Dynamics of Early Stage Spinodal Decomposition of Multicomponent Polymer Systems

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ABSTRACT: The Cahn−Hilliard−Cook (CHC) theory with random phase approximation (RPA) for the time change in the structure factor in multicomponent polymer systems is used to describe the dynamics of the early stage spinodal decomposition. Explicit expressions on the time change in the structure factor for the block copolymer/homopolymer mixture have been obtained with the dynamics of microphase/macrophase separations of the mixture presented in detail.

I. Introduction

Multicomponent polymer systems have been a fascinating subject of material science in recent years because of their remarkable physical properties. Tanaka and Hashimoto[1] studied the phase diagram of a mixture of block copolymer A−B and homopolymer B (A−B/B) and that of a mixture of homopolymer A, homopolymer B, and A−B (A−B/A/B) by using the random phase approximation (RPA). Hong and Noolandi[2] and Whitemore and Noolandi[3] developed a theory for the phase diagram of a mixture of A−B and homopolymer C (A−B/C) where C has a chemical structure different from A−B. Jin Kon Kim et al.[4] studied the phase diagrams of 4-component polymer systems by using the RPA.

de Gennes[5] first introduced the RPA to calculate the structure factor of macromolecules with heavy-atom labels in polymer melts. Leibler[6] studied the structure factor of monodisperse A−B by the RPA. Tanaka and Hashimoto[1] calculated the structure factors of A−B/A and A−B/A/B systems. Ijichi and Hashimoto[7] obtained an explicit expression for the structure factor of three-component polymer systems. Jin Kon Kim et al.[4] and Benoit et al.[8] derived the structure factor for multicomponent polymer systems.

de Gennes,[9] Pincus,[10] and Binder[11] studied the dynamics of a binary polymer blend in one-phase and two-phase regions. Akcasu et al.[12] applied the RPA to the dynamics of a binary polymer blend and a diblock copolymer in the one-phase region in terms of the dynamic scattering structure factor. Akcasu and Tombakoglu[13] then developed the theory for the dynamic structure factor in multicomponent polymer systems by using the RPA.

Akcasu[14] derived the generalized Cahn−Hilliard−Cook (CHC) theory[15,16] and applied it with Rouse dynamics to the short time dynamics of binary polymer blends. Kawasaki and Sekimoto[17−19] presented a new stochastic equation for the multicomponent systems by adopting the biased reptation model in the mean field approximation. The Kawasaki and Sekimoto theory considered q-dependent kinetic coefficients which replace the Onsager kinetic coefficients in the usual time-dependent Ginzburg−Landau equation. They, however, did not show the practical expressions needed to calculate the structure factors for real experimental systems. Hence we present here a method to stimulate the long time dynamics for multicomponent polymer systems by using the generalized CHC theory and the RPA with a q-dependent kinetic coefficient based on the Kawasaki and Sekimoto theory. This method should permit us to calculate the time change in the structure factor of multicomponent polymer systems during the early stage of spinodal decomposition. We shall apply our results to an A−B/B system and obtain the necessary explicit expressions in order to describe the dynamics of the phase separation process via spinodal decomposition. By using the derived expressions, we can calculate the time change in the structure factor of the system quenched into the unstable region where macrophase separation and microphase separation occur.

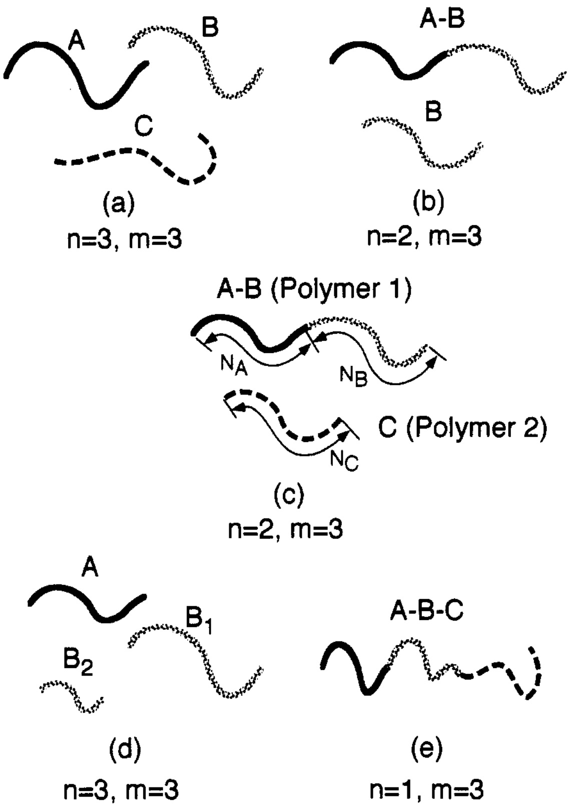

Figure 1. Examples of polymer systems considered in this study: (a) A/B/C, (b) A−B/B, (c) A−B/C, (d) A/B_1/B_2, and (e) A−B−C. m and n denote the number of "polymer" and that of "component" in the system, respectively.

II. Theory

Let us consider the dynamics of spinodal decomposition by quenching a mixture of m polymers consisting

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of n components into an unstable region. Figure 1 illustrates the examples of polymer systems considered in this study. Here "m polymers" means that the mixture has m kinds of copolymers of homopolymers. The homopolymers made of the same species with different molecular weights are considered as different polymers. Hence, an A/B/C system, an A–B/B system, an A–B/C system, an A/B_1/B_2 system, and a triblock copolymer A–B–C system are considered as a three-polymer system, a two-polymer system, a two-polymer system, a three-polymer system, and a one-polymer system, respectively, where B_1 and B_2 consist of identical species but have different molecular weights. The definitions of a "component" are as follows: (i) the homopolymers made of a different species are identified as different components; (ii) the homopolymers made of the same species with different molecular weights are considered as different components; (iii) different species in a block copolymer are identified as different components. Therefore an A/B/C system, an A–B/B system, an A–B/C system, an A/B_1/B_2 system, and a triblock copolymer A–B–C system are all considered as a three-component mixture.

The structure of an m-polymer system consisting of n components is characterized by concentration fluctuations $\varrho_i(q,t)$ of the ith component at wavenumber q and time t. The structure factor $S_{ij}(q,t)$ which characterizes the concentration fluctuation of the system at q and t is defined by

$$S_{ij}(q,t) = \langle \varrho_i(q,t)\varrho_j(q,t)\rangle_T \qquad (1)$$

where $\langle ...\rangle_T$ denotes a thermal average. The scattered intensity $I(q,t)$ at q and t is given by

$$I(q,t) \sim \sum_{i,j=1}^{n} a_i a_j S_{ij}(q,t) \qquad (2)$$

where a_i (i = 1, 2, ..., n) corresponds to the scattering amplitude per monomer of component i. By using the incompressible constraint and the symmetry property ($S_{ij}(q,t) = S_{ji}(q,t)$) eq 2 becomes

$$I(q,t) \sim \sum_{i,j=1}^{n-1} (a_i - a_n)(a_j - a_n)S_{ij}(q,t) \qquad (3)$$

According to the CHC equation by Akcasu,[14] the time change in the structure factor matrix $\mathbf{S}(q,t)$ is given by

$$\mathbf{S}(q,t) = \mathbf{S}_{\mathrm{eq}}(q) + \mathbf{L}(q,t)[\mathbf{S}(q,0) - \mathbf{S}_{\mathrm{eq}}(q)]\mathbf{L}^{\dagger}(q,t) \qquad (4)$$

where $\mathbf{S}(q,0)$, $\mathbf{S}_{\mathrm{eq}}(q)$, and $\mathbf{L}(q,t)$ are the structure factor matrix at $t = 0$, the virtual structure factor matrix, and the normalized dynamic structure matrix, respectively, with $\mathbf{L}^{\dagger}(q,t)$ being the hermitian conjugate of $\mathbf{L}(q,t)$. These matrices are $(n - 1) \times (n - 1)$ matrices and the component n is eliminated by using the incompressible constraint.

$\mathbf{S}(q,0)$ and $\mathbf{S}_{\mathrm{eq}}(q)$ can be calculated by using the RPA. If the mixture contains at least one homopolymer, we can use the method developed by Benoit et al.[8] where one of homopolymers in the mixture can be eliminated as the component n. According to the method developed by Benoit et al., $\mathbf{S}(q,0)$ and $\mathbf{S}_{\mathrm{eq}}(q)$ are given by

$$[\mathbf{S}(q,0)]^{-1} = [\mathbf{S}_0(q)]^{-1} + \mathbf{v}_0(q) \qquad (5)$$

and

$$[\mathbf{S}_{\mathrm{eq}}(q)]^{-1} = [\mathbf{S}_0(q)]^{-1} + \mathbf{v}_{\mathrm{T}}(q) \qquad (6)$$

respectively. It should be noted that eq 6 is valid only in the early stages of spinodal decomposition[14] when the system is still in a state of equilibrium. If the system moves away from equilibrium after a quench into the spinodal region, $\mathbf{S}_{\mathrm{eq}}(q)$ becomes nonphysical in nature and is referred to as a "virtual structure factor". In any case, the procedure (eq 6) should be considered an approximation even in a shallow quench. $\mathbf{S}_0(q)$ is the bare structure factor matrix and the components $S_{0,ij}(q)$ of $\mathbf{S}_0(q)$ depend on the structure of constituent polymers in the system. For example, if all n-constituent polymers are homopolymers, $S_{0,ij}(q)$ is given by

$$S_{0,ii}(q) = \phi_i N_i g(q,N_i,b) \qquad (7)$$

and

$$S_{0,ij}(q) = 0 \qquad \text{for } i \neq j \qquad (8)$$

where ϕ_i and N_i are respectively the volume fraction and the polymerization index of i and b is the statistical segment length. It is noted that the statistical segment length of each component in the system is assumed to be identical for simplicity. $g(q,N_i,b)$ is the Debye function, defined by

$$g(q,N_i,b) = \frac{2}{x_i^2}[\exp(-x_i) + x_i - 1] \qquad (9)$$

where

$$x_i = \frac{N_i b^2 q^2}{6} \qquad (10)$$

$\mathbf{v}_0(q)$ and $\mathbf{v}_{\mathrm{T}}(q)$ are the interaction matrices before and after quench, respectively. The elements $v_{0,ij}(q)$ of $\mathbf{v}_0(q)$ are given by

$$v_{0,ii}(q) = \frac{1}{S_{0,nn}(q)} - 2\chi_{0,in} \qquad \text{for } i = j \qquad (11)$$

and

$$v_{0,ij}(q) = \frac{1}{S_{0,nn}(q)} - (\chi_{0,in} + \chi_{0,jn} - \chi_{0,ij}) \qquad \text{for } i \neq j \qquad (12)$$

where $\chi_{0,kl}$ are the Flory–Huggins segmental interaction parameters between k and l before quench. Similarly, the elements $v_{\mathrm{T},ij}(q)$ of $\mathbf{v}_{\mathrm{T}}(q)$ are given by

$$v_{\mathrm{T},ii}(q) = \frac{1}{S_{0,nn}(q)} - 2\chi_{\mathrm{T},in} \qquad (13)$$

and

$$v_{\mathrm{T},ij}(q) = \frac{1}{S_{0,nn}(q)} - (\chi_{\mathrm{T},in} + \chi_{\mathrm{T},jn} - \chi_{\mathrm{T},ij}) \qquad (14)$$

where $\chi_{\mathrm{T},kl}$ are the Flory–Huggins segmental interaction parameters between k and l after quench. If there is no homopolymer in the mixture, we use the following method proposed by Kim et al.[4] The components $S_{ij}(q,0)$ of $\mathbf{S}(q,0)$ are expressed by

$$S_{ij}(q,0) = \sum_{k=1}^{n-1} C_{ik}(q)[S_{0,kj}(q) - w_k(q)S_{0,kj}(q)] \quad (15)$$

where $C_{ik}(q)$ is the component of the $(n-1) \times (n-1)$ matrix $\mathbf{C}(q)$. $\mathbf{C}(q)$ is given by

$$\mathbf{C}(q) = \mathbf{A}^{-1}(q) \quad (16)$$

with

$$A_{ij}(q) = \sum_{p=1}^{n} [S_{0,ip}(q) - w_i(q)S_{0,mp}(q)][\chi_{0,pj} - \chi_{0,pm}] + w_j(q) + \delta_{ij} \quad (17)$$

and $w_i(q)$ is given by

$$w_i(q) = \frac{t_i(q)}{t_m(q)} \quad (18)$$

with

$$t_j(q) = \sum_{r=1}^{m} S_{0,jr}(q) \quad (19)$$

$\mathbf{S}_{\text{eq}}(q)$ can be obtained by replacing $\chi_{0,ij}$ with $\chi_{\text{T},ij}$.

$\mathbf{L}(q,t)$ is expressed by

$$\mathbf{L}(q,t) = \exp(\mathbf{D}(q)t) \quad (20)$$

where $\mathbf{D}(q)$ is the collective diffusion matrix and is given by

$$\mathbf{D}(q) = -q^2 \mathbf{\Lambda}(q)[\mathbf{S}_{\text{eq}}(q)]^{-1} \quad (21)$$

$\mathbf{\Lambda}(q)$ is the mobility matrix and the elements $\Lambda_{ij}(q)$ of $\mathbf{\Lambda}(q)$ are given by

$$\Lambda_{ij}(q) = \Lambda_{0,ij}(q) - \frac{\sum_{p}^{m} \Lambda_{0,ip}(q) \sum_{q}^{m} \Lambda_{0,jq}(q)}{\sum_{k,l}^{m} \Lambda_{0,kl}(q)} \quad (22)$$

if we assume that the system obeys the slow theory,[9-11] where the slow component controls the collective diffusion of the system. On the other hand, if the system obeys the fast theory,[13,14,20,21] where the fast component controls the collective diffusion of the system, then $\Lambda_{ij}(q)$ is given by

$$\Lambda_{ij}(q) = \Lambda_{ij,0}(q) - \phi_j \sum_{p=1}^{n} \Lambda_{ip,0}(q) - \phi_i \sum_{q=1}^{n} \Lambda_{qj,0}(q) + \phi_i \phi_j \sum_{r=1}^{n} \sum_{s=1}^{n} \Lambda_{rs,0}(q) \quad (23)$$

It is noted that if the i and j components ($i \neq j$) are those of a block copolymer then $\Lambda_{0,ij}(q)$ is nonvanishing. For examples, $\Lambda_{0,\text{AB}}(q)$ [$=\Lambda_{0,\text{BA}}(q)$], $\Lambda_{0,\text{BC}}(q)$ [$=\Lambda_{0,\text{CB}}(q)$], and $\Lambda_{0,\text{CA}}(q)$ [$=\Lambda_{0,\text{AC}}(q)$] are zero for an A/B/C system (Figure 1a), whereas these parameters are not zero for an A–B–C system (Figure 1e). Our result is somewhat different from the Akcasu et al. result[13] because they calculated only the short time bare mobility matrix, which is diagonal in the Rouse limit, whereas in this study we are considering the long time mobility. Kawasaki and Sekimoto[17-19] proposed the expression for $\Lambda_{0,ij}(q)$ by using the biased reptation model. According to their theory, $\Lambda_{0,ij}(q)$ is given by

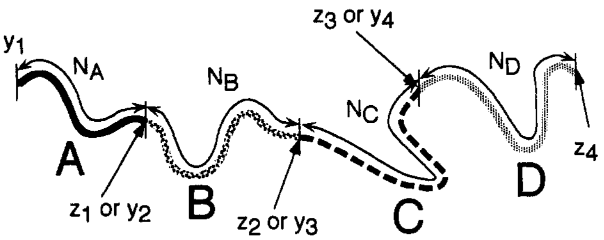

Figure 2. Schematic illustration of an A–B–C–D block copolymer of which A and D are assumed to be, respectively, the head and the tail of the copolymer.

$$\Lambda_{0,ij}(q) = 3D_k N_k \phi_k \bar{P}_{ij}(q) \quad (24)$$

where D_k is the self-diffusion coefficient of the k polymer, and ϕ_k and N_k are respectively the volume fraction and the polymerization index of the k polymer given by

$$\phi_k = \sum_{(k)} \phi_x \quad (25)$$

and

$$N_k = \sum_{(k)} N_x \quad (26)$$

Here the summation in eqs 25 and 26 denotes that in the k polymer. For example, in the case of an A–B/C system as shown in Figure 1c, N_1 and N_2 are $N_\text{A} + N_\text{B}$ and N_C, respectively. If the monomeric diffusion coefficient and the polymerization index between entanglements of each component in the k polymer are identical, D_k is expressed by

$$D_k = D_{1k} \frac{N_\text{e}}{N_k^{\,2}} \quad (27)$$

where D_{1k} and N_e are respectively the monomeric diffusion coefficient and the polymerization index between entanglements. If $i \neq j$ and the i component is not present in the same polymer containing the j component, $\Lambda_{0,ij}(q)$ is 0. $\bar{P}_{ij}(q)$ is given by

$$\bar{P}_{ij}(q) = \frac{1}{N_k b^2 q^2}[P_{y_i y_j}(q) - P_{y_i z_j}(q) - P_{z_i y_j}(q) + P_{z_i z_j}(q)] \quad (28)$$

with

$$P_{y_i z_j}(q) = \exp\left(-\frac{1}{6}\left|y_i - z_j\right| b^2 q^2\right) \quad (29)$$

where y_i and z_i are respectively the head point and the tail point of the i component. For example, let us consider the A–B–C–D copolymer as shown in Figure 2. If A and D are assumed to be the head and tail, respectively, y_i and z_i of each component are expressed by

$$y_\text{A} = 0, \qquad z_\text{A} = N_\text{A},$$

$$y_\text{B} = N_\text{A}, \qquad z_\text{B} = N_\text{A} + N_\text{B},$$

$$y_C = N_A + N_B, \quad z_C = N_A + N_B + N_C,$$

and

$$y_D = N_A + N_B + N_C, \quad z_D = N_A + N_B + N_C + N_D \tag{30}$$

It should be noted that Schwahn et al.[22] reported a discrepancy between the theoretical results and their experimental results in the q-dependent Onsager kinetic coefficient. Kawasaki and Koga[23] suggested that this discrepancy was caused by the stress effects. In this paper, the Kawasaki and Sekimoto theory is assumed to be valid.

$\mathbf{D}(q)$ is not symmetric so that we have to diagonalize $\mathbf{D}(q)$ by a similarity transformation to calculate $\mathbf{L}(q)$,

$$\mathbf{d}(q) = \mathbf{QDQ}^{-1} = \begin{pmatrix} \lambda_1(q) & & & \mathbf{0} \\ & \lambda_2(q) & & \\ & & \ddots & \\ \mathbf{0} & & & \lambda_{n-1}(q) \end{pmatrix} \tag{31}$$

where $\mathbf{d}(q)$ is the diagonal matrix of $\mathbf{D}(q)$, $\lambda_K(q)$ are the eigenvalues of $\mathbf{D}(q)$, and $\mathbf{Q}$ is given by

$$\mathbf{Q}^{-1} = [\mathbf{q}_1, \mathbf{q}_2, ..., \mathbf{q}_{n-1}] \tag{32}$$

where $\mathbf{q}_K$ are the eigenvectors of $\mathbf{D}(q)$. By using eq 31, $\mathbf{L}(q,t)$ is expressed by

$$\mathbf{L}(q,t) = \mathbf{Q}^{-1}\mathbf{Q}\exp(\mathbf{D}(q)t)\mathbf{Q}^{-1}\mathbf{Q} = \mathbf{Q}^{-1}\exp(\mathbf{d}(q)t)\mathbf{Q} = \mathbf{Q}^{-1}\mathbf{l}(q,t)\mathbf{Q} \tag{33}$$

where $\mathbf{l}(q)$ is given by

$$\mathbf{l}(q,t) = \begin{pmatrix} e^{\lambda_1 t} & & & 0 \\ & e^{\lambda_2 t} & & \\ & & \ddots & \\ 0 & & & e^{\lambda_{n-1} t} \end{pmatrix} \tag{34}$$

By substituting eq 33 into eq 4, we obtain

$$\mathbf{S}(q,t) = \mathbf{S}_{eq}(q) + \mathbf{Ql}^{-1}(q,t)\mathbf{Q}[\mathbf{S}(q,0) - \mathbf{S}_{eq}(q)][\mathbf{Ql}^{-1}(q,t)\mathbf{Q}]^{\dagger} \tag{35}$$

The procedure to calculate $\mathbf{S}(q,t)$ is as follows: (i) the calculation of $\mathbf{S}(q,0)$ and $\mathbf{S}_{eq}(q)$ by using eqs 5, 6, 11, and 12, (ii) the calculation of $\mathbf{D}(q)$ by using $\mathbf{S}_{eq}(q)$ and eqs 21–24, (iii) the calculation of $\lambda_K(q)$ from $\mathbf{D}(q)$, (iv) the calculation of $\mathbf{Q}$ by using $\lambda_K(q)$, and (v) the calculation of $\mathbf{S}(q,t)$ by using eq 35.

III. Dynamics of Spinodal Decomposition in an A–B/B Mixture

Let us consider the dynamics of spinodal decomposition in an A–B/B mixture as an application of the CHC theory. It is noted that the dynamic structure factor of the system in the one-phase region have been considered by Tombakoglu and Akcasu.[24] The mixture referred to A in A–B, B in A–B, and homopolymer B as 1, 2, and 3. We identify homopolymer B or component 3 as the matrix. $I(q,t)$ of the mixture is, according to eq 3, given by

$$I(q,t) \sim (a_1 - a_3)^2 S_{11}(q,t) \tag{36}$$

First, we shall calculate $\mathbf{S}(q,0)$ and $\mathbf{S}_{eq}(q)$ which are 2 × 2 matrices. The components $S_{0,ij}(q)$ (i, j = 1, 2) of $\mathbf{S}_0(q)$ are given by

$$S_{0,11}(q) = N_b\phi_b h(f,N_b,b,q) \tag{37}$$

$$S_{0,22}(q) = N_b\phi_b h(1 - f,N_b,b,q) \tag{38}$$

and

$$S_{0,12}(q) = S_{0,21}(q) = \frac{N_b}{2}\phi_b[h(1,N_b,b,q) - h(f,N_b,b,q) - h(1 - f,N_b,b,q)] \tag{39}$$

where

$$\phi_b = \phi_1 + \phi_2 \tag{40}$$

$$N_b = N_1 + N_2 \tag{41}$$

$$f = N_1/(N_1 + N_2) \tag{42}$$

and

$$h(f,N,b,q) = \frac{2}{x^2}[fx + e^{-fx} - f] \tag{43}$$

with

$$x = \frac{Nb^2q^2}{6} \tag{44}$$

The elements $v_{0,ij}(q)$ and $v_{T,ij}(q)$ of the interaction matrices are given by

$$v_{0,11}(q) = \frac{1}{S_{0,33}(q)} - 2\chi_{0,AB} \tag{45}$$

$$v_{0,12}(q) = v_{0,21}(q) = v_{0,22}(q) = \frac{1}{S_{0,33}(q)} \tag{46}$$

and

$$v_{T,11}(q) = \frac{1}{S_{0,33}(q)} - 2\chi_{T,AB} \tag{47}$$

$$v_{T,12}(q) = v_{T,21}(q) = v_{T,22}(q) = \frac{1}{S_{0,33}(q)} \tag{48}$$

respectively, where

$$S_{0,33}(q) = N_3\phi_3 h(1,N_3,b,q) \tag{49}$$

By substitution of eqs 45 and 46 into eq 5, $\mathbf{S}(q,0)$ can be obtained explicitly as follows:

$$\mathbf{S}(q,0) = \begin{bmatrix} (S_{0,11}(q)S_{0,33}(q) + \Delta^0) & (S_{0,12}(q)S_{0,33}(q) + \Delta^0) \\ (S_{0,12}(q)S_{0,33}(q) + \Delta^0) & (S_{0,22}(q)S_{0,33}(q) + \Delta^0 - 2\chi_{0,AB}) \end{bmatrix} \Bigg/ \Delta \tag{50}$$

where

$$\Delta = S_{0,11}(q) + S_{0,22}(q) + 2S_{0,11}(q) + S_{0,33}(q) - 2\chi_{0,AB}(S_{0,11}(q)S_{0,33}(q) + \Delta^0) \tag{51}$$

and

$$\Delta^0 = S_{0,11}(q)S_{0,22}(q) - [S_{0,12}(q)]^2 \tag{52}$$

Similarly, $\mathbf{S}_{\mathrm{eq}}(q)$ is given by

$$\mathbf{S}_{\mathrm{eq}}(q) = \left.\begin{bmatrix} (S_{0,11}(q)S_{0,33}(q) + \Delta^0) & (S_{0,12}(q)S_{0,33}(q) + \Delta^0) \\ (S_{0,12}(q)S_{0,33}(q) + \Delta^0) & (S_{0,22}(q)S_{0,33}(q) + \Delta^0 - 2\chi_{\mathrm{T,AB}}) \end{bmatrix}\right/\Delta \tag{53}$$

Next, we shall calculate $\mathbf{D}(q)$. Here it is assumed that the A–B/B system obeys the slow theory. The elements $\Lambda_{ij}(q)$ of $\Lambda(q)$ are given by

$$\Lambda_{11}(q) = \frac{\Lambda_{0,11}(q)[\Lambda_{0,22}(q) + \Lambda_{0,33}(q)] - [\Lambda_{0,12}(q)]^2}{\Lambda_{0,33}(q) + \Lambda_{0,11}(q) + \Lambda_{0,22}(q) + 2\Lambda_{0,12}(q)} \tag{54}$$

$$\Lambda_{22}(q) = \frac{\Lambda_{0,22}(q)[\Lambda_{0,11}(q) + \Lambda_{0,33}(q)] - [\Lambda_{0,12}(q)]^2}{\Lambda_{0,33}(q) + \Lambda_{0,11}(q) + \Lambda_{0,22}(q) + 2\Lambda_{0,12}(q)} \tag{55}$$

and

$$\Lambda_{21}(q) = \Lambda_{12}(q) = \frac{\Lambda_{0,12}(q)[\Lambda_{0,12}(q) + \Lambda_{0,33}(q)] - \Lambda_{0,11}(q)\Lambda_{0,22}(q)}{\Lambda_{0,33}(q) + \Lambda_{0,11}(q) + \Lambda_{0,22}(q) + 2\Lambda_{0,12}(q)} \tag{56}$$

where

$$\Lambda_{0,11}(q) = \frac{6D_{\mathrm{b}}\phi_{\mathrm{b}}}{b^2q^2}\eta(N_1) \tag{57}$$

$$\Lambda_{0,22}(q) = \frac{6D_{\mathrm{b}}\phi_{\mathrm{b}}}{b^2q^2}\eta(N_2) \tag{58}$$

$$\Lambda_{0,12}(q) = -\frac{3D_3\phi_3}{b^2q^2}\eta(N_1)\eta(N_2) \tag{59}$$

and

$$\Lambda_{0,33}(q) = \frac{6D_3\phi_3}{b^2q^2}\eta(N_3) \tag{60}$$

with

$$\eta(N_k) = 1 - \exp(-N_k b^2q^2/6) \tag{60a}$$

where D_{b} and D_3 are the self-diffusion coefficient of block copolymer and homopolymer B, respectively.

By using eqs 21 and 53–56 the elements $D_{ij}(q)$ of $\mathbf{D}(q)$ are expressed by

$$D_{11}(q) = -q^2\left\{\Lambda_{11}(q)\left[\frac{S_{0,22}(q)}{\Delta^0} + \frac{1}{S_{0,33}(q)} - 2\chi_{\mathrm{T,AB}}\right] + \Lambda_{12}(q)\left[-\frac{S_{0,12}(q)}{\Delta^0} + \frac{1}{S_{0,33}(q)}\right]\right\} \tag{61}$$

$$D_{12}(q) = -q^2\left\{\Lambda_{11}(q)\left[-\frac{S_{0,12}(q)}{\Delta^0} + \frac{1}{S_{0,33}(q)}\right] + \Lambda_{12}(q)\left[-\frac{S_{0,11}(q)}{\Delta^0} + \frac{1}{S_{0,33}(q)}\right]\right\} \tag{62}$$

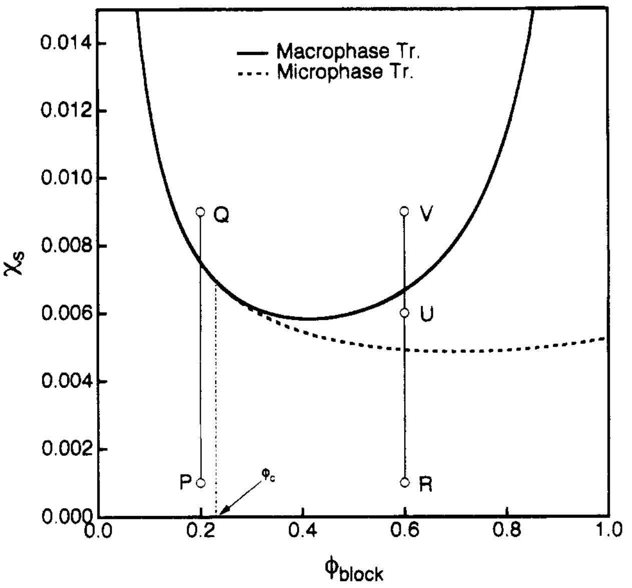

Figure 3. Stability limit of macrophase separation (solid line) and microphase separation (broken line) for the A–B/B mixture with $N_1 = N_2 = 1000$ and $N_3 = 1000$.

Table 1. Characteristic Parameters Used in This Study

N_1	1000	D_{b}, nm^2/s	0.25
N_2	1000	D_3, nm^2/s	1
N_3	1000	b, nm	0.7

$$D_{21}(q) = -q^2\left\{\Lambda_{12}(q)\left[\frac{S_{0,22}(q)}{\Delta^0} + \frac{1}{S_{0,33}(q)} - 2\chi_{\mathrm{T,AB}}\right] + \Lambda_{22}(q)\left[-\frac{S_{0,12}(q)}{\Delta^0} + \frac{1}{S_{0,33}(q)}\right]\right\} \tag{63}$$

and

$$D_{22}(q) = -q^2\left\{\Lambda_{12}(q)\left[-\frac{S_{0,12}(q)}{\Delta^0} + \frac{1}{S_{0,33}(q)}\right] + \Lambda_{22}(q)\left[-\frac{S_{0,11}(q)}{\Delta^0} + \frac{1}{S_{0,33}(q)}\right]\right\} \tag{64}$$

Finally, we calculate $S_{11}(q,t)$. Before the calculation, we have to obtain the diagonalized matrix $\mathbf{d}(q,t)$, $\mathbf{Q}$, and $\mathbf{Q}^{-1}$. The eigenvalues $\lambda_1(q)$ and $\lambda_2(q)$ are the solution of

$$[D_{11}(q) - \lambda(q)][D_{22}(q) - \lambda(q)] - D_{12}(q)D_{21}(q) = 0 \tag{65}$$

$\mathbf{Q}$ is

$$\mathbf{Q} = \begin{bmatrix} D_{12} & D_{12} \\ (\lambda_1 - D_{11}) & (\lambda_2 - D_{11}) \end{bmatrix} \tag{66}$$

Substituting eqs 65 and 66 into eq 35, we obtain $S_{11}(q,t)$:

$$S_{11}(q,t) = S_{\mathrm{eq},11}(q) + \frac{1}{(\lambda_1(q) - \lambda_2(q))^2}[a_1(q)\mathrm{e}^{2\lambda_1(q)t} + a_2(q)\mathrm{e}^{(\lambda_1(q)+\lambda_2(q))t} + a_3(q)\mathrm{e}^{2\lambda_2(q)}] \tag{67}$$

where

$$a_1(q) = (S_{11}(q,0) - S_{\mathrm{eq},11}(q))(\lambda_1(q) - D_{22}(q))^2 + 2(S_{12}(q,0) - S_{\mathrm{eq},12}(q))(\lambda_1(q) - D_{22}(q))D_{12}(q) + D_{12}(q)^2(S_{22}(q,0) - S_{\mathrm{eq},22}(q)) \tag{68}$$

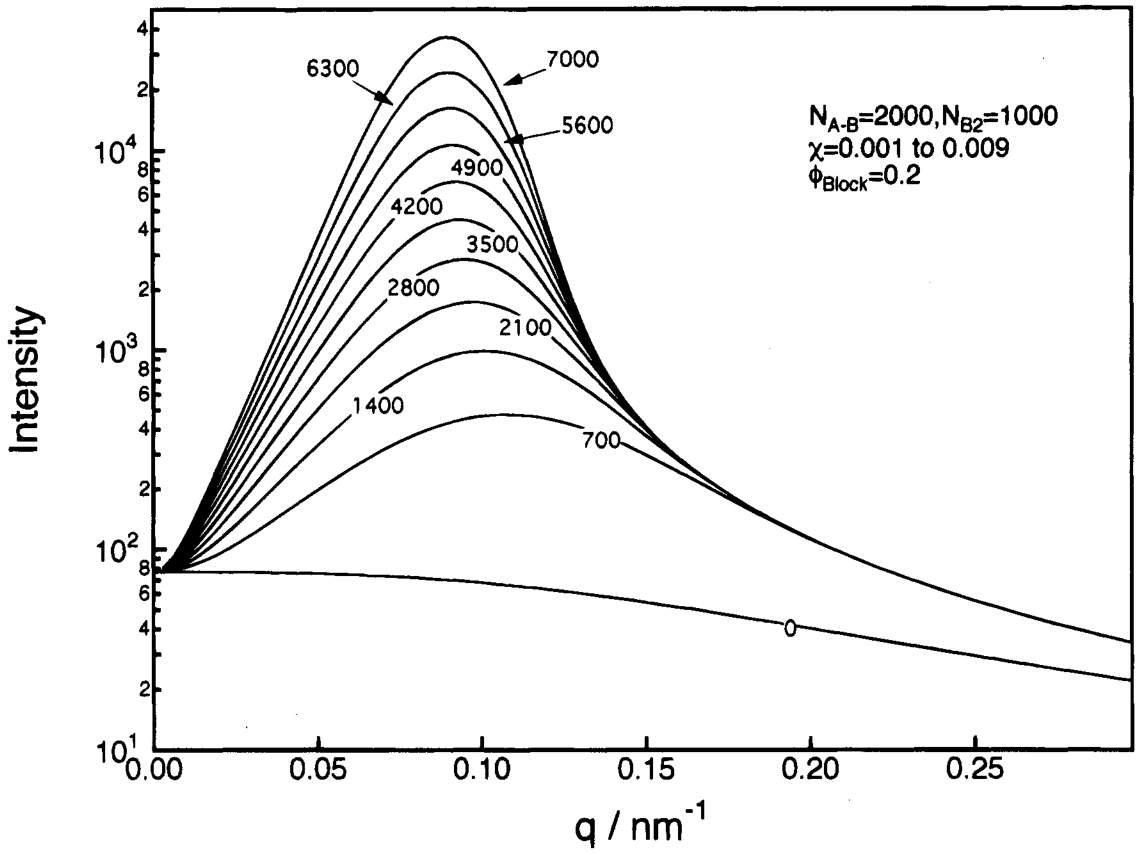

Figure 4. Time change in the structure factor for the A–B/B system with $\phi_b = 0.2$ quenched from $\chi = 0.001$ to $\chi = 0.009$. The unit of time indicated in the graph is seconds.

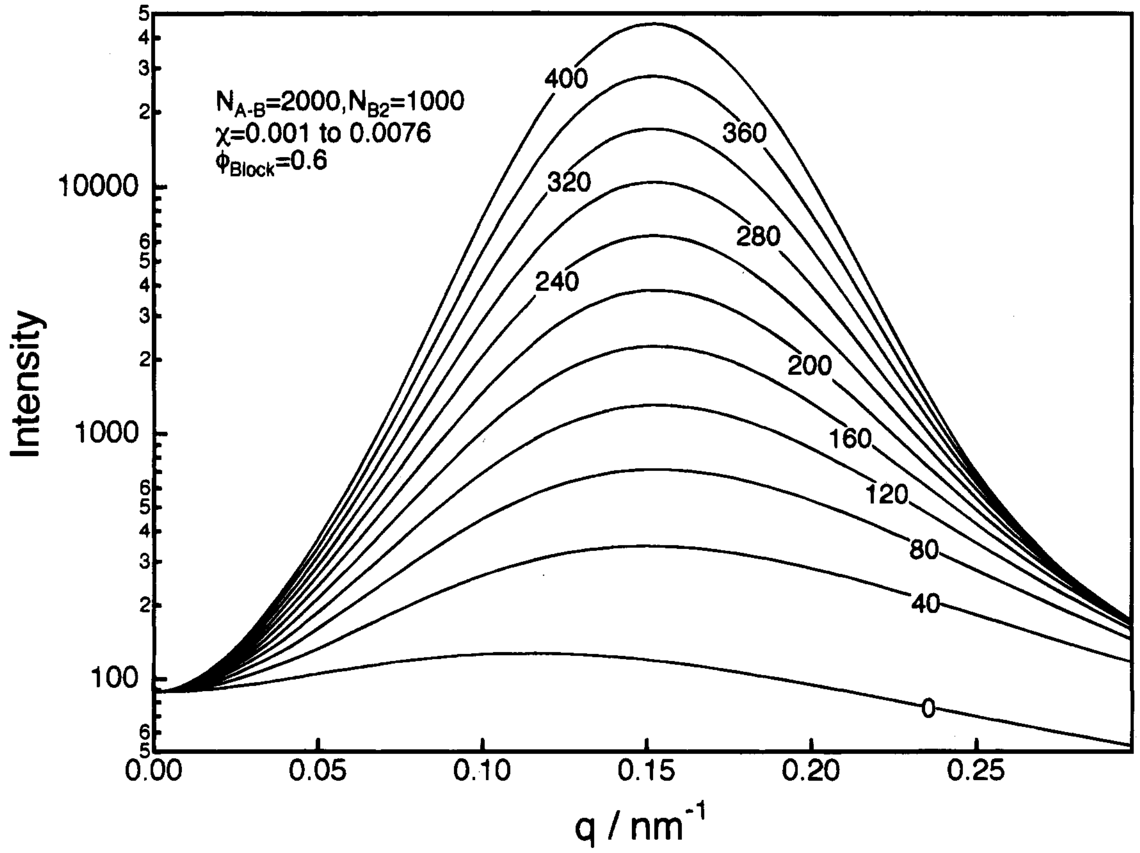

Figure 5. Time change in the structure factor for the A–B/B system with $\phi_b = 0.6$ quenched from $\chi = 0.001$ to $\chi = 0.0076$.

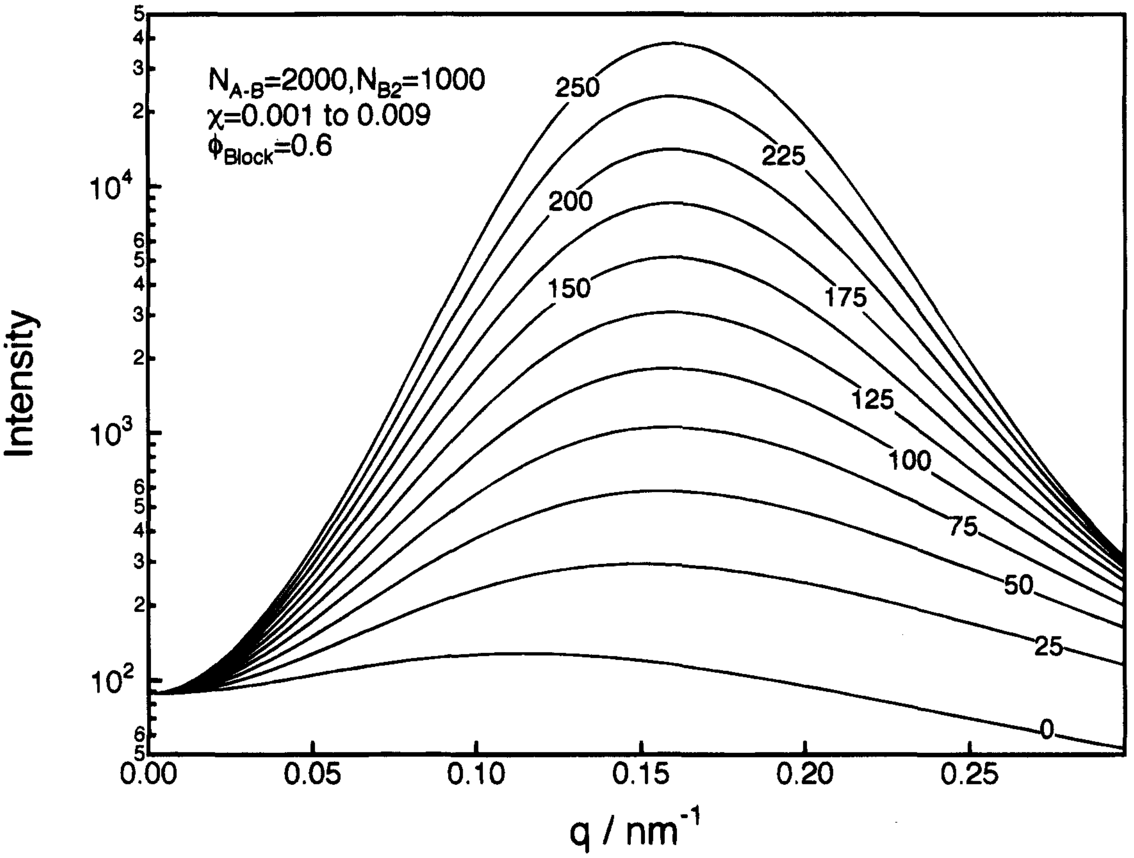

Figure 6. Time change in the structure factor for the A–B/B system with $\phi_b = 0.6$ quenched from $\chi = 0.001$ to $\chi = 0.009$.

$$a_2(q) = 2(\lambda_1(q) - D_{22}(q))(D_{22}(q) - \lambda_2(q))(S_{11}(q,0) - S_{eq,11}(q)) + 2D_{12}(q)(2D_{22}(q) - \lambda_1(q) - \lambda_2(q))(S_{12}(q,0) - S_{eq,12}(q)) - 2D_{12}(q)^2(S_{22}(q,0) - S_{eq,22}(q)) \quad (69)$$

and

$$a_3(q) = (S_{11}(q,0) - S_{eq,11}(q))(D_{22}(q) - \lambda_2(q))^2 - 2(D_{22}(q) - \lambda_2(q))D_{12}(q)(S_{12}(q,0) - S_{eq,12}(q)) + (S_{22}(q,0) - S_{eq,22}(q))D_{12}(q)^2 \quad (70)$$

Let us analyze the dynamics of spinodal decomposition in the A–B/B mixture by using eq 67. Tanaka and Hashimoto[1] investigated the phase diagram of the A–B/B mixture in detail by RPA. The stability limit of the mixture for macro separation can be calculated by setting the condition

$$S_{11}(q{=}0)^{-1} = 0 \quad (71)$$

If $S_{11}(q)$ has a peak at $q = q_m$, $S_{11}(q)$ has the microphase separation and the stability limit for the microphase separation can be calculated by setting

$$S_{11}(q{=}q_m)^{-1} = 0 \quad (72)$$

The results suggest that the mixture has both a microphase separation and a macrophase separation. Both phenomena depend on the volume fraction and the molecular weight of the constituent polymers in the mixture.

As an example, we calculated the dynamics of the A–B/B mixture shown in Table 1, where we assumed that the diffusion coefficient is independent of temperature. Figure 3 shows the phase diagram of the mixture used in this calculation. As indicated by Hashimoto and Tanaka,[1] the mixture showed only macrophase separation at $\phi_b < \phi_c$ but macrophase separation and/or microphase separation at $\phi_b > \phi_c$. We calculated three cases: (i) The quench from P to Q. This quench is expected to induce only the macrophase separation. (ii) The quench from R to U. The point S is below the stability limit of the macrophase separation but above that of the microphase separation. Thus only microphase separation progresses. (iii) The quench from R to V where both micro- and macrophase separation are expected to occur.

Figure 4 shows the time change in the structure factor of the A–B/B system with $\phi_b = 0.2$ quenched from P ($\chi = 0.001$) to Q ($\chi = 0.009$). The peak appears at $q = 0.11$ nm^{-1} and $t = 700$ s and the peak shifts to a small q region. This shift was also shown in the time change of the scattered intensity of homopolymer blends calculated by Strobl.[25]

The time change in the structure factor of the A–B/B system with $\phi_b = 0.6$ quenched from R ($\chi = 0.001$) to U ($\chi = 0.0076$) is plotted as a function of q in Figure 5. The interesting feature on the time change in the structure factor is that the peak at $q = 0.11$ nm^{-1} and $t = 0$ s shifts to larger q values with time in the early time region. This is because the effects of thermal fluctuations. After $t = 80$ s, the peak shifts to smaller q values.

The calculated results for the system quenched from R ($\chi = 0.001$) to V ($\chi = 0.009$) where the concentration fluctuation mode at $q = 0$ is unstable are shown in Figure 6. The same tendency shown in Figure 5 is observed in Figure 6. This is because the q value at which the structure factor grows with the maximum rate for Figure 5 is almost the same for Figure 6, even though the concentration fluctuation mode at $q = 0$ is unstable. Unfortunately, this equation is valid only in the early stage of spinodal decomposition, where the concentration fluctuations are small, so that we cannot simulate the microphase separation induced by macrophase separation. We should observe the difference in the time change in the structure factor between the quench from R to U and that from R to V at a further time region where nonlinear effects become important.

IV. Conclusion

In this paper, we have proposed a method to calculate the dynamics of the early stage spinodal decomposition for multicomponent polymer systems by using the generalized CHC theory and the RPA. We considered the q-dependent Onsager kinetic coefficient by following the Kawasaki and Sekimoto theory and obtained explicit expressions to describe the time change in the structure factor for an A−B/B mixture. The time change for three quench conditions have been calculated as an example. In a forthcoming paper,[26] we plan to calculate the compatibilizer effects of the A−B block copolymer in the dynamics of A/B/A−B mixtures.

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