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# Concentration Fluctuations in Polymer–Polymer–Solvent Systems

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*Received November 1, 1986*

ABSTRACT: We examine the dynamics of concentration fluctuations and spinodal decomposition in ternary systems composed of two polymers and a single solvent, assumed to be well-described by the Flory–Huggins model. The dynamic light-scattering spectrum in the one-phase region is calculated for systems in which one of the polymers is isorefractive with the solvent. It is shown that the spectrum in this case is well represented, in the limit $qR_G < 1$, by a sum of two exponentials. Only in the limit where the probe species is infinitely dilute does single-exponential behavior occur. Recent experimental results showing nonsingle-exponential behavior and in some cases the existence of two distinct modes of decay are discussed in light of these predictions. The theory of spinodal decomposition as formulated for binary systems is extended to the ternary case. It is shown that the light-scattering spectrum will evolve as the sum of three exponentials after quenches into the spinodal region. Recent experimental results are in qualitative agreement with this finding.

## Introduction

Concentration fluctuations in polymer–solvent systems have been studied extensively in recent years. Both dynamic and static light scattering techniques have been used to provide much new information on the behavior of dilute and semidilute solutions. These developments, along with numerous theoretical advances, notably the scaling laws,[1] have greatly increased our understanding of polymer–solvent systems in the one-phase region. Much less work has been done on polymer–polymer systems, both as a consequence of the comparative rarity of compatible polymer systems and as a result of the experimental difficulties that arise when studying such systems. Dynamic light scattering has been applied to low molecular weight polymer mixtures as studied recently by Murschall et al.[2] For higher molecular weights, Rutherford back-scattering spectrometry[3] have been found to be extremely useful. While considerable effort is being made to understand polymer–solvent and polymer–polymer systems in the one-phase region, there is also increased interest in the dynamics of phase separation in such systems. In particular, recent developments in the theory of spinodal decomposition in polymer–polymer mixtures have led to several experimental studies.[4-6] de Gennes[7] has shown that for quenches into the spinodal region, the structure factor associated with the total intensity at time $t$, $\langle|\delta\phi_A(q,t)|^2\rangle$, can be described in the early stages of spinodal decomposition by

$$\langle|\delta\phi_A(q,t)|^2\rangle = \langle|\delta\phi_A(q,0)|^2\rangle e^{-2\tau^{-1}(q)t} \quad (1)$$

where $\phi_A$ is the volume fraction of polymer A and the relaxation time, $\tau(q)$, is given by

$$\tau^{-1}(q) = q^2\Lambda(q)\left(\frac{1}{N\phi_A\phi_B} - 2\chi_{AB} + \frac{a^2q^2}{18\phi_A\phi_B}\right) \quad (2)$$

where $q$ is the scattering wave vector, $\Lambda(q)$ the $q$-dependent Onsager coefficient of the binary system, $N$ the degree of polymerization of both species, $\chi_{AB}$ the Flory interaction parameter, and $a$ the statistical segment length of each polymer. Binder[8] has modified the above approach to take account of random thermal fluctuations and obtains

$$\langle|\delta\phi_A(q,t)|^2\rangle = \langle|\delta\phi_A(q,0)|^2\rangle e^{-2\tau^{-1}(q)t} + \langle|\delta\phi_A(q,\infty)|^2\rangle(1 - e^{-2\tau^{-1}(q)t}) \quad (3)$$

where $\langle|\delta\phi_A(q,\infty)|^2\rangle$ is the structure factor as $t \rightarrow \infty$. In the early stages of spinodal decomposition and for $q$-values such that $q < q_c$, $q_c$ being the wave vector at which $\tau(q)$ changes sign, both equations predict that the structure factor will grow exponentially with time for quenches into the spinodal region, but for quenches in the one-phase region, Binder's approach predicts that the structure factor will decay to a finite value $\langle|\delta\phi_A(q,\infty)|^2\rangle$ rather than zero, in agreement with experiment. It should be stressed, however, that both theories are linear in nature and will not be able to describe the later stages of spinodal decomposition where nonlinear effects will be dominant.

The above predictions have largely been confirmed in recent experiments on polymer–polymer phase separation. For example, Snyder et al.[6] have used light scattering to monitor the time evolution of the structure factor after quenches into the spinodal region of a polystyrene–poly(vinyl methyl ether) mixture. In the early stages of spinodal decomposition, a plot of the logarithm of the total intensity vs. time yields a straight line in agreement with the predictions of theory. In the later stages of phase separation considerable deviation occurs due to the increased importance of nonlinear processes.

Less well understood are the dynamics in ternary systems composed of two polymers and a solvent. Recent experiments on both rigid[9] and flexible[10] polymers indicate that the dynamic light scattering spectrum in the one-phase region is well approximated (in the limit $qR_G < 1$ where $R_G$ is the radius of gyration) by a sum of two exponentials. In addition, many authors[11-16] have investigated dynamics in "isorefractive" systems, i.e., systems in which one of the polymer species is refractive-index matched to the solvent and hence presumably contributes very little to the excess scattering from the solution. At very low concentrations of the "optically labeled" or probe species, initial experiments[14] found single-exponential behavior of the correlation function, i.e.,

$$\langle\delta\phi_A(q,t)\delta\phi_A(-q,0)\rangle = \langle|\delta\phi_A(q,0)|^2\rangle e^{-q^2\lambda_1 t} \quad (4)$$

where $\lambda_1$ has been taken to be identical with the tracer

0024-9297/87/2220-1891$01.50/0

diffusion coefficient of the probe species. Recently, however, it has been found that even in the regime $qR_g < 1$ where internal polymer modes are not probed, the spectrum of the isorefractive system cannot be described by a single exponential as in eq 4. Chu et al.,[13] for example, have studied a pseudoternary system composed of two polymers and a cosolvent mixture and find that even when one of the polymers is index matched to the solvent mixture, two modes of decay, similar to those observed in nonisorefractive systems, are detected. Similar results have been obtained by Nemoto et al.[16] for a ternary system spanning a wide range of compositions of the isorefractive polymer. Other authors have observed nonexponential behavior of the correlation function but have not resolved their spectrum into two distinct modes of decay. Lodge and co-workers,[15] for example, have proposed that polydispersity effects play a major role and have presented an analysis on this basis. On a different but related topic, the study of phase separation in polymer–polymer–solvent systems is still at an early stage of investigation. Sasaki and Hashimoto[17] have studied a nonisorefractive ternary system and find significant deviation from the theories developed by de Gennes and Binder for binary systems. They interpreted this phenomenon as a consequence of the finite time required to quench into the spinodal region but did not discuss the applicability of binary theory to ternary systems.

In this paper we present an analysis of concentration fluctuations in ternary systems in general and isorefractive systems in particular. In the one-phase region we review the steps involved in calculating the light-scattering spectrum with the aim of offering an explanation for some of the recent experimental results. Finally, we extend the available theory of spinodal decomposition to the ternary case in order to provide a framework for the analysis of spinodal decomposition in ternary systems.

## Equations Governing the Dynamics of Concentration Fluctuations

We consider a system composed of two polymers, A and B, of degrees of polymerization $N_A$ and $N_B$, in a solvent, S. We assume that the free energy of mixing (per lattice site) is given by the usual Flory–Huggins[1] expression for concentrated solutions

$$\Delta f_{FH}/kT = \phi_S(\mathbf{r}) \ln \phi_S(\mathbf{r}) + (1/N_A)\phi_A(\mathbf{r}) \ln \phi_A(\mathbf{r}) + (1/N_B)\phi_B(\mathbf{r}) \ln \phi_B(\mathbf{r}) + \chi_S\phi_S(\mathbf{r})[\phi_A(\mathbf{r}) + \phi_B(\mathbf{r})] + \chi_p\phi_A(\mathbf{r})\phi_B(\mathbf{r}) \quad (5)$$

where the $\phi_i(\mathbf{r})$ are the spatially varying volume fractions and where we have assumed for convenience that the solvent–polymer interaction parameters are equal and given by $\chi_S$. This assumption simplifies the expressions for the diffusion coefficients obtained below but does not affect the conclusions of this work. The polymer–polymer interaction parameter is denoted by $\chi_p$. Equation 5 can be extended to include contributions to the free energy from concentration fluctuations. These contributions can be expressed in terms of the gradients of the volume fractions[18] giving a relation of the form

$$\Delta f/kT = (\Delta f_{FH}/kT) + k_{AA}[\nabla\phi_A(\mathbf{r})]^2 + k_{AB}\nabla\phi_A(\mathbf{r})\nabla\phi_B(\mathbf{r}) + k_{BB}[\nabla\phi_B(\mathbf{r})]^2 \quad (6)$$

In general the coefficients, $k_{ij}$, will be functions of composition as expressed, for example, by de Gennes[7] in the binary case. In order to give a detailed description of spinodal decomposition over a somewhat wider range of wave vectors, we must include these gradient terms. A brief treatment of this aspect of the problem is given in Appendix A along with a calculation of the coefficients $k_{ij}$ based on de Gennes' results for binary systems. However, for the purpose of simplifying the main body of this paper, where our aim is to stress the multiexponential nature of dynamics in ternary systems, we will consider the $q \rightarrow 0$ limit where the gradient terms in eq 6 are negligible. We assume also that the system is completely incompressible so that density fluctuations can be neglected. Recent light-scattering experiments[2] have shown this to be a good assumption in polymer–polymer mixtures; we expect similar behavior in concentrated polymer–polymer–solvent systems. Finally we consider long time scales such that[8]

$$t \gg R_A^2/D_A \quad (7)$$

and

$$t \gg R_B^2/D_B \quad (8)$$

where the $R_i^2$ are radii of gyration and the $D_i$ are the tracer diffusion coefficients of polymers A and B. Thus, we do not consider the possibility of coupling between intermolecular and intramolecular dynamics. From eq 5 we can derive expressions for the chemical potential per segment of each component, giving

$$(\mu_S - \mu_S^0)/kT = \ln \phi_S(\mathbf{r}) + \phi_A(\mathbf{r})[1 - (1/N_A)] + \phi_B(\mathbf{r})[1 - (1/N_B)] + \chi_S[\phi_A^2(\mathbf{r}) + \phi_B^2(\mathbf{r})] + (2\chi_S - \chi_p)\phi_A(\mathbf{r})\phi_B(\mathbf{r}) \quad (9)$$

$$(\mu_A - \mu_A^0)/N_AkT = (1/N_A) \ln \phi_A(\mathbf{r}) - \phi_S(\mathbf{r})[1 - (1/N_A)] + \phi_B(\mathbf{r})[(1/N_A) - (1/N_B)] + \chi_S\phi_S^2(\mathbf{r}) + \chi_p\phi_B(\mathbf{r})(\phi_S(\mathbf{r}) + \phi_B(\mathbf{r})) \quad (10)$$

$$(\mu_B - \mu_B^0)/N_BkT = (1/N_B) \ln \phi_B(\mathbf{r}) - \phi_S(\mathbf{r})[1 - (1/N_B)] + \phi_A(\mathbf{r})[(1/N_B) - (1/N_A)] + \chi_S\phi_S^2(\mathbf{r}) + \chi_p\phi_A(\mathbf{r})[\phi_S(\mathbf{r}) + \phi_A(\mathbf{r})] \quad (11)$$

With the necessary thermodynamic description of our system in place, we now need to formulate the continuity equations of our system. Assuming the system to be completely incompressible, we have two independent equations of continuity

$$\frac{\partial\phi_A(\mathbf{r})}{\partial t} + \nabla\cdot j_A(\mathbf{r}) = 0 \quad (12)$$

$$\frac{\partial\phi_B(\mathbf{r})}{\partial t} + \nabla\cdot j_B(\mathbf{r}) = 0 \quad (13)$$

The fluxes, $j_i(\mathbf{r})$, are given by

$$j_A(\mathbf{r}) = -\frac{\bar{v}_A\Lambda_{AA}}{m_SkT}\nabla[\mu_A(\mathbf{r})/N_A - \mu_S(\mathbf{r})] \quad (14)$$

$$j_B(\mathbf{r}) = -\frac{\bar{v}_B\Lambda_{BB}}{m_SkT}\nabla[\mu_B(\mathbf{r})/N_B - m_S(\mathbf{r})] \quad (15)$$

where $\bar{v}_A$ and $\bar{v}_B$ are the specific volume of component A and B, respectively, and $m_S$ is the molecular mass of the solvent. Equations 12–15 are derived in Appendix B and we have made the additional assumption that the Onsager coefficient, $\Lambda_{AB}$, can be neglected. This assumption does not affect the main points of our analysis in any significant way. We have also assumed that $\Lambda_{AA}$ and $\Lambda_{BB}$ are independent of the wave vector, $q$. This is justified for the length scales of interest in this paper; the $q$ dependence of the Onsager coefficients will in general be important only on length scales shorter than the radius of gyration of the polymer species.[8,19]

Equations 12 and 13 can be Fourier transformed and written in matrix form as

$$\frac{\partial}{\partial t}\begin{pmatrix}\phi_{\rm A}(q,t)\\ \phi_{\rm B}(q,t)\end{pmatrix} + q^2\begin{pmatrix}\bar{v}_{\rm A}\Lambda_{\rm AA}/kTm_{\rm s} & 0\\ 0 & \bar{v}_{\rm B}\Lambda_{\rm BB}/kTm_{\rm s}\end{pmatrix}\begin{pmatrix}\mu_{\rm A}(q)/N_{\rm A} - \mu_{\rm S}(q)\\ \mu_{\rm B}(q)/{\rm N}_{\rm B} - \mu_{\rm S}(q)\end{pmatrix} = 0 \quad (16)$$

To progress further we make the usual linear approximation: we let $\delta\phi_{\rm i}(q)$ be the deviation from the mean volume fraction, $\phi_{\rm i0}$, i.e.,

$$\delta\phi_{\rm i}(q) = \phi_{\rm i}(q) - \phi_{\rm i0} \quad (17)$$

and get the linearized chemical potentials per site

$$[\mu_{\rm A}(q)/N_{\rm A} - \mu_{\rm S}(q)]/kT = {\rm const} + \left(\frac{1}{N_{\rm A}\phi_{\rm A0}} + \frac{1}{\phi_{\rm S0}} - 2\chi_{\rm S}\right)\delta\phi_{\rm A}(q) + \left(\frac{1}{\phi_{\rm S0}} + \chi_{\rm p} - 2\chi_{\rm S}\right)\delta\phi_{\rm B}(q) \quad (18)$$

$$[\mu_{\rm B}(q)/N_{\rm B} - \mu_{\rm S}(q)]/kT = {\rm const} + \left(\frac{1}{N_{\rm B}\phi_{\rm B0}} + \frac{1}{\phi_{\rm S0}} - 2\chi_{\rm S}\right)\delta\phi_{\rm B}(q) + \left(\frac{1}{\phi_{\rm S0}} + \chi_{\rm p} - 2\chi_{\rm S}\right)\delta\phi_{\rm A}(q) \quad (19)$$

One obtains, then, by using these expressions in eq 16,

$$\frac{\partial}{\partial t}\begin{pmatrix}\delta\phi_{\rm A}(q,t)\\ \delta\phi_{\rm B}(q,t)\end{pmatrix} + q^2\begin{pmatrix}D_{\rm AA} & D_{\rm AB}\\ D_{\rm BA} & D_{\rm BB}\end{pmatrix}\begin{pmatrix}\delta\phi_{\rm A}(q,t)\\ \delta\phi_{\rm B}(q,t)\end{pmatrix} = 0 \quad (20)$$

where the diffusion coefficients, $D_{ij}$, are given by

$$D_{\rm AA} = (\bar{v}_{\rm A}\Lambda_{\rm AA}/m_{\rm S})\left(\frac{1}{N_{\rm A}\phi_{\rm A0}} + \frac{1}{\phi_{\rm S0}} - 2\chi_{\rm S}\right) \quad (21)$$

$$D_{\rm AB} = (\bar{v}_{\rm A}\Lambda_{\rm AA}/m_{\rm S})\left(\frac{1}{\phi_{\rm S0}} + \chi_{\rm p} - 2\chi_{\rm S}\right) \quad (22)$$

$$D_{\rm BA} = (\bar{v}_{\rm B}\Lambda_{\rm BB}/m_{\rm S})\left(\frac{1}{\phi_{\rm S0}} + \chi_{\rm p} - 2\chi_{\rm S}\right) \quad (23)$$

$$D_{\rm BB} = (\bar{v}_{\rm B}\Lambda_{\rm BB}/m_{\rm S})\left(\frac{1}{N_{\rm B}\phi_{\rm B0}} + \frac{1}{\phi_{\rm S0}} - 2\chi_{\rm S}\right) \quad (24)$$

The Onsager coefficients cannot be calculated a priori so that we must retain them as parameters of the model. We note, however, that they must be such as to give the following limiting values of the diffusion coefficients, $D_{\rm ij}$:[20]

$$\lim_{\phi_{\rm i}\to 0} D_{\rm ij} = D_{\rm i},\ {\rm i} = {\rm j}$$
$$= 0,\ {\rm i} \neq {\rm j} \quad (25)$$

where $D_{\rm i}$ is the tracer (self) diffusion coefficient of i in the ternary system.

Equation 20 can easily be solved by taking Laplace transforms and inverting to give

$$\delta\phi_{\rm A}(q,t) = \left[\frac{\lambda_1 - D_{\rm BB}}{\lambda_1 - \lambda_2}\delta\phi_{\rm A}(q,0) + \frac{D_{\rm AB}}{\lambda_1 - \lambda_2}\delta\phi_{\rm B}(q,0)\right]e^{-q^2\lambda_1 t} + \left[\frac{\lambda_2 - D_{\rm BB}}{\lambda_2 - \lambda_1}\delta\phi_{\rm A}(q,0) + \frac{D_{\rm AB}}{\lambda_2 - \lambda_1}\delta\phi_{\rm B}(q,0)\right]e^{-q^2\lambda_2 t} \quad (26)$$

$$\delta\phi_{\rm B}(q,t) = \left[\frac{\lambda_1 - D_{\rm AA}}{\lambda_1 - \lambda_2}\delta\phi_{\rm B}(q,0) + \frac{D_{\rm BA}}{\lambda_1 - \lambda_2}\delta\phi_{\rm A}(q,0)\right]e^{-q^2\lambda_1 t} + \left[\frac{\lambda_2 - D_{\rm AA}}{\lambda_2 - \lambda_1}\delta\phi_{\rm B}(q,0) + \frac{D_{\rm BA}}{\lambda_2 - \lambda_1}\delta\phi_{\rm A}(q,0)\right]e^{-q^2\lambda_2 t} \quad (27)$$

where the eigenvalues $\lambda_1$ and $\lambda_2$ are given by

$$\lambda_{1,2} = \tfrac{1}{2}[D_{\rm AA} + D_{\rm BB} \pm [(D_{\rm AA} - D_{\rm BB})^2 + 4D_{\rm AB}D_{\rm BA}]^{1/2}] \quad (28)$$

In the following section, eq 21–28 will be used to calculate the dynamic light-scattering spectrum in isorefractive systems. Next, they will be used to calculate the time evolution of the equal-time structure factor for quenches from the one-phase region into the spinodal region.

## Dynamic Light Scattering in Isorefractive Systems

The quantity of interest in dyanmic light scattering is $\langle\delta\epsilon(q,t)\delta\epsilon(-q,0)\rangle$ where $\delta\epsilon$ is the fluctuation in the dielectric constant, $\epsilon$, of the system. By defining the quantities $\epsilon_{\rm i}$ as

$$\epsilon_{\rm i} = (\partial\epsilon/\partial\phi_{\rm i})_{\phi_{\rm j},T,p} \quad (29)$$

we have at constant temperature and pressure

$$\delta\epsilon = \epsilon_{\rm A}\delta\phi_{\rm A} + \epsilon_{\rm B}\,\delta\phi_{\rm B} \quad (30)$$

so that

$$\langle\delta\epsilon(q,t)\delta\epsilon(-q,0)\rangle = \langle[\epsilon_{\rm A}\delta\phi_{\rm A}(q,t) + \epsilon_{\rm B}\delta\phi_{\rm B}(q,t)][\epsilon_{\rm A}\delta\phi_{\rm A}(-q,0) + \epsilon_{\rm B}\delta\phi_{\rm B}(-q,0)]\rangle \quad (31)$$

In a perfectly matched isorefractive system, we have $\epsilon_{\rm B} = 0$, giving

$$\langle\delta\epsilon(q,t)\delta\epsilon(-q,0)\rangle = \epsilon_{\rm A}{}^2\langle\delta\phi_{\rm A}(q,t)\delta\phi_{\rm A}(-q,0)\rangle \quad (32)$$

The right-hand side of eq 32 can be calculated directly from eq 26 so that the dynamic light-scattering spectrum from an isorefractive ternary system can be written as

$$\langle\delta\epsilon(q,t)\delta\epsilon(-q,0)\rangle = \epsilon_{\rm A}{}^2\langle|\delta\phi_{\rm A}(q,0)|^2\rangle \times \left[\left[\frac{\lambda_1 - D_{\rm BB}}{\lambda_1 - \lambda_2} + \frac{D_{\rm AB}}{\lambda_1 - \lambda_2}\frac{\langle\delta\phi_{\rm B}(q,0)\delta\phi_{\rm A}(-q,0)\rangle}{\langle|\delta\phi_{\rm A}(q,0)|^2\rangle}\right]e^{-q^2\lambda_1 t} + \left[\frac{\lambda_2 - D_{\rm BB}}{\lambda_2 - \lambda_1} + \frac{D_{\rm AB}}{\lambda_2 - \lambda_1}\frac{\langle\delta\phi_{\rm B}(q,0)\delta\phi_{\rm A}(-q,0)\rangle}{\langle|\delta\phi_{\rm A}(q,0)|^2\rangle}\right]e^{-q^2\lambda_2 t}\right] \quad (33)$$

Therefore, even in isorefractive systems, the spectrum at arbitrary concentrations is described by a sum of two exponentials with $q^2$ dependent relaxation times. Only in the limit $\phi_{\rm A} \to 0$, where, by using eq 25 and 28 we obtain

$$D_{\rm AB} = 0 \quad (34)$$

$$\lambda_1 = D_{\rm A} \quad (35)$$

$$\lambda_2 = D_{\rm BB} \quad (36)$$

does the spectrum reduce to a single exponential, i.e.,

$$\lim_{\phi_{\rm A}\to 0}\langle\delta\epsilon(q,t)\delta\epsilon(-q,0)\rangle = \epsilon_{\rm A}{}^2\langle|\delta\phi_{\rm A}(q,0)|^2\rangle e^{-q^2 D_{\rm A} t} \quad (37)$$

An origin of the nonsingle exponential which one observes even in isorefractive systems may be the thermodynamic coupling that occurs between the two variables $\delta\phi_{\rm A}$ and $\delta\phi_{\rm B}$. This is an intrinsic property of all ternary systems and is observed in systems of flexible polymers,[10] rodlike polymers,[9] and colloidal particles.[21]

Attempts to interpret observations of two-exponential decay behavior in isorefractive polymer systems in terms of entanglements between the probe species and the isorefractive polymer[13] should not be necessary. In recent experiments on isorefractive systems where nonsingle exponential behavior is observed, it is possible that aside from the effect of polydispersity,[15] contributions from both coupled diffusion coefficients through modes $\lambda_1$ and $\lambda_2$ are being detected due to the finite concentration of the labeled species. Experiments on polymer–polymer systems[22] indicate that the effect of concentration on the diffusion coefficient persists even at very low concentrations so that actually attaining the infinite dilution limit is quite difficult without extrapolation of the data. This effect is particularly pronounced in systems which show limited miscibility and becomes more significant as the coexistence curve is approached. While deviations from single-exponential behavior have been observed in isorefractive systems composed of two compatible polymers and a solvent, it is interesting to note that the most severe deviations have been detected in systems where the polymers are incompatible. Chu and co-workers[13] and Nemoto et al.[16] have detected two distinct modes of decay in polystyrene (PS)–poly(methyl methacrylate) (PMMA)–solvent systems, while, using the same polymers, Numasawa et al. have noticed significant deviation from single-exponential behavior. It seems likely, therefore, that thermodynamic coupling between the polymer species, particularly if they are incompatible, must be considered even at very low concentrations of the probe polymer. The infinite-dilution limit might not be easily attainable so that eq 33 may not be accurately approximated by eq 37. Other factors such as polydispersity treated by Lodge et al.[15] and incomplete refractive index matching will also be important. The latter issue is investigated further in Appendix C.

## Dynamics of Spinodal Decomposition in Ternary Systems

In this section we examine the dynamics of spinodal decomposition in ternary systems. We shall show that the light scattering spectrum from ternary systems will not exhibit the single-exponential behavior which is predicted to occur in binary systems. This is true whether or not the system is isorefractive, since in most experimental situations, spinodal decomposition will be observed when both polymer species have appreciable compositions. In our ternary system in which $\phi_A + \phi_B + \phi_S = 1$, we have three independent correlations, i.e., eq 20 can be rewritten in terms of the quantities $\langle \delta\phi_i(q,t)\delta\phi_j(-q,t)\rangle$ as

$$\frac{\partial}{\partial t}\begin{bmatrix} \langle |\delta\phi_A(q,t)|^2\rangle \\ \langle \phi_A(q,t)\delta\phi_B(-q,t)\rangle \\ \langle |\delta\phi_B(q,t)|^2\rangle \end{bmatrix} + q^2\begin{bmatrix} 2D_{AA} & 2D_{AB} & 0 \\ D_{BA} & D_{AA}+D_{BB} & D_{AB} \\ 0 & 2D_{BA} & 2D_{BB} \end{bmatrix}\begin{bmatrix} \langle |\delta\phi_A(q,t)|^2\rangle \\ \langle \delta\phi_A(q,t)\delta\phi_B(-q,t)\rangle \\ \langle |\delta\phi_B(q,t)|^2\rangle \end{bmatrix} = 0 \quad (38)$$

Equation 38 describes the time dependence of the correlations $\langle \delta\phi_i(q,t)\delta\phi_j(-q,t)\rangle$ as the system passes from its initial state at $T_0$, to its final state at $T_f$. It is clear that we can expect our spectrum to be composed of three exponentials and to be more complex than in the binary case where there exists one independent correlation and single-exponential behavior occurs. From eq 26 and 27 we expect our spectrum to be of the form

$$\langle \delta\epsilon(q,t)\delta\epsilon(-q,t)\rangle = Ae^{-2q^2\lambda_1 t} + Be^{-2q^2\lambda_2 t} + Ce^{-q^2(\lambda_1+\lambda_2)t} \quad (39)$$

In isorefractive systems the amplitudes $A$, $B$, and $C$ are given by

$$A = \epsilon_A{}^2\left[\left(\frac{\lambda_1 - D_{BB}}{\lambda_1-\lambda_2}\right)^2\langle|\delta\phi_A(q,0)|^2\rangle + \left(\frac{D_{AB}}{\lambda_1-\lambda_2}\right)^2\langle|\delta\phi_B(q,0)|^2\rangle + 2\left(\frac{\lambda_1 - D_{BB}}{\lambda_1-\lambda_2}\right)\left(\frac{D_{AB}}{\lambda_1-\lambda_2}\right)\langle\delta\phi_A(q,0)\delta\phi_B(-q,0)\rangle\right] \quad (40)$$

$$B = \epsilon_A{}^2\left[\left(\frac{\lambda_2 - D_{BB}}{\lambda_1-\lambda_2}\right)^2\langle|\delta\phi_A(q,0)|^2\rangle + \left(\frac{D_{AB}}{\lambda_1-\lambda_2}\right)^2\langle|\delta\phi_B(q,0)|^2\rangle + 2\left(\frac{\lambda_2 - D_{BB}}{\lambda_1-\lambda_2}\right)\left(\frac{D_{AB}}{\lambda_1-\lambda_2}\right)\langle\delta\phi_A(q,0)\delta\phi_B(-q,0)|\rangle\right] \quad (41)$$

$$C = -2\epsilon_A{}^2\left[\left(\frac{\lambda_1 - D_{BB}}{\lambda_1-\lambda_2}\right)\left(\frac{\lambda_2 - D_{BB}}{\lambda_1-\lambda_2}\right)\langle|\delta\phi_A(q,0)|^2\rangle + \left(\frac{D_{AB}}{\lambda_1-\lambda_2}\right)^2\langle|\delta\phi_B(q,0)|^2\rangle + \frac{D_{AB}}{\lambda_1-\lambda_2}\left(\frac{\lambda_2 - D_{BB}}{\lambda_1-\lambda_2} + \frac{\lambda_1 - D_{BB}}{\lambda_1-\lambda_2}\right)\langle\delta\phi_A(q,0)\delta\phi_B(-q,0)\rangle\right] \quad (42)$$

In the limit $\phi_A \rightarrow 0$, eq 39 will reduce in the isorefractive case to a single exponential, i.e.,

$$\lim_{\phi_A\rightarrow 0}\langle\delta\epsilon(q,t)\delta\epsilon(-q,0)\rangle = \epsilon_A{}^2\langle|\delta\phi_A(q,0)|^2\rangle e^{-2q^2D_{AA}t} \quad (43)$$

However, we are interested in concentrated solutions so that the full expression, eq 39, must be used. For quenches close to the spinodal curve, some simplification may be expected. In this case $\lambda_1$ will be slightly negative and $\lambda_2$ will be positive. If $|\lambda_2| > |\lambda_1|$, then the spectrum will consist of two exponentially decaying terms and a single exponentially increasing term. Thus at large times, the spectrum will be approximated by

$$\langle\delta\epsilon(q,t)\delta\epsilon(-q,t)\rangle = Ae^{-q^2\lambda_1 t} \quad (44)$$

so that single-exponential behavior will be expected. At very short times, contributions from the exponentially decaying terms must be included so that deviations from single-exponential behavior will be expected. Sasaki and Hashimoto[17] have studied phase separation in polymer–polymer–solvent systems and have indeed observed deviation from single-exponential behavior in the early stages of spinodal decomposition. The authors interpreted this phenomenon as a consequence of the finite time required to quench into the two-phase region but such an explanation may not be needed in light of our findings. It is difficult, however, to carry out a quantitative comparison of the data with eq 39, since there are only limited data available and there are five adjustable parameters. However, the qualitative trends exhibited by the data are encouraging so that further study on such systems should be carried out.

## Conclusion

Dynamics of concentration fluctuations in ternary systems are seen to be more complex than in the binary case. Even in isorefractive systems, the light scattering spectrum will be quite complicated. At least two exponentials should be revealed by dynamic light scattering in the one-phase region. In the infinite-dilution limit where the probe species is present in only trace amounts, the spectrum should in theory reduce to a single-exponential decay. This limit may be difficult to attain in practice so that the use of refractive-index matching as a means of measuring tracer diffusion coefficients without extrapolation procedures may be limited in scope. The early stages of spinodal decomposition as measured by light scattering from isorefractive systems will be quite complex, requiring at least three exponentials to fit the data. A simplification results in that these three decays involve only two independent variables, $\lambda_1$ and $\lambda_2$, which for shallow quenches are likely to be of considerably different magnitudes. Although more data are clearly needed, the limited results available in the literature so far are in qualitative agreement with our conclusions.

**Acknowledgment.** This work was supported by the Polymers Program of the National Science Foundation under Grant DMR-841150.

### Appendix A: Extended Free Energy Expression in Ternary Systems

In binary systems, the Flory–Huggins equation can be extended to include gradient terms such that[7]

$$\frac{\Delta f}{kT} = \frac{\Delta f_{FH}}{kT} + K(\nabla\phi)^2 \qquad (A.1)$$

where

$$K = \frac{a^2}{36\phi(1-\phi)} \qquad (A.2)$$

and $a$ is the statistical segment length which is assumed to be the same for both species. Extending this approach to a ternary system composed of two polymers and a solvent we write

$$\frac{\Delta f}{kT} = \frac{\Delta f_{FH}}{kT} + K_{AA}(\nabla\phi_A)^2 + K_{AB}\nabla\phi_A\nabla\phi_B + K_{BB}(\nabla\phi_B)^2 \qquad (A.3)$$

where

$$K_{AA} = a^2/36\phi_A \qquad (A.4)$$

$$K_{AB} = 0 \qquad (A.5)$$

$$K_{BB} = a^2/36\phi_B \qquad (A.6)$$

As in de Gennes' derivation[7] we have assumed (i) we are in the low-$q$ limit where the Ornstein–Zernike equation holds, i.e., we consider terms up to $q^2$ in our free energy expression; (ii) the polymer chains obey Gaussian statistics; (iii) the interaction parameters do not contribute to the gradient terms, i.e.,

$$\chi_S, \chi_P \ll 1 \qquad (A.7)$$

and (iv) the polymers have the save segment length, $a$.

In the limit as $\phi_S \rightarrow 0$, we have, assuming no volume changes on mixing,

$$\nabla\phi_A = -\nabla\phi_B \qquad (A.8)$$

so that eq A.3 becomes

$$\frac{\Delta f}{kT} = \frac{\Delta f_{FH}}{kT} + \frac{a^2}{36\phi_A\phi_B}(\nabla\phi_A)^2 \qquad (A.9)$$

which is simply the expression obtained earlier by de Gennes for polymer–polymer systems as should be expected. On the other hand, since

$$\nabla\phi_A + \nabla\phi_B + \nabla\phi_S = 0 \qquad (A.10)$$

we can write, from eq A.3, for our ternary system

$$\frac{\Delta f}{kT} = \frac{\Delta f_{FH}}{kT} + \frac{a^2}{36}\left(\frac{1}{\phi_A} + \frac{1}{\phi_B}\right)(\nabla\phi_A)^2 + \frac{a^2}{36\phi_B}(\nabla\phi_S)^2 + \frac{a^2}{18\phi_B}\nabla\phi_A\nabla\phi_S \qquad (A.11)$$

Now, in the limit $\phi_B \rightarrow 0$ we have

$$\nabla\phi_A = -\nabla\phi_S \qquad (A.12)$$

giving

$$\frac{\Delta f}{kT} = \frac{\Delta f_{FH}}{kT} + \frac{a^2}{36\phi_A}(\nabla\phi_A)^2 \qquad (A.13)$$

The chemical potential difference per site, $\mu_A/N_A - \mu_S$, is then given by functional differentiation as

$$\frac{1}{kT}(\mu_A/N_A - \mu_S) = \frac{1}{kT}\frac{\partial\Delta f_{FH}}{\partial\phi_A} + \frac{a^2}{36\phi_A{}^2}(\nabla\phi_A)^2 - \frac{a^2}{18\phi_A}\nabla^2\phi_A \qquad (A.14)$$

This is identical with Binder's expression (eq 6.6 of ref 8) for the chemical potential difference for a binary polymer–solvent system. Thus our proposed equation for the free energy in ternary systems of two polymers and a solvent, eq A.3, gives previously obtained limiting expressions for the free energy in binary polymer–polymer and polymer–solvent systems. It can therefore be used as the starting point for a more detailed theory of spinodal decomposition in ternary systems, incorporating terms up to fourth order in the wave vector, $q$.

### Appendix B: Conservation Equations

The continuity equation for component i in a mixture is given by

$$\frac{\partial\rho_i}{\partial t} + \nabla\cdot\rho_i\mathbf{u}_i = 0 \qquad (B.1)$$

The most useful fluxes for formulating the phenomenological relations in their simplest form are the fluxes $\mathbf{J}_i$'s with respect to the velocity $\mathbf{u}^m$ of the local center of mass where[23]

$$\mathbf{J}_i = \rho_i(\mathbf{u}_i - \mathbf{u}^m) \qquad (B.2)$$

and

$$\sum_i \mathbf{J}_i = 0 \qquad (B.3)$$

Equation B.1 can then be written as

$$(\partial\rho_i/\partial t) + \mathbf{u}^m\cdot\nabla\rho_i = -\nabla\cdot\mathbf{J}_i - \rho_i\nabla\cdot\mathbf{u}^m \qquad (B.4)$$

In our ternary system where i = A, B, or S for solvent, the three equations represented in (B.4) can be rewritten in terms of the continuity equation for the mixture by summing (B.4) over all components and two equations for A and B, respectively. One has then

$$\partial\rho/\partial t = -\nabla\cdot\rho\mathbf{u}^m \qquad (B.5)$$

$$\frac{\partial\rho_A}{\partial t} + \mathbf{u}^m\cdot\nabla\rho_A = -\nabla\cdot\mathbf{J}_A - \rho_A\nabla\cdot\mathbf{u}^m \qquad (B.6)$$

and an equation similar to (B.6) for component B. The mass fluxes $\mathbf{J}_A$ and $\mathbf{J}_B$ are given in terms of Onsager coefficients $\Lambda$'s as[23]

$$\mathbf{J}_A = -\frac{\Lambda_{AA}}{kT}\nabla(\mu_A/m_A - \mu_S/m_S) - \frac{\Lambda_{AB}}{kT}\nabla(\mu_B/m_B - \mu_S/m_S) \qquad (B.7)$$

$$\mathbf{J}_B = -\frac{\Lambda_{BB}}{kT}\nabla(\mu_B/m_B - \mu_S/m_S) - \frac{\Lambda_{AB}}{kT}\nabla(\mu_A/m_A - \mu_S/m_S) \qquad (B.8)$$

when $\mu_i$ is the chemical potential of molecule i and $m_i$ is its mass.

For an incompressible mixture, $\rho$ is constant and $\nabla\cdot\mathbf{u}^m = 0$; eq B.5 is automatically satisfied and the last term in (B.6) drops out. Finally, since we shall be considering only small fluctuations away from equilibrium, we neglect nonlinear terms such as $\mathbf{u}^m\cdot\nabla\rho_A$ in (B.6). We are then left with the two governing equations

$$\partial\rho_A/\partial t = -\nabla\cdot\mathbf{J}_A \qquad \text{(B.9)}$$

and

$$\partial\rho_B/\partial t = -\nabla\cdot\mathbf{J}_B \qquad \text{(B.10)}$$

Equations 12–15 follow from (B.7)–(B.10) by letting $\phi_i = \rho_i\bar{v}_i$ where $\bar{v}_i$ is the specific volume of component i and neglecting the cross-coefficient terms involving $\Lambda_{AB}$.

## Appendix C: Effect of Incomplete Refractive-Index Matching

We saw earlier that in a perfectly matched isorefractive system we have $\epsilon_B = 0$ so that eq 31 simplified to give eq 32. In this way the spectrum could be calculated directly from eq 26 to give eq 33. In this Appendix we investigate the effect of including terms linear in $\epsilon_B$ in eq 31. Since the equations get quite cumbersome we use the following notation:

$$S_{AA} = \langle|\delta\phi_A(q,0)|^2\rangle \qquad \text{(C.1)}$$

$$S_{AB} = \langle\delta\phi_A(q,0)\delta\phi_B(-q,0)\rangle \qquad \text{(C.2)}$$

$$S_{BB} = \langle|\delta\phi_B(q,0)|^2\rangle \qquad \text{(C.3)}$$

From eq 31, 26, and 27, our spectrum becomes

$$\langle\delta\epsilon(q,t)\delta\epsilon(-q,0)\rangle = A_1e^{-q^2\lambda_1t} + A_2e^{-q^2\lambda_2t} \qquad \text{(C.4)}$$

where

$$A_1 = \frac{\lambda_1 - D_{BB}}{\lambda_1 - \lambda_2} + \frac{S_{AB}}{S_{AA}}\frac{D_{AB}}{\lambda_1 - \lambda_2} + \frac{\epsilon_B}{\epsilon_A}\left[\frac{D_{BA}}{\lambda_1 - \lambda_2} + \frac{S_{BB}}{S_{AA}}\frac{D_{AB}}{\lambda_1 - \lambda_2} + \frac{S_{AB}}{S_{AA}}\left(\frac{\lambda_1 - D_{BB}}{\lambda_1 - \lambda_2} + \frac{\lambda_1 - D_{AA}}{\lambda_1 - \lambda_2}\right)\right] \qquad \text{(C.5)}$$

$$A_2 = \frac{\lambda_2 - D_{BB}}{\lambda_2 - \lambda_1} + \frac{S_{AB}}{S_{AA}}\frac{D_{AB}}{\lambda_1 - \lambda_2} + \frac{\epsilon_B}{\epsilon_A}\left[\frac{D_{BA}}{\lambda_2 - \lambda_1} + \frac{S_{BB}}{S_{AA}}\frac{D_{AB}}{\lambda_2 - \lambda_1} + \frac{S_{AB}}{S_{AA}}\left(\frac{\lambda_2 - D_{BB}}{\lambda_2 - \lambda_1} + \frac{\lambda_2 - D_{AA}}{\lambda_2 - \lambda_1}\right)\right] \qquad \text{(C.6)}$$

In general we want $A_1 \gg A_2$ so that the $\lambda_1$ mode will dominate. For simplicity we consider some special cases. In the limit where $\phi_A$ and $\phi_B$ became infinitely dilute we can use eq 25 to give

$$\frac{A_1}{A_2} = \frac{1 + \dfrac{\epsilon_B}{\epsilon_B}\dfrac{S_{AB}}{S_{AA}}}{\dfrac{\epsilon_B}{\epsilon_A}\dfrac{S_{AB}}{S_{AA}}} \qquad \text{(C.7)}$$

Therefore, in this case, $A_1$ will be much greater than $A_2$ when

$$\frac{\epsilon_B}{\epsilon_A}\frac{S_{AB}}{S_{AA}} \ll 1 \qquad \text{(C.8)}$$

which is essentially the result of Hanley et al.[14] If we now consider a situation where only the probe species is infinitely dilute, we get

$$\frac{A_1}{A_2} = \frac{1 + \dfrac{\epsilon_B}{\epsilon_A}\left[\left(\dfrac{D_{BA}}{D_{AA} - D_{BB}}\right) + \dfrac{S_{AB}}{S_{AA}}\right]}{\dfrac{\epsilon_B}{\epsilon_A}\left[\left(\dfrac{D_{BA}}{D_{BB} - D_{AA}}\right) + \dfrac{S_{AB}}{S_{AA}}\right]} \qquad \text{(C.9)}$$

Interestingly, this expression includes diffusion coefficients as well as the thermodynamic quantities $S_{ij}$. Since the diffusion term in the numerator is the negative of that in the denominator, these terms will cancel for the total intensity as expected from eq C.4 at $t = 0$. However, at any time, $t$, they will have an effect on the amplitude ratio $A_1/A_2$ of the two decay modes. In a situation where

$$\frac{S_{AB}}{S_{AA}} \gg \left|\frac{D_{BA}}{D_{AA} - D_{BB}}\right| \qquad \text{(C.10)}$$

we simply return to eq C.8 as our criterion of adequate index matching. If, however, we have

$$\frac{S_{AB}}{S_{AA}} \ll \left|\frac{D_{BA}}{D_{AA} - D_{BB}}\right| \qquad \text{(C.11)}$$

we then require

$$\frac{\epsilon_B}{\epsilon_A}\left|\frac{D_{BA}}{D_{AA} - D_{BB}}\right| \ll 1 \qquad \text{(C.12)}$$

The data of Daivis et al. indicate that[10]

$$\left|\frac{D_{BA}}{D_{AA} - D_{BB}}\right| \simeq 8 \qquad \text{(C.13)}$$

in their system. Putting this into eq C.12 then gives as a rough estimate

$$\epsilon_B/\epsilon_A \ll 0.1 \qquad \text{(C.14)}$$

In general one must therefore be careful in deciding what values of $\epsilon_B$ and $\epsilon_A$ constitute a genuinely isorefractive system for light-scattering purpose. Effects of this kind may have some bearing on the recent data showing non-single-exponential behavior in isorefractive systems.

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