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A Nonlinear Theory of Transients Following Step Temperature Changes in Polymer Blends

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ABSTRACT: A nonlinear theory for the scattering intensity $I(q,t)$ during spinodal decomposition, dissolution (reverse quench), and transients following step temperature changes within the one-phase region is developed including coupling among density modes. It is shown analytically that the peak position $q_m(t)$ of $I(q,t)$ behaves as $q_m(t) \sim t^{-1/3}$ asymptotically during spinodal decomposition, and $I(q,t)$ scales approximately as $I(q,t) \sim q_m(t)^{-3}y^2/(2 + y^6)$, where $y = q/q_m(t)$, with a calculable temperature-dependent proportionality constant. The possibility of a power law $q_m(t) \sim t^{-1/2}$ during dissolution after a reverse quench within an intermediate time interval is demonstrated. An asymptotic power law $q_m(t) \sim t^{1/3}$ during transients following step temperature changes within the one-phase region is obtained. A discussion of various interpretations of the fluctuation-dissipation relation in nonlinear systems is also included.

Introduction

This paper presents a nonlinear theory of transients in the intensity of scattered radiation in light or neutron scattering experiments on polymer blends, initiated by a step change in the temperature of the sample. These include the transients after a step change from a temperature in the one-phase region to a temperature in the two-phase region, involving spinodal decomposition, followed by a step temperature change from the two-phase region into the one-phase region (reverse quench), involving dissolution of inhomogeneities formed during the period of spinodal decomposition, and the transients caused by step temperature changes within the one-phase region. The theoretical approach taken in this study is similar in principle to those by Langer et al.,[1,2] originally developed for spinodal decomposition in fluid mixtures, and by Fredrickson,[3] developed to study transients caused by temperature changes in the one-phase region in polymer blends. There are, however, differences in the way the fluctuations are treated in the presence of nonlinearities and in the details of the derivations arising from the chain connectivity (polymer effect) in the case of polymer blends. A summary of the numerical predictions based on the analytical results obtained in this paper, concerning the variation of the intensity as a function of time following step temperature changes described above, has been presented elsewhere.[4] In the case of dissolution, the numerical results have been compared with experimental data.[5]

In this paper, we first present a critical discussion of various methods for the investigation of fluctuations in Markovian nonlinear systems in general, with particular attention to the implementation of the fluctuation-dissipation theorem in such systems. We then derive a nonlinear equation describing the temporal behavior of the intensity in polymer blends during transients. Using this nonlinear description, we investigate analytically the scaling properties of the intensity during spinodal decomposition and dissolution, as well as during transients following a step temperature jump toward the spinodal temperature within the one-phase region. In particular, we obtain, in each case, the exponents in the power-law dependence of the wavenumber corresponding to the peak intensity during transients. Finally, we also obtain an expression for the dynamic scattering function in an equilibrium state, within the same mathematical framework, and comment on the effect of nonlinearities on its relaxation frequency.

Foundations of the Theoretical Approach

We consider a melt of two homopolymer species A and B. The local volume fractions of monomers belonging to these components at a point $\mathbf{r}$ and time t are denoted by $\Phi_A(\mathbf{r},t)$ and $\Phi_B(\mathbf{r},t)$. The mixture is assumed to be incompressible so that $\Phi_A(\mathbf{r},t) + \Phi_B(\mathbf{r},t) = 1$. When the mixture is in a homogeneous equilibrium state, the volume fractions are uniform and denoted by $\Phi_A = \Phi_0$ and $\Phi_B = 1 - \Phi_0$. The incremental volume fraction of the A component is defined as $\varphi(\mathbf{r},t) \equiv \Phi_A(\mathbf{r},t) - \Phi_0$, which serves as the order parameter in this problem because of the incompressibility assumption.

The intensity $I(q,t)$ of the scattered beam is related to the Fourier transform $\varphi_{\mathbf{q}}(t)$ of $\varphi(\mathbf{r},t)$:

$$I(q,t) = \frac{1}{Vv_0}\langle|\varphi_{\mathbf{q}}(t)|^2\rangle \qquad (1)$$

where $\mathbf{q}$ is the momentum transfer vector, V is the volume of the system, and v_0 is a reference volume defined in Appendix A. With the normalization chosen in eq 1, $I(q,t)$ is a dimensionless quantity, and its equilibrium value $I_{eq}(q)$ coincides with the mean field expression of the static structure factor $S(q)$ at the final state, given in eqs A2 and A4.

The main assumption of the present theoretical approach is that the fluctuations in $\Phi(\mathbf{r},t)$ can be treated as a Markov process. The implications of this assumption can be presented in a generic form by dividing space into cubic cells of side l labeled i with a position $\mathbf{r}_i$ and introducing a discrete set of numbers $\Phi_i(t) = l^3\Phi(\mathbf{r}_i,t)$, which we denote collectively by a vector $\mathbf{\Phi}(t)$ = column $[\Phi_1(t), \Phi_2(t), ...]$. Then, the following moment equations are obtained when the vector process $\{\mathbf{\Phi}(t)\}$ is a Markov process[6,7]

$$\frac{d}{dt}\langle\mathbf{\Phi}(t)\rangle = \langle\mathbf{A}(\mathbf{\Phi}(t))\rangle \qquad (2a)$$

$$\frac{d}{dt}\langle\mathbf{\Phi}(t)\mathbf{\Phi}(t)^T\rangle = \langle\mathbf{A}(\mathbf{\Phi}(t))\mathbf{\Phi}(t)^T\rangle + \langle\mathbf{\Phi}(t)\mathbf{A}(\mathbf{\Phi}(t))^T\rangle + \langle\mathbf{B}(\mathbf{\Phi}(t))\rangle \qquad (2b)$$

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$$\frac{d}{dt}\langle \mathbf{\Phi}(t)\mathbf{\Phi}(t')^{T}\rangle = \langle \mathbf{A}(\mathbf{\Phi}(t))\mathbf{\Phi}(t')^{T}\rangle \tag{2c}$$

where the drift vector $\mathbf{A}(\mathbf{\Phi})$ and the diffusion matrix[7] $\mathbf{B}(\mathbf{\Phi})$ are defined by

$$\mathbf{A}(\mathbf{\Phi}) = \int d\alpha\, \alpha W(\alpha|\mathbf{\Phi}) \tag{3a}$$

$$\mathbf{B}(\mathbf{\Phi}) = \int d\alpha\, \alpha\alpha^{T} W(\alpha|\mathbf{\Phi}) \tag{3b}$$

in terms of the transition rate $W(\alpha|\mathbf{\Phi})$ from a state $\mathbf{\Phi}$ at time t to another state $\mathbf{\Phi} + \alpha$ per unit time. Here we assumed that the Markov process is homogeneous in time so that $W(\alpha|\mathbf{\Phi})$ does not depend on time. The deterministic evolution of the state vector is given by

$$\frac{d}{dt}\mathbf{\Phi}(t) = \mathbf{A}(\mathbf{\Phi}(t)) \tag{4}$$

which are the nonlinear macroscopic equations of the system.

The one-time and two-time averages in eqs 2 denote averages over the probability density $P(\mathbf{\Phi},t)$, and the transition probability density $P(\mathbf{\Phi},t|\mathbf{\Phi}',t')$, $t > t'$, both of which satisfy the master equation characterizing the underlying Markov processes. The point we make here is that the time evolution of these averages described by eqs 2 require only the first two moments, i.e., $\mathbf{A}(\mathbf{\Phi})$ and $\mathbf{B}(\mathbf{\Phi})$ of the transition rate $W(\alpha|\mathbf{\Phi})$. In many applications to physical problems, the underlying Markov process is not known in sufficient detail, and $W(\alpha|\mathbf{\Phi})$ is not available explicitly. One can still determine the required averages of $\mathbf{A}(\mathbf{\Phi})$ and $\mathbf{B}(\mathbf{\Phi})$ in eqs 2, at least approximately, using the macroscopic description of the system, and its equilibrium properties. The macroscopic equations of motion in eq 4 are either obtained systematically starting from the Liouville equation or written down phenomenologically as an adequate description of the system with the chosen set of variables included in the state vector $\mathbf{\Phi}(t)$, e.g., the hydrodynamic equations in fluids. In either case one has an appropriate expression of $\mathbf{A}(\mathbf{\Phi})$. In order to find an appropriate expression for $\langle \mathbf{B}(\mathbf{\Phi}(t))\rangle$ in eq 2b, which contains statistical information related to fluctuations in the state vector, one assumes that the perturbed system asymptotically approaches an equilibrium state, in which the moments of $\mathbf{\Phi}(t)$ are independent of time. Thus, eq 2b leads to

$$\langle \mathbf{B}(\mathbf{\Phi})\rangle_{eq} = -\langle \mathbf{A}(\mathbf{\Phi})\mathbf{\Phi}^{T}\rangle_{eq} - \langle \mathbf{\Phi}\mathbf{A}(\mathbf{\Phi})^{T}\rangle_{eq} \tag{5}$$

where $\langle\cdots\rangle_{eq}$ denote equilibrium averages. This relation, which is the nonlinear version of the generalized Einstein relation,[6,7] enables one to determine only the equilibrium average of $\mathbf{B}(\mathbf{\Phi})$, but not $\langle \mathbf{B}(\mathbf{\Phi}(t))\rangle$ needed in eq 2b. Only in linear systems, in which $\mathbf{A}(\mathbf{\Phi})$ and $\mathbf{B}(\mathbf{\Phi})$ are linear functions of their argument, can $\mathbf{B}(\mathbf{\Phi})$ be determined from eq 5 uniquely. In nonlinear systems one has to resort to further approximations in order to obtain $\langle \mathbf{B}(\mathbf{\Phi}(t))\rangle$ from eq 5. The difficulties in analyzing fluctuations of macrovariables in nonlinear systems in general have been pointed out by various authors.[7-11] In particular, van Kampen[10] introduced his system size expansion to develop a systematic procedure for this purpose. In this paper, we treat eq 5 as a relationship that must be satisfied consistently at any level of approximation one adopts for $\mathbf{A}(\mathbf{\Phi})$, $\mathbf{B}(\mathbf{\Phi})$, and the moments of $\mathbf{\Phi}(t)$ which are implicit in eq 5 and on the right-hand side of eqs 2.

There are two other mathematically equivalent approaches to the study of fluctuations in nonlinear systems that are often used in the literature. Although they are well-known, we comment on them to put the above description into a better perspective. One of them is based on the Fokker–Planck equation for $P(\mathbf{\Phi},t)$, which is obtained from the master equation by truncating the Kramers–Moyal expansion after the second derivatives in $\mathbf{\Phi}$:[8]

$$\frac{\partial P(\mathbf{\Phi},t)}{\partial t} = -\frac{\partial}{\partial \Phi_j}\{A_j(\mathbf{\Phi})P(\mathbf{\Phi},t)\} + \frac{1}{2}\frac{\partial^2}{\partial \Phi_j \partial \Phi_k}\{B_{jk}(\mathbf{\Phi})P(\mathbf{\Phi},t)\} \tag{6}$$

The transition probability $P(\mathbf{\Phi},t|\mathbf{\Phi}',t')$, $t > t'$, also satisfies eq 6 with the initial condition $P(\mathbf{\Phi},t|\mathbf{\Phi}',t') \to \delta(\mathbf{\Phi} - \mathbf{\Phi}')$ as $t \to t'$. The validity of the Fokker–Planck equation as an approximation to the master equation has been discussed by van Kampen[8,10] using the system size expansion. One finds that it is justified either in the limit of large cell size at a fixed concentration or in the limit of high concentration at fixed cell size.[8] It is clear that eqs 2 follow also from the Fokker–Planck equation by calculating $\langle \mathbf{\Phi}(t)\rangle$, $\langle \mathbf{\Phi}(t)\cdot\mathbf{\Phi}(t)^{T}\rangle$, and $\langle \mathbf{\Phi}(t)\mathbf{\Phi}(t')^{T}\rangle$ using eq 6. One can determine the full diffusion matrix $\mathbf{B}(\mathbf{\Phi})$ by requiring that the equilibrium distribution $P_{eq}(\mathbf{\Phi})$ be the steady-state solution of eq 6, provided $P_{eq}(\mathbf{\Phi})$ is known independently.

The second approach is based on the Langevin equation[6,7] for the instantaneous value of the state vector $\mathbf{\Phi}(t)$:

$$\frac{d}{dt}\mathbf{\Phi}(t) = \mathbf{A}(\mathbf{\Phi}(t)) + \mathbf{s}(t) \tag{7}$$

where the statistical properties of the random driving force $\mathbf{s}(t)$ are obtained[7] as

$$\langle \mathbf{s}(t)\rangle = 0 \tag{8a}$$

$$\langle \mathbf{s}(t)\mathbf{\Phi}(t)^{T}\rangle + \langle \mathbf{\Phi}(t)\mathbf{s}(t)^{T}\rangle = \langle \mathbf{B}(\mathbf{\Phi}(t))\rangle \tag{8b}$$

$$\langle \mathbf{s}(t)\mathbf{s}(t')^{T}\rangle = \langle \mathbf{B}(\mathbf{\Phi}(t))\rangle\delta(t - t') \tag{8c}$$

$$\langle \mathbf{s}(t)\mathbf{\Phi}(t')^{T}\rangle = 0, \quad t > t' \tag{8d}$$

These properties are obtained such that the moment equations in eqs 2 are reproducd when they are calculated directly from the Langevin equation. The property in eq 8c is a direct consequence of the assumption that the fluctuations in $\mathbf{\Phi}(t)$ can be treated as a Markov random process. The property in eq 8d expresses the causality. The physical content of the Langevin equation method in nonlinear systems is discussed by van Kampen[9,10] and Akcasu[7] using the system size expansion. The Fokker–Planck equation can be obtained directly from the Langevin equations by interpreting the averages in eqs 8 as conditional averages such that $\mathbf{\Phi}(t)$ at t is specified as $\mathbf{\Phi}$.[8]

Since both approaches lead to the same moment equations by their construction and require also only $\mathbf{A}(\mathbf{\Phi})$ and $\mathbf{B}(\mathbf{\Phi})$ as inputs, we start directly from eqs 2 to analyze the transients in polymer blends.

Continuum Limit of the Moment Equations. We first take the continuum limit[8] of eqs 2 by letting the cell size l^3 shrink to zero, denoting $\Phi(\mathbf{r}_j) = \lim l^{-3}\Phi_j$, and using $A(\mathbf{r}_j,\{\mathbf{\Phi}\}) = \lim l^{-3}[\mathbf{A}(\mathbf{\Phi})]_j$ and $B(\mathbf{r}_j,\mathbf{r}_k,\{\mathbf{\Phi}\}) = \lim l^{-6}[\mathbf{B}(\mathbf{\Phi})]_{jk}$:

$$\frac{\partial}{\partial t}\langle \varphi(\mathbf{r},t)\rangle = \langle A(\mathbf{r},\{\mathbf{\Phi}(t)\})\rangle \tag{9a}$$

$$\frac{\partial}{\partial t}\langle \varphi(\mathbf{r},t)\varphi(\mathbf{r}',t)\rangle = \langle A(\mathbf{r},\{\mathbf{\Phi}(t)\})\varphi(\mathbf{r}',t)\rangle + \langle A(\mathbf{r}',\{\mathbf{\Phi}(t)\})\varphi(\mathbf{r},t)\rangle + \langle B(\mathbf{r},\mathbf{r}',\{\mathbf{\Phi}(t)\})\rangle \tag{9b}$$

$$\frac{\partial}{\partial t}\langle \varphi(\mathbf{r},t)\varphi(\mathbf{r}',t')\rangle = \langle A(\mathbf{r},\{\mathbf{\Phi}(t)\})\varphi(\mathbf{r}',t')\rangle \tag{9c}$$

In these equations, $A(\mathbf{r},\{\mathbf{\Phi}(t)\})$ and $\langle B(\mathbf{r},\mathbf{r}',\{\mathbf{\Phi}(t)\})\rangle$ are functionals of $\mathbf{\Phi}(\mathbf{r},t)$ at time t. We recall that $\mathbf{\Phi}(\mathbf{r},t)$ is the local density of monomers belonging to one of the components in the binary mixture, and $\varphi(\mathbf{r},t) = \mathbf{\Phi}(\mathbf{r},t)$ −

Φ_0 denotes the deviations from the uniform equilibrium density Φ_0. In the continuum limit, the generalized Einstein relation in eq 5 reads

$$\langle B(\mathbf{r},\mathbf{r}',\{\Phi\})\rangle_{\rm eq} = -\langle A(\mathbf{r},\{\Phi\})\varphi(\mathbf{r}')\rangle_{\rm eq} - \langle A(\mathbf{r}',\{\Phi\})\varphi(\mathbf{r})\rangle_{\rm eq} \tag{10}$$

and the deterministic equation 4 becomes

$$\frac{\partial}{\partial t}\varphi(\mathbf{r},t) = A(\mathbf{r},\{\Phi(t)\}) \tag{11a}$$

The continuum limit of the Fokker–Planck equation follows from eq 6 as[8]

$$\frac{\partial P(\{\Phi\},t)}{\partial t} = -\int \mathrm{d}\mathbf{r}\,\frac{\partial}{\partial\Phi(\mathbf{r})}\Big[A(\mathbf{r},\{\Phi\}) - \frac{1}{2}\int \mathrm{d}\mathbf{r}'\,\frac{\partial}{\partial\Phi(\mathbf{r}')}B(\mathbf{r},\mathbf{r}',\{\Phi\})\Big]P(\{\Phi\},t) \tag{11b}$$

In order to illustrate the procedure we wish to follow to study the transients in polymer blends using eqs 9–11, we consider as an example the pure diffusion of particles with a diffusion coefficient D. In this simple example the deterministic diffusion equation is linear: $\partial\varphi(\mathbf{r},t)/\partial t = D\nabla^2\varphi(\mathbf{r},t)$. Comparison with eq 11a shows that $A(\mathbf{r},\{\Phi(t)\}) = D\nabla^2\varphi(\mathbf{r},t)$. Substitution of the latter into eq 10 yields $\langle B(\mathbf{r},\mathbf{r}',\{\Phi\})\rangle_{\rm eq} = -2D\nabla^2\langle\varphi(\mathbf{r})\varphi(\mathbf{r}')\rangle_{\rm eq}$. The static correlation function $\langle\varphi(\mathbf{r})\varphi(\mathbf{r}')\rangle_{\rm eq}$ in this case is known to be governed by Poisson statistics,[8] i.e., $\langle\varphi(\mathbf{r})\varphi(\mathbf{r}')\rangle_{\rm eq} = \langle\Phi(\mathbf{r})\rangle_{\rm eq}\delta(\mathbf{r}-\mathbf{r}')$, so that one obtains from eq 10

$$\langle B(\mathbf{r},\mathbf{r}',\{\Phi\})\rangle_{\rm eq} = -2D\nabla^2\langle\Phi(\mathbf{r})\rangle_{\rm eq}\delta(\mathbf{r}-\mathbf{r}') \tag{12a}$$

where $\langle\Phi(\mathbf{r})\rangle_{\rm eq} = \Phi_0$. A direct calculation based on cell description and the transition rates using eq 3b shows[8] that $B(\mathbf{r},\mathbf{r}',\{\Phi\}) = -2D\nabla^2\Phi(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}')$, which is consistent with eq 12a. However, in eq 9b, we need $\langle B(\mathbf{r},\mathbf{r}',\{\Phi(t)\})\rangle$, rather than its equilibrium average, which can be written as

$$\langle B(\mathbf{r},\mathbf{r}',\{\Phi(t)\})\rangle = -2D\nabla^2[\Phi_0 + \langle\varphi(\mathbf{r},t)\rangle]\delta(\mathbf{r}-\mathbf{r}') \tag{12b}$$

Equation 12b shows, as we wished to point out by considering this example, that $\langle B(\mathbf{r},\mathbf{r}',\{\Phi(t)\})\rangle$ in this example depends on time through the mean $\langle\varphi(\mathbf{r},t)\rangle$ of the fluctuations. The time evolution of the latter is given by eq 9a, so that one has to solve eqs 9a and 9b simultaneously to obtain the time evolution of $\langle\varphi(\mathbf{r},t)\cdot\varphi(\mathbf{r}',t)\rangle$. However, when the transients do not involve perturbations in the mean so that $\langle\varphi(\mathbf{r},t)\rangle = 0$ for all times, such as step temperature changes in polymer blends within the one-phase region where the mean density remains homogeneous during transients, then $\langle B(\mathbf{r},\mathbf{r}',\{\Phi(t)\})\rangle$ becomes time-independent and is given by

$$\langle B(\mathbf{r},\mathbf{r}',\{\Phi(t)\})\rangle = -2D\Phi_0\nabla^2\delta(\mathbf{r}-\mathbf{r}') \tag{13}$$

In such cases, the system is translationally invariant, and the two space-point correlations $\langle\varphi(\mathbf{r},t)\varphi(\mathbf{r}',t)\rangle$ and $\langle\varphi(\mathbf{r},t)\varphi(\mathbf{r}',t')\rangle$ are functions of $\mathbf{r} - \mathbf{r}'$. The moment equations 9 can then be written directly in the Fourier space as

$$\frac{\partial}{\partial t}\langle\varphi_{\mathbf{q}}(t)\rangle = \langle A_{\mathbf{q}}(\{\Phi(t)\})\rangle \tag{14a}$$

$$\frac{\partial}{\partial t}I(q,t) = \frac{1}{Vv_0}[\langle A_{\mathbf{q}}(\{\Phi(t)\})\varphi_{-\mathbf{q}}(t)\rangle + \langle A_{-\mathbf{q}}(\{\Phi(t)\})\varphi_{\mathbf{q}}(t)\rangle + \langle B_{\mathbf{q},-\mathbf{q}}(\{\Phi\})\rangle] \tag{14b}$$

$$\frac{\partial}{\partial t}\langle\varphi_{\mathbf{q}}(t)\varphi_{-\mathbf{q}}(t')\rangle = \langle A_{\mathbf{q}}(\{\Phi(t)\})\varphi_{-\mathbf{q}}(t')\rangle \tag{14c}$$

In these equations $A_{\mathbf{q}}(\{\Phi\})$ and $B_{\mathbf{q}}(\{\Phi\})$ are functionals of $\{\Phi_{\mathbf{q}}\}$. Since the intensity $I(q,t)$ is defined as $I(q,t) = \langle|\varphi_{\mathbf{q}}(t)|^2\rangle/Vv_0$, we have divided eq 14b by Vv_0. We note in passing that translational invariance implies $\langle\varphi_{\mathbf{q}}(t)\varphi_{\mathbf{q}}'(t)\rangle = (2\pi)^3\delta(\mathbf{q}+\mathbf{q}')I(q,t)v_0$ in which $\delta(\mathbf{q}+\mathbf{q}')$ denotes the Dirac delta function. The generalized Einstein relation in eq 10 in the q-space reads

$$\langle B_{\mathbf{q},\mathbf{q}'}(\{\Phi\})\rangle_{\rm eq} = -\langle A_{\mathbf{q}}(\{\Phi\})\varphi_{\mathbf{q}'}\rangle_{\rm eq} - \langle\varphi_{\mathbf{q}}A_{\mathbf{q}'}(\{\Phi\})\rangle_{\rm eq} \tag{15a}$$

Subtracting eq 15a from eq 14b, we find

$$\frac{\partial}{\partial t}I(q,t) = \frac{1}{Vv_0}[\langle A_{\mathbf{q}}(\{\Phi(t)\})\varphi_{-\mathbf{q}}(t)\rangle - \langle A_{\mathbf{q}}(\{\Phi\})\varphi_{-\mathbf{q}}\rangle_{\rm eq} + \langle A_{-\mathbf{q}}(\{\Phi(t)\})\varphi_{\mathbf{q}}(t)\rangle - \langle A_{-\mathbf{q}}(\{\Phi\})\varphi_{\mathbf{q}}\rangle_{\rm eq}] + \frac{1}{Vv_0}[\langle B_{\mathbf{q},-\mathbf{q}}(\{\Phi(t)\})\rangle - \langle B_{\mathbf{q},-\mathbf{q}}(\{\Phi\})\rangle_{\rm eq}] \tag{15b}$$

which now incorporates the generalized Einstein relation in the sense that it automatically implies $\partial I(q,t)/\partial t \to 0$ as $t \to \infty$. It is important to note that the last term in eq 15b in general is not zero because, whereas $\langle B_{\mathbf{q},-\mathbf{q}}(\{\Phi\})\rangle_{\rm eq}$ is independent of time, $\langle B_{\mathbf{q},-\mathbf{q}}(\{\Phi(t)\})\rangle$ depends on time implicitly through the moments of $\Phi(t)$.[7,10,12] We have already demonstrated this point in the case of pure diffusion discussed above in eqs 12. In many applications one assumes, as an approximation, that $B_{\mathbf{q},-\mathbf{q}}(\{\Phi\})$ is independent of $\{\Phi\}$, or that $\langle B_{\mathbf{q},-\mathbf{q}}(\{\Phi(t)\})\rangle$ is independent of time, so that the last term in eq 15b vanishes. Then eq 15b becomes

$$\frac{\partial}{\partial t}I(q,t) = \frac{1}{Vv_0}[\langle A_{\mathbf{q}}(\{\Phi(t)\})\varphi_{-\mathbf{q}}(t)\rangle + \langle A_{-\mathbf{q}}(\{\Phi(t)\})\varphi_{\mathbf{q}}(t)\rangle] + B(q) \tag{15c}$$

with

$$B(q) = -\frac{1}{Vv_0}[\langle A_{\mathbf{q}}(\{\Phi\})\varphi_{-\mathbf{q}}\rangle_{\rm eq} + \langle A_{-\mathbf{q}}(\{\Phi\})\varphi_{\mathbf{q}}\rangle_{\rm eq}] \tag{15d}$$

Equations 14 and 15 will serve as the starting equations in the following applications.

Application to Polymer Blends

The deterministic evolution of $\varphi_{\mathbf{q}}(t)$ in polymer blends[3,13,14] in the absence of momentum effects is given by

$$\frac{\partial\varphi_{\mathbf{q}}(t)}{\partial t} = -q^2\Lambda_{\mathbf{q}}\frac{\delta F}{\delta\Phi_{-\mathbf{q}}} \tag{16}$$

where $F(\{\Phi\})$ denotes the free energy which is a functional of $\{\Phi_q\}$ and where $[\delta F/\delta\Phi(\mathbf{r})]_{\mathbf{k}} = \delta F/\delta\Phi_{-\mathbf{k}}$ has been used (see Appendix B for notations and definitions of functional derivatives). The quantity $\Lambda_{\mathbf{q}}$ is the Fourier transform of the nonlocal Onsager coefficient.[14] The explicit functional form of F will be presented later. Comparison with the Fourier transform of eq 11 shows that $A_{\mathbf{q}}(\{\Phi\}) = -q^2\Lambda_{\mathbf{q}}\delta F/\delta\Phi_{-\mathbf{q}}$ in this case. Since the equilibrium distribution function is related to the free energy by $P_{\rm eq}(\{\Phi\}) \sim \exp(-F(\{\Phi\})$, the equilibrium averages eq 15a can be calculated exactly using integration by parts after substitution of the above expression of $A_{\mathbf{q}}\{(\Phi\})$:

$$\langle B_{\mathbf{q},\mathbf{q}'}(\{\Phi\})\rangle_{\rm eq} = 2q^2\Lambda_{\mathbf{q}}\delta_{\mathbf{q}+\mathbf{q}'} \tag{17}$$

where we used the fact that $\Lambda_{\mathbf{q}}$ is real and $\delta_{\mathbf{q}+\mathbf{q}'} \equiv (2\pi)^3\cdot\delta(\mathbf{q}+\mathbf{q}')$. (See Appendix B for definitions.) Since $(2\pi)^3\cdot\delta(\mathbf{q}+\mathbf{q}')/V$ approaches to a Kronecker delta when $V \to \infty$, eq 17 yields $\langle B_{\mathbf{q},-\mathbf{q}}(\{\Phi\})\rangle_{\rm eq} = 2q^2\Lambda_{\mathbf{q}}V$. Although the latter shows that $\langle B_{\mathbf{q},-\mathbf{q}}(\{\Phi\})\rangle_{\rm eq}$ is independent of the moments of Φ, it does not necessarily imply that $B_{\mathbf{q},-\mathbf{q}'}(\{\Phi\})$ is independent of $\{\Phi\}$. Consequently, $\langle B_{\mathbf{q},-\mathbf{q}}(\{\Phi(t)\})\rangle$ may still depend on time implicitly through the moments of $\Phi(t)$, because it involves an average over the time-dependent distribution function. Only with the additional assumption $\langle B_{\mathbf{q},-\mathbf{q}}(\{\Phi(t)\})\rangle \approx \langle B_{\mathbf{q},-\mathbf{q}}(\{\Phi\})\rangle_{\mathrm{eq}}$ we are allowed to calculate $B(q)$ in eq 15c using its definition in eq 15d as $B(q) = 2q^2\Lambda(q)$, where, and henceforth, we have introduced $\Lambda(q) \equiv \Lambda_{\mathbf{q}}/v_0$. When these expressions of $A_{\mathbf{q}}(\{\Phi\})$ and $B(q)$ are used in eq 11b, one obtains the following Fokker–Planck equation in k-space for the distribution function $P(\{\Phi\},t)$:

$$\frac{\partial P(\{\Phi\},t)}{\delta t} = \int_{\mathbf{k}} \frac{\delta}{\delta \Phi_{\mathbf{k}}}\left[k^2\Lambda_{\mathbf{k}}\left[\frac{\delta F}{\delta \Phi_{-\mathbf{k}}} + \frac{\delta}{\delta \Phi_{-\mathbf{k}}}\right]\right]P(\{\Phi\},t) \qquad (18\mathrm{a})$$

which is automatically satisfied by $P_{\mathrm{eq}}(\{\Phi\}) \sim \exp(-F)$. This point is made more transparent by rewriting eq 18a in terms of $P_{\mathrm{eq}}(\{\Phi\})$ as

$$\frac{\partial P(\{\Phi\},t)}{\partial t} = \int_{\mathbf{k}} \frac{\delta}{\delta \Phi_{\mathbf{k}}}\left[k^2\Lambda_{\mathbf{k}}\left[-\frac{\delta \ln P_{\mathrm{eq}}(\{\Phi\})}{\delta \Phi_{-\mathbf{k}}} + \frac{\delta}{\delta \Phi_{-\mathbf{k}}}\right]\right]P(\{\Phi\},t) \qquad (18\mathrm{b})$$

Equation 18a is identical to eq 2.12 obtained by Fredrickson[3] when the coupling to the hydrodynamic modes is neglected. We shall include this coupling later in a separate publication.

The above procedure to determine $A_{\mathbf{q}}(\{\Phi\})$ and $B_{\mathbf{q}}(\{\Phi\})$ starting from a given expression for the free energy functional is consistent and unambiguous. But, it cannot be implemented exactly because the resulting equation for $\mathrm{d}I(q,t)/\mathrm{d}t$ after $A_{\mathbf{q}}(\{\Phi\}) = -q^2\Lambda_{\mathbf{q}}\delta F/\delta\Phi_{-\mathbf{q}}$ has been substituted into eq 15c is not a closed equation in $I(q,t)$. One has to introduce approximations to obtain a closed nonlinear equation involving only $I(q,t)$, as we discuss below. The same approximations must be used in calculating $B(q)$ with eq 15d.

We start with eq 14b and substitute $A_{\mathbf{q}}(\{\Phi\}) = -q^2\Lambda_{\mathbf{q}}\delta F/\delta\Phi_{-\mathbf{q}}$. An expression for $\delta F/\delta\Phi_{-\mathbf{q}}$ is presented in the form of a truncated power series in powers of $\varphi_{\mathbf{q}}(t)$ in eq A8, which is obtained starting from a slightly modified version of the free energy functional given by Binder.[14] When eq A8 is used in eq 14b, one obtains

$$\frac{\mathrm{d}I(q,t)}{\mathrm{d}t} = -2R(q)\Bigg\{I(q,t) + \frac{S(q)}{Vv_0}\Big[\int_{\mathbf{k}_1}\int_{\mathbf{k}_2}\Gamma_2(\mathbf{q},\mathbf{k}_1,\mathbf{k}_2)\delta_{\mathbf{q}+\mathbf{k}_1+\mathbf{k}_2}\langle\varphi_{\mathbf{k}_1}(t)\varphi_{\mathbf{k}_2}(t)\varphi_{-\mathbf{q}}(t)\rangle + \int_{\mathbf{k}_1}\int_{\mathbf{k}_2}\int_{\mathbf{k}_3}\Gamma_3(\mathbf{q},\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_3)\delta_{\mathbf{q}+\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3} \times \langle\varphi_{\mathbf{k}_1}\varphi_{\mathbf{k}_2}\varphi_{\mathbf{k}_3}\varphi_{-\mathbf{q}}(t)\rangle\Big]\Bigg\} + B(q) \qquad (19)$$

where we approximated $\langle B(q,\{\Phi\})\rangle$ as $B(q)$ assuming that $B(q,\{\Phi\})$ is independent of $\{\Phi\}$ as we discussed above. The relaxation frequency $R(q)$ follows as

$$R(q) = q^2\frac{\Lambda(q)}{S(q)} \qquad (20\mathrm{a})$$

where $S(q)$ is given in eq A4. In the small-q limit, we obtain the more familiar expression of $R(q)$:

$$R(q) = 2q^2\Lambda(q)\left\{\chi_{\mathrm{s}} - \chi + \frac{q^2}{36}\left[\frac{\sigma_{\mathrm{A}}^2}{z_{\mathrm{A}}\Phi_0} + \frac{\sigma_{\mathrm{B}}^2}{z_{\mathrm{B}}(1-\Phi_0)}\right]\right\} \qquad (20\mathrm{b})$$

As we mentioned earlier, eq 19 is not closed in $I(q,t)$. Before discussing the additional approximation needed to obtain a closed equation for $I(q,t)$, we first consider the linear theory, in which eq 19 is approximated by

$$\frac{\mathrm{d}I(q,t)}{\mathrm{d}t} = -2R(q)I(q,t) + B \qquad (21\mathrm{a})$$

with a solution

$$I(q,t) = I_{\mathrm{in}}(q,t)\mathrm{e}^{-2R(q)t} + I_{\mathrm{eq}}(q)[1 - \mathrm{e}^{-2R(q)t}] \qquad (21\mathrm{b})$$

which is the celebrated Cahn–Hilliard–Cook form (CHC) for polymer mixtures.[13,15] In obtaining eq 21b, we have eliminated $B(q)$ requiring that $I(q,t) \to I_{\mathrm{eq}}(q)$ as $t \to \infty$. This leads to

$$B(q) = 2R(q)I_{\mathrm{eq}}(q) \qquad (22\mathrm{a})$$

which is equivalent to eq 15. Since $I_{\mathrm{eq}}(q) = S(q)$, by the construction of the free energy functional in eq A1 or A6, eq 22 yields

$$B(q) = 2q^2\Lambda(q) \qquad (22\mathrm{b})$$

which was arrived at above starting from eq 15a. Thus, to obtain this expression of $B(q)$ by either using the requirement $I(q,t) \to I_{\mathrm{eq}}(q)$ as $t \to \infty$ or by implementing Einstein's relation in eq 15a leads to identical results in linear theory.

In the nonlinear theory, however, one has to introduce approximations to express the third- and fourth-order correlation functions in eq 19 in terms of $I(q,t)$. If we assume that $\varphi_{\mathbf{q}}(t)$ for different values of $\mathbf{q}$ are Gaussian random variables with zero mean, then we have

$$\langle\varphi_{\mathbf{k}_1}(t)\varphi_{\mathbf{k}_2}(t)\varphi_{-\mathbf{q}}(t)\rangle = 0 \qquad (23)$$

$$\langle\varphi_{\mathbf{k}_1}(t)\varphi_{\mathbf{k}_2}(t)\varphi_{\mathbf{k}_3}(t)\varphi_{-\mathbf{q}}(t)\rangle = \langle\varphi_{\mathbf{k}_1}(t)\varphi_{\mathbf{k}_2}(t)\rangle\langle\varphi_{\mathbf{k}_3}(t)\varphi_{-\mathbf{q}}(t)\rangle + \langle\varphi_{\mathbf{k}_1}(t)\varphi_{\mathbf{k}_3}(t)\rangle\langle\varphi_{\mathbf{k}_2}(t)\varphi_{-\mathbf{q}}(t)\rangle + \langle\varphi_{\mathbf{k}_1}(t)\varphi_{-\mathbf{q}}(t)\rangle\langle\varphi_{\mathbf{k}_2}(t)\varphi_{\mathbf{k}_3}(t)\rangle$$

Using

$$\langle\varphi_{\mathbf{k}}(t)\varphi_{\mathbf{k}'}(t)\rangle = I(k,t)v_0\delta_{\mathbf{k}+\mathbf{k}'}$$

and the permutational symmetry of $\Gamma(\mathbf{q},\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_3)\delta_{\mathbf{q}+\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3}$ with respect to the order of $\mathbf{k}_1$, $\mathbf{k}_2$, and $\mathbf{k}_3$ in eq 19, we obtain

$$\langle\varphi_{\mathbf{k}_1}(t)\varphi_{\mathbf{k}_2}(t)\varphi_{\mathbf{k}_3}(t)\varphi_{-\mathbf{q}}(t)\rangle = 3I(q,t)I(k_2,t){v_0}^2\delta_{\mathbf{k}_1-\mathbf{q}}\delta_{\mathbf{k}_2+\mathbf{k}_3} \qquad (24)$$

Substitution of eqs 23 and 24 into eq 19 yields

$$\mathrm{d}I(q,t)/\mathrm{d}t = -2R(q)I(q,t)[1 + Z(q,t)] + B(q) \qquad (25)$$

where

$$Z(q,t) = v_0\int_{\mathbf{k}}\gamma(q,k)I(k,t) \qquad (26)$$

In eq 26 we have introduced

$$\gamma(q,k) = 3\Gamma_3(\mathbf{q},-\mathbf{q},\mathbf{k},-\mathbf{k})S(q) \qquad (27\mathrm{a})$$

where $\Gamma_3(\mathbf{q},-\mathbf{q},\mathbf{k},-\mathbf{k})$ is to be obtained from eq A 10b with obvious changes in the arguments, and $S(q)$ is given in eq A4b. In the small-q limit, for example, one has

$$\gamma(q,k) = \frac{3}{2}\,\frac{Z_1 + \frac{Z_2}{3}(q^2 + k^2)}{\chi_{\mathrm{s}} - \chi + \frac{q^2}{36}\left[\frac{\sigma_{\mathrm{A}}^2}{z_{\mathrm{A}}\Phi_0} + \frac{\sigma_{\mathrm{B}}^2}{z_{\mathrm{B}}(1-\Phi_0)}\right]} \qquad (27\mathrm{b})$$

where Z_1 and Z_2 are defined in eqs A10d and A10e.

Equation 26 shows that the function $Z(q,t)$ represents the effect of mode coupling on the time evolution of $I(q,t)$. Indeed, by introducing a time-dependent instantaneous relaxation frequency as

$$\Omega(q,t) = R(q)[1 + Z(q,t)] \tag{28}$$

we can write eq 25 in a form similar to that in the linear theory given in eq 21a:

$$\mathrm{d}I(q,t)/\mathrm{d}t = -2\Omega(q,t)I(q,t) + B(q) \tag{29a}$$

with a solution

$$I(q,t) = I_{\mathrm{in}}(q)\exp[-2\int_0^t \mathrm{d}t'\ \Omega(q,t')] + B(q)\int_0^t \mathrm{d}u \exp[-2\int_0^u \mathrm{d}t'\ \Omega(q,t-t')] \tag{29b}$$

which is of the same form as the linear solution in eq 21b. In the nonlinear case, also, the first term represents the relaxation of the initial intensity, and the second term accounts for the buildup of the fluctuations in the final equilibrium state. The only difference between the results of the nonlinear and the linear theories is that the relaxation frequency becomes time dependent in the former, whereas it is constant in the latter. The magnitude of the noise source, $B(q)$, in eq 25 is determined by requiring, as in the linear theory, that $I(q,t) \rightarrow I_{\mathrm{eq}}(q)$ as $t \rightarrow \infty$:

$$B(\mathrm{q}) = 2R(q)I_{\mathrm{eq}}(q)[1 + Z_{\mathrm{eq}}(q)] \tag{30a}$$

where

$$Z_{\mathrm{eq}}(q) = v_0 \int_{\mathbf{k}} \gamma(q,k) Ie_{\mathrm{q}}(k) \tag{30b}$$

The same result is also obtained directly from eq 15d by evaluating its right-hand side consistently using the same truncation and Gaussian approximation as used in obtaining a closed equation for $I(q,t)$. Thus, eq 30 enables one to calculate $B(q)$ in terms of the equilibrium intensity $I_{\mathrm{eq}}(q)$ consistently with the above approximations. The $I_{\mathrm{eq}}(q)$ must be specified by independent calculations. For example, in the linear theory eq 30a reduces to $B(q) = 2R(q)I_{\mathrm{eq}}(q)$ (cf. eqs 22), which yields $B(q) = 2q^2\Lambda(q)$ when $I_{\mathrm{eq}}(q)$ is calculated with the mean field theory, i.e., when $I_{\mathrm{eq}}(q) = S(q)$. In the nonlinear theory, one does not have to chose $I_{\mathrm{eq}}(q)$ this same way. But, since the mean field expression of $I_{\mathrm{eq}}(q)$ is found to be an excellent approximation to the equilibrium structure factor,[3] even relatively close to the critical points ($|1 - \chi/\chi_{\mathrm{s}}| \geq 0.01$), we choose $I_{\mathrm{eq}}(q) = S(q)$ in eq 30a in the nonlinear case also and obtain

$$B(q) = 2q^2\Lambda(q)[1 + Z_{\mathrm{eq}}(q)] \tag{31}$$

Once $B(q)$ is specified, eq 25 enables one to investigate the temporal behavior of the intensity $I(q,t)$ during transients following step temperature changes, either numerically as reported elsewhere[4] or analytically as we do in the following sections.

Before proceeding further we wish to point out that eq 30a has been interpreted in the literature[3] somewhat differently by choosing $B(q)$ as $B(q) = 2q^2\Lambda(q)$, which is obtained from eq 15d by evaluating its right-hand side exactly using the equilibrium distribution $P_{\mathrm{eq}}(\{\Phi\}) \sim \exp(-F(\{\Phi\}))$, as we have demonstrated above. With this specification of $B(q)$, eq 30a becomes an integral equation for the equilibrium intensity $I_{\mathrm{eq}}(q)$ in the presence of nonlinearities, which would yield a different expression for $I_{\mathrm{eq}}(q)$ from its mean field expression as $I_{\mathrm{eq}}(q) = S(q)$. If, on the other hand, one further insists on choosing $I_{\mathrm{eq}}(q)$ as $I_{\mathrm{eq}}(q) = S(q)$, on the basis of experimental success of the mean field expression, then eq 30a becomes overspecified and cannot be satisfied unless one modifies (or renormalizes) the relaxation rate $R(q)$, as suggested by Fredrickson.[3] This difficulty seems to be an artifact of calculating $\langle A_{\mathbf{q}}(\{\Phi(t)\})\varphi_{-\mathbf{q}}(t)\rangle$ in eq 15c with the truncation and Gaussian approximation, while calculating $\langle A_{\mathbf{q}}(\{\Phi\})\varphi_{-\mathbf{q}}\rangle_{\mathrm{eq}}$ exactly, even though both appear in the same equation. As a result of this somewhat inconsistent procedure, the long-time limit of $\langle A_{\mathbf{q}}(\{\Phi(t)\})\varphi_{-\mathbf{q}}(t)\rangle$ does not coincide with $\langle A_{\mathbf{q}}(\{\Phi\})\varphi_{-\mathbf{q}}\rangle_{\mathrm{eq}}$ precisely. When both quantities are evaluated with the truncation and Gaussian approximation, as we have done in the derivation of eq 30, the need for a modification of the relaxation rate does not arise.

We now proceed with the calculation of $Z_{\mathrm{eq}}(q)$ using eq 30b:

$$Z_{\mathrm{eq}}(q) = \frac{v_0}{2\pi^2}\int_0^{q_{\mathrm{c}}} \mathrm{d}k\ k^2\gamma(q,k)S(k) \tag{32}$$

The upper cutoff wavenumber q_{c} is introduced because the integral in eq 32, in which $S(k)$ is to be substituted from eq A4, is divergent. The physical implication of the cutoff is that only the modes with wavenumbers between zero and q_{c} are coupled to each other. It is therefore reasonable to choose[1,2] q_{c} of the order of the inverse of the correlation length ζ, which is defined by expressing $S(k)$ in eq A2 in the small-q limit as $S(k) = S(0)/[1 + k^2\zeta^2]$:

$$\frac{1}{q_{\mathrm{c}}} = \zeta = \left\{\frac{1}{36|\chi_{\mathrm{s}} - \chi|}\left[\frac{\sigma_{\mathrm{A}}^2}{z_{\mathrm{A}}\phi_0} + \frac{\sigma_{\mathrm{B}}^2}{z_{\mathrm{B}}(1 - \phi_0)}\right]\right\}^{1/2} \tag{33}$$

In evaluating the integral in eq 32 with $q_{\mathrm{cut}} \leq q_{\mathrm{c}}$, we can use the small-$q$ limits of $S(k)$ given in eq A2 and of $\gamma(q,k)$ given in eq 27b. The result can be obtained analytically[4] as follows:

$$Z_{\mathrm{eq}}(q) = \frac{3}{8\pi^2}\frac{v_0 q_{\mathrm{c}}^3}{(\chi_{\mathrm{s}} - \chi)^2}\frac{1}{1 + q^2\zeta^2}\left\{(\alpha - \tan^{-1}\alpha)\left(Z_1 + \frac{Z_2 q^2}{3}\right) + \left(\tan^{-1}\alpha + \frac{\alpha^3}{3} - \alpha\right)\frac{Z_2 q_{\mathrm{c}}^2}{3}\right\} \tag{34}$$

where Z_1 and Z_2 are given in eqs A10. In eq 34 we have introduced $\alpha = q_{\mathrm{cut}}/q_{\mathrm{c}}$, as a measure of the range of mode coupling. We treat α as an adjustable parameter in the theory, with values $\alpha \leq 1$.

The $Z(q,t)$ in eq 26 is also to be calculated with the same cutoff:

$$Z(q,t) = \frac{v_0}{2\pi^2}\int_0^{q_{\mathrm{cut}}} \mathrm{d}k\ k^2\gamma(q,k)I(k,t) \tag{35a}$$

or substituting $\gamma(q,k)$ from eq A10a

$$Z(q,t) = \frac{3}{4\pi^2}\frac{v_0 q_{\mathrm{c}}^3}{\chi_{\mathrm{s}} - \chi}\frac{1}{1 + q^2\zeta^2}\left\{\int_0^{\alpha} \mathrm{d}x\ x^2\left[Z_1 + \frac{Z_2}{3}(q^2 + x^2 q_{\mathrm{c}}^2)\right]I(xq_{\mathrm{c}},t)\right\} \tag{35b}$$

where we have defined $x = k/q_{\mathrm{c}}$.

Equation 25 can now be solved numerically[4] starting from a given initial intensity $I_{\mathrm{in}}(q)$, calculating $Z(q,0)$ from eq 35 with the given $I_{\mathrm{in}}(q)$ and finding $I(q,\Delta t)$. One continues to compute $I(q,2\Delta t)$, $I(q,3\Delta t)$, and so on, successively, updating $Z(q,n\Delta t)$ at each step using $I(q,n\Delta t)$ in eq 35. The value of $B(q)$ in eq 25 is calculated only once with eq 31, in which $Z_{\mathrm{eq}}(q)$ is determined from eq 32 numerically or from eq 34 analytically for the parameters at the final temperature. Since the intensities in a scattering experiment are measured in arbitrary units, one has to introduce a scaling factor to convert the experimental values to the absolute intensities as $I_{\mathrm{in}}(q) = A_0 I_{\mathrm{in}}^{\mathrm{exp}}$.

(q), where the conversion factor A_0 is to be treated as an adjustable parameter. The number α in eqs 34 and 35 is also to be considered as an adjustable parameter with $\alpha \le 1$. The results of such a numerical analysis in the case of a temperature drop from the spinodal region into the single-phase region, resulting in a dissolution process, has recently been presented and compared with experimental data.[5] In this paper we concentrate more on the analytical properties of the intensity based on eq 25.

Dimensionless Equations

It is convenient to rewrite eq 25 in terms of dimensionless variables in order to bring about the universal aspects of the transients involving dissolution and demixing processes by introducing the dimensionless wavenumber $k = q/q_c$ and the dimensionless time $\tau = q_c^2 D_{\text{int}} t$, where q_c is the inverse correlation length ζ and D_{int} is the interdiffusion coefficient. The q_c is defined in eq 33, which reduces to

$$q_c^2 = \frac{3}{R_g^2}\left[1 - \frac{\chi(T_f)}{\chi_s}\right] \tag{36}$$

where, and henceforth, we specialize to a completely symmetric mixture in which the chains of the components are identical: $N_A = N_B = N$, $z_A = z_B = 1$, $\sigma_A = \sigma_B$, and $v_A = v_B = v_0$ and $\Phi_0 = 1/2$. The critical interaction parameter in this case is given by $\chi_s = 2/N$, where N is the number of statistical segments in a chain. The interdiffusion coefficient is defined as $D_{\text{int}} = \lim\, (R(q)/q^2)$ as $q \to 0$, i.e.

$$D_{\text{int}} = 2\Lambda(0)[\chi_s - \chi] \tag{37}$$

where both $\Lambda(q)$ and χ are evaluated at the final temperature. In these definitions, the final state is assumed to be in the single-phase region so that $\chi < \chi_s$. The case of $\chi > \chi_s$, corresponding to spinodal decomposition, will be treated separately. In the definition of τ, $(q_c^2 D_{\text{int}})^{-1}$ is the time for a molecule to diffuse one correlation length. In terms of the above dimensionless variables, eq 25 reads

$$\mathrm{d}I(k,\tau)/\mathrm{d}\tau = -2r(k)I(k,\tau)[1 + Z(k,\tau)] + B(k) \tag{38}$$

where $r(k) = k^2(1 + k^2)$ and $B(k) = 2r(k)I_{\text{eq}}(k)[1 + Z_{\text{eq}}(k)]$, or explicitly

$$B(k) = \frac{k^2}{\chi_s - \chi}[1 + Z_{\text{eq}}(k)] \tag{39a}$$

and

$$I_{\text{eq}}(k) = \frac{1}{2(\chi_s - \chi)(1 + k^2)} \tag{39b}$$

The expression of $Z_{\text{eq}}(k)$ needed to evaluate $B(k)$ follows from eq 34 in dimensionless form as

$$Z_{\text{eq}}(k) = \frac{3\sqrt{3}}{\pi^2}\frac{v_0}{\chi_s R_g^3}\frac{(1 - \chi/\chi_s)^{-1/2}}{1 + k^2} \times \left\{\left(1 + \frac{R_g^2 q_c^2}{3}k^2\right)(\alpha - \tan^{-1}\alpha) + \frac{R_g^2 q_c^2}{3}\left(\tan^{-1}\alpha + \frac{\alpha^3}{3} - \alpha\right)\right\} \tag{40}$$

It is to be noted that $Z_{\text{eq}}(k)$ diverges as $(1 - \chi/\chi_s)^{-1/2}$ when $\chi \to \chi_s$, i.e., when the final state approaches the spinodal line from the one-phase region.

The expression of $Z(k,t)$ in eq 38 in dimensionless form is obtained from eq 35b as

$$Z(k,\tau) = \frac{6\sqrt{3}}{\pi^2}\frac{v_0}{R_g^3}\frac{(1 - \chi/\chi_s)^{1/2}}{1 + k^2}\int_0^\alpha \mathrm{d}x\, x^2\left[1 + \frac{R_g^2 q_c^2}{3}(k^2 + x^2)\right] I(x,\tau) \tag{41}$$

Equations 38–41 describe transients from an initial intensity $I_{\text{in}}(k)$ to the final intensity $I_{\text{eq}}(k)$ following step temperature changes in which the final temperature is in the one-phase region. The input parameters to be specified to solve these equations are χ_s, χ at the final temperature, v_0, and R_g. The α is an adjustable parameter in the theory with values $\alpha \le 1$ as mentioned earlier. $I_{\text{in}}(k)$ is the equilibrium intensity at the initial temperature, when the initial and final temperatures are within the one-phase region. In a reverse quench experiment, in which the initial temperature is in the spinodal region, $I_{\text{in}}(k)$ denotes the intensity at the end of a period of spinodal decomposition, and thus must be specified experimentally or must be obtained by solving eq 25 for a quench from a temperature in the one-phase region to another in the spinodal region and by allowing the system to phase separate through spinodal decomposition. (The computational details of such a calculation in dimensionless form will be discussed presently.)

Equation 41 shows that $Z(k,\tau)$ is positive at all times when the system relaxes toward an equilibrium state. This means that the effect of nonlinearity, and mode coupling arising from it, always enhances the relaxation rate given by $\Omega(k,\tau) = r(k)[1 + Z(k,\tau)]$. At large times, $Z(k,\tau) \to Z_{\text{eq}}(k)$, so that the relaxation frequency asymptotically approaches $\Omega(k) = r(k)[1 + Z_{\text{eq}}(k)]$. When the final state in the one-phase region is sufficiently away from the spinodal line, i.e., when $\chi \ll \chi_s$, the magnitude of $Z_{\text{eq}}(k)$ is small compared to unity, so that the relaxation of the intensity approximately follows the linear theory. Otherwise the linear theory is not valid even asymptotically.

In order to describe the spinodal decomposition analytically, the above equations must be modified slightly for two reasons: First, in this case, $\chi(T_f) \equiv \chi > \chi_s$ at the final state following the temperature change from T_i in the one-phase region to T_f in the two-phase region, which leads to the following sign changes:

$$\mathrm{d}I(k,\tau)/\mathrm{d}\tau = 2r(k)I(k,\tau)[1 + Z(k,\tau)] + B(k) \tag{42}$$

where $r(k) = k^2(1 - k^2)$ with $k = q/q_c$ as before, and

$$Z(k,\tau) = -\frac{6\sqrt{3}}{\pi^2}\frac{v_0}{R_g^3}\frac{(\chi/\chi_s - 1)^{1/2}}{1 - k^2}\int_0^\alpha \mathrm{d}x\, x^2\left[1 + \frac{R_g^2 q_c^2}{3}(k^2 + x^2)\right] I(x,\tau) \tag{43}$$

In eqs 42 and 43, $q_c^2 = (3/R_g^2)(\chi/\chi_s - 1)$ and $\tau = q_c^2 D_{\text{int}} t$, where the interdiffusion coefficient is modified as $D_{\text{int}} = 2\Lambda(0)(\chi - \chi_s)$. It is noted in eq 43 that $r(k)Z(k,\tau)$ is always negative at any wavenumber, thus indicating that the nonlinearity slows down the growth rates but enhances the decay rates. The initial intensity, which is the equilibrium intensity at the initial temperature T_i, is

$$I_{\text{in}}(k) = \frac{1}{2[\chi_s - \chi(T_i)]}\left[1 + \frac{\chi(T_f) - \chi_s}{\chi_s - \chi(T_i)}k^2\right]^{-1} \tag{44}$$

The factor in front of k^2 in eq 44 arises from the fact that k is normalized in eqs 42–44 relative to the correlation length $q_c(T_f)$ at the final state.

The second modification involves the specification of $B(k)$ in eq 42. Since the final two-phase equilibrium state at T_f is not accessible, the procedure followed above to determine $B(k)$ by requiring $I(k,t\to\infty) = I_{eq}(k,T_f)$ cannot be used. We therefore assume here (other alternatives are possible) that the temperature difference $T_f - T_i$ is sufficiently small so that $B(k,T_f) \cong B(k,T_i)$.[4,12] The latter is given by eq 31 in terms of the initial equilibrium intensity $I_{eq}(q,T_i)$ before the normalization of the variables. With the scaled variable used in eqs 42–44, we obtain $B(k)$ to be used in eq 42 as

$$B(k) \cong \frac{k^2}{\chi(T_f) - \chi_s} \frac{\Lambda(k,T_i)}{\Lambda(k,T_f)}[1 + Z_{eq}(k,T_i)] \qquad (45)$$

where the factor $\Lambda(k,T_i)/\Lambda(k,T_f)$ arises from the scaling of the variables. The $Z_{eq}(k,T_i)$ in eq 45 is given by

$$Z_{eq}(k,T_i) = \frac{3\sqrt{3}}{\pi^2} \frac{v_0}{\chi_s R_g^{\ 3}}[1 - \chi(T_i)/\chi_s]^{-1/2}\left[1 + \frac{\chi(T_f) - \chi_s}{\chi_s - \chi(T_i)}k^2\right]^{-1} \times \left\{\left(1 + \frac{R_g^{\ 2} q_c^{\ 2}(T_i)}{3}k^2\right)(\alpha - \tan^{-1}\alpha) + \frac{R_g^{\ 2} q_c^{\ 2}(T_i)}{3}\left(\tan^{-1}\alpha + \frac{\alpha^3}{3} - \alpha\right)\right\} \qquad (46)$$

where $q_c^{\ 2}(T_i) = (3/R_g^{\ 2})[1 - \chi(T_i)/\chi_s]$. The input parameters needed for numerical calculations in the case of spinodal decomposition are $\chi(T_i)$, $\chi(T_f)$, $\chi(T_s)$, v_0, and R_g. Again, the parameter $\alpha = q_{cut}/q_c(T_f)$ is to be adjusted around unity.

The scaled equations (38) and (42) have been integrated numerically[4] to obtain the variation of the intensity $I(k,\tau)$ during a complete cycle starting from a temperature T_i, jumping to T_f and allowing spinodal decomposition for a period of time, and then dropping it back to T_i, as well as during transients following step temperature changes within the one-phase region. The results have been reported elsewhere.[4,5] In the following sections we present the analytical derivation of the scaling behavior of the intensity during these transients which have been observed in these numerical calculations.

Scaling during Spinodal Decomposition

It is suspected that[16–19] the behavior of the intensity $I(k,\tau)$ during spinodal decomposition may be scaled (in three dimensions) as

$$I(k,\tau) = k_m^{\ -3}(\tau) f\left(\frac{k}{k_m(\tau)}\right) \qquad (47)$$

for k values about its peak occurring at $k_m(\tau)$ as $\tau \to \infty$, where the scale function $f(x)$ is such that $f'(1) = 0$ by its construction. $k_m(\tau)$ is a decreasing function of time accounting for the coarsening due to phase separation. In this section we attempt to determine the asymptotic time dependence of $k_m(\tau)$ as $\tau \to \infty$ and to estimate the shape of $f(x)$ as a function of its argument.

Since this behavior is expected to prevail in the k regions and time intervals where the contribution of the thermal fluctuations to the intensity is not significant, we start with eq 42 without $B(k)$. The latter is important in the very early stages of spinodal decomposition in which the coarsening has not yet been developed or during the approach to the final equilibrium state. We rewrite eq 42 without $B(q)$ as

$$\frac{d \ln I(k,\tau)}{d\tau} = 2k^2\left[1 - k^2 - C\int_0^{\alpha} dx\, x^2[1 + D(k^2 + x^2)]I(x,\tau)\right] \qquad (48)$$

where the constants C and D are

$$C = \frac{6\sqrt{3}}{\pi^2} \frac{v_0}{R_g^{\ 3}}(\chi/\chi_s - 1)^{1/2} \qquad (49a)$$

$$D = \frac{q_c^{\ 2} R_g^{\ 2}}{3} = \frac{\chi - \chi_s}{\chi_s} \qquad (49b)$$

We point out that the expression of q_c used in eq 49b is taken from eq 33, which was obtained by using the small-q limit of $S(q)$ in eq A.2 and therefore contains inherently the restriction $(q_c R_g)^2 < 1$, which in turn imposes a restriction on the interaction parameter as $\chi < 2\chi_s$. Substituting eq 47 into eq 48, evaluating the resulting equation at $k = k_m(\tau)$, and using $f'(1) = 0$, one obtains

$$\frac{3}{4}\frac{d}{d\tau}\left(\frac{1}{k_m^{\ 2}(\tau)}\right) = 1 - k_m^{\ 2}(\tau) - C\int_0^{\alpha/k_m(\tau)} dy\, y^2 f(y)[1 + Dk_m^{\ 2}(\tau)(1 + y^2)] \qquad (50)$$

which is an equation for $k_m(\tau)$. Since the latter is a decreasing function of time, the right-hand side of this equation must be positive and should approach zero asymptotically as $\tau \to \infty$ so that $dk_m(\tau)/d\tau$ also vanish in this limit together with $k_m(\tau)$. When used in eq 50, this requirement leads to

$$C\int_0^{\infty} dy\, y^2 f(y) = 1 \qquad (51)$$

which specifies the magnitude of $f(y)$, for example $f(1)$, in terms of C. Substituting eq 51 into eq 50 yields

$$\frac{3}{4}\frac{d}{d\tau}\left(\frac{1}{k_m^{\ 2}(\tau)}\right) = C\int_{\alpha/k_m(\tau)}^{\infty} dy\, y^2 f(y) - k_m^{\ 2}(\tau)\left\{1 + CD\int_0^{\alpha/k_m(\tau)} dy\, y^2 f(y)[1 + y^2]\right\} \qquad (52)$$

The asymptotic behavior of $k_m(\tau)$ is determined by the leading term in the expansion of the right-hand side of eq 52 in powers of $k_m(\tau)$. Since the second term is always negative, the first term, which is positive, must vanish with the first power of $k_m(\tau)$. The asymptotic behavior of the integral in the first term in powers of $k_m(\tau)$, on the other hand, depends on the limiting behavior of $f(y)$ as $y \to \infty$. We assume that $f(y) \to a_0/y^n$ as $y \to \infty$. Then, using

$$\lim_{x\to\infty}\int_x^{\infty} dy\, y^2 f(y) = \frac{a_0}{n - 3}x^{3-n}, \qquad n > 3$$

we find that the first term behaves as $a_0 k_m(\tau)/\alpha$ when $n = 4$ and as $a_0[k_m(\tau)/\alpha]^3/3$ when $n = 6$. Since in the latter case the second term on the right-hand side of eq 52, which is negative, becomes the leading term, we conclude that only $n = 4$ is permitted; i.e., $f(y) \to a_0/y^4$ as $y \to \infty$ has been established. The behavior of $f(y)$ for small arguments can be obtained, somewhat crudely, from eq 48 by evaluating its right-hand side in the small-k limit and casting it into the following form:

$$I(k,\tau) \to I_{eq}(0)\left\{1 + 2k^2\int_0^{\tau} d\tau'\left[1 - C\int_0^{\alpha} dx\, x^2(1 + Dx^2)I(x,\tau')\right]\right\}$$

where $I_{eq}(k)$ is the initial equilibrium intensity. Since the noise term is not included in eq 48, this result is valid for large values of τ for which the second term on the right-hand side exceeds one. Thus, there is a range of values of k and τ in which $I(k,\tau)$ is proportional to k^2 for fixed τ. This conclusion implies that $f(y)$ must behave as y^2 for $y \ll 1$. By interpolating $f(y)$ between the above small and large argument limits, we obtain the following closed but approximate form for $f(y)$:

$$f(y) = f(1)\frac{3y^2}{2 + y^6} \tag{53}$$

which satisfies $f'(1) = 0$, and $a_0 = 3f(1)$. The magnitude $f(1)$ is obtained from the condition in eq 51 using[20]

$$\int_0^\infty \mathrm{d}y \frac{y^4}{2 + y^6} = \frac{1}{2^{1/6}}\frac{\pi}{3} \cong 0.933$$

as $f(1) = 0.357/C$, in which C is given in eq 49a. Clearly, $f(1)$ depends on the interaction parameters χ and χ_s and on the final temperature through χ.

Having determined the form of the shape function of $f(y)$, we return to eq 52 to obtain the asymptotic behavior of $k_m(\tau)$. We note that eq 52 can be regarded as an integral equation for $k_m(\tau)$ once $f(y)$ is specified and can be solved numerically. We use it only asymptotically for large times. Expanding both the first and second terms in powers of $k_m(\tau)$ in eq 52, we find

$$\frac{3}{4}\frac{\mathrm{d}}{\mathrm{d}\tau}\left(\frac{1}{k_m^{\,2}(\tau)}\right) = a_0 C k_m(\tau)(1 - \alpha^2 D)/\alpha + o(k_m^{\,2}) \tag{54}$$

which leads to the following $\tau^{-1/3}$ power law for $k_m(\tau)$:

$$k_m^{\,3}(\tau) \rightarrow \frac{\alpha}{2a_0 C(1 - \alpha^2 D)}\frac{1}{\tau} \tag{55a}$$

Substituting $a_0 = 3f(1)$ and using the numerical value of $f(1)C$, obtained above, we arrive at

$$k_m^{\,3}(\tau) \rightarrow 0.518\left(\frac{\alpha}{1 - \alpha^2 D}\right)\frac{1}{\tau} \tag{55b}$$

This result was verified by a numerical integration of eq 42 with $\alpha = 1$ and $\chi = 1.1\chi_s$.[4] In eq 55b, $\alpha^2 D = (q_{\mathrm{cut}}R_g)^2/3$ (cf. eq 49b). Since we have been carrying out the derivations in the small-q limit, $(q_{\mathrm{cut}}R_g)^2 \ll 1$ must be used to be consistent, so that eq 55b can be simplified as $k_m(\tau)^3 \rightarrow 0.518\alpha/\tau$. It is interesting to note that the prefactor in this power law depends on $\alpha = q_{\mathrm{cut}}/q_c$, which is an adjustable parameter in the theory. In a log–log representation eq 55b reads $\ln k_m(\tau) = -0.219 + (1/3) \ln \alpha - (1/3) \ln \tau$. Hence, one can estimate the value of α in principle by presenting the experimental values of $k_m(\tau)$ also in a log–log plane, provided the intensity is measured in time intervals where the scaling behavior prevails. The numerical integration showed[4] that the $\tau^{-1/3}$ power law is reached very slowly only for $\tau \geq 512$. It may not be possible to reach this region experimentally.

The right-hand side of eq 48 is the instantaneous relaxation frequency $\Omega(k,\tau)$ in dimensionless units which was introduced in eq 28. Since the above derivation crucially depended on the asymptotic behavior of $\Omega(k,\tau)$, we present the results of the numerical integration showing its variation with k and τ in Figure 1. The curves in the figure were obtained for a quench corresponding to a change in the interaction parameter from $\chi_{\mathrm{in}} = 0.95\chi_s$ to $\chi_f = 1.1\chi_s$, with $\alpha = 1$. These inputs are chosen just for illustration purposes and have no physical significance. In the linear theory, $\Omega(k,\tau)/k^2 = 1 - k^2$ and is independent of time. In this case, the modes for which $k < 1$ are unstable. In the nonlinear theory, as depicted in Figure 1, the growth rate decreases with time, and at the same time the range of k values corresponding to the unstable modes shrinks to zero asymptotically. There is a slight change in the curvature and the overall slope of the curves.

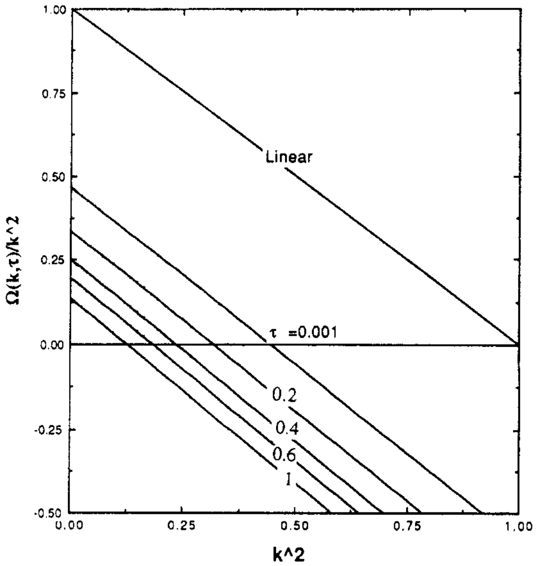

Figure 1. Variation of the instantaneous relaxation frequency with the normalized wavenumber (k) during spinodal decomposition at different normalized times (τ) following a quench.

Two remarks on the scaling properties of $I(k,\tau)$ during spinodal decomposition are to be made at this stage: The first is that the form of the scaling function in eq 53 is proposed in the literature[16-19] for strongly off-critical quenches (cluster regime), but yet it is obtained here for a symmetrical mixture with $\Phi_0 = 0.5$. The second is that the peak position $k_m(\tau)$ of the intensity is found in this paper to shift to smaller values of k according to the power law $k_m(\tau) \rightarrow \tau^{-1/3}$, which also corresponds to growth of the radius of spherical grains in the A-rich phase on the background of the B-phase. This power law differs from $k_m(\tau) \sim \tau^{-1/4}$ obtained by Binder,[21] even though both derivations are essentially based on the Langer–Baron–Miller theory.[1] The $\tau^{-1/3}$ behavior obtained in this paper has been verified[4] by a numerical integration of eq 42 as stated earlier.

An alternative and more detailed derivation of the power law $k_m(\tau) \rightarrow \tau^{-1/3}$, which describes the approach of $I(k,\tau)$ to its scaling form, is presented in Appendix C.

Power-Law Behavior during Dissolution

Variation of $k_m(\tau)$ during dissolution processes also may display a power-law behavior in a limited time interval following a reverse quench from an initial temperature in the two-phase region to one within the one-phase region. Relaxation of $I(k,\tau)$ from the initial intensity $I_{\mathrm{in}}(k)$ to the equilibrium intensity $I_{\mathrm{eq}}(k)$ at the final temperature is described by eq 29b, which we reproduce here in normalized variables introduced in eq 38:

$$I(k,\tau) = I_{\mathrm{in}}(k) \exp[-2\int_0^\tau \mathrm{d}\tau' \, \Omega(k,\tau')] + B(k)\int_0^\tau \mathrm{d}\tau' \exp[-2\int_0^u \mathrm{d}t' \, \Omega(k,\tau-\tau')] \tag{56}$$

where $\Omega(k,\tau) = k^2(1 + k^2)[1 + Z(k,\tau)]$ and $Z(k,t)$ is defined in eq 41. In a reverse quench experiment, the initial intensity $I_{\mathrm{in}}(k)$ is prepared by spinodal decomposition by allowing the system to phase separate sufficiently at the initial temperature in the two-phase region, so that the scaling behavior is attained. Hence, $I_{\mathrm{in}}(k) = k_m^{-3}f(1)3y^2/(2 + y^6)$, where $y = k/k_m$. The first term in eq 56 represents the dissolution of the inhomogeneities characterized by the initial peak at k_m, and the second term accounts for the contribution of density fluctuations in the final equilibrium state. The intensity $I(k,\tau)$ after the quench displays a peak at $k_m(\tau)$ which, as we see presently, decreases with time starting from $k_m(0) = k_m$. Its time dependence can be obtained by differentiating eq 56 with respect to k (more conveniently, with respect to k^2), evaluating the resulting equation at $k = k_m(\tau)$, and using $\mathrm{d}I(k,\tau)/\mathrm{d}k^2 = 0$ at $k = k_m(\tau)$. A power-law behavior in $k_m(\tau)$ occurs in the early stages of dissolution in which the effect of thermal fluctuations represented by the second term in eq 56 is not yet important in the vicinity of $k_m(\tau)$. Ignoring this term, we find

$$\left.\frac{\mathrm{d}\ln I_{\mathrm{in}}(k)}{\mathrm{d}k^2}\right|_{k=k_m(\tau)} = 2\frac{\mathrm{d}}{\mathrm{d}k^2}\{k^2(1+k^2)[\tau + \int_0^\tau \mathrm{d}\tau'\, Z(k,\tau')]\}_{k=k_m(\tau)}$$

We evaluate this equation in the limit of $\tau \to \infty$ and $k_m(\tau) \to 0$. Since $I(k,\tau)$ must vanish in this limit when the effect of the thermal fluctuations are not present, $Z(k,\tau\to\infty) = 0$ for large times. Hence, we obtain

$$\left.\frac{\mathrm{d}\ln I_{\mathrm{in}}(k)}{\mathrm{d}k^2}\right|_{k=k_m(\tau)} = 2\tau \tag{57}$$

The crucial quantity in eq 57 that dictates the asymptotic behavior of $k_m(\tau)$ is the variation of $\ln I_{\mathrm{in}}(k)$ with k, which depends on the preparation of the initial state, as we pointed out earlier. Using its scaled form given above, we find $\mathrm{d}\ln I_{\mathrm{in}}(k)/\mathrm{d}k^2|_{k=k_m(\tau)} = k_m(\tau)^{-2}$ in the limit of $k_m(\tau) \to 0$. Substitution of this result into eq 57 yields

$$k_m(\tau)^2 \to 1/(2\tau) \tag{58}$$

This $\tau^{-0.5}$ dependence has been obtained by numerical integration of eq 38[4] for a reverse quench from $\chi = 1.1\chi_s$ to $\chi = 0.95\chi_s$ with $\alpha = 1$ and verified experimentally by Han and his collaborators.[5]

It is important to note that the derivation of the above power law crucially depends on the behavior of the initial intensity as a function of k in the small-k region. Had the initial intensity been prepared differently, instead of by spinodal decomposition, then $k_m(t)$ could conceivably display a different time dependence. The power-law behavior will be reached in a k-region and a time interval in which the first term in eq 56 remains much larger than the second term. Since only the thermal fluctuations contribute to the scattering intensity in the final homogeneous equilibrium state, the intensity $I(k,\tau)$ should eventually deviate from the power-law behavior after the dissolution of the initial inhomogeneities. Therefore, the time interval in which the power-law behavior may be observed depends on the extent of the phase separation by spinodal decomposition prior to the reverse quench.

Power-Law Behavior in Transients within the One-Phase Region

Numerical integration of eq 38 shows that the intensity $I(k,\tau)$ passes through a peak at $k_m(\tau)$ as a function of k also during the transients following step temperature jumps toward the spinodal line within the one-phase region.[4] This peak has been observed also experimentally by Schwahn et al.[22] The location of the peak moves in time toward smaller wavenumbers, as in the case of spinodal decomposition. More interestingly, $k_m = k_m(\tau)$ seems to approach asymptotically also to a $\tau^{-1/3}$ power law. In this section, we investigate analytically how such a power law may arise in the solution of eq 38.

The intensity $I(k,\tau)$ in such an experiment grows asymptotically from the initial equilibrium intensity $I_{\mathrm{eq}}(k,\chi_{\mathrm{in}})$ corresponding to an interaction parameter χ_{in} to $I_{\mathrm{eq}}(k,\chi_f)$ in the final equilibrium state corresponding to an interaction parameter $\chi_f > \chi_{\mathrm{in}}$. Since the $I(k,\tau)$ saturates toward $I_{\mathrm{eq}}(k,\chi_f)$ as $\tau \to \infty$, we expect $I(k_m,\tau) = I_{\mathrm{eq}}(k_m,\chi_f)$ to hold asymptotically. We henceforth drop χ_f in the argument of $I_{\mathrm{eq}}(k,\chi_f)$. Using $\mathrm{d}I_{\mathrm{eq}}(k_m)/\mathrm{d}\tau = I_{\mathrm{eq}}(k_m)'\mathrm{d}k_m(\tau)^2/\mathrm{d}\tau$, where $I_{\mathrm{eq}}(k)' = \mathrm{d}I_{\mathrm{eq}}(k)/\mathrm{d}k^2$, and $\mathrm{d}I(k_m,\tau)/\mathrm{d}\tau = \partial I(k_m,\tau)/\partial\tau$ because $\partial I(k,\tau)/\partial k^2 = 0$ at $k = k_m(\tau)$, we obtain from eq 38

$$I'_{\mathrm{eq}}(k_m)\frac{\mathrm{d}k_m^{\ 2}}{\mathrm{d}\tau} = -2r(k_m)\{[1 + Z(k_m,\tau)]I(k_m,\tau) - [1 + Z_{\mathrm{eq}}(k_m)]I_{\mathrm{eq}}(k_m)\}$$

Evaluating this equation in the limit of $k_m \to 0$ and $\tau \to \infty$ and using $I(k_m,\tau) = I_{\mathrm{eq}}(k_m)$ and $I_{\mathrm{eq}}(k_m)'/I_{\mathrm{eq}}(k_m) \to -1$ in this limit, we find

$$\mathrm{d}k_m/\mathrm{d}\tau = k_m[Z(k_m,\tau) - Z_{\mathrm{eq}}(k_m)] \tag{59}$$

The question now is to determine how the right-hand side of eq 59 vanishes as $k_m \to 0$ and $\tau \to \infty$. Substitution of $Z(k_m,\tau)$ from eq 41 into eq 59 yields in the limit of $k_m \to 0$

$$\mathrm{d}k_m/\mathrm{d}\tau = k_m C\int_0^\alpha \mathrm{d}x\, x^2[1 + D(k_m^{\ 2} + x^2)][I(x,\tau) - I_{\mathrm{eq}}(x)]$$

where C and D are defined in eqs 49. Since the modes for which $k > k_m(\tau)$ relax to their equilibrium values faster than the long-wavelength modes, we let $I(x,\tau) - I_{\mathrm{eq}}(x) \cong 0$ for $x > k_m(\tau)$ and replace the upper limit of the integral by $k_m(\tau)$. Finally, we use $I(0,\tau) = I_{\mathrm{eq}}(0,\chi_i)$ because the $k = 0$ modes do not grow and obtain $\mathrm{d}k_m(\tau)/\mathrm{d}\tau = -\Delta C k_m^4(\tau)/3$, which leads to the $\tau^{-1/3}$ power law for $k_m(\tau)$:

$$k_m^{\ 3}(\tau) \to 1/\Delta C\tau \tag{60}$$

where $\Delta = I_{\mathrm{eq}}(0,\chi_f) - I_{\mathrm{eq}}(0,\chi_i)$. The above derivation is meant to be an analytical explanation of the $\tau^{-1/3}$ power law observed in the numerical results rather than to be a rigorous mathematical proof. It demonstrates that, as in the case of spinodal decomposition, the power-law behavior in eq 60 is a consequence of the mode coupling arising from nonlinearity. Both the appearance and its time dependence of the peak are somewhat surprising because there is no coarsening during the transition from an initial equilibrium intensity to one closer to the spinodal. The change in the intensity during transients is due to both the increase in the magnitude of the thermal fluctuations and in the correlation length. The latter may be interpreted as a "coarsening" in a statistical sense, in which the size of the correlated domains increases in time.

Effect of Nonlinearities on the Dynamic Scattering Function in Equilibrium

The dynamic scattering function, $S_D(q,t)$, in an equilibrium state can also be calculated within the above mathematical framework starting from eq 14c using the same approximations as the ones introduced in the calculation of the intensity. Defining $S_D(q,t) = \langle\varphi_q(t)\varphi_{-q}(0)\rangle_{\mathrm{eq}}/Vv_0$ so that $S_D(q,0) = I_{\mathrm{eq}}(q)$, we obtain from eq 14c

$$\frac{\partial}{\partial t}S_D(q,t) = \frac{1}{Vv_0}\langle A(\{\Phi(t)\})\varphi_{-q}(0)\rangle_{\mathrm{eq}}, \quad t \geq 0$$

The right-hand side of this equation can be approximated using the truncation and Gaussian approximation introduced in eq 24. The result is

$$\frac{\partial}{\partial t}S_D(q,t) = -\Omega(q)S_D(q,t) \tag{61a}$$

where

$$\Omega(q) = q^2\frac{\Lambda(q)}{S(q)}[1 + Z_{\mathrm{eq}}(q)] \qquad (61b)$$

in which $Z_{\mathrm{eq}}(q)$ is defined in eq 32 and calculated explicitly in eq 34. It is observed that $S_{\mathrm{D}}(q,t)$ relaxes exponentially as in the case of the linear theory as $S_{\mathrm{D}}(q,t) = \exp[-\Omega(q)t]S(q)$, but its relaxation rate is modified by the factor $[1 + Z_{\mathrm{eq}}(q)]$. The latter represents the effect of mode coupling arising from the nonlinear nature of the relaxation process. This result shows that the linear theory is not valid even asymptotically unless $Z_{\mathrm{eq}}(q) \ll 1$ in the final state. The effect of nonlinearity is therefore expected to be appreciable when the final state is near the spinodal point, where the magnitude of the thermal density fluctuations is enhanced.

Discussion and Conclusions

In this paper we first briefly summarized various methods to investigate fluctuations in macrovariables in nonlinear systems in general and in interacting binary polymer mixtures in particular, with special attention to the interpretation of the fluctuation–dissipation theorem, or the generalized Einstein relation, in the presence of nonlinearities. We have pointed out that all these methods are mathematically equivalent and are based on the assumption that the fluctuations in the macrovariables, e.g., in the order parameter, can be treated as a Markov process. We have shown that when the power spectral density $B(q)$ of the random force appearing in the nonlinear equation describing the temporal behavior of the intensity during transients is determined from the generalized Einstein relation, consistently using the truncation and Gaussian approximation introduced to obtain this equation, $B(q)$ is renormalized as $B(q) = 2q^2\Lambda(q)[1 + Z_{\mathrm{eq}}(q)]$, where $Z_{\mathrm{eq}}(q)$ represents the effect of coupling of density modes. With this expression of $B(q)$, the intensity approaches asymptotically to the static structure factor in the final equilibrium state, without requiring renormalization of the relaxation rate.[3]

We then investigated analytically the scaling properties of the intensity during transients in a symmetrical binary polymer mixture. We have shown that the intensity during spinodal decomposition is approximately scaled as $I(k,\tau) \sim k_{\mathrm{m}}(\tau)^{-3}y^2/(2 + y^6)$, where $y = k/k_{\mathrm{m}}(\tau)$, and calculated the proportionality constant explicitly in terms of the interaction parameters. The extended derivation in Appendix C sheds light also on how this scaling behavior is approached as $\tau \rightarrow \infty$. This scaling function is of the same form as the one proposed by Furukawa for strongly off-critical quenches and exhibits "Porod's law", $I(k,\tau) \sim k^{-4}$, in three dimensions for large k values. The peak position $k_{\mathrm{m}}(\tau)$ of the intensity has been found to shift to smaller values of k with a power law $k_{\mathrm{m}}(\tau) \sim \tau^{-1/3}$. Since our theoretical approach is essentially the same as that of Langer, Baron, and Miller (LBM) and contains the same Gaussian approximation, this result shows that the LBM theory is capable of predicting $\tau^{-1/3}$ behavior,[21] which is characteristic to the growth of the radius of spherical grains of an A-rich phase on the background of a B phase. This power law has been obtained also in numerical calculation of the intensity.[4]

We have shown that the peak position $k_{\mathrm{m}}(\tau)$ of the intensity shifts to smaller values of k also during dissolution following a reverse quench. Depending on the conditions of the reverse quench, $k_{\mathrm{m}}(\tau)$ may exhibit a power law $k_{\mathrm{m}}(\tau) \sim \tau^{-1/2}$ in a limited time interval. Such a power-law dependence has been observed experimentally[5] and demonstrated by a numerical calculation of $I(k,\tau)$.[4] These numerical calculations also showed that the peak position of the intensity moves to smaller values of k asymptotically with a power law $k_{\mathrm{m}}(\tau) \sim \tau^{-1/3}$, also during transients following step temperature changes toward the spinodal line. We have provided an analytical derivation to demonstrate the possibility of such a power-law behavior.

Finally, we have calculated, within the same mathematical framework used for the intensity, the dynamic scattering function in an equilibrium state and showed that it is an exponential function of time with a relaxation frequency modified by a factor $[1 + Z_{\mathrm{eq}}(q)]$, which again accounts for the effect of mode coupling.

In this paper we have considered the mode coupling only among the density modes. It is possible to include in the present formulation also the coupling to the hydrodynamic modes.[3] We leave this extension to a future publication.

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Appendix A. Expansion of the Free Energy

Following Binder,[14] we start with the free energy excess for a binary mixture of A and B homopolymers, choosing the unit of energy as $k_{\mathrm{B}}T$:

$$F = \int \mathrm{d}^3r\frac{1}{v_0}\left\{f[\Phi(\mathbf{r})] + \frac{1}{36}\left[\frac{\sigma_{\mathrm{A}}^2}{z_{\mathrm{A}}\Phi(\mathbf{r})} + \frac{\sigma_{\mathrm{B}}^2}{z_{\mathrm{B}}[1 - \Phi(r)]}\right]|\nabla\Phi(\mathbf{r})|^2\right\} \qquad (A1a)$$

where $\Phi(\mathbf{r}) = \Phi_{\mathrm{A}}(\mathbf{r})$, and

$$f(\Phi) = \frac{\Phi}{z_{\mathrm{A}}N_{\mathrm{A}}}\ln\Phi + \frac{1 - \Phi}{z_{\mathrm{B}}N_{\mathrm{B}}}\ln(1 - \Phi) + \chi\Phi(1 - \Phi) \qquad (A1b)$$

In eq A1a, σ_α and N_α denote, respectively, the statistical segment length and the number of monomers in a chain of kind α = A,B. $z_\alpha = v_\alpha/v_0$ denotes the normalized monomeric volumes relative to a reference volume v_0. The quantity χ in eq A1b denotes the Flory interaction parameter. When $v_{\mathrm{A}} = v_{\mathrm{B}} = v_0$ and v_0 is set equal to unity, eqs A1 reduce to eq 2.1 and 2.2 of Binder,[14] which is valid for slow spatial variations. The reference volume v_0 can be chosen[23] as $v_0 = (v_{\mathrm{A}}v_{\mathrm{B}})^{1/2}$. Although the choice of v_0 is arbitrary, this particular one has the advantage that it leads to $z_{\mathrm{A}}z_{\mathrm{B}} = 1$ and thus makes the quantity in the curly bracket a function of the ratio of the segmental volumes only. The coefficient of $|\nabla\Phi(\mathbf{r})|^2$ in eq A1a was chosen by de Gennes[24] in such a way that the above expression for F leads to the small-q limit of the static structure factor $S(q)$:

$$\left.\frac{\delta F}{\delta\Phi(\mathbf{r})}\right|_{\Phi(\mathbf{r})=\Phi_0} = \frac{1}{v_0S(q)}$$

where

$$\frac{1}{S(q)} = 2\left\{\chi_{\mathrm{s}} - \chi + \frac{q^2}{36}\left[\frac{\sigma_{\mathrm{A}}^2}{z_{\mathrm{A}}\Phi_0} + \frac{\sigma_{\mathrm{B}}^2}{z_{\mathrm{B}}(1 - \Phi_0)}\right]\right\} \qquad (A2)$$

in which χ_{s} denotes the value of the interaction parameter on the spinodal:

$$\chi_s = \frac{1}{2}\left[\frac{1}{z_A N_A \Phi_0} + \frac{1}{z_B N_B (1-\Phi_0)}\right] \qquad \text{(A3)}$$

The $S(q)$ is related to the static structure factor in volume fraction through

$$\langle|\varphi_{\mathbf{q}}|^2\rangle = V\upsilon_0 S(q) \qquad \text{(A4a)}$$

The full expression of $S(q)$ in the random phase approximation is

$$\frac{1}{S(q)} = \frac{1}{z_A N_A \Phi_0 f_D(q^2 R_{gA}^2)} + \frac{1}{z_B N_B (1-\Phi_0) f_D(q^2 R_{gB}^2)} - 2\chi \qquad \text{(A4b)}$$

where $f_D(x)$ is the conventional Debye function

$$f_D(x) = \frac{2}{x^2}(x - 1 + e^{-x}) \qquad \text{(A5)}$$

Equation A2 follows from eq A4 by expanding the Debye function as $f_D(x) = 1 - x/3$ for small arguments. It is possible to modify the expression of the free energy, as shown by Akcasu and Sanchez,[25] in such a way that it will reproduce the full expression of $S(q)$ in eq 4 for all wavenumbers:

$$F = \int d^3r \frac{1}{\upsilon_0}\left\{\frac{\ln \Phi_A}{z_A N_A} F_A(\nabla^2)\Phi_A + \frac{\ln \Phi_B}{z_B N_B} F_B(\nabla^2)\Phi_B + \chi\Phi_A\Phi_B\right\} \qquad \text{(A6a)}$$

where $\Phi_A = \Phi(\mathbf{r})$, $\Phi_B = 1 - \phi(\mathbf{r})$, and the operator $F_\alpha(\nabla^2)$ is a function of the Laplacian ∇^2 and defined by

$$F_\alpha(\nabla^2) = \frac{1}{2}\left[1 + \frac{1}{f_D(-R_{g\alpha}^2\nabla^2)}\right] \qquad \text{(A6b)}$$

When the Debye function is approximated by $f_D(x) = 1 - x/3$ in eq A6, the latter reduces to the form of the free energy given in eqs A1. We shall present the expansion of F both in the small-q limit and in its extended form.

The functional derivative of $\delta F/\delta\Phi(\mathbf{r})$ yields the local chemical potential difference:[14]

$$\frac{\delta F}{\delta\Phi(\mathbf{r})} = \frac{1}{\upsilon_0}\left\{\frac{1}{z_A N_A}\left[F_A(\nabla^2)\ln\Phi_A + \frac{1}{\phi_A}F_A(\nabla^2)\Phi_A\right] + \chi(1 - 2\Phi_A) + \frac{1}{z_B N_B}\left[F_B(\nabla^2)\ln\Phi_B + \frac{1}{\phi_B}F_B(\nabla^2)\Phi_B\right]\right\} \qquad \text{(A7a)}$$

In the limit of slow spatial variations, eq A7a reduces to

$$\frac{\delta F}{\delta\Phi(\mathbf{r})} = \frac{1}{\upsilon_0}\left\{\frac{1}{z_A N_A}[1 + \ln\Phi_A] - \frac{1}{z_B N_B}[1 + \ln\Phi_B] + \chi(1 - 2\Phi_A) - \frac{1}{18}\left[\frac{\sigma_A^2}{z_A\Phi_A} + \frac{\sigma_B^2}{z_B\Phi_B}\right]\nabla^2\Phi_A + \frac{1}{36}\left[\frac{\sigma_A^2}{z_A\Phi_A^2} - \frac{\sigma_B^2}{z_B\Phi_B^2}\right]|\nabla\Phi_A|^2\right\} \qquad \text{(A7b)}$$

When $\upsilon_A = \upsilon_B = \upsilon_0$ and υ_0 is set equal to unity, one reproduces eq 2.7 of Binder.[14]

In order to calculate $\delta F/\delta\varphi_{\mathbf{k}}$ as a power series in $\varphi_{\mathbf{k}}$, we let $\Phi(\mathbf{r},t) = \Phi_0 + \varphi(\mathbf{r})$ in eqs A7, expand it in powers of $\varphi(\mathbf{r})$, and then take the Fourier transform of the resulting series. After lengthy but straightforward calculations, one obtains

$$\frac{\delta F}{\delta\varphi_{-\mathbf{q}}} = \frac{1}{\upsilon_0}\left[\frac{1}{S(q)}\varphi_{\mathbf{q}} + \int_{\mathbf{k}_1}\int_{\mathbf{k}_2}\Gamma_2(\mathbf{q},\mathbf{k}_1,\mathbf{k}_2)\delta_{\mathbf{q}-\mathbf{k}_1-\mathbf{k}_2}\varphi_{\mathbf{k}_1}\varphi_{\mathbf{k}_2} + \int_{\mathbf{k}_1}\int_{\mathbf{k}_2}\int_{\mathbf{k}_3}\Gamma_3(\mathbf{q},\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_3)\delta_{\mathbf{q}-\mathbf{k}_1-\mathbf{k}_2-\mathbf{k}_3}\varphi_{\mathbf{k}_1}\varphi_{\mathbf{k}_2}\varphi_{\mathbf{k}_3}\right] \qquad \text{(A8)}$$

where the terms of the order of $\varphi(\mathbf{r})^4$ and higher have been neglected. The vertex function $\Gamma_2(\mathbf{q},\mathbf{k}_1,\mathbf{k}_2)$ in eq A8 is obtained as follows:

$$\Gamma_2(\mathbf{q},\mathbf{k}_1,\mathbf{k}_2) = \frac{1}{z_A N_A}\left[1 - \frac{1}{2}F_A(-q^2) - F_A(-k_2^2)\right] - \frac{1}{z_B N_B}\left[1 - \frac{1}{2}F_B(-q^2) - F_B(-k_2^2)\right] \qquad \text{(A9a)}$$

where the functions $F_\alpha(-q^2)$ are defined in eq A6b. In the small-q limit, eq A9a reduces to

$$\Gamma_2(\mathbf{q},\mathbf{k}_1,\mathbf{k}_2) = U_1 - U_2\frac{1}{2}(q^2 + k_1^2 + k_2^2) \qquad \text{(A9b)}$$

with

$$U_1 = \frac{1}{2}\left[\frac{1}{z_B N_B(1-\Phi_0)^2} - \frac{1}{z_A N_A \Phi_0^2}\right] \qquad \text{(A9c)}$$

$$U_2 = \frac{1}{36}\left[\frac{\sigma_A^2}{z_A\Phi_0^2} - \frac{\sigma_B^2}{z_B(1-\Phi_0)^2}\right] \qquad \text{(A9d)}$$

In obtaining eq A9b, we symmetrized the second term in eq A8 by interchanging $\mathbf{k}_1$ and $\mathbf{k}_2$, adding the resulting equations, and dividing by 2. It is to be noted that $\Gamma_2(\mathbf{q},\mathbf{k}_1,\mathbf{k}_2)$ vanishes in the case of a symmetric mixture in which the molecules of the two species are identical to each other so that $N_A = N_B$, $z_a = z_B$, $\sigma_A = \sigma_B$, and $\upsilon_A = \upsilon_B$ and their volume fractions are equal, i.e., $\Phi_0 = 1/2$.

The vertex function $\Gamma_3(\mathbf{q},\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_3)$ is calculated after symmetrization as

$$\Gamma_3(\mathbf{q},\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_3) = \frac{1}{3z_A N_A \Phi_0^3}\left[-3 + F_A(-q^2) + \sum_{j=1}^{3}F_A(-k_j^2)\right] + \frac{1}{3z_B N_B(1-\Phi_0)^3}\left[-3 + F_B(-q^2) + \sum_{j=1}^{3}F_B(-k_j^2)\right] \qquad \text{(A10a)}$$

Substituting $F_\alpha(-k^2)$ from eq A6b, one can express the above in terms of the Debye function:

$$\Gamma_3(\mathbf{q},\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_3) = -Z_1 + \frac{1}{6z_A N_A \Phi_0^3}\left[f_D^{-1}(q^2 R_{gA}^2) + \sum_{j=1}^{3}f_D^{-1}(k_j^2 R_{gA}^2)\right] + \frac{1}{6z_B N_B(1-\Phi_0)^3}\left[f_D^{-1}(q^2 R_{gB}^2) + \sum_{j=1}^{3}f_D^{-1}(k_j^2 R_{gB}^2)\right] \qquad \text{(A10b)}$$

where Z_1 is given below. In the small-q limit we have

$$\Gamma_3(\mathbf{q},\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_3) = Z_1 + \frac{Z_2}{6}(q^2 + k_1^2 + k_2^2 + k_3^2) \qquad \text{(A10c)}$$

with

$$Z_1 = \frac{1}{3}\left[\frac{1}{z_A N_A \Phi_0^3} + \frac{1}{z_B N_B(1-\Phi_0)^3}\right] \qquad \text{(A10d)}$$

$$Z_2 = \frac{1}{18}\left[\frac{\sigma_A^{\,2}}{z_A\Phi_0^{\,3}} + \frac{\sigma_B^{\,2}}{z_B(1-\Phi_0)^3}\right] \tag{A10e}$$

In eq A8 we terminated the expansion in powers of $\varphi(\mathbf{r})$ after the cubic term. An exact expansion of the chemical potential in q-space in terms of vertex functions was given by Hong and Noolandi.[26]

Appendix B. Relations Involving Functionals

We follow the notations introduced by Fredrickson.[3] The Fourier transform of a function of position $\varphi(\mathbf{r})$ is defined as usual: $\varphi_\mathbf{k} = \int \mathrm{d}\mathbf{r}\, \exp(\mathrm{i}\mathbf{k}\cdot\mathbf{r})\varphi(\mathbf{r})$. Its inverse transform is written as $\varphi(\mathbf{r}) = \int_\mathbf{k} \exp(-\mathrm{i}\mathbf{k}\cdot\mathbf{r})\varphi_\mathbf{k}$, introducing

$$\int_\mathbf{k} = (2\pi)^{-3}\int \mathrm{d}\mathbf{k} \tag{B1}$$

Also introduced is $\delta_{\mathbf{k}-\mathbf{k}'} = (2\pi)^3\delta(\mathbf{k}-\mathbf{k}')$, where $\delta(\mathbf{k}-\mathbf{k}')$ is the conventional Dirac delta function. The functional derivative in k-space is defined as

$$\delta\varphi_\mathbf{k}/\delta\varphi_{\mathbf{k}'} = \delta_{\mathbf{k}-\mathbf{k}'} \tag{B2}$$

which absorbs a factor $(2\pi)^3$. With this definition one has $\delta\varphi(\mathbf{r})/\delta\varphi_\mathbf{k} = \exp(-\mathrm{i}\mathbf{k}\cdot\mathbf{r})$ and $\delta\varphi_\mathbf{k}/\delta\varphi(\mathbf{r}) = \exp(\mathrm{i}\mathbf{k}\cdot\mathbf{r})$. The functional derivative $\delta F/\delta\varphi_\mathbf{k}$, where F is a functional of $\{\varphi_\mathbf{k}\}$, can be calculated as

$$\frac{\delta F}{\delta\varphi_\mathbf{k}} = \int \mathrm{d}\mathbf{r}\, \frac{\delta F}{\delta\varphi(\mathbf{r})}\frac{\delta\varphi(\mathbf{r})}{\delta\varphi_\mathbf{k}} = \int \mathrm{d}\mathbf{r}\, \frac{\delta F}{\delta\varphi(\mathbf{r})}\mathrm{e}^{-\mathrm{i}\mathbf{k}\cdot\mathbf{r}}$$

or

$$\frac{\delta F}{\delta\varphi_{-\mathbf{k}}} = \left[\frac{\delta F}{\delta\varphi(\mathbf{r})}\right]_\mathbf{k} \tag{B3}$$

where the right-hand side is the Fourier transform of the functional derivative of F with respect to $\varphi(\mathbf{r})$. In this relation we have used the same symbol F on both sides even though F on the left is a functional of $\{\varphi_\mathbf{k}\}$, whereas it is a functional of $\{\varphi(\mathbf{r})\}$.

Finally, for a functional $Z(\mathbf{r},\{\Phi\})$, which explicitly depends on position $\mathbf{r}$, one can show by first expressing $Z(\mathbf{r},\{\Phi\})$ as the inverse transform of $Z_\mathbf{k}(\{\Phi\})$ that

$$\int \mathrm{d}\mathbf{r}\, \frac{\delta Z(\mathbf{r},\{\Phi\})}{\delta\varphi(\mathbf{r})} = \int_\mathbf{k} \frac{\delta Z_\mathbf{k}(\{\Phi\})}{\delta\varphi_\mathbf{k}(\mathbf{r})} \tag{B4}$$

Appendix C. An Alternative Derivation of $t^{-1/3}$ Behavior during Spinodal Decomposition

We start with eq 48, in which we set $D = 0$ for simplicity because the presence of this term is not crucial in the derivation:

$$\frac{\mathrm{d}\ln I(k,\tau)}{\mathrm{d}\tau} = 2k^2[1 - k^2 - z(\tau)] \tag{C1a}$$

where

$$z(\tau) \equiv C\int_0^\alpha \mathrm{d}x\, x^2 I(x,\tau) \tag{C1b}$$

We want to construct the asymptotic solution of this equation for $I(k,\tau)$ as $\tau \to \infty$. We let

$$I(k,\tau) = k_\mathrm{m}^{\;-3}(\tau)f(x)\mathrm{e}^{-2k^4\tau} \tag{C2}$$

with $x = k/k_\mathrm{m}(\tau)$ and try to determine the new unknown functions $f(x)$ and $k_\mathrm{m}(\tau)$ asymptotically. The function $k_\mathrm{m}(\tau)$ is not the value of k, at which $I(k,\tau)$ attains its maximum for a given τ, but it approaches to it as $\tau \to \infty$ if we choose $f(x)$ to satisfy $f'(1) = 0$, where $f'(x) = \mathrm{d}f(x)/\mathrm{d}x$. We demonstrate this assertion later.

The form of $I(k,\tau)$ in eq C2 does not yet correspond to "scaling", which we expect $I(k,\tau)$ to approach in the limit of $\tau \to \infty$, keeping x fixed. However, it approaches to it as $\tau \to \infty$. Indeed, we can write eq C2 as

$$I(k,\tau) = k_\mathrm{m}^{\;-3}(\tau)f(x)\mathrm{e}^{-2x^4\tau k_\mathrm{m}^{\,4}(\tau)} \tag{C3}$$

It will be found after we determine the asymptotic behavior of $k_\mathrm{m}(\tau)$ that the following limit is true:

$$\lim_{\tau\to\infty} \tau k_\mathrm{m}^{\;4}(\tau) = 0 \tag{C4}$$

so that eq C3 yields the expected scaling form $I(k,\tau) = k_\mathrm{m}^{-3}(\tau)f(x)$ when $\tau \to \infty$. At this stage the condition in eq C4 requires $k_\mathrm{m}(\tau)$ to vanish faster than $1/\tau^{1/4}$.

Substitution of eq C2 into eq C1 yields

$$-\frac{3}{k_\mathrm{m}(\tau)}\frac{\mathrm{d}k_\mathrm{m}(\tau)}{\mathrm{d}\tau} - \frac{k}{k_\mathrm{m}^{\;2}(\tau)}\frac{\mathrm{d}k_\mathrm{m}(\tau)}{\mathrm{d}\tau}\frac{\mathrm{d}\ln f(x)}{\mathrm{d}x} = 2k^2[1 - z(\tau)] \tag{C5a}$$

where

$$z(\tau) = C\int_0^{\alpha/k_\mathrm{m}(\tau)} \mathrm{d}y\, y^2 f(y)\mathrm{e}^{-2y^4 k_\mathrm{m}^{\,4}(\tau)\tau} \tag{C5b}$$

We note that the term k^4 in eq C1 is canceled by the exponential factor in eq C2 and that the exponential factor reappears in eq C5b. Evaluating eq C5a at $x = 1$, using $f'(1) = 0$, taking the large-τ limit in the integrand of eq 5b, and using eq C4, we obtain

$$\frac{3}{4}\frac{\mathrm{d}}{\mathrm{d}\tau}\left(\frac{1}{k_\mathrm{m}^{\;2}(\tau)}\right) = 1 - C\int_0^{\alpha/k_\mathrm{m}(\tau)} \mathrm{d}y\, y^2 f(y) \tag{C6}$$

which is the same as eq 50 of the main text with $D = 0$ and without the $k_\mathrm{m}(\tau)^2$ term on the right-hand side. The rest of the derivation is the same as described in the text and leads to $k_\mathrm{m}(\tau) \sim \tau^{-1/3}$ so that the condition in eq C4 is satisfied.

The value of k where $I(k,\tau)$ its maximum, denoted by $K_\mathrm{m}(\tau)$, is obtained by differentiating the right-hand side of eq C2 with respect to k and equating to zero:

$$f'\left[\frac{K_\mathrm{m}(\tau)}{k_\mathrm{m}(\tau)}\right] = 8\left[\frac{K_\mathrm{m}(\tau)}{k_\mathrm{m}(\tau)}\right]^3 f\left[\frac{K_\mathrm{m}(\tau)}{k_\mathrm{m}(\tau)}\right]\tau k_\mathrm{m}^{\;4}(\tau)$$

which yields $K_\mathrm{m}(\tau)$ in terms of $k_\mathrm{m}(\tau)$ at each τ. Defining $K_\mathrm{m}(\tau)/k_\mathrm{m}(\tau) = 1 + \epsilon(\tau)$, expanding $f'(1 + \epsilon(\tau))$ in powers of $\epsilon(\tau)$, and using $f'(1) = 0$, one finds that $\epsilon(\tau)$ vanishes as $\tau^{-1/3}$. Hence, we are permitted to interpret $k_\mathrm{m}(\tau)$, asymptotically, as the value of k corresponding to the peak of $I(k,\tau)$.

It is to be noted that the exponential term in eq C2 accounts for the decay of modes with large k, as in the case of the linear theory.

The above derivation also shows how the scaling solution $I(k,\tau) = k_\mathrm{m}^{-3}(\tau)f(x)$ is reached as $\tau \to \infty$, through the exponential factor in eq 3, which approaches in this limit to unity as $\exp[-(\text{constant})2x^4/\tau^{1/3}]$ for a fixed x.

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