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# Critical Fluctuations in Ternary Polymer Solutions

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ABSTRACT: The dynamics of critical fluctuations and spinodal decomposition in ternary mixtures of two polymers and a solvent are studied. The special case of a symmetrical mixture where concentration and composition fluctuations are decoupled is considered. The dynamical structure factor $S_I(q,t)$ which is directly measurable in the zero-average contrast condition is examined in detail. Its decay rate $\Gamma_I$ is calculated in the presence of hydrodynamic interaction, and various scaling properties with the wavevector $q$ are identified. These are found to be sensitive to the approximation made for the chain form factor $P(q)$, and a particular scaling not found in polymer blends is obtained in the intermediate $q$-range. The hydrodynamic interactions identified with mode coupling effects in critical mixtures are also discussed in detail. The kinetics of spinodal decomposition in the early stages is examined only in the linear approximations.

## 1. Introduction

The scattering properties of ternary polymer solutions were the subject of intensive studies in the last decade.[1-12] A large number of systems was studied either by static or dynamic light and neutron scattering, and the data were analyzed by various theoretical models. In some cases, special experimental conditions were chosen in order to observe particular phenomena or to check theoretical predictions. For instance, in the early experiments the mixtures were chosen in such a way that one polymer is isorefractive with the solvent and the second polymer has a finite increment of refractive index and its concentration is very low (trace amount). The aim of these experiments was to investigate the self-diffusion coefficient $D_s$ and check if the prediction of the reptation model[13] and in particular the scaling behavior of $D_s$ with the concentration and molecular weight could be observed. Further theoretical and experimental developments allowed for more progress along these lines, and several other systems were examined. In some systems, new properties were obtained by choosing the composition and the increments of refractive indices in such a way that the average contrast is zero: the so-called optical Θ condition. The experiments were, in general, carried out at room temperature and in a concentration range where the system remains in a stable monophasic state far from the critical point. The purpose of this paper is to explore the behavior of ternary polymer solutions satisfying the zero-average contrast conditions as a function of temperature and concentration. In the first part, we study the static and dynamic properties when the system is brought, by small temperature drops, close to the critical point C as illustrated by line (i) in Figure 1. In the second part, we discuss the kinetics of phase separation for ternary polymer solutions when the system is brought from the one-phase regime into the two-phase region as shown by line (ii) in Figure 1. This process can be implemented either by small drops of the temperature or by a single quench from $T_0$ to $T_f < T_0$. For ternary polymer solutions, unlike pure blends, there is another possibility of bringing the system from the uniphasic to the biphasic regions, which is to increase the concentration of the polymer, keeping the temperature and composition constant. This can be done by evaporation of the solvent which means that the spinodal curve is shifted downward from (a) to (b) as illustrated in Figure 1. In this case, one observes that the structure factor initially increases with time, and this initial growth will be examined including some new properties emerging from the presence of a low molecular weight solvent. The other process which can be examined concerns the reverse jump experiment where the system is brought from the initial two-phase region into the monophasic state by a reverse process as (ii) in Figure 1.

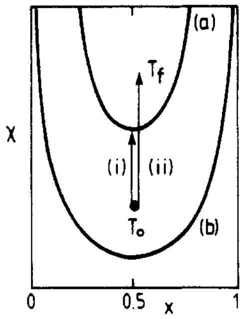

**Figure 1.** Phase diagram of a ternary mixture of polymer 1/polymer 2/solvent. The spinodal curve (a) corresponds to a smaller polymer concentration than (b).

## 2. Compatibility Enhancement and Fluctuations in the Presence of Solvent

When the solvent is added to a polymer blend, new properties emerge. First, the compatibility of the mixture is substantially enhanced by increasing the solvent concentration, which implies that the critical temperature $T_c$ is decreased for mixtures with UCST. It is clear that this compatibility enhancement or decrease of $T_c$ (i.e., increase of the critical parameter $\chi_c$) is due to the increase of entropy of mixing resulting from the presence of low molecular weight solvent. The complete expression of the critical parameter $\chi_c$ above which a phase separation takes place will be given shortly after in terms of polymer concentration, composition, molecular weight, and polymer–solvent interaction parameters. One can anticipate its limit in the high concentration regime for polymers having approximately the same degree of polymerization $N$:

$$\chi_c = \frac{1}{2\phi N x(1-x)} \qquad (1)$$

where $x$ is the composition of polymer 1 which is expressed as the ratio of its volume fraction $\phi_1$ and the total polymer volume fraction $\phi = \phi_1 + \phi_2$. It is clear that $\chi_c$(solution) < $\chi_c$(bulk) since $\phi < 1$, and this is illustrated in Figure 1 by a translation upward of the curve (b) into (a) when $\phi$

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decreases as more solvent with volume fraction $\phi_s = 1 - \phi$ is added. Moreover, the presence of solvent in the blend produces concentration fluctuations in addition to the composition fluctuations. The concentration fluctuations, which are absent in the bulk state, are particularly sensitive to the polymer–solvent interactions. The *chain conformations* are also modified since in good-solvent conditions, the chains are swollen and their *dimensions* are governed by critical exponents, which are more like *Ising exponents* such as $\nu = 0.6$. In Θ-solvent conditions, the chain statistics are essentially Gaussian and their dimensions governed by mean-field exponents ($\nu = 0.5$). In poor-solvent conditions, the chain is in the collapsed state, the exponents are modified, and in particular $\nu = {}^1/_3$. Additional complications arise in the presence of selective solvents, which can be good for one polymer and poor for the other, and a mixture of statistics takes place along with preferential adsorption phenomena. These complications will be avoided here. Concerning the dynamical properties, one considers two types of critical dynamics. The first one is the critical dynamics for composition fluctuations, which is similar to the one observed in the blend. The second one is the critical dynamics for concentration fluctuations which are similar to the ones observed in binary polymer–solvent solutions. The latter fluctuations are not of real interest here, and it will be assumed that the Θ temperature or solvent quality is roughly the same for both polymers, i.e., $\chi_{1s} = \chi_{2s} = \chi_{PS}$. Moreover, one knows that $\chi_c \ll \chi_{c,PS}$ since $\chi_c \sim 1/N$ as indicated by eq 1, whereas $\chi_{c,PS}$ is equal to ${}^1/_2$. This implies that when the temperature is increased, one reaches the critical temperature for polymer–polymer phase separation first, before the critical temperature for polymer–solvent phase separation is reached, and, consequently, the critical dynamics for *composition fluctuations* takes place first. Concentration and composition fluctuations are coupled, and one can define two correlation lengths: $\xi_0$ and $\xi$ are the correlation lengths for concentration and composition fluctuations, respectively. The approximate forms of $\xi_0$ and $\xi$ will be given later.

There are two different ways of decoupling the fluctuations of concentrations and composition. The first one is by choosing a symmetrical mixture which satisfies the following properties:

$$N_1 = N_2 = N;\quad P_1(q) = P_2(q) = P(q);\quad \chi_{1s} = \chi_{2s} = \chi_{PS};\quad x = {}^1/_2 \tag{2}$$

and for the dynamics, equal friction coefficients per monomer:

$$\zeta_1 = \zeta_2 = \zeta \tag{3}$$

The $P(q)$'s are form factors of the chains. This system will be discussed in the next section, and the decoupling will be shown explicitly.

The second way of probing the concentration and composition fluctuations separately is to choose the constrast factors $\nu_1$ and $\nu_2$ properly. The latter quantities represent in light scattering the increments of refractive indices and in neutron scattering the difference of scattering lengths per monomer 1 and 2 and a solvent molecule, respectively. They should not be confused with the critical exponent $\nu$ which will be introduced later. For example, in order to observe the composition fluctuations, it is sufficient to choose the system fulfilling the condition of zero-average contrast or optical Θ condition

$$x\nu_1 + (1 - x)\nu_2 = 0 \tag{4}$$

In this case the measured intensity is proportional to the structure factor $S_I(q)$:

$$S_I(q) = \frac{S_{11}(q)}{x^2} + \frac{S_{22}(q)}{(1-x)^2} - \frac{2S_{12}(q)}{x(1-x)} \tag{5}$$

This quantity represents the correlations of the order parameter $\rho_I(q)$:

$$\rho_I(q) = \rho_1(q)/x - \rho_2(q)/(1-x) \tag{6}$$

with

$$S_I(q) = \langle \rho_I(q)\, \rho_I(-q) \rangle \tag{7}$$

where the symbol $\langle\ \rangle$ indicates the ensemble average with respect to the equilibrium distribution. Likewise, in dynamic scattering experiments, the relaxation processes of the concentration and composition fluctuations are coupled if one measures the eigenmodes of the partial dynamic structure factors. However, the initial decay rate of $S_I(q,t)$, measured under the conditions of eq 4, gives directly the interdiffusive relaxation frequency. The critical slowing down, which bears a strong similarity with the pure polymer blends, can be monitored through the decay rate of $S_I(q,t)$.

## 3. Static Scattering Functions and Critical Behavior

The static scattering intensity for a ternary mixture of polymer 1, polymer 2, and a solvent has been obtained before as[14]

$$I(q) = \frac{\nu_1^2 S_1^\circ(q) + \nu_2^2 S_2^\circ(q) + (\nu_1^2 \vartheta_{22} + \nu_2^2 \vartheta_{11} - 2\nu_1\nu_2\vartheta_{12}) S_1^\circ(q)\, S_2^\circ(q)}{\mathrm{D}(q)} \tag{8}$$

where the bare structure factors $S_i^\circ(q)$ ($i = 1, 2$) are defined in terms of the total polymer volume fraction $\phi$, the composition $x$, and the form factors $P_1(q)$ and $P_2(q)$ as

$$S_1^\circ(q) = x\phi N_1 P_1(q),\quad S_2^\circ(q) = (1-x)\phi N_2 P_2(q) \tag{9}$$

The excluded-volume parameters can also be expressed in terms of the solvent volume fraction $\phi_s$ and the Flory–Huggins interaction parameters as[15]

$$\vartheta_{11} = 1/\phi_s - 2\chi_{1s} \tag{10a}$$

$$\vartheta_{22} = 1/\phi_s - 2\chi_{2s} \tag{10b}$$

$$\vartheta_{12} = 1/\phi_s - \chi_{1s} - \chi_{2s} + \chi \tag{10c}$$

The denominator $\mathrm{D}(q)$ of eq 8 is

$$\mathrm{D}(q) = S_1^\circ(q)\, S_2^\circ(q) \left[\left(\frac{1}{S_1^\circ(q)} + \vartheta_{11}\right)\left(\frac{1}{S_2^\circ(q)} + \vartheta_{22}\right) - \vartheta_{12}^2\right] \tag{11}$$

The intensity $I(q)$ should be positive or zero, which means that the denominator $\mathrm{D}(q)$ should also remain positive or zero. The stability condition of the mixture requires that

$$\mathrm{D}(q) \geq 0 \quad \forall q \tag{12}$$

In the case of a mixture of homopolymers, there is no microphase-separation transition, and therefore it is sufficient to examine the stability condition in the thermodynamic limit where $q = 0$. The spinodal equation defining the conditions under which a macrophase separation takes place is given by

$$\mathrm{D}(q=0) = 0 \tag{13a}$$

Combining this equation with eqs 10 and 11 yields the critical parameter $\chi_c$.

$$\chi_c = \chi_{1s} + \chi_{2s} - \frac{1}{\phi_s} + \left[\left(\frac{1}{\phi_1 N_1} + \frac{1}{\phi_s} - 2\chi_{1s}\right)\left(\frac{1}{\phi_2 N_2} + \frac{1}{\phi_s} - 2\chi_{2s}\right)\right]^{1/2} \quad (13b)$$

In the case of a symmetrical mixture eq 13b becomes

$$\chi_c = 2\chi_{PS} - \frac{1}{\phi_s} + \left[\left(\frac{1}{x\phi N} + \frac{1}{\phi_s} - 2\chi_{PS}\right)\left(\frac{1}{(1-x)\phi N} + \frac{1}{\phi_s} - 2\chi_{PS}\right)\right]^{1/2} \quad (13c)$$

and in the high concentration limit, the above result reduces to eq 1. This stability condition and the values of $\chi_c$ are deduced from $\mathrm{D}(q)$, which is common to $I(q)$ and all the partial structure factors $S_{ij}(q)$, and, therefore, they are independent of the optical conditions. We shall focus our attention on the different structure factors which can be deduced from eq 8. The first one $S_{11}(q)$ in the conditions of eq 2, keeping $x$ arbitrary, has the form

$$S_{11}(q) = \frac{x\phi NP(q)\,[1 + \vartheta(1-x)\phi NP(q)]}{\mathrm{D}(q)} \quad (14)$$

$$\mathrm{D}(q) = 1 + \vartheta\phi NP(q) - \chi(2\vartheta + \chi)x(1-x)\phi^2 N^2 P^2(q) \quad (15)$$

The second structure factor $S_I(q)$, which is defined by eq 5, takes a simple form in the symmetrical case with an arbitrary composition $x$:

$$S_I(q) = \frac{\phi NP(q)\,\{1 + [\vartheta + 2\chi x(1-x)]\phi NP(q)\}}{x(1-x)\mathrm{D}(q)} \quad (16)$$

When $x$ is equal to $^1/_2$, one has a further important simplification by noting that the denominator $\mathrm{D}(q)$ can be factorized as follows:

$$\mathrm{D}(q) = [1 + (\vartheta + \chi/2)\phi NP(q)][1 - (\chi/2)\phi NP(q)] \quad (17)$$

Substituting this equation into eq 16 yields

$$4S_{11}(q) = S_T(q) + (1/4)S_I(q) \quad (18)$$

$$S_T(q) = \frac{\phi NP(q)}{1 + (\vartheta + \chi/2)\phi NP(q)} \quad (19)$$

$$S_I(q) = \frac{4\phi NP(q)}{1 - (\chi/2)\phi NP(q)} \quad (20)$$

where $S_T(q)$ is the total structure factor describing the space correlations of the local total polymer concentration; i.e.

$$S_T(q) = S_{11}(q) + S_{22}(q) + 2S_{12}(q) \quad (21)$$

or

$$S_T(q) = \langle \rho_T(q)\,\rho_T(-q)\rangle \quad (22a)$$

with

$$\rho_T(q) = \rho_1(q) + \rho_2(q) \quad (22b)$$

This result calls for several comments. (i) One observes that the fluctuations of concentration and composition are completely *decoupled*. (ii) It appears from eq 6a that the zero-average contrast condition reads $\nu_1 = -\nu_2$ and the structure factor $S_I(q)$ has a form similar to the result obtained in the bulk limit. In the framework of the present mean-field approach this means that one has a direct access to the parameter $\chi$ as a function of *temperature* and *concentration* by *static scattering*. (iii) If this measurement of $\chi$ is made under the condition $\nu_1 = -\nu_2$, then it is clear that the *stability condition* is defined by the denominator of eq 20 which yields the critical parameter $\chi_c$ as

$$\chi_c = 2/\phi N \quad (23)$$

It is interesting to note that in this formalism the result in eq 23 is valid for *any concentration*, from the infinite dilution limit (single chain $\phi \to 0$ and $\chi_c \to \infty$) to the bulk limit $\phi = 1$ and $\chi_c = 2/N$. Similar observations were made by Onuki and Hashimoto[6b] from renormalization group theory arguments in the semidilute regime and in the $\Theta$-solvent conditions. (iv) The correlation lengths $\xi_0$ and $\xi$ will be examined shortly after as a function of the concentration, degree of polymerization, and temperature.

**3.1. On the Form Factor $P(q)$.** The essential result in eq 8 can be obtained by several methods. Stockmayer,[16] in 1950, derived its thermodynamic limit at $q = 0$ using pure statistical mechanical arguments. His result was the basis for establishing phase diagrams and measuring $\chi$ parameters by various techniques until the early 1980s. Its extension to a finite value of $q$ was first derived by using the chains of single contacts[14] as a direct extension of the Zimm equation[17] to ternary systems. It was then obtained by various other techniques, and some of them are reviewed in a recent paper.[18] In the framework of the random-phase approximation (RPA) method, the main result expresses the scattering functions ($S_{ij}(q)$, $I(q)$, etc., ...) in terms of bare structure factors $S_i{}^\circ(q)$ or single-chain form factors $P_i(q)$ and excluded-volume parameters $\vartheta_{ij}$. It was suggested[19] that the RPA (or mean-field approximation) can be extended by a renormalization argument assuming that the quantities $P_i(q)$ and $\vartheta_{ij}$ appearing in eq 8 are *renormalized form factors* and *excluded-volume parameters*. These quantities become concentration dependent, and hence they include the effect of higher order interactions (three-body and higher interaction terms). One may also include critical exponents (e.g., Ising exponents) to account for deviations from the mean-field variations with the temperature, molecular weight, and concentration of these quantities. With regards to the renormalization of the excluded volumes $\vartheta$'s or the interaction parameters $\chi$'s, detailed discussions can be found in the literature,[6] where pseudobinary models are developed for blends in the presence of a low molecular weight solvent. These models use a single renormalized $\chi$-parameter which describes the interaction between blobs of the two species since the blobs constitute the renormalized units. This point will not be developed further here; instead we turn to the discussion of the renormalized form factor $P(q)$. A first guess would be to assume that it is given by the Debye function but allowing the radius of gyration $R_g$ to be temperature and concentration dependent. This function can be used in its full form

$$P(q) = \frac{2}{u^2}(e^{-u} + u - 1), \quad u = q^2 R_g{}^2 \quad (24a)$$

or in its simplified approximate form[20]

$$P(q) = \frac{1}{1 + \frac{1}{2}q^2 R_g{}^2} \quad (24b)$$

The factor $^1/_2$ is used in the denominator to fit the high $qR_g$ range, but one can adjust this parameter to achieve a better fit of the desired range of $q$. This last form is convenient because it enables one to have analytical results in the study of dynamical properties. Other forms of $P(q)$ are available, and a particularly interesting model uses the blob picture which defines a crossover transition for chemical length $n$ along the chains which are either below or above the blob size $N_0$. This crossover is expressed as follows:

$$n < N_0, \quad R_n^{\,2} = n^{2\nu}a^2 \tag{25a}$$

$$n > N_0, \quad R_n^{\,2} = \left(\frac{n}{N_0}\right)\xi_0^{\,2} \tag{25b}$$

where $R_n$ is the end-to-end distance of a section of the chain having a chemical length $n$, $a$ is the statistical length, and $\xi_0$ is the size of the blob or the correlation length for concentration fluctuations:

$$\xi_0^{\,2} = N_0^{\,2\nu}a^2 \tag{25c}$$

The scaling behavior of $\xi_0$ and $N_0$ with $\phi$ is found as[13,21,22]

$$\xi_0 \sim \phi^{-3/4}, \quad N_0 \sim \phi^{-5/4} \tag{25d}$$

The form factor can easily be calculated from this model, and the result is[23]

$$NP(q) = 1 + \frac{N_0}{\nu a_1^{\,1/2\nu}}\left[F\left(\frac{1}{2\nu},a_1\right) - \frac{z}{a_1^{\,1/2\nu}}F\left(\frac{1}{\nu},a_1\right)\right] + \frac{2N}{a_2}\left[(1-z)e^{-za_2} + \frac{1}{a_2}(e^{-a_2} - e^{-za_2})\right] \tag{26a}$$

where

$$F(\mu,a_1) \equiv \gamma(\mu,a_1) - \gamma(\mu,a_1/N_0^{\,2\nu}) \tag{26b}$$

$\gamma(\mu,a_1)$ is the incomplete Gamma function

$$\gamma(\mu,a_1) = \int_0^{a_1}\mathrm{d}x\, x^{\mu-1}e^{-x} \tag{26c}$$

$$a_1 = q^2\xi_0^{\,2}/6; \quad a_2 = a_1/z; \quad z = N_0/N \tag{26d}$$

The exponent $\nu$ is usually chosen as 0.6 for good-solvent conditions, but one can choose another value such as the Ising exponent $\nu = 0.63$ to express, for example, the transition from mean field to Ising behavior near $T_c$. The second term on the right-hand side of eq 26a describes a single-chain behavior within blobs which is perturbed by excluded-volume interactions and hence governed by a critical exponent $\nu \neq 0.5$. The third term describes a cooperative behavior due to the interactions with other chains in the medium, and, therefore, it reflects mean-field behavior with an exponent $\nu = 0.5$ due to the screening of excluded-volume interactions. This expression can be used in the previous equations to calculate various structure factors numerically. It is useful in exploring the internal structure of the chains in the $q$ range corresponding to $qR_g \geq 1$. This is possible with light scattering for high molecular weight and with neutron scattering for practically any polymer mixture that can be considered. Furthermore, the blob picture given in this calculation of $P(q)$ is reasonable only in the semidilute range where $\xi_0 \leq R_g$, but all our considerations in this study, either in the one-phase or in the two-phase regions, are meaningful only for concentrations above the overlap threshold $\phi^*$ since in the dilute range $\chi_c$ is very high and one cannot reach the critical region easily by lowering the temperature. The introduction of a swelling behavior within blobs is due to polymer–solvent interactions or excluded-volume interactions. Additional conformational changes of the chains have been suggested[24,25] when the mixture is brought close to the critical point. These changes are due to the incompatibility of polymers and can be included through the composition correlation length $\xi$ which is very sensitive to the Flory–Huggins parameter $\chi$ since it diverges as one approaches the critical point $\chi = \chi_c$. To our knowledge, this renormalized form factor $P(q)$ as given by eq 26a has not been explicitly included before in the investigation of structural properties of ternary polymer mixtures. It could be useful in the interpretation of scattering data, especially if one needs to study the scaling behavior for high molecular weight polymers in a wide range of wavevectors $q$. To proceed further in seeking a simple analytical result, one can use the expression given by eq 24b as a first-order approximation and introduce the critical exponent $\nu$ in the final results to account for deviations from the mean-field behavior to the critical or Ising like behavior. Therefore, substituting eq 19 for eq 24b yields

$$\frac{S_T(q)}{S_T(0)} = \frac{\xi_0^{\,-2}}{q^2 + \xi_0^{\,-2}} \tag{27a}$$

with

$$S_T(0) = \frac{\phi N}{1 + (\vartheta + \chi/2)\phi N} \tag{27b}$$

and

$$\xi_0 = \frac{R_g}{2^{1/2}}[1 + (\vartheta + \chi/2)\phi N]^{-1/2} \tag{27c}$$

It is possible to make a connection between this result and the expression of $P(q)$ given by eq 26a. This is done by expanding $P(q)$ in the small $q$ range as

$$P(q) = 1 - \frac{1}{3}q^2R_g^{\,2} \tag{27d}$$

Assuming Gaussian chains of $(N/N_0)$ blobs of size $\xi_0 = N_0^{\nu}a$ from the blob hypothesis, one finds that $R_g$ is roughly given by

$$R_g^{\,2} = \frac{1}{6}\left(\frac{N}{N_0}\right)\xi_0^{\,2}, \quad \xi_0^{\,2} = N_0^{\,2\nu}a^2 \tag{27e}$$

The scaling behavior of $R_g$ with $N$ and $\phi$ is

$$R_g \sim \phi^{-1/8}N^{1/2} \tag{27f}$$

The same scaling behavior can be obtained from eq 27c by recalling that the renormalized second virial coefficient or excluded-volume[14,21,22] parameter $\vartheta$ scales with $\phi$ as $\vartheta \sim \phi^{1/4}$. Likewise $S_I(q)$ in eq 20 can be written as

$$\frac{S_I(q)}{S_I(0)} = \frac{\xi^{-2}}{q^2 + \xi^{-2}} \tag{28a}$$

where

$$\frac{S_I(q{=}0)}{4\phi N} = \frac{\chi_c}{\chi_c - \chi} \tag{28b}$$

and

$$\xi = \frac{R_g}{2^{1/2}}\left(\frac{\chi_c}{\chi_c - \chi}\right)^{1/2} \tag{28c}$$

with

$$\chi_c = 2/\phi N \tag{28d}$$

In the case where polymer 2 is isorefractive with the solvent, one has from eqs 18, 27a, and 28a

$$4S_{11}(q) = \frac{S_T(q{=}0)}{1 + q^2\xi_0^{\,2}} + \frac{S_I(q{=}0)}{4(1 + q^2\xi^2)} \tag{29}$$

where $S_T(q{=}0)$ and $S_I(q{=}0)$ are given by eqs 27b and 28b. Equation 28a,b shows that it is the correlation function for composition fluctuations which is more important when $\chi \to \chi_c$ as one approaches the critical temperature. The structure factor at $q = 0$ and the correlation length $\xi$ both diverge, indicating strong and long-range composition fluctuations. Let us assume that $\chi(T)$ satisfies the inverse temperature law:[26,27]

$$\chi(T) = \chi_a/T - \chi_b \tag{30}$$

where the constants $\chi_a$ and $\chi_b$ are due to enthalpic and entropic contributions, respectively. Substituting eq 30 for eq 28a,b yields

$$\frac{S_I(q{=}0)}{4\phi N} = \frac{T_c\chi_c}{\chi_a}\left(\frac{T - T_c}{T}\right)^{-1} \tag{31}$$

and

$$\xi = R_g\left[\frac{T_c\chi_c}{2\chi_a}\right]^{1/2}\left(\frac{T - T_c}{T}\right)^{-0.5} \tag{32}$$

One observes that the exponents governing the scaling of $S_I(q{=}0)$ and $\xi$ with $\epsilon \equiv |T - T_c|/T$ are mean-field exponents:

$$S_I(q{=}0) = \text{constant} \times \epsilon^{-\gamma}, \quad \gamma = 1 \tag{33}$$

and

$$\xi = \text{constant} \times \epsilon^{-\nu}, \quad \nu = 0.5 \tag{34}$$

This behavior is partly due to the approximate Gaussian forms of $P(q)$ in eq 24a,b. One can introduce corrections into the final results by using the critical exponents $\nu$ and $\gamma$ which are of the Ising type:

$$\gamma = 1.24 \quad \text{and} \quad \nu = 0.63 \tag{35a}$$

The scaling relationship between the exponents $\gamma$ and $\nu$ is

$$(2 - \eta)\nu = \gamma \tag{35b}$$

In the mean-field approximation $\eta = 0$, and in the Ising model, $\eta$ is found to be 0.032. This exponent was recently evaluated by neutron scattering for a blend of deuterated polybutadiene and plystyrene, and the result was approximately equal to the value given above.[28]

### 3.2. On the Ginzburg Criterion.

We have seen in section 2 that the presence of solvent in the mixture induces an enhanced compatibility which is expressed by a lower $T_c$ for mixtures characterized by an upper critical solution temperature (UCST). This behavior results also in a wider transition region $\epsilon = \Delta T = T - T_c$ as described by the Ginzburg criterion. In comparison with blends, one observes that, by adding a low molecular weight solvent, the transition from the mean-field to critical (or Ising-like) behavior should be smoother. To estimate the width of the transition region $\epsilon$ as a function of the polymer volume fraction $\phi = 1 - \phi_s$, we adopt the criterion used before for bulk[25-27] to polymer solutions and write

$$\epsilon = \text{constant} \times \tilde{\vartheta}_m{}^2 \frac{\left(\dfrac{1}{N_1\phi_1{}^3} + \dfrac{1}{N_2\phi_2{}^3}\right)^2}{\left(\dfrac{1}{N_1\phi_1} + \dfrac{1}{N_2\phi_2}\right)\left(\dfrac{R_{g1}{}^2}{N_1\phi_1} + \dfrac{R_{g2}{}^2}{N_2\phi_2}\right)^3} \tag{36}$$

where the constant is approximately 0.3; $\tilde{\vartheta}_m$ the volume of a unit segment is of the order $a^3$. If one assumes that this expression *remains valid* in the presence of solvent, its application to the symmetrical mixture ($\phi_1 = \phi_2 = \phi/2$) yields

$$\epsilon = \text{constant} \times \tilde{\vartheta}_m{}^2 \frac{N^2}{\phi^2}\frac{1}{R_g{}^6} \tag{37a}$$

Using eq 27e for the radius of gyration yields

$$\epsilon = \text{constant} \times \left(\frac{\tilde{\vartheta}_m}{a^3}\right)^2 N_0{}^{3(1-2\nu)}\frac{1}{N\phi^2} \tag{37b}$$

In the bulk limit $\phi = 1$ and $N_0 = 1$, one recovers the known result,[25-27] $\epsilon \sim 1/N$. In the presence of solvent, the Ginzburg domain $|T - T_c|$ is much wider and its size depends on the critical exponent $\nu$. If $\nu$ has the mean-field value 0.5, one obtains $\epsilon \sim 1/N\phi^2$, and if $\nu \neq 0.5$, recalling that[21-23] $N_0 \sim \phi^{-\delta}$ with $\delta = 1/(3\nu - 1)$, one finds

$$\epsilon \sim 1/N\phi^{\delta} \tag{37c}$$

if $\nu = 0.6$

$$\epsilon \sim N^{-1}\phi^{-5/4} \sim N^{-1}\phi^{-1.25} \tag{37d}$$

and if $\nu = 0.63$

$$\epsilon \sim N^{-1}\phi^{-1.1} \tag{37e}$$

This means that the range of temperatures defined by the Ginzburg criterion is much wider in the presence of solvent, and the transition from mean field to Ising models is smoother with some slight differences depending on the value of $\nu$. Obviously, these conclusions are only speculative at this stage because the extension of eq 36 to blends in the presence of solvent has not yet been shown rigorously. Furthermore, there are no data available at present which show the changes of the scattering properties in the vicinity of the critical temperature (i.e., the Ginzburg region) for such ternary mixtures. Static and dynamic light scattering experiments along these lines are in progress, and we hope to report on their results in the near future.

## 4. Dynamic Scattering Functions and Critical Slowing Down

The dynamic scattering from ternary mixtures of two polymers and a solvent has been the subject of intensive studies in the last decade. It is not our intention to review this subject here, but we would like to mention a few things. From the theoretical point of view, various models[22-31] are available in the study of dynamic scattering from ternary mixtures of two polymers and a solvent. A review of these models is not in the scope of this work, but it would be useful to make a few remarks concerning the random-phase approximation (RPA) and the single-exponential model in the calculation of the dynamic structure matrix. The standard RPA expresses the inverse dynamical response matrix $\chi(q,p)$ in the interacting system as a sum of the inverse dynamical bare response matrix $\chi_0(q,p)$ in the noninteracting systems and the excluded-volume matrix $\vartheta$.

$$\chi^{-1}(q,p) = \chi_0{}^{-1}(q,p) + \vartheta \tag{38}$$

$p$ represents the frequency variable since the response functions are expressed here in terms of their Laplace transforms. The relationship between response matrices and dynamical structure matrices is given by the linear response theory result which in the time domain reads

$$kT\chi(q,t) = -\frac{\partial}{\partial t}\mathbf{S}(q,t) \tag{39}$$

and the same equation is valid for bare quantities. One needs to specify the bare response functions or bare dynamic structure factors to solve this problem. These functions can be obtained, for example, from the model of Dubois-Violette and de Gennes,[32] who derived $S_0(q,t)$ for a single-chain including hydrodynamic interaction. This method has been used by Csiba, Jannink, and co-workers[12] to analyze spin-echo neutron experiments from mixtures of deuterated and ordinary poly(dimethylsiloxane) in a solvent itself made from a mixture of deuterated and ordinary benzene. The drawback of this model is that it cannot account for hydrodynamic interaction between different chains, besides the fact that it is a mean-field approximation neglecting memory effects (except in the bare dynamic structure factor as given in ref 32). Another method starts from the generalized Langevin equation describing the time evolution of $\mathbf{S}(q,t)$ and neglecting memory effects. This leads to a single-exponential decay of $\mathbf{S}(q,t)$ whose decay rate is given by the first cumulant matrix $\mathbf{\Omega}(q)$:

$$\mathbf{S}(q,t) = e^{-\mathbf{\Omega}(q)t}\mathbf{S}(q) \tag{40}$$

where $\mathbf{\Omega}(q)$ is given by the known equation

$$\mathbf{\Omega}(q) = q^2kT\mathbf{M}(q)\,\mathbf{S}^{-1}(q) \tag{41}$$

The mobility matrix $\mathbf{M}(q)$ is expressed in terms of $\mathbf{S}(q)$ using hydrodynamic interaction through the Oseen tensor model:

$$\mathbf{M}(q) = \mathbf{M}_0(\text{Rouse}) + \frac{1}{(2\pi)^2\eta}\int_0^\infty \mathrm{d}K\, f(K/q)\,\mathbf{S}(K) \tag{42a}$$

$\eta$ is the viscosity of the medium and $f(x)$ is given by

$$f(x) = x^2\left\{\frac{x^2+1}{2x}\log\left|\frac{x+1}{x-1}\right| - 1\right\} \tag{42b}$$

$\mathbf{M}_0$(Rouse) is the mobility in the Rouse limit, and its elements are

$$M_{ii}^\circ = \phi_i/\zeta_i \quad\text{and}\quad M_{ij}^\circ = 0 \tag{42c}$$

$\zeta_i$ is the friction coefficient of monomer $i$ having segment length $a_i$; $\zeta_i = 3\pi\eta a_i$. This model has been used to analyze quasielastic light scattering (QELS) experiments on various ternary mixtures.[5] Its drawback is due to the absence of memory effects, and hence it provides only the early stages in the decay of $\mathbf{S}(q,t)$. Solving eq 40 for a ternary mixture yields the partial dynamic correlation function $S_{ij}(q,t)$ as a sum of two exponentials

$$S_{ij}(q,t) = A_{ij}e^{-\Gamma t} + A'_{ij}e^{-\Gamma' t}\ (i,j = 1,2) \tag{43}$$

where $\Gamma$ and $\Gamma'$ are the eigenvalues of $\mathbf{\Omega}$:

$$\Gamma, \Gamma' = \Omega_{\text{av}} \pm [\Omega_{\text{av}}^2 - \Delta(\Omega)]^{1/2} \tag{44a}$$

$$\Omega_{\text{av}} = \frac{\Omega_{11} + \Omega_{22}}{2},\quad \Delta(\Omega) = \Omega_{11}\Omega_{22} - \Omega_{12}\Omega_{21} \tag{44b}$$

The $\Omega_{ij}$'s are the elements of $\mathbf{\Omega}$, and the amplitudes $A_{ij}$ can in general be written in terms of $\Omega_{ij}$ and $S_{ij}(q)$. We are essentially interested in the simple case of a symmetrical mixture satisfying eq 3. The important observation here is that the eigenmodes can be rigorously identified as the cooperative and the interdiffusive modes corresponding to the relaxation of concentration and composition fluctuations, respectively. By noting the identities

$$S_{11} = S_{22} = S(q);\quad S_{12}(q) = S_{21}(q) = S'(q) \tag{45a}$$

$$\Omega_{11} = \Omega_{22} = \Omega(q);\quad \Omega_{12} = \Omega_{21} = \Omega' \tag{45b}$$

and the definitions

$$\Gamma_{\text{T}} = q^2kT\frac{M_{\text{T}}(q)}{S_{\text{T}}(q)} \tag{46a}$$

$$\Gamma_{\text{I}} = q^2kT\frac{M_{\text{I}}(q)}{S_{\text{I}}(q)} \tag{46b}$$

where $M_{\text{T}}(q) = \sum M_{ij}$ and $M_{\text{I}}(q) = \sum(-1)^{(i+j)}M_{ij}/x_ix_j$, $i$ and $j$ taking the values 1 and 2. One easily finds[33]

$$\Gamma = \Gamma_{\text{T}} = q^2D_0\left\{\frac{\phi N}{S_{\text{T}}(q)} + \frac{N\zeta}{(2\pi)^2\eta}\int_0^\infty \mathrm{d}K\, f\!\left(\frac{K}{q}\right)\frac{S_{\text{T}}(K)}{S_{\text{T}}(q)}\right\} \tag{47a}$$

and

$$\Gamma' = \Gamma_{\text{I}} = q^2D_0\left\{\frac{4\phi N}{S_{\text{I}}(q)} + \frac{N\zeta}{(2\pi)^2\eta}\int_0^\infty \mathrm{d}K\, f\!\left(\frac{K}{q}\right)\frac{S_{\text{I}}(K)}{S_{\text{I}}(q)}\right\} \tag{47b}$$

$$D_0 = kT/N\zeta \tag{48}$$

$D_0$ is the single-chain diffusion coefficient in the Rouse limit; $S_{\text{T}}(q)$ and $S_{\text{I}}(q)$ are given by eqs 19 and 20, respectively. Substituting these results in eqs 47 and 48 yields

$$\Gamma_{\text{T}} = q^2D_0\left\{\frac{1}{P(q)} + \left(\vartheta + \frac{\chi}{2}\right)\phi N\right\} + q^2\frac{kT}{(2\pi)^2\eta}\int_0^\infty \mathrm{d}K\, f\!\left(\frac{K}{q}\right)\frac{\dfrac{1}{P(K)} + \left(\vartheta + \dfrac{\chi}{2}\right)\phi N}{P(q) + \left(\vartheta + \dfrac{\chi}{2}\right)\phi N} \tag{49a}$$

and

$$\Gamma_{\text{I}} = q^2D_0\left[\frac{1}{P(q)} - \frac{\chi}{\chi_{\text{c}}}\right] + q^2\frac{kT}{(2\pi)^2\eta}\int_0^\infty \mathrm{d}K\, f\!\left(\frac{K}{q}\right)\frac{P(K)}{P(q)}\frac{\left[1 - \dfrac{\chi}{\chi_{\text{c}}}P(q)\right]}{\left[1 - \dfrac{\chi}{\chi_{\text{c}}}P(K)\right]} \tag{49b}$$

The first terms on the right-hand side of these equations represent the Rouse contributions and the second terms the effects of hydrodynamic interactions. In the study of critical dynamics of polymers blends, these two terms are described as the non-mode-coupling and mode-coupling contributions, respectively. For the present problem, the second term describes the actual long-range hydrodynamic backflow effects. $\Gamma_{\text{T}}$ and $\Gamma_{\text{I}}$ are entirely defined in terms of the single-chain form factor $P(q)$. If one uses eq 26a of the blob hypothesis, the calculation of $\Gamma_{\text{T}}$ and $\Gamma_{\text{I}}$ becomes tedious and should be done numerically since the form of $P(q)$ is quite complicated. But, if one adopts the Ornstein–Zernike form as is usually done, simple analytical results are obtained. We shall consider both limits and discuss their implications in terms of the scaling behavior of $\Gamma_{\text{I}}(q)$.

**4.1. $q$-Dependence of $\Gamma_I$. (a) Using the Approximation in Equation 24b for $P(q)$.** Adopting eq 24b for $P(q)$ yields $S_I(q)$ in the Ornstein–Zernike form as given by eq 28a. In this case, one can calculate the integral in the expression of $\Gamma_I(q)$ analytically by noting that

$$\frac{1}{(2\pi)^2\eta}\int_0^\infty \mathrm{d}K\, f\left(\frac{K}{q}\right)\frac{1+q^2\xi^2}{1+K^2\xi^2} = \frac{F(q\xi)}{6\pi\eta\xi} \tag{50a}$$

where $F(x)$ is the so-called Kawasaki function:[20]

$$F(x) = \frac{3}{4}\frac{1+x^2}{x^3}[x + (x^2-1)\arctan x] \tag{50b}$$

Substituting eq 50a into eq 48b yields

$$\Gamma_I = q^2 D_0 \frac{(1+q^2\xi^2)(\chi_c - \chi)}{\chi_c} + q^2\frac{kT}{6\pi\eta\xi}F(q\xi) \tag{51}$$

It is known that, in the zero-average condition and for a symmetrical system, the only relaxation mode which is measured is the interdiffusive mode related with composition fluctuations and expressed by the dynamic structure factor:

$$S_I(q,t) = S_I(q)e^{-\Gamma_I t} \tag{52}$$

where $S_I(q)$ is given by eq 28. The scaling behavior of $\Gamma_I$ as displayed by eq 51 is very simple. One essentially distinguishes two regimes: (i) The critical regime where $\chi \rightarrow \chi_c$ and hence $\xi \rightarrow \infty$, implying $q\xi \gg 1$. In this case, by noting that $F(x) \rightarrow (3\pi/8)x$ when $x \rightarrow \infty$, one obtains from eq 51

$$\Gamma_I = q^4\frac{D_0 R_g^{\,2}}{2} + q^3\frac{kT}{16\eta} \tag{53}$$

Using the relationship between $R_g$ and $\xi_0$ given by the blob model in eq 27a, one can write the non-mode-coupling term as $q^4(kT/12N_0\zeta)\xi_0^2$. This is a known result[23] for Gaussian chains made of unit segments of length $\xi_0$ and friction coefficient $N_0\zeta$. The coefficient $^1/_{16} = 0.063$ is also consistent with a known result for Gaussian chains in the presence of hydrodynamic interaction.[23] (ii) Away from the critical point $\chi \ll \chi_c$, $\xi$ is small, and, therefore, $q\xi$ should remain small as compared to 1 in light scattering experiments. Noting that $F(x)$ goes to $^3/_4$ when $x \rightarrow 0$, one obtains approximately

$$\Gamma_I = q^2 D_0\left(1 - \frac{\chi}{\chi_c}\right) + q^2\frac{kT}{8\pi\eta\xi} \tag{54a}$$

Both processes in the non-mode-coupling limit and in the mode-coupling limit are diffusive, and the corresponding diffusion coefficient scales with $q$ and $\epsilon = |T - T_c|$ as

$$\Gamma_I \simeq q^2\epsilon^{2\nu} + q^2\epsilon^{\nu}\ (\nu = 0.5) \tag{54b}$$

Similar results were also obtained in the case of pure mixtures of homopolymers.[25-27]

**(b) Using the Blob Model for $P(q)$.** In this description, there is an additional crossover which is introduced in the blob model and taking place for $q = q^* = \xi_0^{-1}$. This crossover was not included before because $P(q)$ was supposed to be Gaussian everywhere in the whole $q$-range by using the approximation in eq 24b. Furthermore, we shall introduce here explicitly a distinction between the ranges of $q$ corresponding to $q < R_g^{-1}$ and $q > R_g^{-1}$. In the $q$-range smaller than $R_g^{-1}$, the chains behave as scattering points and their motion is diffusivelike, whereas for $q > R_g^{-1}$, internal modes should be taken into account.

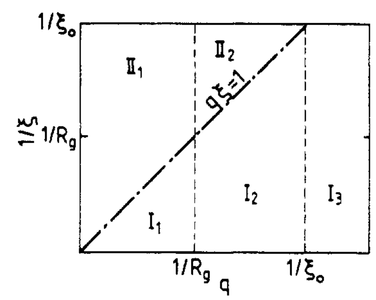

**Figure 2.** $q$-Regimes of $\Gamma_I$.

The various regimes of the $q$-dependence of $\Gamma_I$ are displayed in Figure 2 where the concentration and temperature effects are introduced explicitly through the correlation lenths $\xi$ and $\xi_0$. The third characteristic length representing the radius of gyration $R_g$ of the chain is also included. We did not extend the range of $\xi$ to smaller values than the blob size $\xi_0$ because the behavior inside blobs characterizes by definition the single-chain properties. The diagonal line in Figure 2 corresponds to $q\xi = 1$ and divides the plane into two regions. The critical lower half-plane ($q\xi > 1$, region I) and the noncritical upper half-plane ($q\xi < 1$, region II). It is observed that the decay rate of the dynamic correlation function $\Gamma_I$ depends crucially on the form factor $P(q)$ as we have discussed earlier. Therefore, a special care is taken when $qR_g > 1$ with regards to the internal structure of the chains. This $q$-range brings in new scaling regimes which were not found before in the critical dynamics of polymer blends. Since the scaling behavior of $\Gamma_I$ depends sensitively on $P(q)$, it would be useful to examine briefly its $q$-dependence in various $q$-ranges. In the small $q$ limit ($q < R_g^{-1}$), $P(q) \approx 1 - (1/3)q^2R_g^{\,2}$ where $R_g$ was given in eq 27e for a Gaussian chain of $N/N_0$ blobs of size $\xi_0$. In the intermediate $q$-range ($R_g^{-1} < q < \xi_0^{-1}$), we obtain the known result for Gaussian chains of $N/N_0$ renormalized units of size $\xi_0$:

$$P(q) = \frac{2}{q^2R_g^{\,2}} = \frac{12}{q^2\xi_0^{\,2}(N/N_0)} \tag{55a}$$

In the high $q$-range ($q > \xi_0^{-1}$), the radiation probes the behavior of a single chain inside the blob:

$$P(q) = \frac{6^{1/2\nu}\Gamma(1/2\nu)}{\nu}\frac{1}{(q\xi_0)^{1/\nu}(N/N_0)} \tag{55b}$$

For $\nu = {}^1/_2$, one recovers the same result as in the Gaussian case of eq 55a, but if $\nu \neq 0.5$, a different scaling behavior is obtained. We shall now examine the implications of these scaling laws on the relaxation frequency $\Gamma_I$ in various regions of $q$ and $\xi^{-1}$.

**(i) Critical Behavior: $q\xi > 1$.** In region $I_1$, $qR_g < 1$ and $q\xi > 1$, one obtains

$$\Gamma_I = q^2D_0\left(1 - \frac{\chi}{\chi_c}\right) + q^3\frac{kT}{6\pi\eta} \tag{56a}$$

In region $I_2$, we have $R_g^{-1} < q < \xi_0^{-1}$ and $q\xi > 1$ so that the behavior of $\Gamma_I$ is

$$\Gamma_I = q^4D_0\frac{R_g^{\,2}}{2} + q^3\frac{kT}{6\pi\eta} \tag{56b}$$

which is identical with the result found earlier in eq 53, except for the numerical factor $1/6\pi$ instead of $^1/_{16}$. In region $I_3$, we have $q\xi_0 > 1$ and $q\xi > 1$ and one obtains a new scaling behavior of $\Gamma_I$:

$$\Gamma_I = q^{(2+1/\nu)}\frac{kT}{\zeta}\frac{\nu a^{1/\nu}}{6^{1/2\nu}\Gamma(1/2\nu)} + q^3\frac{kT}{\eta}\frac{\Gamma\left(\frac{1-\nu}{2\nu}\right)}{\Gamma(1/2\nu)}\frac{1}{6\pi\sqrt{\pi}} \tag{56c}$$

If $\nu = 0.5$, one recovers the same behavior as in region $I_2$, but if $\nu \neq 0.5$, one obtains a different $q$-dependence of $\Gamma_I$, which has not been predicted before for blends.

**(ii) Noncritical Behavior: $q\xi < 1$.** We distinguish two regions in the half-plane corresponding to $q\xi < 1$ in Figure 2. The first one $II_1$ is limited by $q < R_g^{-1}$ and $\xi > \xi_0$ without making a distinction between the regions where $\xi > R_g$ and $\xi_0 < \xi < R_g$ since $\xi$ is not very large even if it is larger than $R_g$. The following variation of $\Gamma_I$ should prevail in region $II_1$:

$$\Gamma_I = q^2 D_0\left(1 - \frac{\chi}{\chi_c}\right) + q^2\frac{kT}{6\pi\eta\xi} \tag{56d}$$

This behavior is similar to the one obtained in eq 54a except for a slight difference in the numerical discrepancy in the second contribution due to the hydrodynamic interaction. The second region in the upper half-plane of Figure 2 corresponds to the intermediate ranges of $q$ and $\xi$ fulfilling the simultaneous conditions $R_g^{-1} < q$ and $\xi^{-1} < \xi_0^{-1}$, which means that $\xi$ is small and that the internal structure of the polymer should be taken into account. $\Gamma_I$ is found as follows:

$$\Gamma_I = q^4 D_0\frac{R_g^2}{2} + q^2\frac{kT}{6\pi\eta\xi} \tag{56e}$$

The Rouse (non-mode-coupling) term is similar to the one obtained in eq 53, but the Zimm (mode-coupling) term is different. This behavior is reasonable since the first contribution essentially reflects the internal structure of the polymer but the second describes long-range coupling between concentration and viscous modes and the $q^3$ behavior found in eq 53 describes the strong coupling in the critical region.

**4.2. Segmental Mobility $w_0$.** Here, we make a few remarks about the segmental mobility $w_0$, which can be introduced into eq 51 as follows:

$$\Gamma_I = q^2 kT\left[\frac{w_0}{S_I(q)} + \frac{1}{6\pi\eta\xi}F(q\xi)\right] \tag{57}$$

In the Rouse dynamics, one has $w_0 = 4\phi/\zeta$ and the factor 4 comes from $1/[x(1-x)] = 4$. This result corresponds to the so-called slow-mode theory since in this theory one has (by extension to the interdiffusion process in solution)

$$kTw_0^{s} = \left(\frac{1}{\phi_1 N_1 D_{10}} + \frac{1}{\phi_2 N_2 D_{20}}\right)^{-1} \tag{58a}$$

For a symmetrical mixture we have $D_{10} = D_{20} = kT/N\zeta$ and $\phi_1 = \phi_2 = \phi/2$, and, therefore, $w_0^{s}$ becomes

$$w_0^{s} = \frac{\phi}{\zeta x(1-x)} = \frac{4\phi}{\zeta} \tag{58b}$$

In the fast-mode theory, one has

$$kTw_0^{f} = N_1\phi_1 D_{10} + N_2\phi_2 D_{20} \tag{58c}$$

or for the symmetrical solution mixture

$$w_0^{f} = \phi/\zeta \tag{58d}$$

This means that the result obtained in eq 51 reproduces the slow-mode theory model. One can also introduce the mobility in the reptation regime if the degree of polymerization exceeds the tube length $N_e$. This is done by writing

$$w_0^{\mathrm{rept}} = \frac{\phi}{\zeta}\frac{N_e}{N} \tag{58e}$$

The reptation regime has been discussed recently by Roby and Joanny,[9,13] and it is possible to reproduce their results within the present formalism. These discussions may appear to be reptitious since they were often reproduced in the literature of polymer blends. Nevertheless, since we are dealing with polymer solutions, we think it is useful to repeat these discussions here not only for comparison with other models but also for a clear characterization of the effect of solvent and in particular the emergence of long-range hydrodynamic backflow interactions.

## 5. Spinodal Decomposition in Ternary Mixtures

We have mentioned earlier that the system can be put into the two-phase region in two different ways. The first possibility is to lower the temperature and hence increase the value of the interaction parameter $\chi$ at a fixed concentration and composition. This is illustrated by the dotted line (ii) in Figure 1. The second possibility is to increase the concentration of polymer without changing the temperature and composition, which means that the spinodal curve is shifted downward without change of the point representing the temperature and composition state of the system as illustrated in Figure 1. For example, the point at temperature $T_0$ and composition $x = 1/2$ which initially was in the one-phase region with respect to the spinodal curve a is finally in the two-phase region when the concentration is increased and the spinodal curve is shifted to curve b. The spinodal curves a and b are defined by eqs 2 and 13c. The critical dynamics describing the slowing down when the symmetric system is brought to the final state[34] by the process described by line (i) in Figure 2 has been discussed in the previous section. In this section, we consider the case where the system undergoes a deep quench from $T_0$ to $T_f < T_c$ into the two-phase region as illustrated by the dotted line (ii) in Figure 1a. The kinetics of spinodal decomposition is, of course, a well-documented subject for blends of homopolymers,[35-38] but only a few attempts were made to examine the case of ternary mixtures in the presence of low molecular weight solvent. Foley and Cohen[39] introduced the properties of the solvent explicitly in the free energy of the mixture and obtained the dynamical equations from the continuity laws. Hashimoto et al.[40] used the same method as in the case of blends by redefining the contrast factor and the interaction parameter. We also note that Binder[41] introduced the effects of vacancies as a third component in the description of the spinodal decomposition in mixtures of homopolymers. We extend the treatments of Foley, Cohen,[39] and Binder[41] by introducing several improvements as we shall see later. To make things clear, we briefly reproduce some known results starting from the continuity equations:

$$\frac{\partial}{\partial t}\rho_1(\mathbf{r},t) + \nabla\cdot j_1(\mathbf{r},t) = 0 \tag{59a}$$

$$\frac{\partial}{\partial t}\rho_2(\mathbf{r},t) + \nabla\cdot j_2(\mathbf{r},t) = 0 \tag{59b}$$

The incompressibility condition requires that the volume fractions of the three components should add up to 1:

$$\rho_1(\mathbf{r},t) + \rho_2(\mathbf{r},t) + \rho_s(\mathbf{r},t) = 1 \tag{59c}$$

The current densities $j_1(\mathbf{r},t)$ and $j_2(\mathbf{r},t)$ are given by the gradients of the chemical potentials:

$$j_1(\mathbf{r},t) = -M_{11}\nabla\left(\frac{\mu_1}{N_1} - \mu_s\right) - M_{12}\nabla\left(\frac{\mu_2}{N_2} - \mu_s\right) \quad (60a)$$

$$j_2(\mathbf{r},t) = -M_{21}\nabla\left(\frac{\mu_1}{N_1} - \mu_s\right) - M_{22}\nabla\left(\frac{\mu_2}{N_2} - \mu_s\right) \quad (60b)$$

where the Onsager coefficients $M_{ij}$ can be identified with the generalized mobilities introduced previously. We note that the cross terms $M_{12}$ and $M_{21}$ were neglected by Foley and Cohen[39] and by Binder[41] in the case of vacancies. To make further progress, we should calculate the chemical potentials per sites $\mu_1/N_1$, $\mu_2/N_2$, and $\mu_s$. This can be done by extending the classical procedure[35-41] to mixtures in the presence of a low molecular weight solvent starting from the free energy functional

$$\frac{\Delta F}{kT} = \int \mathrm{d}^3r \left\{\frac{f_{\mathrm{FH}}[\rho(r)]}{kT} + \frac{1}{36}\left[\frac{{\sigma_1}^2}{\rho_1(r)}\left|\nabla\rho_1(r)\right|^2 + \frac{{\sigma_2}^2}{\rho_2(r)}\left|\nabla\rho_2(r)\right|^2\right]\right\} \quad (61a)$$

where $f_{\mathrm{FH}}[\rho]$ is the Flory–Huggins free energy per site:

$$\frac{f_{\mathrm{FH}}[\rho]}{kT} = \frac{\rho_1}{N_1}\ln\rho_1 + \frac{\rho_2}{N_2}\ln\rho_2 + \rho_2\ln\rho_s + \rho_s(\chi_{1s}\rho_1 + \rho_{2s}\rho_2) + \chi\rho_1\rho_2 \quad (61b)$$

The chemical potentials $\mu_s$, $\mu_1$, and $\mu_2$ can be obtained from the functional derivatives of eq 61a, and the final results are

$$\frac{1}{kT}\left(\frac{\mu_1}{N_1} - \mu_s\right) = \frac{\ln\rho_1 + 1}{N_1} + \chi\rho_2 + \chi_{1s}\rho_s - (\ln\rho_s + 1 + \chi_{1s}\rho_1 + \chi_{2s}\rho_2) \quad (62a)$$

$$\frac{1}{kT}\left(\frac{\mu_2}{N_2} - \mu_s\right) = \frac{\ln\rho_2 + 1}{N_2} + \chi\rho_1 + \chi_{2s}\rho_s - (\ln\rho_s + 1 + \chi_{1s}\rho_1 + \chi_{2s}\rho_2) \quad (62b)$$

Combining eqs 59 and 60, after having taken Fourier transforms, yields

$$\frac{\partial}{\partial t}\rho(q,t) = -q^2kT\mathbf{M}(q)\cdot\mu(q,t) \quad (63a)$$

where

$$\rho(q,t) = \begin{pmatrix}\rho_1(q,t)\\ \rho_2(q,t)\end{pmatrix};\quad \mu(q,t) = \begin{pmatrix}\dfrac{\mu_1(q,t)}{N_1} - \mu_s(q,t)\\ \dfrac{\mu_2(q,t)}{N_2} - \mu_s(q,t)\end{pmatrix} \quad (63b)$$

and

$$\mathbf{M} = \begin{pmatrix}M_{11} & M_{12}\\ M_{21} & M_{22}\end{pmatrix} \quad (63c)$$

**M** has already been defined in eq 42a and includes both Rouse frictional terms and long-range hydrodynamic effects which were neglected in refs 39 and 41. These terms are particularly important in solutions in the critical condition. To make further progress, we shall solve these equations in terms of the Fourier components $\delta\rho_1(q,t)$ and $\delta\rho_2(q,t)$ which represent the fluctuations in the volume fractions of polymers 1 and 2 from their average values $\rho_{01} \equiv \phi_1$ and $\rho_{02} \equiv \phi_2$, namely

$$\rho_1(q,t) = \phi_1 + \delta\rho_1(q,t) \quad (64a)$$

$$\rho_2(q,t) = \phi_2 + \delta\rho_2(q,t) \quad (64b)$$

$$\rho_s(q,t) = 1 - \rho_1(q,t) - \rho_2(q,t);\quad \rho_{s0} \equiv \phi_s \quad (64c)$$

After straightforward manipulations keeping only linear terms in $\delta\rho_1(q,t)$ and $\delta\rho_2(q,t)$, one obtains

$$\frac{\partial}{\partial t}\delta\rho(q,t) = -q^2kT\mathbf{M}\cdot\mathbf{S}^{-1}(q)\,\delta\rho(q,t) \quad (65a)$$

where $\delta\rho(q,t)$ is the column vector

$$\delta\rho(q,t) = \begin{pmatrix}\delta\rho_1(q,t)\\ \delta\rho_2(q,t)\end{pmatrix} \quad (65b)$$

and $\mathbf{S}^{-1}(q)$ is yielded by

$$\mathbf{S}^{-1}(q) = \begin{pmatrix}\dfrac{1}{\phi_1N_1} + \dfrac{q^2{\sigma_1}^2}{18\phi_1} + \dfrac{1}{\phi_s} - 2\chi_{1s} & \dfrac{1}{\phi_s} - \chi_{1s} - \chi_{2s} + \chi\\ \dfrac{1}{\phi_s} - \chi_{1s} - \chi_{2s} + \chi & \dfrac{1}{\phi_2N_2} + \dfrac{q^2{\sigma_2}^2}{18\phi_2} + \dfrac{1}{\phi_s} - 2\chi_{2s}\end{pmatrix} \quad (65c)$$

The latter equation can also be written in the standard form[18]

$$\mathbf{S}^{-1}(q) = {\mathbf{S}_0}^{-1}(q) + \vartheta$$

But in eq 65c only the small $q$-limit of $P_i(q)$ is used since in the starting free energy only the squares of gradient terms were introduced. Therefore, one can rewrite eq 65a in the more general form

$$\frac{\partial}{\partial t}\delta\rho(q,t) = -\mathbf{\Omega}(q)\,\delta\rho(q,t) \quad (65d)$$

where $\mathbf{\Omega}(q)$ is the first cumulant matrix already defined in the first part of this paper. The remaining task is to solve this equation and to introduce the effect of random noises as suggested by Cook[37] for binary alloys and by Binder[36] for blends of polymers. For simplicity and to keep in contact with our discussions in the first part of this paper, we shall consider the case of a symmetrical mixture having a composition $x = {}^1/_2$ and satisfying the conditions

$$N_1 = N_2 = N;\ P_1 = P_2 = P;\ \zeta_1 = \zeta_2 = \zeta;\ \chi_{1s} = \chi_{2s} = \chi_{\mathrm{PS}}$$

In this case, the solution of eq 65d simply is

$$\delta\rho_1(q,t) = \frac{1}{2}\left[\delta\rho_{\mathrm{T}}(q)\,e^{-\Gamma_{\mathrm{T}}t} + \frac{1}{2}\delta\rho_{\mathrm{I}}(q)\,e^{-\Gamma_{\mathrm{I}}t}\right] \quad (66a)$$

$$\delta\rho_2(q,t) = \frac{1}{2}\left[\delta\rho_{\mathrm{T}}(q)\,e^{-\Gamma_{\mathrm{T}}t} - \frac{1}{2}\delta\rho_{\mathrm{I}}(q)\,e^{-\Gamma_{\mathrm{I}}t}\right] \quad (66b)$$

where

$$\delta\rho_{\mathrm{T}}(q) = \delta\rho_1(q) + \delta\rho_2(q) \quad (66c)$$

$$\delta\rho_{\mathrm{I}}(q) = 2[\delta\rho_1(q) - \delta\rho_2(q)] \quad (66d)$$

The frequencies $\Gamma_{\mathrm{T}}$ and $\Gamma_{\mathrm{I}}$ coincide with the eigenvalues of $\mathbf{\Omega}$ and were discussed before. The factor ${}^1/_2$ in front of $\delta\rho_{1,2}(q)$ in eqs 66a and 66b is due to the definition of $\rho_{\mathrm{I}}$ in eq 6. The following time-dependent static structure factors are introduced:

$$S_{11}^{t}(q) = \langle|\delta\rho_1(q,t)|^2\rangle \qquad (67a)$$

$$S_{\rm I}^{t}(q) = \langle|\delta\rho_{\rm I}(q,t)|^2\rangle \qquad (67b)$$

$$S_{\rm T}^{t}(q) = \langle|\delta\rho_{\rm T}(q,t)|^2\rangle \qquad (67c)$$

Their time evolutions are obtained from eq 65 as

$$4S_{11}^{t}(q) = S_{\rm T}^{t}(q) + \frac{1}{4}S_{\rm I}^{t}(q) \qquad (68a)$$

with

$$S_{\rm T}^{t}(q) = \langle|\delta\rho_{\rm T}(q)|^2\rangle e^{-2\Gamma_{\rm T}t} \qquad (68b)$$

and

$$S_{\rm I}^{t}(q) = \langle|\delta\rho_{\rm I}(q)|^2\rangle e^{-2\Gamma_{\rm I}t} \qquad (68c)$$

The quantities $\langle|\delta\rho_{\rm T}(q)|^2\rangle = S_{\rm T}^{0}(q)$ and $\langle|\delta\rho_{\rm I}(q)|^2\rangle = S_{\rm I}^{0}(q)$ are the equilibrium static structure factors given by eqs 19 and 20, respectively, since the initial state is the equilibrium state. One recovers the correct relationship between $S_{11}^{0}(q)$, $S_{\rm T}^{0}(q)$, and $S_{\rm I}^{0}(q)$ consistently with eq 29. These results call for the following remarks: (i) in the case where polymer 2 is isorefractive with the solvent, one measures $S_{11}^{t}(q)$, which, as shown by eqs 4, 5, and 8, is a sum of two exponentials. The third-exponential term obtained by Foley and Cohen is due to the coupling between the concentration and composition fluctuations which for our symmetrical system reduces to zero. (ii) If the mixture is such that $\nu_1 = -\nu_2$ (i.e., zero-average contrast condition), one measures directly $S_{\rm I}^{t}(q)$, which evolves in time following a single exponential. (iii) A single-exponential behavior is also found in $S_{\rm T}^{t}(q)$, which is accessible when $\nu_1 = \nu_2$. In good-solvent conditions, the system is stable with regards to a phase-separation polymer/solvent and, therefore, $S_{\rm T}^{t}(q)$ should decay exponentially in time. This is, of course, not the case for $S_{\rm I}^{t}(q)$ and $S_{11}^{t}(q)$ when the system is brought from the equilibrium initial state at the temperature $T_0$ to the final state at the temperature $T$ as shown by line (ii) of Figure 1. Since the system is in the two-phase region with $\chi > \chi_{\rm c}$, $S_{\rm I}^{t}(q)$ grows exponentially in time. The growth rate $\gamma_{\rm I}(q)$ is given by eq 51:

$$\gamma_{\rm I}(q) = q^2 D_0(1 + q^2\xi^2)\frac{\chi - \chi_{\rm c}}{\chi_{\rm c}} + q^2\frac{kT}{6\pi\eta\xi}F(q\xi) \qquad (69)$$

The variation of $\gamma_{\rm I}(q)$ with the wavevector $q$ has been discussed in detail above as a function of temperature and volume fraction, and hence we do not reproduce this discussion here. We only note that the hydrodynamic effect on $\gamma_{\rm I}(q)$ plays a dominant role for ternary polymer solutions, and in this sense the present model brings a substantial improvement upon the model of Foley and Cohen where hydrodynamic interaction was neglected. In the case where polymer 2 is isorefractive with the solvent, although one measures $S_{11}^{t}(q)$, its time evolution is dominated by the growth of $S_{\rm I}^{t}(q)$ since $S_{\rm T}^{t}(q)$ relaxes quickly in time, $\Gamma_{\rm T}(q)$ being always positive in good-solvent conditions. (iv) The procedure described here applies also to a jump experiment where the system initially is in the two-phase region and is brought into the uniphasic state by a temperature jump. Similar expressions are obtained for the time-dependent structure factors $S_{11}^{t}(q)$, $S_{\rm T}^{t}(q)$, and $S_{\rm I}^{t}(q)$, but here these quantities relax exponentially to the equilibrium state and the relaxation rates $\Gamma_{\rm T}(q)$ and $\Gamma_{\rm I}(q)$ are positive since $\chi < \chi_{\rm c}$. This will be the subject of a future paper.

**Effect of the Random Noise.** We have solved the continuity eqs 57 or 61a without taking into account the effect of the random noise which modifies eq 61a in the following way:

$$\frac{\partial}{\partial t}\rho(q,t) = -q^2 kT\mathbf{M}(q)\cdot\mu(q,t) + \mathbf{f}(q,t) \qquad (70)$$

This effect was first introduced by Cook[27] for binary alloys and by Binder[36] for polymer blends. In the case of interest to us, the relevant structure factor $S_{\rm I}^{t}(q)$ is measured under the zero-average contrast conditions. Its time evolution is not simply given by eq 68c, but due to the effect of the random noise it should be modifed as follows:

$$S_{\rm I}^{t}(q) = S_{\rm I}^{T_{\rm f}}(q) + [S_{\rm I}^{T_0}(q) - S_{\rm I}^{T_{\rm f}}(q)]e^{-2\Gamma_{\rm I}(q)t} \qquad (71)$$

where $S_{\rm I}^{T_{\rm f}}(q)$ and $S_{\rm I}^{T_0}(q)$ are the structure factors at the final temperature $T_{\rm f}$ and the initial temperature $T_0$, respectively. Similar modifications should be introduced for the time evolutions of $S_{11}^{t}(q)$ and $S_{\rm T}^{t}(q)$ when the effects of the random noise are included.

## 6. Conclusions

In this paper, we examined the dynamics of critical fluctuations and spinodal decomposition in ternary mixtures of two polymers and a solvent. The importance of optical conditions emerge essentially noting that when the average contrast is zero the measured dynamic structure factor decays following a single exponential which we tried to investigate in detail. This system shows properties similar to those in the pure polymer mixture problem, and the new effects that emerge are due to the presence of a low molecular weight solvent. These effects can be summarized in the following points:

(i) The polymer mixture becomes more compatible as the solvent concentration $\phi_{\rm s} = 1 - \phi$ increases since the critical interaction parameter $\chi_{\rm c}$ is inversely proportional to $\phi$ as shown by eq 1.

(ii) The transition from mean-field behavior to Ising-like (or critical) behavior is less rapid as in the blend. This is found by extending the Ginzburg criterion to polymer solutions and showing that the region where this transition takes place is inversely proportional to the polymer concentration, and, therefore, it becomes much wider as the solvent content is increased.

(iii) The hydrodynamic interaction becomes also dominant as the solvent concentration is increased. It was recognized before that, even for polymer blends close to the critical conditions, the hydrodynamic coupling between the long-range viscous modes and the composition fluctuation modes plays a crucial role in the critical slowing down. Here, such a coupling exists not only because of critical conditions but also because of the presence of solvent as well. Far from the critical conditions, the usual hydrodynamic interaction is introduced with a viscosity $\eta$ affected only by the polymer concentration. When the latter increases, $\eta$ increases and the effect of hydrodynamic interaction is reduced because of the screening introduced by Edwards.[20] If the system is taken close to the critical conditions and if the polymer concentration is sufficiently high, one should correct the viscosity for the temperature effect as is usually done for polymer blends.[26,27]

In the last part of this paper, we examined the kinetics of spinodal decomposition in ternary polymer solutions. This is a particularly important subject which has had only moderate attention in the literature from an experimental point of view.[40,45,46] We have extended earlier treatment[39,41] in many respects. First, we have taken into account the effects of concentration gradients to all orders by introducing the full form factor $P(q)$ instead of the $q^2$ term only. The replacement of $P(q)$ by the approximate form in eq 24b was chosen only for convenience in order to have analytical results, but other more elaborate forms could be used as shown in eq 26. We have introduced the effect of hydrodynamic interaction both in the diagonal and in the off-diagonal Onsager coefficients. This is particularly important for polymer solutions as shown in the early part where the effects of hydrodynamic interaction on the scaling behavior of the decay rates were examined. In the treatment of spinodal decomposition, we have not included the effect of nonlinearities which can be introduced by expanding the chemical potentials to higher orders in $\delta\rho(q,t)$ and using methods similar to the ones applied to polymer blends by Akcasu and coworkers.[42] A similar treatment can be used to describe the kinetics of polymer mixing in a temperature jump experiment by taking the system from an initial state in the two-phase region to a final state in the one-phase region. The present work will be the basis for the interpretation of light scattering experiments on the mixture PMMA/PDMS/chloroform in approximately the conditions of zero-average contrast as defined earlier. This system has been studied before[43,44] in the uniphasic region, and more experimental work is in progress to characterize the concentration and temperature effects on the dynamical properties of this system.

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$$\vartheta_{ii} = \frac{\tilde{\vartheta}_i^{\,2}}{\tilde{\vartheta}_s}\left(\frac{1}{\phi_s} - 2\chi_{is}\right); \ (i = 1, 2)$$

$$\vartheta_{12} = \frac{\tilde{\vartheta}_1\tilde{\vartheta}_2}{\tilde{\vartheta}_s}\left(\frac{1}{\phi_s} - \chi_{is} - \chi_{2s} + \chi_{12}\right)$$

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