Dynamic correlation effect in reversible diffusion-influenced reactions: Brownian dynamics simulation in three dimensions

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A Brownian dynamics (BD) simulation for a pseudo-first-order diffusion-influenced reversible association–dissociation reaction of a target system in three dimensions with spherical symmetry is presented. The exact Green function for a reversible geminate dissociation that we obtained recently is utilized in the simulation. We compare the results of simulation with two successful theoretical predictions, the enhanced version of the superposition approximation approach (SA) and the more rigorous kinetic theoretical approach (KT). The KT predicts the correct power law behavior of $\sim t^{-3/2}$ with a slightly higher amplitude in the long-time region, but it is in good agreement with the BD result in the transient region. On the other hand, a faster relaxation is observed in the transient region for the SA, but the correct power law behavior with numerically exact amplitude is predicted for the exact target system. An interesting interplay between the mobility of the system and the dynamic correlation effect incorporated with many-body problems is also revealed. © *1999 American Institute of Physics.* [S0021-9606(99)51227-0]

I. INTRODUCTION

Recently, diffusion-influenced reversible reactions have attracted growing interest. Typically, the reversible association–dissociation reaction $[A+B \leftrightarrow C]$ has been studied by many authors.[1–10] In order to check the validity of various theoretical predictions, one has to compare any theoretical result with that of a reliable simulation study.

Edelstein and Agmon[3] developed an efficient Brownian dynamics (BD) simulation method in one dimension (1D) based on the exact Green function for the reversible geminate dissociation. The main advantage of this method over other conventional BD simulations and random walk simulations on the lattice is that the time step can be larger due to the incorporation of the exact solution. For a reversible trap, the probability located near the trap is higher than that for an irreversible one. Therefore the time step should be very small with the conventional BD method. Their simulation study has been a standard reference ever since for comparisons with theoretical works in 1D. Recently, Naumann *et al.*[9] compared their theory of the enhanced superposition approximation for the reversible association–dissociation reaction with the BD result of Edelstein and Agmon[11] in 1D. Essentially the same BD algorithm was adopted by Kim *et al.* to investigate the asymptotic behavior of the pseudo-first-order reversible association–dissociation with photolysis in 1D.[10]

Edelstein and Agmon tried to extend their method to three dimensions (3D) by using three (*x*,*y*,*z* directions) random numbers at each coordinate.[12] This algorithm is superior to other conventional simulation methods in 3D. However, they utilized the 1D Green function to simulate the movement and reaction of particles. Therefore, the error arising from the correlation between coordinates forces their method to have a smaller time step. Zhou[13] proposed his own BD simulation method to study the enzyme-catalyzed reactions. He used the spherically symmetric irreversible 3D probability functions. Since his method neglects the correlation between association and dissociation reactions, the time step again should be small. Note that the crudest BD simulation can give the exact result only if the time step is sufficiently small. Recently, Kim and Shin[14] obtained the exact field-free Green function for the ground-state reversible geminate dissociation in 3D with spherical symmetry. This opens a door to reliable BD studies in 3D. Shortly after the work of Kim and Shin, Gopich and Agmon worked out the exact solution for the excited state with two different lifetimes and with the contact quenching in 3D.[15] They also discovered an interesting transition in the long-time behavior of the solution. As a first attempt to apply the exact solution to the BD simulation in 3D, we investigate, in the present work, the ground-state reversible association–dissociation reaction without the contact quenching for which various theoretical predictions are available.

On the theoretical side, Naumann *et al.*[9] and Sung *et al.*[4] investigated the same system with the enhanced version of the well-known approach of the superposition approximation (SA). In obtaining some analytical results, they adopted the linearized version (LSA). The SA is based on the hierarchical Smoluchowski equations. Sung *et al.*[4] also analyzed the present system depending on the mobility of the system, the target, and the trap problems. For the target problem, *A* is fixed while *B*s can move around, and vice versa for the trap case. A more rigorous kinetic theoretical approach (KT) based on the renormalized kinetic theory has been recently applied to the same system by Yang *et al.*[7] One of the salient

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features of the KT is to reveal the contribution of the dynamic correlation effect of a third particle incorporated with the inherent nature of many-body problems. In Ref. 7, several conventional theories including the SA were critically discussed in this context.

In this paper, we perform the BD simulations in 3D with spherical symmetry for the target problem, and the results are compared with those of the KT and the target version of the SA. Since the KT is originally formulated for the mobile system, it may not be justifiable to compare it directly with the target BD results. But, in doing so, we find some interesting interplay between the mobility of the system and the dynamic correlation effect which is not properly incorporated in the SA.

This paper is organized as follows. In Sec. II, we review theoretical approaches mentioned above and make some critical comparisons between the SA (and the LSA) and the KT. The BD simulation method is described in Sec. III. Simulation results and discussions are presented in Sec. IV, followed by some concluding remarks in Sec. V.

II. THEORETICAL BACKGROUND

The SA, based on the formulation of Lee and Karplus,[1] has been applied rather successfully to many phenomena.[16–20] They derived a rate equation which is coupled to the hierarchical evolution equations of the pair correlation function, starting from the many-body Smoluchowski equation, and truncated the hierarchy by the simple superposition approximation. They also introduced two additional approximations. One is the low concentration of B particle, and the other is the separability of time scales of the bulk concentration and the pair distribution function. The latter can be removed by the linearization technique of Szabo,[2] who showed that the SA could also give the power law behavior of $\sim t^{-d/2}$ in d dimensions in the long-time limit. The enhanced linearized version of SA (LSA) was recently developed by Sung *et al.*[4] They removed the former approximation and thus obtained improved amplitude of the power law behavior. At the same time, Naumann *et al.*[9] also reported the same result independently, focusing on the long-time behavior. They reported that the LSA predicts the exact long-time behavior by comparing with the BD simulation results of Edelstein and Agmon[11] in 1D for the target problem. Despite the successful prediction of the LSA at long times, it still shows unsatisfactory behavior at short and intermediate times, which seems to arise from both the superposition and linearization approximations. In particular, the weakness of the LSA due to the superposition approximation was discussed by Yang *et al.*[7,21,22] as the improper treatment of the dynamic correlation effect inherent with the many-body problem.

Consider a pseudo-first-order reversible reaction system $A+B\leftrightarrow C$ with the equilibrium constant, $K_{\mathrm{eq}}=[C]_{\mathrm{eq}}/c_B[A]_{\mathrm{eq}}=k_r/k_d$, where c_B is the constant bulk concentration of B, and k_r and k_d are the intrinsic recombination and dissociation rate constants, respectively. The main results of the SA for this system, before the linearization step is taken, are the following coupled evolution equations of concentrations and pair correlation functions:[4]

$$\frac{d[A]}{dt}=-k_r\rho_{AB}(\sigma,t)[A]c_B-k_d[C], \tag{2.1a}$$

$$\frac{\partial}{\partial t}\rho_{AB}(r,t)=L_{AB}\rho_{AB}(r,t)-S(r)[k_r\rho_{AB}(r,t)-k_r[C]/[A]c_B]+k_r[\rho_{CB}(r,t)-\rho_{AB}(r,t)][C]/[A], \tag{2.1b}$$

$$\frac{\partial}{\partial t}\rho_{CB}(r,t)=L_{CB}\rho_{CB}(r,t)+k_r\rho_{AB}(\sigma,t)[\rho_{AB}(r,t)-\rho_{CB}(r,t)]\times[A]c_B/[C], \tag{2.1c}$$

where $\rho(r,t)$ is the nonequilibrium pair correlation function, σ the reaction distance, L the Smoluchowski operator, and $S(r)$ denotes the sink function which is assumed to be a contact reactivity here. The initial condition that we consider here is that there are only As ($[A(0)]=1$ normalized such that $[A(t)]+[C(t)]=1$) is surrounded by an equilibrium distribution of Bs[$\rho_{AB}(r,0)=\rho_{CB}(r,0)=1$]. The superposition approximation, compromising both the exact mobility of the system as shown below and the full information on the many-body dynamic correlation effect on the doublet distribution function, was already employed to obtain Eqs. (2.1). Further progress can be made by introducing another approximation regarding L_{CB} which could also change the mobility of the system. Since the mobility of the system, altered by these approximations, is closely coupled to the many-body dynamic correlation effect, it may be appropriate to look into both aspects more carefully.

A. Mobility of the system

In a pure binary problem, only the relative motion of two particles determines the reaction dynamics, and consequently we do not have to distinguish the target from trap or/and mobile systems. The exact mobility of the system starts to be compromised as one considers the ternary dynamics in connection with the dynamic correlation effect that will be discussed in the next section. For a three-particle system in which two B particles (B_1 and B_2) randomly move around a fixed A particle (the target problem), $A-B_1$ and $A-B_2$ pair dynamics can be independent of each other only if there is no interaction between B particles. In this case, it is well-known that the simple superposition approximation becomes exact even for the pseudo-first-order irreversible system.[23] On the other hand, for the system in which two B particles are fixed and an A particle moves around (the trap problem), two pair dynamics ($A-B_1$ and $A-B_2$) could not be independent because there is only one degree of freedom due to the moving A particle. In this case, the superposition approximation cannot be exact with respect to the mobility, even in the irreversible system.

Up to the stage of Eqs. (2.1), the SA formulation is carried out defining neither the target nor the trap problem. Strictly speaking, the SA starts from a certain system in

which the mobility of particles is described by the self-diffusion constants of each particle at various levels of the hierarchy. In principle, the mobility of the system can be described exactly by this infinite hierarchy. However, by taking the superposition approximation to make a closed set of equations up to the doublet level, the exact description of the mobility of the system is also compromised.

In fact, the usual practice is that the target problem (it actually is a pseudo-target problem) is defined by setting $L_{CB}=L_{AB}$ (and, thus, $D_{CB}=D_{AB}$) in Eqs. (2.1). In the pseudo-first-order case ($[A]$ or $[C]\ll c_B$), this relation could approximately describe a system in which A (and thus C) particles are fixed while B particles are mobile with the diffusion constant $D_B=D$; thus, the target problem. However, it is interesting to note that, even if Eqs. (2.1) were exact for the target problem, the relation $D_{CB}=D_{AB}$ holds not only for the target problem but also for the system in which both A and C particles are mobile with the same diffusion constant, $D_A=D_C$, and B particles can have a different mobility with D_B. This makes the uniqueness of Eqs. (2.1) questionable regarding the mobility of the system, which is inevitable as long as one introduces any approximation to many-body problem such as the truncation of the hierarchical equations. Therefore, we believe that the mobility of a system should be handled rather carefully in connection with the truncation which alters the nature of the dynamic correlation effect. Nevertheless, the approximation of $D_{CB}=D_{AB}$ is usually taken for the target problem and, somehow, the long-time behavior of the LSA is known to be numerically in good agreement, in 1D, with the BD simulation for the exact target problem. The usual trap problem is defined by setting $L_{CB}=0$, which represents the system in which B (and thus C) particles are fixed ($D_B=D_C=0$) while A particles are mobile with the diffusion constant, $D_A=D$. There appears to be no problem in the uniqueness, if Eqs. (2.1) were exact, for the trap problem.

In the LSA formulation, the linearization technique is employed to Eqs. (2.1) and, also, the usual target or the trap problem has to be chosen in order to get approximate analytical expressions. For the usual target problem, the concentration deviation $\xi(t)\equiv[A]-[A]_{\rm eq}$ is obtained in the Laplace transformed domain, $\hat{f}(z)\equiv\int_0^\infty f(t)\exp(-zt)dt$, as follows:[4]

$$\hat{\xi}_{\rm LSA}^{\rm target}(z)=[z+(c_B+K_{\rm eq}^{-1})\hat{\kappa}_{\rm LSA}(z)]^{-1}, \tag{2.2a}$$

$$\frac{1}{\hat{\kappa}_{\rm LSA}(z)}=\frac{1}{k_r}+\frac{c_BK_{\rm eq}}{1+c_BK_{\rm eq}}\cdot\frac{1}{\hat{k}_D(s)}\bigg|_{s=z+(c_B+K_{\rm eq}^{-1})k_r}+\frac{1}{1+c_BK_{\rm eq}}\cdot\frac{1}{\hat{k}_D(z)}, \tag{2.2b}$$

$$\hat{k}_D(z)=k_D[1+\sqrt{\sigma^2z/D}], \tag{2.2c}$$

where D is the diffusion constant of B particles relative to fixed A (and thus C) particles and $k_D=4\pi\sigma D$. The superscript *target* denotes that the relation $L_{AB}=L_{CB}$ is utilized to solve Eqs. (2.1b) and (2.1c). From Eqs. (2.2a)–(2.2c), one can obtain the long-time asymptotic expression of the concentration deviation as

$$\lim_{t\to\infty}\xi_{\rm LSA}^{\rm target}(t)\sim\frac{K_{\rm eq}}{(1+c_BK_{\rm eq})^2}(4\pi Dt)^{-3/2}. \tag{2.3}$$

For the usual trap case, the concentration deviation is obtained as

$$\hat{\xi}_{\rm LSA}^{\rm trap}(z)=\left[z+\frac{k_rc_B+k_d}{1+\hat{k}_D(z+k_rc_Bz/(z+k_d))}\right]^{-1}, \tag{2.4}$$

and the long-time asymptotic expression is given by

$$\lim_{t\to\infty}\xi_{\rm LSA}^{\rm trap}(t)\sim\frac{K_{\rm eq}}{\sqrt{1+c_BK_{\rm eq}}}(4\pi Dt)^{-3/2}. \tag{2.5}$$

Note that the above equation was first obtained by Gopich and Doktorov[8] using the scale transformation of exact series without their average t-matrix approximation.

Recently, Yang *et al.* applied the fully renormalized kinetic theory to the present reaction scheme.[7] They started with a reaction-Liouville equation satisfying in the phase space for all particles of the system. They derived a memory equation for the singlet field of reactants by use of the Mori's projection operator technique. A many-body effect is incorporated into the memory kernel with a renormalized hierarchical structure, which was truncated by the disconnected approximation. This formulation was quite successfully applied to the steady-state fluorescence quenching kinetics,[21] and the reversible reaction kinetics of $A+B\leftrightarrow C+B$.[22] In the application to the current system, the KT predicted a satisfactory behavior in the transient region. The predictions of the KT are given by

$$\hat{\xi}_{\rm KT}(z)=[z+(c_B+K_{\rm eq}^{-1})\hat{\kappa}_{\rm KT}(z)]^{-1}, \tag{2.6a}$$

$$\frac{1}{\hat{\kappa}_{\rm KT}(z)}=\frac{1}{k_r}+\frac{c_BK_{\rm eq}}{1+c_BK_{\rm eq}}\cdot\frac{1}{\hat{k}_D(s)}\bigg|_{s=z+(c_B+K_{\rm eq}^{-1})\hat{\kappa}_{\rm KT}(z)}+\frac{1}{1+c_BK_{\rm eq}}\cdot\frac{1}{\hat{k}_D(z)}. \tag{2.6b}$$

The same initial condition as in the SA was employed here. In deriving Eqs. (2.6), the off-diagonal elements of the diffusion tensor were neglected, and it was also assumed that $D_{AB}=D_{CB}$. The latter assumption is in the same spirit as that employed in the LSA for the usual target problem. As mentioned earlier, however, this may also correspond to a mobile system approximately, namely, A and C particles with the same mobility and B particles with a different mobility. Previously, we attempted to interpret our system as mobile rather than as the usual target problem.[22] Whether a system can be treated as the target problem or as mobile can only be determined *a posteriori* from the comparison with

the simulation study which is designed exactly, from the beginning, as one of those unless the exact description of the dynamic correlation effect is provided.

B. The dynamic correlation effect

The LSA and the KT are similar to each other in the sense that Eqs. (2.2a) and (2.6a) can be rewritten as memory (rate kernel) equations for the concentration deviation in the time domain. However, two theories are different in the second terms of Eqs. (2.2b) and (2.6b), which contain the many-body effect influencing the dynamics of a specific pair of particles via the rate kernels in the argument of the diffusive rate kernel $\hat{k}_D(z)$. Both theories require certain truncation steps for the hierarchical set of equations in the formulation. The simple superposition approximation is employed at the level of the doublet reduced distribution function (SA), and the disconnected approximation is employed to the propagator at the level of the doublet density field (KT); it was pointed out earlier that the latter approximation is more fine-grained than the former.[21] As a result, the dynamic correlation effect of the third bath molecule is included self-consistently in the KT while the Markovian description resulted in the LSA. Based on this difference in both approaches, Yang *et al.* suggested that the shortcoming of the LSA should result from the neglect of the dynamic correlation effect of the third particle on the evolution of the reactive pair of particles. Namely, the LSA describes the system that a specific pair propagates while other B particles are at equilibrium, which makes the relaxation faster and causes the error of the faster decay of the deviation function in the transient region. The KT also shows the same power law behavior in the long-time limit as in the SA but with different amplitude. The long-time asymptotic expression of the deviation function is given by

$$\lim_{t\to\infty} \xi_{\mathrm{KT}}(t) \sim \frac{K_{\mathrm{eq}}}{(1+c_B K_{\mathrm{eq}})^2 (1-P)} (4\pi D t)^{-3/2}, \qquad (2.7)$$

where the factor P incorporates the dynamical correlation effect still remaining in the power law region, which the LSA neglects [see Eq. (2.3)]. The expression for that can be found in Ref. 7. By comparing Eqs. (2.3) and (2.7), even though the numerical value of the LSA is indiscernible from the simulation data, Yang *et al.* questioned Naumann *et al.*'s claim that Eq. (2.3) should be exact.

However, the LSA which is a limiting case of the SA, as given by Eqs. (2.1), could represent the latter only near the equilibrium, and thus the above limitation of the LSA may not be relevant to the prediction of the SA in the transient time region. This motivates us to examine the dynamic information contained in the SA before the linearization technique is introduced. In fact, Sung *et al.* reported that the results of the LSA were hardly distinguishable from those of the SA, even in the transient region.[4] Based on their report and assuming that the linearization technique is valid near the equilibrium, Yang *et al.* pointed out earlier that the lack of the dynamic correlation (which should exist in a real system even near the equilibrium) in the LSA should be ascribed to the superposition approximation itself.[12] However,

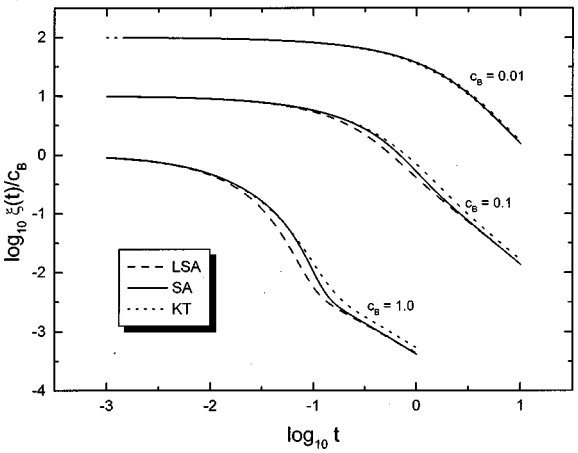

FIG. 1. Comparison between the SA and the LSA through the time dependence of the concentration deviation for several values of c_B. The KT result is also plotted for a reference. $k_r=125.0$, $k_d=5.0$, and $D=\sigma=1$.

it may be required to compare the LSA with the SA for a wide range of parameter sets to confirm their coincident predictions.

In Fig. 1, we plot the results of the LSA and the SA for several concentrations of B for a comparison. The parameters used are $D=\sigma=1$, $k_r=125.0$, and $k_d=5.0$. We add the result of the KT as a reference. We use the FLINV routine in the IMSL[24] in order to invert the results of the LSA and the KT in the Laplace transformed domain and the numerical method of Kim *et al.*[25,26] to obtain those of the SA. The deviation among all three theories is small for $c_B=0.01$, where the dynamic correlation effect is expected to be small, but becomes larger as c_B increases. It should be noted that the results of the LSA and the SA are already indistinguishable prior to the $t^{-3/2}$ power-law phase. (The slope is about -1.0 at the value of $\log_{10} t=-0.5$ in the curve of $c_B=1.0$.) As previously mentioned, the neglect of the dynamic correlation effect in the LSA is shown to make the relaxation faster. From this comparison, one can see that the dynamic correlation effect is partially included in the SA in contrast with the LSA. Based on this observation, we can conclude that the lack of the dynamical correlation effect in the LSA may be due not only to the superposition approximation but also, at least partially, to the linearization approximation. We can also find, from the coincidence of the amplitude of the power law behavior predicted by both the SA and the LSA, that the dynamic correlation effect incorporated into the SA does not seem to affect the long-time dynamics. A possible explanation of this fact is that the long-time dynamic correlation effect in the SA may have a higher order contribution (e.g., $\sim t^{-5/2}$) than the long-time power law behavior ($t^{-3/2}$) of the evolution of the pair.

On the other hand, the long-time behavior predicted by the KT shows a slightly higher amplitude compared with the SA (and the LSA) due to the correction factor P in Eq. (2.7). The difference between the SA and the KT in the prediction of the amplitude of the power law behavior was ascribed to the different ways of treating the dynamic correlation effect as discussed previously.[22] Recalling the discussion of the mobility in Sec. II A, the difference may well have arisen

from introducing the usual target relation at different stages of the formulation in two theories. Moreover, it is probable that the dynamic correlation effect and the mobility assumption are closely coupled to each other. The possibility of interpreting the usual target relation as describing a mobile system makes the situation more difficult. This confusion can be cleared when we compare these theoretical predictions with a computer simulation. At present, the KT is developed only for the case of 3D, and the computer simulation in 3D is required to compare with the KT and the SA (and the LSA). This motivates us to develop a BD simulation method in 3D.

III. BD SIMULATION

The overall method of the present BD simulation is very similar to that of Edelstein and Agmon[3] in 1D. We assumed that the direct correlations between the noninteracting like particles (Bs) may be ignored and the particle A (or C) is immobile, which represents an exact target problem. From these assumptions, we can realize the pseudo-first-order system taking advantage of the exact Green functions for an isolate pair without loss of accuracy. One assumption to realize in the many-particle system is that the remaining particles are fixed when one particle moves or reacts, which may cause error at short times less than one time step.

From the practical viewpoint, the main difficulty for the 3D simulation is that one cannot increase the boundary (R) easily as in the 1D case because the number of particles, $N \sim R^3$ to maintain the same concentration, namely, a thousand times N, are needed to increase R ten times. Therefore, one should be very careful of the finite system size error.

In our simulation, an A (or C) particle is regarded as a fixed target, representing the *real* target problem. Only B particles can move around in our simulation. We put one target (A or C) at the origin of the spherically symmetric radial coordinate, r, and N particles of B into the interval $[\sigma,R]$ randomly. Note that a uniform distribution in the 3D space corresponds to the distribution $p(r)=3r^2/(R^3-\sigma^3)$ in the radial coordinate.[13]

Then, the particle B may move or react with A one by one. Each particle has only one chance to change its position during one time step by generating a random list. After the trials of all particles, one can continue the next step.

One particle is randomly selected and moved to a new location, which is calculated as follows. When the selected particle is in the bound state (*), it will remain there with the probability of $p(*,\Delta t|*)$ or move to r with the probability of

$$\int_\sigma^r dr'\, 4\pi r'^2 p(r',\Delta t|*)$$

after Δt. When an unbound particle at r_0 is selected, it will end up at the target with the probability of $p(*,\Delta t|r_0)$ or move to r with the probability of

$$\int_\sigma^r dr'\, 4\pi r'^2 p(r',\Delta t|r_0).$$

All the necessary probability functions were obtained by Kim and Shin[14] from their exact Green function in 3D as follows:

$$\begin{aligned} p(r,t|r_0)4\pi r r_0\sqrt{D} &= \frac{1}{\sqrt{4\pi t}}\left\{\exp\left[-\frac{(r-r_0)^2}{4Dt}\right]+\exp\left[-\frac{(r+r_0-2\sigma)^2}{4Dt}\right]\right\} \\ &+\frac{\alpha(\gamma+\alpha)(\alpha+\beta)}{(\gamma-\alpha)(\alpha-\beta)}W\left(\frac{r+r_0-2\sigma}{\sqrt{4Dt}},\alpha\sqrt{t}\right) \\ &+\frac{\beta(\alpha+\beta)(\beta+\gamma)}{(\alpha-\beta)(\beta-\gamma)}W\left(\frac{r+r_0-2\sigma}{\sqrt{4Dt}},\beta\sqrt{t}\right) \\ &+\frac{\gamma(\beta+\gamma)(\gamma+\alpha)}{(\beta-\gamma)(\gamma-\alpha)}W\left(\frac{r+r_0-2\sigma}{\sqrt{4Dt}},\gamma\sqrt{t}\right), \end{aligned} \tag{3.1}$$

$$\begin{aligned} p(*,t|r_0) &= \frac{k_r}{4\pi r_0\sigma\sqrt{D}}\left\{\frac{\alpha}{(\gamma-\alpha)(\alpha-\beta)}W\left(\frac{r_0-\sigma}{\sqrt{4Dt}},\alpha\sqrt{t}\right)\right. \\ &+\frac{\beta}{(\alpha-\beta)(\beta-\gamma)}W\left(\frac{r_0-\sigma}{\sqrt{4Dt}},\beta\sqrt{t}\right) \\ &\left.+\frac{\gamma}{(\beta-\gamma)(\gamma-\alpha)}W\left(\frac{r_0-\sigma}{\sqrt{4Dt}},\gamma\sqrt{t}\right)\right\}, \end{aligned} \tag{3.2}$$

$$\begin{aligned} p(r,t|*) &= \frac{k_d}{4\pi r\sigma\sqrt{D}}\left\{\frac{\alpha}{(\gamma-\alpha)(\alpha-\beta)}W\left(\frac{r-\sigma}{\sqrt{4Dt}},\alpha\sqrt{t}\right)\right. \\ &+\frac{\beta}{(\alpha-\beta)(\beta-\gamma)}W\left(\frac{r-\sigma}{\sqrt{4Dt}},\beta\sqrt{t}\right) \\ &\left.+\frac{\gamma}{(\beta-\gamma)(\gamma-\alpha)}W\left(\frac{r-\sigma}{\sqrt{4Dt}},\gamma\sqrt{t}\right)\right\}, \end{aligned} \tag{3.3}$$

$$\begin{aligned} p(*,t|*) &= \frac{\alpha(\beta+\gamma)}{(\gamma-\alpha)(\alpha-\beta)}\Omega(\alpha\sqrt{t}) \\ &+\frac{\beta(\gamma+\alpha)}{(\alpha-\beta)(\beta-\gamma)}\Omega(\beta\sqrt{t}) \\ &+\frac{\gamma(\alpha+\beta)}{(\beta-\gamma)(\gamma-\alpha)}\Omega(\gamma\sqrt{t}), \end{aligned} \tag{3.4}$$

where $W(a,b)\equiv\exp(2ab+b^2)\mathrm{erfc}(a+b)$, $\Omega(a)\equiv\exp(a^2)\mathrm{erfc}(a)$ and $\mathrm{erfc}(x)$ denotes the complementary error function. α, β, and γ satisfy the following relations:

$$\alpha+\beta+\gamma=(1+k_r/k_D)\sqrt{D}/\sigma, \tag{3.5}$$

$$\alpha\beta+\beta\gamma+\gamma\alpha=k_d, \tag{3.6}$$

$$\alpha\beta\gamma=k_d\sqrt{D}/\sigma. \tag{3.7}$$

It is worthwhile to note the detailed balance condition, $k_r p(r,t|*)=k_d p(*,t|r)$.

The endpoint of the stochastic trajectory (r_ξ) can be

found by comparing a uniform distribution random number, $0<\xi<1$, such that

$$\xi - p(*,\Delta t) = \int_{\sigma}^{r_\xi} p(r,\Delta t)\,dr. \tag{3.8}$$

The calculation of the trajectory for every particle at every step is the most time-consuming part. We introduce the precalculated look-up tables constructed from the above probability functions. The look-up table method reduces the computing time greatly, but requires much more memory space. The following relations are useful to construct the look-up tables:

$$\begin{aligned}
Q(r,t|r_0) &\equiv \int_{\sigma}^{r} dr'\, 4\pi r'^2 p(r',t|r_0) + p(*,t|r_0) \\
&= -\frac{\sqrt{Dt}}{r_0\sqrt{\pi}}\left(\exp\left(-\frac{(r-r_0)^2}{4Dt}\right) - \exp\left(-\frac{(r+r_0-2\sigma)^2}{4Dt}\right)\right) + \frac{1}{2}\left(\operatorname{erf}\left(\frac{r-r_0}{\sqrt{4Dt}}\right)\right. \\
&\quad \left. + \operatorname{erf}\left(\frac{r+r_0-2\sigma}{\sqrt{4Dt}}\right)\right) + \frac{1}{r_0}\left(r-\frac{\sqrt{D}}{\alpha}\right)\frac{(\gamma+\alpha)(\alpha+\beta)}{(\gamma-\alpha)(\alpha-\beta)} W\left(\frac{r+r_0-2\sigma}{\sqrt{4Dt}}, \alpha\sqrt{t}\right) \\
&\quad + \frac{1}{r_0}\left(r-\frac{\sqrt{D}}{\beta}\right)\frac{(\alpha+\beta)(\beta+\gamma)}{(\alpha-\beta)(\beta-\gamma)} W\left(\frac{r+r_0-2\sigma}{\sqrt{4Dt}}, \beta\sqrt{t}\right) + \frac{1}{r_0}\left(r-\frac{\sqrt{D}}{\gamma}\right)\frac{(\beta+\gamma)(\gamma+\alpha)}{(\beta-\gamma)(\gamma-\alpha)} W\left(\frac{r+r_0-2\sigma}{\sqrt{4Dt}}, \beta\sqrt{t}\right),
\end{aligned} \tag{3.9}$$

$$\begin{aligned}
Q(r,t|*) &\equiv \int_{\sigma}^{r} dr'\, 4\pi r'^2 p(r',t|*) + p(*,t|*) \\
&= \operatorname{erf}\left(\frac{r-\sigma}{\sqrt{4Dt}}\right) + \frac{k_d}{\sigma}\left(r-\frac{\sqrt{D}}{\alpha}\right)\frac{1}{(\gamma-\alpha)(\alpha-\beta)} W\left(\frac{r-\sigma}{\sqrt{4Dt}}, \alpha\sqrt{t}\right) + \frac{k_d}{\sigma}\left(r-\frac{\sqrt{D}}{\beta}\right)\frac{1}{(\alpha-\beta)(\beta-\gamma)} W\left(\frac{r-\sigma}{\sqrt{4Dt}}, \beta\sqrt{t}\right) \\
&\quad + \frac{k_d}{\sigma}\left(r-\frac{\sqrt{D}}{\gamma}\right)\frac{1}{(\beta-\gamma)(\gamma-\alpha)} W\left(\frac{r-\sigma}{\sqrt{4Dt}}, \gamma\sqrt{t}\right).
\end{aligned} \tag{3.10}$$

One can confirm $Q(\infty,t)=1$ easily. The look-up tables can be constructed monotonic in order to perform the easy look-up procedure.

The reflecting boundary condition is used in the present simulations at the outer boundary ($r=R$). And when a particle is already bound to the fixed target, namely, transformed to the C state, the inner boundary ($r=\sigma$) is also regarded as the reflecting one because other particles cannot react with the target anymore. The probability functions should be changed to the following well-known Green function with the reflecting boundary, instead of Eq. (3.1):

$$\begin{aligned}
p(r,t|r_0) 4\pi r r_0 \sqrt{D} &= \frac{1}{\sqrt{4\pi t}}\left\{\exp\left[-\frac{(r-r_0)^2}{4Dt}\right] + \exp\left[-\frac{(r+r_0-2\sigma)^2}{4Dt}\right]\right\} \\
&\quad - \frac{\sqrt{D}}{\sigma} W\left(\frac{r+r_0-2\sigma}{\sqrt{4Dt}}, \frac{\sqrt{Dt}}{\sigma}\right).
\end{aligned} \tag{3.11}$$

IV. RESULTS AND DISCUSSION

In order to verify the methodology of the present simulation, we compare the simulation result with those of the SA and the KT in Fig. 2. The time dependence of the concentration deviation, $\xi(t)$, is plotted in the log–log scale. The chosen values of parameters are $c_B=0.001$, $k_r=125.0$, $k_d=5.0$, and $D=\sigma=1$. For these parameters, both the SA and the KT predict almost the same results. The result of simulation is also shown to be indistinguishable from the theoretical predictions. The different descriptions of the mobility of the system as well as the dynamic correlation effect by the SA and the KT do not appear at this low concentration of B. Interestingly, we found that the finite system size error makes the relaxation slower in 3D, while it is faster in 1D. We increased the size of the simulation system until the converged results were obtained.

In Fig. 3, the relaxation curves of the concentration deviation are plotted but the values of parameters are changed, such that $c_B=1.0$, $k_r=125.0$, and $k_d=50.0$. For these values, two theories predict the different behaviors in both the transient and the long-time regions. Furthermore, the simulation result supports neither the KT nor the SA for the entire time domain. Prior to the asymptotic power law region, the simulation results follow the prediction of the KT but support the SA in the long-time power law region. This trend is again found in Fig. 4, where the values of parameters are the same as those of Fig. 3, except $k_d=5.0$. Note that, in general, the larger $c_B K_{\mathrm{eq}}$, the more severe test for the theories. For these parameters, the deviation of the SA from the BD simulation is larger than that in Fig. 3 in the transient region, but the SA is still good in the power law region at long times. The good

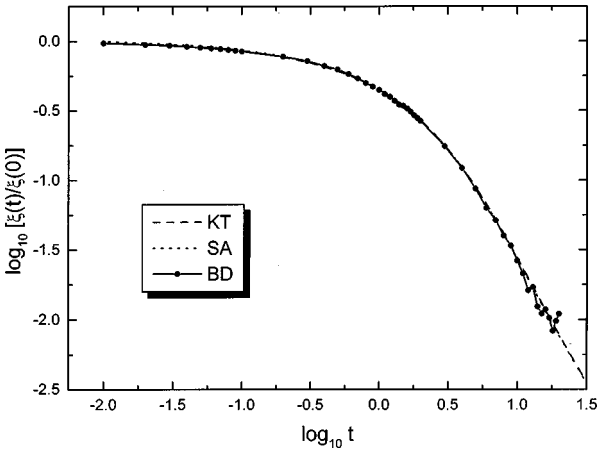

FIG. 2. Comparison of the BD result with those of the SA and the KT through the time dependence of the concentration deviation. $c_B=0.001$, $k_r=125.0$, $k_d=5.0$, and $D=\sigma=1$.

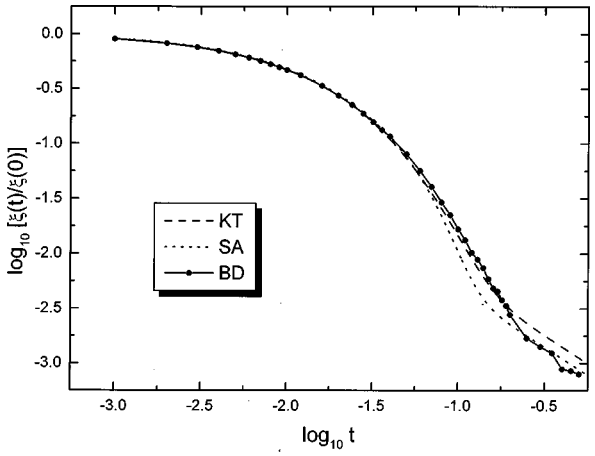

FIG. 4. The same as Fig. 2, except $c_B=1.0$.

agreement of the KT with the simulation in the transient region shows that the dynamical correlation effect plays an important role during the transient relaxation period to make a slower relaxation compared with the SA, which accounts for it only partially. On the other hand, the coincidence of the SA and the BD results in the power law region tells us that, since the BD simulation is designed for the exact target problem, the SA for the usual target problem is also numerically exact for the exact target problem in the long-time power law region in 3D. This is in line with the previous result of Naumann *et al.* that the usual target version of the LSA for the present reversible system becomes numerically exact in the long-time limit in 1D. Of course, it is well-known that the SA for the irreversible reaction system describes the target system exactly. For the reversible system, it is now confirmed that the LSA is also exact in 3D, at least numerically, in the long-time limit for the exact target problem.

The dynamic correlation effect does not seem to appear in the SA in the power law behavior of the target system. This may not mean the absence of the dynamic correlation effect in the SA formulation in the power law region. Rather, we suspect that it has a higher order contribution than $t^{-3/2}$ to the relaxation kinetics and is not exposed in the lowest-order term to have any effect on the power law behavior. A similar explanation may also be given for the long-time dynamic correlation effect of the BD simulation for the exact target system. On the other hand, the long-time dynamic correlation effect in the KT makes a contribution to the lowest-order ($t^{-3/2}$) relaxation behavior, and this alters the amplitude of the power law from that of the SA (or the BD).

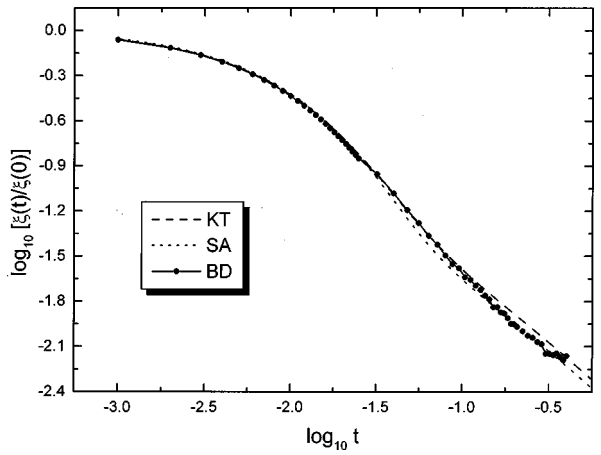

FIG. 3. The same as Fig. 2, except $c_B=1.0$, and $k_d=50.0$.

In the KT formulation, the long-time dynamic correlation effect is included through the factor P in Eq. (2.7), which is absent in the LSA result of Eq. (2.3). From the observation of a slightly higher amplitude of the KT result compared with that of the BD in the power law region, we can conclude that the dynamic correlation effect self-consistently considered by the KT does not represent that of the exact target system. This fact was discussed previously,[22] in which the irreversible survival probability predicted by the KT is a little bit different from that of the exact target system (presented in Fig. 1(b) in Ref. 22). In our previous works, we suggested that the KT is an approximate model for a mobile system, although we employed the approximation of $D_{AB}=D_{CB}$, since this relation can represent not only the usual target problem but also a mobile system, as we pointed out in Sec. II A.

From the above discussions, we believe that a system with a certain mobility (say, the exact target problem) has a different dynamic correlation effect from that of another system with different mobility (say, a mobile system). The different dynamic correlation effect associated with the different mobility appears as a faster (or a slower) relaxation behavior in the transient region, or in the different amplitude of the power law behavior in the long-time limit. The origin of the difference in the amplitude of the power law behavior between the SA and the KT can actually be investigated from the comparison with a reliable simulation study for the mobile system. As of now, neither the reliable simulation study nor the exact theory is available for the mobile system.

V. CONCLUDING REMARKS

We have investigated the pseudo-first-order diffusion-influenced association–dissociation reaction with the BD

simulation study in 3D for a spherically symmetric system, with the aid of the exact field-free ground-state Green function for the reversible geminate dissociation recently obtained by Kim and Shin.[14] The simulation results are compared with those of the SA and the KT formulations. The main conclusions are as follows:

(1) The dynamic correlation effect appears to be closely associated with the mobility of the system. The exact mobility is known only for the BD simulation for the exact target problem. In the SA (or the LSA), the usual target assumption may not be justified as the target approximation.
(2) The dynamic correlation effect is partially accounted for in the SA, and the lack of the dynamic correlation effect in the LSA is due not only to the simple superposition approximation but also to the linearization technique.
(3) The long-time behaviors of the SA and the LSA are coincident, indicating that the dynamic correlation effect as accounted for in the SA may have a higher order contribution to the long-time relaxation kinetics than the power law behavior of $t^{-3/2}$. A similar behavior may also be ascribed to the BD simulation.
(4) The BD simulation for the exact target problem is in good agreement with the KT in the transient region and with the SA for the usual target problem in the power law region, respectively. This tells us that the dynamic correlation effect is important in the transient dynamics. However, the long-time behavior of the SA for the usual target problem is numerically exact in 3D also for the exact target problem.
(5) A slightly higher amplitude of the power law behavior in the KT shows that the KT formulation may not be appropriate for the exact target problem in the long-time region. It can be easily figured out that the usual target assumption may also be employed for a mobile system, a reliable simulation study for the mobile system is required in order to clarify this point.

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