Long time behavior of reversible diffusion-influenced reaction perturbed by photolysis: Brownian dynamics simulation

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New power law behavior ($t^{-3/2}$) in the asymptotic relaxation of pseudo-first-order reversible diffusion-influenced reaction, $A+B\leftrightarrow AB$ perturbed by photolysis is confirmed by a Brownian dynamics simulation in one dimension when the photolytic dissociation distance is equal to the thermal dissociation distance as predicted by Yang *et al.* [Phys. Rev. Lett. **79**, 3783 (1997)]. For larger photolytic dissociation distances, however, our simulation curves follow the thermal relaxation curve at the beginning and deviate from the latter to show $t^{-3/2}$ power law behavior at longer times. The effect of photolytic perturbation on various nonequilibrium initial states is also examined by Brownian dynamics simulations. © *1999 American Institute of Physics.* [S0021-9606(99)51208-7]

I. INTRODUCTION

Recently, the relaxation kinetics of the diffusion-influenced reversible reaction, $A+B\leftrightarrow AB$, has been widely investigated theoretically. The superposition approximation (SA) approach proposed by Lee and Karplus[1] was modified to predict the asymptotic $t^{-d/2}$ power law for the pseudo-first-order system.[2,3] More refined results along this approach have been reported to describe the relaxation kinetics in not only the asymptotic but also the transient regions.[4–6] Computer simulation studies confirmed $t^{-1/2}$ power law behavior in one dimension for the pseudo-first-order system by several workers with their Monte Carlo[3,7] and Brownian dynamics (BD)[8–10] simulation methods.

Although these theories all predict the $t^{-1/2}$ asymptotic power law behavior in one dimension, they all show some discrepancy with the simulation in the transient region, more distinct at high concentration. A rigorous kinetic theoretical investigation[11] revealed that the dynamical correlation effect is not properly incorporated in the above theories. All the above theories and simulations considered the case of the thermal perturbation of the initial equilibrium system by an abrupt temperature change.

Recently, Yang *et al.*[12] predicted a new power law behavior ($t^{-3/2}$ and $t^{-5/2}$ in one and three dimensions, respectively) in the asymptotic relaxation of the concentration deviation of the same reversible reaction system perturbed by *photolysis*. The initial equilibrium system is perturbed by a photoflash with a short duration which is turned on at time zero abruptly to break up some fraction of *AB* molecules to produce geminate pairs of *A* and *B* molecules separated by a distance r_0 . The role of these geminate pairs, which does not exist in the thermal perturbation case, is proven to be so crucial as to change the power law behavior in the long time limit. They presented a simple probabilistic arguments under the condition that the photolytic dissociation distance, r_0 , is the same as the thermal dissociation distance, σ , which is the reaction distance.

The main purposes of this article are (1) to confirm the new power law behavior predicted by Yang *et al.*[12] for the case of $r_0=\sigma$ by the BD simulation method and (2) to examine the relaxation behavior for any r_0 larger than σ for which no theoretical explanation is available, and (3) to investigate the effect of the photolytic perturbation on the nonequilibrium initial state.

II. THEORETICAL BACKGROUND

Consider a reversible reaction $A+B\leftrightarrow AB$ with the equilibrium constant, $K_{\mathrm{eq}}=[AB]_{\mathrm{eq}}/c_B[A]_{\mathrm{eq}}$ where c_B is the constant bulk concentration of *B* (the pseudo-first-order model). When the initial equilibrium system is perturbed by photolysis, each of *A*'s dissociated from *AB*'s by the perturbation sees a geminate partner *B* separated by the photolytic dissociation distance r_0 and the equilibrium distribution of other *B*'s. Then the concentration deviation of *A*, defined by $\xi(t)\equiv([A(t)]-[A]_{\mathrm{eq}})/([A]_0-[A]_{\mathrm{eq}})$, can be expressed by[12]

$$\xi(t)=\mathcal{S}(t|r_0)-\mathcal{S}(t|*), \tag{1}$$

where $[A]_0$ is the initial concentration of *A.* Since one can set $[A]_{\mathrm{eq}}+[AB]_{\mathrm{eq}}$ as a constant, $[A]_{\mathrm{eq}}$ can be determined exactly in terms of c_B and K_{eq}.$S(t|*)$ and $S(t|r_0)$ are the conditional probabilities of finding *A*'s in the unbound state at time *t* for initially bound *A*'s and for initially geminate pairs with *A*-*B* separation r_0, respectively.

When $r_0=\sigma$, we can utilize the relation[13]

$$S(t|*)=k_d\int_0^t d\tau\, e^{-k_d\tau}S(t-\tau|\sigma), \tag{2}$$

where k_d is the thermal dissociation constant and Eq. (1) can be simplified as

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$$\xi(t)=\frac{1}{k_d}\frac{d}{dt}S(t|*). \tag{3}$$

The long time behavior of $S(t|*)$ is well known in one dimension as[2,3,14]

$$S(t|*) \underset{t\to\infty}{\sim} [1-b(4\pi Dt)^{-1/2}], \tag{4}$$

where D is the diffusion constant and b a time-independent constant. Hence the long time power law behavior of $\xi(t)$ in one dimension is given by[12]

$$\xi(t) \underset{t\to\infty}{\sim} t^{-3/2}. \tag{5}$$

In general, however, r_0 need not be the same as σ and one cannot utilize Eq. (2) in this case and the asymptotic behavior of $\xi(t)$ is yet to be determined. Another interesting phenomenon would be the effect of photolytic perturbation to the *nonequilibrium* initial states for which no theoretical explanation has been provided yet. Our simulation results for these cases will be presented after a brief review of the BD simulation method.

III. BD SIMULATION

We perform the BD simulations with the aid of the method of Edelstein and Agmon[8] with minor technical variations. Their simulation method utilizes the exact analytical solutions of one-dimensional reversible diffusion equation for a geminate pair[15,16] under the assumptions that direct correlations between noninteracting like particles may be ignored and the particle *A* or *AB* is immobile, namely, regarded as a static trap. Under these assumptions as many theories also do, the method can be applied to a pseudo-first-order system of our concern.

To simulate N particles in the system of size L, 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 (*AB*), it will remain there with the probability of $p(*,\Delta t|*)$ after Δt given by[8]

$$p(*,t|*)=\frac{1}{\Delta}\left[\lambda_+\Omega\left(\lambda_-\sqrt{\frac{t}{D}}\right)-\lambda_-\Omega\left(\lambda_+\sqrt{\frac{t}{D}}\right)\right], \tag{6}$$

where $\Omega(x)=\exp(x^2)\mathrm{erfc}(x)$, $\lambda_\pm\equiv(k_r\pm\Delta)/2$, $\Delta^2\equiv k_r^2-4Dk_d$, $\mathrm{erf}(x)$ and $\mathrm{erfc}(x)$denote the error and the complementary error functions, respectively, and k_r the recombination rate constant. Otherwise it will move to x with the probability of $\int_0^x dx'\,p(x',\Delta t|*)$ with[8]

$$p(x,t|*)=\frac{k_d}{\Delta}\left[W\left(\frac{x}{\sqrt{4Dt}},\lambda_-\sqrt{\frac{t}{D}}\right)-W\left(\frac{x}{\sqrt{4Dt}},\lambda_+\sqrt{\frac{t}{D}}\right)\right], \tag{7}$$

where $W(a,b)\equiv\exp(2ab+b^2)erfc(a+b)$. When an unbound particle at x_0 is selected, it will end up in the trap with the probability of $p(*,\Delta t|x_0)$ given by[8]

$$p(*,t|x_0)=\frac{k_r}{\Delta}\left[W\left(\frac{x_0}{\sqrt{4Dt}},\lambda_-\sqrt{\frac{t}{D}}\right)-W\left(\frac{x_0}{\sqrt{4Dt}},\lambda_+\sqrt{\frac{t}{D}}\right)\right], \tag{8}$$

or move to x with the probability of $\int_0^x dx'\,p(x',\Delta t|x_0)$ with[8]

$$p(x,t|x_0)=\frac{1}{\sqrt{4\pi Dt}}\left\{\exp\left(-\frac{(x-x_0)^2}{4Dt}\right)+\exp\left(-\frac{(x+x_0)^2}{4Dt}\right)\right\}-\frac{k_r}{D}W\left(\frac{x+x_0}{\sqrt{4Dt}},k_r\sqrt{\frac{t}{D}}\right). \tag{9}$$

Here we assume that the remaining $N-1$ particles are fixed during the time interval, Δt , which may cause error at short times less than Δt . The endpoint of the stochastic trajectory is found by comparing a uniformly distributed random number, $0<\xi<1$, with the integral of the exact solution. The particle ends up in the trap if $\xi<p(*,\Delta t)$ and it ends up being unbound if $\xi>p(*,\Delta t)$. In the latter case, the endpoint (x_ξ) is found from the following relation:[8]

$$\xi=p(*,\Delta t)+\int_0^{x_\xi}p(x,\Delta t)dx. \tag{10}$$

The calculation of the trajectory for every particle at every step is the most time consuming part and the precalculated look-up tables are constructed from the above probability functions. Since Eqs. (7) and (9) can be integrated analytically, the following relations turn out to be useful to construct the look-up tables more efficiently:

$$p(*,t|*)+\int_0^x dx'\,p(x',t|*)=\mathrm{erf}(x/\sqrt{4Dt})+\frac{1}{\Delta}\exp(-x^2/4Dt)[\lambda_+\Omega(x/\sqrt{4Dt}+\lambda_-\sqrt{t/D})-\lambda_-\Omega(x/\sqrt{4Dt}+\lambda_+\sqrt{t/D})], \tag{11a}$$

$$p(*,t|x_0)+\int_0^x dx'\,p(x',t|x_0)=\frac{1}{2}\mathrm{erf}[(x+x_0)/\sqrt{4Dt}]+\frac{1}{2}\mathrm{erf}[(x-x_0)/\sqrt{4Dt}]+\frac{k_r}{\Delta}\exp[-(x+x_0)^2/4Dt]\times\{\Omega[(x+x_0)/\sqrt{4Dt}+\lambda_-\sqrt{t/D}]-\Omega[(x+x_0)/\sqrt{4Dt}+\lambda_+\sqrt{t/D}]\}. \tag{11b}$$

The look-up table method reduces the computing time greatly but requires much more memory space. We use the interpolation method to reduce the memory space.

In our simulation, each particle has only one chance to move or to remain during Δt by generating a ''random list'' which is found to help reducing errors during the first few time steps. The reflecting boundary conditions are used at the inner ($x = 0$) and the outer ($x = L$) boundaries, respectively, when a particle is bound to the trap. After the trials of all particles, one can continue the next step. Incorporating the exact solutions into the calculation of the trajectory, Δt can be much larger than that in the conventional BD or in the lattice random walk simulations.

In order to reduce the computing time of the trajectory, the radius of influence of the reversible trap, x_{rev}, is also introduced.[8] In the interval $[0, x_{\mathrm{rev}}]$ the reaction dynamics is calculated by using the precalculated look-up tables constructed from the exact solutions but free diffusion is assumed in the interval $[x_{\mathrm{rev}}, L]$.

The initial photolysis is represented by a compulsory dissociation of the particle *AB* by planting the *B* particle at the photolytic dissociation distance, $r_0 - \sigma$ away from $x = 0$. Note that only one *A* or *AB* can exist in each realization of the system and all the other *B* particles are in their equilibrium distribution. The numbers of realizations with and without the initial photolysis can be estimated from the ratio of $[AB]_{\mathrm{eq}}/[A]_{\mathrm{eq}} = c_B K_{\mathrm{eq}}$.

The effect of photolytic perturbation on the nonequilibrium initial state is examined as follows. The initial equilibrium system is first perturbed thermally and we wait until a nonequilibrium state is reached after a certain period of time. Then the photolytic perturbation is turned on and the relaxation behavior thereafter is monitored as described above.

The converged result for the photolytically perturbed system is much more difficult to obtain than that of previous $t^{-1/2}$ decay simulations since more rapid decay requires more accurate results. Up to 3×10^9 realizations are averaged to obtain the present results. Since all realizations are independent of each other, we can reduce the computing time greatly by the parallel programming method. The simulations are performed on an IBM SP2 model massively parallel processing (MPP) computer with 40 nodes.

IV. RESULTS AND DISCUSSION

The values of parameters in our simulations are $k_r = D = 1$, $k_d = 1$, $c_B = 0.01$, and $N = 10$ ($L = 1000$). The values are chosen to obtain the converged results easily in a physically reasonable condition. In order to check the validity of the present simulation, we compare, in Fig. 1, the simulation result for the thermal perturbation case in one dimension with that of the SA-based theory[4–6] which predicts $t^{-1/2}$ asymptotic power law behavior. The SA-based theory is chosen because the more rigorous kinetic theoretical prediction is not available in one dimension and the former is known to yield rather good agreement with the simulation at low concentrations.[5] Since the concentration of our system is low enough, the simulation result is in good agreement with the theory at all times. The numerical integration of the kinetic equations [Eqs. (2.9), (2.10), (2.12), and (2.17) of Ref. 6] in the theory is carried out by using our previously developed method.[17] Actually, we use this comparison to check the finite system size error due to the artificial reflecting boundary condition. This error makes the concentration of the system higher than the given value[7] and therefore the slope becomes more steep. For a given concentration, the smaller the boundary, the smaller number of particles can be used. By this comparison we could find an optimum size of the system. To reduce the computing time, we set the size of the system as small as possible.

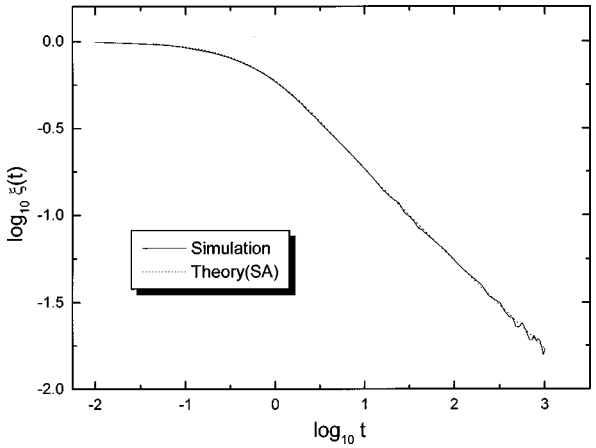

FIG. 1. Time dependence of the concentration deviation for a thermally perturbed case. The present BD simulation result (solid) is compared with the theoretical prediction (dots). See the text for the parameters.

The time dependence of the concentration of *A* for the photolytic perturbation case is plotted for several values of r_0 in Fig. 2. The thermal perturbation case is also plotted for comparison. Indeed the equilibrium is reached more rapidly in the photolytic perturbation case. Note that the deviation from the thermal perturbation case starts at about $t = 10^{-1/2}$ when $r_0 - \sigma = 2$, and at about $t = 10$ when $r_0 - \sigma = 10$, which is consistent with the Einstein–Smoluchowski law in the form of $\Delta r_2/\Delta r_1 \sim \sqrt{\Delta t_2/\Delta t_1}$. We can infer that the geminate correlations affect dynamics seriously from this deviation starting point.

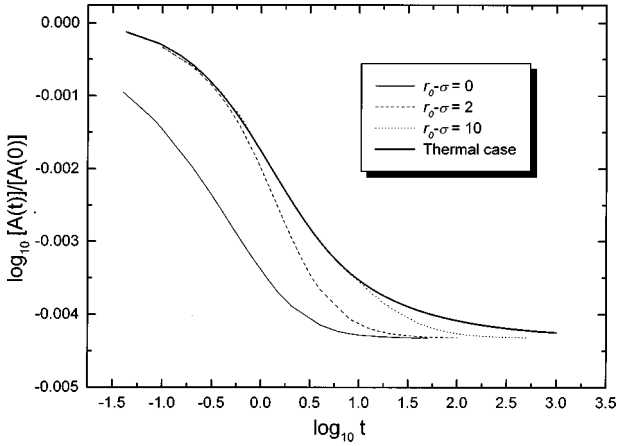

FIG. 2. Survival probabilities of *A* for several values of r_0 for the photolytically perturbed case. Thermally perturbed case (thick solid) is also plotted for comparison. The parameters are the same as those in Fig. 1.

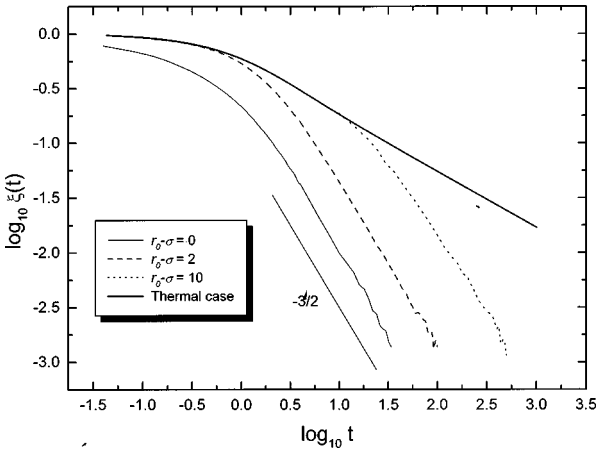

FIG. 3. Time dependence of the concentration deviations for several values of r_0 for the photolytically perturbed cases. The parameters are the same as those in Fig. 1.

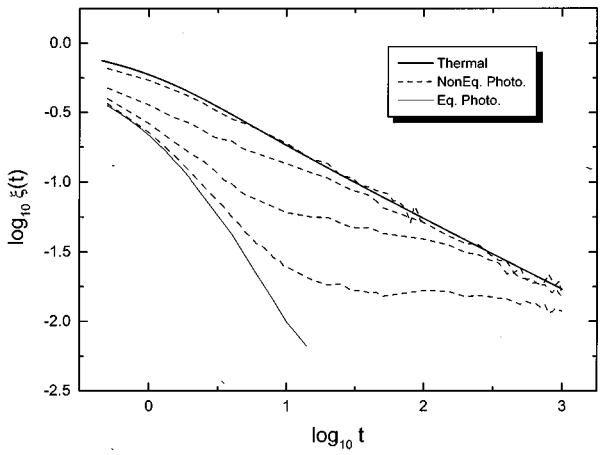

FIG. 4. Time dependence of the concentration deviations (dots) for $r_0=\sigma$ and for the nonequilibrium photolysis. The times (t_p) when the perturbation is turned on are 1, 10, 100, and 1000 from top to bottom, respectively. Other parameters are the same as those in Fig. 1. Thermal (thick solid) and photolytically (solid) perturbed cases for the equilibrium initial state are plotted for comparison.

In Fig. 3, the time dependence of the concentration deviation, $\xi(t)$, for the photolytic perturbation case is plotted for several values of r_0 . Again, the thermal perturbation case is plotted for comparison. As a reference, we add a straight line with the slope $=-3/2$. For the photolytic perturbation cases, $t^{-3/2}$ asymptotic power law behavior is clearly observed for $r_0=\sigma$ as Yang *et al.*[12] predicted. For larger values of r_0 , however, our simulation curves follow the thermal relaxation curve at the beginning and deviate from the latter to show $t^{-3/2}$ power law behavior at longer times. A slightly less steep slope ($<3/2$) detected for a very large values of r_0 (e.g., $r_0-\sigma=10$) may indicate that the asymptotic power law region has not been reached yet. As r_0 gets even larger, the departure from the thermal relaxation curve would be further delayed reminding us the fact that the relaxation behavior should be the same as that of the thermally perturbed case for $r_0\rightarrow\infty$.

We could not carry out the simulation below $\xi(t)=1.0\times10^{-3}$. In order to obtain noise-free data at the value of $\xi(t)=1.0\times10^{-4}$, the hundredfold more realizations than those at $\xi(t)=1.0\times10^{-3}$ should be averaged. That means the average over 3×10^{11} realizations is beyond the limitation of our computing power.

For all the above results, the photolytic perturbation is applied to the initial equilibrium states. Although there is no theoretical explanation, it would be interesting to examine the nonequilibrium photolysis by the present BD simulation method. In order to obtain a nonequilibrium initial state, the original equilibrium state is first perturbed thermally and wait until t_p when the photolytic perturbation is turned on. The relaxation behavior of $\xi(t)$ is monitored afterward and the results are plotted in Fig. 4. All curves are for the case of $r_0=\sigma$. For comparison, we add the thermal (A) and the photolytic (B) perturbation curves both for the *equilibrium* initial states. The results show that the nonequilibrium photolysis curves follow the curve B at short times, but approach the curve A at long times. It is very interesting to note that the plateau region is observed for the curve for $t_p=1000$. The value of $\xi(t)$ at the beginning of the plateau region is very close to that of the curve A at $t=1000$. This implies that the curve reaches a pseudoequilibrium state at the level of the initial nonequilibrium state. We infer that the large difference between the relaxation times for the bulk (curve A) and the geminate (curve B) correlations may cause the pseudoequilibrium state.

From the above observation, the photolytic perturbation technique is found to be useful in making the early stage of the relaxation kinetics toward equilibrium from a given nonequilibrium initial state faster than that without it.

In summary, the asymptotic power law behavior in the pseudo-first-order reversible diffusion-influenced reaction, $A+B\leftrightarrow AB$ perturbed by photolysis in one dimension is investigated by the BD simulation method. $t^{-3/2}$ asymptotic power law behavior is clearly observed for $r_0=\sigma$ as Yang *et al.*[12] predicted. For larger values of r_0 , however, the departure from the thermal relaxation curve at longer time is observed to show $t^{-3/2}$ asymptotic power law behavior. For the nonequilibrium photolysis, we find the plateau region which implies a pseudoequilibrium state due to the difference between the relaxation times of the bulk and the geminate correlations.

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