# Multicomponent Diffusion Theory and Its Applications to Polymer-Solvent Systems

**Peter E. Price, Jr., and Ilyess Hadj Romdhane**
3M Engineering Systems Technology Center, St. Paul, MN 55144

*Recent publications by Zielinski and Hanley and by Alsoy and Duda have proposed relationships between self- and mutual-diffusion coefficients in multicomponent systems that can be derived from Bearman's friction-based theory. Subsequently, Zielinski and Alsoy published an article calling into question the ability of these new theories to satisfy the Onsager reciprocal relations, and Nauman and Savoca also reported that the Zielinski and Hanley theory can, in some cases, fail to satisfy material balance constraints. Here, the existing friction-based theories are reviewed and then previous approaches to relating self- and mutual-diffusion coefficients are generalized. The result is an expression that both unifies previous results and is itself a previous result. This generalization prompts us to address the issues raised regarding the existing theories. Some example calculations are also presented, and some directions for future areas of research are suggested.*

## Introduction

As process engineers responsible for understanding the drying behavior of coated webs, we have relied heavily on process models. These models use simplifications of Bearman's (1961) friction-based theory to relate self- and mutual-diffusion coefficients and Vrentas and Duda's (1977a,b) free-volume theory to describe self-diffusion coefficients. We were very excited when, first, Vrentas and Vrentas (1993) extended the range of the binary theory beyond its original dilute-region approximation, and then, in seemingly rapid succession, Dabral (1997), Zielinski and Hanley (1999), and Alsoy and Duda (1999) developed theories that allowed practical application of the Bearman−Vrentas−Duda approach to multicomponent systems. The latter two articles, in particular, gave us tools that dramatically improved our ability to model the drying behavior in multisolvent systems.

Two subsequent articles dampened our excitement as they called into question the validity of these new multicomponent theories. The first article, by Zielinski and Alsoy (2001), suggested that Zielinski and Hanley's (1999) and Alsoy and Duda's (1999) multicomponent theories failed to satisfy the Onsager reciprocal relations (ORR). Particularly disconcerting was Zielinski and Alsoy's contention that the generalized Bearman theory did satisfy the ORR, while the particular cases of the Zielinski and Hanley theory and the Alsoy and Duda theory did not. If theories based on particular assumptions about the ratios of friction factors failed to satisfy the ORR, how could the general theory, a theory that certainly admitted their conditions as special cases, satisfy the ORR? We found it disturbing that the creators of these wonderful new tools were calling into question their own results.

The second and even more troubling article, by Nauman and Savoca (2001), stated that Zielinski and Hanley's theory could, under certain circumstances, fail to obey the required material-balance constraints. Shortly after the publication of that article, we began to find real examples of material-balance failure in some of our process calculations. The theories of Dabral (1997) and Alsoy and Duda (1999) faired no better. Only by dropping the cross-diffusion terms could we seemingly assure reasonable results. Unfortunately, this can lead to significant errors in drying predictions (Zielinski and Alsoy, 2001).

In an attempt to understand these issues, we developed a theory that unifies all of the previous Bearman-derived, friction-based theories and found that the generalized theory was already known. In deriving this generalized theory, we find a natural resolution to the concerns of Zielinski and Alsoy (2001). The generalized theory also allows us to postulate a solution to the concerns of Nauman and Savoca (2001) that

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Correspondence concerning this article should be addressed to P. E. Price, Jr.

seems to assure reasonable results while retaining the cross-diffusion terms. Below, we review existing friction-based theories, present the generalized theory, show how the previous theories are admitted as special cases, address the concerns just mentioned, and suggest areas of focus for future research.

In the equations that follow, all partial derivatives are taken with the usual restrictions of constant temperature and pressure. In addition, when derivatives are taken with respect to a concentration, only the concentration of interest and the balancing component concentration are allowed to vary. All other concentrations are held constant.

## Review of Friction-Based Diffusion Theories

Bearman (1961) described gradients in chemical potential, $\mu_i$, in terms of the frictional force due to the relative motion of components in a solution

$$\nabla\mu_i = -\sum_{j=1}^{N}\frac{\rho_j}{M_j}\zeta_{ij}(v_i - v_j) \tag{1}$$

with the following relation between friction factors

$$\zeta_{ij} = \zeta_{ji} \tag{2}$$

Here $\rho_j$ is the local mass concentration of component $j$, and $M_j$ is the molecular weight of component $j$. To simplify the notation, we have recast the theory into molar, rather than the original molecular, form. Bearman also showed that the self-diffusion coefficients, $D_i$, can be expressed in terms of the friction factors

$$D_i = \frac{RT}{\sum_{j=1}^{N}\frac{\rho_j}{M_j}\zeta_{ij}} \tag{3}$$

We can relate Bearman's friction-factor expressions to the usual Fickian diffusion coefficients using the equations for the diffusive flux relative to the volume-average velocity, $v^{\neq}$

$$j_i^{\neq} = -\sum_{j=1}^{N-1} D_{ij}\nabla\rho_j = \rho_i(v_i - v^{\neq}) \tag{5}$$

$$v^{\neq} = \sum_{i=1}^{N}\phi_i v_i \tag{5}$$

$$\sum_{i=1}^{N} j_i^{\neq}\hat{V}_i = 0 \tag{6}$$

where $j_i^{\neq}$ is the flux of component $i$ relative to the volume-average velocity, $v^{\neq}$; $D_{ij}$ is the Fickian mutual-diffusion coefficient for component $i$ with respect to a gradient in component $j$; $v_i$ is the velocity of component $i$; $\phi_i$ is the volume fraction of component $i$; and $\hat{V}_i$ is the partial specific volume of component $i$.

By subtracting and adding the volume-average velocity to $v_i$ and $v_j$ respectively, in Eq. 1, we can then substitute the generalized Fick's Law given by Eq. 4 into Eq. 1. This allows us to express the diffusion coefficients, $D_{ij}$, in terms of the friction factors $\zeta_{ij}$.

### *Binary case*

Making the preceding substitution for a binary, for example, solvent(1)–polymer(2), solution leads to

$$D_{11} = \frac{\hat{V}_2 M_2\rho_1}{\zeta_{12}}\frac{\partial\mu_1}{\partial\rho_1} \tag{7}$$

Following Vrentas and Duda (1977a), we can write this as

$$D_{11} = \rho_2\hat{V}_2\frac{D_1}{1-\frac{D_1}{D_1^*}}\left(\frac{\rho_1}{RT}\frac{\partial\mu_1}{\partial\rho_1}\right) = \rho_2\hat{V}_2\frac{D_1}{1-\frac{D_1}{D_1^*}}Q \tag{8}$$

where

$$D_1^* = \frac{RTM_1}{\rho_1\zeta_{11}} \tag{9}$$

Vrentas and Duda (1977a) considered solvent–polymer systems and argued that if $\zeta_{11}$ remains bounded in the pure polymer limit, for sufficiently small solvent concentrations

$$1-\frac{D_1}{D_1^*} = \frac{1}{\frac{\rho_1}{\rho_2}\frac{M_2}{M_1}\frac{\zeta_{11}}{\zeta_{12}}+1} \cong 1 \tag{10}$$

We refer to this as the dilute-solvent region. In this region

$$D_{11} = \rho_2\hat{V}_2 D_1\left(\frac{\rho_1}{RT}\frac{\partial\mu_1}{\partial\rho_1}\right) = \phi_2 D_1 Q \tag{11}$$

Equation 11 is the relationship that has appeared most commonly in applications to binary solvent–polymer systems. Indeed, the dilute region form and its multicomponent extension described below appear to be the only forms considered herein for which the assumptions upon which they are based limit their application to solvent–polymer systems.

In a later article, seeking to derive a more robust relationship between the self- and mutual-diffusion coefficients in a binary system, Vrentas and Vrentas (1993) postulated

$$1-\frac{D_1}{D_1^*} = A + B\phi_2 + C\phi_2^2 + E\phi_2^3 \tag{12}$$

Applying restrictions based on known limits (Eqs. 13, 15 and 16) and expected behavior (Eq. 14): the expectation is that in the dilute region, the model approaches Eq. 11

$$\frac{D_1}{D_1^*} = 0 \qquad \text{at } \omega_1 = 0 \tag{13}$$

$$\left[\frac{\partial\left(\frac{D_{11}}{QD_1}\right)}{\phi_2}\right] = 1 \qquad \text{at } \omega_1 = 0 \tag{14}$$

$$\frac{D_1}{D_1^*} = 1 \qquad \text{at } \omega_1 = 1 \tag{15}$$

$$D_{11} = D_2 \qquad \text{at } \omega_1 = 1 \tag{16}$$

where $\omega_1$ is the solvent mass fraction, Vrentas and Vrentas found

$$1-\frac{D_1}{D_1^*}=\phi_1^2\phi_2\left(\frac{QD_1}{D_2}\right)_{\phi_1=1}+\phi_2^2(1+2\phi_1) \qquad (17)$$

or

$$D_{11}=\frac{D_1Q}{\phi_1^2\left(\frac{QD_1}{D_2}\right)_{\phi_1=1}+(1-\phi_1)(1+2\phi_1)} \qquad (18)$$

Vrentas and Vrentas (2000) recently presented an alternative approach to diffusion in binary systems that eliminates the thermodynamic term from the expression for the mutual-diffusion coefficient. Their results are very interesting and demand further study, but they fall outside the scope of our present analysis.

Zielinski and Hanley (1999) developed a theory for multicomponent diffusion. Their results are tantamount to assuming that the ratios of the friction factors are equal to the ratios of molecular weights

$$\frac{\zeta_{ij}}{\zeta_{ik}}=\frac{M_j}{M_k} \qquad (19)$$

From Eqs. 1 through 6, it follows that the binary limit of their theory gives

$$D_{11}=\left(1-\rho_1\left(\hat{V}_1-\hat{V}_2\right)\right)D_1\left(\frac{\rho_1}{RT}\frac{\partial\mu_1}{\partial\rho_1}\right)=\frac{\phi_2}{\omega_2}D_1Q \qquad (20)$$

For their theory

$$1-\frac{D_1}{D_1^*}=1-\omega_1=\omega_2 \qquad (21)$$

Alsoy and Duda (1999) presented a theory for multicomponent drying, with more details available in Alsoy (1998). In their article, they present several expressions relating self- and mutual-diffusion coefficients. Their Case 4 is equivalent to Dabral's (1997) theory, described below. In their Case 1, hereafter referred to as the theory of Alsoy and Duda, the ratio of friction factors is assumed to be equal to the ratio of partial molar-specific volumes $\tilde{V}_i$

$$\frac{\zeta_{ij}}{\zeta_{ik}}=\frac{\tilde{V}_j}{\tilde{V}_k}=\frac{\hat{V}_j}{\hat{V}_k}\frac{M_j}{M_k} \qquad (22)$$

This leads to

$$D_{11}=D_1\left(\frac{\rho_1}{RT}\frac{\partial\mu_1}{\partial\rho_1}\right)=D_1Q \qquad (23)$$

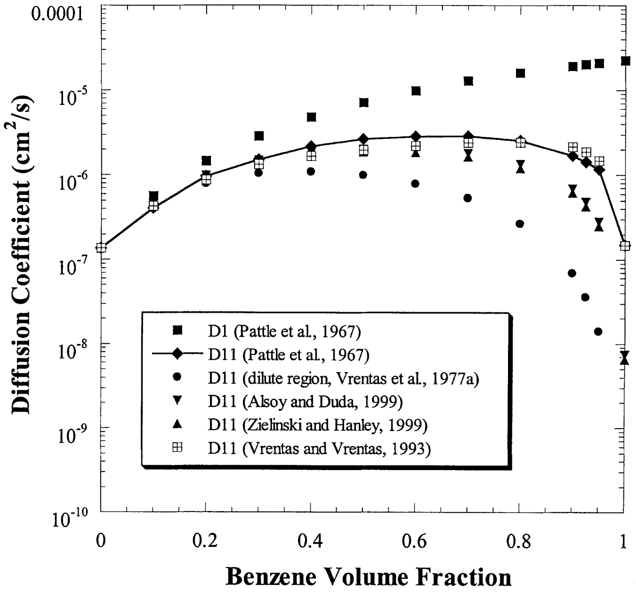

**Figure 1. Diffusion coefficients for benzene in rubber from experimental data (Pattle et al., 1967) and various model forms.**

For their theory

$$1-\frac{D_1}{D_1^*}=1-\phi_1=\phi_2. \qquad (24)$$

For binary polymer–solvent systems, we expect Alsoy and Duda's (1999) and Zielinski and Hanley's (1999) theories to be more robust than the dilute-solvent region approximation, but not as robust as Vrentas and Vrentas' (1993) theory. This is shown clearly by considering the self-diffusion, mutual-diffusion, and thermodynamic data published by Pattle et al. (1967) for benzene in rubber. Following Vrentas and Vrentas (1993), we can test the various theories by using the published self-diffusion data and thermodynamic factors to predict the mutual-diffusion coefficients and compare them with the published values. The results are shown in Figure 1. All of the forms do well at low solvent concentrations. At high solvent concentrations, the dilute region form dramatically underpredicts the mutual-diffusion coefficients. Alsoy and Duda's and Zielinski and Hanley's forms yield almost identical predictions that are significantly better than the dilute region form, though they fall precipitously at high solvent concentrations. Finally, Vrentas and Vrentas' theory gives the best predictions of the mutual-diffusion coefficients.

Clearly, Vrentas and Vrentas' theory is the only form designed to cover the full concentration range. Nonetheless, many applications, for example, drying models, require computations that span the range from high solvent to low solvent concentrations. Figure 1 shows clearly the potential for error when the various theories are used to predict mutual-diffusion coefficients based on self-diffusion and thermodynamic data. In practice, the various theories may show less dramatic differences in application to binary systems when the binary forms are used to fit binary mutual-diffusion data or to fit experimental data in inverse problems (Verros and

Malamataris, 1999, 2001; Doumenc and Guerrier, 2001). An example of such fitting is shown later in Figure 3. One can, however, expect significant differences in applications of the various multicomponent forms described below to multicomponent systems when the diffusion parameters are determined from data for the constituent binary systems.

### *Ternary case*

For ternary, for example, solvent(1)–solvent(2)–polymer(3), systems, subtracting and adding the volume-average velocity to each of the species velocity difference terms in the ternary form of Eq. 1, then substituting in the ternary form of Eq. 4 leads to

$$D_{11}=-\frac{\Phi_{22}\frac{\partial\mu_1}{\partial\rho_1}-\Phi_{12}\frac{\partial\mu_2}{\partial\rho_1}}{|\Phi|} \tag{25}$$

$$D_{12}=-\frac{\Phi_{22}\frac{\partial\mu_1}{\partial\rho_2}-\Phi_{12}\frac{\partial\mu_2}{\partial\rho_2}}{|\Phi|} \tag{26}$$

$$D_{21}=-\frac{\Phi_{11}\frac{\partial\mu_2}{\partial\rho_1}-\Phi_{21}\frac{\partial\mu_1}{\partial\rho_1}}{|\Phi|} \tag{27}$$

$$D_{22}=-\frac{\Phi_{11}\frac{\partial\mu_2}{\partial\rho_2}-\Phi_{21}\frac{\partial\mu_1}{\partial\rho_2}}{|\Phi|} \tag{28}$$

where

$$\Phi_{11}=-\frac{\rho_2\hat{V}_3M_3\zeta_{12}+M_2\left(1-\rho_2\hat{V}_2\right)\zeta_{13}}{\rho_1\hat{V}_3M_2M_3} \tag{29}$$

$$\Phi_{12}=\frac{\hat{V}_3M_3\zeta_{12}-\hat{V}_2M_2\zeta_{13}}{\hat{V}_3M_2M_3} \tag{30}$$

$$\Phi_{21}=\frac{\hat{V}_3M_3\zeta_{12}-\hat{V}_1M_1\zeta_{23}}{\hat{V}_3M_1M_3} \tag{31}$$

$$\Phi_{22}=-\frac{\rho_1\hat{V}_3M_3\zeta_{12}+M_1\left(1-\rho_1\hat{V}_1\right)\zeta_{23}}{\rho_2\hat{V}_3M_1M_3} \tag{32}$$

$$|\Phi|=\frac{\zeta_{12}}{\hat{V}_3M_3}\left[\frac{\zeta_{23}}{\rho_1M_2}+\frac{\zeta_{13}}{\rho_2M_1}\right]+\left[\frac{\rho_3\zeta_{13}\zeta_{23}}{\rho_1\rho_2\hat{V}_3M_3^2}\right] \tag{33}$$

Equations 25 through 33 relate the mutual-diffusion coefficients to the friction factors. Equation 3 relates the self-diffusion coefficients to the friction factors. Unfortunately, there are more friction factors than self-diffusion coefficients, so we cannot relate the self- and mutual-diffusion coefficients directly without additional assumptions. Given this, we now examine the assumptions and resultant forms of several published and unpublished efforts to relate the self- and mutual-diffusion coefficients in ternary systems.

Vrentas et al. (1985) considered the limit as the solvent concentrations, $\rho_1$ and $\rho_2$, go to zero. In this limit, the cross-diffusion terms, $D_{12}$ and $D_{21}$, go to zero, and the main terms, $D_{11}$ and $D_{22}$, approach the corresponding self-diffusion coefficients, $D_1$ and $D_2$. They assumed that in the low solvent concentration range they were interested in, the volumetric and thermodynamic effects on the concentration dependencies of $D_{11}$ and $D_{22}$ were small with respect to those inherent in the self-diffusion coefficients. Thus, they applied the latter directly. Zielinski and Hanley (1999) state that this is the inevitable practical application.

In a private communication to 3M in 1988, Vrentas considered the region of dilute solvents, where

$$1-\frac{D_1}{D_1^*}=1-\frac{D_1}{\dfrac{RTM_1}{\rho_1\zeta_{11}}}\cong 1 \qquad 1-\frac{D_2}{D_2^*}=1-\frac{D_2}{\dfrac{RTM_2}{\rho_2\zeta_{22}}}\cong 1 \tag{34}$$

Vrentas also assumed that the cross-solvent friction factor, $\zeta_{12}$, and the cross-diffusion coefficients, $D_{12}$ and $D_{21}$, were equal to zero. The resultant main-term diffusion coefficients are

$$D_{ii}=\left(1-\rho_i\hat{V}_i\right)\rho_iD_i\left(\frac{1}{RT}\frac{\partial\mu_i}{\partial\rho_i}\right)-\sum_{\substack{j=1\\ j\neq i}}^{2}\rho_j\hat{V}_j\rho_iD_j\left(\frac{1}{RT}\frac{\partial\mu_j}{\partial\rho_i}\right) \qquad i=1,2 \tag{35}$$

Dabral (1997) also considered the low solvent concentration region. He postulated that since the solvent–solvent friction factors, $\zeta_{11}$, $\zeta_{12}$, and $\zeta_{22}$, are much smaller than the solvent–polymer friction factors, $\zeta_{13}$ and $\zeta_{23}$, and the polymer–polymer friction factor, $\zeta_{33}$, they ($\zeta_{11}$, $\zeta_{12}$, and $\zeta_{22}$) can be effectively set to zero in Eqs. 29 to 33. This results in the same main-term diffusion coefficients as Vrentas (private communication to 3M, 1988), although Dabral maintained the crossterms. The resulting diffusion coefficients are

$$D_{ik}=\left(1-\rho_i\hat{V}_i\right)\rho_iD_i\left(\frac{1}{RT}\frac{\partial\mu_i}{\partial\rho_k}\right)-\sum_{\substack{j=1\\ j\neq i}}^{2}\rho_j\hat{V}_j\rho_iD_j\left(\frac{1}{RT}\frac{\partial\mu_j}{\partial\rho_k}\right) \qquad i,k=1,2 \tag{36}$$

Zielinski and Hanley's (1999) approach is equivalent to assuming that the ratios of the friction factors are equal to the ratios of molecular weights, Eq. 19. The resultant diffusion coefficients are

$$D_{ik}=\left[1-\rho_i\left(\hat{V}_i-\hat{V}_3\right)\right]\rho_iD_i\left(\frac{1}{RT}\frac{\partial\mu_i}{\partial\rho_k}\right)-\sum_{\substack{j=1\\ j\neq i}}^{2}\left(\hat{V}_j-\hat{V}_3\right)\rho_j\rho_iD_j\left(\frac{1}{RT}\frac{\partial\mu_j}{\partial\rho_k}\right) \qquad i,k=1,2 \tag{37}$$

Finally, Alsoy and Duda (1999) assumed that the ratios of friction factors were equal to the ratios of the partial molar-specific volumes, Eq. 22. The resultant diffusion coefficients are

$$D_{ik} = \rho_i D_i \left( \frac{1}{RT} \frac{\partial \mu_i}{\partial \rho_k} \right). \qquad i, k = 1, 2 \tag{38}$$

## Generalized Friction-Based Approach

Each of the above approaches can be generalized to more components. After suffering through some additional algebra, one can also unify and generalize all of the approaches in terms of a ratio of friction factors. Let us assume that the ratio of friction factors is given by

$$\frac{\zeta_{ij}}{\zeta_{ik}} = \frac{\alpha_j}{\alpha_k} \frac{\tilde{V}_j}{\tilde{V}_k} = \frac{\alpha_j}{\alpha_k} \frac{\hat{V}_j}{\hat{V}_k} \frac{M_j}{M_k} \tag{39}$$

where the $\alpha_j$ are constants or functions that can be used to scale the friction factor ratios. We show below that this form is just a rearrangement of a common mixing rule for friction factors and ultimately connects the various theories to results that have been known for some time.

Equation 39 leads to the following form for the mutual diffusion coefficients

$$\begin{aligned} D_{ik} = {} & \left[ 1 - \rho_i \hat{V}_i \left( 1 - \frac{\alpha_i}{\alpha_N} \right) \right] \rho_i D_i \left( \frac{1}{RT} \frac{\partial \mu_i}{\partial \rho_k} \right) \\ & - \sum_{\substack{j=1 \\ j \neq i}}^{N-1} \left( 1 - \frac{\alpha_j}{\alpha_N} \right) \rho_j \hat{V}_j \rho_i D_j \left( \frac{1}{RT} \frac{\partial \mu_j}{\partial \rho_k} \right) \\ & i, k = 1, \ldots, N-1 \end{aligned} \tag{40}$$

where index $N$ typically corresponds to the polymer in solvent–polymer systems. There is, however, nothing in the derivation of Eq. 40 that restricts its applications to such systems.

It can be easily shown that setting

$$\alpha_i = 0 \qquad i \neq N \qquad \alpha_N \neq 0 \tag{41}$$

gives the theory of Dabral (1997) and the dilute region theory in the binary limit. Again, this appears to be the only form for which the stated assumptions limit application to solvent–polymer systems

Setting

$$\alpha_i = \frac{1}{\hat{V}_i} \qquad i = 1, \ldots, N \tag{42}$$

gives the theory of Zielinski and Hanley (1999), and setting

$$\alpha_i = 1 \qquad i = 1, \ldots, N \tag{43}$$

gives the theory of Alsoy and Duda (1999). Finally, setting

$$\frac{\alpha_1}{\alpha_2} = \frac{1}{\phi_1 \left[ \phi_1^2 \left( \frac{QD_1}{D_2} \right)_{\phi_1 = 1} + \phi_2 (1 + 2\phi_1) \right]} - \frac{\phi_2}{\phi_1} \tag{44}$$

gives the theory of Vrentas and Vrentas (1993) for binary solutions.

Equation 40 can also be viewed as a new, generalized theory that yields an extra parameter or function, $\alpha_i / \alpha_N$, for each solvent–solute pair in the system of interest. This in itself would be useful, but deeper insight comes from examining the relations between self-diffusion coefficients when the ratios between friction factors are considered (see Appendix A)

$$\frac{D_k}{D_j} = \frac{\alpha_j}{\alpha_k} \frac{\hat{V}_j}{\hat{V}_k} \frac{M_j}{M_k} = \frac{\zeta_{ij}}{\zeta_{ik}} = \frac{\zeta_{jj}}{\zeta_{jk}} \tag{45}$$

This equation allows us to interpret the $\alpha_i$ given earlier in terms of the self-diffusion coefficients. It is clear from Eqs. 41 through 44 that, of the existing theories, only Vrentas and Vrentas' (1993) binary theory allows for any concentration dependence in the ratios of self-diffusion coefficients.

We believe that Eq. 45 holds the key to resolving most of the perceived difficulties with the previously proposed theories. Let us rearrange and substitute this expression into Eq. 40

$$\begin{aligned} D_{ik} = {} & \left[ 1 - \rho_i \hat{V}_i \left( 1 - \frac{D_N \hat{V}_N M_N}{D_i \hat{V}_i M_i} \right) \right] \rho_i D_i \left( \frac{1}{RT} \frac{\partial \mu_i}{\partial \rho_k} \right) \\ & - \sum_{\substack{j=1 \\ j \neq i}}^{N-1} \left( 1 - \frac{D_N \hat{V}_N M_N}{D_j \hat{V}_j M_j} \right) \rho_j \hat{V}_j \rho_i D_j \left( \frac{1}{RT} \frac{\partial \mu_j}{\partial \rho_k} \right) \\ & i, k = 1, \ldots, N-1 \end{aligned} \tag{46}$$

Using the Gibbs–Duhem equation, one can rewrite this theory in a much more aesthetically pleasing form

$$\begin{aligned} D_{ik} = {} & \frac{\rho_i}{RT} \sum_{\substack{j=1 \\ j \neq i}}^{N} \phi_j \left( D_i \frac{\partial \mu_i}{\partial \rho_k} - D_j \frac{\partial \mu_j}{\partial \rho_k} \right) \\ & i, k = 1, \ldots, N-1 \end{aligned} \tag{47}$$

The corresponding species flux equations become

$$j_i^{\neq} = \frac{\rho_i}{RT} \sum_{\substack{j=1 \\ j \neq i}}^{N} \phi_j \left( D_j \nabla \mu_j - D_i \nabla \mu_i \right) \tag{48}$$

These expressions appear to be a multicomponent extension of the well-known Darken (1948) equation for binary systems. For binary systems, this form is generally associated with the geometric mean approximation for the friction factors, and it is trivial to show that the assumed form for friction-factor ratios, Eq. 39, does satisfy the geometric mean assumption

$$\zeta_{ij} = \left( \zeta_{ii} \zeta_{jj} \right)^{1/2} \tag{49}$$

This shows that all of the recently proposed theories can be viewed as particular cases of the general geometric mean assumption. Although we did not seek its origin, the literature reveals that the general result is also nothing new (van Loo et al., 1987; Rönkä et al., 1996). We can, however, gain new insight into the perceived difficulties with multicomponent diffusion calculations by examining those difficulties in light of the generalized theory and Eq. 45. Before doing so, let us examine how the generalized theory performs for a binary solvent–polymer system.

### *Binary case revisited*

In the binary limit, Eq. 46 has the form

$$D_{11}=\left[1-\rho_1\hat{V}_1\left(1-\frac{D_2\hat{V}_2M_2}{D_1\hat{V}_1M_1}\right)\right]D_1\left(\frac{\rho_1}{RT}\frac{\partial\mu_1}{\partial\rho_1}\right). \tag{50}$$

When one substitutes the usual Flory–Huggins expression for the chemical potential, we have

$$D_{11}=\left[1-\rho_1\hat{V}_1\left(1-\frac{D_2\hat{V}_2M_2}{D_1\hat{V}_1M_1}\right)\right]D_1\left[(1-\phi_1)(1-2\chi\phi_1)+\phi_1\frac{\hat{V}_1M_1}{\hat{V}_2M_2}\right] \tag{51}$$

This expression satisfies all of Vrentas and Vrentas' (1993) proposed limits, but when we apply it to real data, we find that some issues remain. Unfortunately, Pattle et al. (1967) did not publish polymer self-diffusion data, so we cannot apply this form to the data shown in Figure 1. Zielinski (1996), however, published graphs of solvent and polymer self- and mutual-diffusion data for toluene in different molecular-weight samples of polystyrene. The data were drawn from several sources. Figure 2 shows the diffusion data for a polystyrene sample with molecular weight of 275,000 at 110°C, where we have corrected the solvent self-diffusion data according to the statement in Waggoner et al. (1993). The figure also shows predictions of the various diffusion theories, where we assumed $\chi=0.4$, a bulk polymer density of 1.072 g/cm$^3$, and no volume change of mixing. To compute the model diffusivities, we fit a smooth curve through the toluene self-diffusion data and fit the polystyrene self-diffusion data with the form $\log(D_2)=-15.595+9.5342\ \omega_1$, recognizing that our confidence in the latter fit decreases rapidly beyond the data.

All five theories agree well with the mutual-diffusion data at low solvent concentrations. The dilute region theory gives mutual-diffusion coefficients that are much too low at higher solvent concentrations. The theories of Zielinski and Hanley (1999) and Alsoy and Duda (1999) fit the mutual-diffusion data well until higher solvent concentrations, where they fall below the experimental values. Vrentas and Vrentas' theory (1993) also fits the mutual-diffusion data well until higher solvent concentrations, where the predicted values are higher than the data. The generalized theory, Eq. 51, yields results that follow the dilute region theory over much of the concentration range, and then make a transition that approaches Vrentas and Vrentas' theory in the neighborhood of the pure-solvent limit. The overall result of the generalized theory is less than satisfactory. Similar results are obtained with the other data published by Zielinski (1996).

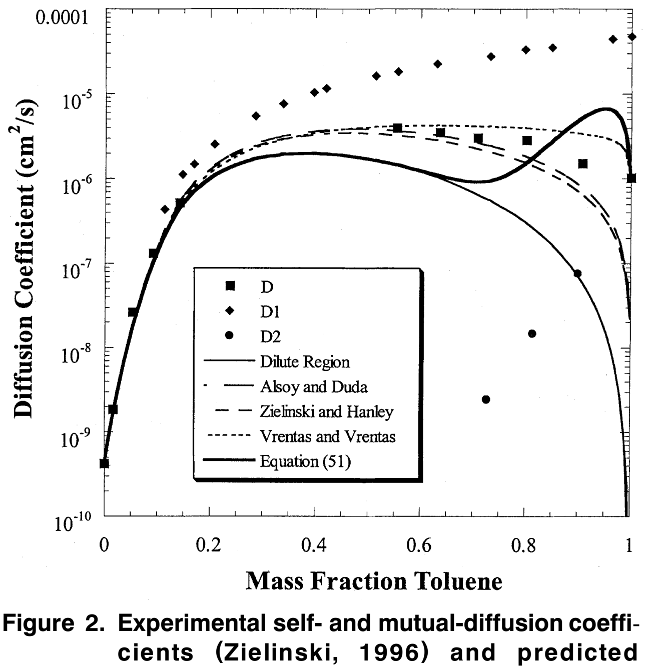

**Figure 2. Experimental self- and mutual-diffusion coefficients (Zielinski, 1996) and predicted mutual-diffusion coefficients for toluene in polystyrene at 110°C.**

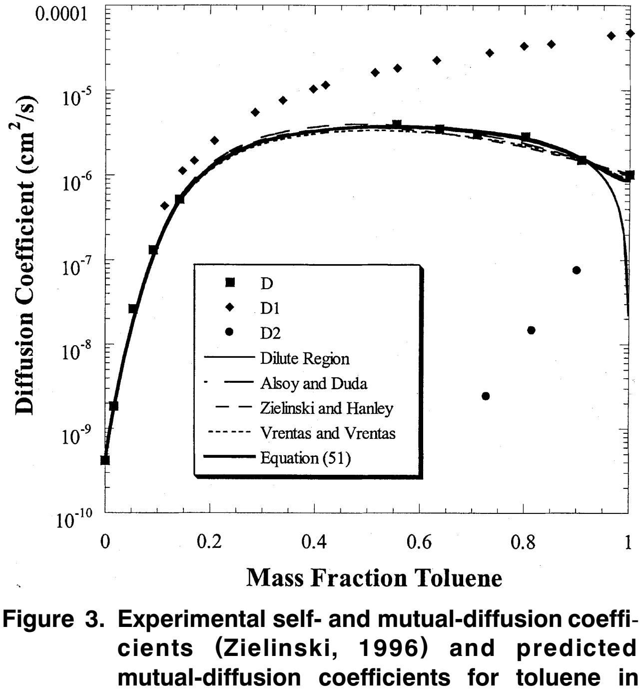

**Figure 3. Experimental self- and mutual-diffusion coefficients (Zielinski, 1996) and predicted mutual-diffusion coefficients for toluene in polystyrene at 110°C.**

Predictions based on modified polymer molecular weights of 206 for the dilute region model, 5,500 for the Alsoy and Duda model, 4,125 for the Zielinski and Hanley model, 8,250 for the Vrentas and Vrentas model, and 220 for the generalized model.

Further scrutiny of the generalized theory suggests three possible sources for its lack of accuracy. First, the generalized theory may not be valid for the system of interest. This is a very real possibility, but one that leads to no further development here. Some of the error may be because our extrapolation of $D_2$ is unrealistic. In the middle of the solvent concentration range, our extrapolation of the $D_2$ data yield values that do nothing to increase the computed mutual-diffusion coefficient. If the $D_2$ values were to decrease less rapidly in the middle concentration range, then the computed mutual-diffusion coefficients would be higher. The final possible source of error is the thermodynamic term(s). At middle to high solvent concentrations, the predicted mutual-diffusion coefficients are quite sensitive to the thermodynamic terms. Specifically, if we reduce $M_2$ in Eq. 51, we find that the theory can fit the data extremely well, as shown in Figure 3. Indeed, by adjusting the value of $M_2$ (without formal optimization) in the last term of the Flory−Huggins expression, we can make all of the theories fit the data quite well. This suggests to us that the thermodynamic behavior, particularly at high solvent concentrations, might warrant additional study. Another possibility is that the thermodynamic terms in the diffusion equation might be better represented by a local composition theory (Li et al., 2001), to reflect the fact that the relevant unit in polymer diffusion is the jumping unit, not the entire polymer chain.

Our critique of the generalized theory leads to the question: What are the Zielinski and Hanley (1999) and Alsoy and Duda (1999) theories doing that results in significantly better predictions than the dilute region theory gives for the mutual-diffusion coefficient? It is clear that neither theory uses the polymer self-diffusion coefficient explicitly. Rather, they use the approximations to it given by Eq. 45 with the appropriate $\alpha$'s

$$D_2 = D_1 \frac{M_1}{M_2} \tag{52}$$

for Zielinski and Hanley (1999), and

$$D_2 = \frac{D_1 \hat{V}_1 M_1}{\hat{V}_2 M_2} \tag{53}$$

for Alsoy and Duda (1999). Since the real polymer self-diffusion coefficients are significantly smaller than the approximate values over most of the concentration range, both theories are, in effect, modifying the thermodynamic terms.

It is well known that the Darken form, Eq. 47, does not represent the binary mutual-diffusion coefficient for polymer−solvent systems over the full concentration range. Our results confirm that, but they also show that all of the proposed friction-based models are really just special cases of this form based on different assumptions about the polymer self-diffusion coefficients. We expect that the actual systems will rarely follow those assumptions. From a practical viewpoint, since the various theories are most often used to relate mutual-diffusion behavior, it may be that the advantages of the general theory described below will allow more robust computations in multicomponent systems. From a fundamental viewpoint, however, the results show that the long-standing need for complete sets of self-diffusion, mutual-diffusion, and thermodynamic data is as critical as ever.

Next, we examine some issues in multicomponent systems.

### *Multicomponent systems and the Onsager reciprocal relations*

The ORR are held by some to be general properties of materials in nature. In application, they seem to have a dual role. Experimentalists use them to check the "consistency" of their data. Theoreticians use them as constraints in their theories.

Zielinski and Alsoy (2001) applied the Onsager relations to ternary systems using various friction-based theories "in an attempt to gauge their validity and ascertain their applicability," where "their" refers to the theories. They conclude that the general Bearman framework and Dabral's (1997) form satisfy the ORR and the theories of Zielinski and Hanley (1999) and Alsoy and Duda (1999) do not. Specifically, the ORR lead to conditions for their theories that

$$\frac{D_1}{D_2} = \frac{M_2}{M_1} \tag{54}$$

in the case of Zielinski and Hanley (1999), and

$$\frac{D_1}{D_2} = \frac{\hat{V}_2 M_2}{\hat{V}_1 M_1} \tag{55}$$

in the case of Alsoy and Duda (1999). They state that these relationships are "not expected to be universally true, in which case this formalism fails the Onsager consistency check."

Zielinski and Alsoy (2001) were apparently hoping that the ORR would give them insight into the diffusion behavior of real materials in nature that they could use to develop better theories, rather than as a "mere" constraint on the consistency of their theories. Because the final result obtained by applying the ORR to the mathematical forms of their theories did not mimic the real behavior of materials in general, they concluded that their theories did not satisfy the ORR. We believe they sold themselves short. Substituting the appropriate $\alpha_i$, Eqs. 42 and 43, into Eq. 45 gives exactly the results of their Onsager analysis. In other words, by not substituting the ratios of friction factors back into Bearman's expressions for the self-diffusion coefficients in terms of the friction factors, they stopped one step short of confirming the Onsager consistency of their theories. In the Bearman formalism, their friction factor relations must hold for the self-diffusion coefficients or the corresponding expressions relating self- and mutual-diffusion coefficients would not hold. In the case of Zielinski and Hanley's (1999) theory, the same result, Eq. 54, follows from the average friction-factor approach used in their original derivation (see Appendix B).

The Onsager consistency of their theories must, of course, hold if the general Bearman formulation is Onsager consistent. In the general form, no restrictions are made on the friction factors. In the Zielinski and Hanley (1999) and Alsoy and Duda (1999) theories, the friction factors are restricted to a subset of those allowed in the general formulation. If the general form is consistent, their forms must also be. In this case, the consistency check should be viewed as a necessary condition for a physically reasonable theory, but not a sufficient condition to assure a theory that describes material behavior in general.

### *Multicomponent systems and material-balance constraints*

In typical applications, one component in a mixture is chosen as the balancing component. The concentration of that species is then computed as the mass balance(s) for the other component(s) is (are) computed based on the fact that the total mass or volume fractions must sum to one. Nauman and Savoca (2001) state that a common problem in multicomponent diffusion calculations is that cross diffusion of this balancing component can lead to computed concentrations that are negative. Of Zielinski and Hanley's (1999) theory, they state, "Also, their methodology can violate the material balance constraint if the self-diffusivities used in their procedure are independent of concentration."

This is a very troubling contention given that the material-balance constraint, Eq. 6, is used in the derivation of the theory without any specific constraint on the concentration dependence of the self-diffusivities. We believe, however, that the solution to this problem lies precisely in the constraints that were imposed. Specifically, from Eqs. 42 and 45, the theory can be strictly valid, within the limitations of the other assumptions made, only when

$$\frac{D_k}{D_j} = \frac{M_j}{M_k} \tag{56}$$

These are the same conditions that result from the Onsager consistency check. It is not the concentration dependence of the self-diffusivities that is an issue, it is the ratio of the self-diffusivities. When the ratio is not as in Eq. 56, violations of the material balance constraint are possible.

Consider a single layer of a ternary mixture bounded by impermeable walls and infinite in the plane of the layer. Let this layer have uniform concentration profiles in the planar direction and initial concentration profiles across its unit thickness (in centimeters) given by

$$\rho_1(0 \le x \le 1, t = 0) = 0.5^* \exp\left[-\left(\frac{x - 0.5}{0.2}\right)^2\right] \tag{57}$$

$$\rho_2(0 \le x \le 1, t = 0) = 0.5 - c_1(x, t = 0)$$

$$\rho_3(0 \le x \le 1, t = 0) = 0.5$$

The dynamics of the concentration profiles in this layer are governed by the one-dimensional diffusion equation

$$\frac{\partial \rho_i}{\partial t} = \frac{\partial}{\partial x}\left(\sum_{j=1}^{2} D_{ij}\frac{\partial \rho_j}{\partial x}\right). \qquad i = 1, 2 \tag{58}$$

Let the components have the properties listed in Table 1. We describe the chemical potentials using the ternary form of the Flory–Huggins theory (Flory, 1953; Favre et al., 1996) and assume no volume change of mixing.

If we compute the mutual diffusion coefficients using the theory of Zielinski and Hanley (1999), Eq. 37, then the system evolves as shown in Figure 4. Here we see that the computed concentrations of the balancing component (component 3) become negative at approximately $t = 0.0125$ s. Another interesting feature of the solution is that the component 2 profile "overshoots" the final equilibrium concentration profile in the center of the domain.

**Table 1. Properties for Components in Material Balance Constraint Calculations**

| | Component 1 | Component 2 | Component 3 |
|---|---|---|---|
| $\hat{V}_i$ (cm$^3$/g) | 1.0 | 1.0 | 1.0 |
| $M_i$ (g/mol) | 1.0 | 10.0 | 1,000.0 |
| $D_i$ (cm$^2$/s) | 1.0 | 1.0 | 1.0$E$-3 |
| $\chi_{i3}$ | 0.3 | 0.3 | |

Now consider a case where both component 1 and component 2 have molecular weights of 1.0, such that the ratio of molecular weights equals the ratio of their self-diffusion coefficients. The evolution of this system is shown in Figure 5. This system remains well behaved throughout its evolution even though the self-diffusion coefficients are constant, in contrast to the assertions of Nauman and Savoca (2001). The

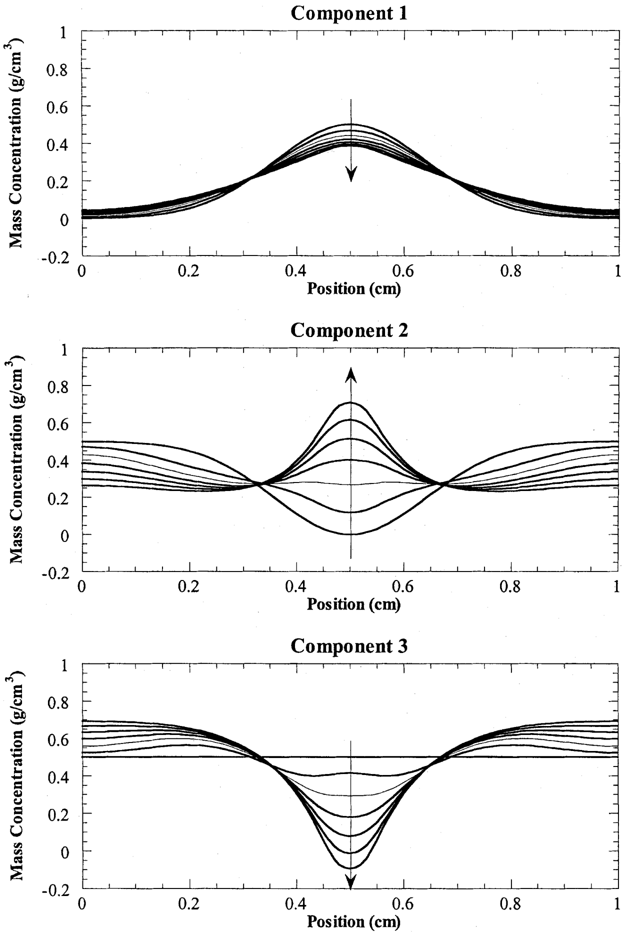
Component 1
Component 2
Component 3

**Figure 4. Evolution of concentration profiles using Zielinski–Hanley mutuals.**

Profiles are shown every 0.0025 s. The arrows indicate the direction in time.

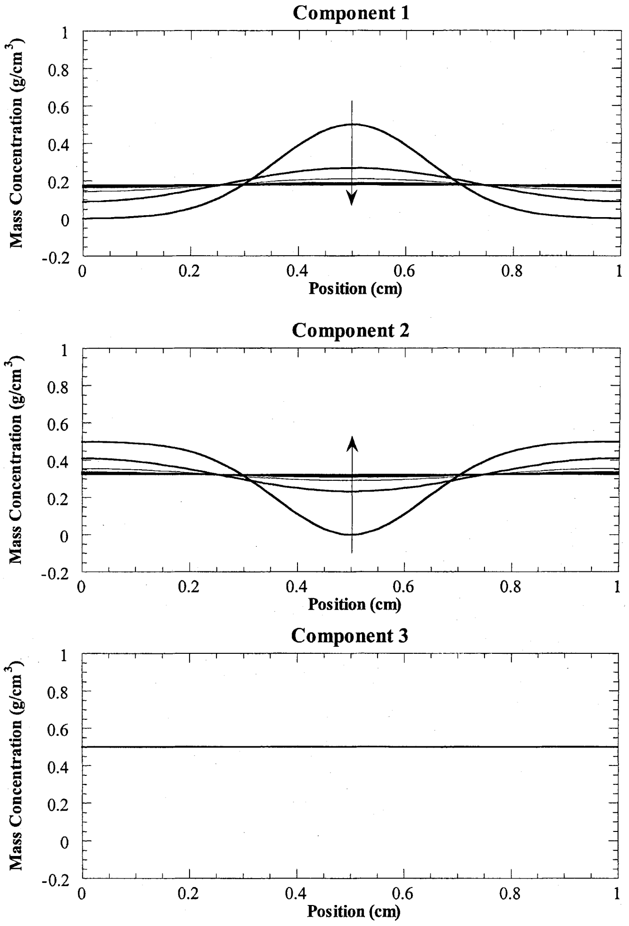

**Figure 5. Evolution of concentration profiles using Zielinski–Hanley mutuals.**

Profiles are shown every 0.015 s. The arrows indicate the direction in time.

profiles also do not exhibit the overshoot behavior observed in the previous case. It is interesting to note that the molecular weights enter into the calculations only through the Flory–Huggins thermodynamic terms in the expressions for the mutual-diffusion coefficients. The necessary molecular-weight dependence appears to stem from the Gibbs–Duhem consistency of the equilibrium thermodynamic model. This suggests that any thermodynamic theory that does not have this consistency could give rise to material-balance constraint violations.

The system is also well behaved if we keep the original molecular weights shown in Table 1, but set the self-diffusion coefficient of component 1 to $D_1 = 10$, so that the ratio of component 1 and 2 self-diffusion coefficients is inversely proportional to the ratio of their molecular weights. The evolution of this system is pictured in Figure 6. We see significant diffusion of the balancing component, component 3, but it goes in the opposite direction of the first case. There is no overshoot of the component 1 and 2 profiles. Rather than drawing component 3 away from the center, as in the first case, the balancing component (3) is drawn toward the center. It does overshoot the equilibrium value there, but the material-balance constraints are not violated.

We recognize that our calculations in no way constitute a rigorous proof, but our conjecture makes intuitive sense. We cannot ignore the ratio of self-diffusion coefficients, violating an assumption of the theory, and expect the theory to perform flawlessly. Similar violations can occur with the Dabral (1997) and Alsoy and Duda (1999) forms.

In practical applications for polymer–multisolvent systems, indeed for most systems, it is highly unlikely that the self-diffusion coefficients would be inversely proportional to the molecular weights, or molar volumes in the case of Alsoy and Duda's (1999) theory, over the entire concentration and temperature range of any such application. Difficulties with the material balance constraints should, therefore, be expected with these theories. This is the fundamental difficulty with the assumption of fixed friction-factor ratios. One advantage of the generalized theory is that this restriction is removed.

### *Drying calculations and the generalized diffusion theory*

Now we return to the issue of model robustness and applications in polymer–solvent systems. There is nothing in our derivations that restricts the $\alpha_i$ to be constant, and, as shown previously, they can be directly related to the component self-diffusion coefficients. The theory does require the rela-

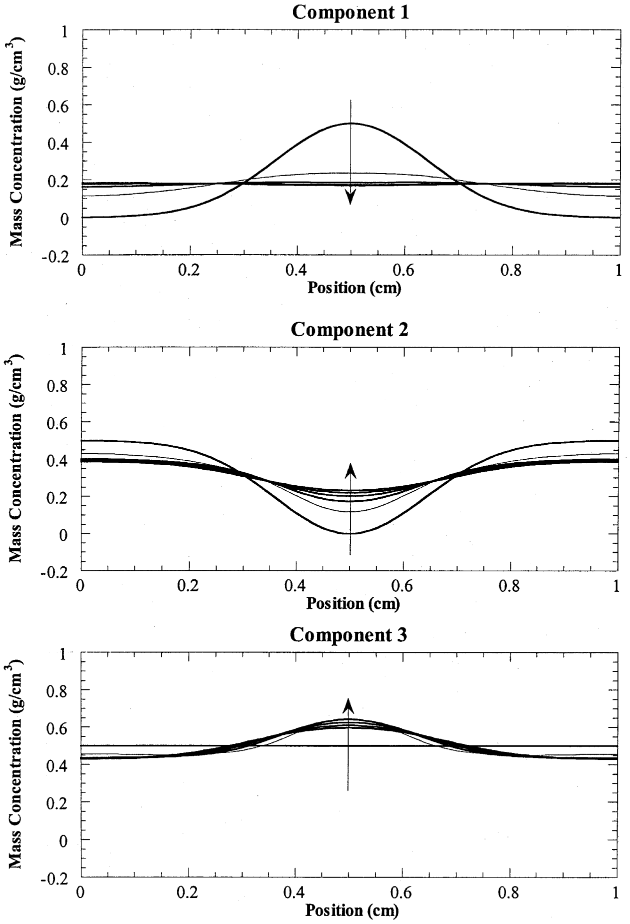

**Figure 6. Evolution of concentration profiles using Zielinski–Hanley mutuals.**

Profiles are shown every 0.004 s. The arrows indicate the direction in time.

tions between self-diffusion coefficients given by Eq. 45. The self-diffusion coefficients in Eq. 46 appear only as ratios of $D_N/D_i$, and the results in Appendix A suggest that any bounded expression for the component self-diffusion coefficients should be applicable without violating the assumptions used to derive Eq. 46. If we proceed in the cautious ignorance of industrial engineers with desktop computers and a job to do, we can simply use what we know about the $D_i$ to predict the mutual-diffusion coefficients and check for violations of material-balance constraints. In most cases, this means we will use the free volume theory expressions for the self-diffusion coefficients of both the solvents and the polymer. This gives rise to two new parameters, a preexponential factor and an activation energy for the polymer self-diffusion coefficient. The free volume theory expressions for the self-diffusion coefficients are

$$D_i = D_{0,i} \exp\left[ \frac{-\gamma \left( \sum_{j=1}^{N} \omega_j \hat{V}_j^* \frac{\xi_{iN}}{\xi_{jN}} \right)}{\hat{V}_{FH}} \right] \tag{59}$$

$$\frac{\hat{V}_{FH}}{\gamma} = \sum_{i=1}^{N} \frac{K_{1i}}{\gamma} \omega_i \left( K_{2i} + T - T_{gi} \right) \tag{60}$$

where $\xi_{NN} = 1$.

To test this approach, we consider a case study presented by Alsoy and Duda (1999) for drying of a polystyrene coating from a blend of toluene and ethylbenzene. We implemented their drying model using Galerkin's method with finite element basis functions, integrating the resulting set of equations with DASSL (Petzold, 1983). All of the necessary parameters can be found in their Tables 2 and 4 except the parameters for the polymer self-diffusion coefficient. We assume a polystyrene molecular molecular weight of 275,000 g/mol and let $D_{0,3} = 3.64 \times 10^{-6}$ (the inverse of the polymer molecular weight) and $E_{\mathrm{act},3} = 0.0$. In this case, the polystyrene self-diffusion parameters are not meant to represent the actual material behavior. Our purpose is only to demonstrate how the generalized theory resolves material-balance constraint violations. Again, we assume no volume change of mixing.

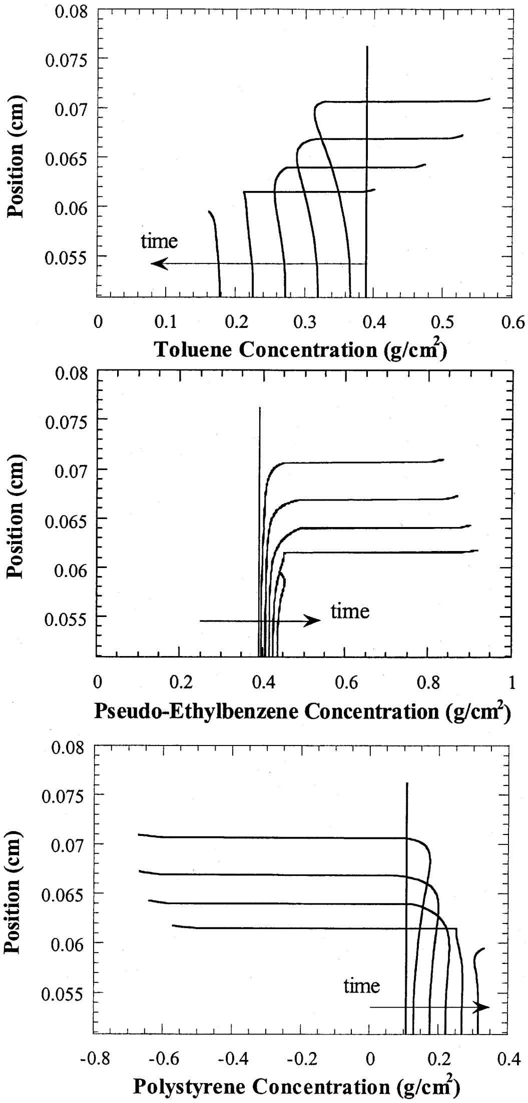

**Figure 8. Concentration profiles at 5-s intervals during drying of a toluene(1)/pseudoethylbenzene(2)/polystyrene(3) coating based on Alsoy and Duda's (1999) diffusion model, Eq. 38.**

Bottom of coating at 0.0508 cm.

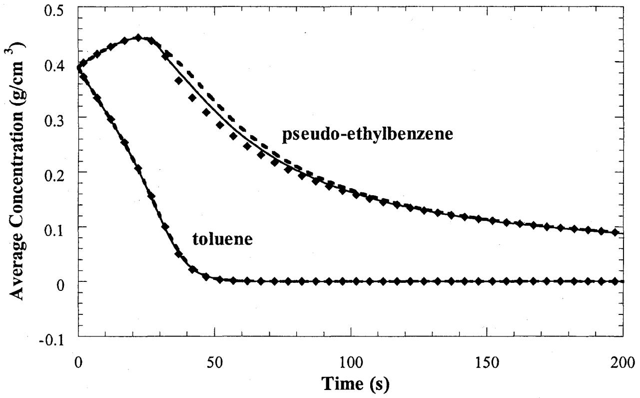

**Figure 7. Average solvent concentration profiles during drying of toluene(1)/pseudoethylbenzene(2)/polystyrene(3) coating based on Alsoy and Duda's diffusion model, Eq. 38 (solid line); Zielinski and Hanley's diffusion model, Eq. 37 (dashed line), and the generalized model, Eq. 46 (diamonds).**

The drying conditions and material properties are described by Alsoy and Duda (1999), except $D_{0,2} = 1.61 \times 10^{-4}$.

The average solvent concentrations in the film computed with Alsoy and Duda's Case 1 diffusion theory, Eq. 38, Zielinski and Hanley's theory, Eq. 37, and the generalized theory, Eq. 46, are all almost identical to Figure 8 in Alsoy and Duda (1999). All three diffusion theories also yield similar smooth and well-behaved concentration profiles within the drying film.

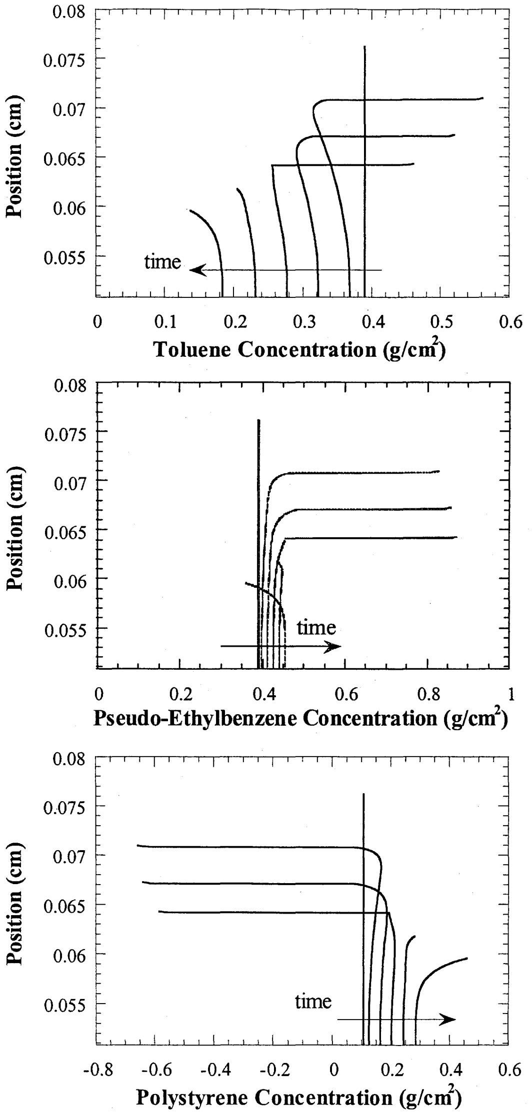

**Figure 9. Concentration profiles at 5-s intervals during drying of a toluene(1)/pseudoethylbenzene(2)/polystyrene(3) coating based on Zielinski and Hanley's (1999) diffusion model, Eq. 37.**

Bottom of coating at 0.0508 cm.

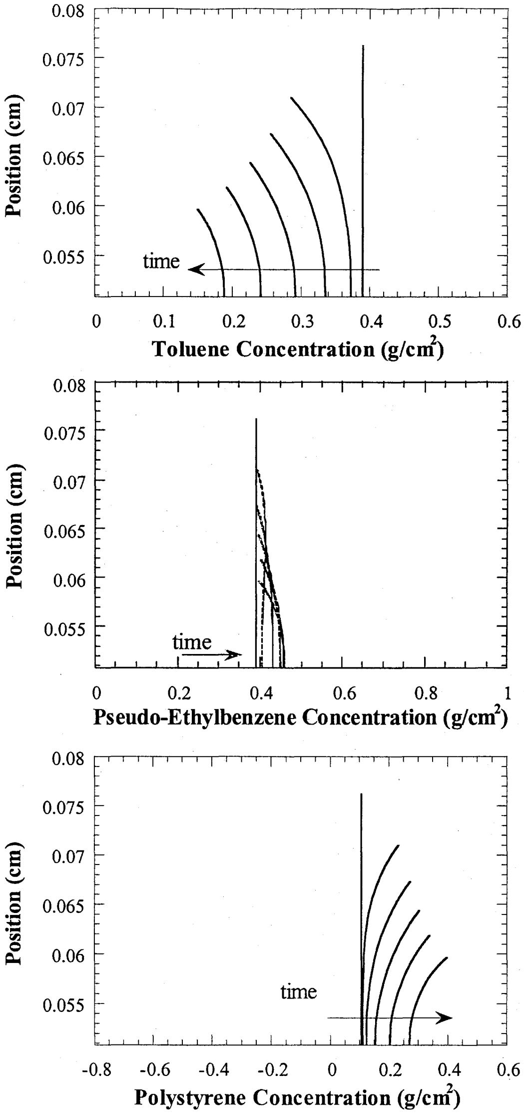

**Figure 10. Concentration profiles at 5-s intervals during drying of a toluene(1)/pseudoethylbenzene(2)/polystyrene(3) coating based on the generalized diffusion model, Eq. 46.**

Bottom of coating at 0.0508 cm.

If we decrease the free volume theory preexponential factor for ethylbenzene from the value given by Alsoy and Duda (1999) to $D_{0,2} = 1.61 \times 10^{-4}$, the macroscopic results for all three theories are, again, almost identical, but we see material-balance violations at the surface of the coating for both the Alsoy and Duda (1999) and Zielinski and Hanley (1999) theories. Figure 7 shows the computed average solvent concentrations for each of the three theories. Figures 8 through 10 show the corresponding computed concentration profiles in the coating during the first 25 s of drying. As in our single-layer calculations earlier, we see that the fixed friction-factor ratio theories cause the third component to diffuse away from the surface until its concentration becomes negative.

One might argue that the agreement in macroscopic results suggests that this is not a critical issue in drying calculations. We contend that if we are interested in understanding microstructure development, as in Dabral et al. (2002), then understanding the evolution of internal concentration profiles is a critical issue. It also seems reasonable to expect that one might encounter conditions where violations of the material balance constraint are not localized at the surface of the coating. This seems to be an area that offers a great deal of potential for experimental studies. Creative use of attenuated total reflectance infrared spectroscopy, as in Elabd and Barbari (2001), during drying of different thickness samples might help elucidate the dynamics of internal solvent concentration profiles during drying.

### *Restrictions on the matrix of diffusion coefficients*

An independent test of the matrix of diffusion coefficients that could indicate potential problems would be very useful. Kirkaldy et al. (1963) examined the behavior of isothermal, isobaric systems and showed that Onsager consistency and thermodynamic stability require that the matrix of diffusion coefficients have real and positive eigenvalues. For constant diffusion coefficients, this assures that computed concentration profiles will relax nonperiodically. For a ternary system, necessary and sufficient conditions for the diffusion matrix to have real and positive eigenvalues are

$$D_{11}+D_{22}>0, \qquad D_{11}D_{22}-D_{12}D_{21}\geq 0, \qquad \text{and}$$
$$(D_{11}+D_{22})^2 \geq 4(D_{11}D_{22}-D_{12}D_{21}) \quad (61)$$

We checked these conditions for all of the case studies presented earlier. None of the physically reasonable results violated these conditions. In the single-layer interdiffusion problem pictured in Figure 4, the determinant condition, listed second in Eq. 61, is violated shortly after the third-component concentration becomes negative. In the nonisothermal drying calculations pictured in Figures 8 and 9, the determinant condition is violated at essentially the same time that the polymer concentration becomes negative. For our case studies, Kirkaldy et al.'s conditions do not supply *a priori* information that the computed behavior is going to violate the material-balance constraints.

Until a more general test of the diffusion-coefficient matrix is available, reasonable behavior seems most likely assured by computing a diffusion-coefficient matrix defined from Eqs. 40 or 46 using a suitable thermodynamic model and satisfying the original assumptions about the friction factors in the self-diffusion coefficients. As shown in Appendix A, it is possible to define friction factors that satisfy the general geometric mean assumption in terms of the component self-diffusion coefficients. Thus, it seems at least possible that a suitable thermodynamic theory can be used in combination with any expression for the self-diffusion coefficients in Eq. 46 while still satisfying the geometric mean assumption and, therefore, achieving well-behaved results. Well-behaved results are not assured if the equilibrium thermodynamic theory indicates phase instabilities. Finally, we have also found that there is always the possibility of material balance violations and other ill-behaved results resulting from numerical integration and/or discretization errors!

## Conclusions

We have presented an analysis of friction-based diffusion theories that includes a review of existing theories and a generalized approach that arrives at a known result from a new direction. The generalized approach shows that all of the proposed multicomponent theories discussed herein are just particular cases obeying a geometric mean relationship between friction factors. In the process, we believe that we have answered questions regarding the Onsager consistency of these theories and offered a solution to material balance constraint violations in the form of a self-consistent framework based on the general geometric-mean relationship.

The generalized theory appears to be well known in the metallurgical literature. Our primary interest is in polymer–solvent systems, and our results suggest two views. From a practical standpoint, the general theory may allow more robust correlation and prediction of binary and/or multicomponent diffusion coefficients with less fear of material-balance constraint violations during process predictions. From a more rigorous standpoint, further experimental understanding of the polymer self-diffusion behavior and the solution thermodynamics is required to determine if the theory is applicable, or can be modified to be made applicable, over the entire solvent–polymer concentration range. In any case, complete sets of polymer and solvent self-diffusion, mutual-diffusion, and thermodynamic data would provide a welcome basis for testing further theoretical developments.

## Acknowledgments

The authors gratefully acknowledge the comments of our reviewers and discussions with Prof. Richard Cairncross, and, particularly, Prof. James S. Vrentas. We also gratefully acknowledge the permission by our laboratory director, Dr. Debra L. Wilfong, to publish these results, and the continuing encouragement of our team leader, Sharon Wang, to pursue better drying models. We hope readers of this work will heed the call to develop better theories and measure more complete sets of data.

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## Appendix A

Bearman's (1961) expression for self-diffusion coefficients in terms of friction factors is

$$D_j = \frac{RT}{\sum_{m=1}^{N} \frac{\rho_m}{M_m} \zeta_{jm}} \tag{A1}$$

Factoring out any one of the friction factors in the denominator and using Eq. 39 gives

$$D_j = \frac{RT}{\zeta_{ji} \sum_{m=1}^{N} \frac{\rho_m}{M_m} \frac{\zeta_{jm}}{\zeta_{ji}}} = \frac{RT}{\zeta_{ji} \sum_{m=1}^{N} \frac{\rho_m}{M_m} \frac{\alpha_m}{\alpha_i} \frac{\hat{V}_m}{\hat{V}_i} \frac{M_m}{M_i}} \quad \text{for all} \quad i = 1, \ldots, N \tag{A2}$$

Thus, the ratio of any two self-diffusion coefficients is

$$\frac{D_k}{D_j} = \frac{\zeta_{ji}}{\zeta_{ki}} = \frac{\zeta_{ij}}{\zeta_{ik}} = \frac{\alpha_j}{\alpha_k} \frac{\hat{V}_j}{\hat{V}_k} \frac{M_j}{M_k} \tag{A3}$$

We can also rearrange Eq. A2 using Eq. A3 to derive a relationship between the friction factors and the component self-diffusion coefficients

$$\zeta_{ji} = \frac{RT}{D_j \sum_{m=1}^{N} \frac{\rho_m}{M_m} \frac{\zeta_{jm}}{\zeta_{ji}}} = \frac{RT}{D_j \sum_{m=1}^{N} \frac{\rho_m}{M_m} \frac{D_i}{D_m}} \tag{A4}$$

These friction factors satisfy the geometric mean assumption

$$\zeta_{ii} \zeta_{jj} = \frac{R^2 T^2}{D_i^2 D_j^2 \left[ \sum_{m=1}^{N} \frac{\rho_m}{M_m} \frac{1}{D_m} \right]^2} = \zeta_{ij}^2 \tag{A5}$$

## Appendix B

Zielinski and Hanley (1999) write the chemical potential gradient in terms of an average resistive force

$$\nabla \mu_i = -f_i M_i (v_i - v) \tag{B1}$$

where $v$ is the mass average velocity of the system

$$v = \sum_{i=1}^{N} \omega_i v_i \tag{B2}$$

and $\omega_i$ is the mass fraction of component $i$. Equation B1 can be written, as in Zielinski and Hanley's (1999) Appendix A, as

$$\nabla \mu_i = -f_i M_i \sum_{j=1}^{N} \omega_j (v_i - v_j) \tag{B3}$$

or

$$\nabla \mu_i = -\frac{f_i M_i}{\rho} \sum_{j=1}^{N} \rho_j (u_i - u_j) \tag{B4}$$

where

$$u_i = v_i - v \tag{B5}$$

is the velocity of component $i$ with respect to the mass average velocity, $v$, of the system. This is the diffusion velocity of component $i$. For isothermal, isobaric systems, the Gibbs–Duhem equation is

$$0 = \sum_{i=1}^{N} \frac{\rho_i}{M_i} \nabla \mu_i . \tag{B6}$$

Using Eq. B4 and multiplying by $-\rho$, we can write the Gibbs–Duhem equation as

$$0 = \sum_{i=1}^{N} \sum_{j=1}^{N} F_{ij} (u_i - u_j) \tag{B7}$$

where

$$F_{ij} = f_i\,\rho_i\,\rho_j \tag{B8}$$

We also have the constraint that the sum of the diffusion fluxes is zero

$$0 = \sum_{i=1}^{N} j_i = \sum_{i=1}^{N} \frac{\rho_i}{f_i M_i}\nabla\mu_i = \sum_{i=1}^{N} \rho_i u_i \tag{B9}$$

For isothermal, isobaric systems with no other body forces, the Gibbs–Duhem equation is essentially a statement of conservation of linear momentum. Following Truesdell (1962), we find that the condition

$$0 = \sum_{j=1}^{N} \left(F_{ij} - F_{ji}\right) \tag{B10}$$

is necessary and sufficient that Zielinski and Hanley's theory be consistent with the Gibbs–Duhem equation. Furthermore, the matrix $F_{ij}$ can be decomposed into a sum of a symmetric and a skew matrix

$$F_{ij} = D_{ij} + W_{ij} \qquad \text{with} \qquad D_{ij} = D_{ji} \qquad \text{and} \qquad W_{ij} = -W_{ji} \tag{B11}$$

where the sum of any row or column of $W_{ij}$ equals zero

$$0 = \sum_{i=1}^{N} W_{ij} = \sum_{j=1}^{N} W_{ij} \tag{B12}$$

For a ternary system, we have

$$\boldsymbol{F} = \begin{bmatrix} f_1\,\rho_1^2 & \frac{f_1+f_2}{2}\rho_1\,\rho_2 & \frac{f_1+f_3}{2}\rho_1\,\rho_3 \\ \frac{f_2+f_1}{2}\rho_2\,\rho_1 & f_2\,\rho_2^2 & \frac{f_2+f_3}{2}\rho_2\,\rho_3 \\ \frac{f_3+f_1}{2}\rho_3\,\rho_1 & \frac{f_3+f_2}{2}\rho_3\,\rho_2 & f_3\,\rho_3^2 \end{bmatrix} + \begin{bmatrix} 0 & \frac{f_1-f_2}{2}\rho_1\,\rho_2 & \frac{f_1-f_3}{2}\rho_1\,\rho_3 \\ \frac{f_2-f_1}{2}\rho_2\,\rho_1 & 0 & \frac{f_2-f_3}{2}\rho_2\,\rho_3 \\ \frac{f_3-f_1}{2}\rho_3\,\rho_1 & \frac{f_3-f_2}{2}\rho_3\,\rho_2 & 0 \end{bmatrix} \tag{B13}$$

where Eq. B12 [Truesdell's (1962) Eq. 31] leads to the skew matrix

$$\begin{bmatrix} 0 & \frac{f_1-f_2}{2}\rho_1\,\rho_2 & \frac{f_1-f_3}{2}\rho_1\,\rho_3 \\ \frac{f_2-f_1}{2}\rho_2\,\rho_1 & 0 & \frac{f_2-f_3}{2}\rho_2\,\rho_3 \\ \frac{f_3-f_1}{2}\rho_3\,\rho_1 & \frac{f_3-f_2}{2}\rho_3\,\rho_2 & 0 \end{bmatrix} = \begin{bmatrix} 0 & \alpha & -\alpha \\ -\alpha & 0 & \alpha \\ \alpha & -\alpha & 0 \end{bmatrix} \tag{B14}$$

It follows that Zielinski and Hanley's (1999) friction factors are equal

$$f_1 = f_2 = f_3 \tag{B15}$$

Upon substituting this result into Zielinski and Hanley's expression for the self-diffusion coefficients

$$D_i = \frac{RT}{M_i f_i} \tag{B16}$$

we find exactly the result given by Zielinski and Alsoy (2001) for the Onsager consistency of the Zielinski and Hanley (1999) theory

$$\frac{D_1}{D_2} = \frac{M_2}{M_1} \tag{B17}$$

*Manuscript received Apr. 22, 2002, and revision received Aug. 16, 2002.*