On the numerical solutions of kinetic equations for diffusion-influenced bimolecular reactions

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Numerical methods for solving kinetic equations for diffusion-influenced bimolecular reactions are presented for three cases. Finite difference method is used to solve diffusion-reaction equations for the pair distribution function. The kinetic equation for the concentration is evolved by the Runge–Kutta method with adaptive time step. The *boundary doubling method* is introduced to study long time dynamics, where the truncation problem of the infinite boundary is crucial. The above methods are applied, in the first case, to the classical Smoluchowski approach to a binary reaction with random initial condition and the results are compared with ones in two dimension. In the second case, an isolated pair recombination dynamics with a delta function initial condition is investigated and the results are compared with analytic expression in three dimension with spherical symmetry. A more complicated system with the hierarchical Smoluchowski approach with the Kirkwood superposition approximation is also investigated in the third case. The efficiency and the accuracy of the numerical calculations are examined against the asymptotic analytical solutions and a Monte Carlo simulation in one dimension. © *1998 American Institute of Physics.* [S0021-9606(98)51814-4]

I. INTRODUCTION

The diffusion equation is one of the most fundamental equations in physical sciences. Since the seminal contribution of Smoluchowski,[1] theories of the diffusion-influenced reactions have been developed by many authors.[2–9] There are many interesting phenomena where the diffusion-reaction equation plays an important role.[2,3] Despite its broad applicability, one can obtain exact analytical solutions of the diffusion equations only for very simple cases and, in general, one has to rely on numerical techniques for finding approximate solutions. There have been constant efforts to find more efficient numerical methods.[10–14] Recently, the effect of like-particle correlations on the bimolecular reactions has attracted considerable interest,[15–17] which shows different behavior from the mean-field predictions. Such studies are primarily concerned with the long time dynamics which requires more exact numerical methods.

The diffusion-reaction equation is an evolution equation for a certain distribution function which is a parabolic-type partial differential equation (PDE) and it cannot, in general, be solved analytically. Therefore, the need for an accurate and efficient algorithm for numerical solutions of diffusion-reaction equations is ever increasing. The main difficulty of solving the equations numerically arises from implementing boundary conditions. The outer spatial boundary needs to be extended to infinity, in principle, but it is truncated at a finite separation for numerical calculations. The error resulting from the truncation grows with time and, as a result, it becomes crucial for long time dynamics. In order to reduce the truncation error as well as to save computing time, we introduce the *boundary doubling method* (BDM). This method is based on the fact that the range covered by diffusive motion is proportional to $t^{1/2}$ according to the Einstein–Smoluchowski relation and thus the outer boundary can be simply doubled at every quadruple time.

In order to demonstrate the merit of employing the BDM we consider three cases. The first case is a simple binary chemical reaction with a random initial condition for the concentrations of reactants. The kinetic equations for this case are those derived from the classical Smoluchowski approach.[1] The second case is the recombination of an isolated pair of A and B molecules with an initial separation of σ_i. The initial condition in this case is given by a δ function which needs to be treated with care numerically. The kinetic equations are those derived from the hierarchical Smoluchowski approach (HSA) with a simple superposition approximation.[18–20] The third case is the same as the first case but the kinetic equations are those derived from the HSA with the Kirkwood superposition approximation[10,11] in which the effect of like-particle correlations becomes important at long times.

The remainder of this paper is organized as follows. In Sec. II, we will explain the numerical method for the classical Smoluchowski approach to a simple binary reaction. As an example of the initially localized system, an isolated pair dynamics will be solved numerically in Sec. III. The effect of like-particle correlations on the bimolecular reaction will be investigated numerically and the results are compared with the Monte Carlo simulation in Sec. IV. Section V concludes the present work.

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II. BIMOLECULAR REACTION WITH RANDOM INITIAL CONDITION

Consider a viscous medium containing molecules of A and B which diffuse independently. The product molecule is created by the instantaneous reaction when the reactants approach within a certain distance. The bimolecular reaction can be represented by $A+B\rightarrow$product. The time evolution of the averaged concentration of A is given by

$$\frac{\partial}{\partial t}[A]=k(t)[A][B], \tag{2.1}$$

where $k(t)$ is the time-dependent rate coefficient and $[A]$ and $[B]$ are the concentrations of reactants A and B at time t, respectively. In the classical Smoluchowski approach, the time-dependent rate coefficient can be calculated from the time-dependent pair distribution function of reactants, $\rho(r,t)$, which is given in d spatial dimension as follows:[21]

$$k(t)=\frac{2\pi^{d/2}D\sigma^{d-1}e^{-\beta U(\sigma)}}{\Gamma(d/2)}\left[\frac{d}{dr}\,e^{\beta U(r)}\rho(r,t)\right]_{r=\sigma}, \tag{2.2}$$

where D is the relative diffusion constant, $\Gamma(x)$ the gamma function, σ the reaction distance, $\beta=(k_BT)^{-1}$, and $U(r)$ the potential of mean force. $\rho(r,t)$ is assumed to satisfy the following diffusion equation:[21]

$$\frac{\partial\rho(r,t)}{\partial t}=D\nabla e^{-\beta U(r)}\nabla e^{\beta U(r)}\rho(r,t). \tag{2.3}$$

This equation is a parabolic-type PDE and requires two boundary conditions at two spatial positions and one initial condition at $t=0$ for $\rho(r,t)$. Therefore, the diffusion equation is usually an initial value problem with respect to time and a boundary value problem with respect to the spatial coordinate. For the diffusion-influenced reaction system, the above PDE is usually considered to be subject to the random initial and Collins–Kimball boundary conditions which are given by

$$\rho(r,0)=e^{-\beta U(r)}, \tag{2.4a}$$

$$\left[\frac{d}{dr}\,e^{\beta U(r)}\rho(r,t)\right]_{r=\sigma}=\frac{k^0\Gamma(d/2)}{2\pi^{d/2}D\sigma^{d-1}e^{-\beta U(\sigma)}}\,\rho(\sigma,t), \tag{2.4b}$$

$$\rho(r\rightarrow\infty,t)=1, \tag{2.4c}$$

where k^0 is the intrinsic rate constant. The Smoluchowski boundary condition can be obtained as $k^0\rightarrow\infty$. For simplicity, let us neglect the effect of the detailed short-range structure in the potential of mean force, namely,

$$U(r)=\begin{cases}0 & \text{for } r\geqslant\sigma\\ \infty & \text{for } r<\sigma\end{cases}. \tag{2.5}$$

The finite difference technique can be used to solve the above equations with the outer boundary truncated at a finite separation, e.g., r_N. The radial and time coordinates are discretized as follows:

$$r_i=\frac{i}{N}(r_N-\sigma)+\sigma \quad (i=0,1,...,N), \tag{2.6a}$$

$$\Delta r=\frac{(r_N-\sigma)}{N}, \tag{2.6b}$$

$$\Delta t=t_j-t_{j-1} \quad (j=1,2,...), \tag{2.6c}$$

where $N+1$ is the number of discrete spatial points. Then the first and second derivatives of the pair distribution function, $\rho(r,t)$, with respect to the spatial coordinate are approximated by

$$\frac{\partial\rho(r_i,t_j)}{\partial r}\approx\frac{\rho(r_{i+1},t_j)-\rho(r_{i-1},t_j)}{2\Delta r}, \tag{2.7a}$$

$$\frac{\partial^2\rho(r_i,t_j)}{\partial r^2}\approx\frac{\rho(r_{i+1},t_j)-2\rho(r_i,t_j)+\rho(_{i-1},t_j)}{\Delta r^2}. \tag{2.7b}$$

With these approximations, we apply the Crank–Nicholson finite difference method[22] to Eq. (2.3) as follows:

$$\begin{aligned}&\frac{\rho(r_i,t_{j+1})-\rho(r_i,t_j)}{\Delta t}\\ &=\frac{D}{2}\left[\frac{\rho(r_{i+1},t_{j+1})-2\rho(r_i,t_{j+1})+\rho(r_{i-1},t_{j+1})}{\Delta r^2}\right.\\ &\quad+\frac{d-1}{2r_i}\,\frac{\rho(r_{i+1},t_{j+1})-\rho(r_{i-1},t_{j+1})}{\Delta r}\\ &\quad+\frac{\rho(r_{i+1},t_j)-2\rho(r_i,t_j)+\rho(r_{i-1},t_j)}{\Delta r^2}\\ &\quad\left.+\frac{d-1}{2r_i}\,\frac{\rho(r_{i+1},t_j)-\rho(r_{i-1},t_j)}{\Delta r}\right].\end{aligned} \tag{2.8}$$

This method is second order in time and stable for any size of Δt. In order to obtain $\rho(r_i,t_{j+1})$, however, a little expensive inversion of the tridiagonal matrix is unavoidable in compensation for the stability. Considering the boundary conditions, Eqs. (2.4b) and (2.4c), the matrix can be given by

$$\begin{bmatrix} m' & u_1 & 0 & & & & \\ l_2 & m & u_2 & & & 0 & \\ 0 & l_3 & m & & & & \\ & & & \ddots & & & \\ & & & & m & u_{N-3} & 0 \\ & 0 & & & l_{N-2} & m & u_{N-2} \\ & & & & 0 & l_{N-1} & m \end{bmatrix} \cdot \begin{bmatrix} \rho(r_1,t_{j+1}) \\ \rho(r_2,t_{j+1}) \\ \vdots \\ \rho(r_{N-2},t_{j+1}) \\ \rho(r_{N-1},t_{j+1}) \end{bmatrix} = \begin{bmatrix} b_1 \\ b_2 \\ \vdots \\ b_{N-2} \\ b_{N-1} \end{bmatrix}, \tag{2.9}$$

where

$$u_i=-\frac{D\Delta t}{2\Delta r}\left(\frac{1}{\Delta r}+\frac{(d-1)}{2r_i}\right) \quad (i=1,...,N-2), \tag{2.10a}$$

$$m=1+\frac{D\Delta t}{\Delta r^2}, \tag{2.10b}$$

$$m' = m + \frac{l_1}{1 + \dfrac{k^0 \Gamma(d/2)\Delta r}{2\pi^{d/2} D \sigma^{d-1}}}, \tag{2.10c}$$

$$l_i = -\frac{D\Delta t}{2\Delta r}\left(\frac{1}{\Delta r} - \frac{(d-1)}{2r_i}\right) \quad (i = 2,...,N-1), \tag{2.10d}$$

$$b_1 = (-u_1)\rho(r_2,t_j) + (-m'+2)\rho(r_1,t_j), \tag{2.10e}$$

$$b_i = (-u_i)\rho(r_{i+1},t_j) + (-m+2)\rho(r_i,t_j) + (-l_i)\rho(r_{i-1},t_j) \quad (i = 2,...,N-2), \tag{2.10f}$$

$$b_{N-1} = (-m+2)\rho(r_{N-1},t_j) + (-l_{N-1})\rho(r_{N-2},t_j) - 2u_{N-1}. \tag{2.10g}$$

Following the above procedure, we can calculate the pair distribution function and therefore the rate coefficient at a given time. Then the rate equation, Eq. (2.1), can be integrated by any of several numerical methods for solving ordinary differential equations. The fourth-order Runge–Kutta method with adaptive step size control by step doubling[22] has very attractive features for the investigation of long time dynamics since the pair distribution function changes very smoothly at long times.

The concentration at $(j+1)$th time step, $[A]_{j+1}$, is obtained as follows:

$$[A]_{j+1} = [A]_j + \frac{\Delta t}{6}(a_1 + 2a_2 + 2a_3 + a_4), \tag{2.11}$$

where

$$a_1 = -k(t_j)[A]_j[B]_j, \tag{2.12a}$$

$$a_2 = -k\left(t_j + \frac{\Delta t}{2}\right)\left([A]_j + \frac{a_1}{2}\right)\left([B]_j + \frac{a_1}{2}\right), \tag{2.12b}$$

$$a_3 = -k\left(t_j + \frac{\Delta t}{2}\right)\left([A]_j + \frac{a_2}{2}\right)\left([B]_j + \frac{a_2}{2}\right), \tag{2.12c}$$

$$a_4 = -k(t_j + \Delta t)([A]_j + a_3)([B]_j + a_3). \tag{2.12d}$$

Let us denote the two approximate solutions, $[A]''$ obtained by using one step of $2\Delta t$ and $[A]'$ by two steps of Δt and define $\delta \equiv [A]' - [A]''$. When we denote δ' as a desired error, the optimum time step size, $\Delta t'$, is calculated by the following equations:[22]

$$\Delta t' = S\Delta t\left|\frac{\delta'}{\delta}\right|^{0.20} \quad (\delta' \geqslant \delta)$$
$$= S\Delta t\left|\frac{\delta'}{\delta}\right|^{0.25} \quad (\delta' < \delta), \tag{2.13}$$

where S is the safety constant. By controlling the value of δ', we can control the accuracy and speed of the calculation. We also note that for the spatial grids, the Richardson extrapolation method can be used to obtain the optimized number of discrete points.[12]

The error resulting from restricting the outer boundary will be significant at long times since the physical value like the pair distribution function at the truncated boundary changes with time. The outer truncated boundary, r_N, should be large enough to satisfy $\rho(r_N,t) = 1$, while Δr needs to be small enough to get converged results, with N as small as possible. This causes a crucial problem for long time dynamics. To minimize the computational cost in some cases, Pedersen and Freed used a variable step size such that Δr is chosen small in the region of $\sigma \leqslant r \leqslant r_M$ with $r_M \ll r_N$ and Δr is taken much larger in $r_M \leqslant r \leqslant r_N$.[10] In this case, the Richardson extrapolation method cannot be used and the error around r_M can be amplified with time. Therefore, their method is not suitable for long time dynamics. Although the asymptotic solution is used for the large r region,[11,14] it is not always possible to get one and the error inherent with it still persists. Transformation methods[12–14,19] have been used to avoid the infinite boundary such that the r-space range of $\{\sigma,\infty\}$ is nonlinearly transformed into the x space with the range of $\{1,0\}$, for example,[19] by a relation such as $x = \exp[-a(r/\sigma - 1)]$. Here a is a dimensionless constant and the grid points for the x space are taken to have equal spacings. This transformation method gives an additional advantage that the grid in the original r space can be more finely spaced near the inner boundary which is the most important region in the Smoluchowski approach. Despite such advantages of the transformation method, however, the problem of truncating infinite outer boundary (infinitesimal inner boundary in the x space) which causes amplification of error at long times still remains due to the finite difference scheme.

We now introduce the boundary doubling method (BDM) with a growing outer boundary which evolves with time. Because of the finite number of discrete grids, this variable outer boundary requires interpolations at new grid points for each time step. We note the fact that the range of regions covered by diffusive motion is proportional to $t^{1/2}$ (the Einstein–Smoluchowski relation), and thus the outer boundary can be simply doubled at every quadruple time without very expensive interpolations. We introduce the following scheme:

$$t(n) = 4t(n-1), \quad n = 1,2,..., \tag{2.14a}$$

$$r_N(t) = c\sqrt{2dDt(n)}, \quad t(n) \leqslant t < t(n+1), \tag{2.14b}$$

$$r_i(t) = \frac{i}{N}(r_N(t) - \sigma) + \sigma, \quad i = 0,1,2,...,N. \tag{2.14c}$$

At every doubling time, $t = t(n)$, the pair distribution function is given by

$$\rho(r_i(t),t) = \begin{cases} \rho(r_{2i}(t),t), & i \leqslant N/2 \\ 1, & i > N/2 \end{cases},$$

where $t(0) \equiv t_0$ and c is an adjustable parameter. Initially, the value of c should be controlled to obtain an optimum outer boundary. At short times, this method can increase accuracy and speed greatly using a finer grid with the same number of grid points (N). For long times, it can minimize the truncation error by using the large outer boundary. One possible drawback of the method is that the error may increase abruptly right after the outer boundary and Δr are doubled. However, the adaptive size Runge–Kutta method can minimize such error by reducing the time step size around the doubling time.

For $d=1$ and 3, the diffusion equation with Smoluchowski boundary condition ($k^0 \to \infty$) for a random initial condition when $[A]_0=[B]_0$ can be solved exactly to give[2]

$$[A]_{1d}=\left(\sqrt{\frac{16Dt}{\pi}}+\frac{1}{[A]_0}\right)^{-1}, \tag{2.15a}$$

$$[A]_{3d}=\left(4\pi\sigma Dt+8\sigma^2\sqrt{\pi Dt}+\frac{1}{[A]_0}\right)^{-1}. \tag{2.15b}$$

But for $d=2$, no closed form solution in terms of elementary functions is available. Instead, the solution of the Laplace transform of rate coefficient, $k(t)$, has been known as follows:[23]

$$\hat{k}(z)_{2d}=\frac{2\pi D\sqrt{z\sigma^2/D}K_1(\sqrt{z\sigma^2/D})}{zK_0(\sqrt{z\sigma^2/D})}, \tag{2.16a}$$

where K_v is a modified Bessel function of the second kind. The inverse Laplace transform of this solution can be given and approximated by[24]

$$\begin{aligned} k(t)_{2d}&=\frac{8D}{\pi}\int_0^\infty \frac{\exp(-\tau x^2)}{x[J_0(x)^2+Y_0(x)^2]}\,dx \\ &\underset{\tau\to 0}{=} 2\pi D((\pi\tau)^{-1/2}+1/2-1/4(\tau/\pi)^{1/2}+\cdots) \\ &\underset{\tau\to\infty}{=} 2\pi D\left(\frac{2}{\ln(4\tau)-2\gamma}-\frac{2\gamma}{(\ln(4\tau)-2\gamma)^2}+\cdots\right) \\ &\cong 2\pi D\left(\frac{\exp(-\sqrt{\pi\tau}/10)}{\sqrt{\pi\tau}}\right. \\ &\quad \left.+\frac{1}{\ln[\sqrt{4\tau\exp(-\gamma)}+\exp(5/3)]}\right), \end{aligned} \tag{2.16b}$$

where γ is the Euler constant, $\tau=Dt/\sigma^2$, and $J_0(x)$ and $Y_0(x)$ are the zero-order Bessel functions of the first and second kind. The last approximation was suggested by Szabo *et al.*[25] They reported that it is accurate to 1.3% for all times. It is not easy to perform the numerical inversion of the Laplace transform containing special functions like K_v with high accuracy. We apply the present numerical method to this two-dimensional Smoluchowski approach. Of course, our method can be applied to more general cases where even the Laplace transformed solution is not available, as will be shown in Sec. IV. Moreover, the magnitude of error in our method can be easily controlled. In Fig. 1, we compare the direct numerical inversion[26] of Eq. (2.16a) with the results of approximate expressions in Eq. (2.16b) to examine the accuracy of them. Indeed, the approximation of Szabo *et al.* is quite accurate for all times.

The concentration of A can be evaluated using Eq. (2.16a) as follows:

$$[A]_{2d}=\left(L^{-1}\left(\frac{2\pi D\sqrt{z\sigma^2/D}K_1(\sqrt{z\sigma^2/D})}{z^2K_0(\sqrt{z\sigma^2/D})}\right)+\frac{1}{[A]_0}\right)^{-1}, \tag{2.17}$$

where L^{-1} denotes the inverse Laplace transform. We can examine the numerical accuracy of the BDM by comparing

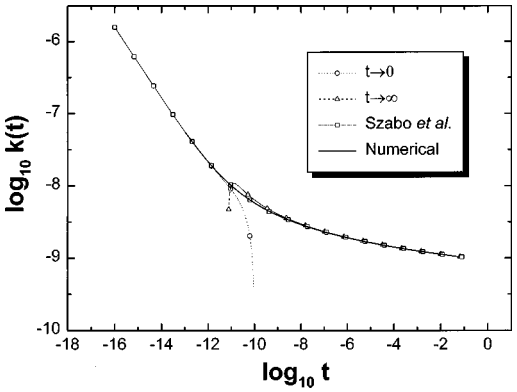

FIG. 1. The rate coefficients in the two-dimensional Smoluchowski approach for the short time limit approximation (the dotted line with circles), long time limit (the dashed line with triangles), Szabo *et al.*'s (Ref. 25) approximation (the dot-dashed line with squares), and direct numerical Laplace transform inversion (the solid line) [see Eqs. (2.16)]. See the text for the values of other parameters.

with the result of the numerical inversion of Eq. (2.17). In Fig. 2, we plot the survival probability curves ($P(t) \equiv [A]/[A]_0$) in log–log scale for several values of N. The values for the parameters are $D=2.0\times10^{-9}$ m^2 s^{-1}, $\sigma=1.0\times10^{10}$ m, $[A]_0=[B]_0=1.0\times10^{19}$ m^{-2}, and the initial time interval $\Delta t=1.0\times10^{-16}$ s. In order to realize the Smoluchowski boundary condition numerically, we take a large value for $k^0(=10^4\times2\pi D)$. If one is interested in the short and intermediate time dynamics, $N=10^3$ will be enough, since it shows an indistinguishable result with the exact one until about 1.0×10^{-9} s (2.0×10^2 in the dimensionless time unit, τ) and it takes about 5 s for computation.[27] $N=10^4$ gives correct results up to about 1.0×10^{-7} s and takes about 1 min, and $N=10^5$ up to 1.0×10^{-6} s with about 12 min. The most time-consuming part is the inversion routine of the tridiagonal matrix [see Eq. (2.9)], hence the computing time is roughly proportional to N. The adaptive size Runge–Kutta method is shown to be very useful. With a fixed time step size algorithm, one should calculate 1.0×10^{10} steps until 1.0×10^{-6} s.

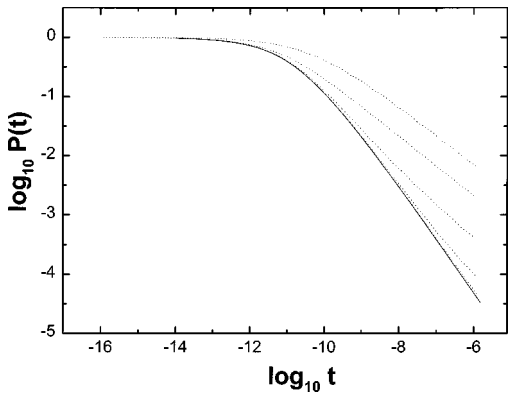

FIG. 2. The survival probabilities in the two-dimensional Smoluchowski approach for several values of N. BDM results (dotted lines) for $N=2$, 10, 10^2, 10^3, 10^4, and 10^5 (from top to bottom) are compared with the numerical Laplace transform inversion (the solid line). All other parameters are the same as those in Fig. 1.

Interestingly we notice in Fig. 2 that the slope of each of the survival probability curves tends to change toward the value of -0.5 in the long time limit. The slope of -0.5 is an exact value in one dimension [see Eq. (2.15a)], and the pair distribution function in one dimension becomes linear with respect to r in the long time limit as[2]

$$\rho(r,t)=\mathrm{erf}\left(\frac{r-\sigma}{2\sqrt{Dt}}\right)\underset{t\to\infty}{\cong}\frac{r-\sigma}{\sqrt{\pi Dt}}\quad(d=1), \tag{2.18}$$

where erf(x) denotes the error function. Therefore we can infer that the slope of -0.5 reflects the fact that the pair distribution function is treated, in this time region, linearly due to the insufficient number of grid points, N. This is why the error increases with time and it does not result from the truncation of the outer boundary. If the BDM is applied to the one-dimensional case, the accuracy will increase greatly. And the BDM can be further improved by adopting, additionally, an appropriate nonlinear transform scheme. Then we can treat the nonlinear pair distribution function with a smaller value of N for a given magnitude of error.

The outer boundary is extended from about $\sigma+1.0\times10^{-13}$ m at beginning up to about $\sigma+1.0\times10^{-8}$ m at time 1.0×10^{-6} s by repeated application of the BDM. On the other hand, with a fixed outer boundary, the error will continuously increase with time, as shown in Fig. 3(a). We compare the time dependence of the rate coefficient for three fixed boundaries, $r_N=10\sigma$, 100σ, and 1000σ with the result of BDM. N for all data is set at 10^4. As expected, when the fixed outer boundary becomes smaller, the result starts to deviate significantly earlier from the correct value. It is interesting to note that the rate coefficient becomes a constant value for a fixed outer boundary case and, therefore, the concentration will show -1 power law behavior in the long time limit. On the other hand, when the fixed outer boundary is set large enough, the error in short and intermediate times will increase since Δr increases for a fixed value of N even though the truncation error becomes small. [See the line of the 1000σ case in Fig. 3(a)]. Therefore, one should find an appropriate value of the fixed outer boundary by trial and error. As previously mentioned, the error increases in the long time due to the insufficiently small value of N for the BDM case. And a larger value of N should be used to examine the longer time dynamics.

In Fig. 3(b), we plot the survival probability curves for several values of N and the fixed boundary, $r_N=10\sigma$. The slope of all curves is -1 at long times due to constant rate coefficient as expected [note $[A]_{2d}\underset{t\to\infty}{\sim}(\ln t)/t$]. This results from the fact that the condition $\rho(r_N,t)=1$ causes the constant input at the boundary and the system reaches a pseudosteady state and has a constant rate. The error due to the small value of N is the early appearance of $-1/2$ power law behavior in the survival probability and the error caused by the fixed boundary is reflected by -1 power law behavior. As a result, the survival probability curve from the fixed boundary method crosses the correct curve due to the fortuitous cancellation of these errors even for a small value of N. However, being free from the fixed boundary error, the BDM shows the correct result as N becomes sufficiently large.

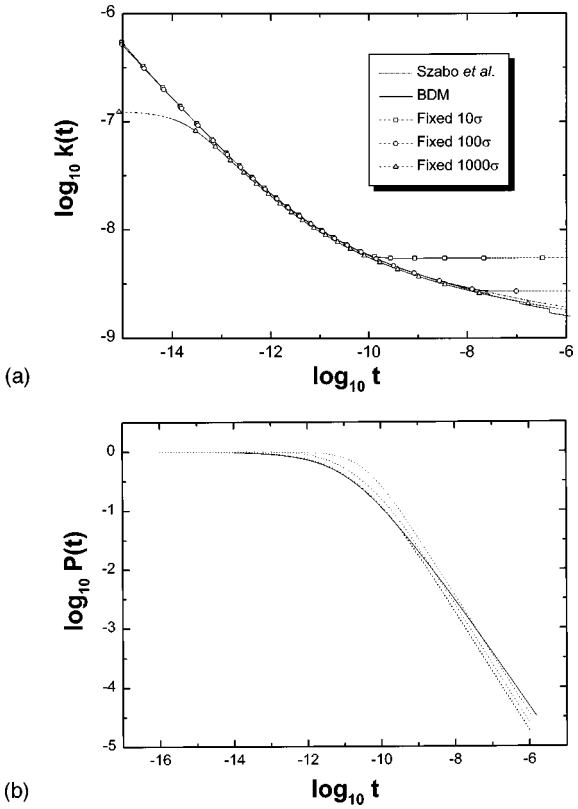

FIG. 3. (a) The rate coefficients in the two-dimensional Smoluchowski approach for three fixed boundaries (dash lines), the BDM result (the solid line), and Szabo *et al.*'s approximation (the dot-dashed line). $N=10000$. (b) The survival probabilities in the two-dimensional Smoluchowski approach for several values of N. The outer boundary is fixed at 10σ. Fixed boundary results (dotted lines) for $N=2$, 10, 10^2, 10^3, and 10^4 (from top to bottom) are compared with the numerical Laplace transform inversion (solid line). All other parameters are the same as those in Fig. 2.

III. RECOMBINATION OF AN ISOLATED PAIR

Despite the success of the classical Smoluchowski approach for some simple problems, it cannot be generally applied to more complex problems. One important example is the recombination dynamics of initially separated pairs. The interplay between bulk and geminate recombinations has been studied by many authors.[6,20,28,29] However, an exact solution has not been given due to its complex dynamics of many particle nature. To examine the numerical procedure for solving the relevant equations, let us consider only one isolated pair which is initially separated by the distance, σ_i, in the system.

Based on the HSA with a simple superposition approximation, one can obtain the following kinetic equations:[20]

$$\frac{d}{dt}P(t)=-k(t)P(t), \tag{3.1a}$$

$$k(t)=\int dr\,\frac{2\pi^{d/2}r^{d-1}}{\Gamma(d/2)}S(r)\rho(r,t), \tag{3.1b}$$

$$\frac{\partial}{\partial t}\rho(r,t)=L(r)\rho(r,t)-S(r)\rho(r,t)+k(t)\rho(r,t), \tag{3.1c}$$

where $P(t)$ is the survival probability at time t, $S(r)$ denotes the reactive sink function at the spatial distance, r, and $L(r)$ represents the nonreactive evolution operator which can be approximated by the Smoluchowski operator if one neglects the effects of hydrodynamic interactions. Namely, $S(r)$ and $L(r)$ can be given as follows:

$$S(r)=\frac{k^0\Gamma(d/2)\,\delta(r-\sigma)}{2\pi^{d/2}\sigma^{d-1}}, \tag{3.2a}$$

$$L(r)=\left(\frac{\partial}{\partial r}+\frac{d-1}{r}\right)D(r)\left(\frac{\partial}{\partial r}+\beta\frac{\partial U(r)}{\partial r}\right)$$
$$\cong D\left(\frac{\partial^2}{\partial r^2}+\frac{d-1}{r}\frac{\partial}{\partial r}\right). \tag{3.2b}$$

The initial distribution is given by

$$\rho(r,0)=\frac{\Gamma(d/2)\,\delta(r-\sigma_i)}{2\pi^{d/2}\sigma_i^{d-1}}. \tag{3.3a}$$

From the viewpoint of numerical calculation, it is not easy to represent the δ-function initial condition which represents an unfavorable singularity. Therefore, we should start from a very small $t(0)\neq 0$, and approximate the initial evolution of pair distribution function as follows:

$$\rho(r,t(0))\cong\frac{\Gamma(d/2)}{2\pi^{d/2}\sigma_i^{d-1}}\,G(r,t(0)|\sigma_i), \tag{3.3b}$$

where $G(r,t(0)|\sigma_i)$ is the Green's function or the propagator for moving from σ_i to r in $t(0)$, which is known for $d=1$, 2, and 3.[23] In applying the BDM described in Sec. II, one should carefully determine the values for the constants given in Eqs. (2.14). Using too small $t(0)$ results in the steep function around σ_i, and requires smaller Δr, while large $t(0)$ causes an initial error for the above approximation. Of course, c should be large enough for the initial outer boundary to be larger than σ_i. If the boundary doubling is done too early, it may result in the loss of information about initial distribution. Initial doubling time, $t(1)$, needs to be carefully treated for a certain class of initial condition, e.g., large σ_i. For this case, $t(1)$ may be modified to $t(1)=4t(0)+c'$, where c' is an adjustable parameter which delays the initial boundary doubling until the sharp initial distribution is somewhat broadened. The localized initial condition needs to be represented more accurately with small enough Δr, which requires using larger N due to the extension of the outer boundary. The nonlinear transformation method[12,19] cannot be easily applied to this kind of problem because of the presence of two separated steep regions (around σ_i and σ).

The δ-function sink used in Eq. (3.2a) is more cumbersome in a numerical calculation than the other equivalent boundary conditions. One can replace the sink function and the reflecting boundary condition with the equivalent radiation boundary condition [see Eq. (2.4b)]. To include the contribution from the last term on the right-hand side of Eq. (3.1c), a similar tridiagonal matrix to that in Eq. (2.9) can be constructed by modifying the previous equations as follows:

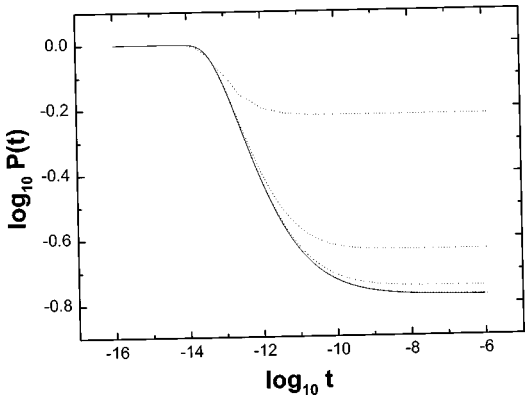

FIG. 4. The survival probabilities of an isolated pair in the three-dimensional Smoluchowski approach for several values of N. BDM results (dotted lines) for $N=10$, 10^2, 10^3, 10^4, and 2×10^4 (from top to bottom) are compared with the exact result (the solid line). See the text for the values of other parameters.

$$m=1+\frac{D\Delta t}{\Delta r^2}-x(t_j), \tag{3.4a}$$

$$b_i=(-u_i)\rho(r_{i+1},t_j)+(-m+2+x(t_j))\rho(r_i,t_j)$$
$$+(-l_i)\rho(r_{i-1},t_j), \tag{3.4b}$$

$$b_1=(-u_1)\rho(r_2,t_j)+(-m'+2+x(t_j))\rho(r_1,t_j), \tag{3.4c}$$

$$b_{N-1}=(-m+2+x(t_j))\rho(r_{N-1},t_j)$$
$$+(-l_{N-1})\rho(r_{N-2},t_j)-2u_{N-1}, \tag{3.4d}$$

where $x(t_j)\equiv k(t_j)\Delta t/2$. To obtain the above equations, we used the following approximation:

$$x(t_{j+1})\cong x(t_j). \tag{3.5}$$

The error due to this approximation can be controlled by adjusting δ' of Eq. (2.13). In other words, one can use a smaller time step to make this error smaller. We can confirm that the error in this approximation is not large by checking the convergence. Using this modified tridiagonal matrix and the Runge–Kutta scheme considering Eq. (3.1a), we can solve Eq. (3.1) in the same manner as before.

In this case, we can solve the diffusion equation with the radiation boundary condition exactly in three dimension with spherical symmetry using the Green's function method and the resulting expression for the survival probability becomes[2,20]

$$P(t)=1-\frac{\sigma}{\sigma_i}\frac{k^0}{k^0+4\pi\sigma D}\left[\Omega(B/\sqrt{t})-\Omega(A\sqrt{t}+B/\sqrt{t})\right]$$
$$\times\exp(-B^2/t), \tag{3.6}$$

where

$$A\equiv\left(1+\frac{k^0}{4\pi\sigma D}\right)\frac{\sqrt{D}}{\sigma},\quad B\equiv\frac{\sigma_i-\sigma}{2\sqrt{D}},$$

$$\Omega(x)\equiv\exp(x^2)\mathrm{erfc}(x).$$

The complementary error function is denoted as erfc(x).

In Fig. 4, we plot numerical results for the survival prob-

abilities in three dimension using several values of N and compare them with the exact result given by Eq. (3.6). We set $\sigma_i = 1.2\times 10^{-10}$ m, $k^0 = 10^4 \times 4\pi\sigma D$, and the other parameters are the same as those in Fig. 1. As expected, the initial value of Δr which is determined by N affects the result significantly. The initial outer boundary set at about 1.1 σ_i is found to give the best results. For all N, the results show similar qualitative behaviors but converge to different values. Deviation from the exact asymptotic value becomes large as N decreases. Since the asymptotic values of $P(t)$ depend only on the initial condition [the exact value is given by $1-\sigma/\sigma_i$ from Eq. (3.6)], the large deviations result from inexact treatment of the initial distribution when using smaller values of N. The larger σ_i requires a larger outer boundary (r_N) which in turn increases Δr for a given N. This causes the larger error. In order to reduce the error in this case, N has to be increased, thereby requiring more computing time.

IV. LIKE-PARTICLE CORRELATION EFFECT

The classical Smoluchowski approach usually shows quite a good result in the short and intermediate times but is incorrect asymptotically due to its lack of consideration for the effects of like-particle correlations. In the long time limit, it is known to be $[A]\sim t^{-\gamma}$ with $\gamma=\min(1,d/4)$, whereas the Smoluchowski approach predicts $[A]\sim t^{-\gamma}$ with $\gamma=\min(1,d/2)$.[15]

Kuzovkov and Kotomin[16] adopted the Kirkwood superposition approximation in the HSA and obtained a set of coupled evolution equations for different pair distribution functions instead of Eq. (2.3). When $D_A=D_B$ and $[A]_0=[B]_0$, these equations can be rewritten, using the sink function formalism, as

$$\frac{\partial \rho_{AB}(r,t)}{\partial t} = L(r)\rho_{AB}(r,t) - S(r)\rho_{AB}(r,t) + 2k(t) \times [A]\rho_{AB}(r,t)[1-X_{AA}(r,t)], \tag{4.1a}$$

$$\frac{\partial \rho_{AA}(r,t)}{\partial t} = L(r)\rho_{AA}(r,t) + 2k(t)[A]\rho_{AA}(r,t) \times [1-X_{AB}(r,t)], \tag{4.1b}$$

$$X_v(r,t) = \frac{\rho_v(r+\sigma,t)+\rho_v(r-\sigma,t)}{2},$$

$$v = AA, AB \quad (d=1). \tag{4.1c}$$

Here, $\rho_{AB}(r,t)$ corresponds to $\rho(r,t)$ of Eq. (2.3) and its evolution is coupled to the like-particle pair distribution function, $\rho_{AA}(r,t)$.

If we define $x(r,t)\equiv k(t)[A][1-X_{AA}(r,t)]\Delta t$, we can construct the following tridiagonal matrix to solve Eq. (4.1a):

$$\begin{bmatrix} m_1 & u_1 & 0 & & & & \\ l_2 & m_2 & u_2 & & & 0 & \\ 0 & l_3 & m_3 & & & & \\ & & & \ddots & & & \\ & & & & m_{N-3} & u_{N-3} & 0 \\ & 0 & & & l_{N-2} & m_{N-2} & u_{N-2} \\ & & & & 0 & l_{N-1} & m_{N-1} \end{bmatrix} \cdot \begin{bmatrix} \rho_{AB}(r_1,t_{j+1}) \\ \rho_{AB}(r_2,t_{j+1}) \\ \vdots \\ \rho_{AB}(r_{N-2},t_{j+1}) \\ \rho_{AB}(r_{N-1},t_{j+1}) \end{bmatrix} = \begin{bmatrix} b_1 \\ b_2 \\ \vdots \\ b_{N-2} \\ b_{N-1} \end{bmatrix}, \tag{4.2}$$

where

$$u_i = -\frac{D\Delta t}{2\Delta r}\left(\frac{1}{\Delta r}+\frac{(d-1)}{2r_i}\right) \quad (i=1,...,N-2), \tag{4.3a}$$

$$m_1 = 1+\frac{D\Delta t}{\Delta r^2} - x(r_1,t_j) + \frac{l_1}{1+\dfrac{k^0\Gamma(d/2)\Delta r}{2\pi^{d/2}D\sigma^{d-1}}}, \tag{4.3b}$$

$$m_i = 1+\frac{D\Delta t}{\Delta r^2} - x(r_i,t_j) \quad (i=2,...,N-1), \tag{4.3c}$$

$$l_i = -\frac{D\Delta t}{2\Delta r}\left(\frac{1}{\Delta r}-\frac{(d-1)}{2r_i}\right) \quad (i=2,...,N-1), \tag{4.3d}$$

$$b_1 = (-u_1)\rho_{AB}(r_2,t_j) + (-m_1+2+x(r_1,t_j)) \times \rho_{AB}(r_1,t_j), \tag{4.3e}$$

$$b_1 = (-u_i)\rho_{AB}(r_{i+1},t_j) + (-m_i+2+x(r_i,t_j)) \times \rho_{AB}(r_i,t_j) + (-l_i)\rho_{AB}(r_{i-1},t_j) \quad (i=2,...,N-2), \tag{4.3f}$$

$$b_{N-1} = (-m_{N-1}+2+x(r_{N-1},t_j))\rho_{AB}(r_{N-1},t_j) + (-l_{N-1})\rho_{AB}(r_{N-2},t_j) - 2u_{N-1}. \tag{4.3g}$$

The above equations can also be used to solve Eq. (4.1b) if we define $x(r,t)\equiv k(t)[A][1-X_{AB}(r,t)]\Delta t$ and modify Eq. (4.3b) as

$$m_1 = 1+\frac{D\Delta t}{\Delta r^2} - x(r_1,t_j) + l_1, \tag{4.4}$$

which considers the reflecting boundary condition. The approximation, $x(r,t_{j+1})\cong x(r,t_j)$ is again used to obtain the above equations and the numerical solution can be obtained as before.

Since no exact solution of the problem has been reported, we carry out a Monte Carlo (MC) simulation in one dimension in order to compare with the numerical solution of Eq. (4.1). The detailed method of our simulation was described in the previous work.[29] The diffusion motion is modeled as simple jumps to neighboring lattice point. Based on the Einstein–Smoluchowski relation, the optimum size of the time step should be found until the simulation results converge. The size of the system should also be chosen to mini-

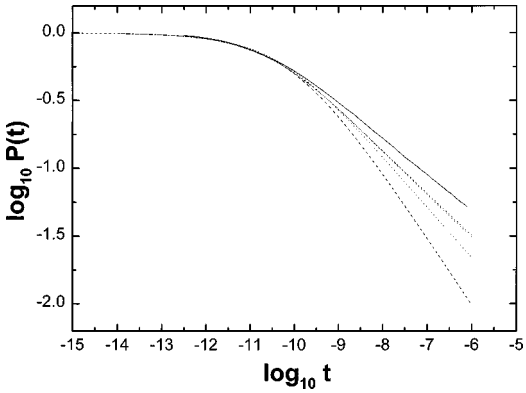

FIG. 5. The survival probabilities in the presence of like-particle correlations in one dimension for several values of N. BDM results (dotted lines) for $N=10$, 10^2, 10^3, and 10^5 (from bottom to top) are compared with that of the Smoluchowski approach (the dashed line) and the Monte Carlo simulation result (the solid line).

mize the finite edge effect. The periodic boundary condition and the minimum image convention are used. The computational cost is reduced greatly by using the parallel programming, MC algorithm with only integer operations, the safe distance method, and the multiple jump method, which are described in our previous work.[29] Our simulations were done on an IBM SP2 model MPP (Massively Parallel Processing) computer with 40 nodes.

The survival probabilities in one dimension are plotted in Fig. 5. We find that the critical exponent, γ, is about 0.31, which is in agreement with the previous calculation,[17] and can be compared with 0.5 obtained from the one-dimensional Smoluchowski approach and 0.25 predicted by the simulation. Therefore the evolution equations with the Kirkwood approximation, which account for the like-particle correlation effect, treat the real binary reaction dynamics better than the Smoluchowski approach but it still remains to be improved to achieve the simulation result.

The effects of nonlinearity of distribution function due to like-particle pair correlations are expected to make the magnitude of error of this problem similar to the previous two-dimensional Smoluchowski approach. Indeed, the converged results up to $t=1.0\times10^{-6}$ s are obtained for $N=10^3$, which is smaller than the two-dimensional Smoluchowski approach ($N=3\times10^4$). This can be explained as follows. The slope of the survival probability curve in the long time limit in two dimension is about -1 (in fact $[A]_{2d} \underset{t\to\infty}{\sim} (\ln t)/t$) while the calculated slope in one-dimensional HSA with the Kirkwood approximation is -0.31, which is the closer value to -0.5—the slope in the one-dimensional Smoluchowski approach. Therefore, we can infer that the pair distribution function in one-dimensional HSA with the Kirkwood approximation is less nonlinear than that of the two-dimensional Smoluchowski approach and can be treated with a smaller value of N.

V. CONCLUDING REMARKS

We have presented accurate and efficient numerical methods for solving various general diffusion-reaction systems. The diffusion-type equations satisfied by the time-dependent pair distribution function with appropriate boundary conditions are solved by the finite difference method. The values of the pair distribution function at the spatial grid points for a particular time are obtained by the inversion of the tridiagonal matrix defined in terms of the quantities at the previous time step. The usual error resulting from restricting the formally infinite outer boundary to a finite distance is avoided by introducing the BDM. The pair distribution function is used to calculate the time-dependent rate coefficient and the kinetic equation for the concentration is integrated by the fourth-order Runge–Kutta method with adaptive time-step size by step doubling.

The BDM is easily applied to the two-dimensional Smoluchowski approach where no exact solution has been known. And more general diffusion-reaction systems described by HSA can also be treated efficiently by this method. The advantage of the BDM over other methods is in the straightforward application to the initially localized system where careful treatment of the initial pair distribution is important. Another important advantage is clearly shown in studying long time phenomena such as the like-particle aggregation since the BDM can effectively minimize the error due to the finite boundary.

Evolution equations obtained from the Kirkwood superposition approximation can describe the effect of like-particle correlations to a certain extent and the BDM can be applied satisfactorily. However, absolute deviation of well-converged numerical result from the exact asymptotic results or with Monte Carlo simulation tells us that the Kirkwood superposition approximation itself in the HSA is yet to be improved.

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