Dynamics of Concentration Fluctuations in Ternary Polymer Solutions

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ABSTRACT: We discuss the relaxation of concentration fluctuations in symmetric ternary solutions of two polymers of the same molecular weight at the same concentration in a common good solvent. The correlations of total concentration and of composition are decoupled, and the two relaxation modes are a pure cooperative mode and a pure interdiffusion mode. The relaxation time of the cooperative mode is the same as for a binary polymer solution at the same concentration. The interdiffusion relaxation rate can be written as the sum of a hydrodynamic contribution and of a contribution due to the friction of the blobs on their environment. The relaxation rates are calculated first within the framework of the Rouse–Zimm model including hydrodynamic interactions; scaling laws are then obtained from the reptation model that take into account entanglements between different chains. The spinodal instability of the mixture is also briefly discussed.

I. Introduction

Segregation effects are extremely strong in polymeric systems and chemically different polymers are in general incompatible.[1,2] Miscibility or partial miscibility can however often be achieved by dissolving the polymer blend in a common good solvent: the polymers are miscible at low concentration and phase separate when the total polymer concentration is increased. The classical description of this phase separation is based on the Flory–Huggins mean field theory[1] which predicts a critical concentration for phase separation much smaller than the overlap concentration and thus well in the dilute regime. This is in contradiction with experimental results that show phase separation only for semidilute solutions. This inadequacy of the classical theory is due to the mean field treatment of the excluded volume interactions. Excluded volume interactions introduce subtle correlation effects that must be included both in the description of the chain conformations and in the thermodynamics of ternary solutions of chemically different polymers in a good solvent.

In recent years, a renormalization group theory[3-5] has been proposed that takes into account more precisely the excluded volume correlations; it allows the description of interpenetration effects between different chains in dilute solution and of the observed phase separation in semidilute solution. For polymers of the same degree of polymerization N, this theory predicts a critical polymer concentration for phase separation $c_K \sim N^{-0.63}$ much larger than the overlap concentration $c^* \sim N^{-0.8}$ and thus well in the semidilute regime. These results are in reasonably good agreement with several sets of experimental data.[6]

More recently, there has been a growing interest in the kinetics of relaxation of concentration fluctuations in ternary polymer solutions which are probed experimentally by quasi-elastic light or neutron scattering. In a series of theoretical papers, Benoît, Benmouna, and their collaborators[7-9] used the so-called dynamic random phase approximation to predict the existence of two relaxation modes that can be roughly identified as a cooperative diffusion mode and a mutual interdiffusion mode. The relaxation times of these modes have been calculated within the framework of the classical mean field theory to describe the static correlations in solution and with the help of the Rouse model to describe the chain dynamics. The theory has also been extended to study the relaxation of fluctuations in diblock copolymer solutions.

Quasi-elastic light scattering experiments by the same group[9,21] show a good agreement with these predictions; however, no quantitative comparison can be made for the scaling of the diffusion constants because of the oversimplifications introduced both by the mean field theory for static correlations and by the Rouse model which ignores hydrodynamic interactions between monomers and entanglements. This was recognized by these authors, who pointed out both that renormalized quantities should be used to describe the static properties of the polymer solution[22] and the important role of hydrodynamic interactions. The aim of this paper is to try to improve the Benoît–Benmouna theory by taking into account the excluded volume correlations, the hydrodynamic interactions, and the effect of entanglements. This is done only for the simplest symmetric case of two polymers of the same molecular weight in a common good solvent and at the same concentration. We also focus mainly on the one-phase region where the concentration is smaller than the critical concentration c_K but is still in the semidilute range ($c > c^*$).

The paper is organized as follows. In the next section we recall the main results for thermodynamics and concentration correlations in ternary polymer solutions using the blob model introduced by Broseta et al.[5] In section III we study the relaxation of long-wavelength fluctuations and calculate the cooperative and the mutual diffusion constants using the Rouse–Zimm model to describe the chain dynamics. The relaxation of short-wavelength fluctuations is discussed in section IV. The Rouse–Zimm model does not take into account correctly the entanglement constraints and allows crossing between different chains. Deep into the semidilute regime, the chain dynamics is dominated by entanglements and must be described by the reptation model. Although we do not have a complete theory of the concentration fluctuations within the reptation model, we present in section V some scaling laws; we also briefly discuss the spinodal decomposition that occurs when the total polymer concentration is larger than the critical concentration for phase separation c_K. The last section is devoted to concluding remarks and presents some possible issues.

II. Thermodynamics and Static Correlations of Polymer Mixtures in a Good Solvent

We study a mixture of two different polymers of different chemical nature 1 and 2 but of same degree of polymer-

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ization N in a common good solvent and we call c_1 and c_2 the respective monomer concentrations. Rather than the concentrations c_1 and c_2, we will often use as thermodynamic variables the total concentration c and the composition $x = c_1/c$. In all the following we discuss the properties of semidilute polymer solutions for which the concentration is larger than the overlap concentration $c^* \sim N^{1-3\nu}$, where ν is the swelling exponent of the polymers in a good solvent ($\nu = {}^3/_5$ in the Flory approximation that we use below). If the two polymers are identical in semidilute solution[10] (binary polymer solution), the bulk correlation length decays with the concentration as

$$\xi \sim c^{-3/4} \tag{1}$$

At length scales larger than this correlation length, the properties of the solution are the same as that of a polymer melt made of renormalized monomers or blobs of size ξ. Each blob contains then $g \sim (\xi/a)^{5/3}$ monomers and each chain contains $Z = N/g$ blobs. The chains are Gaussian and their radius of gyration is

$$R_g = Z^{1/2}\xi = (N/g)^{1/2}\xi \tag{2}$$

The picture that emerges from the renormalization theory of mixtures[3-5] of chemically different polymers is an extension of this renormalized melt description. At length scales larger than the correlation length ξ the properties of the semidilute solution are the same as those of a blend of chains of blobs in the melt. In particular, the free energy of mixing can be calculated from the classical Flory–Huggins theory after renormalization of the monomers to the blob size. Each chain contains then Z blobs and the volume fraction of blobs of type 1 is x (or the site fraction in the lattice description). The renormalization group theory gives a value of the equivalent Flory interaction parameter between blobs that increases with the total concentration:

$$\chi \sim c^{\alpha} \tag{3}$$

where α is a crossover exponent roughly equal to 0.29. The Flory–Huggins theory gives then the following free energy density F:

$$F\xi^3/k_BT = x/Z \log x + (1-x)/Z \log(1-x) + \chi x(1-x) + K \tag{4}$$

The first two terms represent the standard translational entropy of the chains, the third term is the interaction between unlike blobs, and the constant K gives the direct excluded volume interactions between monomers. The spinodal line where the solution becomes unstable is given by the usual relation:

$$\chi_K = \frac{g}{2Nx(1-x)} \tag{5}$$

Notice that as the interaction parameter between blobs χ essentially depends on the total concentration c if the temperature is kept constant, this defines a spinodal concentration for each composition x above which the solution is unstable and cannot remain monophasic. The critical concentration is obtained for $x = {}^1/_2$, $c_K \sim N^{-0.63}$.[5]

The concentration static correlation functions $S_{ij}(\mathbf{q}) = \int e^{i\mathbf{q}\cdot\mathbf{r}}\langle c_i(0)c_j(r)\rangle \, d\mathbf{r} = \int e^{i\mathbf{q}\cdot\mathbf{r}} g_{ij}(r) \, d\mathbf{r}$ for ternary polymer solutions have also been calculated in ref 5. They can be expressed as functions of the correlation functions $S_{cc}(\mathbf{q})$, $S_{xc}(\mathbf{q})$, and $S_{xx}(\mathbf{q})$ of the concentration c and the composition x:

$$[S_{ij}] = S_{cc}[A_{ij}] + c^2S_{xx}[B_{ij}] + 2cS_{xc}[C_{ij}] \tag{6}$$

where the matrices $[A_{ij}]$, $[B_{ij}]$, and $[C_{ij}]$ are defined as

$$[A_{ij}] = \begin{bmatrix} x^2 & x(1-x) \\ x(1-x) & (1-x)^2 \end{bmatrix}$$

$$[B_{ij}] = \begin{bmatrix} 1 & -1 \\ -1 & 1 \end{bmatrix}$$

$$[C_{ij}] = \begin{bmatrix} x & (1/2)-x \\ (1/2)-x & x-1 \end{bmatrix}$$

The concentration correlation function is essentially the same as for a single polymer in a good solvent solution:[10]

$$S_{cc}(\mathbf{q}) = \frac{c^2\xi^3}{1 + q^2\xi^2} \tag{7}$$

The classical random phase approximation has been applied to the semidilute solution considered as a melt of blobs in ref 5. It allows the calculation of the composition correlation function:

$$S_{xx}(\mathbf{q}) = \frac{\xi^3 x(1-x)}{\frac{g}{N}\left(1 - \frac{\chi}{\chi_K}\right) + q^2\xi^2} \tag{8}$$

The width of this function defines the composition correlation length ξ_T of the solution:

$$\xi_T = \xi\left[\frac{g}{N}\left(1 - \frac{\chi}{\chi_K}\right)\right]^{-1/2} = R_g\left(1 - \frac{\chi}{\chi_K}\right)^{-1/2} \tag{9}$$

where R_g is the radius of gyration of the chains in the semidilute solution given by eq 2. The correlation length is equal to the radius of the chains if the concentration is smaller than the spinodal concentration ($\chi < \chi_K$) and diverges on the spinodal line as expected. Notice that, in this approach, the fluctuations of composition are treated in a mean field manner and the composition correlation length diverges with the mean field exponent ${}^1/_2$. As discussed in ref 5, very close to the spinodal line the divergence is governed by the Ising critical exponent $\nu_I = 0.63$. Similarly, the divergence of the composition correlation function $S_{xx}(\mathbf{q}{=}0)$ is governed by the Ising exponent $\gamma_I = 1.25$ close to the critical point; this is different from the value 1 predicted by eq 8.

The blob model does not allow the calculation of the crossed correlation function $S_{xc}(\mathbf{q})$; to our knowledge this correlation function has not yet been calculated for a finite wave vector $\mathbf{q}$. For symmetry reasons, however, it is clear that if the mixture is symmetric ($x = {}^1/_2$) the correlations of concentration and of composition are uncoupled and $S_{xc}(\mathbf{q}{=}0)$.[11] In the following we will ignore the crossed correlation function $S_{xc}(\mathbf{q})$ and thus consider only the vicinity of $x = {}^1/_2$. One could test the validity of this approximation by calculating the value of $S_{xc}(\mathbf{q}{=}0)$ from the derivatives of the free energy (4) and by comparing at $\mathbf{q} = 0$ the third term to the other two in eq 6.

We will often need below the correlation functions not in Fourier space but in direct space; these are obtained by Fourier inversion of eq 6–8:

$$g_{cc}(r) = c^2\xi\frac{1}{4\pi r}e^{-r/\xi}, \qquad g_{xx}(r) = x(1-x)\xi\frac{1}{4\pi r}e^{-r/\xi_T} \tag{10}$$

The blob model does not describe correctly the properties of the solution at length scales smaller than the concentration correlation length or blob size ξ. The correlation functions given by eqs 7, 8, and 10 are thus not accurate when $r < \xi$ or when $q\xi > 1$. Inside the blobs the chains behave as individual chains and

$$g_{11}(r) \sim xcr^{-4/3}, \qquad g_{22}(r) \sim (1-x)cr^{-4/3} \qquad (r < \xi) \tag{11}$$

This gives the concentration and composition correlation functions:

$$g_{cc}(r) \sim cr^{-4/3}, \qquad g_{xx}(r) \sim x(1-x)c^{-1}r^{-4/3} \qquad (r < \xi) \tag{11'}$$

When r is equal to ξ these formulas crossover smoothly to eq 10.

III. Diffusion Constants: Rouse–Zimm Model

The relaxation of concentration fluctuations is in general probed by quasielastic light or neutron scattering; one then directly measures the matrix of the time correlation functions of the concentration:

$$S_{ij}(\mathbf{q},t) = \int e^{i\mathbf{q}\cdot\mathbf{r}}\langle c_i(0,0)c_j(r,t)\rangle \, \mathrm{d}\mathbf{r} \tag{12}$$

We will discuss here only the initial decay rate or first cumulant matrix defined as

$$[\Omega_{ij}(\mathbf{q})] = -\lim_{t\to 0}\frac{\partial}{\partial t}[S_{ij}(\mathbf{q},t)][S_{ij}^{-1}(\mathbf{q})] \tag{13}$$

The eigenvalues of this matrix give the decay rates of the concentration fluctuations in the solution. In the limit where the wave vector vanishes, the relaxation is in general diffusive and we may define a diffusion matrix by $[\Omega_{ij}(\mathbf{q})] = q^2[D_{ij}(\mathbf{q})]$.

If there is a fluctuation of the monomer concentrations in the solution, there exist locally gradients in the chemical potentials of the two types of monomers $\nabla\mu_i$. These thermodynamic forces induce fluxes of monomers that tend to equalize the chemical potentials. In the linear response approximation, the fluxes are proportional to the forces:

$$J_i(\mathbf{q}) = -[M_{ij}(\mathbf{q})]\nabla\mu_j(\mathbf{q}) \tag{14}$$

where the summation is implicit over the repeated indices. The matrix of Onsager coefficients $[M_{ij}(\mathbf{q})]$ will be referred to in the following as the mobility matrix. The chemical potential gradients are proportional to the concentration gradients:

$$\nabla\mu_i(\mathbf{q}) = [X_{ij}^{-1}(\mathbf{q})]\nabla c_j(\mathbf{q}) \tag{15}$$

The linear response theory relates the response function $[X_{ij}(\mathbf{q})]$ to the concentration correlation functions: $[S_{ij}(\mathbf{q})] = k_{\mathrm{B}}T[X_{ij}(\mathbf{q})]$. Equation 14 and 15 give then the diffusion matrix as

$$[D_{ij}(\mathbf{q})] = k_{\mathrm{B}}T[M_{ij}(\mathbf{q})][S_{\mathrm{ij}}^{-1}(\mathbf{q})] \tag{16}$$

To determine the diffusion matrix, we thus need to calculate the mobility matrix. We will assume in this section that the relaxation of concentration fluctuations is a purely hydrodynamic process: the motion of the monomers create backflows in the surrounding viscous medium of viscosity η that are responsible for hydrodynamic interactions between the monomers. The backflow effects must thus be taken into account through the so-called Oseen tensor. The classical Kawasaki–Ferrell mode coupling approximation allows then the calculation of the mobility matrix as a function of the concentration correlation matrix $[g_{ij}(r)]$; in the limit of vanishing wave vector[10,12]

$$[M_{ij}] = \int\frac{1}{6\pi\eta r}[g_{ij}(r)]\,\mathrm{d}\mathbf{r} \tag{17}$$

Using eqs 6 and 16 we can write the diffusion matrix at zero wave vector as

$$[D_{ij}] = D_{cc}\begin{bmatrix} x & x \\ 1-x & 1-x \end{bmatrix} + D_{xx}\begin{bmatrix} 1-x & -x \\ x-1 & x \end{bmatrix} \tag{18}$$

The cooperative diffusion constant D_{cc} and the mutual diffusion constant D_{xx} are the eigenvalues of the diffusion matrix. They govern respectively the relaxations of the fluctuations of the total concentration c and of the composition x and are expressed as

$$D_{cc} = k_{\mathrm{B}}TM_{cc}/S_{cc}, \qquad D_{xx} = k_{\mathrm{B}}TM_{xx}/S_{xx}c^2 \tag{19}$$

The relevant mobilities are

$$M_{cc} = \int\frac{1}{6\pi\eta r}g_{cc}(r)\,\mathrm{d}\mathbf{r}, \qquad M_{xx} = c^2\int\frac{1}{6\pi\eta r}g_{xx}(r)\,\mathrm{d}\mathbf{r} \tag{20}$$

The viscosity that enters the calculation of these two mobilities through the Oseen tensor is the viscosity of the medium between two monomers at a distance r. For polymer solutions, however, this viscosity depends on the length scale r. A full treatment of concentration fluctuations relaxation would require a detailed consideration of the nonlinear couplings between concentration fluctuations and hydrodynamic motions. As in ref 13, we use here a more empirical approach and take these couplings into account by introducing a priori an effective size-dependent viscosity $\eta(r)$ in eq 20. If the distance r is smaller than the blob size ξ, the effective viscosity is clearly that of the pure solvent η_0. If the distance between the monomers r is larger than the radius R_{g} of the polymer chains, the hydrodynamic interaction is mediated by the macroscopic polymer solution and the effective viscosity is the macroscopic viscosity of the solution η_{M}. Our hydrodynamic model only considers phantom chains that can freely cross each other; it thus overlooks the role of entanglements. At this level of analysis, it is therefore consistent to use the Rouse model to determine the viscosity of the solution. For a semidilute solution where the hydrodynamic interactions are screened over a length ξ, the blob description leads to $\eta_{\mathrm{M}} = (N/g)\eta_0$. Between $r = \xi$ and $r = R_{\mathrm{g}}$, the viscosity increases smoothly; within a naive Rouse model, a scaling analysis leads to $\eta(r) \sim r^2$. However, we are interested here only in scaling laws and for this purpose it is sufficient to use a discontinuous viscosity $\eta(r) = \eta_0$ if $r < \xi$ and $\eta(r) = \eta_{\mathrm{M}}$ if $r > \xi$.

In the calculation of the cooperative mobility M_{cc} the correlation function g_{cc} decreases exponentially when $r > \xi$; the relevant viscosity is thus the solvent viscosity η_0. Equations 10, 19, and 20 give the cooperative diffusion constant as

$$D_{cc} \sim \frac{k_{\mathrm{B}}T}{6\pi\eta_0\xi} \tag{21}$$

The fluctuations of concentration and of composition being uncoupled for symmetric systems, the relaxation of the total concentration does not depend on the composition of the polymer solution and the cooperative diffusion constant D_{cc} is the same as that of a binary polymer solution in a good solvent[10] at the same concentration c; it increases with the concentration as $c^{3/4}$.

To determine the mutual diffusion constant we divide the integral of eq 20 for M_{xx} into two parts, an integral from 0 to ξ where the effective viscosity is the solvent viscosity and an integral between ξ and ∞ where the effective mobility is the macroscopic viscosity η_M. We thus write the mutual diffusion constant as the sum of two terms $D_{xx} = D'_{xx} + D''_{xx}$ with

$$D'_{xx} = \frac{k_B T[1 - (\chi/\chi_K)]}{6\pi\eta_0(N/g)\xi}, \qquad D''_{xx} = \frac{k_B T}{6\pi\eta_M\xi_T} \tag{22}$$

The contribution D''_{xx} to the mutual diffusion constant is dominated by the hydrodynamic interactions between monomers separated by a distance much larger than the blob size ξ. It has exactly the same structure as the cooperative diffusion constant in simple liquid binary mixtures as calculated by Kawasaki[14] and Ferrell.[15] This contribution decreases with the concentration as $c^{-9/8}$ if $\chi \ll \chi_K$ and vanishes as the inverse of the composition correlation length on the spinodal line of the solution when $\chi = \chi_K$ or $c = c_K$. In the mean field model that does not incorporate composition fluctuations, it vanishes as $[1 - (\chi/\chi_K)]^{1/2}$; in the vicinity of the critical point the composition fluctuations are relevant and D''_{xx} vanishes with the Ising exponent ν_I. The only specific polymeric feature of D''_{xx} is the very large value of the solution viscosity η_M that considerably decreases the value of D''_{xx}. An analogous contribution to the mutual diffusion constant of polymer blends in the melt has been proposed by de Gennes.[10]

The contribution D'_{xx} to the mutual diffusion constant is dominated by hydrodynamic interactions at the scale of the blob. In the limit where the two types of polymers are identical, the blob interaction parameter χ is small and D'_{xx} is the Rouse diffusion constant[12] of a chain of blobs; when the polymers are chemically different, there is an extra thermodynamic factor that takes into account the interactions between unlike monomers. D'_{xx} decreases with the concentration as $c^{-1/2}$ when $\chi \ll \chi_K$ and vanishes on the spinodal line in the same way as $S_{xx}(\mathbf{q}=0)$, with an exponent 1 in the mean field theory and with the Ising exponent γ_I when composition fluctuations are relevant.

In the vicinity of the spinodal line, the mutual diffusion constant is dominated by D''_{xx}; it thus vanishes as the inverse of the composition correlation length ξ_T as in usual binary liquid mixtures. This is however true only in a very small range of χ close to χ_K ($1 - \chi/\chi_K \sim g/N$), and in most of the concentration range between the overlap concentration c^* and the critical concentration c_K, the mutual diffusion constant is given by the Rouse value, $D_{xx} = D'_{xx}$. One must notice however that the model presented so far does not take into account the role of entanglements that is dominant in the dynamic properties of semidilute polymer solutions; due to the entanglement effects, the Rouse model that we have used does not give a correct description of the dynamic properties of polymer solutions and the reptation model must be used. This point will be addressed in section V.

IV. Relaxation of Finite-Wavelength Fluctuations: Rouse–Zimm Model

Neutron scattering experiments can probe the dynamics of polymer solutions at finite wave vectors $\mathbf{q}$; it is thus interesting to extend the above results to nonvanishing wave vectors $\mathbf{q}$. The initial decay rate matrix $[\Omega_{ij}(\mathbf{q})]$ is related to the concentration correlation functions by a Kubo formula:[12]

$$[\Omega_{ij}(\mathbf{q})] = k_B T \int \frac{d\mathbf{k}}{(2\pi)^3}[S_{ij}(\mathbf{k}+\mathbf{q})]\frac{q^2 - (\mathbf{q}\cdot\hat{\mathbf{k}})^2}{\eta(\mathbf{k})k^2}[S_{ij}^{-1}(\mathbf{q})] \tag{23}$$

where $\hat{\mathbf{k}} = \mathbf{k}/|\mathbf{k}|$ is a unit wave vector; the fraction $[q^2 - (q\cdot\hat{\mathbf{k}})^2]/\eta(\mathbf{k})k^2$ is the Oseen tensor which takes into account the hydrodynamic interactions between monomers. As in the previous section, η is an effective viscosity that depends on the length scale i.e., on the wave vector $\mathbf{k}$. At short length scales, $k\xi > 1$, η is the solvent viscosity η_0; in the same approximation as above, at large length scales ($k\xi < 1$) we use for η the macroscopic viscosity of the solution η_M.

As for zero wave vector, the relaxation modes are given by the eigenmodes of the relaxation matrix. We find again a cooperative mode and a mutual diffusion mode. The decay rate of the cooperative mode is equal to

$$\Omega_{cc}(\mathbf{q}) = \frac{k_B T}{S_{cc}(\mathbf{q})}\int \frac{d\mathbf{k}}{(2\pi)^3}S_{cc}(\mathbf{k}+\mathbf{q})\frac{q^2 - (\mathbf{q}\cdot\hat{\mathbf{k}})^2}{\eta(\mathbf{k})k^2} \tag{24}$$

The integral is always dominated by wave vectors such that $k\xi > 1$ and we can use the solvent viscosity η_0 as the effective viscosity. This is then the same as the concentration decay rate of a single polymer semidilute solution at the same concentration c. If $q\xi < 1$, $\Omega_{cc} = q^2 D_{cc}$, where the cooperative diffusion constant D_{cc} is given by eq 21; if $q\xi > 1$, the decay rate only depends on the wave vector and $\Omega_{cc}(\mathbf{q}) \sim k_B T q^3/\eta_0$.

The decay rate for the mutual interdiffusion mode is given by

$$\Omega_{xx}(\mathbf{q}) = \frac{k_B T}{S_{xx}(\mathbf{q})}\int \frac{d\mathbf{k}}{(2\pi)^3}S_{xx}(\mathbf{k}+\mathbf{q})\frac{q^2 - (\mathbf{q}\cdot\hat{\mathbf{k}})^2}{\eta(\mathbf{k})k^2} \tag{24'}$$

We must here split the integral into two parts: $\Omega_{xx} = \Omega'_{xx} + \Omega''_{xx}$. The first part Ω'_{xx} contains wave vectors $\mathbf{k}$ such that $k\xi \gg 1$ for which the viscosity is the solvent viscosity η_0; Ω''_{xx} is the contribution to the integral of the small wave vectors ($k\xi \ll 1$) where we use the solution viscosity η_M. In the limit where $q\xi < 1$, the two contributions to the decay rate can be explicitly calculated from eq 24. In the short-wavelength contribution to the decay rate Ω'_{xx}, the wave vector $\mathbf{k}$ in the integral is always larger than $\mathbf{q}$ and we may expand the integrand in powers of k/q. We find

$$\Omega'_{xx}(\mathbf{q}) \sim \frac{k_B T\xi}{8\pi^2\eta_0\xi_T^2 S_{xx}(\mathbf{q})}q^2 \sim \frac{k_B T\xi}{8\pi^2\eta_0\xi_T^2}(1 + q^2\xi_T^2)q^2 \tag{25}$$

In the limit where $q\xi_T \ll 1$ eq 25 gives back the mutual diffusion constant of eq 22. When $q\xi_T \gg 1$, $\Omega'_{xx}(\mathbf{q}) \sim k_B T q^4\xi/\eta_0$; this is the relaxation rate expected in the Rouse model for a melt of blobs of size ξ.[10,12]

The long-wavelength contribution to the decay rate can be calculated by extending the integral to infinity. We find the same result as for usual binary mixtures:[14]

$$\Omega''_{xx}(\mathbf{q}) = \frac{k_B T q^2}{6\pi\eta_M\xi_T}F(\mathbf{q}\xi_T) \tag{26}$$

where

$$F(x) = \frac{3}{4}\frac{1 + x^2}{x^3}[x + (x^2 - 1)\arctan(x)]$$

is the so-called Kawasaki function. In the limit $q\xi_T \ll 1$, the relaxation is diffusive with a diffusion constant given by eq 22. When $q\xi_T \gg 1$, $\Omega''_{xx} \sim k_B T q^3/\eta_M$. This has the same structure as the classical Zimm relaxation rate of polymer solutions but the viscosity is here the macroscopic viscosity of the solution η_M, which is in general very large.

The results for the decay rate of the mutual interdiffusion mode are summarized in Figure 1, where we plot in a diagram ξ/ξ_T versus $q\xi$ for various regions where we

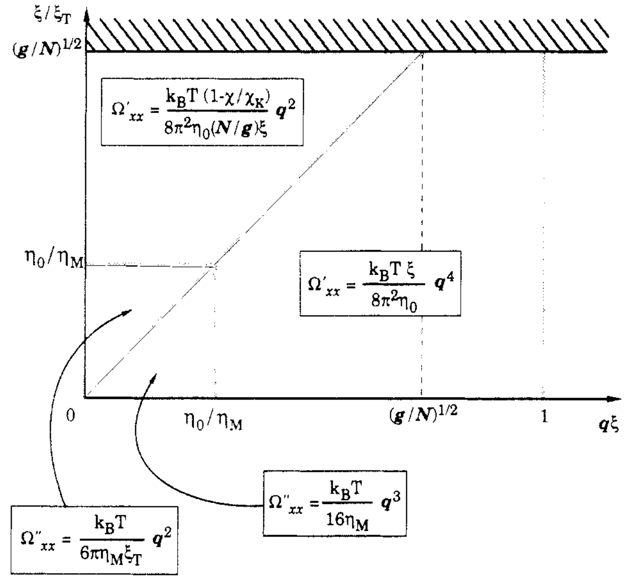

Figure 1. Dominant contributions to the relaxation rate of the interdiffusion mode in the Rouse–Zimm model when the total concentration c and the wave vector **q** are varied. ξ is the blob size or concentration correlation length given in eq 1. ξ_T is the composition correlation length given by eq 9.

give the dominant contributions to the mutual initial decay rate Ω_{xx}. Whenever $q\xi_T \ll 1$, the relaxation is diffusive, the crossover between the Rouse-like diffusion D'_{xx} and the Zimm-like diffusion D''_{xx} occurring when $\xi/\xi_T \sim \eta_0/\eta_M$. Whenever $q\xi_T \gg 1$, the relaxation rate is independent of ξ_T, the crossover between the q^4 Rouse behavior and the hydrodynamic q^3 behavior occurring for $q\xi \sim \eta_0/\eta_M$. One must however be careful in using this diagram because the dependences of the two axes on the total concentration c is rather complicated and the constant concentration curves are not straight lines.

V. Reptation Model

In the previous sections we have treated the dynamics of semidilute polymer solutions within the framework of the Rouse–Zimm model, which takes into account correctly the hydrodynamic interactions between monomers. This model, however, only considers phantom polymer chains and allows crossing between them; it thus ignores the role of entanglements in the dynamics of the solution. When the concentration is well in the semidilute range, entanglements are known to play a dominant role in the hydrodynamic properties of polymer solutions;[10,12] the critical concentration for phase separation being much larger than the overlap concentration c^*, we must therefore modify the Rouse–Zimm model to take entanglement constraints into account. We do not have a detailed hydrodynamic theory of relaxation of concentration fluctuations within the reptation model; we will only give here scaling laws assuming that the physical picture that emerges from the Rouse–Zimm model remains valid and including the effect of entanglements with the help of reptation theory. We first study the relaxation of concentration fluctuations in a monophasic solution and then briefly discuss the initial stages of the spinodal instability for solutions with a concentration larger than the spinodal value.

1. Relaxation Modes for a Monophasic Solution. We only discuss here the relaxation of concentration fluctuations in symmetric solutions where the two polymers have the same molecular weights and are at the same concentration. The fluctuations of concentration c and of composition x are then uncoupled. The relaxation of the total concentration fluctuations is governed by the breathing modes of the semidilute solution that do not depend on the existence of entanglements. Their decay rate is given by eqs 21 and 24. We thus need only to discuss the relaxation of composition fluctuations.

We first consider the limit of zero wave vector for which the relaxation is diffusive and we assume that the mutual diffusion constant has the same structure as that obtained in the Rouse–Zimm model and can be written as the sum of two contributions: $D_{xx} = D'_{xx} + D''_{xx}$.

The contribution D''_{xx} is dominated by the long-range hydrodynamic interactions between blobs and has the same Kawasaki–Ferrell form as the diffusion constant of simple liquid mixtures given by eq 22: $D''_{xx} = k_BT/6\pi\eta_M\xi_T$, where η_M is the macroscopic viscosity of the solution. In the reptation model, the viscosity of a semidilute polymer solution scales as

$$\eta_M \sim \eta_0(N/g)^3 \sim N^3c^{15/4} \qquad (27)$$

The contribution D''_{xx} to the mutual diffusion constant is thus considerably reduced when the effect of entanglements is included. It scales as

$$D''_{xx} = \frac{k_BT[1-(\chi/\chi_K)]^{1/2}}{6\pi\eta_0(N/g)^{7/2}\xi} \sim N^{-7/2}c^{-29/8}[1-(\chi/\chi_K)]^{1/2}$$

The other contribution D'_{xx} to the diffusion constant includes hydrodynamic interactions at the level of a blob. The Rouse–Zimm result of eq 22 suggests to write

$$D'_{xx} = D_0[1-(\chi/\chi_K)] \qquad (28)$$

where D_0 is the self-diffusion constant of a tagged chain in a semidilute solution. In the Rouse model D_0 is equal to $k_BT(g/N)\xi^{-1}$ and eq 28 gives back the diffusion constant of eq 22. In the reptation model

$$D_0 \sim k_BT(g/N)^2\xi^{-1} \sim N^{-2}c^{-7/4}$$

$$D'_{xx} = \frac{k_BT[1-(\chi/\chi_K)]}{\eta_0(N/g)^2\xi} \sim N^{-2}c^{-7/4}[1-(\chi/\chi_K)] \qquad (29)$$

In the vicinity of the spinodal line, the hydrodynamic contribution D''_{xx} dominates the mutual interdiffusion constant; however, this is true only in a very small range of concentration such that $[1-(\chi/\chi_K)] < (g/N)^3 \ll 1$ and in most of the concentration range between the overlap concentration c^* and the critical concentration c_K the mutual diffusion constant is given by eq 29.

At a finite wave vector such that $q\xi_T > 1$, we also split the initial decay rate into two contributions $\Omega_{xx}(\mathbf{q}) = \Omega'_{xx}(\mathbf{q}) + \Omega''_{xx}(\mathbf{q})$.

The contribution of the hydrodynamic interactions at large length scales $\Omega''_{xx}(\mathbf{q})$ is still given by eq 26 where the viscosity η_M is now the reptation viscosity (27).

The local contribution $\Omega'_{xx}(\mathbf{q})$ is governed by the local reptative motions of the chains. To estimate it, we consider the semidilute solution as a melt of blobs and use the results obtained for polymer melts. Pincus[16] has calculated the mobility M_{xx} of a blend of two homopolymers in the melt using the reptation model; if we renormalize the size of the monomers to the blob size ξ and the microscopic friction on a monomer to the friction on a blob $6\pi\eta_0\xi$, the

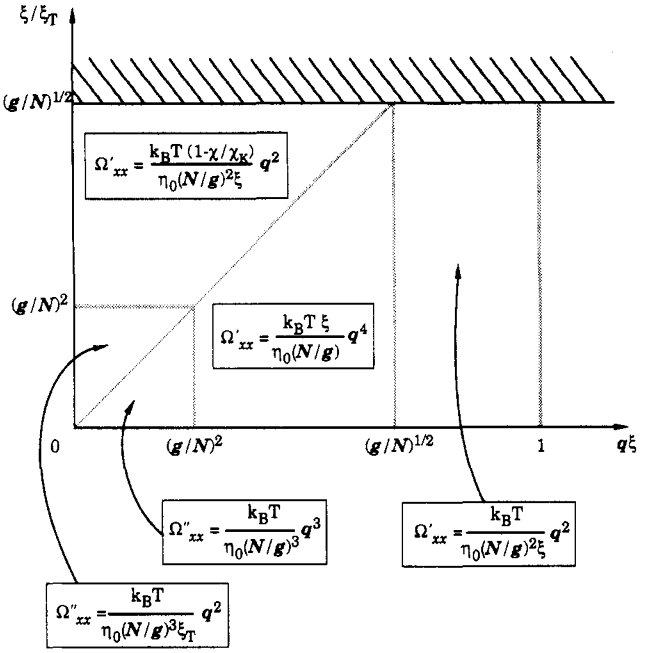

Figure 2. Dominant contributions to the relaxation rate of the interdiffusion mode in the reptation model.

mobility is

$$M'_{xx}(\mathbf{q}) = c^2\frac{x(1-x)}{\eta_0(qL)^2}\xi^2\left[1-\exp\left(\frac{-q^2R_g^{\,2}}{6}\right)\right] \tag{30}$$

where R_g is the radius of gyration of the chain given by eq 2 and $L = (N/g)\xi$ is the contour length of the chain along its tube of radius ξ. The mobility is independent of the wave vector and equal to

$$M'_{xx}(\mathbf{q}) \sim \frac{c^2x(1-x)\xi^2}{(N/g)\eta_0} \quad \text{when } qR_g < 1$$

It decreases with the wave vector as

$$M'_{xx}(\mathbf{q}) \sim c^2\frac{x(1-x)}{\eta_0(qN/g)^2} \quad \text{when } qR_g > 1$$

The contribution Ω'_{xx} to the initial decay rate is then given by eq 16:

$$\Omega_{xx}(\mathbf{q}) = k_BTq^2M'_{xx}(\mathbf{q})/c^2S_{xx}(\mathbf{q}) \tag{31}$$

In the limit of vanishing wave vector, this gives back the mutual diffusion constant (29). When $\xi_T^{-1} < q < R_g^{-1}$ we obtain

$$\Omega'_{xx}(\mathbf{q}) = \frac{k_BT\xi}{\eta_0N/g}q^4 \sim q^4N^{-1}c^{-2} \tag{32}$$

Finally, when $qR_g \gg 1$ and $q\xi < 1$, the relaxation rate is

$$\Omega'_{xx}(\mathbf{q}) = \frac{k_BT}{\eta_0(N/g)^2\xi}q^2 \sim q^2N^{-2}c^{-7/4} \tag{33}$$

These last two scaling laws are characteristic of the reptative motion of the chains. All our results are summarized in Figure 2, where in the various regions of the plane $[\xi/\xi_T, q\xi]$ we give the dominant contribution to the initial decay rate Ω_{xx}. It should be noticed that the region in this plane where Ω''_{xx} is the dominant contribution is a very narrow region in the vicinity of $q = 0$ and $\chi = \chi_K$ and that in most of the diagram $\Omega_{xx}(\mathbf{q}) = \Omega'_{xx}(\mathbf{q})$.

2. Spinodal Decomposition. When the concentration is larger than the spinodal value given by eq 5, the polymer solution is unstable and fluctuations of large wavelength do not relax but grow. It is clear that the unstable mode is the mutual diffusion mode. We now briefly discuss the initial stages of the spinodal decomposition;[17] our results are very similar to those of Pincus for polymer blends in the melt and can also be simply derived by renormalization of the monomer size to the blob size and of the friction constant of a monomer to the Stokes friction constant of a blob.

It is usually accepted that the relaxation rates obtained for a monophasic solution can still be used in the spinodal region. If the quench into the spinodal region is not too shallow, the relaxation rate of a fluctuation of composition of wave vector $\mathbf{q}$ is given by eqs 31–30 and 8:

$$\Omega_{xx}(\mathbf{q}) = \frac{k_BT}{L^2\xi\eta_0}\left[1-\exp\left(\frac{-q^2R_g^{\,2}}{6}\right)\right]\left[\frac{g}{N}\left(1-\frac{\chi}{\chi_K}\right)+q^2\xi^2\right] \tag{34}$$

This relaxation rate is indeed negative for small values of $\mathbf{q}$ corresponding to a growth of the composition fluctuations and reaches a minimum for a finite wave vector $\mathbf{q}^*$ that is the fastest growing mode of the instability.

If $\chi \gg \chi_K$, for a deep quench in the spinodal region, the fastest growing mode has a wave vector such that

$$\frac{1}{\mathbf{q}^*} = R_g(\ln(6\chi/\chi_K))^{-1/2} \sim N^{1/2}c^{-1/8} \tag{35}$$

the characteristic time for the growth of the fluctuations is $\tau(\mathbf{q}^*)$:

$$1/\tau(\mathbf{q}^*) = -\Omega_{xx}(\mathbf{q}^*) = T_{\text{rep}}^{\;-1}(\chi/\chi_K) \tag{36}$$

where $T_{\text{rep}} = (N/g)^3(\eta_0\xi^3/k_BT) \sim N^3c^{3/2}$ is the reptation time.

For a quench close to the spinodal line, $1/\mathbf{q}^*$ is of the order of the correlation length of the composition fluctuations:

$$\frac{1}{\mathbf{q}^*} = R_g[(\chi/\chi_K)-1]^{-1/2} \tag{37}$$

and the growth rate is

$$1/\tau(\mathbf{q}^*) = -\Omega_{xx}(\mathbf{q}^*) = T_{\text{rep}}^{\;-1}[(\chi/\chi_K)-1]^2 \tag{38}$$

The concentration is here close to the critical concentration c_K and the reptation time must be evaluated for this value of the concentration. The growth rate tends to zero on the spinodal line, showing the classical critical slowing down.

VI. Concluding Remarks

We have presented in this paper a scaling description of the relaxation of concentration fluctuations in ternary polymer solutions that takes into account the excluded volume correlations, the hydrodynamic interactions, and the effect of entanglements. This has been possible only in the symmetric case where the two polymers have the same molecular weight and the same concentration (composition $x = {}^1/_2$ or close to ${}^1/_2$). For symmetric solutions the fluctuations of concentration and of composition in the solution are not correlated, and the two relaxation modes correspond to a cooperative concentration mode and to a mutual interdiffusion mode.

The cooperative concentration mode has a relaxation time identical to that of a single polymer in semidilute solution in a good solvent at the same concentration.

The Rouse–Zimm model neglects the effect of entanglements between the polymer chains, but the hydrodynamic theory can be carried out more quantitatively. One of the key points is the variation with the length scale of the viscosity of the solution. We have introduced here a priori in the relaxation equations a viscosity that increases with the length scale and which is equal to the solvent viscosity at length scales smaller than the blob size of the solution and equal to the macroscopic viscosity of the polymer solution at length scales larger than the blob size. We have checked that the precise functional form of this viscosity is not very relevant and that functional forms which extrapolate more smoothly between the two limiting values of the viscosity lead to the same scaling laws. A more complete theory should consider explicitly the nonlinear couplings between concentration fluctuations and the hydrodynamic motions of the chains that we take into account through this renormalized viscosity, but it does not seem to be available at present. Within our empirical approach, the relaxation rate of the composition fluctuations can be written as the sum of two terms: one takes into account the hydrodynamic long-range interactions between monomers or blobs and has the same form as in simple liquid binary mixtures with a viscosity equal to the macroscopic viscosity; the other term is a Rouse-like relaxation rate due to the local friction of the blob on the neighboring fluid.

A detailed theory that takes into account quantitatively the interplay between entanglement effects and hydrodynamic interactions does not exist to our knowledge. Starting from the structure of the relaxation rates in the Rouse–Zimm model, we have forced the reptation scaling laws in order to take into account the entanglements between chains. This can be done by considering the solution as a melt of blobs and by using the known results for polymer blends in the melt.[18,19] Our results are summarized in Figure 2 which could be directly compared to experiments. As already noted however the composition fluctuations have been treated at the mean field level and this is a poor approximation in the vicinity of the critical concentration for phase separation where the Ising critical exponents are expected. A Ginzburg criterion has been constructed in ref 5 which shows that the composition flutuations are relevant in a range $(1 - \chi/\chi_K) < g/N$ in the vicinity of the critical concentration; within this temperature range, the scaling laws for the diffusion constants must be modified. Following the lines of ref 5 we obtain $D'_{xx} = (k_B T[1 - (\chi/\chi_K)]^{\gamma_I})/\eta_0(N/g)^{3-\gamma_I}\xi$ and $D''_{xx} = (k_B T/6\pi\eta_M)(g/N)^{1-\nu_I}[1 - (\chi/\chi_K)]^{\nu_I}$, where ν_I and γ_I are the usual Ising exponents.

The main limitation of our work is the restriction to symmetric solutions. To extend our results to polymers of different molecular weights one needs a careful analysis of the mutual interdiffusion of two polymers of different molecular weights. This problem has generated a lot of controversies on how one should average the diffusion constants of the two polymers.[10] To our knowledge also, the mobility at finite wave vector has not been calculated. In asymmetric solutions, one must also include the crossed correlations between concentration and composition that introduce couplings between the pure interdiffusion and the pure cooperative modes that we have discussed here.

Possible developments of this study include the generalization to other solvency conditions (polymers in a Θ solvent or in a selective solvent) and to copolymer solutions as done within the framework of the mean field theory by Benoît and Benmouna.

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