erican Chemical Society: Washington, D.C.; Symposium Series, 1984; Vol. 266, pp 293-310.
(22) Harrah, L. A.; Zeigler, J. M. In *Photophysics of Polymers*; Hoyle, C. E., Torkelson, J. M., Eds.; ACS Symposium Series 358; American Chemical Society: Washington, D.C., 1987; pp 482-498.
(23) Harrah, L. A.; Zeigler, J. M. *Bull. Am. Phys. Soc.* **1985**, *30*, 540.
(24) Cotts, P. M.; Miller, R. D.; Trefonas, P., III; West, R.; Fickes, G. N. *Macromolecules* **1987**, *20*, 1046.
(25) Lim, K. C.; Heeger, A. J. *J. Chem. Phys.* **1985**, *82*, 522.
(26) Plachetta, C.; Rau, N. O.; Schulz, R. C. *Mol. Cryst. Liq. Cryst.* **1983**, *96*, 141.

Concentration Dynamics in Polymer Blends and Block Copolymer Melts

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ABSTRACT: The theory of slow dynamics of monomer concentrations in polymer blends and block copolymer melts developed earlier by the present authors is reconsidered when the incompressibility condition is replaced by the condition of constant chemical potential for the total monomer density. This results in modifications of earlier results even for the symmetric polymer blends where the same results are obtained for macroscopic interdiffusion. Linearized equations of motion for concentration deviations from homogeneous states as well as from the equilibrium lamellar state are derived, the latter giving rise to phase equations for long-wavelength deformations of lamellae. For blends in the strong segregation regime, we find the diffusion along interfaces of the type considered by Mullins, giving rise to the $^1/_4$ power law for the domain growth in time. This process, however, is masked by faster hydrodynamic growth process.

1. Introduction

Dynamics of macroscopic phase separation in polymer blends and microphase separation in block copolymers is one of the most interesting but still poorly understood problems in phase transition studies and in polymer sciences.[1] A major source of difficulty resides, of course, in our incomplete understanding of chain dynamics in polymer melts. Nevertheless, a wealth of experimental studies has been accumulated that motivates one to attempt theoretical understanding of these problems. We presented such attempts[2] stimulated by the pioneering works of de Gennes, Pincus, Binder, and others.[3] One of the crucial assumptions made in these theories is that the system is totally incompressible. A consequence of this is that polymer chains cannot move independently even for the mean field type reptation model, but correlations are introduced among moving parts of chains that form temporary rings.[2,4]

Difficulty of polymer chain dynamics in melts, however, precludes a priori judgement of validity of incompressibility, for which we must rely on tests by laboratory experiments or computer simulations.

Experimental tests of the incompressibility assumption have been performed recently for the related but somewhat different problem of interdiffusion in compatible polymer blends. Here two theories have so far been put forward that give quite different predictions. One is based on the incompressibility assumption[5] (slow process) whereas the other assumes the constant chemical potential for the total monomer density[6] (fast process). The available experimental evidence seems to exclude the prediction based on the incompressibility assumption.[6] In Appendix A we discuss the problem of bulk flow in the context of this work. This development thus necessitates reconsideration of earlier theories of phase-separation dynamics, which is the purpose of this paper.

In the next section we summarize the main results of this work and intuitive discussions will be given wherever appropriate. Derivations of these results and some formal developments are contained in the sections that follow. This reconsideration is important even for the so-called symmetric polymer blends[6] where the difference between the two theories vanishes for macroscopic interdiffusion taking place in the homogeneous background (Appendix A). In section 3 we develop a general theory of concentration dynamics for polymer blends and diblock polymers in which only relative monomer concentrations are the slow variables. This means that the total monomer density is eliminated by requiring that the chemical potential associated with the total monomer density is constant. The theory is first applied in section 4 to the simplest problem of dynamics of small concentration deviations from the uniform background in blends and diblocks. Section 5 deals with linear dynamics of small concentration deviations in the equilibrium lamellar phase of diblocks. The result is used in section 6 to investigate dynamics of smooth deformations of lamellar structure, which can be shown to be described by a phase equation. Explicit results are obtained for the weak segregation regime. In section 7 we are concerned with the late-stage phase separation of blends where the problem can be reduced to dynamics of interfaces.

2. Main Results with Intuitive Discussions

In this section we summarize main concrete results of this paper and also give intuitive explanations wherever appropriate. We first take up the slow dynamics of the smooth deformation field $u(\mathbf{r}, t)$ of the lamellar mesophase pattern of the block copolymer system. This is an analogue of the deformation of roll patterns in Rayleigh-Benard convection or of layers in the smectic A phase of liquid crystals.[7] Here, $u(\mathbf{r}, t)$ is found to satisfy the following phase equation[8] when the undeformed lamellae are in the xy plane

$$\frac{\partial}{\partial t}u(\mathbf{r}, t) = \left(D_z\frac{\partial^2}{\partial z^2} + D_\perp\nabla_\perp{}^4\right)u(\mathbf{r}, t) \qquad (2.1)$$

where $\nabla_\perp{}^4 = (\nabla_\perp{}^2)^2$ with $\nabla_\perp{}^2 \equiv (\partial/\partial x)^2 + (\partial/\partial y)^2$. The two terms in (2.1) describe the two types of deformations shown, respectively, by the left and right figures of Figure 1. For the compressible case now under consideration and in the weak segregation regime the coefficients in (2.1) are

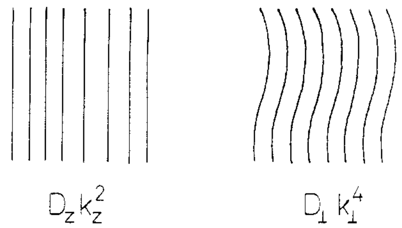

Figure 1. Lines of constant phase of lamellar structure associated with the two types of deformations in (6.12).

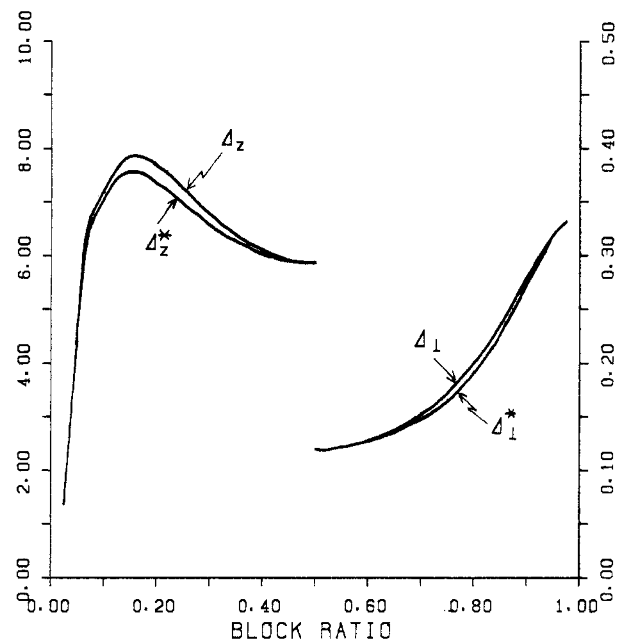

Figure 2. Values of Δ_z, Δ_z^*, $\Delta_\perp$, and $\Delta_\perp^*$ plotted as functions of the block ratio. Only half of the curves are shown in view of the symmetry about 0.5 of the block ratio.

obtained explicitly by employing the reptation model[9] and are found to be given by

$$D_z = \frac{D_1}{N^2}\Delta_z \qquad D_\perp = \frac{D_1 b^2}{4N}\Delta_\perp \tag{2.2}$$

where N, b, and D_1 are the polymerization index, the Kuhn length, and the monomer diffusion constant, respectively. Δ_z and $\Delta_\perp$ are functions of the block ratio and are shown in Figure 2, where the corresponding functions with asterisks for the previously obtained incompressible case[10] are also depicted. We see that the results are very close to each other. This is to be more or less anticipated because here we are dealing with the same type of chains in contrast to blends where different center of mass motions of different molecular species come into play. Hence, we expect the situation to be quite different for multicomponent systems like blends of two block copolymers. The same remark applies to the wavenumber-dependent Onsager kinetic coefficient in (2.9) as will be discussed at the end of section 4.

We now consider a polymer blend in the strong segregation regime (SSR) with sharp interfaces dividing A-rich and B-rich domains, which occur at late stage of phase separation. For the incompressible case that we have already considered[2] the dominant mechanism for morphology change is the correlated reptation loop process as depicted in Figure 3 where solid and wavy lines represent, respectively, the A-type and B-type chains lined up to form a loop that moves in the direction of arrows. Note that loop processes of this kind need not be restricted to the naive reptation process[9] but can include processes where the loop is formed from portions of chains that perform concerted motions along the loop such as the one considered by Pakula.[4] The process is characterized by a pair of a source and a sink of $\rho_A(\mathbf{r})$ on the domain wall, respectively, indicated by Q_0 and Q_i in the Figure 3. Thus, if we consider a region containing either one of the source or the sink but not both, there is a net increase or decrease of the A-type monomers within the region. In other words, there is an apparent violation of the conservation law on a small scale. This leads to the familiar Lifshitz–Allen–Cahn law of curvature-driven domain wall motion without conservation[11]

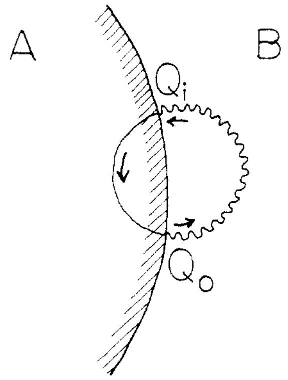

Figure 3. Correlated reptation loop passing through a domain wall. Solid and wavy lines represent portions of the loop involving A- and B-type chain segments, respectively.

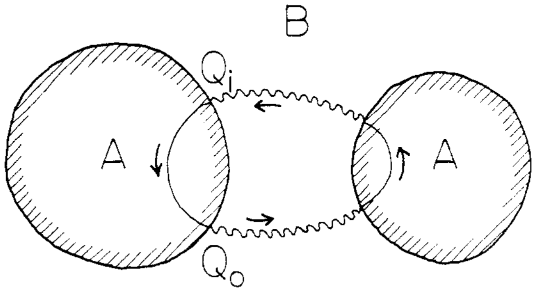

Figure 4. Correlated reptation loop connecting two isolated domains.

$$v = D\mathcal{H} \tag{2.3}$$

where v is the velocity along the wall normal, $\mathcal{H}$ is the mean curvature, and D is the polymer self-diffusion constant apart from some dimensionless numerical factor, which may take large values if only small portions of chains are involved. This gives rise to the $t^{1/2}$ law of coarsening at some early stages characterized by small length scales.[2] We note that the result obtained here is a consequence of the *effective* long-distance hopping of monomers and is not restricted to the particular kinds of processes considered here. Here, the incompressibility condition may not be indispensable but helps to extend the hopping distance by introducing correlations ("rigidity") into the system as will be discussed below.

For later stages of coarsening where length scales are greater than the typical distance of a source–sink pair, the conservation law manifests itself and the $t^{1/3}$-growth law was recovered. However, it is important to point out a special feature of this case distinguishing it from the more usual Lifshitz–Slyozov type processes for small molecules.[12] This arises from the fact that in SSR a polymer chain (e.g. of the A-type) practically cannot move through wrong domains (e.g. consisting of the B-type chains). To illustrate the point consider two isolated A-type domains floating in the sea of B-type domain as depicted in Figure 4 where a loop passing through the two A-type domains is also

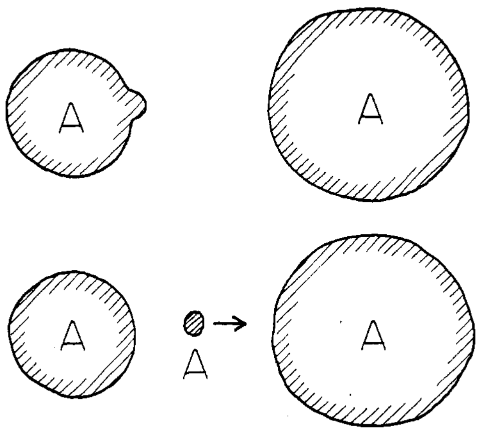

Figure 5. Material transfer between two isolated domains for small molecular system.

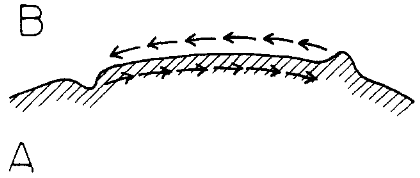

Figure 6. Material transfer along a domain wall.

shown. There is no net transfer of A-type monomers between the two A-type domains. This is contrasted with the Lifshitz–Slyozov type process as depicted in Figure 5, where net transfer is permitted, and thus each isolated domain can act as a net source or a sink. For the polymer case, on the other hand, each domain can contain only a pair of source and sink (i.e. a dipole) and no net transfer into or out of an isolated domain is permitted. This is explicitly demonstrated in Appendix E of ref 2a for the naive reptation process. Late-stage phase-separation kinetics of polymer blends for the incompressible case based on the reptation picture was discussed in ref 2 and will not be repeated.

We now turn to the case where the incompressibility condition is replaced by the other extreme condition that the total density adiabatically follows change of the relative concentration (the so-called fast diffusion case) expressed as the requirement of the constant chemical potential conjugate to the total density. In SSR a change of the relative concentration, which is again limited to the vicinity of domain walls since a polymer chain practically cannot wander into "wrong" domains here also, is accompanied by a change in the total density, i.e. a change in the number density of vacancies in the lattice model. (Actually, here we mean the total density change, which still remains after the bulk flow has taken place; see Appendix A.) In the present case the total density variation cannot propagate far away from the domain wall region since the relative concentration is fixed there. "Vacancies" and hence the relative concentration change will then be transported along the domain wall as is shown in Figure 6. The elementary steps associated with such a transport will extend only over finite distances in the absence of rigidity. In the absence of the total density change associated with a relative concentration change, basically the same picture holds where the relative concentration is directly transported along the domain walls. We denote this distance by R_T. The situation like this where, however, R_T is of atomic scale has been considered by Mullins.[13] He showed that when the length R_T is much smaller than the radii of curvature of domains, (2.3) is to be replaced by

$$v = D'R_T^2 \nabla_a^2 \mathcal{K} \tag{2.4}$$

with D' another diffusion constant than D where ∇_a^2 is the Laplacian acting on the domain wall. It is also known that this leads to the $t^{1/4}$ law of coarsening.[14] Note that here again no net material transfer occurs between isolated domains as in the incompressible case. The reptation model estimate gives

$$D'R_T^2 \sim D_{\text{rep}} R_G \xi \tag{2.5}$$

where D_{rep} is the reptation result for the self-diffusion constant, R_G the gyration radius of a chain, and ξ thickness of the interface. The very slow process considered here, however, is normally masked by much faster hydrodynamic process.[24]

It is instructive to compare (2.3) with D equated to D_{rep} and (2.4) with (2.5). The ratio of (2.3) and (2.4) is

$$(2.4)/(2.3) \sim D_{\text{rep}} R_G \xi \nabla_a^2 \mathcal{K} / D_{\text{rep}} \mathcal{K} \tag{2.6}$$

For $\mathcal{K} \sim l^{-1}$, l being the average domain size, we estimate for $l < R_G^2/\xi$ where (2.1) is valid, (2.6) $\sim R_G \xi / l^2$, which is very small for the length scale of our interest l much greater than R_G. For $l > R_G^2/\xi$ where the right-hand side (rhs) of (2.1) acquires an additional factor $R_G^2/\xi l$ (see ref 2), the above ratio becomes $\xi^2/R_G l$, which is again very small. Thus we see that the process described by (2.4) is indeed a very slow process counteracting with our expectation that the fast process should give rise to faster domain growth. This is due to the fact that the words fast and slow processes[5,6] are appropriate only when one is dealing with diffusion in a uniform background.[5,6] The condition of constant chemical potential in fact gives rise to another constraint than incompressibility, which restricts the chain movements effectively to very narrow regions of the width ξ surrounding the interface.

Here, we have examined the two extreme cases where the total density cannot change at all or adiabatically follows the concentration change. These are the two special cases of a more general situation in which the total density behaves as an independent dynamical variable. An example of theory that deals with such a situation in the framework of a lattice model is the work of Schichtel and Binder[15] where vacancies are permitted to move independently. In a continuum theory this can be done by introducing the heat mode since the remaining sound wave modes vary too fast and drop out in the slow concentration dynamics.

As byproducts of this work we obtain the explicit expressions for the wavenumber-dependent Onsager kinetic coefficients denoted as $\hat{\Lambda}_S(k)$, which are associated with the decay rates of the concentration deviation from uniform background for both polymer blend and block copolymer system in the compressible case. This is summarized here.

For a blend with the relative concentration S_0 of two kinds of polymer with polymerization indices N_A and N_B we have

$$\hat{\Lambda}_S(k) = \frac{2D_1}{T\rho_0 b^2} S_0(1 - S_0)\left[\frac{1 - S_0}{N_A^2}\eta_k(N_A) + \frac{S_0}{N_B^2}\eta_k(N_B)\right] \tag{2.7}$$

where T is the temperature, ρ_0 is the total number density of monomer, and

$$\eta_k(N) \equiv 1 - \exp\left(-\frac{1}{6}k^2 b^2 N\right) \tag{2.8}$$

The corresponding expression for a diblock copolymer system with the polymerization index N and the block ratio S_0 is

$$\hat{\Lambda}_S(k) = \frac{2D_1}{T\rho_0(Nb)^2}[(1 - S_0)^2\eta_k(NS_0) + S_0{}^2\eta_k[N(1 - S_0)] + S_0(1 - S_0)\eta_k(NS_0)\eta_k[N(1 - S_0)]] \tag{2.9}$$

3. Equation of Motion for Monomer Concentrations

We consider a general multicomponent polymer system whose chains contain monomers of various species K = A, B, ... We will be interested in very slow morphology change, which is assumed to be described by a set $\{\rho\}$ of the local monomer density fields[7] $\rho_K(\mathbf{r}, t)$, K = A, B, ... Then we can start from the general kinetic equations of change for $\{\rho\}$ as follows (the random force will be consistently omitted here and the argument t is suppressed for simplicity)[2]

$$\frac{\partial}{\partial t}\rho_K(\mathbf{r}) = -\sum_{K'}\int \mathrm{d}\mathbf{r}'\ \Lambda_{KK'}(\mathbf{rr}')\mu_{K'}(\mathbf{r}') \tag{3.1}$$

$$\mu_K(\mathbf{r}) \equiv \delta H\{\rho\}/\delta\rho_K(\mathbf{r}) \tag{3.2}$$

$$\Lambda_{KK'}(\mathbf{rr}') \equiv \left\langle \frac{\partial\hat{\rho}_K(\mathbf{r})}{\partial\mathbf{c}}\cdot\hat{\Lambda}(\mathbf{c})\cdot\frac{\partial\hat{\rho}_{K'}(\mathbf{r}')}{\partial\mathbf{c}} \right\rangle_{\{\rho\}} \tag{3.3}$$

$$H\{\rho\} \equiv -k_{\mathrm{B}}T \ln \int_{\{\rho\}}\mathrm{d}\mathbf{c}\ e^{-\hat{H}\{\mathbf{c}\}/k_{\mathrm{B}}T} \tag{3.4}$$

Here, $\mathbf{c}$ denotes a configuration of the entire system of chains with the free energy $\hat{H}(\mathbf{c})$. Then chain dynamics is formally expressed as

$$\frac{\partial}{\partial t}\mathbf{c} = -\hat{\Lambda}(\mathbf{c})\cdot\partial\hat{H}(\mathbf{c})/\partial\mathbf{c} + \text{random force term} \tag{3.5}$$

where $\mathbf{c}$ is thought to be arranged as a vector in the chain configuration space and $\hat{\Lambda}(\mathbf{c})$ is the symmetric kinetic matrix in this space. $\hat{\rho}_K(\mathbf{r})$ is the microscopic expression in terms of $\mathbf{c}$ for the monomer density $\rho_K(\mathbf{r})$. The angular bracket in (3.3) denotes the local equilibrium averages with the constraint $\hat{\rho}_K(\mathbf{r}) = \rho_K(\mathbf{r})$ for every K and $\mathbf{r}$, and the integration in (3.3) is restricted to the region satisfying $\hat{\rho}_K(\mathbf{r}) = \rho_K(\mathbf{r})$. The explicit formal details can be found in section 2 of ref 2a. Here we point out that $\Lambda_{KK'}(\mathbf{rr}')$ has contributions mainly from $|\mathbf{r} - \mathbf{r}'|$ less than about the end-to-end distance of polymer provided that each chain is assumed to move independently in the mean field formed by other chains like the reptation model.[9] The fundamental assumption for (2.1) is that there exists a dynamical regime in which the local monomer densities are the only slow variables, to which all other variables are "slaved", i.e. assume their local equilibrium values. This is a nontrivial assumption. For instance the local segment orientation may take very long times to relax, for instance, in lamellar phase of block copolymers where chains are already elongated in the equilibrium state.[17] Nevertheless, in this work we adopt this assumption since this is the simplest one to make for studying morphology dynamics and work out its consequence, which can be tested by experiments and computer simulations. We also remark here that the local quantities such as $\hat{\rho}_K$, ρ_K, and μ_K should in fact be defined over a suitably chosen coarse-graining volume. The linear size of this volume must be much greater than the chain segment length to justify the continuum description but must be much smaller than the linear size of a chain in order to see polymer effects such as apparent violation of conservation for the incompressible case.

$H\{\rho\}$ is the free-energy functional, $\mu_K(\mathbf{r})$ is the local chemical potential, and $\Lambda_{KK'}(\mathbf{rr}')$ represents a generalization of the Onsager kinetic coefficient. All these quantities depend functionally on $\{\rho\}$ and hence can change in time.

In the following it is convenient to use the matrix notation in the $\mathbf{r}$ space so that ρ_K and μ_K denote vectors with their $\mathbf{r}$ components $\rho_K(\mathbf{r})$ and $\mu_K(\mathbf{r})$, respectively, and $\Lambda_{KK'}$ the matrix with the $\mathbf{rr}'$ elements given by

$$\langle\mathbf{r}|\Lambda_{KK'}|\mathbf{r}'\rangle = \Lambda_{KK'}(\mathbf{rr}') \tag{3.6}$$

Thus (3.1) is written simply as

$$\frac{\partial}{\partial t}\rho_K = -\sum_{K'}\Lambda_{KK'}\mu_{K'} \tag{3.7}$$

Here we note two properties of $\Lambda_{KK'}$ which also follow directly from (3.3). One is the Onsager reciprocity reflecting the symmetry of $\hat{\Lambda}(\mathbf{c})$:

$$\langle\mathbf{r}|\Lambda_{KK'}|\mathbf{r}'\rangle = \langle\mathbf{r}'|\Lambda_{K'K}|\mathbf{r}\rangle \tag{3.8}$$

Another comes from the conservation law for each species:

$$\int \frac{\partial}{\partial t}\ \rho_K(\mathbf{r}, t)\ \mathrm{d}\mathbf{r} = 0 \tag{3.9}$$

That is

$$\int \langle\mathbf{r}|\Lambda_{KK'}|\mathbf{r}'\rangle\ \mathrm{d}\mathbf{r}' = \int \langle\mathbf{r}|\Lambda_{KK'}|\mathbf{r}'\rangle\ \mathrm{d}\mathbf{r} = 0 \tag{3.10}$$

The last result implies that $\mu_K(\mathbf{r})$ is arbitrary up to an additive constant.

Before proceeding further we encounter a problem. Even though variations of relative concentrations of different species of monomers can be very slow since driving forces for them are chemical rather than mechanical, this is not so for the total density

$$\rho_T \equiv \sum_K \rho_K \tag{3.11}$$

which can be driven by mechanical forces. There are two simple ways to deal with the total density. One is to assume that the system is completely incompressible as we have done previously.[2,3] This leaves no room for free volume to play a role in the system and brings in certain rigidity in a general sense[18] and hence long-range dynamical correlations such as correlated reptations of polymer chains.[2,4] Another approach is to assume that the total density is also slaved to the assumed slowly varying relative concentration fields defined by

$$S_K \equiv \rho_K/\rho_T \tag{3.12}$$

This assumption is formally expressed by requiring that the total chemical potential

$$\mu_T(\mathbf{r}) \equiv \delta H\{\rho\}/\delta\rho_T(\mathbf{r}) = \sum_K S_K(\mathbf{r})\mu_K(\mathbf{r}) \tag{3.13}$$

takes on a constant value, say, μ_0.[19] This assumption, in fact, is equivalent to that made by Kramer and co-workers[6] in interpreting the experimental results of interdiffusion of compatible polymer blends. Expressing $H\{\rho\}$ as a functional of S_K and ρ_T, we have (we often suppress the arguments $\mathbf{r}$ unless confusion arises)

$$\mu_K = \mu_0 + \sum_{K'}\frac{\partial S_{K'}}{\partial\rho_K}\mu^S_{K'} \tag{3.14}$$

with

$$\mu^S_K \equiv \delta H\{\rho_T, S\}/\delta S_K \tag{3.15}$$

$$\partial S_K/\partial\rho_{K'} = \delta_{KK'}/\rho - \rho_K/\rho^2 \tag{3.16}$$

From (3.7) we find using (3.14) and (3.10) the following equation of motion for S_K

$$\frac{\partial}{\partial t}S_K = -\sum_{K'}\Lambda^S_{KK'}\mu^S_{K'} \tag{3.17}$$

with

$$\Lambda^S_{KK'} \equiv \sum_{\bar{K}\bar{K}'}(\partial S_K/\partial\rho_{\bar{K}})\Lambda_{\bar{K}\bar{K}'}(\partial S_{K'}/\partial\rho_{\bar{K}'}) \tag{3.18}$$

In (3.15) the derivative is taken with fixed ρ_T. However, we can include the variation of ρ_T in the definition since using $\mu_T(\mathbf{r}) = \mu_0$ the difference amounts to

$$\int \frac{\delta H}{\delta\rho_T(\mathbf{r}')}\frac{\delta\rho_T(\mathbf{r}')}{\delta S_K(\mathbf{r})}\,d\mathbf{r}' = \mu_0\frac{\delta}{\delta S_K(\mathbf{r})}\int\rho_T(\mathbf{r}')\,d\mathbf{r}' = 0 \tag{3.19}$$

by constancy of the total segment number. The set of equations (3.17) are of course not completely independent because of the identity $\sum_K S_K = 1$.

Here, of course, abandoning of incompressibility does not immediately imply that the system is infinitely compressible. Since we assume the local equilibrium throughout, the total density is given by the usual thermodynamic relation (constitutive relation) $\rho_T = \rho_T(T, \mu_T, \{S\})$ where $\{S\}$ represents the set S_K. The incompressibility condition means that ρ_T is fixed to the same value everywhere in the system, which can be done by varing μ_T. Here, we are replacing this condition by the requirement that μ_T is fixed to the same value μ_0 everywhere. Physically, this implies that ρ_T follows very rapidly to the variation of $\{S\}$. This automatically determines ρ_T, which, however, need no longer assume the same value throughout the system since $\{S\}$ need not be the same everywhere.

In the following we shall limit ourselves to the binary system K = A and B and denote $S_{\rm A}$ and ρ_T simply as S and ρ, respectively, so that $S_{\rm B} = 1 - S$. Then (3.17) reduces using (3.16) to

$$\frac{\partial}{\partial t}S = -\Lambda_S\mu_S \tag{3.20}$$

where

$$\mu_S = \delta H/\delta S \tag{3.21}$$

$$\Lambda_S \equiv \frac{1-S}{\rho}\Lambda_{\rm AA}\frac{1-S}{\rho} + \frac{S}{\rho}\Lambda_{\rm BB}\frac{S}{\rho} - \frac{1-S}{\rho}\Lambda_{\rm AB}\frac{S}{\rho} - \frac{S}{\rho}\Lambda_{\rm BA}\frac{1-S}{\rho} \tag{3.22}$$

For later convenience here we give an alternative expression for $\Lambda_{KK'}$, (3.3). For this purpose we write out (3.3) more explicitly as

$$\Lambda_{KK'}(\mathbf{r}\mathbf{r}') = \left\langle \sum_{ij}\sum_{\tau}^{(K)}\sum_{\tau'}^{(K')}\frac{\partial\hat{\rho}^i_\tau(\mathbf{r})}{\partial\mathbf{c}^i_\tau}\cdot\hat{\Lambda}^{ij}_{\tau\tau'}(\mathbf{c})\cdot\frac{\partial\hat{\rho}^j_{\tau'}(\mathbf{r}')}{\partial\mathbf{c}^j_{\tau'}}\right\rangle_{\{\rho\}} \tag{3.23}$$

where $\mathbf{c}^i_\tau$ is the position vector of the τth segment of the ith chain, the sum over $\tau(\tau')$ is limited to the $K(K')$-type segments and

$$\hat{\rho}^i_\tau(\mathbf{r}) \equiv \delta(\mathbf{r} - \mathbf{c}^i_\tau) \tag{3.24}$$

× 3 tensor. Since

$${}^i_\tau(\mathbf{r}) = -\nabla\hat{\rho}^i_\tau(\mathbf{r}) \tag{3.25}$$

ases, say,
phase state

$${}^i_\tau(\mathbf{r})\cdot\hat{\Lambda}^{ij}_{\tau\tau'}(\mathbf{c})\cdot\nabla'\hat{\rho}^j_{\tau'}(\mathbf{r}')\rangle_{\{\rho\}} \tag{3.26}$$

This expression shows that $\Lambda_{KK'}(\mathbf{r}\mathbf{r}')$ is nonvanishing only if the K-type monomer density and the K'-type monomer density are nonvanishing at $\mathbf{r}$ and $\mathbf{r}'$, respectively.

Finally, we here reproduce the concrete expressions for $\Lambda_{KK'}$ obtained earlier[2] when the biased reptation model[20] in the mean field due to averaged chain interactions is adopted for chain dynamics.

For binary blend we have

$$\Lambda_{KK'} = \Lambda_K\delta_{KK'} \tag{3.27}$$

$$\langle\mathbf{r}|\Lambda_K|\mathbf{r}'\rangle = \frac{2D^K_{\rm c}}{T}[p_K(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}') - P_{0,N_K}(\mathbf{r}\mathbf{r}')] \tag{3.28}$$

where $D^K_{\rm c}$ is the diffusion constant of a K-type chain along the tube, $P_{0,N_K}(\mathbf{r}\mathbf{r}')$ is the density correlation of two end segments of K-type chains at $\mathbf{r}$ and $\mathbf{r}'$ normalized such that

$$p_K(\mathbf{r}) = \int P_{0,N_K}(\mathbf{r}\mathbf{r}')\,d\mathbf{r}' \tag{3.29}$$

gives the density of one end of chains, all evaluated in the local equilibrium state of fixed concentration distribution $\{\rho\}$.

For AB diblocks, we give an abbreviated matrix expression for $\Lambda_{KK'}$ as ($D_{\rm c}$ is the tube diffusion constant of a whole chain)

$$\Lambda_{\rm AA} = \frac{D_{\rm c}}{T}(P_{00} - P_{0J} - P_{J0} + P_{JJ})$$

$$\Lambda_{\rm AB} = \frac{D_{\rm c}}{T}(P_{0J} - P_{0N} - P_{JJ} + P_{JN})$$

$$\Lambda_{\rm BA} = \frac{D_{\rm c}}{T}(P_{J0} - P_{N0} - P_{JJ} + P_{NJ})$$

$$\Lambda_{\rm BB} = \frac{D_{\rm c}}{T}(P_{JJ} - P_{JN} - P_{NJ} + P_{NN}) \tag{3.30}$$

where 0, J, and N denote the segments at τ = 0, $N_{\rm A}$, and $N = N_{\rm A} + N_{\rm B}$, respectively, and

$$\langle\mathbf{r}|P_{00}|\mathbf{r}'\rangle = p_0(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}'),\ \text{etc.} \tag{3.31}$$

P_{0J}, etc., denote various density correlations involving polymer ends and junction points, etc., which are normalized as in (3.29).

We observe here that in any mean-field-type dynamical model where individual chains move independently in the mean field determined by fixed configurations of other chains, $\hat{\Lambda}^{ij}_{\tau\tau'}(\mathbf{c})$ is nonvanishing only for $i = j$. This means that in each term in (3.26) a single chain must pass through $\mathbf{r}$ and $\mathbf{r}'$ implying that $\Lambda_{KK'}(\mathbf{r}\mathbf{r}')$ has the range of the size of a single chain.

4. Linear Dynamics of Concentration Deviations from Uniform Background

Here we consider linear dynamics of concentration deviation $\delta S(\mathbf{r}, t)$ from its uniform background value S_0. It is then sufficient to consider a single Fourier component $\hat{S}_{\mathbf{k}}(t)$ of $\delta S(\mathbf{r}, t)$ in view of the translation invariance of the uniform background state where $\langle\mathbf{r}|\Lambda_S|\mathbf{r}'\rangle$ in the uniform state and $\mu_S(\mathbf{r})$ have Fourier components $\hat{\Lambda}_S(k)$ and $\hat{H}_{SS}(k)\hat{S}_{\mathbf{k}}$, respectively, where $\hat{H}_{SS}(k)$ is the Fourier component of $\delta^2H\{S\}/\delta S(\mathbf{r})\delta S(\mathbf{r}')$ evaluated also in the uniform state where $H\{S\}$ is interpreted to be $H(\{\rho_T\{S\}\}, \{S\})$ with $\rho_T\{S\}$ adiabatically determined as was discussed in section 2. We then find

$$\frac{\partial}{\partial t}\hat{S}_{\mathbf{k}} = -\Gamma_k\hat{S}_{\mathbf{k}} \tag{4.1}$$

$$\Gamma_k \equiv \hat{\Lambda}_S(k)\hat{H}_{SS}(k) \tag{4.2}$$

In the following we adopt the biased reptation model and consider blends and diblocks in turn.

Blend. Here we use (3.28). p_K is then a constant equal to the uniform chain number density so that $p_A = \rho_0 S_0/N_A$ and $p_B = \rho_0(1 - S_0)/N_B$ with ρ_0 the uniform constant value of ρ_T. For Gaussian chains with the Kuhn length b we also find that $P_{0N}(\mathbf{rr}')$ has the Fourier component given by[9]

$$\hat{P}_{0,N_K}(k) = p_K \exp\left(-\frac{1}{6}k^2b^2N_K\right) \tag{4.3}$$

Therefore, we have for the Fourier components of Λ_K the following:

$$\hat{\Lambda}_K(k) = \frac{2D_c^K}{T}p_K\eta_k(N_K) \tag{4.4}$$

with

$$\eta_k(N) \equiv 1 - \exp\left(-\frac{1}{6}k^2b^2N\right) \tag{4.5}$$

Substituting (3.27) into (3.22) we find

$$\hat{\Lambda}_S(k) = \left(\frac{1 - S_0}{\rho_0}\right)^2\hat{\Lambda}_A(k) + \left(\frac{S_0}{\rho_0}\right)^2\hat{\Lambda}_B(k) \tag{4.6}$$

We follow the reptation model[9] to put

$$D_c^K = D_1/N_Kb^2 \tag{4.7}$$

with D_1 the monomer self-diffusion constant and use (4.4) and (4.6) to obtain

$$\hat{\Lambda}_S(k) = \frac{2D_1}{T\rho_0b^2}S_0(1 - S_0)\left[\frac{1 - S_0}{N_A^2}\eta_k(N_A) + \frac{S_0}{N_B^2}\eta_k(N_B)\right] \tag{4.8}$$

If we combine the result (4.8) with more well-known expressions for $\hat{H}_{SS}(k)$ (which is equal to the inverse of the variance of $\hat{S}_K$ in equilibrium and metastable states),[9] we obtain the complete expressions for the linear decay or growth rates of deviations from uniformity depending on the signs of $\hat{H}_{SS}(k)$.

For the limit of small k, (4.1) should reduce to the diffusion equation since one can see that $\hat{\Lambda}_S(k)$ goes as k^2 from (4.8) and $\hat{H}_{SS}(k)$ remains finite as $k \to 0$. The latter reduces to $\mathrm{d}^2\bar{H}(S_0)/\mathrm{d}S_0^2$ with $\bar{H}(S_0)$ the free energy density for the state with a uniform concentration S_0. If we take the Flory–Huggins form for $\bar{H}(S)$[9]

$$\bar{H}(S) = \rho_0k_BT\left[\frac{S}{N_A}\ln S + \frac{1 - S}{N_B}\ln(1 - S) + \chi S(1 - S)\right] \tag{4.9}$$

χ being the Flory–Huggins interaction parameters, we obtain (ρ_0 can be taken as the overall average density, which is taken to be fixed since explicit consideration of ρ_T is not necessary under the slaving assumption made in section 3)

$$\hat{H}_{SS}(0) = \mathrm{d}^2\bar{H}(S_0)/\mathrm{d}S_0^2 = \frac{\rho_0k_BT}{S_0(1 - S_0)}\left[\frac{1 - S_0}{N_A} + \frac{S_0}{N_B} - 2\chi S_0(1 - S_0)\right] \tag{4.10}$$

The final result for $k \to 0$ is

$$\Gamma_k = D_mk^2 \tag{4.11}$$

where D_m is the mutual diffusion constant given by

$$D_m \equiv \frac{k_BT}{\rho_0}\left(\frac{1 - S_0}{S_0}M_A + \frac{S_0}{1 - S_0}M_B\right) \times \left[\frac{1 - S_0}{N_A} + \frac{S_0}{N_B} - 2\chi S_0(1 - S_0)\right] \tag{4.12}$$

M_K being the mobilities defined by $\hat{\Lambda}_K(k)/k^2$ with $k \to 0$:

$$M_A \equiv \frac{D_1\rho_0}{3T}\frac{S_0}{N_A} \qquad M_B \equiv \frac{D_1\rho_0}{3T}\frac{1 - S_0}{N_B} \tag{4.13}$$

The expression (4.12) exactly coincides with that obtained by Kramer et al.[6a] Hence, our work can be regarded as a generalization of their "fast" mutual diffusion theory.

Diblocks. Here the Fourier components $\hat{P}(k)$ of the P's are given by

$$\begin{aligned}\hat{P}_{00}(k) &= \hat{P}_{NN}(k) = \hat{P}_{JJ}(k) = c_0 \equiv \rho_0/N\\ \hat{P}_{J0}(k) &= \hat{P}_{0J}(k) = c_0[1 - \eta_k(N_A)]\\ \hat{P}_{JN}(k) &= \hat{P}_{NJ}(k) = c_0[1 - \eta_k(N_B)]\\ \hat{P}_{0N}(k) &= \hat{P}_{N0}(k) = c_0[1 - \eta_k(N)]\end{aligned} \tag{4.14}$$

where c_0 is nothing but the constant chain number density. The Fourier components $\hat{\Lambda}(k)$ of the Λ's, (3.30), now become, using also the definition in (4.5)

$$\begin{aligned}\hat{\Lambda}_{AA}(k) &= 2\frac{c_0D_c}{T}\eta_k(N_A)\\ \hat{\Lambda}_{AB}(k) = \hat{\Lambda}_{BA}(k) &= -\frac{c_0D_c}{T}\eta_k(N_A)\eta_k(N_B)\\ \hat{\Lambda}_{BB}(k) &= 2\frac{c_0D_c}{T}\eta_k(N_B)\end{aligned} \tag{4.15}$$

Using (3.22) where S and ρ are now the constants $S_0 = N_A/N$ and ρ_0, respectively, we find

$$\hat{\Lambda}_S(k) = \frac{2c_0D_c}{\rho_0^2T}[(1 - S_0)^2\eta_k(N_A) + S_0^2\eta_k(N_B) + S_0(1 - S_0)\eta_k(N_A)\eta_k(N_B)] \tag{4.16}$$

For the linear case $S(\mathbf{r})$ is conserved in contrast to more general situation. Thus, we find, for $(kb)^2 \ll 6/N_A, 6/N_B$

$$\hat{\Lambda}_S(k) \cong \frac{b^2D_c}{3\rho_0T}S_0(1 - S_0)k^2 \tag{4.17}$$

and for $(kb)^2 \gg 6/N_A, 6/N_B$

$$\hat{\Lambda}_S(k) \cong \frac{2c_0D_c}{\rho_0{}^2T}(1 - S_0 + S_0{}^2) \tag{4.18}$$

For diblocks, however, the most interesting k regions are those corresponding to the incipient microphase separation.

Note here the similarity of these results for $\hat{\Lambda}_S(k)$ with those obtained for the incompressible case.[2d] In fact, (4.17) is identical with that for the incompressible case. So is (4.18) for the special case of $S_0 = 1/2$. The reason for this similarity was discussed in section 2.

The theoretical results obtained here can be used to analyze experimental results on the early-stage dynamics[3] in quenched polymer blends and diblocks and also on the decay rates of concentration fluctuations in equilibrium states of these systems.

5. Linear Dynamics of Concentration Deviatio in Lamellar States

Here we consider diblocks in one of the mesop lamellar phase. Although an equilibrium mes corresponds to straight and regular lamellar microstructure, most electron micrographs show irregularities such as distorted lamellae.[21] It is thus of interest to study dynamics of distorted microstructures. Here we consider linear dynamics of small concentration fluctuations in the equilibrium lamellar structure. This problem was already taken up by us[2c,10] adopting the reptation model and assuming the incompressibility. Our starting point is the linearized version of (3.20) for the deviation $\delta S(\mathbf{r})$

$$\frac{\partial}{\partial t}\delta S(\mathbf{r}) = -\int \Lambda_0(\mathbf{r}, \mathbf{r}')\mu_S(\mathbf{r}')\,\mathrm{d}\mathbf{r}' \tag{5.1}$$

$$\Lambda_0(\mathbf{r}, \mathbf{r}') \equiv \langle \mathbf{r}|\Lambda_S|\mathbf{r}'\rangle_0 \tag{5.2}$$

where a subscript 0 in this section indicates that the quantity is evaluated for the equilibrium lamellar state, and $\mu_S(\mathbf{r})$ is already linear in the deviation

$$\mu_S(\mathbf{r}) = \int B(\mathbf{r}, \mathbf{r}')\delta S(\mathbf{r}')\,\mathrm{d}\mathbf{r}' \tag{5.3}$$

$$B(\mathbf{r}, \mathbf{r}') \equiv [\delta^2 H\{S\}/\delta S(\mathbf{r})\delta S(\mathbf{r}')]_0 \tag{5.4}$$

We choose the z axis to be perpendicular to the lamellar plane. The lamellar state is invariant under translations in the lamellar plane as well as by integer multiples of vectors $l\hat{\mathbf{z}}$, $\hat{\mathbf{z}}$ being the unit vector along the z direction and l the period. This invariance is reflected by the following properties of $\Lambda_0(\mathbf{r}, \mathbf{r}')$ and $B(\mathbf{r}, \mathbf{r}')$:

$$\Lambda_0(\mathbf{r} + \mathbf{a} + ml\hat{\mathbf{z}}, \mathbf{r}' + \mathbf{a} + ml\hat{\mathbf{z}}) = \Lambda_0(\mathbf{r}, \mathbf{r}'), \quad \text{etc.} \tag{5.5}$$

with m an arbitrary integer and $\mathbf{a}$ an arbitrary vector in the xy plane, where we adopt the periodic boundary condition for the entire system.

We now transform relations like (5.1) and (5.3) into forms that reflect the invariance like (5.5). We first introduce Fourier transforms by

$$\delta S(\mathbf{r}) = \int_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}}\hat{S}(\mathbf{k}), \quad \text{etc.} \tag{5.6}$$

with

$$\int_{\mathbf{k}} = \frac{1}{(2\pi)^3}\int \mathrm{d}\mathbf{k} \tag{5.7}$$

Hence (4.1) becomes

$$\frac{\partial}{\partial t}\hat{S}(\mathbf{k}) = -\int_{\mathbf{k}'}\hat{\Lambda}(\mathbf{k}, \mathbf{k}')\hat{\mu}_S(\mathbf{k}') \tag{5.8}$$

$$\hat{\Lambda}(\mathbf{k}, \mathbf{k}') \equiv \int\int \mathrm{d}\mathbf{r}\,\mathrm{d}\mathbf{r}'\, e^{-i\mathbf{k}\cdot\mathbf{r}+i\mathbf{k}'\cdot\mathbf{r}'}\Lambda_0(\mathbf{r}, \mathbf{r}') = \int\int \mathrm{d}\xi\,\mathrm{d}\zeta\, e^{-i(\mathbf{k}-\mathbf{k}')\cdot\xi-(i/2)(\mathbf{k}+\mathbf{k}')\cdot\zeta}\Lambda_0\left(\xi + \frac{1}{2}\zeta, \xi - \frac{1}{2}\zeta\right) \tag{5.9}$$

We now put with m a suitable integer

$$\boldsymbol{\xi} = (\xi_0 + ml)\hat{\mathbf{z}} + \boldsymbol{\xi}_\perp \tag{5.10}$$

where ξ_0 is restricted to

$$0 \le \xi_0 < l \tag{5.11}$$

and $\xi_\perp$ is in the xy plane. Then

$$\int \mathrm{d}\xi \ldots = \sum_m \oint \mathrm{d}\xi_0 \int \mathrm{d}\xi_\perp \ldots \tag{5.12}$$

where the integral with circle is over the interval (5.11). In view of (5.5) the expression on the right-hand side of (5.9) then contains the factor

$$\int \mathrm{d}\boldsymbol{\xi}_\perp \sum_{m=-\infty}^{\infty} e^{-i(\mathbf{k}-\mathbf{k}')(\hat{\mathbf{z}}ml+\boldsymbol{\xi}_\perp)} = \frac{(2\pi)^3}{l}\sum_{m=-\infty}^{\infty}\delta\left(\mathbf{k} - \mathbf{k}' - \frac{2\pi}{l}m\hat{\mathbf{z}}\right) \tag{5.13}$$

where the following identity has been used to obtain the right-hand side.

$$\sum_{m=-\infty}^{\infty} e^{2\pi imx} = \sum_{m=-\infty}^{\infty}\delta(x - m) \tag{5.14}$$

(5.9) is thus transformed using (5.5) further into

$$\hat{\Lambda}(\mathbf{k}, \mathbf{k}') = \int \mathrm{d}\zeta \oint \mathrm{d}\xi_0\, e^{-i(\mathbf{k}-\mathbf{k}')\cdot\hat{\mathbf{z}}\xi_0-(i/2)(\mathbf{k}+\mathbf{k}')\cdot\zeta}\frac{(2\pi)^3}{l}\sum_m \delta\left(\mathbf{k} - \mathbf{k}' - \frac{2\pi}{l}m\hat{\mathbf{z}}\right)\Lambda_0\left(\xi_0\hat{\mathbf{z}} + \frac{1}{2}\zeta, \xi_0\hat{\mathbf{z}} - \frac{1}{2}\zeta\right) \tag{5.15}$$

From now on we replace $\mathbf{k}$, etc., by $\mathbf{k} + (2\pi/l)m\hat{\mathbf{z}}$ where m is a suitable integer and $\mathbf{k}$ is restricted to the first Brillouin zone given by

$$-\pi/l \le k < \pi/l \tag{5.16}$$

(5.15) is written after some algebra as

$$\hat{\Lambda}\left(\mathbf{k} + \frac{2\pi}{l}m\hat{\mathbf{z}}, \mathbf{k}' + \frac{2\pi}{l}m'\hat{\mathbf{z}}\right) = (2\pi)^2\delta(\mathbf{k}_\perp - \mathbf{k}_\perp{}')\int \mathrm{d}\zeta_\perp\, e^{-i\mathbf{k}_\perp\cdot\zeta_\perp}\frac{2\pi}{l}\oint \mathrm{d}\xi_0 \times \int \mathrm{d}\zeta_z \sum_{\bar{m}} e^{-i(k_z+(2\pi/l)m)\zeta_z}e^{i(2\pi/l)\bar{m}(-\xi_0+(1/2)\zeta_z)}\delta\left(k_z - k_z{}' + \frac{2\pi}{l}(m - m' - \bar{m})\right)\Lambda_0\left(\xi_0\hat{\mathbf{z}} + \frac{\zeta}{2}, \xi_0\hat{\mathbf{z}} - \frac{\zeta}{2}\right) \tag{5.17}$$

Since k_z and $k_z{}'$ are restricted by (5.16), we have $|k_z - k_z{}'| < 2\pi/l$, which in turn requires $m - m' - \bar{m} = 0$ in (5.17). Hence, (5.17) becomes

$$\hat{\Lambda}\left(\mathbf{k} + \frac{2\pi}{l}m\hat{\mathbf{z}}, \mathbf{k}' + \frac{2\pi}{l}m'\hat{\mathbf{z}}\right) = \frac{(2\pi)^3}{l}\delta(\mathbf{k} - \mathbf{k}')\int \mathrm{d}\zeta_\perp\, e^{-i\mathbf{k}_\perp\cdot\zeta_\perp}\int \mathrm{d}\zeta_z \oint \mathrm{d}\xi_0 \times e^{-i(k_z+\pi(m+m')/l)\zeta_z}e^{-i(2\pi/l)(m-m')\xi_0}\Lambda_0\left(\xi_0\hat{\mathbf{z}} + \frac{1}{2}\zeta, \xi_0\hat{\mathbf{z}} - \frac{1}{2}\zeta\right) \tag{5.18}$$

We now introduce a new Bloch-type representation for $\delta S(\mathbf{r})$, etc., as follows

$$\delta S(\mathbf{r}) = \oint_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}}\tilde{S}_{\mathbf{k}}(z), \quad \text{etc.} \tag{5.19}$$

with $\tilde{S}_{\mathbf{k}}(z)$ the l-periodic function of z defined by

$$\tilde{S}_{\mathbf{k}}(z) \equiv \sum_{m=-\infty}^{\infty}\hat{S}\left(\mathbf{k} + \frac{2\pi}{l}m\hat{\mathbf{z}}\right)e^{2\pi imz/l} \tag{5.20}$$

where the integral in (5.19) is over the first Brillouin zone. Using (5.14), we can also find the inverse of (5.20) as

$$\hat{S}\left(\mathbf{k} + \frac{2\pi}{l}m\hat{\mathbf{z}}\right) = \frac{1}{l}\oint \mathrm{d}z\,\tilde{S}_{\mathbf{k}}(z)e^{-2\pi imz/l} \tag{5.21}$$

The equation of motion (5.8) can now be recast into the equation for $\tilde{S}_{\mathbf{k}}(z)$. Thus, using (5.20), (5.8), and (5.18), we have

$$\frac{\partial}{\partial t}\tilde{S}_{\mathbf{k}}(z) = -\frac{1}{l}\oint \mathrm{d}z'\,\tilde{\Lambda}_{\mathbf{k}}(zz')\tilde{\mu}_{S\mathbf{k}}(z') \tag{5.22}$$

where

$$\tilde{\Lambda}_{\mathbf{k}}(zz') = \frac{2\pi}{l}\int \mathrm{d}\zeta_\perp e^{-i\mathbf{k}_\perp\cdot\zeta_\perp}\int \mathrm{d}\zeta_z \oint \mathrm{d}\xi_0 \times e^{-ik_z\zeta_z}\sum_m \exp\left[\frac{2\pi i}{l}m\left(z - \frac{1}{2}\zeta_z - \xi_0\right)\right]\sum_{m'}\exp\left[\frac{2\pi i}{l}m'\left(-z' - \frac{1}{2}\zeta_z + \xi_0\right)\right]\Lambda_0\left(\xi_0\hat{\mathbf{z}} + \frac{1}{2}\zeta, \xi_0\hat{\mathbf{z}} - \frac{1}{2}\zeta\right) \tag{5.23}$$

We use the identity (5.14) for product of the two sums in (5.23) to transform it into

$$l^2\sum_m\sum_{m'}\delta\left(z-\frac{1}{2}\zeta_z-\xi_0-ml\right)\delta\left(z'+\frac{1}{2}\zeta_z-\xi_0-m'l\right)= l^2\sum_m\sum_{m'}\delta(\zeta_z+z'-z+ml-m'l)\delta\left(\frac{z+z'}{2}-\xi_0-\frac{m+m'}{2}l\right)=l^2\sum_m\sum_{m'}\delta(\zeta_z+z'-z+ml)\delta\times\left(\frac{z+z'}{2}-\xi_0-\frac{m}{2}l-m'l\right)\quad(5.24)$$

where m was changed to $m+m'$ in the last line. Now, because of the δ functions, Λ_0 in (5.23) can be written as

$$\Lambda_0\left((z+m'l)\hat{\mathbf{z}}+\frac{1}{2}\zeta_\perp,(z'+ml+m'l)\hat{\mathbf{z}}-\frac{1}{2}\zeta_\perp\right)=\Lambda_0\left(z\hat{\mathbf{z}}+\frac{1}{2}\zeta_\perp,(z'+ml)\hat{\mathbf{z}}-\frac{1}{2}\zeta_\perp\right)\quad(5.25)$$

and is brought behind the summation sign of (5.24) where ξ_0 now appears only in the second δ function of (5.24) in the entire expression for Λ. Since the integration over ξ_0 is limited by (5.11), only one term remains in the sum over m'. These considerations amount to the following result:

$$\tilde{\Lambda}_{\mathbf{k}}(zz')=2\pi l\int\mathrm{d}\zeta_\perp\,e^{-i\mathbf{k}_\perp\cdot\zeta_\perp}\sum_{m=-\infty}^{\infty}e^{-ik_z(z-z'-ml)}\Lambda_0\left(z\hat{\mathbf{z}}+\frac{1}{2}\zeta_\perp,(z'+ml)\hat{\mathbf{z}}-\frac{1}{2}\zeta_\perp\right)\quad(5.26)$$

Equations 5.22 and 5.26 thus describe the linear dynamics of deviation in the lamellar phase where k and z (and z' too) are restricted to be in the intervals (5.16) and (5.11), respectively.

The above procedure used to transform (5.1) into (5.22) can be followed verbatim to transform (5.3) into the following form

$$\tilde{\mu}_{S\mathbf{k}}(z)=\frac{1}{l}\fint\mathrm{d}z'\,\tilde{B}_{\mathbf{k}}(zz')\tilde{S}_{\mathbf{k}}(z')\quad(5.27)$$

where $\tilde{B}_{\mathbf{k}}$ is defined by a formula analogous to (5.26).

Combining (5.22) and (5.27), we find the closed linear equation of motion for $S_{\mathbf{k}}(z)$ as follows

$$\frac{\partial}{\partial t}\tilde{S}_{\mathbf{k}}(z)=-\frac{1}{l}\fint\mathrm{d}z'\,\tilde{\omega}_{\mathbf{k}}(zz')\tilde{S}_{\mathbf{k}}(z')\quad(5.28)$$

with

$$\tilde{\omega}_{\mathbf{k}}(zz')\equiv\frac{1}{l}\fint\mathrm{d}\bar{z}\;\tilde{\Lambda}_{\mathbf{k}}(z\bar{z})\tilde{B}_{\mathbf{k}}(\bar{z}z')\quad(5.29)$$

The normal-mode analysis of (5.28) provides us with various excitation modes in the lamellar state. Note that $\tilde{\omega}_{\mathbf{k}}(zz')$ is not equal to $\tilde{\omega}_{-\mathbf{k}}(z'z)$ in general and hence the oscillatory behavior of δS cannot be a priori excluded at this stage.

6. Lamellar Phase Equation

The equation of motion (5.28) for a small concentration deviation in the equilibrium lamellar state is still the integral equation not easy to solve in general. Here, we consider smooth deformations, which vary very slowly in space on the length scale of l; that is, $kl \ll 1$ in (5.28). Such deformations occur in the z direction and can be described in terms of a slowly varying displacement field $u(\mathbf{r})$ which enters $S(\mathbf{r})$ as

$$S(\mathbf{r})=\bar{S}(z)-u(\mathbf{r})\bar{S}'(z)$$

where $\bar{S}(z)$ now describes the equilibrium lamellar state and the prime denotes differentiation. In view of the slowly varying nature of $u(\mathbf{r})$ we can put in (5.19)

$$\tilde{S}_{\mathbf{k}}(z)=-\hat{u}_{\mathbf{k}}\bar{S}'(z)\quad(6.1)$$

where $\hat{u}_{\mathbf{k}}$ is the Fourier component of $u(\mathbf{r})$. Substituting this expression for $\tilde{S}_{\mathbf{k}}(z)$ into (4.29) and integrating over z from 0 to l after multiplying on both sides by $S'(z)$, we obtain the equation of motion for $\hat{u}_{\mathbf{k}}$ (the so-called phase equation[15]) as

$$\frac{\partial}{\partial t}\hat{u}_{\mathbf{k}}=-\omega_{\mathbf{k}}\hat{u}_{\mathbf{k}}\quad(6.2)$$

$$\omega_{\mathbf{k}}\equiv\fint\mathrm{d}z\;\fint\mathrm{d}z'\,\bar{S}'(z)\tilde{\omega}_{\mathbf{k}}(zz')\bar{S}'(z')/l\fint\mathrm{d}z\;\bar{S}'(z)^2\quad(6.3)$$

For small k, (6.3) can be further reduced by making use of the eigenfunction expansion of $\tilde{B}_{\mathbf{k}}(zz')$. In order to find this we go back to (5.4) and consider a change δH of $H\{S\}$ due to $\delta S(\mathbf{r})$:

$$\delta H=\frac{1}{2}\int\int\mathrm{d}\mathbf{r}\,\mathrm{d}\mathbf{r}'\,B(\mathbf{r},\mathbf{r}')\delta S(\mathbf{r})\delta S(\mathbf{r}')=\frac{1}{2}\int\mathrm{d}\mathbf{r}\,\delta S(\mathbf{r})\mu_S(\mathbf{r})=\frac{1}{2l}\fint_{\mathbf{k}}\fint\mathrm{d}z\;\tilde{S}_{\mathbf{k}}(z)^*\tilde{\mu}_{\mathbf{k}}(z)=\frac{1}{2l^2}\fint_{\mathbf{k}}\fint\mathrm{d}z\;\fint\mathrm{d}z'\,\tilde{S}_{\mathbf{k}}(z)^*\tilde{B}_{\mathbf{k}}(zz')\tilde{S}_{\mathbf{k}}(z')\quad(6.4)$$

where the identity (5.14) has been used together with (5.16), and (5.27) was used in the last step. If we further substitute (6.1) into (6.4), we find

$$\delta H=\frac{1}{2}\fint_{\mathbf{k}}\bar{B}_{\mathbf{k}}|\hat{u}_{\mathbf{k}}|^2\quad(6.5)$$

with

$$\bar{B}_{\mathbf{k}}\equiv\frac{1}{l^2}\fint\mathrm{d}z\;\fint\mathrm{d}z'\,\bar{S}'(z)\tilde{B}_{\mathbf{k}}(zz')\bar{S}'(z')\quad(6.6)$$

(6.5) gives the free energy associated with smooth deformation field of the lamellar structure. On the other hand, this result implies that the integral operator whose kernel is $\tilde{B}_{\mathbf{k}}(zz')$ has the eigenfunction $\bar{S}'(z)$ with the corresponding eigenvalue

$$l^2\bar{B}_{\mathbf{k}}/\fint\bar{S}'(z)^2\,\mathrm{d}z$$

This gives rise to the following eigenfunction expansion of $\tilde{B}_{\mathbf{k}}(zz')$

$$\tilde{B}_{\mathbf{k}}(zz')=[l^2\bar{B}_{\mathbf{k}}/\mathcal{S}^2]\bar{S}'(z)\bar{S}'(z')+\ldots\quad(6.7)$$

where

$$\mathcal{S}\equiv\fint\mathrm{d}z\;\bar{S}'(z)^2\quad(6.8)$$

and the ellipsis stands for the contribution from eigenfunctions orthogonal to $\bar{S}'(z)$. Then from (5.29) and (6.3) only the first term of (6.7) contributes to $\omega_{\mathbf{k}}$. The result is

$$\omega_{\mathbf{k}}=\frac{l^2}{\mathcal{S}^2}\bar{\Lambda}_{\mathbf{k}}\bar{B}_{\mathbf{k}}\quad(6.9)$$

where

$$\bar{\Lambda}_{\mathbf{k}}\equiv\frac{1}{l_2}\fint\mathrm{d}z\;\fint\mathrm{d}z'\,\bar{S}'(z)\tilde{\Lambda}_{\mathbf{k}}(zz')\bar{S}'(z')\quad(6.10)$$

This is the result found in ref 2c, which we have rederived here in a slightly more transparent manner. The uniaxial symmetry gives for small k.

$$\bar{B}_{\mathbf{k}}=B_zk_z{}^2+B_\perp k_\perp{}^4\quad(6.11)$$

and $\bar{\Lambda}_{\mathbf{k}}$ can be replaced by $\bar{\Lambda}_0$, which is finite. The final result for $\omega_{\mathbf{k}}$ takes the following diffusive form

$$\omega_{\mathbf{k}} = D_z k_z^2 + D_\perp k_\perp^4 \tag{6.12}$$

with

$$D_z \equiv \frac{l^2}{\mathscr{S}^2} \bar{\Lambda}_0 B_z \tag{6.13}$$

$$D_\perp \equiv \frac{l^2}{\mathscr{S}^2} \bar{\Lambda}_0 B_\perp \tag{6.14}$$

The B's can be obtained if elastic properties of the lamellar structure are known on the basis of specific models of diblocks (see below (6.18) and (6.19)) whereas $\bar{\Lambda}_0$ is generally more difficult to find. Further reduction of $\bar{\Lambda}_0$ is possible if the spatial modulation of $\bar{S}(z)$ is weak, that is, in the weak segregation regime (WSR) where $\bar{S}(z)$ is sinusoidal with the small amplitude h:

$$\bar{S}(z) = h \sin (2\pi z/l) \tag{6.15}$$

This then permits $\hat{\Lambda}_{\mathbf{k}}(zz')$ in (6.10) to be replaced by that for the homogeneous state found in section 3 where Λ_0 in (5.26) takes the form

$$\int_{\bar{\mathbf{k}}} \hat{\Lambda}_S(\bar{\mathbf{k}}) \exp[i\bar{\mathbf{k}}_\perp \cdot \zeta_\perp + i\bar{k}_z(z - z' - ml)]$$

with $\hat{\Lambda}_S(\mathbf{k})$ given by (4.16). In this way we obtain with the help of (5.14)

$$\tilde{\Lambda}_{\mathbf{k}}(z, z') = \sum_{m=-\infty}^{\infty} \hat{\Lambda}_S\left(\mathbf{k}_\perp, k_z + \frac{2\pi}{l}m\right) \exp\left[i\frac{2\pi}{l}m(z - z')\right] \tag{6.16}$$

(6.15) and (6.16) are substituted into (6.10) to yield

$$\Lambda_{\mathbf{k}} = \pi^2\left(\frac{h}{l}\right)^2\left[\hat{\Lambda}_S\left(\mathbf{k}_\perp, k_z + \frac{2\pi}{l}\right) + \hat{\Lambda}_S\left(\mathbf{k}_\perp, k_z - \frac{2\pi}{l}\right)\right] \tag{6.17}$$

B_z and $B_\perp$ in WSR have been obtained elsewhere[22] as (now $S_0 = N_A/N$)

$$B_z = \frac{T\rho_0 b^2}{2S_0(1 - S_0)} h^2 \left(\frac{2\pi}{l}\right)^2 \tag{6.18}$$

$$B_\perp = \frac{T\rho_0 b^2}{8S_0(1 - S_0)} h^2 \tag{6.19}$$

where we have combined (4.25) of ref 23 and (5.35) and (5.36) of ref 22, the latter having been obtained by putting the coefficient $b^2/4S_0(1 - S_0)\rho_0$ equal to unity (note h equals ρ_0^{-1} times the amplitude of the density modulation). $\mathscr{S}$ now becomes $2\pi^2h^2/l$ and from (4.16) with $D_c = D_1/Nb^2$, D_1 being the monomer diffusion constant, we find

$$l^2\Lambda_0/\mathscr{S}^2 = (2\pi^2)^{-1}(l/h)^2(D_1/\rho_0 TN^2b^2)\lambda_1 \tag{6.20}$$

with

$$\lambda_1 \equiv 2[(1 - S_0)^2\eta_c(N_A) + S_0^2\eta_c(N_B) + S_0(1 - S_0)\eta_c(N_A)\eta_c(N_B)] \tag{6.21}$$

$$\eta_c(N) \equiv 1 - \exp(-2\pi^2b^2N/3l^2) \tag{6.22}$$

The final results for the D's are

$$D_z = \frac{D_1}{N^2}\Delta_z \qquad D_\perp = \frac{D_1b^2}{4N}\Delta_\perp \tag{6.23}$$

with

$$\Delta_z \equiv \frac{\lambda_1}{S_0(1 - S_0)} \qquad \Delta_\perp \equiv \left(\frac{l}{2\pi b}\right)^2 \frac{1}{N} \frac{\lambda_1}{S_0(1 - S_0)} \tag{6.24}$$

We now compare these results with the earlier ones obtained by assuming incompressibility[10] where the only difference is in the value of λ_1. This value, which is now denoted as λ_1^*, is given by

$$\lambda_1^* = 2\eta_c(N_A)\eta_c(N_B)\left[1 - \frac{1}{4}\eta_c(N_A)\eta_c(N_B)\right] \Big/ \eta_c(N) \tag{6.25}$$

It is interesting to note that despite quite different appearances, λ_1 and λ_1^* are very similar. Indeed, for the two limiting cases of $S_0 \ll 1$ (and hence $S_0 \cong 1$) and $S_0 \cong {}^1/_2$, the two are approximately the same:

$$\begin{aligned} \lambda_1 \cong \lambda_1^* &\cong 2\eta_c(N_A), \quad S_0 \ll 1 \\ &\simeq \eta_c(N_A)[1 + \tfrac{1}{2}\eta_c(N_A)], \quad S_0 \cong \tfrac{1}{2} \end{aligned} \tag{6.26}$$

The numerical values of Δ_z and $\Delta_\perp$ as well as Δ_z^* and $\Delta_\perp^*$ corresponding to λ_1^* are shown in Figure 1. The intuitive meanings of D_z and $D_\perp$ are explained in Figure 2 where two types of deformations are shown whose decay rates are given by the two terms in (6.12). Experimental tests of these results on decay rates of deformations of lamellar structure will provide a new channel of investigations into chain dynamics in the mesophases of block copolymers although this is not a good test for validity of the incompressibility condition.

7. Interface Dynamics in Phase-Separating Polymer Blends

For binary polymer melts in which monomers of different species repel each other, the enthalpic cost of bringing a large portion of the A-type chain inside the region that consists of the B-type segments is very high when the polymerization indices are very large. Thus at low temperatures still above the glass transition, the system is divided into domains consisting exclusively of the A-type or the B-type segments separated by the domain walls (interfaces) whose thickness is very small compared with the typical linear size of domains. This is called the strong segregation regime (SSR) and is realized typically in microphase-separated block copolymers and at late stages of phase separation of polymer blends. Here the relative concentration S can change only near the domain walls since $S(\mathbf{r}, t)$ is equal to 1 (or 0) in the A-rich (or B-rich) domains. Such variations of S in turn induce domain wall movements. Hence, we here derive the equation of motion of domain walls. We now remind the reader that from the argument of section 2 $\langle \mathbf{r}|\Lambda_{KK'}|\mathbf{r}'\rangle$ practially vanishes if $\mathbf{r}$ is in the K-poor domain *or* $\mathbf{r}'$ is in the K'-poor domain. This fact combined with the form of Λ_S given by (3.22) implies that $\langle \mathbf{r}|\Lambda_S|\mathbf{r}'\rangle$ should vanish unless both $\mathbf{r}$ and $\mathbf{r}'$ are located near the domain walls, which we had expected. Then we can employ the standard prescription to obtain the interface equation of motion from (3.20). We parametrize a location on the interface by the set of variables a and the coordinate along the normal direction is denoted as n and the speed of interfacial motion and the virtual infinitesimal interfacial displacement along n by $v(a)$ and $\delta q(a)$, respectively. If we consider the usual situation where the average radius of interfacial curvature $l(t)$ is much greater than its thickness, $S(\mathbf{r})$ near the interface is very close to that for the equilibrium concentration profile of a flat interface denoted as $S(n)$. Thus we find

$$\frac{\partial}{\partial t}S(\mathbf{r}, t) = -\bar{S}'(n)v(a), \quad \text{etc.} \tag{7.1}$$

where the prime denotes differentiation. We also find the infinitesimal change of H expressed in two ways

$$\delta H = -\int \mathrm{d}a\ \delta q(a) \int \mathrm{d}n\ \bar{S}'(n)\mu_S(\mathbf{r}) = -\int \mathrm{d}a\ \delta q(a)f(a) \tag{7.2}$$

where $f(a)$ is the static force for interfacial displacement defined through (7.2). For polymer blends in which H is given, apart from a trivial additive constant, by the interfacial tension σ times the total interfacial area, we have[2]

$$f(a) = \sigma\mathcal{H}(a) \qquad \text{(blend)} \tag{7.3}$$

For block copolymers the connectivity of molecules introduces an additional contribution to H, which takes the form of interaction energy among interfacial elements. If we adopt the simplified model for diblock copolymer systems proposed in ref 23, $f(a)$ takes the following form

$$f(a) = \sigma\mathcal{H}(a) + \alpha\int \mathrm{d}\mathbf{r}' \frac{1}{|\mathbf{r}_a - \mathbf{r}'|}\bar{S}(\mathbf{r}') \qquad \text{(diblock)} \tag{7.4}$$

where α is some positive constant, $\mathbf{r}_a$ the position vector at the interfacial element a, and $\bar{S}(\mathbf{r})$ the concentration profile in SSR. Since in (3.20) we need $\mu_S(\mathbf{r})$ only near the interface, we can put in view of (7.2)

$$\mu_S(\mathbf{r}) = f(a)\mu^*(n) \tag{7.5}$$

where $\mu^*(n)$ fulfills the condition

$$\int \bar{S}'(n)\mu^*(n)\,\mathrm{d}n = 1 \tag{7.6}$$

Substituting (7.1) and (7.5) into (3.20) and integrating over n after multiplying by $\bar{S}'(n)$, we obtain

$$v(a) = \int \mathrm{d}a'\,\Psi(a, a')f(a') \tag{7.7}$$

where

$$\Psi(a, a') \equiv \frac{1}{\mathcal{S}_b}\int\int \mathrm{d}n\,\mathrm{d}n'\,\bar{S}'(n)\langle\mathbf{r}|\Lambda_S|\mathbf{r}'\rangle\mu^*(n') \tag{7.8}$$

$$\mathcal{S}_b \equiv \int \bar{S}'(n)^2\,\mathrm{d}n \tag{7.9}$$

and $\mathbf{r}$ is now expressed as (n, a) near the interface. Since $\Psi(aa')$ is the Onsager kinetic "coefficient" for the interfacial motion, the reciprocity demands $\Psi(a'a) = \Psi(aa')$. This is satisfied if we take, in view of (7.6)

$$\mu^*(n) = \mathcal{S}_b^{-1}\bar{S}'(n) + (\text{terms orthogonal to } \bar{S}'(n))$$

Hence, (7.8) is replaced by

$$\Psi(aa') = \frac{1}{\mathcal{S}_b^{2}}\int\int \mathrm{d}n\,\mathrm{d}n'\,\bar{S}'(n)\langle\mathbf{r}|\Lambda_S|\mathbf{r}'\rangle\bar{S}'(n') \tag{7.10}$$

Note that so far we have not used any specific model for polymer chain dynamics.

The interface equation like (7.7) has been obtained earlier[2] when the incompressibility is required. Our equation differs from the previous one in the following two respects. One is that if the mean-field-like chain dynamics is assumed, $\Psi(aa')$ here is nonvanishing mainly for $|\mathbf{r}_a - \mathbf{r}_{a'}|$ less than about the end-to-end distance of polymer chains whereas previously $\Psi(aa')$ contained the Coulomb-like long-range contributions arising from the incompressibility requirement. The second is that, in the absence of incompressibility requirement, the conservation law for the relative concentration $S(\mathbf{r}, t)$ need not generally hold. Regarding the latter point, however, if $\rho_T(\mathbf{r})$ is locally determined by $S(\mathbf{r})$, that is, if $\mu_T(\mathbf{r}) = \mu_0$ reduces to the local relation between $\rho_T(\mathbf{r})$ and $S(\mathbf{r})$ like $\rho_T(\mathbf{r}) = \bar{\rho}_T(S(\mathbf{r}))$, the conservation law for $S(\mathbf{r})$ is asymptotically satisfied in the limit of strong segregations. This is because here we have

$$\rho_A(\mathbf{r}) = \bar{\rho}_T(S(\mathbf{r}))S(\mathbf{r}) = \rho_T(1)S(\mathbf{r})$$

except in the very thin interfacial regions since $S(\mathbf{r})$ is 1 or 0. Therefore, the conservation law for $\rho_A(\mathbf{r})$ immediately leads to that for $S(\mathbf{r})$. We may call this the local limit, which is more likely to be realized in blends than in block copolymers. The conservation law then gives

$$\int \Psi(aa')\,\mathrm{d}a = 0 \tag{7.11}$$

When this condition is satisfied, then, for the region of interface where the radius of curvature as well as the distance to the nearest element of other interfaces is much greater than the size of a chain, the interface equation (7.7) for any mean-field model of chain dynamics takes the following form

$$v(a) = D_s\nabla_a^2 f(a) \tag{7.12}$$

where ∇_a^2 is the Laplacian on the interface and D_s the coefficient of surface diffusion. For the case of blends with (7.3) this reduces to the equation obtained by Mullins[13] for surface diffusion:

$$v(a) = \sigma D_s\nabla_a^2\mathcal{H}(a) \tag{7.13}$$

In the late stage of phase separation when the length scale characterizing the random domain structure is again denoted as $l(t)$, a simple dimensional analysis of (7.13) predicts for $l(t) \gg R_G$, the chain gyration radius, the following behavior:[14]

$$l(t) \propto t^{1/4} \tag{7.14}$$

If we adopt the reptation model of chain dynamics,[9] we estimate in Appendix B that $\sigma D_s \sim D_{\mathrm{rep}}R_G\xi$ where D_{rep} is the chain self-diffusion constant. Thus (7.14) becomes

$$l(t) \sim (D_{\mathrm{rep}}R_G\xi t)^{1/4} \tag{7.15}$$

At much later times but still in the interconnected morphology of domain structure, the hydrodynamic domain growth[24] takes place yielding

$$l(t) \sim (\sigma/\eta)t \tag{7.16}$$

where η is the shear viscosity. The crossover then occurs at $l = \bar{l}_h \propto N^{1/2}$ or $t = \bar{t}_h \propto N^{7/2}$ given respectively by

$$\bar{l}_h = (D_{\mathrm{rep}}R_G\xi\eta/\sigma)^{1/3} = (R_G\xi/l_h^2)^{1/3}l_h \ll l_h \tag{7.17}$$

$$\bar{t}_h = (D_{\mathrm{rep}}R_G\xi)^{1/3}(\eta/\sigma)^{4/3} = (R_G\xi/l_h^2)^{1/3}t_h \ll t_h \tag{7.18}$$

where l_h and t_h designate the crossover from the Allen–Cahn $t^{1/2}$ behavior of the incompressible case to the hydrodynamic behavior. Thus, we observe that the hydrodynamic regime $l \sim t$ is reached much earlier than the previous incompressible case[2] since $l_h = \eta D_{\mathrm{rep}}/\sigma \propto N$ is much greater than $R_G \propto N^{1/2}$. Indeed the $t^{1/4}$ growth behavior may not be observable experimentally since $\bar{l}_h \propto N^{1/2}$ is only of the same order as $R_G \propto N^{1/2}$ or even smaller. More explicitly, we find $\bar{l}_h/R_G \sim \chi^{-1/3}N_e^{-2/3}$ where χ is the Flory–Huggins interaction parameter and N_e is the number of monomers between adjacent entanglements.

When the domains are no longer interconnected but consist of separated droplets, the hydrodynamic growth originating from the hydrodynamic instability of interconnected domain structure is no longer important and, for small molecular systems, the Lifshitz–Slyozov–Wagner (LSW) evaporation–condensation mechanism[12] dominates the coarsening.[20] For blends of long polymer chains in SSR, the situation can be drastically different. Here a chain of one species is unlikely to be found in the domain of another species as was mentioned earlier, which prohibits diffusion processes needed in the LSW mechanism. Indeed, for morphology with droplets whose radii and average droplet separations are much greater than the chain size, $\Psi(aa')$ of the mean-field model is nonvanishing only for those a and a' that are on the surface of the same droplet. Here, (7.12) is approximately valid and hence the volume of each droplet no longer changes in time. Alternatively, one may start from (3.1) and (3.26) and can show by integrating by parts that the total A-type segment number contained in a A-rich precipitate does not change in time in the mean-field model where use is made of the fact that no A-type segment exists in the B-rich domain outside the droplet. The suppression of coarsening described seems to be in accord with the recent experimental finding that coarsening virtually stops when interconnected domain morphology changes into separate droplets.[25]

8. Discussion

We have presented the dynamical theory of concentrations in polymer blends and diblocks with the assumption of constant chemical potential for the total monomer density in a general way. However, specific predictions made are all based on the mean-field-type chain dynamics such as the biased reptation in which individual chain movements are uncorrelated, which are reflected in specific assumptions for $\Lambda(c)$ in (2.3). Such mean-field models can be quite inadequate as recent computer simulations seem to indicate.[4,26] There is also a work claiming that inclusion of constraint release mechanism largely eliminates the controversy over slow and fast diffusion processes.[27] However, there is a recent report supporting the reptation picture on the basis of extensive molecular dynamics.[28] Correlated chain movements generally introduce long-range components in the kernels of equations of motion such as $\langle \mathbf{r}|\Lambda_S|\mathbf{r}'\rangle$ and $\Psi(aa')$. If this range is finite, our predictions will still hold qualitatively if the chain dimension is replaced by this finite range of correlations. However, if the correlation range is infinite reflected by power law decays of kernels as we have encountered earlier,[2] the situation will drastically change. Hence, we definitely need further information on dynamics of individual chains as well as cooperative motion of many chains in polymer melts. On the other hand, experimental tests of our predictions should in turn shed light on the nature of chain dynamics in polymer melts.

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Appendix A

Here we consider the question of the bulk flow for polymer blends[6] in the present context. We follow the notations of section 3 and formally write the equation of motion of the density variables for blends as

$$\frac{\partial}{\partial t}\rho_K = -\Lambda_K \mu_K \qquad K = \mathrm{A, B} \tag{A.1}$$

Assuming existence of the inverses of Λ_K, we rewrite this as

$$\Lambda_K^{-1}\frac{\partial}{\partial t}\rho_K = -\mu_K \tag{A.2}$$

Then the condition of the constant total chemical potential (3.13) can be expressed in terms of the densities as

$$\sum_K S_K \Lambda_K^{-1}\frac{\partial}{\partial t}\rho_K = 0 \tag{A.3}$$

Here we have set this constant equal to zero by supposing that we are dealing with an extremely large system and changes are taking place in some large but finite regions in the system, and very far from the region where the density variations are taking place, the left-hand side of (A.3) should vanish. If we note that the right-hand side and the left-hand side of (A.2) express, respectively, the static and frictional forces for the density variations acting on a unit quantity of the component K; (A.3) can be interpreted as expressing the balance of frictional forces on each component per unit quantity of the blend. This, in fact, is the condition in disguise of the one used by Brochard[6c,29] to study interdiffusion of compatible polymer blends (also note that $\partial\rho_K/\partial t = (\dot\rho_K)_{\mathrm{real}} - (\dot\rho_K)_{\mathrm{bulk}}$ as will be shown below).

Now, the system described by (A.1) generates inhomogeneous total density and hence pressure differences when the blend consists of polymer chains of widely different polymerization indices. Such pressure differences must be equilibrated. This equilibration process cannot be described by (A.1), which only contains dissipative processes arising from random thermal motions (fluctuation dissipation theorems). In order to examine the situation, we consider the simple case where the total density in equilibrium states does not depend on the relative concentration. We then rewrite (A.1) using $\rho_K = \rho_T S_K$ where ρ_T is the total dendity and S_K is the fraction of K

$$\rho_T\frac{\partial}{\partial t}S_K = \frac{\partial}{\partial t}\rho_K - S_K\frac{\partial}{\partial t}\rho_T \tag{A.4}$$

We now reinterpret (A.4) as follows. We regard the left-hand side of (A.4) to be the actual rate of density change really taking place in the system, which is denoted as $(\dot\rho_K)_{\mathrm{real}}$. The first term on the right-hand side (A.4) represents the intrinsic change due to random fluctuations and is denoted as $(\dot\rho_K)_{\mathrm{intrinsic}}$. The second term then represents the bulk flow term $(\dot\rho_K)_{\mathrm{bulk}}$ associated with the equilibration process mentioned above. With this new interpretation (A.4) represents the correct density change with the bulk flow. Obviously

$$\sum_K (\dot\rho_K)_{\mathrm{real}} = 0 \tag{A.5}$$

implying that the total density change does not actually take place. The bulk flow term is readily found from (A.1), (A.3), and (A.4) as

$$(\dot\rho_K)_{\mathrm{bulk}} = S_K(\dot\rho_T)_{\mathrm{bulk}}$$

$$(\dot\rho_T)_{\mathrm{bulk}} \equiv \sum_K (\dot\rho_k)_{\mathrm{bulk}} = -\frac{\partial}{\partial t}\rho_T = [S\Lambda_{\mathrm{A}}^{-1}S + (1-S)\Lambda_{\mathrm{B}}^{-1}S]^{-1}[S\Lambda_{\mathrm{A}}^{-1} - (1-S)\Lambda_{\mathrm{B}}^{-1}]\rho_T\frac{\partial}{\partial t}S \tag{A.6}$$

where we have denoted $S_{\mathrm{A}} = S$ and $S_{\mathrm{B}} = 1 - S$. The rate of change of S_K of course is not affected by the bulk flow, and the results for S_K described in the test remains the same in this new interpretation.

For small deviations from the homogeneous equilibrium state treated in section 4, (A.6) reduces after Fourier transform to

$$(\dot\rho_T)_{\mathrm{bulk}} = [S_0^2\Lambda_{\mathrm{A}}(k)^{-1} + (1-S_0)^2\Lambda_{\mathrm{B}}(k)^{-1}]^{-1}[S_0\Lambda_{\mathrm{A}}(k)^{-1} - (1-S_0)\Lambda_{\mathrm{B}}(k)^{-1}]\rho_0\frac{\partial}{\partial t}S \tag{A.7}$$

This is a straightforward generalization to finite k of the known results for bulk flow density variation.[6] For small k where

$$\hat\Lambda_K(\mathbf{k}) \simeq \frac{k^2b^2}{3T}\rho_0 S_K D_c^{\ K} \tag{A.8}$$

the macroscopic ($k \to 0$) bulk flow can be made to vanish by the choice $D_c^A = D_c^B$. (Here we are allowing D_1 in (3.7) to be unequal for A and B.) Since the self-diffusion constant D_S^K is proportional to D_c^K/N_K, this condition is $N_A D_S^A = N_B D_S^B$, which is already given in ref 6. Even with this choice, however, the bulk flow is generally nonvanishing when viewed on a smaller scale (finite k) unless $N_A = N_B$ or when the system is inhomogeneous.

When the equilibrium value of the total density can depend on the relative concentration, this introduces the following additional contribution to the bulk flow term (A.7):

$$\left(\frac{\partial \rho_T}{\partial S}\right)_{\mu_T} \frac{\partial}{\partial t} S \tag{A.9}$$

The real concentration change then becomes

$$(\dot{\rho}_K)_{\mathrm{real}} = \rho_T \frac{\partial}{\partial t} S_K + S_K \left(\frac{\partial \rho_T}{\partial S}\right)_{\mu_T} \frac{\partial}{\partial t} S \tag{A.10}$$

Appendix B

Here we estimate the magnitude of σD_s appearing in (7.13). For a blend, where $f(a) = \sigma \mathcal{K}(a)$ is slowly varying over the distance of $O(\xi)$ on the interface, we can expand $f(a')$ in (7.7) as

$$f(a') = f(a) + (\mathbf{a} - \mathbf{a}')\cdot\nabla_a f(a) + \frac{1}{2}(\mathbf{a} - \mathbf{a}')(\mathbf{a} - \mathbf{a}'):\nabla_a \nabla_a f(a) + \ldots$$

where $\mathbf{a}$ denotes the location on the interface and we have neglected the curvature except in $f(a)$. Substituting this into (7.7) and using the conservation law (7.11) and the symmetry we find

$$v(a) = \sigma D_S \nabla_a^2 \mathcal{K}(a) \tag{B.1}$$

with

$$D_S \equiv \frac{1}{4} \int \mathrm{d}a' \, |a - a'|^2 \Psi(a, a') \tag{B.2}$$

Hence, we only need $\Psi(a, a')$ with $a \neq a'$. Then, using (3.22), (3.28), and

$$P_{0,N_K}(\mathbf{r}\mathbf{r}') \sim \frac{\rho}{N_K} Q_{N_K}(\mathbf{r}\mathbf{r}') \sim \frac{\rho}{N_K} \frac{1}{R_G{}^3} Q^*(|\mathbf{r} - \mathbf{r}'|/R_G) \tag{B.3}$$

where $Q_N(\mathbf{r}\mathbf{r}')$ is the Helfand function[30] and $Q^*(x)$ is some function decaying to zero for x for the order unity, we readily estimate

$$\langle \mathbf{r}|\Lambda_S|\mathbf{r}'\rangle \sim \frac{D_c}{\rho T N} \frac{1}{R_G{}^3} Q^*(|\mathbf{r} - \mathbf{r}'|/R_G) \tag{B.4}$$

Thus, noting $\mathcal{S}_b \sim \xi^{-1}$, we estimate from (7.10)

$$\Psi(a, a') \sim \frac{D_c \xi^2}{\rho T N} \frac{1}{R_G{}^3} Q^*(|a - a'|/R_G) \tag{B.5}$$

Therefore we obtain from (A.2) using $D_c \sim N D_{\mathrm{rep}}/b^2$ and $\sigma \sim \rho b^2 T/\xi$[27]

$$\sigma D_S \sim \sigma R_G{}^4 \Psi(|a - a'| \sim R_G) \sim \sigma R_G \frac{D_c \xi^2}{\rho T N} \sim D_{\mathrm{rep}} \xi R_G \tag{B.6}$$

Note Added in Proof. In response to the comment made by one of the referees regarding the assumption of constant total chemical potential in section 2, we point out that this assumption in fact is equivalent to the use of the Gibbs–Duhem relation at constant pressure and temperature, which was also used by Silescu.[6b] This is valid as long as the local equilibrium assumption familiar in thermodynamics of irreversible processes is correct.

References and Notes

(1) Hashimoto, T. In *Current Topics in Polymer Science*; Ottenbrite, R. M., Utracki, L. A., Inoue, S., Eds.; Hanser Publishers: Munich, 1987; Vol. II. Hashimoto, T. In *Physical Optics of Dynamic Phenomena in Macromolecular Systems*; Sedlacek, B., Ed.; de Gruyter: Berlin, 1985.

(2) (a) Kawasaki, K.; Sekimoto, K. *Physica* **1987**, *143A*, 349. The Bessel function referred to below eq F.2 is $J_0(ka)$ obtained by first integrating over all the directions of **k** in this equation. (b) *Europhys. Lett.* **1987**, *4*, 339. (c) *Physica* **1988**, *148A*, 361. (d) Kawasaki, K. In *Competing Interactions and Microstructures: Statics and Dynamics*; Bishop, A., Heffner, R., LeSar, R., Eds.; Springer: Heidelberg, 1988.

(3) de Gennes, P.-G. *J. Chem. Phys.* **1980**, *72*, 4756. Pincus, P. *J. Chem. Phys.* **1981**, *75*, 1996. Binder, K. *J. Chem. Phys.* **1983**, *79*, 6387. Strobl, G. R. *Macromolecules* **1985**, *18*, 558.

(4) Pakula, T. *Macromolecules* **1987**, *20*, 679. *Polymer* **1987**, *28*, 1293. Pakula, T.; Geyler, S. *Macromolecules* **1987**, *20*, 2909.

(5) Brochard, F.; Jouffroy, J.; Levinson, P. *Macromolecules* **1983**, *16*, 1638. *J. Phys., Lett.* **1983**, *44*, L-455.

(6) (a) Kramer, E. J.; Green, P.; Palmstrøm, C. J. *Polymer* **1984**, *25*, 473. Composto, R. J.; Kramer, E. J.; White, D. M. *Nature* **1987**, *328*, 234; *Macromolecules* **1988**, *21*, 2580. (b) Sillescu, H. *Makromol. Chem., Rapid Commun.* **1984**, *5*, 519; **1987**, *8*, 393. (c) Brochard-Wyart, F. *C. R. Hebd. Seances Acad. Sci.* **1987**, *305*, 657.

(7) Hohenberg, P. C.; Cross, M. C. In *Fluctuation and Stochastic Phenomena in Condensed Matter*; Garrido, L., Ed.; Springer: Heidelberg, 1987. Guazzelli, E.; Guyon, E.; Wesfreid, J. E. *Philos. Mag.* **1983**, *A48*, 709.

(8) Pomeau, Y.; Manneville, P. *J. Phys., Lett.* **1979**, *40*, L-609.

(9) de Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell: Ithaca, NY, 1979. Doi, M.; Edwards, S. F. *Theory of Polymer Dynamics*; Oxford University: Oxford, 1986.

(10) Kawasaki, K.; Sekimoto, K. In *Dynamics of Ordering Processes in Condensed Matter*; Komura, S., Furukawa, H., Eds.; Plenum Press: New York, 1988.

(11) Lifshitz, I. M. *Sov. Phys.—JETP* (*Engl. Transl.*) **1962**, *15*, 932. Allen, S. M.; Cahn, J. W. *Acta Metall.* **1979**, *27*, 1085.

(12) Lifshitz, I. M.; Slyozov, V. V. *J. Phys. Chem. Solids* **1961**, *19*, 35.

(13) Mullins, W. W. *J. Appl. Phys.* **1959**, *30*, 77.

(14) Furukawa, H. *Adv. Phys.* **1985**, *34*, 703.

(15) (a) Schichtel, T. E.; Binder, K. *Macromolecules* **1987**, *20*, 1671. (b) Kehr, K. W.; Binder, K.; Reulein, S. M., preprint, 1988.

(16) The definition of monomer densities appears to be immaterial. Here, for definiteness, we choose the segment number density as in ref 2.

(17) Bates, F. S. *Macromolecules* **1984**, *17*, 2607.

(18) Anderson, P. W. *Basic Notions of Condensed Matter Physics*; Benjamin: Menlo Park, CA, 1984.

(19) For a single-component system in the uniform state, $H\{\rho\}$ reduces to the Helmholtz free energy $F(M,T,V)$ with $M \equiv \rho_T V$, V being the system volume. Then μ_T reduces to the usual chemical potential. In this connection the statements (1) and (2) of section 6 of ref 2c are not correct. The total density fluctuations can, of course, decay also through the heat mode. However, the heat mode generally decays much faster than the concentration fluctuation.

(20) Slater, G. W.; Noolandi, J. *Phys. Rev. Lett.* **1985**, *55*, 1579. Lumpkin, O. J.; Dejardin, P.; Zimm, B. H. *Biopolymers* **1985**, *24*, 1573.

(21) For instance, see: Hashimoto, T.; Shibayama, M.; Fujimura, M.; Kawai, H. *Mem. Fac. Eng., Kyoto Univ.* **1981**, *18*, 184.

(22) Kawasaki, K.; Ohta, T. *Physica* **1986**, *139A*, 223.

(23) Ohta, T.; Kawasaki, K. *Macromolecules* **1986**, *19*, 2621.

(24) McMaster, L. P. In *Copolymers, Blends and Composites*; Platzer, N. A. J., Ed.; American Chemical Society: Washington, DC, 1975. Siggia, E. D. *Phys. Rev.* **1979**, *20*, 595.

(25) See the articles by Hashimoto, T. and by Hasegawa, H.; Shiwaku, A.; Nakai, A.; Hashimoto, T. In *Dynamics of Oredering Processes in Condensed Matter*; Komura, S., Furukawa, H., Eds.; Plenum Press: New York, 1988.

(26) Kolinski, A.; Skolnick, J.; Yaris, R. *J. Chem. Phys.* **1987**, *86*, 1567.

(27) Hess, W.; Akcasu, A. Z. *J. Phys.* (*Les Ulis, Fr.*) **1988**, *49*, 1261.

Macromolecules **1989**, *22*, 3075-3080

(28) Kremer, K.; Grest, G. S.; Carmesin, I. *Phys. Rev. Lett.* 1988, *61*, 566.

(29) Brochard's condition is expressed in terms of the velocities of the two types of chains and the matrix. We use time variations of the density variables, which are related to the current densities and hence to the velocities through the equations of continuity.

(30) Helfand, E.; Wasserman, Z. R. In *Developments in Block Copolymers*; Goodman, I., Ed.; Applied Science Publishers: London, 1982; Vol. 1.

Functional Form for the Stress Relaxation Moduli of Binary Blends Consisting of Nearly Monodisperse Polymers and the Effect of Tube Size Enlargement. 1

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ABSTRACT: It has been concluded that the tube renewal process is negligible in (nearly) monodisperse polymers from the successful line-shape analyses of the viscoelastic spectra in terms of the proposed general theory (the monodisperse theory). In the case of binary blends, however, it is clearly visible in the measured spectra that the stress anisotropy in the regions of a long-chain tube, where entanglements with the short chains occur, relaxes as the short chains reptate away (referred to as the *regional* tube renewal or constraint release process). (Note: The word "regional" is added to distinguish the process considered here from the tube renewal or constraint release process, which involves the whole polymer chain and is often treated as a "Rouse tube" motion.[18-21]) A related phenomenon is the tube size enlargement effect, which can be observed very clearly in the terminal region of the long-chain component. Considering the regional constraint release process, a functional form for the stress relaxation moduli of binary blends (the binary theory) was previously proposed in brief. Here, the binary theory is described in detail. Specifically the effect of tube size enlargement is analyzed. The results of the analyses are in good agreement with the theoretical predictions. The relations between the monodisperse theory and the binary theory are discussed in light of the present and previous data analyses.

I. Introduction

On the basis of the Doi–Edwards theory,[1-4] a general linear viscoelastic theory for monodisperse flexible linear polymer melts and concentrated solutions (also referred to as the monodisperse theory below)[5] has been developed by including the chain contour length fluctuation effect and two additional relaxation processes: the Rouse motion of an entanglement strand (assuming the entanglement points are fixed in the short time region) and the chain slippage through entanglement links. The theory has been very successful in describing quantitatively the line shapes of the linear viscoelastic relaxation spectra of nearly monodisperse polystyrene melts[6,7] and concentrated solutions[8] and explaining the universal observations: the molecular weight (MW) dependence of the zero-shear viscosity and the steady-state compliance and their respective transition points, M_c and M_c'.[5-8] It has also been shown that the theory correlates quantitatively the viscoelasticity data and the diffusion data.[9]

An important conclusion derived from the successful comparisons of the monodisperse theory and the experimental results of polymer viscoelasticity is that the tube renewal (or constraint release) process is negligible in a monodisperse system to MW as low as $1.24M_e$. This conclusion has been physically explained by the fact that the number of entanglement strands per cubed tube diameter, n_t, which has been shown to be topologically a universal constant, is quite large ($\sim$17).[10]

In the case of binary blends consisting of two far separated monodisperse components, however, it is clearly visible in the measured spectra that the stress anisotropy in the region of a long-chain tube, where entanglements with the short chains occur, relaxes as the short chains reptate away (the regional constraint release process). As early as 1983,[11] we have recognized this effect and by including it proposed a functional form for the stress relaxation moduli, $G(t)$, for binary blends. Our functional form was published as a note in ref 6[12] with some preliminary experimental results. In the Appendix of ref 8, it was shown how the functional form can be reduced to that for a concentrated solution (denoted here as $G_s(t)$) consisting of a high MW polymer with MW $\gg M_e$ (as the polymer) and a low MW polymer with MW $< M_e$ (as the solvent). The high MW part of the $G_s(t)$ function is identical with that for the pure monodisperse melt as the MW is normalized with respect to the entanglement MW of the concentrated solution, M_e', given as

$$M_e' = M_e W_H^{-1} \tag{1}$$

where M_e is the entangle MW of the pure melt and W_H is the weight fraction of the high MW component. And the low MW part of $G_s(t)$ is described by the Rouse theory of a free chain.[13] The line shapes of the linear viscoelastic spectra of a series of concentrated polystyrene solutions have been very successfully analyzed in terms of the $G_s(t)$ function. It has been shown from the analyses that within experimental error the friction factor (K) in the Rouse part (for the low MW chains) and in the general theory part (for the high MW chains, with M_e' given by eq 1) are identical.[8] This strongly supports that the general theory has bridged the gap between the Rouse theory and the Doi–Edwards theory.

On the basis of the study, it was first pointed out[8] that in a binary blend consisting of a high MW (M_H) monodisperse component and a low MW (M_L) monodisperse component, both MWs being greater than M_e, tube size in the terminal region associated with the high MW component should enlarge gradually with decreasing M_L (at

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