Excited-state diffusion-influenced reversible association–dissociation reaction: Brownian dynamics simulation in three dimensions

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Excited-state diffusion-influenced reversible reaction, $A^*+B\rightleftarrows C^*$, is investigated in three dimensions by suitably modifying the Brownian dynamics simulation algorithm of Edelstein and Agmon [J. Chem. Phys. **99**, 5396 (1993)] which requires the exact Green functions of the geminate system. The proposed simulation algorithm is based on using the mixed look-up tables. For the excited bound state, the unimolecular decay is coupled to the reactive movement and its trajectory can be calculated with the aid of the excited-state look-up table. On the other hand, the unimolecular decay of the excited unbound state is assumed to be independent of the reactive movement and its trajectory is calculated with the ground-state look-up table. The optimum size of the time step is found by fitting simulations performed for the geminate case to the analytic result. The simulation results with varying concentration of *B* particles as well as the ratio of unimolecular decay constants are in excellent agreement with the kinetic theoretical predictions of Kwac *et al.* [J. Chem. Phys. **114**, 3883 (2001)]. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1492282]

I. INTRODUCTION

Recently, the excited-state diffusion-influenced reaction, $A^*+B\rightleftarrows C^*$, has been investigated. For the geminate case, Gopich and Agmon[1–4] succeeded in obtaining exact Green functions for the geminate system in three dimensions (3D) as well as an interesting kinetic transition behavior in the long time asymptotic region. When the lifetime of the unbound state (A^*) is different from that of the bound state (C^*), they discovered a transition between two types of behaviors. In the *A* regime, the excited bound pair decays as $t^{-3/2}\exp(-k_0' t)$, where $k_0'^{-1}$ is the lifetime of the unbound state. A pure exponential decay is obtained in the *AB* regime. These two regimes are connected at the critical value of the parameters and the transition decay follows $t^{-1/2}\exp(-k_0' t)$ behavior.

Extension of Gopich and Agmon's work[1–4] to the pseudo-first-order system in which $[A^*]$, $[C^*] \ll [B]=c_B$ (constant in time) has been recently carried out by Kwac *et al.*[5] by reformulating the renormalized kinetic theoretical formulation of Yang *et al.*[6] in the configuration space. Differently from the geminate system, they found that the evolution of the effective survival probability in the pseudo-first-order system shows exponentially increasing or decreasing regions separated by a transition region depending on the ratio of two lifetimes. The transition line appears when the lifetimes of bound and unbound states are equal ($k_0=k_0'$) and its asymptotic value is equal to the equilibrium value for the ground-state system.

The purpose of the present work is to verify the theoretical predictions of Kwac *et al.*[5] with the Brownian dynamics (BD) simulation. Some time ago, Edelstein and Agmon[7] developed an efficient BD simulation method for the ground-state pseudo-first-order reversible reaction of $A+B\rightleftarrows C$ in one dimension (1D). Their method is based on the exact Green function for the ground-state reversible geminate dissociation in 1D obtained by Agmon.[8] The main advantage of this method is that the time step can be larger compared to other conventional BD simulations due to the incorporation of the exact solution.

The exact Green function for the ground-state reversible geminate dissociation in 3D with spherical symmetry obtained by Kim and Shin[9] makes it possible to extend the above BD simulation method to 3D. Actually, Kim *et al.*[10] performed the BD simulation for the pseudo-first-order reaction system of $A+B\rightleftarrows C$ in 3D to investigate the long time asymptotic behavior but it turned out that, due to large fluctuations inherent in 3D simulations, their simulation could not reach the true power-law long time asymptotic region. Recently, Popov and Agmon[11] modified their original algorithm and succeeded in carrying out the BD simulation in 3D to sufficiently long times revealing the ultimate power-law asymptotic behavior.

However, the above efficient BD simulation has not been carried out for the excited-state reversible dissociation reaction. With the exact Green functions for the excited-state reversible dissociation reaction in 3D obtained by Gopich and Agmon[4] and in 1D by Kim *et al.*,[12] we should be able to perform the BD simulations for the excited-state reaction system in both dimensions. Since the theoretical predictions of Kwac *et al.*[5] in 3D shows only exponentially increasing or decreasing behavior at long times, we believe that the earlier BD simulation algorithm of Edelstein and Agmon[7] extended to 3D should be sufficient enough to confirm the theoretical results without resorting to more elaborate algorithm of Popov and Agmon.[11]

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In this paper, we perform BD simulations for the excited-state pseudo-first-order reversible diffusion-influenced reaction ($A^*+B\rightleftarrows C^*$) in 3D by suitably adapting the algorithm of Edelstein and Agmon and the results are compared with the kinetic theoretical predictions of Kwac *et al.*[5]

This paper is organized as follows. In Sec. II we review the theoretical backgrounds on the excited-state reversible reaction for both the geminate and pseudo-first-order systems. In Sec. III, we propose an appropriate BD simulation method in the excited-state reaction by utilizing the mixed look-up tables. The simulation results are presented in Sec. IV followed by a summary with some concluding remarks presented in Sec. V.

II. THEORETICAL BACKGROUND

The reaction system of interest is schematically written as

$$A^*+B\underset{k_d}{\overset{k_a}{\rightleftarrows}}C^*,$$

$$A^*\xrightarrow{k_0'}A,$$

$$C^*\xrightarrow{k_0}C,$$

where* denotes the excited state, k_a and k_d are the rate constants for association and dissociation, respectively. Unimolecular decay rate constants for the bound (C^*) and unbound (A^*) excited states are denoted as k_0 and k_0', respectively.

A. Geminate case

Let $p(r,t|r_0)$ be the probability of finding the unbound excited pair (A^* and B) separated by a distance r at time t given that it was initially separated by r_0. Gopich and Agmon[4] assumed that the time evolution of $p(r,t|r_0)$ obeys a Smoluchowski-type equation which is coupled to a kinetic equation for the probability $p(*,t|r_0)$ of finding the geminate pair in the excited bound state (C^*) at time t. For the case without interaction potential between A^* and B, they obtained

$$p(r,t|r_0)e^{k_0't}=\frac{1}{4\pi r r_0}\left\{\frac{1}{\sqrt{4\pi Dt}}\left\{\exp\left[\frac{(r-r_0)^2}{4Dt}\right]+\exp\left[-\frac{(r+r_0-2\sigma)^2}{4Dt}\right]\right\}-\frac{\alpha(\gamma+\alpha)(\alpha+\beta)}{(\gamma-\alpha)(\alpha-\beta)}W\left(\frac{r+r_0-2\sigma}{\sqrt{4Dt}},-\alpha\sqrt{Dt}\right)\right.$$
$$\left.-\frac{\beta(\alpha+\beta)(\beta+\gamma)}{(\alpha-\beta)(\beta-\gamma)}W\left(\frac{r+r_0-2\sigma}{\sqrt{4Dt}},-\beta\sqrt{Dt}\right)-\frac{\gamma(\beta+\gamma)(\gamma+\alpha)}{(\beta-\gamma)(\gamma-\alpha)}W\left(\frac{r+r_0-2\sigma}{\sqrt{4Dt}},-\gamma\sqrt{Dt}\right)\right\}, \tag{2.1}$$

where $W(p,q)\equiv\exp(2pq+q^2)\mathrm{erfc}(p+q)$, σ is the reaction distance, and $\mathrm{erfc}(x)$ denotes the complementary error function. α, β, and γ satisfy the following relations:

$$\alpha+\beta+\gamma=-(k_D+k_a)/(\sigma k_D), \tag{2.2a}$$

$$\alpha\beta+\beta\gamma+\gamma\alpha=(k_0-k_0'+k_d)/D, \tag{2.2b}$$

$$\alpha\beta\gamma=-[(k_D+k_a)(k_0-k_0'+k_d)-k_ak_d]/(D\sigma k_D), \tag{2.2c}$$

with $k_D=4\pi D\sigma$ the diffusion-controlled rate constant. D is the relative diffusion constant between A^* and B. They also obtained other Green functions,

$$p(*,t|r_0)e^{k_0't}=-\frac{k_a}{r_0k_D}\left[\frac{\alpha}{(\gamma-\alpha)(\alpha-\beta)}W\left(\frac{r_0-\sigma}{\sqrt{4Dt}},-\alpha\sqrt{Dt}\right)\right.$$
$$+\frac{\beta}{(\alpha-\beta)(\beta-\gamma)}W\left(\frac{r_0-\sigma}{\sqrt{4Dt}},-\beta\sqrt{Dt}\right)$$
$$\left.+\frac{\gamma}{(\beta-\gamma)(\gamma-\alpha)}W\left(\frac{r_0-\sigma}{\sqrt{4Dt}},-\gamma\sqrt{Dt}\right)\right], \tag{2.3}$$

$$p(r,t|*)e^{k_0't}=-\frac{k_d}{rk_D}\left[\frac{\alpha}{(\gamma-\alpha)(\alpha-\beta)}W\left(\frac{r-\sigma}{\sqrt{4Dt}},-\alpha\sqrt{Dt}\right)\right.$$
$$+\frac{\beta}{(\alpha-\beta)(\beta-\gamma)}W\left(\frac{r-\sigma}{\sqrt{4Dt}},-\beta\sqrt{Dt}\right)$$
$$\left.+\frac{\gamma}{(\beta-\gamma)(\gamma-\alpha)}W\left(\frac{r-\sigma}{\sqrt{4Dt}},-\gamma\sqrt{Dt}\right)\right], \tag{2.4}$$

$$p(*,t|*)e^{k_0't}=\frac{\alpha(\beta+\gamma)}{(\gamma-\alpha)(\alpha-\beta)}\Omega(-\alpha\sqrt{Dt})$$
$$+\frac{\beta(\gamma+\alpha)}{(\alpha-\beta)(\beta-\gamma)}\Omega(-\beta\sqrt{Dt})$$
$$+\frac{\gamma(\alpha+\beta)}{(\beta-\gamma)(\gamma-\alpha)}\Omega(-\gamma\sqrt{Dt}), \tag{2.5}$$

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

The survival probability of initially bound state is given by[4]

$$S(t|*)=4\pi\int_{\sigma}^{\infty}r^2p(r,t|*)dr$$
$$=-e^{-k_0't}\frac{k_d}{D\sigma}\left[\frac{1}{\alpha\beta\gamma}+\frac{1+\alpha\sigma}{\alpha(\gamma-\alpha)(\alpha-\beta)}\Omega(-\alpha\sqrt{Dt})\right.$$
$$+\frac{1+\beta\sigma}{\beta(\alpha-\beta)(\beta-\gamma)}\Omega(-\beta\sqrt{Dt})$$
$$\left.+\frac{1+\gamma\sigma}{\gamma(\beta-\gamma)(\gamma-\alpha)}\Omega(-\gamma\sqrt{Dt})\right]. \quad (2.6)$$

The long time asymptotic behavior of the effective binding probability $p'(*,t|*)\equiv p(*,t|*)e^{k_0't}$ reveals an interesting kinetic transition behavior depending on the sign of the following quantity:

$$q\equiv k_0'-k_0-\frac{k_dk_D}{k_a+k_D}. \quad (2.7)$$

When $q<0$ (the A regime), $p'(*,t|*)$ decays as $t^{-3/2}$ but it shows an exponentially increasing behavior when $q>0$ (the AB regime). In the transition region ($q=0$), it decays as $t^{-1/2}$. The effective survival probability $S'(t|*)\equiv S(t|*)e^{k_0't}$ shows a different transition behavior at long times: An exponential behavior in the AB regime, the $t^{1/2}$ power-law behavior in the transition region, and the approach to a constant value in the A regime.

B. Pseudo-first-order case

The same reaction scheme in the pseudo-first-order case was originally treated by Yang *et al.*[6] in their fully renormalized kinetic theoretical formulation of bimolecular reactions in liquid. Although they obtained general expressions of various survival probabilities for the excited-state system, only the ground-state system was analyzed at that time. Reformulating the kinetic theory in the configuration space, Kwac *et al.*[5] obtained the same results of Yang *et al.*[6] and the excited-state system was analyzed to compare with the excited-state geminate system of Gopich and Agmon.[4]

The pseudo-first-order binding and survival probabilities of initially bound state are given, respectively, in the Laplace transformed expressions as[5,6]

$$S(z|*)=[\kappa_f(z)/K_{\mathrm{eq}}]/d(z), \quad (2.8)$$

$$p(*,z|*)=[z+k_0'+c_B\kappa_f(z)]/d(z), \quad (2.9)$$

with

$$d(z)\equiv(z+k_0')[z+k_0+\kappa_f(z)/K_{\mathrm{eq}}]+(z+k_0)c_B\kappa_f(z), \quad (2.10)$$

where z is the variable of the Laplace transform $f(z)=\int_0^{\infty}f(t)e^{-zt}dt$. The forward rate kernel $\kappa_f(z)$ is given by

$$\kappa_f(z)=\frac{k_a}{1+k_a/k_{DR}(z)}. \quad (2.11)$$

The reaction–diffusion kernel $k_{DR}(z)$ can be obtained from

$$\frac{1}{k_{DR}(z)}=\left.\frac{\Gamma_1(z)}{k_D(s)}\right|_{s=z+\alpha_1(z)}+\left.\frac{\Gamma_2(z)}{k_D(s)}\right|_{s=z+\alpha_2(z)}, \quad (2.12)$$

where

$$\Gamma_1(z)\equiv\frac{\alpha_1(z)-k_0-\kappa_f(z)/K_{\mathrm{eq}}}{\alpha_1(z)-\alpha_2(z)}, \quad (2.13)$$

$$\Gamma_2(z)\equiv 1-\Gamma_1(z), \quad (2.14)$$

$$\alpha_1(z)\equiv\{\alpha(z)+[\alpha^2(z)-4\beta(z)]^{1/2}\}/2, \quad (2.15)$$

$$\alpha_2(z)\equiv\{\alpha(z)-[\alpha^2(z)-4\beta(z)]^{1/2}\}/2, \quad (2.16)$$

$$\alpha(z)\equiv k_0+k_0'+(c_B+K_{\mathrm{eq}}^{-1})\kappa_f(z), \quad (2.17)$$

$$\beta(z)\equiv k_0k_0'+(c_Bk_0+k_0'/K_{\mathrm{eq}})\kappa_f(z), \quad (2.18)$$

where $K_{\mathrm{eq}}\equiv k_a/k_d$. Here, the diffusion rate kernel $k_D(s)$ from the Collins–Kimball model is given by

$$k_D(s)\equiv k_D(1+\sigma\sqrt{s/D}). \quad (2.19)$$

The long time asymptotic behavior of the effective binding probability $p'(*,t|*)$ of the pseudo-first-order system shows a different kinetic transition from that of the geminate case. It shows exponentially decreasing or increasing regions separated by the transition line which appears when the two lifetimes are equal. The asymptotic value of the transition line is equal to the equilibrium value for the ground-state system given by

$$p'(*,\infty|*)=\frac{c_BK_{\mathrm{eq}}}{1+c_BK_{\mathrm{eq}}}. \quad (2.20)$$

The long-time asymptotic behavior of the effective survival probability $S'(t|*)$ of the pseudo-first-order system also shows exponentially increasing or decreasing regions separated by the transition line with the asymptotic equilibrium value given by

$$S'(\infty|*)=\frac{1}{1+c_BK_{\mathrm{eq}}}. \quad (2.21)$$

III. BROWNIAN DYNAMICS SIMULATION

A. Ground-state system

In the ground-state BD simulation algorithm of Edelstein and Agmon,[4] an A (or C) particle is located at the origin and N particles of B are randomly distributed. We also assume that direct correlations between noninteracting B particles may be neglected. This arrangement insures that A (or C) particle with the radius of σ is a fixed target and only B particles are moving around. We can realize the pseudo-first-order system taking advantage of the exact Green function for a geminate pair of particles without loss of accuracy. Another assumption to realize the many-particle system is that the remaining particles are fixed while one particle moves or reacts, which may cause error at short times less than one time step.

When the bound state (C) is selected at the origin, it will remain there with the probability of $p^0(*,\Delta t|*)$ after the first time interval Δt. The binding probability $p^0(*,\Delta t|*)$ is given by[9]

$$p^0(*,t|*)=\frac{a(b+c)}{(c-a)(a-b)}\Omega(a\sqrt{t})+\frac{b(c+a)}{(a-b)(b-c)}\Omega(b\sqrt{t})+\frac{c(a+b)}{(b-c)(c-a)}\Omega(c\sqrt{t}), \tag{3.1}$$

where a, b, and c satisfy the following relations:

$$a+b+c=(1+k_a/k_D)\sqrt{D}/\sigma, \tag{3.2a}$$

$$ab+bc+ca=k_d, \tag{3.2b}$$

$$abc=k_d\sqrt{D}/\sigma. \tag{3.2c}$$

Otherwise, it will undergo dissociation reaction and the leaving B particle moves to r after Δt with the probability of $\int_\sigma^r dr'\,4\pi r'^2 p^0(r',\Delta t|*)$ where[9]

$$p^0(r,t|*)=\frac{k_d}{4\pi r\sigma\sqrt{D}}\left\{\frac{a}{(c-a)(a-b)}W\left(\frac{r-\sigma}{\sqrt{4Dt}},a\sqrt{t}\right)+\frac{b}{(a-b)(b-c)}W\left(\frac{r-\sigma}{\sqrt{4Dt}},b\sqrt{t}\right)+\frac{c}{(b-c)(c-a)}W\left(\frac{r-\sigma}{\sqrt{4Dt}},c\sqrt{t}\right)\right\}. \tag{3.3}$$

Other B particles are moved with free diffusion within a time step.

When the unbound particle (A) is found at the origin, a B particle at r_0 is selected and it undergoes association reaction ending up as a bound particle at the origin with the probability of $p^0(*,\Delta t|r_0)$ given by[9]

$$p^0(*,t|r_0)=\frac{k_a}{4\pi r_0\sigma\sqrt{D}}\left\{\frac{a}{(c-a)(a-b)}W\left(\frac{r_0-\sigma}{\sqrt{4Dt}},a\sqrt{t}\right)+\frac{b}{(a-b)(b-c)}W\left(\frac{r_0-\sigma}{\sqrt{4Dt}},b\sqrt{t}\right)+\frac{c}{(b-c)(c-a)}W\left(\frac{r_0-\sigma}{\sqrt{4Dt}},c\sqrt{t}\right)\right\}. \tag{3.4}$$

Otherwise, it does not react with A and just moved to r after Δt with the probability of $\int_\sigma^r dr'\,4\pi r'^2 p^0(r',\Delta t|r_0)$ with[9]

$$p^0(r,t|r_0)4\pi r r_0\sqrt{D}=\frac{1}{\sqrt{4\pi t}}\left\{\exp\left[-\frac{(r-r_0)^2}{4Dt}\right]+\exp\left[-\frac{(r+r_0-2\sigma)^2}{4Dt}\right]\right\}+\frac{a(c+a)(a+b)}{(c-a)(a-b)}W\left(\frac{r+r_0-2\sigma}{\sqrt{4Dt}},a\sqrt{t}\right)+\frac{b(a+b)(b+c)}{(a-b)(b-c)}W\left(\frac{r+r_0-2\sigma}{\sqrt{4Dt}},b\sqrt{t}\right)+\frac{c(b+c)(c+a)}{(b-c)(c-a)}W\left(\frac{r+r_0-2\sigma}{\sqrt{4Dt}},c\sqrt{t}\right). \tag{3.5}$$

B. Excited-state system

In carrying out BD simulations for the excited-state case, we also have to take into consideration of unimolecular decays of excited-states, both bound and unbound. Therefore, the fate of the excited bound state (C^*) at the origin is one of the following.

(1) Stays there with the probability of $p_b=p(*,\Delta t|*)$ given by Eq. (2.5).

(2) Dissociates into A^* (at the origin) and B (separated by r) with the probability of $\int_\sigma^r dr'\,4\pi r'^2 p(r',\Delta t|*)$ with $p(r,t|*)$ given by Eq. (2.4).

(3) Undergoes a unimolecular decay to C with the probability of $U_b=1-p_b-S_b$, where $S_b\equiv\int_\sigma^\infty dr'\,4\pi r'^2 p(r',\Delta t|*)$ is the survival probability of dissociated B particle from the bound state. In the meantime, other B particles are moved by free diffusion. Notice that the fate of C^* is independent of other B particles and C^* undergoes unimolecular decay only once during a time step.

On the other hand, the fate of A^* found at the origin depends critically on B particles at large. For a randomly selected B particle at r_0, A^* undergoes one of the following.

(1) Associates with the B particle to become the bound state C^* with the probability of $p_u=p(*,\Delta t|r_0)$ given by Eq. (2.3).

(2) The B particle does not react with A^* and moves to r with the probability of $\int_\sigma^r dr'\,4\pi r'^2 p(r',\Delta t|r_0)$ with $p(r,t|r_0)$ given by Eq. (2.1).

(3) Decays to A with the probability of $U_u=1-p_u-S_u$, where $S_u\equiv\int_\sigma^\infty dr'\,4\pi r'^2 p(r',\Delta t|r_0)$ is the survival probability of B particle in the unbound state.

If we perform BD simulations for the geminate system, we can now move to the next time step. However, for the pseudo-first-order system in which there are many particles of B, we have to choose other B particles one by one and let them move before going to the next time step. For the next B particle selected, A^* survived in (2) will experience again three possible pathways: (1)–(3). Now the problem is that the unimolecular decay in the step (3) occurs twice to the same A^* particle. Within a time step, every B particle has to be given a chance to move and if the step (3) is open to each of N particles of B, the unimolecular decay of A^* occurs N times as much as that of C^* within a time step. This causes erroneously rapid relaxation of the system. Notice that once A^* (or C^*) decays to A (or C), the simulation is terminated.

In order to avoid this difficulty, we introduce the following assumption in our simulation. That is, the unimolecular decay of the A^* particle is independent of the reactive movement of B particles within a short enough time step. Then the reactive movements of B particles are considered as those in the ground state. Thus in the simulation for the initially unbound state, we first ask A^* particle whether it will undergo unimolecular decay with the probability of $U_u=1-e^{-k_0' t}$ or not before selecting a B particle. If it does not, then a B particle at r_0 is selected and we ask whether A^* undergoes association with the B particle or not. The association occurs with the probability of $p^0(*,\Delta t|r_0)$. Otherwise, A^* remains at the origin while the B particle moves to r with the probability of $\int_\sigma^r dr'\,4\pi r'^2 p^0(r',\Delta t|r_0)$. Notice that probabili-

ties are given in terms of those of the ground state system since we assume that there is no unimolecular decay during a sufficiently small time step.

The calculation of the trajectory for particles at every time step is the most time consuming part and the precalculated look-up tables can be constructed from the above probability functions to reduce the computing time. Since Eq. (2.4) can be integrated analytically, the following relation turns out to be useful to construct the look-up table for the bound state:

$$
\begin{aligned}
Q(r,t|*) &= p(*,t|*) + \int_{\sigma}^{r} dr'\, 4\pi r'^2 p(r',t|*) \\
&= e^{-k_0' t}\Bigg\{ \frac{1}{D\sigma}\left(\frac{k_d}{\alpha}+k_d r\right)\frac{W\left(\frac{r-\sigma}{\sqrt{4Dt}}, -\alpha\sqrt{Dt}\right)}{(\gamma-\alpha)(\alpha-\beta)} + \frac{1}{D\sigma}\left(\frac{k_d}{\beta}+k_d r\right)\frac{W\left(\frac{r-\sigma}{\sqrt{4Dt}}, -\beta\sqrt{Dt}\right)}{(\alpha-\beta)(\beta-\gamma)} + \frac{1}{D\sigma}\left(\frac{k_d}{\gamma}+k_d r\right) \\
&\quad \times \frac{W\left(\frac{r-\sigma}{\sqrt{4Dt}}, -\gamma\sqrt{Dt}\right)}{(\beta-\gamma)(\gamma-\alpha)} - \left[\frac{k_d}{D}\left(1+\frac{1}{\alpha\sigma}\right) - \alpha(\beta+\gamma)\right]\frac{\Omega(-\alpha\sqrt{Dt})}{(\gamma-\alpha)(\alpha-\beta)} - \left[\frac{k_d}{D}\left(1+\frac{1}{\beta\sigma}\right) - \beta(\gamma+\alpha)\right] \\
&\quad \times \frac{\Omega(-\beta\sqrt{Dt})}{(\alpha-\beta)(\beta-\gamma)} - \left[\frac{k_d}{D}\left(1+\frac{1}{\gamma\sigma}\right) - \gamma(\alpha+\beta)\right]\frac{\Omega(-\gamma\sqrt{Dt})}{(\beta-\gamma)(\gamma-\alpha)} - \frac{k_d}{\alpha\beta\gamma D\sigma}\,\mathrm{erf}\left(\frac{r-\sigma}{\sqrt{4Dt}}\right)\Bigg\},
\end{aligned}
\tag{3.6}
$$

where erf(x) is the error function. Notice that $p_b + S_b = Q(\infty,t|*) < 1$ which implies that the probability of the bound state to be in the ground state is $1-Q(\infty,t|*)$.

For the unbound state particle we can utilize the following relation for the ground-state system:[10]

$$
\begin{aligned}
Q^0(r,t|r_0) &\equiv p^0(*,t|r_0) + \int_{\sigma}^{r} dr'\, 4\pi r'^2 p^0(r',t|r_0) \\
&= -\frac{\sqrt{Dt}}{r_0\sqrt{\pi}}\left\{\exp\left[-\frac{(r-r_0)^2}{4Dt}\right] - \exp\left[-\frac{(r+r_0-2\sigma)^2}{4Dt}\right]\right\} + \frac{1}{2}\left[\mathrm{erf}\left(\frac{r-r_0}{\sqrt{4Dt}}\right) + \mathrm{erf}\left(\frac{r+r_0-2\sigma}{\sqrt{4Dt}}\right)\right] \\
&\quad + \frac{1}{r_0}\left(r-\frac{\sqrt{D}}{a}\right)\frac{(c+a)(a+b)}{(c-a)(a-b)} W\left(\frac{r+r_0-2\sigma}{\sqrt{4Dt}}, a\sqrt{t}\right) + \frac{1}{r_0}\left(r-\frac{\sqrt{D}}{b}\right)\frac{(a+b)(b+c)}{(a-b)(b-c)} W\left(\frac{r+r_0-2\sigma}{\sqrt{4Dt}}, b\sqrt{t}\right) \\
&\quad + \frac{1}{r_0}\left(r-\frac{\sqrt{D}}{c}\right)\frac{(b+c)(c+a)}{(b-c)(c-a)} W\left(\frac{r+r_0-2\sigma}{\sqrt{4Dt}}, c\sqrt{t}\right).
\end{aligned}
\tag{3.7}
$$

By using the excited-state look-up table constructed from Eq. (3.6) for the bound state and the ground-state look-up table constructed from Eq. (3.7) for the unbound state, we are actually utilizing the mixed look-up tables in our simulation of the excited-state reaction system.

If the BD simulation is performed for the geminate system, the following relation can be used to construct the look-up table for the unbound state particle:

$$
\begin{aligned}
Q(r,t|r_0) &= p(*,t|r_0) + \int_{\sigma}^{r} dr' 4\pi r'^2 p(r',t|r_0) \\
&= \frac{e^{-k_0' t}}{r_0}\Bigg\{ \left(r+\frac{1}{\alpha}\right)\frac{(\gamma+\alpha)(\alpha+\beta)}{(\gamma-\alpha)(\alpha-\beta)} W\left(\frac{r+r_0-2\sigma}{\sqrt{4Dt}}, -\alpha\sqrt{Dt}\right) \\
&\quad + \left(r+\frac{1}{\beta}\right)\frac{(\alpha+\beta)(\beta+\gamma)}{(\alpha-\beta)(\beta-\gamma)} W\left(\frac{r+r_0-2\sigma}{\sqrt{4Dt}}, -\beta\sqrt{Dt}\right) + \left(r+\frac{1}{\gamma}\right)\frac{(\beta+\gamma)(\gamma+\alpha)}{(\beta-\gamma)(\gamma-\alpha)} W\left(\frac{r+r_0-2\sigma}{\sqrt{4Dt}}, -\gamma\sqrt{Dt}\right)
\end{aligned}
$$

$$-\left[\left(\sigma+\frac{1}{\alpha}\right)(\gamma+\alpha)(\alpha+\beta)+\frac{k_a}{k_D}\alpha\right]\frac{W\left(\frac{r_0-\sigma}{\sqrt{4Dt}},-\alpha\sqrt{Dt}\right)}{(\gamma-\alpha)(\alpha-\beta)}-\left[\left(\sigma+\frac{1}{\beta}\right)(\alpha+\beta)(\beta+\gamma)+\frac{k_a}{k_D}\beta\right]$$

$$\times\frac{W\left(\frac{r_0-\sigma}{\sqrt{4Dt}},-\beta\sqrt{Dt}\right)}{(\alpha-\beta)(\beta-\gamma)}-\left[\left(\sigma+\frac{1}{\gamma}\right)(\beta+\gamma)(\gamma+\alpha)+\frac{k_a}{k_D}\gamma\right]\frac{W\left(\frac{r_0-\sigma}{\sqrt{4Dt}},-\gamma\sqrt{Dt}\right)}{(\beta-\gamma)(\gamma-\alpha)}$$

$$+\sqrt{\frac{Dt}{\pi}}\left\{2\exp\left[-\frac{(r+r_0-2\sigma)^2}{4Dt}\right]-\exp\left[-\frac{(r-r_0)^2}{4dt}\right]-\exp\left[-\frac{(r-r_0)^2}{4Dt}\right]-3\exp\left[-\frac{(r_0-\sigma)^2}{4Dt}\right]\right\}$$

$$-\left(\sigma-\frac{r_0}{2}+\frac{1}{\alpha}+\frac{1}{\beta}+\frac{1}{\gamma}\right)\left[\operatorname{erf}\left(\frac{r+r_0-2\sigma}{\sqrt{4Dt}}\right)-\operatorname{erf}\left(\frac{r_0-\sigma}{\sqrt{4Dt}}\right)\right]+\frac{r_0}{2}\left[\operatorname{erf}\left(\frac{r-r_0}{\sqrt{4Dt}}\right)-3\operatorname{erf}\left(\frac{r_0-\sigma}{\sqrt{4Dt}}\right)\right]\Bigg\}. \tag{3.8}$$

The reflecting boundary condition is used at the outer boundary when a particle is in the unbound state. When a particle is already bound to the fixed target, the reflecting boundary condition is used both at the inner and outer boundaries. In this case, the probability functions, Eq. (3.5) and Eq. (2.1) for the ground- and excited-state simulations, respectively, should all be changed to the following well-known Green function with the reflecting boundary:

$$p(r,t|r_0)4\pi r r_0\sqrt{D}=\frac{1}{\sqrt{4\pi t}}\left\{\exp\left[-\frac{(r-r_0)^2}{4Dt}\right]+\exp\left[-\frac{(r+r_0-2\sigma)^2}{4Dt}\right]\right\}-\frac{\sqrt{D}}{\sigma}W\left(\frac{r+r_0-2\sigma}{\sqrt{4Dt}},\frac{\sqrt{Dt}}{\sigma}\right). \tag{3.9}$$

IV. RESULTS AND DISCUSSIONS

In order to reduce the simulation time, we must find out the optimum size of a time step. For this purpose, we perform BD simulations of the geminate system for several values of the size of time step with mixed look-up tables: the excited-state look-up table given by Eq. (3.6) for the bound state and the ground-state look-up table given by Eq. (3.7) for the unbound state. The unimolecular decay of the unbound state is treated with the probability of $U_u=1-e^{-k_0't}$. The results are compared with analytic result calculated from Eq. (2.5). Once the optimum size of the time step is found, it will be used in other simulations for the pseudo-first-order system. In Fig. 1, simulation results of the time dependence of the effective binding probability $p'(*,t|*)\equiv p(*,t|*)e^{k_0't}$ of the geminate case for several different sizes of time step (Δt) are plotted. The parameter values are $k_a=10.0$, $k_d=10.0$, $k_0=0.5$, $k_0'=0.1$, $D=1.0$, and $\sigma=0.1$. According to Eq. (2.7), the system is in the A regime ($q<0$) in which $p'(*,t|*)$ decays as $t^{-3/2}$. The power-law behavior at long times may be a better choice than the exponential behavior (as in the AB regime) for comparison between results of simulations and the analytic theory. The time steps are 0.05, 0.1, 0.5, and 1.0, respectively. The larger the time step is, the faster the result is obtained but the more inaccurate the result is. Since the time step 0.05 is in good agreement with the analytic result for the present parameter values, it will be chosen as the optimum size to be used for simulations of the pseudo-first-order system with the same parameter values.

The effect of lifetimes (in terms of several values of the ratio, k_0'/k_0) on the evolution of the effective binding probability $p'(*,t|*)$ of the geminate case from the analytic expression of Eq. (2.5) is plotted in Fig. 2 for later comparison with the simulation results of the pseudo-first-order system. Other parameter values are the same as those in Fig. 1. The asymptotic kinetic transition behaviors at long times are clearly shown for the geminate system.

Our BD simulation results of the effect of lifetimes on the time dependence of $p'(*,t|*)$ for the pseudo-first-order case with $c_B=10.0$ are plotted in Fig. 3. The asymptotic power-law decay region with respect to the variation of the ratio of the lifetimes of the excited states shown in Fig. 2

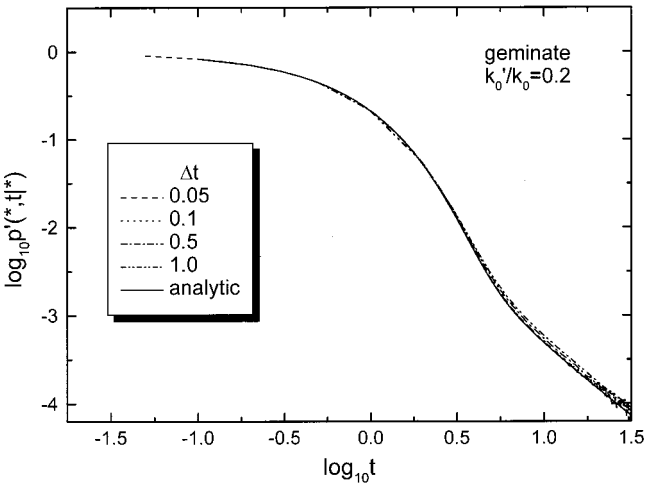

FIG. 1. Simulation results of the time-dependence of the effective binding probability $p'(*,t|*)\equiv p(*,t|*)e^{k_0't}$ in the geminate case for several different values of the size of time step. The solid line is the analytic result. Parameter values are $k_a=10.0$, $k_d=10.0$, $k_0=0.5$, $k_0'=0.1$, $D=1.0$, and $\sigma=0.1$.

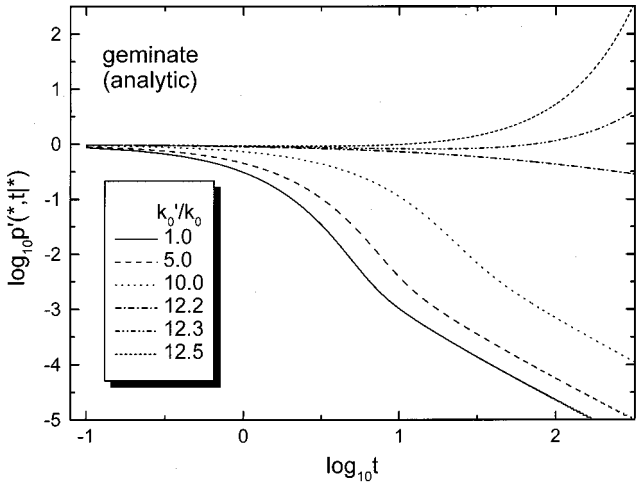

FIG. 2. The time dependence of $p'(*,t|*)$ in the geminate case evaluated analytically for several values of k_0'/k_0. Other parameters are the same as in Fig. 1.

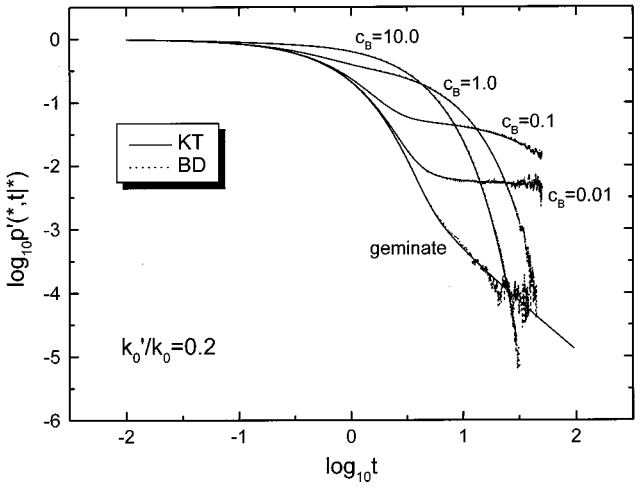

FIG. 4. Simulation results of the effect of increasing c_B on the time dependence of $p'(*,t|*)$ for $k_0'/k_0=0.2$. The solid lines are the KT results. Other parameters are the same as in Fig. 1.

does not appears in Fig. 3. When $k_0>k_0'$, the exponentially decreasing behavior is observed in the long time region. On the other hand, it increases exponentially when $k_0<k_0'$. When $k_0=k_0'$, the ultimate fate of $p'(*,t|*)$ is to reach the equilibrium value. The kinetic theoretical (KT) results calculated from Eq. (2.9) is also plotted. The agreement between the theory and simulations is very good.

In Fig. 4, simulation results of the effect of increasing c_B on the time dependence of $p'(*,t|*)$ are plotted when $k_0>k_0'$ ($k_0=0.5$ and $k_0'=0.1$). Other parameters are the same as those in Fig. 1. The geminate case shows the power law decay, but exponentially decreasing behavior is observed in the pseudo-first-order cases. As c_B increases, the exponentially decreasing behavior appears in the shorter time region. The simulation results are in good agreement with the prediction of the KT.

Simulation results of the effect of increasing c_B in the time dependence of $p'(*,t|*)$ are plotted in Fig. 5 when $k_0=k_0'(=0.1)$. Other parameters are the same as those in Fig. 1. The geminate case shows the power law ($t^{-3/2}$) in the long time region. In the pseudo-first-order case, $p'(*,t|*)$ approaches to the equilibrium value at long times. Since the case of $k_0=k_0'$ corresponds to the ground-state system, the ultimate value of $p'(*,t|*)$ can be determined by Eq. (2.20). Again the agreement between BD simulation and the KT results is very good.

When $k_0<k_0'$ ($k_0=0.1$, $k_0'=0.2$), simulation results of the effect of increasing c_B on the time dependence of $p'(*,t|*)$ are plotted in Fig. 6. Other parameters are the same as those in Fig. 1. The long time behavior of the geminate case shows power law decay, but that of the pseudo-first-order case shows an exponentially increasing behavior. As c_B is increased, the exponential behavior appears in the shorter time region. Notice that the agreement between BD simulation and the KT results is also very good.

Simulation results of the time dependence of the effective survival probability $S'(t|*)\equiv S(t|*)e^{k_0't}$ are plotted in

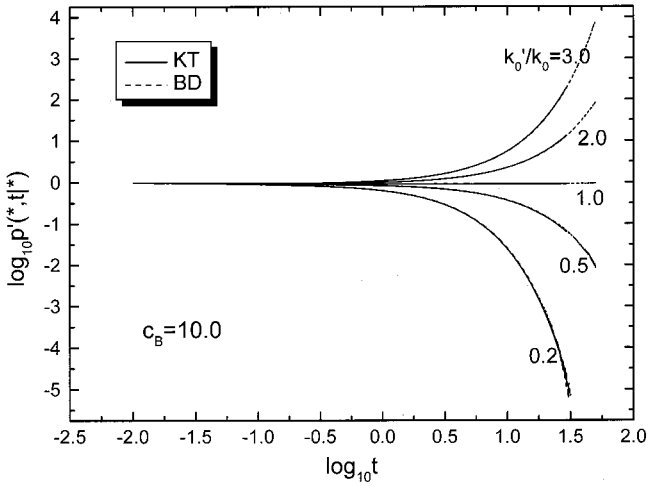

FIG. 3. Simulation results of the time dependence of $p'(*,t|*)$ in the pseudo-first-order case with $c_B=10.0$ for several values of k_0'/k_0. The solid lines are the KT results. Other parameters are the same as in Fig. 1.

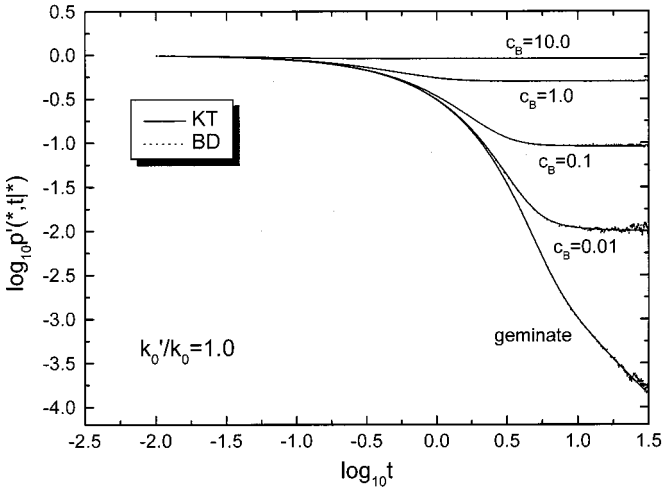

FIG. 5. Same as Fig. 4 except for $k_0'/k_0=1.0$.

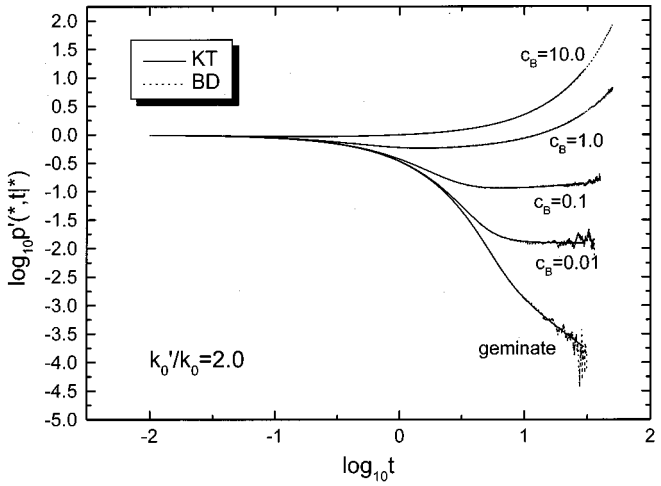

FIG. 6. Same as Fig. 4 except for $k_0'/k_0=2.0$.

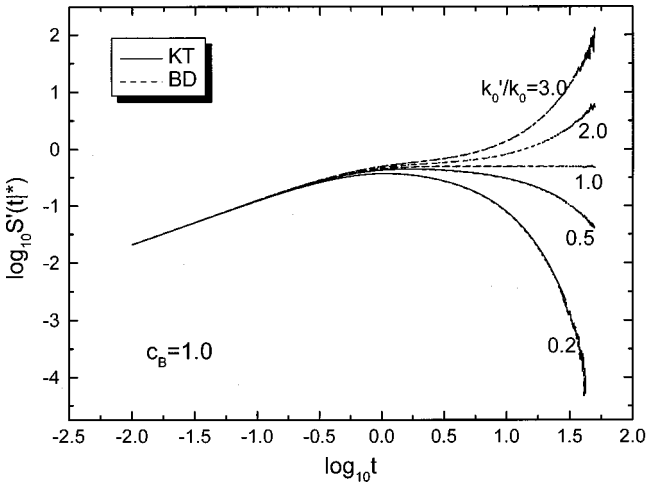

FIG. 8. Same as Fig. 7 except for the pseudo-first-order case with $c_B=1.0$.

Fig. 7 for several values of k_0'/k_0 in the geminate case and compared with the analytic results calculated from Eq. (2.6). In the geminate case, $S'(t|*)$ the effective survival probability also shows a kinetic transition behavior as in $p'(*,t|*)$. In the *A* regime, it approaches to the equilibrium and shows exponential behavior in the *AB* regime. In the transition region, $t^{1/2}$ behavior appears in the long time region.

In Fig. 8, simulation results of the time dependence of $S'(t|*)$ for the pseudo-first-order case ($c_B=1.0$) are plotted for several values of k_0'/k_0 and compared with the KT results calculated from Eq. (2.8). Instead of the power law behavior that appeared in the geminate case, exponentially increasing or decreasing behavior is shown in the pseudo-first-order system. When $k_0=k_0'$, the curve reaches the equilibrium value in the long time region like that of $p'(*,t|*)$. The equilibrium value of $S'(t|*)$ can be obtained from Eq. (2.21).

When k_0 is not much larger than k_0', the time dependence of the effective binding probability shows a plateau region. This behavior was observed at long times in the analysis of experiments of Huppert *et al.*[13] on the excited-state proton transfer of HPTS (8-hydroxypyrene 1,3,6-trisulfonate) in water. However, kinetic theoretical prediction of Kwac *et al.*[12] shows that the plateau region appears in the transient time region and the exponential behavior appears at long times. The effective binding probability in this case is defined by $p(*,t|*)e^{k_0t}$ rather than $p(*,t|*)e^{k_0't}$ because the former was used in analyzing experimental results. Simulation results of the time dependence of $p(*,t|*)e^{k_0t}$ are plotted in Fig. 9. The unimolecular decay constants are $k_0=0.11$ and $k_0'=0.10$, respectively. We can observe the plateau in the transient time region and the exponentially increasing behavior at long times. The simulation results are in good agreement with the KT results.

V. SUMMARY

We have presented the Brownian dynamics simulation results of the excited-state diffusion influenced reversible reaction of $A^*+B\rightleftarrows C^*$ in 3D without a quenching process.

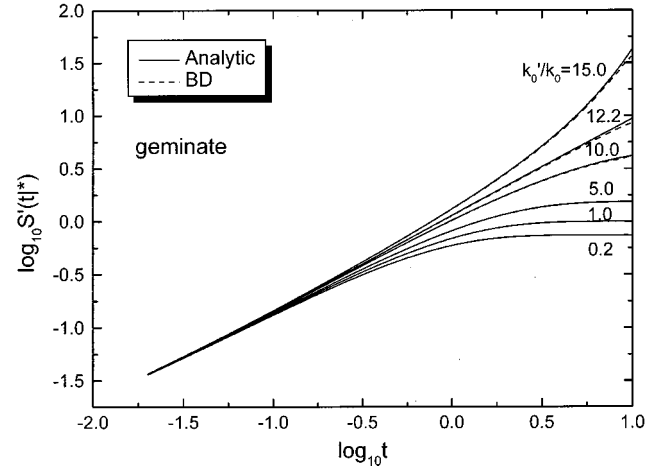

FIG. 7. Simulation results of the time dependence of the effective survival probability $S'(t|*)$ for several values of k_0'/k_0 in the geminate case. The solid lines are the KT results. Other parameters are the same as in Fig. 1.

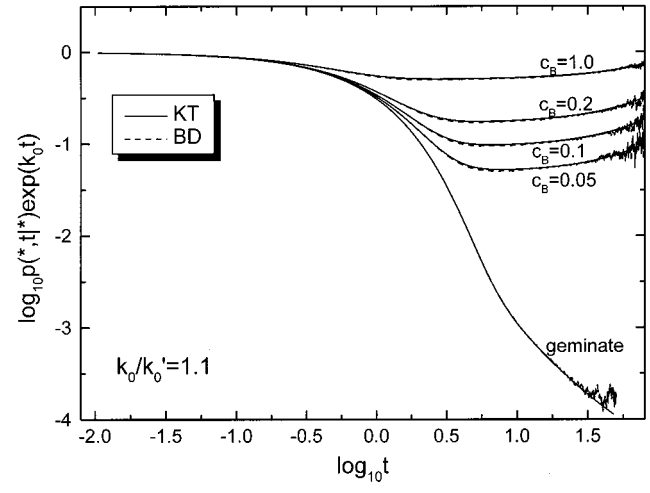

FIG. 9. Simulation results of the time dependence of $p(*,t|*)\exp(k_0t)$ for $k_0'/k_0=1.1$. The solid lines are the KT results. Other parameters are the same as in Fig. 1.

We performed the simulation using the mixed look-up tables which are divided into two parts. For the initially bound state, the unimolecular decay is coupled to the reactive movement and the excited-state look-up table is constructed. On the other hand, the unimolecular decay is assumed to be independent of the reactive movement for the initially unbound state and the ground-state look-up table is used. The unimolecular decay occurs independently with the probability of $1-e^{-k_0't}$ and the reactive movement can be traced as if the system is in the ground state. This assumption can be justified if the size of a time step is sufficiently small. Since the small time step requires more simulation time, we find the optimum size by performing simulations for the excited-state geminate system for which analytic results are available.

The present simulation results for the pseudo-first-order system are in good agreement with the kinetic theoretical predictions of Kwac *et al.*[5] In particular, their theory predicts that the long time asymptotic behavior of the effective binding probability $p'(*,t|*)$ of the pseudo-first-order system shows a different kinetic transition behavior from that of the geminate case: Exponentially increasing (when $k_0<k_0'$) and decreasing (when $k_0>k_0'$) regions separated by the transition line (when $k_0=k_0'$). The ultimate destination of the transition line is the equilibrium value reached also by the ground-state system. All these theoretical predictions are confirmed by the present simulation study.

ACKNOWLEDGMENT

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