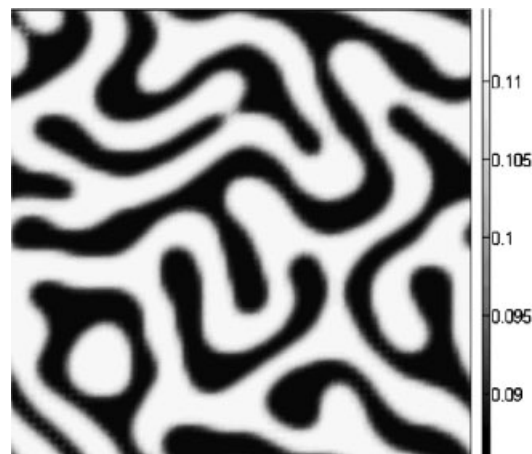


# Spinodal Decomposition in Ternary Systems with Significantly Different Component Diffusivities

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A numerical method for simulating spinodal decomposition in ternary systems with order-of-magnitude differences in diffusion coefficients is presented. The method has been partially verified by molecular dynamic simulations and gives results equivalent to the standard technique when the diffusivities are equal. A two-dimensional simulation of an asymmetric polymer/polymer/polymer system reproduces an experimentally observed bimodal distribution of dispersed-phase particle sizes. The ripening exponent for the larger particles is near the expected value of 0.33, but that for the smaller particles is only about 0.1. The method was also used for a polymer/polymer/solvent system.



## Introduction

Understanding phase transitions in multicomponent systems is a key tool for improving polymer properties. Polymer composites can be made in several different ways. Reaction induced phase separation produces polymer blends such as impact polystyrene and poly(propylene). Mechanical blending is common and in some instances, reaction is combined with reaction in reactive-blending. Compositional quenching<sup>[1]</sup> uses a solvent to achieve a

single-phase mixture and then induces phase separation by rapidly removing the solvent by flash devolatilization.

Binary polymer blends usually give particulate morphologies, but co-continuous blends are also possible. Ternary blends show a wealth of morphologies.<sup>[2]</sup> Some ternary systems have two phases with a third component that is too low in concentration to form a separate phase but which is strongly segregated at the interface.

The present paper demonstrates a method for diffusion calculations in ternary systems undergoing spinodal decomposition. Applications include coagulation and membrane formation involving a polymer/solvent/solvent system, drying and reaction blending involving polymer-polymer-solvent or polymer/polymer/monomer systems, and thermal or compositional quenching involving three polymers. Simulation of such systems is relatively simple when the components have equal

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diffusivities. We call such systems “symmetric.” In many cases, the assumption of symmetry in polymer/polymer/polymer systems has given predictions in quite good agreement with experiments.<sup>[3,4]</sup> However, differences in diffusivity are apparent in some experiment morphologies.

The traditional approach to an  $N$ -component diffusion problem is to treat  $N - 1$  of the variables as independent and to calculate the concentration of the remaining component from a material balance, typically in the form of constant mass density for a liquid system. This approach is satisfactory when the component diffusivities are equal or when there is one dominant component.<sup>[5]</sup> In the more general case, it can predict non-physical results such as negative concentrations.<sup>[6]</sup> This possibility arises in simulations of spinodal decomposition in polymer systems where mutual solubilities are low. The problem is theoretically resolved by a sufficiently elaborate set of compositionally dependent diffusion coefficients for the  $N - 1$  independent compositions, but this approach is impractical in terms of available data. Another theoretical resolution is the use of the Stefan-Maxwell equations that reflect the dependence of the diffusive flux of any one component on the fluxes of all the other components. Equations of the Stefan-Maxwell form have recently been developed for asymmetric polymer systems in the single-phase region.<sup>[7]</sup> It is possible in principle to derive the Stefan-Maxwell counterpart to the modified Cahn-Hilliard equation,<sup>[8]</sup> but this would impose a complicated and computational intense methodology on a problem that is already complicated and computationally challenging, particularly when the Cahn-Hilliard equation is coupled to the equations of motion through compositionally dependent body force terms.<sup>[9–11]</sup> Instead, we choose a simple and robust model that accounts for the fluxes of all components, that avoids anomalous behavior, and perhaps most importantly, allows simple and even constant estimates of diffusion coefficients that are allowed to differ by orders of magnitude. The proportional flux method<sup>[6]</sup> has been tested using molecular dynamics for the diffusion of short-chain alkanes.<sup>[12]</sup> In the following part the proportional flux model is applied to spinodal decomposition in ternary, asymmetric systems of polymers and solvents.

## Mathematical Description of the System

The free energy at a point in the system is assumed to depend on concentration gradients as well as the

concentrations at the point.<sup>[13,14]</sup> We assume constant density so that:

$$\phi_1 + \phi_2 + \phi_3 = 1 \quad (1)$$

where the  $\phi_i$  are volume fractions. The variational free energy<sup>[15]</sup> is given by:

$$\left(\frac{\delta G}{\delta \phi_1}\right)_{\phi_2, \phi_3} = \frac{\partial g}{\partial \phi_1} - \kappa_A \nabla^2 \phi_1 - \kappa_C \nabla^2 \phi_2 \quad (2)$$

$$\left(\frac{\delta G}{\delta \phi_2}\right)_{\phi_1, \phi_3} = \frac{\partial g}{\partial \phi_2} - \kappa_C \nabla^2 \phi_1 - \kappa_B \nabla^2 \phi_2 \quad (3)$$

$$\left(\frac{\delta G}{\delta \phi_3}\right)_{\phi_1, \phi_2} = \frac{\partial g}{\partial \phi_3} \quad (4)$$

where  $g$  is the free energy of the system in the absence of concentrations gradients. We assume a Flory-Huggins form:

$$g = \frac{\phi_1 \ln(\phi_1)}{N_1} + \frac{\phi_2 \ln(\phi_2)}{N_2} + \frac{\phi_3 \ln(\phi_3)}{N_3} + \chi_{12} \phi_1 \phi_2 + \chi_{13} \phi_1 \phi_3 + \chi_{23} \phi_2 \phi_3 \quad (5)$$

where the  $N_i$  are chain lengths and the  $\chi$  are binary interaction parameters. The kappa in Equation (2) and (3) are gradient energy parameters that are known functions of the radius of gyration and the interaction parameters.<sup>[16,17]</sup> The composition and gradient dependent chemical potentials are given by:

$$\nabla \mu_i = (1 - \phi_i) \nabla \left( \frac{\delta G}{\delta \phi_i} \right) - \sum_{j=1, j \neq i}^N \phi_j \nabla \left( \frac{\delta G}{\delta \phi_j} \right) \quad (6)$$

$i, j = 1, \dots, N$

It is the chemical potential gradients that drive diffusion:

$$-j_i = \phi_i D_i \nabla \mu_i \quad i = 1, \dots, N \quad (7)$$

Note that any cross diffusion terms have been ignored. Also, the inclusion of  $\phi_i$  as a pre-multiplier allows the system to reduce to Fickian diffusion when the mixture is ideal. The traditional approach at this point is to derive the component continuity equations. For component 1,

$$\left( \frac{\partial \phi_1}{\partial t} = \nabla \cdot D_1 \phi_1 \left\{ (1 - \phi_1) \nabla \left( \frac{\partial g}{\partial \phi_1} - \kappa_A \nabla^2 \phi_1 - \kappa_C \nabla^2 \phi_2 \right) - \phi_2 \nabla \left( \frac{\partial g}{\partial \phi_2} - \kappa_C \nabla^2 \phi_1 - \kappa_B \nabla^2 \phi_2 \right) - \phi_3 \nabla \left( \frac{\partial g}{\partial \phi_3} \right) \right\} \right) \quad (8)$$

This is a ternary extension of the modified Cahn-Hilliard equation<sup>[15]</sup> and is normally solved assuming constant and equal values of  $D_1$  for each component. When the  $D_1$  are significantly different, material balance violations can occur during spinodal decomposition just they are observed for Fickian diffusion. Indeed, non-physical behavior is most easily observed when the concentration of one component is small, and this situation commonly occurs at the interface between incompatible polymers. The present approach avoids the problem by calculating the fluxes for each component and then imposing a material balance constraint that forces the sum of fluxes into a point to be zero:

$$\sum_{i=1}^3 j_i = 0 \quad (9)$$

The proportional flux method uses Equation (9) to calculate input and output fluxes for each component at a given point in the system. Incoming fluxes, positive, and outgoing fluxes, negative, are then summed. The larger in magnitude of the positive and negative fluxes is scaled down to match the other flux, the scaling being done proportionately for the individual species. This approach insures satisfaction of the material balance without imposing restrictions on the choice of the diffusion coefficients. They are independently chosen and can be either constant or compositionally dependent which gives greater flexibility.

### Simulation of a Symmetric Polymer/ Polymer/Polymer System

The model was first tested for a symmetric system using a case studied by Nauman and He.<sup>[2]</sup> The initial concentrations for this system and the other systems reported here are within the spinodal region. The interaction parameters for the system are as follows:  $\chi_{12} = 0.003$ ,  $\chi_{13} = 0.006$  and  $\chi_{23} = 0.003$ . Homogenous initial concentrations of  $\phi_1 = 0.7$ ,  $\phi_2 = 0.2$  and  $\phi_3 = 0.1$  were assumed. Additionally, it was assumed that  $M_1 = M_2 = M_3 = 1000$ . The gradient parameters were calculated from:

$$\kappa_A = \frac{2}{3} (R_g^2) \chi_{13} \quad (10)$$

$$\kappa_B = \frac{2}{3} (R_g^2) \chi_{23} \quad (11)$$

$$\kappa_C = \frac{1}{3} R_g^2 (\chi_{13} + \chi_{23} - \chi_{12}) \quad (12)$$

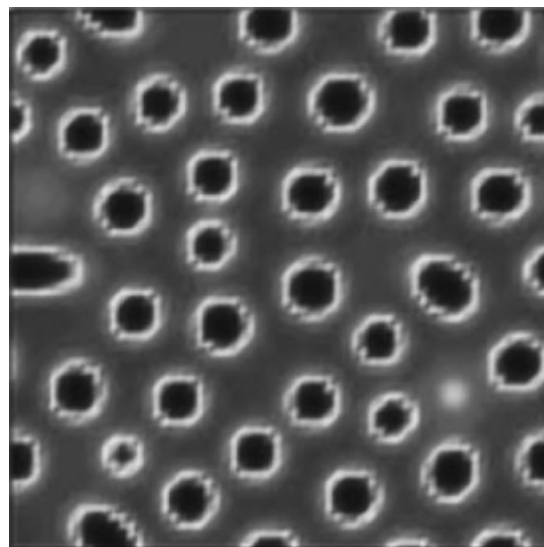
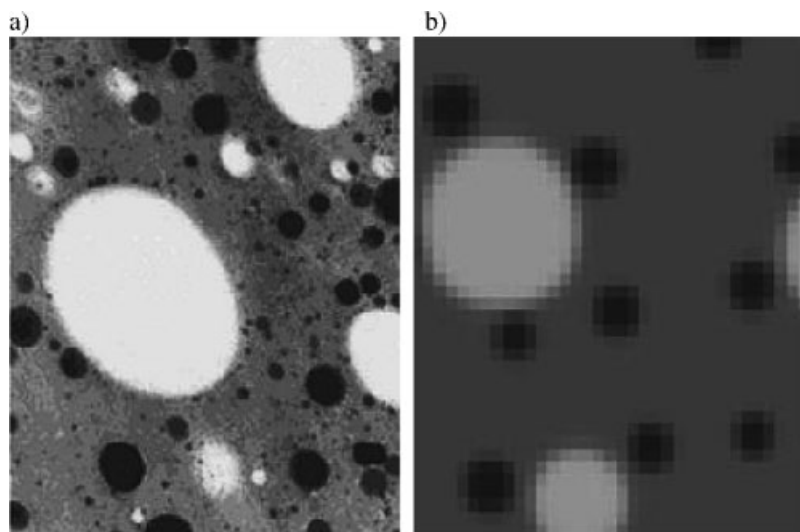


Figure 1. Core and shell morphology for a symmetric ternary system.

where all three polymers are assumed to have equal radii of gyration,  $R_g$ . For concreteness, a diffusion coefficient of  $10^{-7} \text{ cm}^2 \cdot \text{s}^{-1}$  was assumed for all three polymers, but the long-term morphology is independent of the magnitude of  $D$ . The system is initially homogenous and then rapidly quenched into the unstable region where phase separation occurs by spinodal decomposition. The fully ripened morphology, core-shell in this example case, shown in Figure 1 is identical to that obtained by Nauman and He.

### Simulation of an Asymmetric Polymer/ Polymer/Polymer System

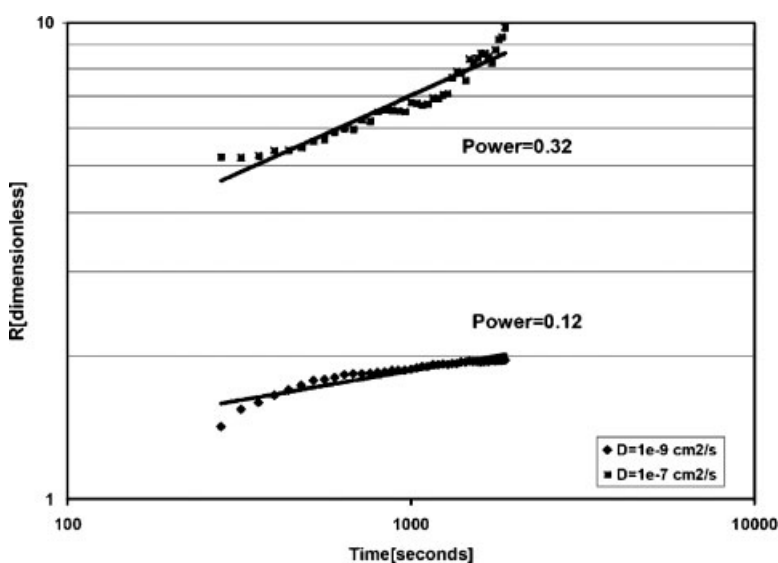
An important ternary structure is the dual discrete particle distribution. The improvement of polymer blend properties with bimodal particle size distributions has been the focus of many studies. Several studies<sup>[18–20]</sup> have shown that a combination of small and large rubber particles in high impact polystyrene (HIPS) will improve product properties. Alfarraj and Nauman<sup>[21]</sup> studied the effect of adding secondary lower modulus rubber particles to the already existing rubber particles in HIPS. Brunswick et al.<sup>[4]</sup> investigated different morphologies in ternary polymer systems. One blend they show is the system of PS/PMMA/PB (77/8/15). The experimental blend, Figure 2(a), shows two sets of discrete particles with the PMMA being the substantially larger white spheres and the PB being the smaller dark spheres. To simulate this system we have initialized our model with the volume fractions used in the experimental sample. Interaction parameters of  $\chi_{\text{PS/PMMA}} = 0.0045$ ,  $\chi_{\text{PS/PB}} = 0.0045$  and  $\chi_{\text{PB/PMMA}} = 0.009$  were



■ Figure 2. Comparison of: (a) experimental, and (b) simulated, PS/PMMA/PB (77/15/8).

assumed. The chain lengths were  $M_{PS} = 1000$ ,  $M_{PMMA} = 1000$  and  $M_{PB} = 2000$ . Both PS and PMMA are expected to diffuse faster than PB. The assumed diffusion coefficients were  $D_{PS} = 1 \times 10^{-7} \text{ cm}^2/\text{s}$ ,  $D_{PMMA} = 1 \times 10^{-7} \text{ cm}^2/\text{s}$  and  $D_{PB} = 1 \times 10^{-9} \text{ cm}^2/\text{s}$ . The gradient energy parameters were calculated using Equation (10)–(12). Figure 2(b) illustrates the results of this case. The simulation predicts a bimodal morphology. Specifically it predicts a much larger size of the PMMA particles compared to the PB particles.

Figure 3 compares the simulated growth rates for the two classes of particles. The results shown are averages of eight runs performed, using an explicit finite difference



■ Figure 3. Particle ripening in an asymmetric system. The upper curve is for the larger particles.

technique on a 64 by 64 grid with periodic boundary conditions. The scaling exponent for the larger particles is near the expected value of 0.33, but finite domain effects are emerging at long times. The scaling exponent for the smaller particles is much less for reasons that are uncertain, and it is unknown whether the difference will persist in a three-dimensional simulation.

The experimental results show a much broader distribution of particle sizes for the PB particles than for the PMMA particles. The reasons for this are unclear. One possibility is polydispersity of the rubber phase. The simulations effectively suppose a monodisperse population. The methods presented here suggest future work in which the effects of polydispersity, with attendant differences in diffusivity, can be studied in detail.

### Simulation of a Polymer/Polymer/Solvent System

In this section we consider a ternary polymer (1)/polymer (2)/solvent (3) system. The interaction parameters between the solvent and the first and second polymers are  $\chi_{13} = 0.2$  and  $\chi_{23} = 0.5$ , respectively, and the polymer-polymer interaction is  $\chi_{12} = 0.0045$ . The initial concentrations are  $\phi_1 = \phi_2 = 0.45$  and  $\phi_3 = 0.10$ . The two polymers are assumed to have an equal diffusion coefficient of  $10^{-7} \text{ cm}^2 \cdot \text{s}^{-1}$ . The solvent diffusion coefficient is set to be three orders of magnitude greater at  $10^{-4} \text{ cm}^2 \cdot \text{s}^{-1}$ . The chain lengths of the two polymers are assumed to be equal and set to  $M_p = 1000$ . The solvent chain length is  $M_s = 1$ . The energy gradients parameters are calculated using:<sup>[17]</sup>

$$\kappa_A = \frac{1}{3} (R_g^2) \chi_{13} \quad (13)$$

$$\kappa_B = \frac{1}{3} (R_g^2) \chi_{23} \quad (14)$$

$$\kappa_C = \frac{1}{6} R_g^2 (\chi_{13} + \chi_{23} - 2\chi_{12}) \quad (15)$$

Figure 4 shows the solvent distribution across the whole domain. The solvent has segregated between the white polymer 1 rich



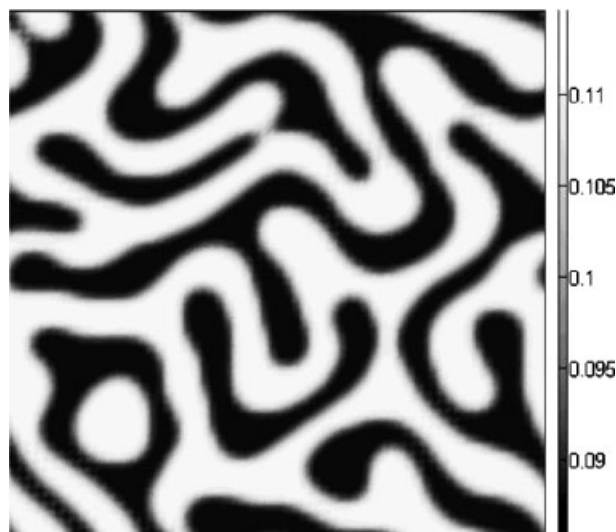


Figure 4. Solvent distribution in an asymmetric polymer/polymer/solvent system.

phase and the black polymer 2 rich phase. One polymer phase has 8.5% solvent and the other has 11.5%. This segregation is due to the difference in interaction of the solvent with the two polymers. The ability to treat true ternary systems will become vital when the concentration of the third component continuously changes, as in reacting monomers.

## Conclusion

The technique demonstrated in this paper greatly extends the parameter set over which spinodal decomposition and diffusion in general can be simulated. Although illustrated here for ternary systems, the extension to more components is relatively straightforward. A key limitation is the need to assume constant density, but this limitation is inherent in the standard theory. Even with this limitation,

many new applications appear possible, including systems involving solvents and reactive monomers in addition to one or more polymers.

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