given by

$$\Pi_2(\mathbf{k},t) = \epsilon_c \tau k^{-2} [2k^2 + S(\mathbf{k},0)\delta(t)] \int_{\mathbf{k}'} 2k_\alpha$$
$$\times T_{\alpha\beta}(\mathbf{k}+\mathbf{k}') k_\beta(k'^2-k^2) S_0(\mathbf{k}',t)$$
$$= \tau[2k^2 + S(\mathbf{k},0)\delta(t)]\Sigma_v(\mathbf{k},t). \qquad (33)$$

As illustrated in Fig. 6, the renormalization of the noise correlation Π_1 is positive for all k and decreases proportional to k^{-4} at large k. Therefore, the renormalization of the noise correlation also tends to amplify the structure factor [see Eq. (35)]. The variation in the structure factor is shown at $t=10$ for various values of ϵ_c and at $\tau=0$ in Fig. 7. The initial value of the structure factor at $t=0$ was assumed to be a simple Lorentzian $S_0(\mathbf{k})=1/(k^2+1)$. The calculation clearly shows that the structure factor is amplified due to the convective nonlinearity, in contrast to the nonlinearity due to the quartic term in the free energy, which damps modes at all wave numbers. Further, the effect of the nonlinearity tends to coarsen the system and the peak wave number decreases as ϵ_c increases. This is shown in Figs. 8 and 9, where the wave number of the peak of the structure factor k_{max} and the peak value S_{max} are shown as a function of time for different values of ϵ_c. Note that the value of k_{max} is not shown near $t=0$ because it depends in this region on the initial form of the structure factor. For the Ornstein–Zernicke form assumed here, the maximum is at $k=0$, and a nonzero maximum appears only at a time near $t=0.5$. In addition, the initial value of the maximum differs from the value $k_{max}=1/\sqrt{2}$ predicted by the Cahn–Hilliard theory due to the presence of the noise correlations (see, for example, Grant et al.[12]). Figure 10 shows the integral of the structure factor

$$\sigma = \int_0^\lambda dk \, k^2 S(k), \qquad (34)$$

where the upper cutoff λ was assumed to be two in the present calculations. This figure indicates that the magnitude of the fluctuations is amplified due to the convective nonlinearity.

The effect of variation in the relaxation time τ on the spinodal decomposition process is also shown in Figs. 7–10. An increase in the relaxation time tends to increase the magnitude of the structure factor and decrease the wave number of the peak value of the structure factor, as shown in Figs. 8, 9, and 10. The effect of the elastic nonlinearity is very similar to that of the convective nonlinearity. However, there is one significant difference associated with the k^4 increase in the elastic self energy at large k. The increase in the self energy at large k is caused by a reduction in the coefficient
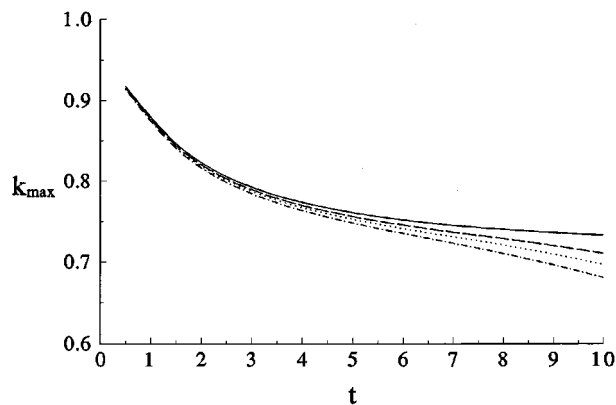
FIG. 8. The wave number of the peak value of the structure factor k_{max} as a function of t. (solid line) ($\epsilon=0.0$, $\tau=0.0$); (broken line) ($\epsilon=2.0$, $\tau=0.0$); (dotted line) ($\epsilon=2.0$, $\tau=2.0$); (dot-dashed line) ($\epsilon=2.0$, $\tau=5.0$).
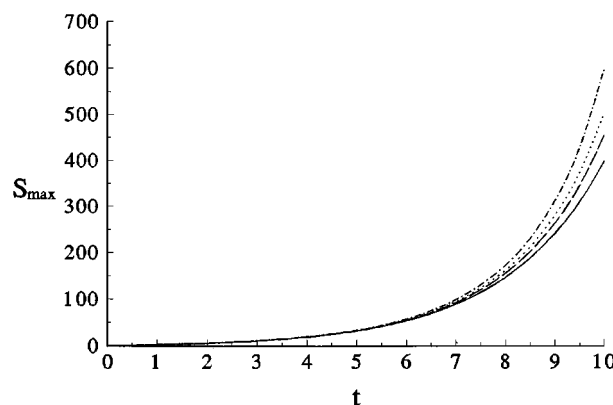

FIG. 9. The peak value of the structure factor S_{max} as a function of t. (solid line) ($\epsilon=0.0$, $\tau=0.0$); (broken line) ($\epsilon=2.0$, $\tau=0.0$); (dotted line) ($\epsilon=2.0$, $\tau=2.0$); (dot-dashed line) ($\epsilon=2.0$, $\tau=5.0$).

of the $O(k^4)$ term in the transport coefficient due to the self-energy Σ_e. This feature is unique to viscoelastic fluids— the nonlinearity arising from the quartic term in the Landau–Ginzburg free energy alters only the $O(k^2)$ term in the transport coefficient, while the self-energy associated with the viscous convective nonlinearity decreases as k^{-2} at large k.

III. CONCLUSIONS

The effect of viscoelasticity on the early stages of spinodal decomposition was analyzed. The model employed in our study consisted of coupled Langevin equations for the concentration, velocity, and stress fields. Novel to the present study was the use of a linear Maxwell model for the stress field. Because of this change in constitutive relation, the phase transformation kinetics depend on the stress relaxation time τ in the Maxwell model as well as the strength of the convective nonlinearity ϵ_c associated with the usual viscous stresses. The nonlinearity arising from the quartic term in the Landau–Ginzburg free energy was neglected for simplicity; its effect has been examined in many earlier studies.

A perturbation expansion was used to calculate the renormalization of the transport coefficient for collective diffusion and the noise correlation. The renormalization of the transport coefficient, which was calculated using the Hartree approximation, depends on the wave number k, in contrast to the renormalization in the usual (nonmode-coupled) solid model which is independent of k. The renormalized transport coefficient contains one contribution due to the elastic term in the stress equation, Σ_e, that is dependent on the relaxation time τ, and one due to the convective nonlinearity, Σ_v, which is independent of the relaxation time. At low k, the forms of Σ_e and Σ_v are similar, and the renormalization of the transport coefficient tends to amplify disturbances with wave number less than about 0.75 and dampen disturbances with wave number greater than 0.75. However, at large k the elastic contribution is positive and diverges proportional to k^2 while the convective contribution is negative and decreases proportional to k^2. Therefore, there is an amplifica-

tion of the large k modes due to the elastic contribution to the transport coefficient, but not due to the convective term.

The present analysis indicates that growth of the structure factor in the presence of convective and elastic nonlinearities is faster than that in the linear regime, and an increase in the relaxation time tends to increase the growth rate. Moreover, coarsening to smaller wave numbers with time is produced by the inclusion of these nonlinearities. The qualitative effect of the elastic nonlinearity in the linear Maxwell model, however, is similar to that due to the convective nonlinearity. Overall, we are hopeful that the results of the present study will shed light on the complex phase transformation kinetics of viscoelastic fluids, such as polymer blends.

ACKNOWLEDGMENT

APPENDIX

In this section, the derivation of the renormalized transport coefficient using the Hartree approximation is discussed. The equation for the structure factor can be written in terms of the renormalized transport coefficient and noise correlation as

$$\partial_t S(\mathbf{k},t) = -[\Gamma_0 - k^2 \Sigma(\mathbf{k},t)] S(k,t) + [2k^2 + k^2 \Pi(\mathbf{k},t)]$$
$$+ \delta(t) S(\mathbf{k},0), \tag{A1}$$

where Σ and Π are the ''self-energies'' for the transport coefficient and the noise correlation and $\Gamma_0(\mathbf{k})$, the bare transport coefficient, is $k^2(k^2-1)$ in scaled variables. The solution of Eq. (A1) is
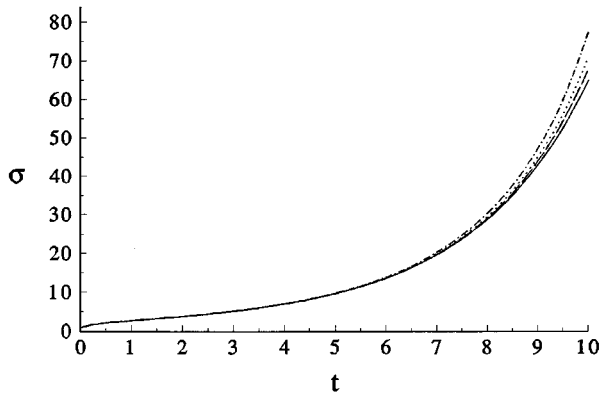
FIG. 10. The amplitude of the concentration fluctuations σ as a function of t. (solid line) ($\epsilon=0.0$, $\tau=0.0$); (broken line) ($\epsilon=2.0$, $\tau=0.0$); (dotted line) ($\epsilon=2.0$, $\tau=2.0$); (dot-dashed line) ($\epsilon=2.0$, $\tau=5.0$).

$$S(\mathbf{k},t) = \exp\left\{-\left[\Gamma_0 t - k^2 \int_0^t dt'\ \Sigma(\mathbf{k},t')\right]\right\}\left(S(\mathbf{k},0)\right.$$
$$+ \int_0^t dt''\ \exp\left\{\left[\Gamma_0 t'' - \int_0^{t''} dt'\ k^2\Sigma(\mathbf{k},t')\right]\right\}$$
$$\left.\times[2k^2 + k^2\Pi(\mathbf{k},t'')]\right). \tag{A2}$$

Thus, the renormalized structure factor can be calculated if the self-energies for the transport coefficient and noise correlation are known.

In the linear approximation, the concentration $\psi(\mathbf{k},t)$ is expressed as

$$\psi(\mathbf{k},t) = U_0(\mathbf{k},t,t')[\zeta(\mathbf{k},t') + \psi(\mathbf{k},0)\delta(t')], \tag{A3}$$

where, by convention, the Dirac delta function $\delta(t')$ is defined so that the integral of $\delta(t')$ from zero to infinity is one. The time propagator $U_0(\mathbf{k},t,t')$, which is an integral operator, is given by

$$U_0(\mathbf{k},t,t') = \exp[-\Gamma_0(\mathbf{k})t]\int_0^t dt'\ \exp[\Gamma_0(\mathbf{k})t']. \tag{A4}$$

The presence of the nonlinear terms leads to a renormalization of the kinetic coefficient $\Gamma(\mathbf{k},t)$, which can be represented by using a time-dependent Dyson equation for the response function. Here, we make a simple "Hartree approximation" for the response function. The Dyson equation for this approximation can be expressed as shown in Fig. 2. The thick lines represent the renormalized response function $U(\mathbf{k},t,t')$ which includes the effect of the nonlinear terms in the Hartree approximation

$$U(\mathbf{k},t,t') = \exp[-\Gamma_0(\mathbf{k})t]\int_0^t dt'\ \exp[\Gamma_0(\mathbf{k})t']A(\mathbf{k},t,t'), \tag{A5}$$

where the renormalization factor $A(\mathbf{k},t,t')$ is to be determined using the Dyson equation. This equation can be written as

$$\exp[-\Gamma_0(\mathbf{k})t]\int_0^t dt'\ \exp[\Gamma_0(\mathbf{k})t']A(\mathbf{k},t,t')$$
$$= \exp[-\Gamma_0(\mathbf{k})t]\left\{\int_0^t dt'\ \exp[\Gamma_0(\mathbf{k})t']\right.$$
$$+ \int_0^t dt''\ A(\mathbf{k},t,t'')k^2\Sigma(t'')\int_0^{t''} dt'\ \exp[\Gamma_0(\mathbf{k})t']\right\}$$
$$= \exp[-\Gamma_0(\mathbf{k})t]\left\{\int_0^t dt'\ \exp[\Gamma_0(\mathbf{k})t']\right.$$
$$+ \int_0^t dt''\ k^2\Sigma(t'')\int_0^{t''} dt'\ \exp[\Gamma_0(\mathbf{k})t']A(\mathbf{k},t'',t')\right\}, \tag{A6}$$

where the $\mathbf{k}$ dependences of the self-energy Σ has been suppressed for simplicity. The quantity $k^2\Sigma(t'')$ represents the loop integral in Fig. 2 and the explicit factor of k^2 in the self-energy is consistent with the concentration field being a conserved dynamical variable. Equation (40) can be rearranged by changing the order of the integration of t' and t'', and can be further simplified to derive the following integral equation for $A(\mathbf{k},t,t')$:

$$A(\mathbf{k},t,t') = 1 + \int_{t'}^t dt''\ A(\mathbf{k},t,t'')k^2\Sigma(t'')$$
$$= 1 + \int_{t'}^t dt''\ A(\mathbf{k},t'',t')k^2\Sigma(t''). \tag{A7}$$

This integral equation can be easily solved to express the unknown function $A(\mathbf{k},t,t')$ in terms of the self-energy $\Sigma(t)$,

$$A(\mathbf{k},t,t') = \exp\left[k^2\int_{t'}^t d\tau\ \Sigma(\tau)\right]. \tag{A8}$$

Using the above expression for $A(\mathbf{k},t,t')$, the propagator $U(\mathbf{k},t,t')$ (renormalized to include the nonlinear terms in the Hartree approximation) is now given by

$$U(\mathbf{k},t,t') = \exp[-\Gamma(\mathbf{k},t)t]\int_0^t dt'\ \exp[\Gamma(\mathbf{k},t')t'], \tag{A9}$$

where

$$\Gamma(\mathbf{k},t)t = \Gamma_0(\mathbf{k})t - k^2\int_0^t dt'\ \Sigma(t'). \tag{A10}$$

[1] P. G. de Gennes, J. Chem. Phys. **72**, 4756 (1980).
[2] P. Pincus, J. Chem. Phys. **75**, 1996 (1981).
[3] K. Binder, J. Chem. Phys. **79**, 6387 (1983).
[4] H. Tanaka, Phys. Rev. Lett. **71**, 3158 (1993).
[5] P. Wiltzius and F. Bates, J. Chem. Phys. **91**, 3258 (1989).
[6] J. W. Cahn, Metall. Soc. AMIE **242**, 166 (1968).
[7] J. E. Hilliard, in *Phase Transformations*, edited by T. Riste (Plenum, New York, 1975).
[8] H. E. Cook, Acta Metall. **18**, 297 (1970).
[9] J. S. Langer, M. Bar-on, and H. D. Miller, Phys. Rev. A **11**, 1417 (1975).
[10] K. Kawasaki and T. Ohta, Prog. Theor. Phys. **67**, 147 (1982).

[11] W. I. Goldburg, C. H. Show, J. S. Huang, and M. S. Pilant, J. Chem. Phys. **68**, 484 (1978).

[12] M. Grant, M. San Miguel, J. Vinals, and J. D. Gunton, Phys. Rev. B **31**, 3027 (1985).

[13] J. S. Langer, Ann. Phys. (N.Y.), **65**, 53 (1970).

[14] A. L. Fetter and J. D. Walecka, *Quantum Theory of Many-Particle Systems* (McGraw-Hill, New York, 1971).

[15] P. C. Hohenberg and B. I. Halperin, Rev. Mod. Phys. **49**, 435 (1977).

[16] R. B. Bird, R. C. Armstrong, and O. Hassager, *Dynamics of Polymeric Fluids* (Wiley, New York, 1977), Vol. I.