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Microscopic Derivation and Extension of the Cahn–Hilliard–Cook Theory in Polymer Blends

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ABSTRACT: A microscopic derivation, based on the linear response theory, of the Cahn–Hilliard–Cook (CHC) expression for the intensity of scattered radiation from binary polymer mixtures during transients following an initial perturbation is presented and compared with the conventional derivation. The microscopic approach leads to a more general expression for the intensity which allows a multicomponent description and nonexponential behavior. It shows that the time dependence of the intensity during the final stages of transients can be expressed quite generally in terms of the normalized dynamic scattering function in the final equilibrium state. An alternative macroscopic derivation based on the Markov assumption and the system-size expansion is also presented to clarify the validity of the inherent approximations in the generalized CHC form. These derivations do not require an incompressibility assumption or a model for the free energy of the mixture. Using a dynamic random phase approximation, an explicit form of the intensity is obtained in the case of an incompressible binary polymer mixture in terms of the interaction parameter. The new expression includes the effect of internal motions of segments on the time behavior of the intensity and extends the conventional theory to higher wavenumbers.

Introduction

The Cahn–Hilliard[1]–Cook[2] (CHC) theory of phase separation for fluids, which has been extended to polymer blends by Pincus[3], de Gennes,[4] and Binder,[5] enables one to investigate the time dependence of the scattered intensity in a scattering experiment on polymer blends, during the transients following an initial perturbation, such as a temperature jump. In the first part of this paper we present a microscopic derivation of the CHC expression for the scattered intensity $I(q,t)$, which elucidates the nature of the approximations inherent in the standard theory and at the same time provides a more general expression for the intensity. In the later part of the paper, we apply the extended form of the theory to a mixture of homopolymers and obtain an expression for $I(q,t)$ that includes the internal chain motions. This part of the paper can be considered as an extended version of the paper by Binder[5] in 1983.

In order to contrast it with the microscopic theory, we first summarize the basic steps and assumptions of the conventional derivation of CHC theory.[5] One considers an incompressible mixture of two polymer species and assumes that the time scales are long enough so that the internal modes have already died out. Since the mixture is assumed to be incompressible, the only slow variable is the volume fraction $\phi(\mathbf{r},t)$ of one of the components. One then adopts the Flory–Huggins expression of the free energy excess for the mixture with the usual square gradient term to account for the interfacial energy density. The local current density appearing in the continuity equation for $\phi(\mathbf{r},t)$ is eliminated in terms of the local chemical potential difference $\mu(\mathbf{r},t)$, postulating a nonlocal linear functional relationship, as an extension of the conventional Onsager relation. The $\mu(\mathbf{r},t)$ is obtained from the free energy by the usual functional differentiation with respect to $\phi(\mathbf{r},t)$. The following nonlinear diffusion equation in Fourier space is obtained:

$$\partial\phi(\mathbf{q},t)/\partial t = -\beta q^2\Lambda(q)\mu(\mathbf{q},t)$$

where $\Lambda(q)$ is the wavelength-dependent Onsager coefficient and β is the inverse temperature. A noise term $\eta(\mathbf{q},t)$ is added[2] to this equation to account for the thermal fluctuations, which are assumed to be a δ-correlated (i.e., white noise) stationary random process with zero mean:

$$\partial\phi(\mathbf{q},t)/\partial t = -\beta q^2\Lambda(q)\mu(\mathbf{q},t) + \eta(\mathbf{q},t)$$

The magnitude of the noise term is determined from the fluctuation–dissipation theorem. This is a nonlinear Langevin equation. The physical content of nonlinear Langevin equations obtained by adding a random force to a deterministic nonlinear equation for the mean values in order to include fluctuations has been questioned by van Kampen[6] in the past two decades. The reason is that a systematic derivation of the Langevin equation in nonlinear systems shows that the statistical properties of the noise depend on all the moments of the dynamical variable,[7] $\phi(\mathbf{q},t)$ in the present case, and the use of fluctuation–dissipation theorem in the phenomenological approach to fix its magnitude becomes questionable. A procedure based on the system size expansion[6] to obtain an appropriate Langevin equation to investigate fluctuations in nonlinear systems has been discussed elsewhere.[7] In Appendix C we present a macroscopic derivation of the CHC theory based on this approach as an alternative to the microscopic derivation. The use of the Langevin equation method in linear systems, however, is standard and not controversial. Linearization is achieved by introducing an incremental volume fraction $\delta\phi(\mathbf{q},t)$ around the mean volume fraction ϕ_0 and expanding $\mu(\mathbf{r},t)$. The scattered intensity (or the time-dependent static structure factor) $I(q,t) = \langle|\delta\phi(\mathbf{q},t)|^2\rangle$ is readily obtained[5] from the linearized diffusion equation as

$$I(q,t) = S_{\mathrm{eq}}(q) + [I_{\mathrm{in}}(q) - S_{\mathrm{eq}}(q)]\exp[-2R(q)t]$$

where $I_{\mathrm{in}}(q)$ is the initial intensity and $S_{\mathrm{eq}}(q)$ is the static structure factor in the final equilibrium state. Here we assume that the system is left in the miscible region after the initial perturbation. The decay constant $R(q)$ is the relaxation frequency of the dynamic structure factor (or the time-displaced correlation function) $S_{\mathrm{D}}(q,t)$, which is also obtained from the linear diffusion equation as

$$S_{\mathrm{D}}(q,t) = S_{\mathrm{eq}}(q)\exp[-R(q)t]$$

The conventional derivation yields $R(q)$ in terms of the q-dependent Onsager coefficient $\Lambda(q)$ but does not provide any expression for the latter. One consequence of the conventional CHC theory is that it predicts a linear decay in time for $\ln[I(q,t) - S_{\mathrm{eq}}(q)]$. Okada and Han[8] interpreted their scattering data from the binary polymer system of polystyrene/poly(vinyl methyl ether) both in one-phase and spinodal regions, fitting a straight line to this quantity. In the latter case both $R(q)$ and $S_{\mathrm{eq}}(q)$ change sign when

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the CHC form is extrapolated into the spinodal region. The nonphysical negative structure factor is referred to as the "virtual" static structure factor and denoted by $S_x(q)$ by Okada and Han.[8]

In the following section we present the microscopic derivation with a very brief summary of the linear response theory, which may not be familiar in the polymer field.

Microscopic Theory

We begin by selecting a set of dynamical variables $\mathbf{a}(\Gamma)$ where Γ is a point in the phase space. These variables are assumed to describe the physical system under consideration with sufficient detail for the class of experiments we perform on it. We assume that when it is unperturbed, the system attains an equilibrium state with a phase space distribution function $\varphi_{eq}(\Gamma)$. The equilibrium averages will be denoted by $\{...\}$. We choose $\{\mathbf{a}(\Gamma)\} = 0$ so that $\mathbf{a}(\Gamma)$ denotes deviations from their equilibrium values. The time evolution of $\mathbf{a}(t;\Gamma)$ is determined by the Liouville equation $\dot{\mathbf{a}} = i\mathcal{L}\mathbf{a}$, where $\mathcal{L}$ is the Liouville operator. Using the projection operator technique, Mori[9] rewrote this equation in the following form:

$$\dot{\mathbf{a}}(t) = i\boldsymbol{\Omega}\mathbf{a}(t) - \int_0^t \mathrm{d}s\ \mathbf{K}(t-s)\mathbf{a}(s) + \mathbf{f}(t) \tag{1}$$

where the frequency matrix $\boldsymbol{\Omega}$ and the memory matrix $\mathbf{K}(t)$ are independent of the initial phase point Γ. Their definitions are not needed at this stage. The dependence of $\mathbf{a}(t;\Gamma)$ and the "noise" term $\mathbf{f}(t;\Gamma)$ on the phase point Γ is suppressed for simplicity of notation. Equation 1 is often referred to as the "generalized Langevin equation" (GLE). Its derivation is straightforward and well documented[9] and need not be repeated here. The noise term $\mathbf{f}(t)$ contains the effect of the initial values of all the remaining variables not included in the set $\mathbf{a}$, as well as the effect of nonlinearities. The following properties of $\mathbf{f}(t)$ are needed in our discussions:

$$\{\mathbf{f}(t)\} = 0 \tag{2}$$

$$\{\mathbf{f}(t)\mathbf{a}^\dagger(0)\} = 0, \qquad t \geq 0 \tag{3}$$

$$\{\mathbf{f}(t)\mathbf{f}^\dagger(0)\} = \mathbf{K}(t)\mathbf{S}_{eq}, \qquad t \geq 0 \tag{4}$$

In these equation $\mathbf{x}^\dagger$ denotes the hermitian conjugate of a vector $\mathbf{x}$. The property (3) implies that $\mathbf{f}(t)$ is orthogonal to $\mathbf{a}$ for all $t \geq 0$, and (4) represents a kind of generalized fluctuation–dissipation theorem. The matrix $\mathbf{S}_{eq}$ is the static structure matrix in the equilibrium state and is defined by

$$\mathbf{S}_{eq} = \{\mathbf{a}\mathbf{a}^\dagger\} \tag{5}$$

The time evolution of $\mathbf{f}(t)$ and hence $\mathbf{K}(t)$ requires the solution of a more complicated dynamical problem than the original Liouville equation, since it involves the projected Liouville operator. Usually, meaningful results are obtained by treating $\mathbf{K}(t)$ approximately. But, such a procedure will not be necessary in the present application of the linear response theory because $\mathbf{K}(t)$ will not appear explicitly in the final expression of the intensity. The frequency matrix $\boldsymbol{\Omega}$ is defined by

$$\boldsymbol{\Omega} = \{\mathbf{a}\mathcal{L}\mathbf{a}^\dagger\}\mathbf{S}_{eq}^{-1} \tag{6}$$

and can often be calculated exactly. The GLE can be solved for $\mathbf{a}(t)$ as

$$\mathbf{a}(t) = \mathbf{L}(t)\mathbf{a}(0) + \int_0^t \mathrm{d}u\ \mathbf{L}(u)\mathbf{f}(t-u) \tag{7}$$

where $\mathbf{L}(t)$ is the inverse Laplace transform of

$$\tilde{\mathbf{L}}(s) = [s\mathbf{I} - i\boldsymbol{\Omega} + \tilde{\mathbf{K}}(s)]^{-1} \tag{8a}$$

Clearly $\mathbf{L}(0) = \mathbf{I}$, and $\mathbf{L}(t)$ is a solution of the GLE without the noise term:

$$\dot{\mathbf{L}}(t) = i\mathbf{L}(t)\boldsymbol{\Omega} - \int_0^t \mathrm{d}u\ \mathbf{L}(u)\mathbf{K}(t-u) \tag{8b}$$

The physical meaning of $\mathbf{L}(t)$ becomes apparent if we multiply the right side of eq 7 by $\mathbf{a}^\dagger(0)$ take the equilibrium average, and use eq 3

$$\mathbf{L}(t) = \mathbf{S}_D(t)\mathbf{S}_{eq}^{-1} \tag{9}$$

where $\mathbf{S}_D(t)$ is the dynamic structure factor defined by

$$\mathbf{S}_D(t) = \{\mathbf{a}(t)\mathbf{a}^\dagger(0)\} \tag{10}$$

Thus, $\mathbf{L}(t)$ is the normalized dynamic structure factor in the equilibrium state.

Equation 7 is exact and describes the instantaneous time dependence of $\mathbf{a}(t)$, both during transients following an initial perturbation and in the equilibrium state. The important feature of this equation is that *it expresses the evolution of* $\mathbf{a}(t)$ *in terms of the normalized dynamic structure factor* $\mathbf{L}(t)$ *in equilibrium, even during transients.* However, its utility depends on the simplicity of the properties of $\mathbf{f}(t)$, some of which are given in eq 2–4. The evolution in time of various moments of $\mathbf{a}(t)$ can be obtained from eq 7, averaging over the initial distribution $\varphi_{in}(\Gamma)$. We denote this average by $\langle...\rangle$ to distinguish it from the equilibrium average $\{...\}$. The initial distribution depends on the preparation of the initial macroscopic state in a given experiment. Often, the mean values of the selected dynamical variables are specified initially, i.e., $\langle\mathbf{a}(0;\Gamma)\rangle = \mathbf{a}_0$. There are many microscopic states consistent with these constraints. A particular choice, due to Mori,[9] is the constrained equilibrium

$$\varphi_{in}(\Gamma) = Z_{in}^{-1}\exp[-\beta(H - k_BT\mathbf{a}^\dagger\mathbf{b})] \tag{11}$$

where H is the system Hamiltonian, and the constant vector $\mathbf{b}$ is chosen such that $\langle\mathbf{a}(0)\rangle = \mathbf{a}_0$. It characterizes the deviation of the initial state from the equilibrium state. The specification of $\varphi_{in}(\Gamma)$ is sufficient to determine the future evolution of the system. It is immaterial how the system is brought to its initial state once $\varphi_{in}(\Gamma)$ is given. This is because the time-dependent phase space distribution function $\varphi_{in}(\Gamma,t)$ of the system is uniquely determined for all $t \geq 0$ by the Liouville equation in terms of $\varphi_{in}(\Gamma)$. The initial distribution can also be calculated, at least in principle, through the Liouville equation if the past history of the external perturbation is known from the preparation of the experiment. As an example, consider a temperature-jump experiment in which the temperature of the system is maintained at T_i for a sufficiently long time and is changed suddenly from T_i to T_f at $t = 0$. In this example

$$\varphi_{in} = Z_{in}^{-1}\exp[-\beta_i H] \tag{12}$$

which is different from the equilibrium distribution φ_{eq} at the new temperature T_f. It can be written in the form of eq 11 by identifying one of the components of $\mathbf{a}$ as $[H(\Gamma) - \{H(\Gamma)\}]$ and the corresponding component of $\mathbf{b}$ as $(\beta_i - \beta_f)$. However, $H(\Gamma)$ need not be included in the set of dynamical variables. The initial values of $\mathbf{a}$ are specified as

$$\mathbf{a}_0 = \{\mathbf{A}(T_i)\} - \{\mathbf{A}(T_f)\} \tag{13}$$

where some of the components may be zero.

When it does not deviate significantly from the final equilibrium state, the initial distribution can be expanded as

$$\varphi_{\mathrm{in}} \cong \varphi_{\mathrm{eq}}(1 + \mathbf{a}^{\dagger}\cdot\mathbf{b}) \tag{14}$$

Using this expansion, Mori[9] showed that the average of $\mathbf{f}(t)$ over the initial distribution is of second order in the deviations from equilibrium measured by $\mathbf{b}$. Indeed, $\langle \mathbf{f}(t) \rangle \cong \{\mathbf{f}(t)\} + \{\mathbf{f}(t)\mathbf{a}^{\dagger}\}\cdot\mathbf{b}$, and both terms vanish by virtue of eq 2 and 3. With this approximation, one obtains the time dependence of the *mean* of $\mathbf{a}(t)$ from eq 7 as

$$\langle \mathbf{a}(t) \rangle \cong \mathbf{L}(t)\mathbf{a}_0 \tag{15}$$

The neglect of $\langle \mathbf{f}(t) \rangle$ in obtaining this result corresponds to "linearization" of the equation of motion of $\langle \mathbf{a}(t) \rangle$.

We now study the time evolution of the second moment matrix, i.e., the intensity, defined by

$$\mathbf{I}(t) = \langle \mathbf{a}(t)\mathbf{a}^{\dagger}(t) \rangle \tag{16}$$

From eq 7 one obtains

$$\mathbf{I}(t) = \mathbf{L}(t)\mathbf{I}_{\mathrm{in}}\mathbf{L}^{\dagger}(t) + \int_0^t \mathrm{d}u\, \mathbf{L}(t-u)\langle \mathbf{f}(u)\mathbf{a}^{\dagger} \rangle \mathbf{L}^{\dagger}(t) + \int_0^t \mathrm{d}u\, \mathbf{L}(t)\langle \mathbf{a}\mathbf{f}^{\dagger}(u) \rangle \mathbf{L}^{\dagger}(t-u) + \int_0^t \mathrm{d}v \int_0^t \mathrm{d}u\, \mathbf{L}(v)\langle \mathbf{f}(t-v)\mathbf{f}^{\dagger}(t-u) \rangle \mathbf{L}^{\dagger}(u) \tag{17}$$

where $\mathbf{I}_{\mathrm{in}} = \langle \mathbf{a}\mathbf{a}^{\dagger} \rangle$ and $\mathbf{a} = \mathbf{a}(0)$. Although $\{\mathbf{f}(s)\mathbf{a}^{\dagger}\} = 0$ for $s \geq 0$, $\langle \mathbf{f}(s)\mathbf{a}^{\dagger} \rangle \neq 0$. Similarly, although $\{\mathbf{f}(t-s)\mathbf{f}^{\dagger}(t-u)\} = \mathbf{K}(u-s)\mathbf{S}_{\mathrm{eq}}$ for $u - s \geq 0$, $\langle \mathbf{f}(t-s)\mathbf{f}^{\dagger}(t-u) \rangle$ does not satisfy such an equality. We now introduce the approximation of replacing the averages over the initial distribution in the last three terms in eq 17 by the equilibrium averages, on the basis of the argument of linearization presented above. We find

$$\mathbf{I}(t) = \mathbf{L}(t)\mathbf{I}_{\mathrm{in}}\mathbf{L}^{\dagger}(t) + \int_0^t \mathrm{d}u \int_0^t \mathrm{d}v\, \mathbf{L}(u) \times [\theta(u-v)\mathbf{K}(u-v)\mathbf{S}_{\mathrm{eq}} + \theta(v-u)\mathbf{S}_{\mathrm{eq}}\mathbf{K}^{\dagger}(v-u)]\mathbf{L}^{\dagger}(v) \tag{18}$$

where we have used the identity

$$\mathbf{K}(-t)\mathbf{S}_{\mathrm{eq}} = \mathbf{S}_{\mathrm{eq}}\mathbf{K}(t)^{\dagger}$$

which can be verified from $\{\mathbf{f}(-t)\mathbf{f}(0)^{\dagger}\} = \{\mathbf{f}(0)\mathbf{f}(t)^{\dagger}\}$, i.e., from the stationarity of equilibrium averages. In eq 18, $\theta(u)$ is the unit step function. From an identity proven by Fox,[10] which we redrive in a different way in Appendix A, eq 18 can be cast into the following form

$$\mathbf{I}(t) = \mathbf{S}_{\mathrm{eq}} + \mathbf{L}(t)(\mathbf{I}_{\mathrm{in}} - \mathbf{S}_{\mathrm{eq}})\mathbf{L}^{\dagger}(t) \tag{19}$$

This equation is the desired generalization of the CHC expression. The main feature of this result is that *the time dependence of the scattered intensity is expressed quite generally in terms of the normalized dynamic scattering function at the final equilibrium state.* Furthermore is derivation does not require the assumptions inherent in the conventional derivation summarized above, such as incompressibility, the use of a nonlocal Onsager relation with a phenomenological q-dependent coefficient, and any reference to a model for the free energy of the mixture.

The remaining task is to investigate the implication of replacing the averages over $\varphi_{\mathrm{in}}(\Gamma)$ by the equilibrium averages. We do this by using the expansion given in eq 14. It is shown in Appendix B that the neglected correction terms (CT) in eq 19 can be grouped as

$$\mathrm{CT} = \mathbf{b}^{\dagger}\cdot\{\mathbf{a}[\mathbf{a}(t)\mathbf{a}^{\dagger}(t) - \mathbf{L}(t)\mathbf{a}\mathbf{a}^{\dagger}\mathbf{L}^{\dagger}(t)]\}_{\mathrm{eq}} + O(|\mathbf{b}|^2) \tag{20}$$

Introducing

$$\mathbf{q}(t) \equiv \mathbf{a}(t) - \mathbf{L}(t)\mathbf{a} = \int_0^t \mathrm{d}u\, \mathbf{L}(t-u)\mathbf{f}(u) \tag{21a}$$

which denotes the deviation from the mean evolution of a particular initial state $\mathbf{a}(\Gamma)$, we express the leading term in eq 20 as

$$\mathrm{CT} = \mathbf{b}^{\dagger}\cdot\{\mathbf{a}[\mathbf{q}(t)\mathbf{q}^{\dagger}(t) + \mathbf{L}(t)\mathbf{a}\mathbf{q}^{\dagger}(t) + \mathbf{q}(t)\mathbf{a}^{\dagger}\mathbf{L}^{\dagger}(t)]\}_{\mathrm{eq}} + O(|\mathbf{b}|^2) \tag{21b}$$

Since the leading term is proportional to $\mathbf{b}$, the neglect of the correction term in eq 19 cannot be justified on the basis of the linearization argument as used by Mori[9] in the calculation of $\langle \mathbf{a}(t) \rangle$. This is expected because the noise term in the linear GLE contains, and hides, the effect of nonlinearities in the evolution of $\mathbf{a}(t)$. The calculation of $\langle \mathbf{a}(t)\mathbf{a}^{\dagger}(t) \rangle$, which is a second-order quantity, keeping track of the nonlinearities in the noise term in the linear Langevin equation is not, in general, the most efficient approach to the problem. The nonlinearities should really be treated explicitly by replacing the set of variables $\{a_j\}$ by an extended set $\{a_j, a_j a_k, ...\}$ containing the products of dynamical variables, as was done by Kawasaki[11] some time ago. The strategies for treating the effect of nonlinearities this way was discussed by Zwanzig[12] in a review article in 1980. Since we are only interested in this paper in obtaining the CHC form, we need not follow this approach. Instead, we try to justify the neclect of the correction term given in eq 21b by a physical argument: We know that $\{\mathbf{q}(t)\mathbf{a}^{\dagger}\} = 0$ at all times (cf. eq 3), which implies that $\mathbf{q}(t)$ and $\mathbf{a}(0)$ are uncorrelated. If we assume that they are also statistically independent, then the leading term in eq 21b vanishes because $\{\mathbf{a}(t)\} = 0$ and $\{\mathbf{q}(t)\} = 0$, and the remaining terms become at least of second order in $|\mathbf{b}|$. This assumption, which is also inherent in the phenomenological derivation of the CHC theory, should be valid for sufficiently long times after the initial perturbation such that the system no longer remembers its initial state, and $\mathbf{q}(t)$ becomes independent of $\mathbf{a}(0)$. It can also be defended if one restricts the selection of the dynamical variables $\mathbf{a}(\Gamma)$ to macrovariables and invokes the Markov assumption. Such a macroscopic derivation of the CHC form is presented in Appendix C for comparison with the microscopic theory. It may be expected that the temporal behavior of the intensity $\mathbf{I}(t)$ immediately after the initial perturbation will depend on the details of the initial state even for small perturbations and cannot be described universally by the normalized dynamic scattering function in the final equilibrium state. In the CHC form, the initial state enters only through the initial intensity $\mathbf{I}_{\mathrm{in}}$ and does not influence the subsequent temporal behavior of $\mathbf{I}(t)$.

Application to Polymer Blends

We consider in this section a binary mixture of two polymer species and choose the density of one of the components in the Fourier space as the dynamical variable:

$$\delta\rho(\mathbf{q}) = \sum_{j=1}^{N_{\mathrm{A}}} \exp(i\mathbf{q}\cdot\mathbf{r}_j) - N_{\mathrm{A}}\delta_{\mathbf{q},0} \tag{22}$$

where N_{A} is the total number of monomers in the component A in the system and $\mathbf{r}_j$ is the position vector of the jth A monomer. All the A monomers are assumed to be identical with identical scattering lengths. The last term in eq 22 represents the uniform density so that $\delta\rho(\mathbf{q},t)$ denotes the fluctuations in the density. It can be dropped whenever $\mathbf{q} \neq 0$.

The A monomers are assumed to be labeled, so that the measured scattered intensity

$$I(q,t) = \langle |\delta\rho(\mathbf{q},t)|^2 \rangle$$

is given, according to eq 19, by

$$I(q,t) = S_{\mathrm{eq}}(q) + [I_{\mathrm{in}}(q) - S_{\mathrm{eq}}(q)]L^2(q,t) \qquad (23)$$

It is assumed that the mixture is left in the miscible region after the initial perturbation. The derivation of this result does not require incompressibility. The remaining task is to calculate the static structure factor $S_{\mathrm{eq}}(q)$ and the normalized dynamic scattering function $L(q,t)$ in the final equilibrium state. The former has already been calculated by de Gennes[13] using the random phase approximation (RPA) in the case of incompressible binary mixtures as

$$\frac{1}{S_{\mathrm{eq}}(q)} = \frac{1}{\phi_{\mathrm{A}}N_{\mathrm{A}}f_{\mathrm{D}}(x_{\mathrm{A}})} + \frac{1}{\phi_{\mathrm{B}}N_{\mathrm{B}}f_{\mathrm{D}}(x_{\mathrm{B}})} - 2\chi \qquad (24)$$

where $x_\alpha = (qR_{\mathrm{g}\alpha})^2$, α = A, B, ϕ_α are the volume fractions with $\phi_{\mathrm{A}} + \phi_{\mathrm{B}} = 1$, χ is the Flory interaction parameter per monomeric volume, N_α and $R_{\mathrm{g}\alpha}$ are the polymerization index and the radius of gyrations of an α-chain, respectively, and $f_{\mathrm{D}}(x)$ is the usual Debye function

$$f_{\mathrm{D}}(x) = \frac{2}{x}\left[1 - \frac{1}{x}(1 - e^{-x})\right] \qquad (25)$$

Here Gaussian statistic is assumed to be valid for a single chain.

The remaining task is the calculation of $L(q,t)$. Although a formal expression for it is available in terms of the memory function $K(q,t)$ and the relaxation frequency $\Omega(q)$ (cf. eq 8) within the frame work of the linear response theory, it is more easily obtained using the the dynamic version of the RPA.[14] It proves convenient to work in the Laplace domain and to introduce to a generalized q- and ω-dependent diffusion coefficient $D(q,s)$ through

$$\tilde{L}(q,s) = [s + q^2D(q,s)]^{-1} \qquad (26)$$

where $\tilde{L}(q,s)$ is the Laplace transform of $L(q,t)$. The microscopic definition of $D(q,s)$ can be obtained by comparing eq 8 and 26. Using the RPA, Akcasu et al.[14] have shown that $D(q,s)$ can be expressed in terms of the corresponding q- and ω-dependent diffusion coefficients of single chains as

$$D(q,s)^{-1} = S_{\mathrm{eq}}(q)\{[\phi_{\mathrm{A}}N_{\mathrm{A}}f_{\mathrm{D}}(x_{\mathrm{A}})D_{\mathrm{A}}(q,s)]^{-1} + [\phi_{\mathrm{B}}N_{\mathrm{B}}f_{\mathrm{D}}(x_{\mathrm{B}})D_{\mathrm{B}}(q,s)]^{-1}\} \qquad (27)$$

The $D_\alpha(q,s)$ are related to the single-chain dynamic scattering functions $S_{\mathrm{D}\alpha}(q,t)$ by

$$S_{\mathrm{D}\alpha}(q,s) = \frac{N_\alpha{}^2f_{\mathrm{D}}(x_\alpha)}{s + q^2D_\alpha(q,s)} \qquad (28)$$

For simplicity in notation, we consider from now on only the case of completely identical chains, i.e., $N_{\mathrm{A}} = N_{\mathrm{B}} = N$, $R_{\mathrm{gA}} = R_{\mathrm{gB}} = R_{\mathrm{g}}$ and $D_{\mathrm{A}}(q,s) = D_{\mathrm{B}}(q,s) = D_0(q,s)$, so that eq 27 simplifies to

$$D(q,s) = \frac{\chi_{\mathrm{c}}(q) - \chi}{\chi_{\mathrm{c}}(q)}D_0(q,s) \qquad (29)$$

where

$$\chi_{\mathrm{c}}(q) = \frac{1}{2}[\phi_0(1 - \phi_0)Nf_{\mathrm{D}}(x)]^{-1} \qquad (30)$$

The problem of calculating $L(q,t)$ has now been reduced to modeling the single-chain dynamic scattering function $S_{\mathrm{D}}(q,t)$. A common procedure has been to adopt the Rouse dynamics[3-5] by which $S_{\mathrm{D}}(q,t)$ is rigorously calculable.[15-17] Since the relationship between $D(q,s)$ and $D_0(q,s)$ in eq 29 is in the Laplace domain, obtaining $L(q,t)$ by first finding the Laplace transform of the exact expression of $S_{\mathrm{D}}(q,t)$ to obtain $D_0(q,s)$ from eq 28 and then obtaining $D(q,s)$ from eq 29 to calculate $L(q,t)$ from eq 26 by taking the inverse Laplace transform are impossible analytically, although this may be feasible numerically. Therefore we resort to simplified descriptions of $S_{\mathrm{D}}(q,t)$ in order to proceed further analytically. In the Markov limit is $t \to \infty$, $q \to 0$ but q^2t fixed, $S_{\mathrm{D}}(q,t)$ is an exponential function of time so that D_0 is independent of q and s. Hence, $L(q,t)$ is also exponential: $L(q,t) = \exp[-R(q)t]$ where the relaxation frequency $R(q)$ follows from eq 26 and 29 as

$$R(q) = q^2\frac{\chi_{\mathrm{c}}(q) - \chi}{\chi_{\mathrm{c}}(q)}D_0 \qquad (31)$$

where D_0 is the translational diffusion coefficient of a single chain in the mixture. It can be written as $D_0 = k_{\mathrm{B}}T/\xi N$, where ξ is the segmental friction coefficient appearing in Rouse dynamics, and should be appropriate to the mixture. The above result is identical with that given by Binder[5] except for an undefined factor c which is claimed to be of the order of unity.

A more detailed description of $S_{\mathrm{D}}(q,t)$ is to represent it as a superposition of two exponentials as

$$N^{-2}S_{\mathrm{D}}(q,t) \cong a_1e^{-\lambda_1(q)t} + a_2e^{-\lambda_2(q)t} \qquad (32)$$

and to determine the parameters a_1, a_2, λ_1, and λ_2 from the exact limits of $S_{\mathrm{D}}(q,t)$:

$$N^{-2}S_{\mathrm{D}}(q,0) = f_{\mathrm{D}}(x)$$

$$\Omega \equiv -\frac{\mathrm{d}}{\mathrm{d}t}\ln S_{\mathrm{D}}(q,t)|_{t=0} = q^2\frac{D_0}{f_{\mathrm{D}}(x)} \qquad \text{(first cumulant)}$$

$$N^{-2}S_{\mathrm{D}}(q,t\to\infty) = P_0(x)e^{-q^2D_0t} \qquad (33a)$$

where

$$P_0(x) = \frac{\pi}{x}\left[\mathrm{erf}\left(\frac{x^{1/2}}{2}\right)\right]^2e^{-x/6} \qquad (33b)$$

$$x = q^2R_{\mathrm{g}}{}^2$$

and where erf (x) is the usual error function.[18] The limit in eq 33 denotes the large time limit for a given q and is different from the Markov limit mentioned above.[19] The parameters in eq 32 are found to be a $a_1 = P_0$, $a_2 = (f_{\mathrm{D}} - P_0)$, $\lambda_1 = \Omega f_{\mathrm{D}}$, and

$$\lambda_2(q) = \Omega f_{\mathrm{D}}(1 - P_0)/(f_{\mathrm{D}} - P_0) \qquad (34)$$

The corresponding normalized scattering function in the interacting system is obtained as

$$L(q,t) = \frac{1}{2}[1 + A(q)]e^{-R_1(q)t} + \frac{1}{2}[1 - A(q)]e^{-R_2(q)t} \qquad (35)$$

where

$$R_1(q) = \frac{\Omega}{2}[\sigma + \eta_{\mathrm{f}} - \Delta]$$

$$R_2(q) = \frac{\Omega}{2}[\sigma + \eta_{\mathrm{f}} + \Delta]$$

which are the roots of the quadratic equation $s^2 + s\Omega(\sigma + \eta_{\mathrm{f}}) + \eta_{\mathrm{f}}\lambda_1\lambda_2 = 0$. The other symbols are

$$A(q) = \frac{\sigma - \eta_{\mathrm{f}}}{\Delta}$$

$$\sigma(q) = P_0(1 - f_{\mathrm{D}})/(f_{\mathrm{D}} - P_0) + f_{\mathrm{D}}$$

$$\Delta^2(q) = (\sigma + \eta_{\mathrm{f}})^2 - 4\eta_{\mathrm{f}}\lambda_1\lambda_2/\Omega^2$$

$$\eta_{\mathrm{f}}(q) = 1 - [\chi_{\mathrm{f}}/\chi_{\mathrm{c}}(q)]$$

We recall that the interaction parameter χ_{f} in the defi-

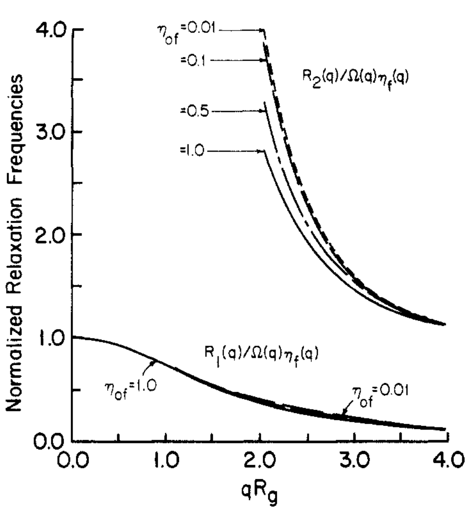

Figure 1. Variation of the normalized relaxation frequencies with qR_g for different values of the interaction parameter.

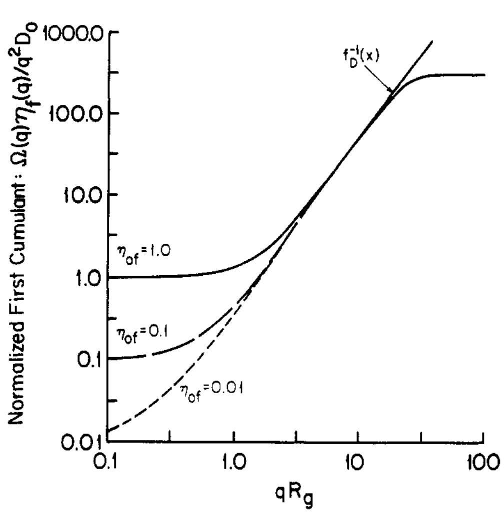

Figure 2. Variation of the first cumulant of the normalized dynamic scattering function $L(q,t)$ with qR_g for various values of the interaction parameter.

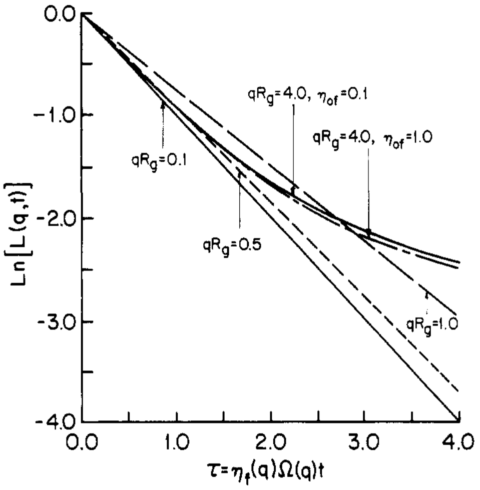

Figure 3. Variation of the normalized dynamic scattering function $L(q,t)$ with the normalized time for different values of qR_g and the interaction parameter.

nition of $\eta_f(q)$ is to be evaluated at the final temperature. Substitution of $L(q,t)$ from eq 35 into

$$I(q,t) = S_{eq}(q) + [I_{in}(q) - S_{eq}(q)]L^2(q,t)$$

yields the scattered intensity in the above extended model. It includes the effect of the internal modes approximately.

It is noted that $L(q,t)$ can be expressed as a universal function $L(\eta_{0f},\tau,\chi)$ of normalized time $\tau = \Omega\eta_f(q)t$ and $x = (qR_g)^2$, and the parameter $\eta_{0f} = \eta_f(0)$, which measures the deviation of the final interaction parameter from its critical value at the spinodal point. Consequently, the intensity $I(q,t)$ can also be written as a universal function of τ and x in a temperature-jump experiment, with the parameters η_{0i} and η_{0f} measuring the relative interaction parameter at the initial and final temperatures, respectively. Another interesting result is that the intensity $I(q,t)$ contains three exponentially decaying terms with relaxation frequencies $2R_1$, $2R_2$, and $R_1 + R_2$ because $L(q,t)$ appears in its expression as squared, in contrast with $L(q,t)$ which contains only two physical relaxation mechanisms associated with the internal modes and the translational diffusion. It is therefore erroneous to try to interpret every decay mode in $I(q,t)$, observed in an experiment, with a physical relaxation mechanism. It should be emphasized here that the multiexponential behavior of $L(q,t)$ may also be due to the coupling of the density to another slowly varying variable, as recently pointed out by Binder et al[20]. In this paper, we have assumed the density to be the only slow variable. In the absence of interactions, i.e., when $\eta_f(q) = 1$, $L(q,t)$ reduces to the single-chain dynamic structure factor given in eq 32. It may also be interesting to consider a few limiting cases in the above results. The first cumulant of $L(q,t)$ in the interacting system is $\Omega_{int}(q) = \eta_f(q)\Omega(q)$ or

$$\Omega_{int}(q) = q^2 D_0\left[\frac{1}{f_D(x)} - \frac{\chi_f}{\chi_c}\right] \tag{36}$$

which is consistent with the general conclusions reached in ref 14. For the values of q for which $\eta_f(q) \leq 0$ holds, $R_1(q)$ is negative, implying spinodal decomposition. But $R_2(q)$ remains always positive. In the small-q limit of $\Omega(q) \to q^2D_0$, $R_1(q) \to q^2\eta_{0f}D_0$ and $L(q,t) \to \exp(-q^2\eta_{0f}D_0t)$, which is consistent with the Markov limit mentioned above. Although $R_2(q)$ approaches a constant, $15D_0/R_g^2$, in this limit, the coefficient of the second exponential in $L(q,t)$ corresponding to $R_2(q)$ vanishes as $q \to 0$. The variations of the normalized relaxation frequencies $R_1(q)/\Omega_{int}(q)$ and $R_2(q)/\Omega_{int}(q)$ with qR_g are shown in Figure 1 for four values of η_{0f}. Since the values of $R_1(q)/\Omega_{int}(q)$ do not differ appreciably from $f_D(x)$ corresponding to $\eta_{0f} = 1$, $R_1(q)$ can be approximated for all values of the interaction parameter by $R_1(q) = q^2D_0\eta_f(q)$. The divergence of $R_2(q)/\Omega_{int}(q)$ as $q \to 0$ is due to the normalization because $R_2(q)$ approaches a constant and the first cumulant vanishes in this limit. Figure 2 shows the variation of the normalized first cumulant in the interacting system as function of qR_g. As seen from eq 36, the curves corresponding to different interaction parameters are obtained by shifting down the first cumulant in the noninteracting system by a constant amount of χ_f/χ_c. The curves with an upper plateau are obtained by using in eq 36 the full expression of the single-chain static structure factor with $N = 300$ (cf. eq 55 of ref 17), instead of the Debye function $f_D(x)$. Here, N is the number of statistical segments. The upper plateau corresponds to segmental diffusion. In Figure 3 we show the variation of $L(q,t)$ as function of the normalized time $\tau = \eta_f(q)\Omega(q)t$ for four values of qR_g. The curves with $\eta_{0f} = 1$ represent the normalized dynamic scattering function of a single chain in Rouse dynamics in the two-exponential approximation. A comparison with the exact calculations available for finite ring polymers (cf. Figure 3 of ref 17) shows that the qualitative aspects of the exact results are reproduced in the two-exponential approximation. As in the exact case, the curves deviate from a single exponential for increasing values of qR_g for a while and approach an exponential when qR_g is further increased. For large values of qR_g, one observes only the initial relaxation of $L(q,t)$ due to the internal motions, whereas the translational diffusion becomes the dominant relaxation mechanism for small values of qR_g. The effect of interactions is illustrated by the curve with $qR_g = 4$ and $\eta_{0f} = 0.1$. It appears that the temporal behavior of $L(q,t)$ is only slightly affected by the interactions when the time is normalized such that the initial slope is −1. Another observation is that there is appreciable deviation from the asymptotic single exponential decay initially when $qR_g \geq 0.5$. We do not plot $I(q,t)$ separately because $I(q,t) - S_{eq}(q)$ is simply proportional to $L^2(q,t)$. These conclusions may provide a more accurate quantitative interpretation of experiments in polymer blends during transients. We do not attempt here to apply these results to the experiments by Okada and Han,[8] for example, because their system was not symmetric, and hence the calculations become too lengthy to be included in this paper. We leave this task to a future publication.

Discussions

In this paper we have shown that the Cahn–Hilliard–Cook form of the intensity $I(q,t)$ can be obtained quite generally by using the linear response theory and discussed the nature and validity of the inherent approximations. In addition of the smallness of the initial perturbations, required by linearization, one also has to assume that the fluctuations of the state vector $\mathbf{a}(t)$ about its time-dependent mean $\mathbf{L}(t)\mathbf{a}(0)$ are statistically independent of the initial value $\mathbf{a}(0)$. This assumption may be expected to be valid for sufficiently long times after the removal of the initial perturbation, especially when th dynamical variables $\mathbf{a}$ are conserved macrovariables. The transients immediately after the initial perturbation should depend on the initial conditions. Only in the final stages of the transients, where the effect of the initial state is completely forgotten, will the time dependence of $I(q,t)$ be governed by the normalized dynamic scattering function in the final equilibrium state for all initial conditions. It is difficult to obtain a quantitative estimate of the waiting time for the CHC form to be valid. Experimentally, one may start from different initial states and always land on the same final state and see whether the same asymptotic behavior is reached in all cases. We have also shown how the random phase approximation (RPA) can be used to determine the dynamic scattering function in the final equilibrium state, in the case of an incompressible binary mixture of homopolymers. We derived an expression for $I(q,t)$ that includes the internal modes of chains and hence extends the results obtained by Binder[5] to higher q values. It seems that the combination of the linear response theory and the RPA provides a clearer and more general derivation of the CHC form than the conventional derivation and elucidates the nature of the inherent approximation. We also included, in Appendix C, an alternative macroscopic derivation of the CHC form based on the Markov assumption and the system size expansion to futher clarify the nature of approximations involved and pointed out the difficulties in extending the Langevin equation to a nonlinear description. Finally, we derived an expression for the intensity of the scattered radiation that takes into account the internal motions of the chain and extends the theory to higher q values.

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Appendix A. Proof of an Identity

The second term (ST) in eq 18 can be written as

$$\mathrm{ST} = \int_0^t \mathrm{d}u \int_u^t \mathrm{d}v\, \mathbf{L}(u)\mathbf{K}(v-u)\mathbf{S}_{eq}\mathbf{L}^\dagger(v) + \int_0^t \mathrm{d}u \int_0^u \mathrm{d}v\, \mathbf{L}(u)\mathbf{S}_{eq}\mathbf{K}^\dagger(u-v)\mathbf{L}^\dagger(v)$$

Using horizontal, instead of vertical, sweep in performing the first surface integral in the v versus u plane and rearranging, we find

$$\mathrm{ST} = \int_0^t \mathrm{d}v \left\{\int_0^v \mathrm{d}u\, \mathbf{L}(u)\mathbf{K}(v-u)\right\}\mathbf{S}_{eq}\mathbf{L}^\dagger(v) + \int_0^t \mathrm{d}u\, \mathbf{L}(u)\mathbf{S}_{eq}\left\{\int_0^u \mathrm{d}v\, \mathbf{K}^\dagger(u-v)\mathbf{L}^\dagger(v)\right\}$$

From eq 8 we find

$$\left\{\int_0^v \mathrm{d}u\, \mathbf{L}(u)\mathbf{K}(v-u)\right\} = -\frac{\mathrm{d}\mathbf{L}(v)}{\mathrm{d}t} + \mathbf{L}(v)i\Omega$$

and its hermitian conjugate

$$\left\{\int_0^u \mathrm{d}v\, \mathbf{K}^\dagger(u-v)\mathbf{L}^\dagger(v)\right\} = -\frac{\mathrm{d}\mathbf{L}^\dagger(u)}{\mathrm{d}t} - i\Omega^\dagger\mathbf{L}^\dagger(u)$$

Using the identity $\Omega\mathbf{S}_{eq} = \mathbf{S}_{eq}\Omega^\dagger$, which follows from the definition of the frequency matrix in eq 6, we obtain the desired identity:

$$\mathrm{ST} = -\int_0^t \mathrm{d}u\, \frac{\mathrm{d}}{\mathrm{d}u}[\mathbf{L}(u)\mathbf{S}_{eq}\mathbf{L}^\dagger(u)] = \mathbf{S}_{eq} - \mathbf{L}(t)\mathbf{S}_{eq}\mathbf{L}^\dagger(t)$$

Appendix B. Calculation of the Correction Term

The lowest order correction terms (CT) in eq 18 can be obtained from eq 17 as

$$\mathrm{CT} = \int_0^t \mathrm{d}u\, \mathbf{L}(u)\{\mathbf{f}(t-u)\mathbf{a}^\dagger(\mathbf{a}^\dagger\cdot\mathbf{b})\}\mathbf{L}^\dagger(t) + \int_0^t \mathrm{d}u\, \mathbf{L}(t)\{(\mathbf{b}^\dagger\cdot\mathbf{a})\mathbf{f}^\dagger(t-u)\}\mathbf{L}^\dagger(u) + \int_0^t \mathrm{d}u \int_0^t \mathrm{d}v\, \mathbf{L}(u)\{\mathbf{f}(t-u)\mathbf{f}^\dagger(t-v)(\mathbf{a}^\dagger\cdot\mathbf{b})\}$$

The equilibrium averages containing the products of $\mathbf{f}(t)$ and $\mathbf{a}$ can be expressed in terms of higher order correlation functions, by multiplying eq 7 by $\mathbf{a}^\dagger(\mathbf{a}^\dagger\cdot\mathbf{b})$, for example, and taking the equilibrium average

$$\int_0^t \mathrm{d}u\, \mathbf{L}(u)\{\mathbf{f}(t-u)\mathbf{a}^\dagger(\mathbf{a}^\dagger\cdot\mathbf{b})\}\mathbf{L}^\dagger(t) = \{[\mathbf{a}(t) - \mathbf{L}(t)\mathbf{a}]\mathbf{a}^\dagger(\mathbf{a}^\dagger\cdot\mathbf{b})\}\mathbf{L}^\dagger(t)$$

Repeating this procedure in the remaining terms, one obtains the forms given in eq 20 and 21.

Appendix C. Macroscopic Theory

In the macroscopic derivation, we select a set of extensive macrovariables A_j, which are assumed to be the superposition of a large number of microscopic quantities. The number of particles of a given kind in microscopically large cells in configuration space is an example of a macrovariable. We assume that the fluctuations of these variables can be treated as a Markov random process, with a known transition probability per unit time, $\mathbf{W}(\mathbf{A},\mathbf{r})$, from

$\mathbf{A}$ to $\mathbf{A} + \mathbf{r}$. It is assumed that W is proportional to the size Ω of the system so that $W(\mathbf{A},\mathbf{r}) = \Omega w(\mathbf{a},\mathbf{r})$, where Ω is the volume of the system and $\mathbf{a} = \mathbf{A}/\Omega$ and $w(\mathbf{a},\mathbf{r})$ are the intensive variables and intensive transition probability, respectively. Starting from the master equation satisfied by the joint probability density of the variables $\mathbf{a}$, one can obtain[7] the following nonlinear Langevin equation:

$$\dot{\mathbf{a}}(t) = \mathbf{c}_1[\mathbf{a}(t)] + \mathbf{f}(t) \qquad \text{(C1)}$$

where $\mathbf{c}_1$ is a nonlinear function of $\mathbf{a}$ and defined by

$$\mathbf{c}_1(\mathbf{a}) = \int \mathrm{d}\mathbf{r}\ \mathbf{r} w(\mathbf{a},\mathbf{r}) \qquad \text{(C2)}$$

Here we assume that the system is time-invariant so that $\mathbf{c}_1$ does not depend on time explicitly. The statistical properties of the noise are also obtained as

$$\langle \mathbf{f}(t) \rangle = 0 \qquad \text{(C3)}$$

$$\langle \mathbf{f}(t)\mathbf{a}^\dagger(0) \rangle = 0, \qquad t > 0 \qquad \text{(C4)}$$

$$\langle \mathbf{f}(t)\mathbf{f}^\dagger(t') \rangle = \langle \mathbf{c}_2[\mathbf{a}(t)] \rangle \delta(t - t') \qquad \text{(C5)}$$

where $\mathbf{c}_2(\mathbf{a})$ is a nonlinear function of vector $\mathbf{a}$, defined by

$$\mathbf{c}_2(\mathbf{a}) = \int \mathrm{d}\mathbf{r}\ \mathbf{r}\mathbf{r}^\dagger w(\mathbf{a},\mathbf{r}) \qquad \text{(C6)}$$

The averages are over the realizations of the Markov process. Equation C5 shows that the autocovariance matrix of the random force depends on all the moments of $\mathbf{a}(t)$. It is this aspect of nonlinear Langevin equations that makes their interpretation ambiguous, as pointed out by van Kampen.[6] In the nonlinear version of the CHC theory, $\langle \mathbf{c}_2[\mathbf{a}(t)] \rangle$ is treated, somewhat arbitrarily, to be a constant and calculated from the fluctuation–dissipation theorem. A systematic procedure to deal with $\langle \mathbf{c}_2[\mathbf{a}(t)] \rangle$ is provided by the method of system size expansion.[7] In this method, one first separates the mean and the fluctuations about the time-dependent mean as $\mathbf{a}(t) = \langle \mathbf{a}(t) \rangle + \epsilon^{1/2}\xi(t)$ and tries to obtain equations satisfied by them separately. This is achieved systematically by expanding them in powers of $\epsilon = 1/\Omega$ as $\langle \mathbf{a}(t) \rangle = \mathbf{a}_0(t) + \epsilon \mathbf{a}_1(t) + \ldots$ and $\xi(t) = \xi_0(t) + \epsilon^{1/2}\xi_1(t) + \ldots$ The following equations are obtained:

$$\dot{\mathbf{a}}_0(t) = \mathbf{c}_1[\mathbf{a}_0(t)] \qquad \text{(C7)}$$

$$\mathrm{d}\xi_0(t)/\mathrm{d}t + \mathbf{R}[\mathbf{a}_0(t)]\xi_0(t) = \mathbf{f}_0(t) \qquad \text{(C8)}$$

where the square matrix $\mathbf{R}(\mathbf{a})$ is defined by $\mathbf{R}(a) \equiv -\partial \mathbf{c}_1(\mathbf{a})/\partial \mathbf{a}$. The statistical properties of the reduced noise term are obtained as

$$\langle \mathbf{f}_0(t) \rangle = 0 \qquad \text{(C9a)}$$

$$\langle \mathbf{f}_0(t)\xi_0(t')^\dagger \rangle = 0, \qquad t > t' \qquad \text{(C9b)}$$

$$\langle \mathbf{f}_0(t)\xi_0(t')^\dagger \rangle + \langle \xi_0(t)\mathbf{f}_0(t)^\dagger \rangle = \mathbf{c}_2[\mathbf{a}_0(t)] \qquad \text{(C9c)}$$

$$\langle \mathbf{f}_0(t)\mathbf{f}_0(t')^\dagger \rangle = \mathbf{c}_2[\mathbf{a}_0(t)]\delta(t - t') \qquad \text{(C9d)}$$

The $\mathbf{a}_0(t)$ denotes the most probable path[21] and is determined by the nonlinear deterministic equation (C7). The fluctuations about the mean satisfy a linear Langevin equation, eq C8, with time-dependent coefficients $\mathbf{R}(t) \equiv \mathbf{R}[\mathbf{a}_0(t)]$. Both these coefficients and the autocovariance of the noise term $\mathbf{c}_2(t) \equiv \mathbf{c}_2[\mathbf{a}_0(t)]$ depend on time implicitly through $\mathbf{a}_0(t)$, which is determined from the deterministic equation, i.e., the fluctuations in nonlinear systems are "driven" by the mean. *The separation of the time evolution of the mean and the fluctuations about the mean is the main difference between the conventional treatment of fluctuations* in the CHC theory and the macroscopic theory presented here.

The two-time correlation function $\mathbf{S}_\mathrm{D}(t,t_0) = \langle \xi_0(t)\xi_0(t_0)^\dagger \rangle$, which depends on both t and t_0 during transients, is obtained from eq C7 by using eq C9b as

$$\mathbf{S}_\mathrm{D}(t,t_0) = \mathbf{L}(t,t_0)\sigma(t_0), \qquad t \geq t_0 \qquad \text{(C10)}$$

where $\mathbf{L}(t,t_0)$ is the solution of

$$\mathrm{d}\mathbf{L}(t,t_0)/\mathrm{d}t = -\mathbf{R}(t)\mathbf{L}(t,t_0) \qquad \text{(C11)}$$

with the initial condition $\mathbf{L}(t_0,t_0) = \mathbf{I}$. The variance $\sigma(t) \equiv \langle \xi_0(t)\xi_0(t)^\ddagger \rangle$ $\langle \xi_0(t)\xi_0(t)^\dagger \rangle$ satisfies

$$\mathrm{d}\sigma(t)/\mathrm{d}t + \mathbf{R}(t)\sigma(t) + \sigma(t)\mathbf{R}(t)^\dagger = \mathbf{c}_2(t) \qquad \text{(C12)}$$

which is obtained from eq C8 by using eq C9c. This equation can be solved as

$$\sigma(t) = \mathbf{L}(t,t_0)\sigma(t_0)\mathbf{L}(t,t_0)^\dagger + \int_{t_0}^{t} \mathrm{d}u\ \mathbf{L}(t,u)\mathbf{c}_2(u)\mathbf{L}(t,u)^\dagger \qquad \text{(C13)}$$

which can be verified by differentiation. The intensity $\mathbf{I}(t) = \langle \mathbf{a}(t)\mathbf{a}(t)^\dagger \rangle$ can be written in the lowest order in ϵ as

$$\mathbf{I}(t) = \mathbf{a}_0(t)\mathbf{a}_0(t)^\dagger + \sigma(t) \qquad \text{(C14)}$$

where we have set $\epsilon = 1$ which is equivalent absorbing ϵ in $\xi_0(t)$ and $\mathbf{c}_2(t)$. Equations C7, C8, and C14 provide a systematic framework to study fluctuations of macrovariables in nonlinear systems during transients following an initial perturbation, as well as at equilibrium. Since we are mainly interested in the linear theory, we consider an equilibrium state $\mathbf{a}_\mathrm{e}$, which is a solution to $\mathbf{c}_1(\mathbf{a}_\mathrm{e}) = 0$, and linearize the deterministic equation (C7) as $\mathrm{d}\delta\mathbf{a}_0(t)/\mathrm{d}t = -\mathbf{R}\delta\mathbf{a}_0(t)$, where $\delta\mathbf{a}_0(t)$ shows the deviations $\delta\mathbf{a}_0(t)$ from $\mathbf{a}_\mathrm{e}$, and $\mathbf{R} = \mathbf{R}(\mathbf{a}_\mathrm{e})$. The equilibrium state is stable if $\mathbf{R}$ is positive definite and unstable otherwise. Defining the intensity as $\mathbf{I}(t) = \delta\mathbf{a}_0(t)\delta\mathbf{a}_0(t)^\dagger + \sigma(t)$ in terms of deviations, we obtain

$$\mathbf{I}(t) = \mathbf{L}(t)\mathbf{I}_\mathrm{in}\mathbf{L}(t)^\dagger + \int_0^t \mathrm{d}u\ \mathbf{L}(u)\mathbf{c}_2[\mathbf{a}_\mathrm{e} + \delta\mathbf{a}_0(u)]\mathbf{L}(u)^\dagger \qquad \text{(C15)}$$

where $\mathbf{L}(t) \equiv \mathbf{L}(t,0) = \exp[-\mathbf{R}t]$. This equation contains only the Markov assumption and linearization. The equilibrium state is not required to be stable, as opposed to the microscopic derivation, so that it can be used in the spinodal region as well. We note that eq C15 is not completely in the CHC form given in eq 19 in the text. The reason is that $\mathbf{c}_2[\mathbf{a}_\mathrm{e} + \delta\mathbf{a}_0(u)]$, which determines the intensity of the noise term in the Langevin equation (C8), is still allowed to depend on time implicitly through $\delta\mathbf{a}_0(u)$. However, if one further simplifies this equation, consistently with the linearization procedure, by ignoring $\delta\mathbf{a}_0(u)$ in the argument of $\mathbf{c}_2$ and introduces $\mathbf{S}_\mathrm{eq}$ through

$$\mathbf{c}_2 = \mathbf{R}\mathbf{S}_\mathrm{eq} + \mathbf{S}_\mathrm{eq}\mathbf{R}^\dagger \qquad \text{(C16)}$$

to eliminate $\mathbf{c}_2 \boxminus \mathbf{c}_2[\mathbf{a}_\mathrm{e}]$, one recaptures the CHC form

$$\mathbf{I}(t) = \mathbf{S}_\mathrm{eq} + \mathbf{L}(t)(\mathbf{I}_\mathrm{in} - \mathbf{S}_\mathrm{eq})\mathbf{L}^\dagger(t) \qquad \text{(C17)}$$

given in the text (cf. eq 19), with the help of the following identity (cf. Appendix A):

$$\int_0^t \mathrm{d}u\ \mathbf{L}(u)\mathbf{c}_2\mathbf{L}(u)^\dagger = \mathbf{S}_\mathrm{eq} - \mathbf{L}(t)\mathbf{S}_\mathrm{eq}\mathbf{L}(t)^\dagger$$

In eq C17, $\mathbf{L}(t) = \exp[-\mathbf{R}t]$ is an exponential function of t, *whereas in the microscopic derivation it was allowed to be nonexponential.* The matrix $\mathbf{S}_\mathrm{eq}$, which was introduced through eq C16 purely as a mathematical change of variable, is clearly identified as the static structure factor in the final equilibrium state when $\mathbf{R}$ is positive definite (stable equilibrium). In this case, eq C16 represents the generalized Einstein relation, or the fluctuation–dissipation theorem. However, one can still use eq C16 to obtain the CHC form even when **R** is negative definite (unstable equilibrium). In this case $\mathbf{S}_{eq}$ is nonphysical, negative, and just a replacement for $\mathbf{c}_2$. It is usually referred to as the "virtual structure factor".

In the macroscopic derivation, the calculation of the intensity requires the knowledge of the relaxation (or growth) matrix **R** and the autocovariance matrix $\mathbf{c}_2$ as the two inputs in the theory. They can be calculated as the first two moments of the transition probability per unit time $w(\mathbf{a},\mathbf{r})$ as in eq C2 and C6, if $w(\mathbf{a},\mathbf{r})$ can be determined from the physical description of the system. In spatially inhomogeneous systems, this can be done by dividing the volume into cells and using discretized formulation of the diffusion process. They can also be determined by using RPA, as was done in the case of microscopic derivation. There are a few differences between the macroscopic and microscopic derivations worth mentioning. Insofar as it describes the time evolution of the mean in the linear regime, $\mathbf{L}(t)$ can be related to the linear response function $\chi(t)$ by

$$\mathbf{L}(t) = \chi(t)\chi(0)^{-1}$$

This relation does not require the stability of the equilibrium state. In the RPA, the response function is expressed in Laplace domain in terms of the mean response functions of the noninteracting components of the mixture[14] as

$$\chi(s)^{-1} = \chi_A(s)^{-1} + \chi_B(s)^{-1} - 2k_BT\chi_F \qquad \text{(C18)}$$

where $\chi_\alpha(t)$ As discussed in ref 14, this relation is valid both in the miscible (stable equilibrium) and in the spinodal (unstable equilibrium) regions. Since noninteracting components are always stable, we can use the linear response theory to express $\chi_\alpha(t)$ in terms of the equilibrium dynamic structure functions $\mathbf{S}_\alpha(t)$, as already discussed in the text (cf. eq 28). Hence, in both the miscible and spinodal regions the calculation of $\mathbf{L}(t)$ has been reduced to the calculation $\mathbf{S}_\alpha(t)$, using for example the Rouse dynamics. *The point is that macroscopic derivation describes the transients in the spinodal region as well as in the one-phase region, in contrast to the microscopic derivation, which is valid in the miscible region only.*

We now return to the calculation of $\mathbf{c}_2$. In the miscible region, it is expressed in terms of the static structure factor $\mathbf{S}_{eq}$ in the final equilibrium state according to Einstein's relation in eq C16, as discussed in the text. The situation is somewhat less straightforward in the dephasing region because the initial state is not a stable equilibrium state, and $\mathbf{S}_{eq}$ is the virtual structure factor. The latter in principle cannot be calculated by de Genne's formula in terms of the static structure factors of the noninteracting components within the framework of the RPA. However, if *one assumes that the temperature jump from the miscible into the spinodal region is sufficiently small so that $\mathbf{c}_2$ remains unchanged during the jump, then it can be calculated from Einstein's relation in terms of the static structure factors at the initial equilibrium state.* This is the procedure that Okada and Han[8] followed to calculate the negative virtual structure factor after a temperature jump.

The system size expansion of van Kampen[6,22] is valid as long as the magnitude of the fluctuations about the mean is of order $\epsilon^{1/2}$ as compared to the mean. Suziki[23] showed some time ago that before the final inhomogeneous equilibrium state is reached, there is a time interval (scaling regime) in which the magnitude of fluctuations becomes comparable to the mean (fluctuation enhancement). Therefore, the macroscopic derivation presented in this appendix is valid only in the early stages of spinodal decomposition.

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