# Excluded Volume Effect on the Diffusion-Influenced Bimolecular Reactions

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By applying the reduced distribution function approach to the diffusion-influenced bimolecular reaction, we evaluate the effect of excluded volume between nonreacting like molecules on the transient kinetics. It is found that concentrations of reactant molecules decay more rapidly with the excluded volume taken into account than without it. Comparison with previous works dealing with the excluded volume effect shows a qualitative agreement, but it appears that previous works underestimate the excluded volume effect.

## I. Introduction

Since the pioneering work of von Smoluchowski[1] many theoretical approaches were proposed to treat the kinetics of diffusion-influenced bimolecular reactions in solution.[2−18] Of the various approaches, those based on a hierarchy of evolution equations for the reduced distribution functions of reactant molecules are particularly attractive, since they provide a systematic theoretical framework for dealing with the diffusion-influenced reaction involved in a complicated reaction mechanism.[8−18]

It was Waite[8] and Monchick *et al.*[9] who initiated this line of theories. Wilemski and Fixman[10] improved the formalism significantly by introducing a sink function in the coupled kinetic equations for the reduced distribution functions rather than employing a boundary condition to model the chemical reaction event. Lee and Karplus reformulated this reduced distribution function (RDF) approach to deal with diffusion-influenced reactions of a more complicated type, e.g., reactions involving reversibility,[11] a gating mode, and orientation-dependent reactivity.[12]

Most RDF theories of diffusion-influenced reactions invoke a simplified version of the superposition approximation which approximates a three-particle RDF as the product of two-particle RDF's for unlike particles undergoing reaction and neglects the correlation between nonreacting like particles. This approximation (that will be called the "dynamic superposition approximation" hereafter) truncates the hierarchy of evolution equations for many-particle RDF's and gives closed kinetic equations for two-particle RDF's, which can be easily solved by numerical analysis and in certain limiting cases yield analytical solutions.

Kalnin[13] and Kuzovkov and Kotomin[14−17] initiated the studies on the effects of the like-particle correlation within the framework of RDF theory. In particular, Kuzovkov and Kotomin found that like particles tend to cluster at long times,[14−18] since a particle located in an environment where nonreacting like particles are more densely populated than reacting partners would have a better chance of surviving. This kind of like-particle correlation effect can be important in the long-time limit. However, there is another kind of like-particle correlation which cannot be negligible even at short times. The dynamic superposition approximation basically assumes that like particles see each other as a point particle, so that the pair correlation function between them is set equal to unity at all separations. But the strong repulsive interaction between the particles does not allow them to overlap, and thus the pair correlation function should vanish when the separation becomes less than the molecular diameter. This kind of like-particle correlation effect, which may be called the *excluded volume effect*, will be important when the particle concentration is high. It may change the reaction rate up to quite a long time and thus the time profiles of reactant concentrations.

Blumen and Manz considered the excluded volume effect on reactions occurring in a solid solution where all reactant molecules are static and the reaction occurs via a multipolar interaction[19] or an exchange mechanism.[20] They used a lattice model and generalized the results to a continuum limit. However, they did not include the molecular diffusion process, which is definitely important for reactions occurring in the liquid solution. More recently, Fayer *et al.* also remarked about the importance of the excluded volume effect in the long-range electron transfer reaction in a solid[21,22] and in a liquid solution.[23,24] They extended the Blumen−Manz theory by including a molecular diffusion process[23] and also devised a new theory using a rather *ad hoc* ansatz, *the separable probability distribution approximation*,[22] as they called it. The theories both of Blumen and Manz and of Fayer *et al.* predicted that when the excluded volume is included, the survival probability falls more rapidly than in the absence of the excluded volume. Fayer *et al.* compared the theoretical results of Blumen and Manz and their own with the Monte Carlo simulation result obtained for the solid solution case, but the agreement was not satisfactory.[22]

Kalnin[13] considered the excluded volume effect by using the RDF approach. However, his analysis was limited to the long-time regime and to the case of small concentration, although the excluded volume effect is most significant in the short-time regime, where reactant concentration can be quite high.

In this paper we study the excluded volume effect in the transient kinetics. The paper is organized as follows. In section II, a general theoretical framework for describing the excluded volume effect is reviewed. In section III, specific reaction models are adopted in the general kinetic equations described in section II, and the resulting equations are solved numerically to determine the time dependence of the reactant concentration. The results are compared with those of Blumen−Manz theory and Fayer *et al.*'s theory for long-range reactions. Judging from the comparison with the simulation result of Swallen *et al.*,[22] we see that the previous works underestimate the excluded volume effect. In section IV, we give some concluding remarks.

## II. RDF Formalism

We consider a simple irreversible reaction between **A** and **B** molecules that gives a chemically inert product,

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$$\mathbf{A} + \mathbf{B} \rightarrow \mathbf{P} \tag{2.1}$$

We assume that the initial distribution of the reactant molecules is random and macroscopically homogeneous in space.

The RDF formalism[8−18] for diffusion-influenced bimolecular reactions gives the usual rate equation for the time dependence of reactant concentration along with a microscopic expression for the rate coefficient:

$$\frac{\mathrm{d}[\mathbf{A}]}{\mathrm{d}t} = -k_{\mathrm{b}}(t)[\mathbf{A}][\mathbf{B}] \tag{2.2}$$

$$k_{\mathrm{b}}(t) = \int \mathrm{d}r\, 4\pi r^2 S_{\mathbf{AB}}(r)\, \rho_{\mathbf{AB}}(r,t) \tag{2.3}$$

Here [**X**] (**X** = **A** or **B**) denotes the bulk number density of the **X** molecules at time $t$. $\rho_{\mathbf{AB}}(r,t)$ is the nonequilibrium pair correlation function between **A** and **B** molecules; $[\mathbf{B}]\rho_{\mathbf{AB}}(r,t)4\pi r^2\,\mathrm{d}r$ gives the average number of **B** molecules located at the distance between $r$ and $r + \mathrm{d}r$ away from an **A** molecule at the coordinate origin at time $t$. $S_{\mathbf{AB}}(r)$ is the sink function which represents the rate of reaction when the **A** and **B** molecules are separated by $r$.

The evolution equation for $\rho_{\mathbf{AB}}(r,t)$ is given by[14−18]

$$\begin{aligned}\frac{\partial}{\partial t}\rho_{\mathbf{AB}}(r,t) = {} & L_{\mathbf{AB}}(r)\, \rho_{\mathbf{AB}}(r,t) - S_{\mathbf{AB}}(r)\, \rho_{\mathbf{AB}}(r,t) + \\ & [\mathbf{A}]\{\textstyle\int \mathrm{d}\mathbf{r}'_{\mathbf{A}}\, S_{\mathbf{AB}}(r_{\mathbf{A'B}})\, \rho_{\mathbf{AB}}(r_{\mathbf{A'B}},t)[1 - \rho_{\mathbf{AA}}(r_{\mathbf{AA'}})]\}\rho_{\mathbf{AB}}(r,t) + \\ & [\mathbf{B}]\{\textstyle\int \mathrm{d}\mathbf{r}'_{\mathbf{B}}\, S_{\mathbf{AB}}(r_{\mathbf{AB'}})\, \rho_{\mathbf{AB}}(r_{\mathbf{AB'}},t)[1 - \rho_{\mathbf{BB}}(r_{\mathbf{BB'}})]\}\rho_{\mathbf{AB}}(r,t)\end{aligned} \tag{2.4}$$

where $L_{\mathbf{AB}}(r)$ is the nonreactive thermal evolution operator for the pair correlation function and $r = |\mathbf{r}_{\mathbf{A}} - \mathbf{r}_{\mathbf{B}}|$ with $\mathbf{r}_{\mathbf{A}}$ and $\mathbf{r}_{\mathbf{B}}$ denoting the positions of the **A** and **B** molecules of the primary reacting pair. $\mathbf{r}'_{\mathbf{A}}$ and $\mathbf{r}'_{\mathbf{B}}$ denote the positions of the **A** and **B** molecules which competitively react with the primary pair of reactant molecules, and $r_{\mathbf{A'B}} = |\mathbf{r}'_{\mathbf{A}} - \mathbf{r}_{\mathbf{B}}|$, $r_{\mathbf{AB'}} = |\mathbf{r}_{\mathbf{A}} - \mathbf{r}'_{\mathbf{B}}|$, and so on.

Recently Molski and Keizer[25] derived an evolution equation for the reactant pair correlation function in the reversible reaction case, $\mathbf{A} + \mathbf{B} \rightleftarrows \mathbf{C}$, using their statistical nonequilibrium thermodynamics formalism. In the irreversible reaction limit their evolution equation also carries terms that are similar to the third and fourth terms in eq 2.4 and which arise from the pair correlation between like particles. However, when they actually calculate the reaction rate coefficient, they neglected those terms by taking the limit of low density.

To solve eq 2.4, we need to know the pair correlation functions between like particles, $\rho_{\mathbf{AA}}$ and $\rho_{\mathbf{BB}}$. Coupled kinetic equations for $\rho_{\mathbf{AA}}$ and $\rho_{\mathbf{BB}}$ can be obtained in a straightforward manner (see refs 14−18). However, we expect that the like-particle correlation effect on the transient kinetics is primarily due to the excluded volume, and thus we approximate $\rho_{\mathbf{AA}}$ and $\rho_{\mathbf{BB}}$ as the equilibrium pair correlation functions:

$$\begin{aligned}\rho_{\mathbf{XX}}(|\mathbf{r}'_{\mathbf{X}} - \mathbf{r}_{\mathbf{X}}|,t) \approx g_{\mathbf{XX}}(|\mathbf{r}'_{\mathbf{X}} - \mathbf{r}_{\mathbf{X}}|) = {} & \\ \exp[-\beta U_{\mathbf{XX}}(|\mathbf{r}'_{\mathbf{X}} - \mathbf{r}_{\mathbf{X}}|)] & \end{aligned} \tag{2.5}$$

where $U_{\mathbf{XX}}$ (**X** = **A** or **B**) denotes the potential of mean force between two **X** molecules and $\beta = 1/k_{\mathrm{B}}T$ with the Boltzmann constant $k_{\mathrm{B}}$ and the absolute temperature $T$. Although the approximations given by eq 2.5 become inaccurate at long times by neglecting the reaction-induced clustering of like molecules[14−18] as mentioned in the Introduction, it is believed that this subtle like-particle correlation may be developed only after the concentrations of reactant molecules drop below the experimentally detectable limit. Anyway, our primary concern in this paper is to consider only the excluded volume effect, as with Blumen and Manz[19,20] and Fayer *et al.*,[21−24] and the excluded volume effect is taken into account through the third and fourth terms on the right hand side of eq 2.4.

We approximate $L_{\mathbf{AB}}(r)$ as the nonreactive Smoluchowski operator, which has the following form in the radial coordinate space,

$$L_{\mathbf{AB}}(r) = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \mathrm{d}(r)\mathrm{e}^{-\beta U_{\mathbf{AB}}(r)}\frac{\partial}{\partial r}\mathrm{e}^{\beta U_{\mathbf{AB}}(r)}\right) \tag{2.6}$$

where d($r$) denotes the relative diffusion coefficient, which depends on $r$ if the hydrodynamic interaction between **A** and **B** molecules is included, and $U_{\mathbf{AB}}(r)$ is the potential of mean force between **A** and **B**. In writing eq 2.6, the dependence of the diffusion coefficient on the solute concentration has been neglected.[4]

When $U_{\mathbf{AB}}(r)$ has a steep repulsive potential wall at $r = \sigma_{\mathbf{AB}}$, we may impose the reflecting boundary condition on eq 2.4 which requires the inward flux at $r = \sigma_{\mathbf{AB}}$ to vanish:

$$\left[\mathrm{d}(r)\mathrm{e}^{-\beta U_{\mathbf{AB}}(r)}\left(\frac{\partial}{\partial r}\mathrm{e}^{\beta U_{\mathbf{AB}}(r)}\rho_{\mathbf{AB}}(r,t)\right)\right]_{\mathrm{r}=\sigma_{\mathbf{AB}}} = 0 \tag{2.7}$$

On the other hand, at infinite separation the pair distribution becomes uncorrelated:

$$\rho_{\mathbf{AB}}(r \rightarrow \infty, t) = 1 \tag{2.8}$$

The initial condition for $\rho_{\mathbf{AB}}(r,t)$ is assumed to be that of equilibrium:

$$\rho_{\mathrm{AB}}(r,0) = g_{\mathbf{AB}}(r) = \exp[-\beta U_{\mathbf{AB}}(r)] \tag{2.9}$$

As did Blumen and Manz[19,20] and Fayer *et al.*,[21−24] we assume for simplicity that equilibrium pair correlations between all solute molecules are set up by the hard-sphere potentials between them, which inhibit the molecules from penetrating through each other; that is,

$$g_{\mathbf{XY}}(r) = \begin{cases} 0 & \text{for } r < \sigma_{\mathbf{XY}} \\ 1 & \text{for } r \geq \sigma_{\mathbf{XY}} \end{cases} \tag{2.10}$$

where $\sigma_{\mathbf{XY}}$ (**X**, **Y** = **A** or **B**) are the contact diameters between **X** and **Y** molecules and $\sigma_{\mathbf{AB}} = (\sigma_{\mathbf{AA}} + \sigma_{\mathbf{BB}})/2$.

With the approximations in eq 2.10, eq 2.4 reduces to

$$\begin{aligned}\frac{\partial}{\partial t}\rho_{\mathbf{AB}}(r,t) = {} & L_{\mathbf{AB}}(r)\, \rho_{\mathbf{AB}}(r,t) - S_{\mathbf{AB}}(r)\, \rho_{\mathbf{AB}}(r,t) + \\ & [\mathbf{A}]\{\textstyle\int \mathrm{d}\mathbf{r}'\, 4\pi r'^2 S_{\mathbf{AB}}(r')\, \rho_{\mathbf{AB}}(r',t)\, \varphi_{\mathbf{A}}(r,r')\}\rho_{\mathbf{AB}}(r,t) + \\ & [\mathbf{B}]\{\textstyle\int \mathrm{d}\mathbf{r}'\, 4\pi r'^2 S_{\mathbf{AB}}(r')\, \rho_{\mathbf{AB}}(r',t)\, \varphi_{\mathbf{B}}(r,r')\}\rho_{\mathbf{AB}}(r,t)\end{aligned} \tag{2.11}$$

where $\varphi_{\mathbf{X}}(r,r')$ (**X** = **A** or **B**) is defined as

$$\varphi_{\mathbf{X}}(r,r') = \begin{cases} 0 & \text{for } |r - r'| \geq \sigma_{\mathbf{XX}} \\ \dfrac{{\sigma_{\mathrm{XX}}}^2 - (r - r')^2}{4rr'} & \text{for } |r - r'| < \sigma_{\mathbf{XX}} \end{cases} \tag{2.12}$$

In eq 2.11, the excluded volume effect is considered through the functions $\varphi_{\mathbf{X}}(r,r')$, which gives a positive contribution to the integral values in the third and fourth terms locally in the range $|r - r'| < \sigma_{\mathbf{XX}}$, so that $\rho_{\mathbf{AB}}(r,t)$ would have a greater value than that in the case without the excluded volume over the whole range of space and time. We may give the following physical interpretation for the excluded volume effect. Suppose that there is a **B** molecule at the origin of the coordinate system. Then $\mathbf{r}$ denotes the position vector of an **A** molecule that is to react with the **B** molecule at the origin, while $\mathbf{r}'$ denotes that of another **A** molecule, which competes with the former **A** molecule to react with the **B** molecule. The short-range repulsive interaction between the **A**'s does not allow the later **A** molecule to come into the region where $|\mathbf{r} - \mathbf{r}'| \approx \sigma_{\mathbf{AA}}$, so that the competition reaction is less salient than that in the case without the excluded volume. The nonequilibrium pair correlation function, $\rho_{\mathbf{AB}}(r,t)$, depletes from the equilibrium value more slowly, and so does the rate coefficient, $k_b(t)$, as defined by eq 2.3. Hence the concentration decays more rapidly according to eq 2.2 than in the case without the excluded volume.

The rate equation in eq 2.2, the rate coefficient expression in eq 2.3, and the evolution equation for the pair correlation function in eq 2.11 together with the associated boundary conditions in eqs 2.7 and 2.8 constitute the working equations to evaluate the excluded volume effect in diffusion-influenced bimolecular reactions. When the potential of mean force takes the simple form of the hard-sphere potential as assumed by eq 2.10 and there is no hydrodynamic interaction, the Smoluchowski operator takes the form

$$L_{\mathbf{AB}}(r) = \frac{D}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) \tag{2.13}$$

where $D$ is the relative diffusion constant for a pair of **A** and **B** molecules.

## III. Numerical Results

We consider two specific reaction models that have often been considered in the theories dealing with diffusion-influenced reactions.[6] Hereafter we omit the subscript **AB** in $\rho_{\mathbf{AB}}$, $S_{\mathbf{AB}}$, and $\sigma_{\mathbf{AB}}$ to simplify the notations.

**A. Contact Reaction.** For many types of diffusion-influenced bimolecular reactions in solution, such as radical recombination,[26,27] fluorescence quenching,[28−31] ligand−protein binding,[32] and so on, it has been assumed that the reaction occurs when two hard-sphere reactants encounter at a certain distance of $r = \sigma$. In this model, the sink function takes the form of a $\delta$-function,

$$S(r) \equiv S_C(r) = k_C\frac{\delta(r-\sigma)}{4\pi\sigma^2} \tag{3.1}$$

where $k_C$ represents the intrinsic reaction rate coefficient that may be observed when the pair correlation maintains the value of unity at $r = \sigma$. The rate coefficient $k_b(t)$ in eq 2.3 is then given by

$$k_b(t) = k_C\rho(\sigma,t) \tag{3.2}$$

and the integrals in eq 2.11 can be easily evaluated to give

$$\frac{\partial}{\partial t}\rho(r,t) = \frac{D}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\rho(r,t)\right) - k_C\frac{\delta(r-\sigma)}{4\pi\sigma^2}\rho(r,t) + k_b(t)\{[\mathbf{A}]\varphi_{\mathbf{A}}(r,\sigma) + [\mathbf{B}]\varphi_{\mathbf{B}}(r,\sigma)\}\rho(r,t) \tag{3.3}$$

The$\delta$-function sink term on the right hand side of eq 3.3 is cumbersome when the equation is solved numerically. But it can be eliminated by replacing the reflecting boundary condition, eq 2.7, with the radiative boundary condition,[10,27,30]

$$4\pi\sigma^2 D\left(\frac{\partial}{\partial r}\rho(r,t)\right)_{r=\sigma} = k_C\rho(\sigma,t) \tag{3.4}$$

The excluded volume effect would be more pronounced in the pseudo-first-order case, where one of the reactant species, say **B**, is very large excess of the other, since the reactive competition among **B** molecules becomes salient. In this case, [**B**] remains essentially at a constant value $C_{\mathbf{B}}$ and $C_{\mathbf{B}} \gg [\mathbf{A}]$ so that the evolution equation for $\rho(r,t)$ is decoupled from the rate equation in eq 2.2:

$$\frac{\partial}{\partial t}\rho(r,t) = \frac{D}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\rho(r,t)\right) + C_{\mathbf{B}}k_b(t)\,\varphi_{\mathbf{B}}(r,\sigma)\,\rho(r,t) \tag{3.5}$$

In addition, the rate equation can be integrated to give the survival probability as

$$R(t) \equiv [\mathbf{A}]_t/[\mathbf{A}]_0 = \exp[-C_{\mathbf{B}}\int_0^t d\tau\, k_b(\tau)] \tag{3.6}$$

Equation 3.5 is the same equation as Kalnin[13] used in his analysis of the excluded volume effect on the steady-state reaction rate coefficient. In the illustrative calculation described below, we will restrict ourselves to the pseudo-first-order case.

The time profile of the survival probability can be calculated by solving the coupled equations in eqs 3.2 and 3.5. We will sketch briefly the overall numerical scheme used. We discretize the continuous time domain with a sufficiently small time step $\Delta t$ and denote the time at the $n$-th step by $t_n = n\Delta t$. Since the equation for $\rho(r,t)$, eq 3.5, involves the rate coefficient $k_b(t)$, which can be determined only if we know $\rho(r,t)$ as in eq 3.2, we should solve it self-consistently at each step. To calculate $\rho(r,t_{n+1})$, we should know the value of $k_b(t_{n+1})$. Taking $k_b(t_{n+1})$ as a trial value for $k_b(t_{n+1})$, we evaluate $\rho(r,t_{n+1})$ by using the finite difference Crank−Nicholson scheme,[33] which gives a better estimate for $k_b(t_{n+1})$ from eq 3.2. In this way, we iterate the calculation of $\rho(r,t_{n+1})$ using the successively better estimate of $k_b(t_{n+1})$ until the relative change in the value of $k_b(t_{n+1})$ becomes less than a tolerance parameter, the value of which is taken to be $1.0 \times 10^{-7}$ in all calculations.

There remains another technical point to discuss. In integrating the diffusion equation for $\rho(r,t)$, the radial coordinate is partitioned into a discrete grid in the finite difference scheme, so that the outer boundary extended to infinity has to be truncated at a finite separation. To reduce the numerical error due to the truncation, one has to keep as many grid points as possible to ensure sufficient spatial extension of the integration range, but this uses much computing time. To avoid this difficulty, we mapped the radial coordinate extending from $\sigma$ to infinity into a new coordinate in the range (0, 1) by using the following nonlinear transformation:[27,30]

$$x = \exp\left[-\alpha\left(\frac{r}{\sigma} - 1\right)\right] \tag{3.7}$$

where $\alpha$ is a positive dimensionless parameter that may be optimized. Since the transformation is nonlinear, a uniformly spaced grid partitioning the $x$-space corresponds to a nonuniform grid in the $r$-space. In fact, the $r$-space grid becomes more finely spaced near $r = \sigma$, and this gives an additional advantage in numerical implementation, since the pair correlation function varies significantly only around the inner boundary region.

We carried out all calculations using dimensionless quantities. There are three independent molecular parameters we can change, which are the reduced diameter of the **B** molecule, $r_{\mathbf{B}} = \sigma_{\mathbf{BB}}/\sigma$, the reduced number density of **B** molecules, $\Phi_{\mathbf{B}} = \sigma^3 C_{\mathbf{B}}$, and the ratio of the intrinsic reaction rate to the diffusion-controlled rate, $\kappa = k_C/4\pi\sigma D$. The time variable is scaled by $\tau_D = \sigma^2/D$.

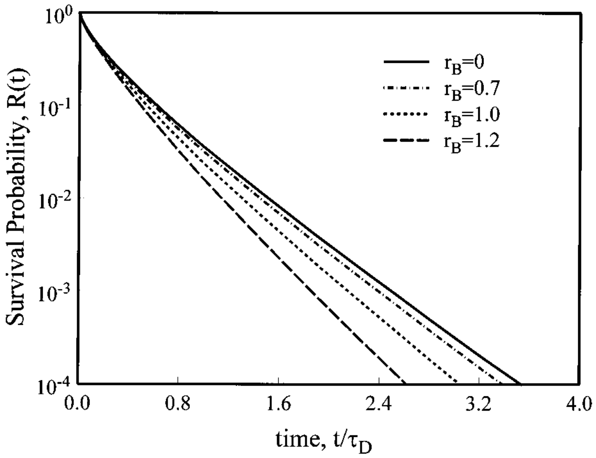

**Figure 1.** Excluded volume effect on the survival probability. Values of the parameters used in the calculation are $\kappa = k_c/4\pi\sigma D = 10$ and $\Phi_{\mathbf{B}} = \sigma^3 C_{\mathbf{B}} = 0.15$. The value of $r_{\mathbf{B}}(=\sigma_{\mathbf{BB}}/\sigma)$ is varied as shown. As $\sigma_{\mathbf{BB}}$ increases, the excluded volume effect becomes more pronounced.

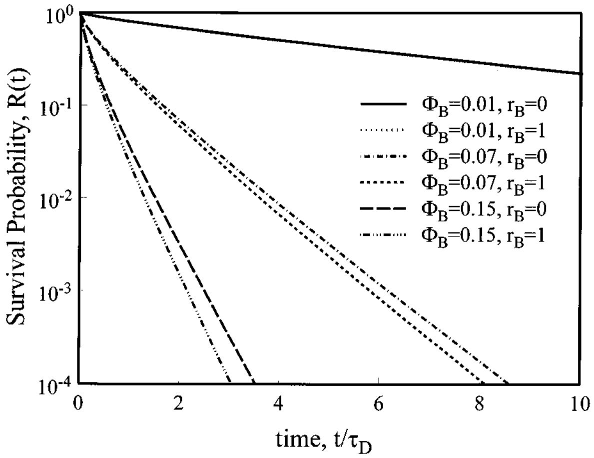

**Figure 2.** Dependence of the excluded volume effect on the concentration of **B** molecules, $\Phi_{\mathbf{B}} = \sigma^3 C_{\mathbf{B}}$. The intrinsic reaction rate parameter $\kappa$ is set equal to 10.

First, we have checked the accuracy of our numerical analysis by comparing the survival probability, calculated numerically from eqs 3.2, 3.5, and 3.6 for the zero excluded volume case, with the analytic survival probability expression[26,32]

$$R(t) = \exp\left[-4\pi\Phi_{\mathbf{B}}\left(\frac{\kappa}{1+\kappa}\right)\left\{\frac{Dt}{\sigma^2} + \frac{\kappa}{1+\kappa}\left(2\sqrt{\frac{Dt}{\sigma^2\pi}} - \frac{1-\Omega((1+\kappa)\sqrt{Dt}/\sigma)}{1+\kappa}\right)\right\}\right] \tag{3.8}$$

where $\Omega(x) = e^{x^2}\,\mathrm{erfc}(x)$. The agreement has been perfect.

Figure 1 displays the excluded volume effect predicted by the RDF theory. As expected, the survival probability decays more rapidly with the increase of the size of **B** molecules. It seems that inclusion of the excluded volume effect is essential in the experimental interpretation of the concentration decay curve, unless the **B** molecules are much smaller than **A** molecules (i.e. $\sigma_{\mathbf{BB}} \ll \sigma$). The importance of the excluded volume effect will be pronounced in reactions involving macromolecules.

In Figures 2 and 3, we compare the decay curve of the survival probability with the excluded volume effect included ($r_{\mathbf{B}} = 1$) and that without the excluded volume effect ($r_{\mathbf{B}} = 0$) for several sets of parameters $\Phi_{\mathbf{B}}$ and $\kappa$. Figure 2 shows that the excluded volume effect is more pronounced for a high concentration of **B** molecules ($\Phi_{\mathbf{B}} = \sigma^3 C_{\mathbf{B}}$). This observation is also consistent with the physical interpretation of the excluded volume effect described in section II; the competition among **B** molecules for the **A** molecule will be more severe when their concentration is high. Figure 3 shows that the excluded volume effect is more pronounced as the intrinsic reaction rate becomes much larger than the diffusion-controlled reaction rate.

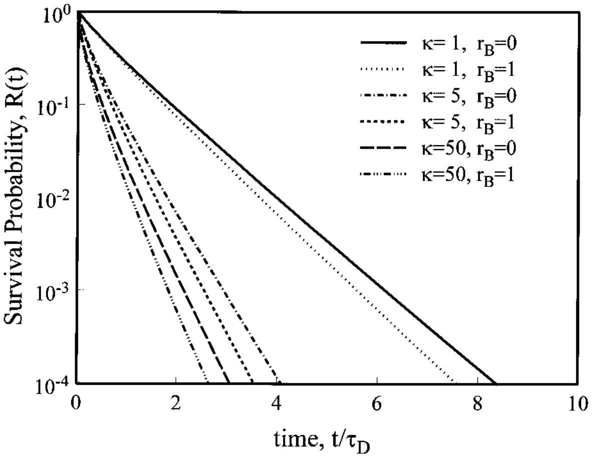

**Figure 3.** Dependence of the excluded volume effect on the intrinsic reaction rate parameter, $\kappa = k_C/4\pi\sigma D$. The **B** molecule concentration parameter $\Phi_{\mathbf{B}}$ is set equal to 0.15.

**B. Long-Range Reaction.** Some types of reactions in solution have been known to occur over a range of spatial separations between the reactants rather than at the specific contact distance.[6] As a long-range reaction model we will consider the excited-state electron-transfer reaction, which was considered by Fayer *et al.*[21−24] in regard to the excluded volume effect:

$$\mathbf{A}^* + \mathbf{B} \xrightarrow{k_b(t)} \mathbf{A}^+ \cdots \mathbf{B}^- \tag{3.9}$$

**A*** molecules are prepared by a very short light pulse in the reaction vessel at $t = 0$. Then they decay with a finite lifetime, $\tau_S$, via radiative or nonradiative channels, or transfer the excitation energy to **B** molecules through electron transfer with the forward rate coefficient $k_b(t)$. The sink function for the forward electron transfer is represented by[6,21−24]

$$S(r) \equiv S_L(r) = k_{ET}\exp\left(-\frac{r-\sigma}{a}\right) \tag{3.10}$$

where $a$ represents the range within which the electron transfer reaction occurs significantly and $k_{ET}$ is the electron transfer rate when an **A*** and a **B** molecule are separated by the contact distance $\sigma$.

Although we did not include the unimolecular decay process in the formalism described in section II, it can be incorporated into the formalism in a straightforward way, as was done in the fluorescence quenching kinetics.[28−31] Again, we concentrate only on the pseudo-first-order case, which represents the most experimental situations when the excitation laser pulse intensity is not too strong. Then the rate equation, including the effect of the unimolecular decay of **A***, becomes

$$\frac{d}{dt}[\mathbf{A}^*] = -\left(\frac{1}{\tau_S} + C_{\mathbf{B}}k_b(t)\right)[\mathbf{A}^*] \tag{3.11}$$

where the rate coefficient is given by

$$k_b(t) = \int_\sigma^\infty dr\, 4\pi r^2 S_L(r)\,\rho(r,t) \tag{3.12}$$

The evolution equation for the nonequilibrium pair correlation function can be shown to be

$$\frac{\partial}{\partial t}\rho(r,t) = \frac{D}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)\rho(r,t) - S_L(r)\,\rho(r,t) + C_{\mathbf{B}}\{\int_\sigma^\infty dr'\,4\pi r'^2 S_L(r')\,\rho(r',t)\,\varphi_{\mathbf{B}}(r,r')\}\rho(r,t) \quad (3.13)$$

where $\varphi_{\mathbf{B}}(r,r')$ is that defined in eq 2.12. We impose the same boundary conditions as given in eqs 2.7 and 2.8.

Unlike the case of contact reaction, we should solve the full partial integro-differential equation, eq 3.13, to obtain $\rho(r,t)$, and integrate the numerically evaluated pair correlation function, multiplied by the sink function, over the radial coordinate to obtain the time-dependent rate coefficient as in eq 3.12. We then integrate eq 3.11 to obtain the decay function for [**A***],

$$R(t)\exp(t/\tau_S) = \exp[-C_{\mathbf{B}}\int_0^t d\tau\, k_b(\tau)] = \exp[-4\pi C_{\mathbf{B}}\int_0^t d\tau \int_\sigma^\infty dr\, r^2 S_L(r)\,\rho(r,\tau)] \quad (3.14)$$

There have been a few approximate theories that consider the excluded volume effect in the long-range reactions. Blumen and Manz[19,20] used the lattice model to treat the long-range energy transfer reaction in a solid solution. By having the immobile acceptor molecules (**B** molecules in our notation) occupy the lattice sites separated by the acceptor diameter, they included the acceptor excluded volume effect. They used a probabilistic argument to obtain the ensemble averaged decay function, which corresponds to the survival probability in our theory. Then they applied the continuum approximation to get the survival probability in a closed form,[19,20]

$$R_{\mathbf{B}M}(t)\exp(t/\tau_S) = \exp\left[\frac{4\pi C_{\mathbf{B}}}{p}\int_\sigma^\infty dr\, r^2 \ln(1 - p + p\exp(-S_L(r)t))\right] \quad (3.15)$$

where $p = \sigma_{\mathbf{BB}}^3 C_{\mathbf{B}}$.

More recently, Fayer *et al.*[21−24] investigated the reaction model represented by eq 3.9. They considered the case where a single excited donor molecule, located at the origin, is surrounded by many acceptor molecules. If the acceptor molecules are point particles, the many-particle radial probability density function for the $N$ acceptor molecules can be separated into a product of $N$ individual two-particle radial probability density functions. Swallen *et al.*[22] argued that this approximation could be made even in the presence of acceptor−acceptor excluded volume if one multiplies each of the two-particle radial probability density functions by an equilibrium radial distribution function $g(r)$ between reactant molecules. Following this "separable probability distribution approximation", they suggested that the expression for the survival probability of the excited donor, derived by Inokuti and Hirayama[34] for the case with acceptor molecules devoid of the excluded volume, may be adapted into the form

$$R_{SW}(t)\exp(t/\tau_S) = \exp[-4\pi C_{\mathbf{B}}\int_\sigma^\infty dr\, r^2(1 - \exp(-S_L(r)t))g(r)] \quad (3.16)$$

When the reactant molecules are point particles, $g(r)$ equals to unity at all values of $r$. For molecules with finite sizes, the analytical solution of the Percus−Yevick equation for the hard-sphere potential was used for $g(r)$.[35,36]

The above two theories can be applied to the electron transfer reaction occurring in a solid solution where all the solute molecules are immobile. However, the formulations can be generalized to include the molecular diffusion. For example, Dorfman and Fayer[23] generalized the theory of Blumen and Manz[19,20] to obtain

$$R_{DF}(t)\exp(t/\tau_S) = \exp\left[\frac{4\pi C_{\mathbf{B}}}{p}\int_\sigma^\infty dr\, r^2 \ln(1 - p + p\rho_o(r,t))\right] \quad (3.17)$$

Although generalization of eq 3.16 has not been made explicitly by Swallen *et al.*,[22,24] the following expression can be readily suggested:

$$R_{SW}(t)\exp(t/\tau_S) = \exp[-4\pi C_{\mathbf{B}}\int_\sigma^\infty dr\, r^2(1 - \rho_o(r,t))g(r)] \quad (3.18)$$

In eqs 3.17 and 3.18, $\rho_o(r,t)$ is the pair correlation function *in the absence of the excluded volume effect*; that is, it is the solution of

$$\frac{\partial}{\partial t}\rho_o(r,t) = \frac{D}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)\rho_o(r,t) - S_L(r)\,\rho_o(r,t) \quad (3.19)$$

with the same initial and boundary conditions as those of $\rho(r,t)$. Note that eqs 3.17 and 3.18 reduce to eqs 3.15 and 3.16, respectively, when the relative diffusion constant $D$ goes to zero in eq 3.19.

Numerical methods used in the calculation of the survival probability in the long-range reaction case are similar to those in the contact reaction case except that in solving the pair correlation function evolution equation, eq 3.13, we should use the reflecting boundary condition in eq 2.7 instead of the radiative boundary condition in eq 3.4 and should include the unimolecular decay term in the rate equation as in eq 3.11. At a given time step we solve the partial integro-differential equation, eq 3.13, by generalizing the finite difference Crank−Nicholson scheme to manipulate the integral term on the right hand side. $\rho(r,t)$ so obtained is then used to calculate the bimolecular rate coefficient from eq 3.12 and in turn the time profile of the concentration decay of **A*** molecules according to eq 3.11.

In Figure 4, the numerical results of the RDF theory are compared with those of Blumen−Manz and Fayer *et al.* In Figure 4a the solute molecules are immobile, while in Figure 4b they are mobile with the relative diffusion constant of $D = 1.0 \times 10^{-6}$ cm$^2$/s. We set the size of **B** molecule equal to that of the **A** molecule; that is, $\sigma_{\mathbf{BB}} = \sigma$. The values of other parameters used are given in the figure caption. First, it can be seen that all three theories predict that the survival probability decays more rapidly when the acceptor−acceptor excluded volume is taken into account regardless of the mobility of the solute molecules. However, the RDF theory predicts the fastest decay of the survival probability due to the excluded volume. For the case depicted in Figure 4a, the numerical result of the Blumen−Manz theory[19,20] is hardly distinguishable from that of Swallen *et al.*'s.[22] At short times the latter predicts faster decay of $R(t)$, but at long times the trend appears to be reversed. We can see a similar trend in the results of Dorfman-Fayer[23] and Swallen *et al.*[22] in Figure 4b. It is also interesting to note that although the difference is small, the excluded volume effect is more pronounced for static reactant molecules than for the mobile ones.

Swallen *et al.* performed Monte Carlo simulations of the electron transfer reaction occurring in a solid solution[22] and in a liquid solution.[24] Their simulation results also show that when the excluded volume is included the survival probability falls off more rapidly than in the absence of the excluded volume.

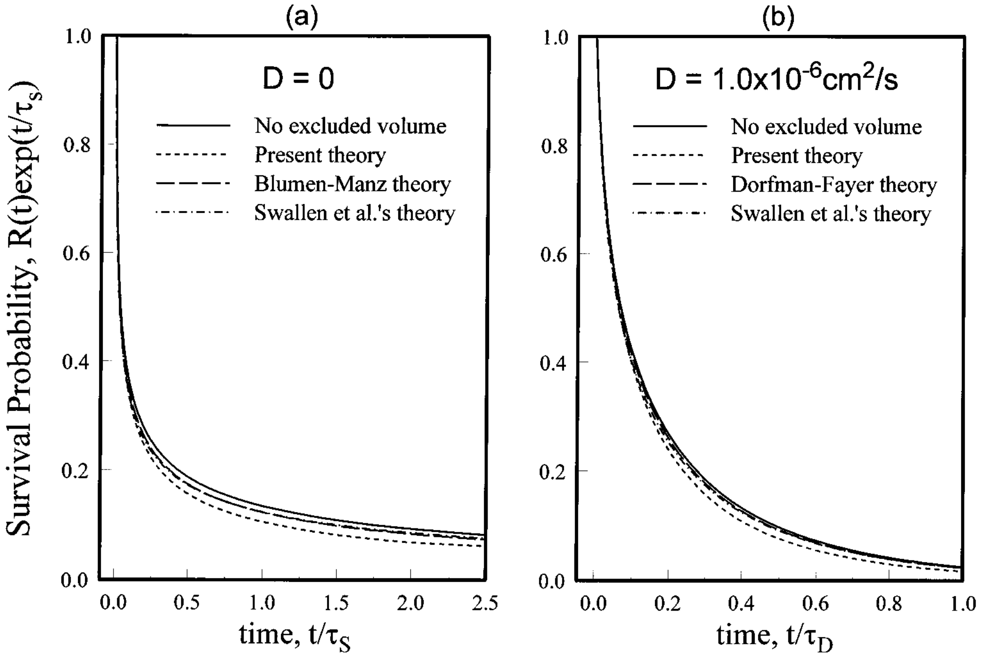

**Figure 4.** Comparison of the various theories accounting for the excluded volume effect in the long-range reaction. All three theories predict that the survival probability decays more rapidly when the excluded volume is taken into account in both cases (a) of solid solution and (b) of liquid solution. The molecular parameters used are $\sigma = \sigma_{\mathrm{BB}} = 7.2$ Å, $a = 0.9$Å, $k_{\mathrm{ET}} = 19.27\ \mathrm{ns}^{-1}$, and $C_{\mathrm{B}} = 0.445$ M, corresponding to $\Phi_{\mathrm{B}} = 0.1$. $D$ is set to zero in part a and to $1.0 \times 10^{-6}$ cm$^2$/s in part b, which gives $\tau_{\mathrm{D}} = 5.18$ ns. Note that we have plotted $R(t)\exp(t/\tau_{\mathrm{S}})$ instead of $R(t)$ to single out the decay rate due to the bimolecular reaction.

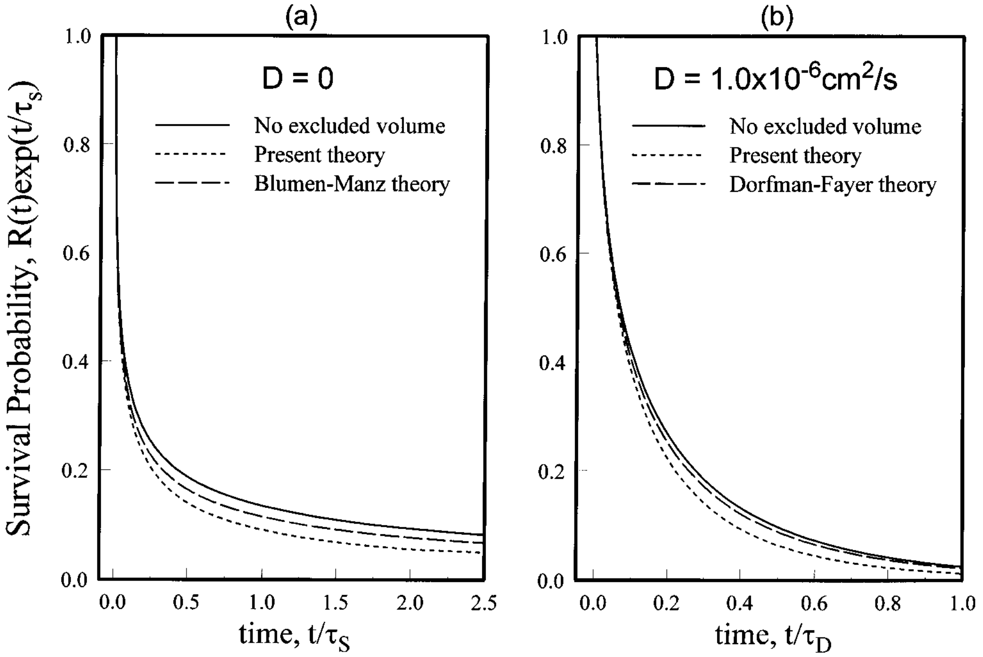

**Figure 5.** Comparison of the various theories when $\sigma_{\mathrm{BB}} = 1.2\sigma$. Other reaction and motional parameters are the same as in Figure 4.

Moreover, the simulation results indicate a faster decay of the survival probability due to the excluded volume effect than that predicted by their theory. Because detailed numerical data of their simulation are not available to us, we are not able to make a direct comparison of the present calculation with their simulation results. Nevertheless, judging from the fact that the RDF theory predicts a larger excluded volume effect than Swallen *et al.*'s theory, we expect that the RDF theory would give results in better accordance with the simulation.

As the size of **B** molecules becomes larger, the excluded volume effect gets more pronounced and the survival probability decay curve calculated from the RDF theory deviates more from those of other theories. This can be seen from the comparison of Figures 4 and 5. In Figure 5, we set $\sigma_{\mathrm{BB}}$ equal to $1.2\sigma$. Other reaction and motional parameters used in the calculations are the same as those in Figure 4. Swallen *et al.*'s theory[22] is not applicable when $\sigma_{\mathrm{BB}} > \sigma$.

## IV. Concluding Remarks

We have investigated the excluded volume effect in the diffusion-influenced bimolecular reaction of the type $\mathbf{A} + \mathbf{B} \rightarrow \mathbf{P}$. Within the framework of the hierarchical RDF approach, the excluded volume between nonreacting like molecules can be taken into account by applying the Kirkwood superposition approximation to the three-particle RDF's. The rate equation in eq 2.2, the rate coefficient expression in eq 2.3, and the kinetic equation for the nonequilibrium pair correlation function in eq

2.11 are the general set of equations that needs to be solved to evaluate the excluded volume effect. For two simple reaction models, the general equations were manipulated to give simpler forms and evaluated by numerical analysis.

We have found that inclusion of the excluded volume renders reactant concentrations to decay more rapidly than in the calculation neglecting it. The physical origin of the excluded volume effect can be attributed to the partial suppression of competition among like molecules for a reacting partner, which makes the pair distribution between reacting molecules deplete more slowly at small separations. The excluded volume effect gets more pronounced, as the size of the reactant molecules increases and the reactant concentration becomes higher. It seems that consideration of the excluded volume is essential in many experimental situations.

Comparison of the numerical results of the RDF theory with those of Blumen and Manz[19,20] and Fayer *et al.*[21−24] shows qualitative agreement. However, the RDF theory predicts a larger excluded volume effect than the other theories, and the deviation becomes larger as the size of reactant molecules increases. In this respect, it is encouraging to note that a recent computer simulation study by Swallen *et al*.[22] predicted a larger excluded volume effect than their theory can explain.

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