

On Relationships Between Diffusion and Friction Coefficients

INTRODUCTION

An important equation in the analysis of translational diffusion in polymer solutions is the relationship between diffusion and friction coefficients.¹⁻⁴ This relationship provides a convenient means of connecting theory and experiment for polymer-solvent systems. Application of statistical mechanics has led to theoretical expressions for the friction coefficient in infinitely dilute⁵ and dilute^{6,7} polymer solutions, whereas utilization of free-volume concepts has yielded corresponding results^{3,8,9} for concentrated solutions. On the other hand, in a diffusion experiment, it is the diffusion coefficient which is the experimentally measurable quantity. The purpose of this paper is to examine three forms of this equation which have been frequently utilized and to deduce which of these relationships appears to be the most appropriate for the analysis of diffusional transport in both dilute and concentrated polymer solutions. In addition, we derive a modified form of the series expansion which describes the concentration dependence of the mutual diffusion coefficient for the important case of dilute polymer-solvent mixtures.

THEORETICAL DEVELOPMENT

We consider isothermal diffusion in polymer-solvent systems under conditions where the effect of pressure gradients on the diffusion process can be neglected. For convenience, and with no loss of generality, the mass transport is assumed to be one dimensional. In the quasi-stationary regime of diffusional transport, the chemical potential gradients and frictional forces are related in the following manner¹⁰:

$$\frac{\partial \mu_1}{\partial x} = -C_2^0 \zeta_{12} (u_1 - u_2) \quad (1)$$

$$\frac{\partial \mu_2}{\partial x} = -C_1^0 \zeta_{12} (u_2 - u_1). \quad (2)$$

Since

$$j_1^2 = \rho_1 (u_1 - u_2) \quad (3)$$

$$j_2^1 = \rho_2 (u_2 - u_1) \quad (4)$$

it can be easily shown that

$$j_1^2 = -\frac{\rho_1 M_2}{\rho_2 N_A^2 \zeta_{12}} \left(\frac{\partial \mu_1}{\partial \rho_1} \right)_{T,P} \frac{\partial \rho_1}{\partial x} \quad (5)$$

$$j_2^1 = -\frac{\rho_2 M_1}{\rho_1 N_A^2 \zeta_{12}} \left(\frac{\partial \mu_2}{\partial \rho_2} \right)_{T,P} \frac{\partial \rho_2}{\partial x}. \quad (6)$$

If diffusion coefficients are defined by the expression

$$j_A^B = -\frac{\rho D_{AB}}{\omega_B} \nabla \omega_A = -\frac{D_{AB} \nabla \rho_A}{\hat{V}_{B \rho B}} \quad (7)$$

it is evident from eqs. (5), (6), and (7) that

$$D_{12} = \frac{M_2 \rho_1 \hat{V}_2}{N_A^2 \zeta_{12}} \left(\frac{\partial \mu_1}{\partial \rho_1} \right)_{T,P} \quad (8)$$

$$D_{21} = \frac{M_1 \rho_2 \hat{V}_1}{N_A^2 \zeta_{12}} \left(\frac{\partial \mu_2}{\partial \rho_2} \right)_{T,P} \quad (9)$$

Furthermore, we have the following result:

$$D_{12} = D_{21} = D. \quad (10)$$

Equations (8) and (9) are equivalent to the diffusivity-frictional coefficient relationship utilized by Bearman,¹⁰ and the diffusion coefficient D is what is commonly called the binary mutual diffusion coefficient.¹¹

On the other hand, if we define diffusion coefficients using the equation

$$j_A^B = -\bar{D}_{AB}\nabla\rho_A \quad (11)$$

it is obvious that

$$\bar{D}_{12} = \frac{\rho_1 M_2}{\rho_2 N_A^2 \zeta_{12}} \left(\frac{\partial \mu_1}{\partial \rho_1} \right)_{T,P} = \frac{D_{12}}{\bar{V}_{2\rho_2}} \quad (12)$$

$$\bar{D}_{21} = \frac{\rho_2 M_1}{\rho_1 N_A^2 \zeta_{12}} \left(\frac{\partial \mu_2}{\partial \rho_2} \right)_{T,P} = \frac{D_{21}}{\bar{V}_{1\rho_1}} \quad (13)$$

In addition, in general, we have

$$\bar{D}_{12} \neq \bar{D}_{21}. \quad (14)$$

This particular form of the relationship between diffusion and friction coefficients has been utilized by Onsager and Fuoss¹² and by Mandelkern and Flory.¹³ Clearly, either of the above results is acceptable since there is, of course, no unique definition of a diffusion coefficient. The differences between the above two formulations are clearly not major, and, indeed, some of these differences disappear in the limit of infinite dilution. For example, as the concentration of the polymer (component 2) approaches zero, we have

$$\lim_{\rho_2 \rightarrow 0} \bar{D}_{21} = \lim_{\rho_2 \rightarrow 0} D_{21}. \quad (15)$$

However, utilization of diffusion coefficients defined by eq. (7) does have discernible advantages over application of those defined by eq. (11), particularly when the analysis is not restricted to a narrow concentration range. Furthermore, these advantages can be achieved with no accompanying complications. In the first place, the first formulation introduced above leads to a symmetrical representation of the diffusion process, and this is desirable since it leads to the introduction of the binary mutual diffusion coefficient. Furthermore, the usual form of the diffusion equation is obtained for a wider variety of diffusion phenomena when eq. (7) rather than eq. (11) is used in conjunction with the species continuity equation.

For example, it is well known that accurate analyses of diffusion phenomena in binary liquid mixtures over wide concentration ranges can be carried out by assuming that the partial specific volumes of the components are constant. For one-dimensional diffusion, the volume average velocity then obeys the following equation:

$$\frac{\partial v^\dagger}{\partial x} = 0. \quad (16)$$

Hence, if the diffusion process is taking place in a closed vessel where the velocity is zero on one of the boundaries, it follows that, everywhere in the diffusion field,

$$v^\dagger = 0. \quad (17)$$

Thus, the species continuity equation reduces to

$$\frac{\partial \rho_2}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial \rho_2}{\partial x} \right) \quad (18)$$

if eq. (7) is used, and to

$$\frac{\partial \rho_2}{\partial t} = \frac{\partial}{\partial x} \left[\bar{D}_{21} (1 - \rho_2 \bar{V}_{20}) \frac{\partial \rho_2}{\partial x} \right] \quad (19)$$

if eq. (11) is applied. The difference between eqs. (18) and (19) is clearly minor, and the application of these equations in the analysis of diffusive transport is effectively equivalent. Nevertheless, there is some merit in utilizing eq. (18), which is the classical form of the diffusion equation, whenever possible since this is the form of the species continuity equation which many investigators use to analyze diffusion experiments, often without bothering to check the validity of this approach. Hence, since it is eq. (18) which serves as the basis for analyzing diffusion phenomena

in liquid systems, we conclude that it is preferable to relate ζ_{12} to D [using eq. (8) or (9)] rather than to \bar{D}_{12} and \bar{D}_{21} [using eqs. (12) and (13)].

A more familiar form of eq. (9) can be derived by noting that eq. (2) can be written as

$$-\frac{\partial \mu_2^0}{\partial x} = f_{12}(u_2 - u_1) \quad (20)$$

where

$$f_{12} = C_{11}^0 \zeta_{12}. \quad (21)$$

Equation (20) better illustrates the role of the friction coefficient f_{12} , which relates the force on a molecule of polymer, $-\partial \mu_2^0 / \partial x$, to the velocity difference of the two components in the mixture. Thus, eq. (9) can be rewritten as

$$D = \frac{(1 - \bar{V}_{2\rho_2})}{N_A f_{12}} \rho_2 \left(\frac{\partial \mu_2}{\partial \rho_2} \right)_{T,p} \quad (22)$$

A third relationship has been utilized by Yamakawa¹⁴ and Tanford,¹⁵ who appear to define diffusion and friction coefficients using the following equations:

$$\rho_2 u_2 = -D^*_{21} \frac{\partial \rho_2}{\partial x} \quad (23)$$

$$-\frac{\partial \mu_2^0}{\partial x} = f^* u_2. \quad (24)$$

This formulation leads to the following form of the species continuity equation

$$\frac{\partial \rho_2}{\partial t} = \frac{\partial}{\partial x} \left(D^*_{21} \frac{\partial \rho_2}{\partial x} \right) \quad (25)$$

and also gives

$$D^*_{21} = \frac{\rho_2}{f^* N_A} \left(\frac{\partial \mu_2}{\partial \rho_2} \right)_{T,p}. \quad (26)$$

However, the exact meaning of D^*_{21} and f^* , when viewed in a general sense, is ambiguous because these material properties are introduced through improper constitutive equations. Equation (23), which is presumably a constitutive equation for the diffusion flux, contains u_2 , the velocity of component 2 with respect to a convenient reference frame. Similarly, the constitutive equation utilized for the frictional force term of eq. (24) also includes u_2 . Since these constitutive equations contain a quantity which is not frame indifferent, the coefficients in these relationships must also be dependent on how the experiment is conducted and who is observing it. Clearly, D^*_{21} and f^* thus lose the status of material properties since they depend on the velocity of the observer and are affected by velocity fields induced by external influences or by volume changes on mixing.

In a general sense, then, eqs. (23) and (24), and hence eq. (26), do not provide a valid basis for interpreting diffusive and frictional behavior. From a limited viewpoint, however, eq. (26) can be appropriately modified to yield a useful result. We suppose that the partial specific volumes are constant, so that there is no volume change on mixing, and that all velocities in a one-dimensional diffusion process are measured with respect to a frame which moves with the volume average velocity. For this particular set of circumstances, it follows that

$$f^* = \frac{f_{12}}{\rho_1 \bar{V}_{10}} \quad (27)$$

$$D^*_{21} = D \quad (28)$$

and, in addition, eq. (26) is equivalent to eq. (22). The formulation of Yamakawa and Tanford can thus be useful in this special case, but it should not be applied to more general diffusion processes. This case is commonly encountered in liquid systems because volume change on mixing effects are often small and because the velocity of the diffusion cell and the volume average velocity are often identical. However, caution must be exercised because small volume changes on mixing can produce velocities which have a substantial effect on the diffusion process.¹⁶

We conclude by deriving a series form of eq. (22) which describes diffusional and frictional be-

havior in dilute polymer solutions. For small concentrations of polymer, we can utilize the series expressions

$$\mu_1 = \mu_1^0 - RT V_1^* \rho_2 \left(\frac{1}{M_2} + A_2 \rho_2 + \dots \right) \quad (29)$$

$$\hat{V}_2 = \hat{V}_{20} [1 + a_1 \rho_2 + \dots] \quad (30)$$

$$\hat{V}_1 = \hat{V}_{10} [1 + b_1 \rho_2 + \dots] \quad (31)$$

$$f_{12} = (f_{12})_0 [1 + k_S \rho_2 + \dots] \quad (32)$$

where the coefficients of ρ_2 are functions of T, p and the nature of the polymer and solvent. Substitution of these equations and the well-known result

$$\left(\frac{\partial \mu_2}{\partial \rho_2} \right)_{T,p} = - \frac{M_2 \rho_1}{M_1 \rho_2} \left(\frac{\partial \mu_1}{\partial \rho_2} \right)_{T,p} \quad (33)$$

into eq. (22) gives the following equations for the concentration dependence of D :

$$D = D_0 (1 + k_D \rho_2 + \dots) \quad (34)$$

$$k_D = 2A_2 M_2 - k_S - b_1 - 2\hat{V}_{20} \quad (35)$$

$$D_0 = \frac{kT}{(f_{12})_0} \quad (36)$$

Hence, the concentration dependence of D is given in terms of quantities $[(f_{12})_0, A_2, k_S]$ which can be deduced from the statistical mechanics of dilute solutions and quantities (\hat{V}_{20}, b_1) which can be easily determined experimentally or can be adequately approximated. Note that k_S refers to the concentration dependence of a friction coefficient which is based on the relative velocities of the components. Equation (35) is a modification and generalization of previous results. Not only are unambiguous material properties (D and f_{12}) used, but the expression allows for volume change on mixing effects. Previous investigators have either ignored^{6,17} the contributions of \hat{V}_{20} and b_1 to k_D or have included \hat{V}_{20} incorrectly due to the formulation of improper constitutive equations.¹⁴ The effect of \hat{V}_{20} and b_1 on k_D will be important when k_D is less than 20 ml/g, as will be the case at low molecular weights for theta solutions¹ and usually in a low to intermediate molecular weight range for nontheta polymer-solvent mixtures.²

In the above development, we have considered two separate but related problems: examinations of various relationships between diffusion and friction coefficients and the derivation of a more general relationship for the quantity k_D which describes the concentration dependence of D . We conclude by citing instances where the effects described above must be considered in the analysis of diffusional phenomena in polymeric systems. First of all, since D_{12} and \bar{D}_{12} (or D_{21} and \bar{D}_{21}) are significantly different when solutions which are not dilute in one of the components are considered, care must be exercised in analyzing diffusional behavior for such solutions. Since eq. (18) is almost always used to analyze diffusion experiments in liquid systems, it must be remembered that it is D , not \bar{D}_{12} or \bar{D}_{21} , which is being determined from the experiment, and an additional calculation is needed to obtain \bar{D}_{12} or \bar{D}_{21} . Also, when diffusion data taken in the middle part of the concentration range are compared, it is necessary to be certain that equivalent diffusion coefficients are being compared.

Secondly, eq. (23) must, of course, never be used to analyze diffusion in flowing polymer solutions since the velocity field in such a system certainly cannot be attributed solely to the effects of concentration gradients. If, in such situations, eq. (23) is interpreted as giving the diffusion flux relative to an appropriate convective velocity, it should be noted that this velocity must, in general, be taken as the volume average velocity. Furthermore, in the experimental determination of diffusion coefficients, sizeable errors can result if eq. (23) is used as the basis of the data analysis even if velocity fields are not induced by external influences. Such errors are caused by the velocity field induced by the volume change on mixing, and these errors can be quite large even though the volume change on mixing itself is quite small. For example, it has been shown¹⁶ that utilization of eq. (23) in the analysis of free diffusion experiments leads to over 50% error in the determination of D even though the volume change on mixing was less than 4%. Free diffusion experiments are frequently used¹⁷ to determine diffusion coefficients in dilute and concentrated polymer solutions.

Finally, it should be noted that significant errors in k_D can result if the modified expression

derived above is not utilized. Even when volume change on mixing effects are small so that b_1 can be set equal to zero, the term $-2\hat{V}_{20}$ is of the order of 2 ml/g and hence will constitute at least a 10% contribution to k_D whenever the absolute value of k_D is less than 20 ml/g. The data of King et al.¹ show that the absolute value of k_D is less than 20 ml/g for molecular weights less than 200,000 for a theta solution (the cyclohexane-polystyrene system). Furthermore, from the data of King et al.,² it is evident that, for diffusion in a mixture of polymer and a mediocre solvent (the methyl ethyl ketone-polystyrene system), the absolute value of k_D is 20 ml/g or less in the molecular weight interval of approximately 50,000–500,000. The error in the prediction of k_D in this wide molecular weight range will be significantly higher than the minimum value of 10%, since k_D changes sign in this molecular weight interval. Hence, appreciable errors can result in the prediction of the *change* of D with concentration if the $-2\hat{V}_{20}$ term is ignored in the calculation of k_D . It is thus fair to conclude that there exist a number of instances where the effects described in this paper can be quite significant in the analysis of diffusional behavior in polymeric systems.

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Nomenclature

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|----------------|--|
| a_1 | coefficient in series for \hat{V}_2 |
| A_2 | second virial coefficient |
| b_1 | coefficient in series for \hat{V}_1 |
| C_I^0 | concentration of species I in units of molecules per unit volume |
| D | binary mutual diffusion coefficient |
| D_0 | value of D in the limit of zero polymer concentration |
| D_{AB} | diffusion coefficient defined by eq. (7) |
| \bar{D}_{AB} | diffusion coefficient defined by eq. (11) |
| D_{21}^* | diffusion coefficient defined by eq. (23) |
| f_{12} | friction coefficient defined by eq. (20) |
| $(f_{12})_0$ | value of f_{12} in the limit of zero polymer concentration |
| f^* | friction coefficient defined by eq. (24) |
| J_A^B | mass diffusion flux of component A relative to the velocity of component B |
| k | Boltzmann's constant |
| k_D | coefficient in series for D |
| k_S | coefficient in series for f_{12} |
| M_A | molecular weight of component A |
| N_A | Avogadro's number |
| p | pressure |
| R | gas constant per mole |
| t | time |
| T | temperature |
| u_A | velocity of component A with respect to a convenient reference frame |
| v^\dagger | volume average velocity with respect to a convenient reference frame |
| \hat{V}_A | partial specific volume of component A |
| \hat{V}_{A0} | value of \hat{V}_A in the limit of zero polymer concentration |
| V_1^* | molar volume of solvent |
| x | distance variable in the direction of diffusion |
| ζ_{12} | friction coefficient defined by eq. (1) |
| μ_I | chemical potential of component I per mole |
| μ_1 | chemical potential of pure solvent per mole |
| μ_1^0 | chemical potential of component I per molecule |
| ρ | mass density of mixture |
| ρ_I | mass density of component I |
| ω_I | mass fraction of component I |
| <i>Indices</i> | |
| 1 | refers to solvent |
| 2 | refers to polymer |

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