Excluded volume effect on diffusion-influenced reactions in one dimension

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(Received 31 January 2003; accepted 6 March 2003)

The excluded volume (EV) effect between nonreactive like-particles of diffusion-influenced pseudo-first-order reaction $A+B\rightarrow C$ is investigated by the hierarchical Smoluchowski approach of Kuzovkov and Kotomin [Rep. Prog. Phys. **51**, 1479 (1988)] and the many-particle kernel formalism of Lee *et al.* [J. Chem. Phys. **113**, 8686 (2000)] in one dimension. Contrary to the three-dimensional analysis, the latter theory can be formulated without additional approximations in one dimension so that more accurate results are obtained. Although formulations and resulting expressions are different, these two theories show almost identical results numerically. The EV effect becomes significant at higher concentrations of *B* molecules as in three dimensions. However, we found that the EV effect in one dimension is more pronounced than in three dimensions. A similar trend appears as the size of the *B* molecule increases. Theoretical results are compared with Monte Carlo simulations. The simulation results reveal much larger EV effect than that predicted by both theories. This behavior may be attributed to the ''cage'' effect which is not considered in both theories. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1570409]

I. INTRODUCTION

Since the pioneering work of Smoluchowski,[1] a great deal of attention has been paid to the diffusion-influenced reaction. Let us consider the following irreversible reaction in which one molecule or a walker (*A*) and many other molecules or traps (*B*'s) diffuse in an inert continuum-like solvent together until they are close enough to react.

$$A+B\rightarrow C. \tag{1}$$

Then what is the survival probability of *A* at time *t*? Although this is one of the simplest reaction models in liquid, the exact solution cannot be obtained in general since it is a many-body problem. It is well known that the Smoluchowski approach becomes exact when (1) the molecule *A* is static and (2) *B* molecules do not interact with each other.[2]

The approximation (1), which is often called the static donor approximation, has attracted much attention[3–6] in the theory of lattice random walks (the trap-target problem) and it has been known that the validity of this approximation improves as the dimensionality increases. In three dimensions (3D), the Smoluchowski solution is highly accurate except at very long times. However, as Szabo noted,[2] the major deficiency of the Smoluchowski approach may be due to the second approximation (2), the neglect of the like-particle correlation between *B* molecules. Even for a hard sphere model, the *B* molecules have the finite excluded volume (EV) not accessible to other molecules. Therefore, for more realistic reactive systems, the Smoluchowski approach could predict erroneous results since *B* molecules are regarded as point particles with no EV.

Numerous approaches which extend the Smoluchowski approach have been presented.[7,8] The importance of the EV effect in reaction dynamics has been noticed by many workers. Kalin[9] and Kuzovkov and Kotomin[10–12] investigated this problem by considering the like-particle correlation in the hierarchical Smoluchowski equation approach. Kuzovkov and Kotomin also predicted microscopic dynamical clustering of similar reactants at long times. Fayer and his coworkers have noted the EV effect between acceptors of the electron transfer reaction model in solid[13] and in liquid.[14] They used approximate methods such as the lattice method of Blumen and Manz[15] and the separable probability distribution method to investigate the EV effect in solid. However, in liquid, they underestimated the EV effect and focused only on the validity of the static donor approximation. Later, Jung and Lee[16] found that the EV effect was larger than that found by the lattice method of Blumen and Manz using their reduced distribution function method.

More recently Lee *et al.*[17] re-investigated the EV effect in 3D with the many-particle kernel (MPK) theory[18] and also with Brownian dynamics simulations. Their theoretical result seemed to agree with Brownian dynamics (BD) simulations for their chosen parameters. However, they introduced a few additional crude approximations in the MPK theory in order to obtain an approximate analytic solution which accounts for the EV effect. This prevents an accurate comparison between theory and simulation. In fact, when the size of a *B* molecule becomes larger, the MPK theory shows that the survival probability decays faster than the BD simulation result. They noted that this dubious behavior maybe due to the additional approximations in the MPK theory or to some statistical errors in their BD simulations.

The purpose of this work is to investigate the EV effect in the above irreversible pseudo-first-order reaction system in one dimension (1D). The 1D model is more interesting one because there is so called the ''bus effect''[19] in which a given pair of *A* and *B* molecules cannot react unless other *B* molecules separating these two disappear. Furthermore, it is

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simpler to apply theories and simulations in 1D.

The physical quantity of our interest is the survival probability of the A molecule. We also consider here the target problem in which the A molecule is static at the origin and only B molecules move around diffusively. Theoretically, we adopt two approaches. The Kuzovkov and Kotomin (KK) theory[12] based on the hierarchical Smoluchowski equations with the Kirkwood superposition approximation incorporates the EV effect in terms of the like-particle correlation. The evolution equations of the pair distribution functions in 1D are readily available in literature. However, the calculation of the survival probability from these evolution equations is nontrivial and requires a rather sophisticated numerical algorithm. In fact, we developed an efficient numerical algorithm for this purpose some time ago[20] and it is utilized in this work.

The other theoretical approach is the MPK theory of Lee *et al.*[17] for which we reformulate to incorporate the EV effect in 1D. We find that additional approximations introduced in 3D formulation are not necessary in 1D and, therefore, the accuracy of the results of the MPK theory is much improved. We find, interestingly, results from both the KK and MPK theories show almost identical results numerically although formulations and resulting expressions are different.

Theoretical results are compared with an efficient Monte Carlo (MC) simulation algorithm that we developed previously.[21] It will be shown that the predictions of the MPK theory deviate significantly from the present Monte Carlo simulations adopting efficient techniques when the EV effect is large.

The outline of this paper is as follows. In Sec. II, we review the KK theory and reformulate the MPK theory to incorporate the EV effect in 1D. An efficient MC algorithm adopted in this work is explained in Sec. III. The results of theory and simulations are compared and discussed in Sec. IV and we conclude the present work in Sec. V.

II. THEORY

We consider the irreversible reaction between A and B molecules given in Eq. (1). The concentration of B molecules, c_B, is assumed to be constant in time. For the target problem, an A molecule is fixed at the origin and only B molecules undergo diffusive motions.

A. The hierarchical Smoluchowski theory

The rate equation for the above reaction scheme, Eq. (1), for the pseudo-first-order case ($[A] \ll [B]=c_B$) and for the contact reactivity is written by[18,22]

$$\frac{d}{dt}[A] = -k(t)[A]c_B = -k_0 C_{AB}(\sigma,t), \tag{2}$$

where $k(t)$ is the rate coefficient, k_0 the intrinsic rate constant, and σ the reaction distance. The evolution of the pair distribution function $C_{AB}(x,t)$, with x the position of B molecule, is given by the following hierarchical kinetic equation:

$$\frac{\partial}{\partial t}C_{AB}(x,t) = L_{AB}(x)C_{AB}(x,t) - S_{AB}(x)C_{AB}(x,t) - \int dx' S_{AB}(x')C_{ABB}(x,x',t), \tag{3}$$

where $C_{ABB}(x,x',t)$ is the three-particle distribution function. The usual Smoluchowski diffusion operator, $L_{\alpha\beta}(x)$, is given by

$$L_{\alpha\beta} = \frac{\partial}{\partial x}D(x)\frac{\partial}{\partial x}, \tag{4}$$

where the diffusion coefficient, $D(x)$, is approximated as a constant, $D=D_\alpha+D_\beta$. The sink function, $S_{AB}(x)$, is assumed to depict a simple contact reactivity

$$S_{AB}(x) = \tfrac{1}{2}k_0\delta(x-\sigma). \tag{5}$$

In order to truncate the hierarchical structure of Eq. (3), Kuzovkov and Kotomin[12] introduced the Kirkwood superposition approximation

$$[A]c_B^2 C_{ABB}(x,x',t) \cong C_{AB}(x,t)C_{AB}(x',t) \times C_{BB}(|x'-x|,t). \tag{6}$$

By rewriting Eq. (3) with the normalized pair correlation function $\rho_{AB}(x,t)$ given by

$$C_{AB}(x,t) \equiv \rho_{AB}(x,t)[A]c_B, \tag{7}$$

the following evolution equations for the pair correlation functions can be obtained:[12]

$$\frac{\partial}{\partial t}\rho_{AB}(x,t) = L_{AB}\rho_{AB}(x,t) - S_{AB}(x)\rho_{AB}(x,t) + k(t)c_B[1-X_{BB}(x,t)]\rho_{AB}(x,t), \tag{8}$$

$$\frac{\partial}{\partial t}\rho_{BB}(x,t) = L_{BB}\rho_{BB}(x,t) + 2k(t)[A] \times [1-X_{AB}(x,t)]\rho_{BB}(x,t). \tag{9}$$

Here, $\rho_{BB}(x,t)$ is the like-particle correlation function for B molecules and $X_{\alpha\beta}(x,t)$ is given, in 1D, as

$$X_{\alpha\beta}(x,t) \equiv \frac{\rho_{\alpha\beta}(x+\sigma,t)+\rho_{\alpha\beta}(x-\sigma,t)}{2}, \quad (\alpha\beta = AB \text{ or } BB). \tag{10}$$

It is worthwhile to note the physical meaning of the third term on the right-hand side of Eq. (8) because it is the only difference from the Smoluchowski solution. The third term can be interpreted as the difference between global concentration decay and local competitive reactions. In the Smoluchowski approach, the two effects are treated as the same. In the KK theory, however, the local environmental fluctuation is treated differently from global one because of the EV effect.

We can ignore the second term on the right-hand side of Eq. (9) because we assume $[A] \to 0$ in the pseudo-first-order limit. And if we assume that the initial distribution of B

molecules is that of equilibrium, the like-particle correlation function $\rho_{BB}(x,t)$ does not evolve in time, that is

$$\rho_{BB}(x,t)\approx\rho_{BB}(x)\equiv g_{BB}(x), \tag{11}$$

where $g_{\alpha\beta}(x)$ is the equilibrium pair correlation function between the molecules α and β. Note that, for the second-order case, $\rho_{BB}(x,t)$ evolves in time due to the presence of the second term in Eq. (9). A similar argument can be extended to the three dimensional pseudo-first-order case for which the KK theory reduces to the Jung and Lee's method[16] which simply regarded the like-particle correlation function as a step function.

Due to the symmetry in 1D, we can consider only half-infinite system for which $S_{AB}(x)=k_0\delta(x-\sigma)$ and $X_{BB}(x,t)$ now becomes

$$X_{BB}(x,t)=\rho_{BB}(x-\sigma,t), \tag{12}$$

which is different from Eq. (10). If we further assume that all the molecules are hard spheres, $X_{BB}(x,t)$ can be simplified as

$$X_{BB}(x,t)=\rho_{BB}(x-\sigma,t)\approx g_{BB}(x-\sigma)=\begin{cases}1 & x\geqslant\sigma+\sigma_{BB}\\ 0 & x<\sigma+\sigma_{BB}\end{cases}, \tag{13}$$

where σ_{BB} is the diameter of a B molecule. When a B molecule is in contact with the A molecule at the reaction distance, the EV effect as shown in the expression of Eq. (13) tells us that the other B molecules should be found in the area $x\geqslant\sigma+\sigma_{BB}$.

With the help of Eq. (13), Eq. (8) can be simplified as

$$\frac{\partial}{\partial t}\rho_{AB}(x,t)=L_{AB}\rho_{AB}(x,t)-S_{AB}(x)\rho_{AB}(x,t)+k(t)c_B[1-g_{BB}(x-\sigma)]\rho_{AB}(x,t). \tag{14}$$

Note that Eq. (14) is now decoupled from Eq. (9) since $g_{BB}(x-\sigma)$ is given by Eq. (13).

It is interesting to consider two limiting cases of Eq. (14):

(i) When $\sigma_{BB}=0$, $g_{BB}(x-\sigma)=1$ [i.e., $X_{BB}(x,t)=1$] for $x\geqslant\sigma$ and Eq. (14) reduces to the usual Smoluchowski equation;

(ii) when $\sigma_{BB}\to\infty$, $g_{BB}(x-\sigma)=0$ [i.e., $X_{BB}(x,t)=0$] and Eq. (14) is written by

$$\frac{\partial}{\partial t}\rho_{AB}(x,t)=L_{AB}\rho_{AB}(x,t)-S_{AB}(x)\rho_{AB}(x,t)+k(t)c_B\rho_{AB}(x,t). \tag{15}$$

Therefore, the global concentration decay term [the last term in Eq. (15)] is due to $\sigma_{BB}\to\infty$, so it can be interpreted as the maximum EV effect. As the EV effect is decreased, so are the last two terms in Eq. (14). That is, the difference between the global concentration decay and the competitive reaction decreases. When $\sigma_{BB}=0$, those terms vanish. This means there is no EV effect. So Eq. (15) is the limiting expression of the maximum EV effect.

It is not easy to solve the coupled differential equations Eqs. (2) and (14) even numerically. We recently presented simple and efficient numerical methods for solving kinetic equations similar to the above equations.[20] These methods utilize the finite-difference method for the pair distribution function and the Runge–Kutta method with adaptive time steps to evolve the kinetic equation for the concentration. Because the main difficulty, especially for the long time dynamics, arises from implementing boundary conditions, we introduced the boundary doubling method to reduce the truncation error, which results from the fact that the outer spatial boundary is truncated at a finite separation instead of infinity. The method is based on the fact that the range covered by diffusive motion is proportional to $t^{1/2}$ and thus the outer boundary can be simply doubled at every quadruple time.

B. The many-particle kernel (MPK) theory

In the MPK theory of Lee *et al.*,[17] the kinetic equation for the pair distribution function is also given by Eq. (3) but the following truncation approximation is introduced instead of Eq. (6):

$$C_{ABB}(x,x',t)\cong C^{NEV}_{ABB}(x,x',t)g_{BB}(|x'-x|), \tag{16}$$

where the superscript *NEV* denotes the system with no EV effect.

Since we consider only the right half-infinite region ($x\geqslant 0$) in this work, $g_{BB}(|x-\sigma|)=g_{BB}(x-\sigma)$. With the help of Eq. (16) and $S_{AB}(x)=k_0\delta(x-\sigma)$ for the sink function, the integration part of Eq. (3) becomes

$$\int dx' k_0\delta(x'-\sigma)C^{NEV}_{ABB}(x,x',t)g_{BB}(|x-x'|) = k_0 C^{NEV}_{ABB}(x,\sigma,t)g_{BB}(|x-\sigma|). \tag{17}$$

With the expression of $g_{BB}(x-\sigma)$ in Eq. (13), Eq. (17) is rewritten as

$$\int dx' k_0\delta(x'-\sigma)C^{NEV}_{ABB}(x,x',t)g_{BB}(|x-x'|) = k_0 C^{NEV}_{ABB}(x,\sigma,t)[1-v_B(x)], \tag{18}$$

where

$$v_B(x)=\begin{cases}1 & \text{for} \quad x<\sigma+\sigma_{BB}\\ 0 & \text{for} \quad x\geqslant\sigma+\sigma_{BB}\end{cases}. \tag{19}$$

Using the MPK theory,[18] the three-particle correlation function with no EV effect can be written as

$$\hat{C}^{NEV}_{ABB}(x,\sigma,s)\cong c_B[g_{AB}(x)+\hat{\xi}^{NEV}(x,s)]\hat{C}_{AB}(\sigma,s), \tag{20}$$

where $\hat{\xi}^{NEV}(x,s)$ is the many particle kernel representing the deviation from equilibrium of the mean distribution of B molecules around an A molecules given that a B molecule is in contact with the A molecule. We have denoted the Laplace transform of a function $f(t)$ by $\hat{f}(s)\equiv\int_0^\infty dt e^{-st}f(t)\equiv\mathcal{L}[f(t)]$.

The survival probability $\hat{Y}(s)=[A]_s/[A]_0$ in the Laplace domain is given by

$$\hat{Y}(s)=\left[s+\frac{k_0c_B}{\hat{F}(s)}\right]^{-1}, \tag{21}$$

where

$$\hat{F}(s)=\hat{F}^{NEV}(s)-\hat{I}_{EV0}(s)-\hat{I}_{EV1}(s), \tag{22}$$

$$\hat{F}^{NEV}(s)=\frac{k_f^{eq}c_B\hat{Y}^{NEV}(s)}{1-s\hat{Y}^{NEV}(s)}, \tag{23}$$

$$\hat{I}_{EV0}(s)=\frac{c_Bk_0}{s}[1-e^{-\sigma_{BB}\sqrt{s/D}}], \tag{24}$$

$$\hat{I}_{EV1}(s)=-\frac{c_B^2k_0}{s[1-s\hat{Y}^{NEV}(s)]}\sqrt{\frac{D}{\pi}}\left\{\left(\sqrt{\frac{\pi}{s}}+\frac{2}{a}\right)\Omega\left(\frac{a}{2\sqrt{s}}\right)-\frac{2}{a}-\left[e^{-\sigma_{BB}\sqrt{s/D}}\mathcal{L}\left[\frac{1}{\sqrt{t}}e^{-a\sqrt{t}}\mathrm{erfc}\left(\frac{b}{\sqrt{t}}\right)\right]-\mathcal{L}\left[\frac{1}{\sqrt{t}}e^{-a\sqrt{t}+st}\mathrm{erfc}\left(\frac{b}{\sqrt{t}}+\sqrt{st}\right)\right]\right]\right\}. \tag{25}$$

In the above equations, $k_f^{eq}[=k_0g_{AB}(\sigma)]$ is the equilibrium rate constant, $a=2c_B\sqrt{D/\pi}$, $b=\sigma_{BB}/(2\sqrt{D})$, and $\Omega(x)=\exp(x^2)\mathrm{erfc}(x)$, where $\mathrm{erfc}(x)$ denotes the complementary error function.

The EV effect in the MPK theory is included via $v_B(x)$ in both $\hat{I}_{EV0}(s)$ and $\hat{I}_{EV1}(s)$. Also $g_{AB}(x)$ contributes to $\hat{I}_{EV0}(s)$ whereas $\hat{\xi}^{NEV}(x,s)$ does to $\hat{I}_{EV1}(s)$. In the three dimensional investigation of the EV effect by Lee *et al.*,[17] the additional ''coarse'' approximations are made for $\hat{\xi}^{NEV}(x,s)$ and also the linearization approximation is introduced for $v_B(x)$ in order to evaluate $\hat{I}_{EV1}(s)$. As they mentioned in their work, these approximations may lead to less reliable predictions of the MPK theory. Fortunately, these approximations are not necessary in 1D case, thereby, the MPK theory can be tested more accurately against other theories as well as against simulations.

Let us also consider the two limiting cases for the MPK theory:

(i) When $\sigma_{BB}=0$, these equations are reduced to the NEV case.

$$\hat{I}_{EV0}(s)=0,\ \hat{I}_{EV1}(s)=0,\quad \text{so}\ \ \hat{F}(s)=\hat{F}^{NEV}(s). \tag{26}$$

In this case, the survival probability reduces to that of the SM theory;

(ii) when $\sigma_{BB}\to\infty$, Eqs. (24) and (25) are reduced to

$$\hat{I}_{EV0}(s)=\frac{c_Bk_0}{s}, \tag{27}$$

$$\hat{I}_{EV1}(s)=-\frac{c_B^2k_0}{s[1-s\hat{Y}^{NEV}(s)]}\sqrt{\frac{D}{\pi}}\left\{\left(\sqrt{\frac{\pi}{s}}+\frac{2}{a}\right)\times\Omega\left(\frac{a}{2\sqrt{s}}\right)-\frac{2}{a}\right\}. \tag{28}$$

In order to evaluate the time-dependence of the survival probability from Eqs. (21)–(25), we used the Fortran Library, IMSL, for the numerical inverse Laplace transform.[23] The complex error function was coded using series expansion expression in a handbook.[24]

III. MONTE CARLO SIMULATIONS

Our MC simulation technique was described in detail in the previous work.[21] The main assumptions of our MC simulations are similar to those of the diffusion equation approach. For the initial conditions in this work, a reactant molecule *A* is fixed at the origin. Then many *B* molecules are randomly distributed in a 1D lattice. Based on the Einstein–Smoluchowski relation the displacement for one MC step is defined as $\Lambda=\sqrt{2Dt}$. The optimum size of the time step should be found until the simulation results converge. The optimum size of the system should be also found to minimize the finite edge effect which can be further minimized by using the periodic boundary condition and the minimum image convention. If one *B* molecule collides with *A* at the reaction distance, the reaction occurs with the probability of unity (corresponds to the Smoluchowski absorbing boundary condition) and the simulation is stopped and the time is recorded. Those records are averaged until the system converges. The EV effect between *B* molecules can be considered by not allowing the overlap between *B* molecules from the implantation time on.

The computational cost is reduced greatly by the parallelized programming, integer operation, and the safe distance method that we introduced in our previous work. The fact that all particles move the same distance in the lattice model leads to additional methods of improving the speed. We define the *safe distance* as the distance a particle can travel without colliding with nearest neighbor particles. Within this distance, one can move the particle safely without checking reactive collisions which is the most time consuming part of the MC simulation. The safe distance should be updated when the particle moves by that distance.

The finite size effect is important at long times. So, the system size should be sufficiently large to investigate the long time phenomena. The number of particles should be also increased proportionally to the system volume to maintain the same concentration. This requirement costs large computing time. Although the inclusion itself of the excluded volume between *B* molecules makes the computations expensive, the faster decay resulted from the EV effect allows us to use the smaller system size and rather lowers the computational cost. Our simulations (including numerical calculations) were done on a LINUX PC cluster with 16 Pentium III cpu's.

IV. RESULTS AND DISCUSSIONS

In this work, we only consider the diffusion-limited case with infinite value of k_0 (practically, $>10^9$) which corresponds to the Smoluchowski absorption boundary condition. The reduced time (τ), the reduced concentration (ϕ_B), and the reduced radius of *B* molecule (ρ_B) are used in all figures as defined by $\tau=t\times(10^9\ \mathrm{s}^{-1})$, $\phi_B=c_B\times(10^{-9}\ \mathrm{m})$, and $\rho_B=r_B\times(10^9\ \mathrm{m}^{-1})$, respectively. For the pseudo-first-order target system in which an *A* molecule is fixed at the origin and only *B* molecules are moving diffusively, the relative diffusion constant appearing in the Smoluchowski operator is actually that of *B* molecules. In all figures, the diffusion constant is given by $D=1.0\times10^{-9}\ \mathrm{m}^2\ \mathrm{s}^{-1}$. Since the present

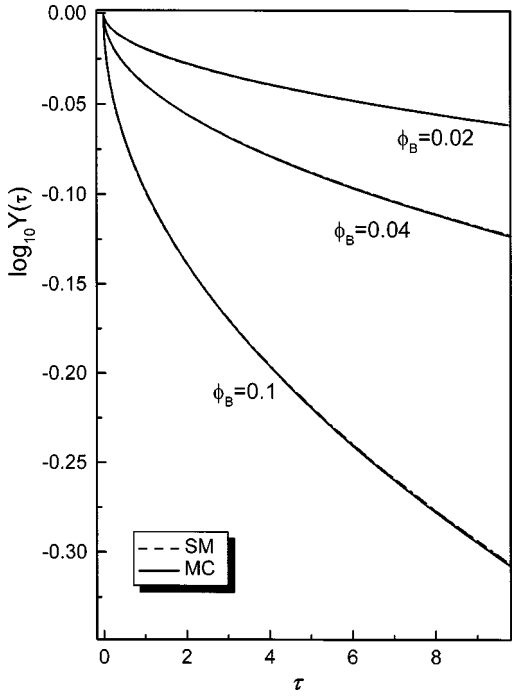

FIG. 1. The time profiles of survival probabilities (with no EV effect) obtained from Smoluchowski's exact solution (SM) and the Monte Carlo simulation (MC) for several values of the concentration of B molecules. The reduced time (τ), the reduced concentration (ϕ_B), and the reduced radius of B molecule (ρ_B) are used in all figures as defined by $\tau=t\times(10^9\ \mathrm{s}^{-1})$, $\phi_B=c_B\times(10^{-9}\ \mathrm{m})$, and $\rho_B=r_B\times(10^9\ \mathrm{m}^{-1})$, respectively. The reduced radius in this figure is $\rho_B=0.0$. The diffusion constant of $D=1.0\times10^{-9}\ \mathrm{m}^2\ \mathrm{s}^{-1}$ is used in all figures.

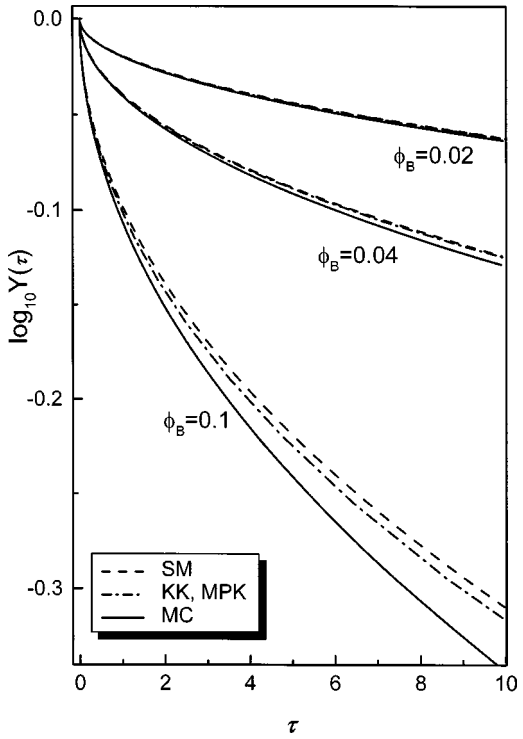

FIG. 2. The EV effect on the time profiles of survival probabilities obtained from the Kuzovkov and Kotomin (KK) theory, the many particle kernel (MPK) theory, and the MC simulation for several values of ϕ_B with $\rho_B=0.5$. The SM result is also plotted for comparison.

MC simulations are performed over the entire interval and the KK and MPK theories are presented over the half interval, the survival probabilities obtained from these theories are squared in order to compare with MC results.

When there is no EV effect, the exact survival probability with the Smoluchowski absorption boundary condition ($k_0\to\infty$) for the half-infinite space is given by[2]

$$Y(t)=\frac{[A]}{[A]_0}=e^{-2c_B\sqrt{Dt/\pi}}. \tag{29}$$

The time profiles of survival probabilities with no EV effect obtained from Smoluchowski's exact solution (SM) [the square of Eq. (29)] and the Monte Carlo simulation (MC) are plotted in Fig. 1 for several values of the concentration of B molecules in order to check the accuracy of the present MC simulation. The reduced radius of B molecule for the case without EV effect is $\rho_B=0.0$. As is well know, the reaction distance σ does not affect the reaction rate in 1D. As shown in the figure, our MC simulation results show good agreement with the SM results at various concentrations of B molecules.

The EV effect on the time profiles of survival probabilities obtained from the KK theory, the MPK theory, and the MC simulation are plotted in Fig. 2 for several values of ϕ_B with $\rho_B=0.5$. The SM result is also plotted for comparison. In the presence of the EV effect, the survival probability from the KK theory should be calculated with Eqs. (8) and (12). The results from the KK theory and the MC simulations show that the values of the survival probabilities are considerably lowered compared to that of the SM theory (with no EV effect) as ϕ_B increases as shown in Fig. 2. However, the MC simulation results become much lower than the KK theory results as ϕ_B increases. It is interesting to notice that the MPK theory also gives almost the same results as the KK theory over a considerable time range with the present parameter values. In either of the KK or MPK theory, the EV effect is incorporated through the three-particle distribution function coupled to the sink function representing the reaction events. However, the EV effect in terms of the like particle correlation is present irrespective of the reaction. The lack of description of this kind of contribution in the KK (or MPK) theory may be the cause of the discrepancy against the MC results.

The reaction-independent like particle correlations can lead to the ''cage'' effect: The B molecules farther away from the A molecule may form a shell-like structure blocking the escape of unreacted B molecules near the A molecule. In the nearer region from A molecule, the concentration of B molecules is lower due to the reaction and this causes the local concentration gradient. Therefore, B molecules are more likely to approach toward A than to escape due to the EV effect.

The dependence of the time profiles of survival probabilities (with the EV effect) on the size of B molecules (ρ_B) from the KK theory, MPK theory, and MC simulations are plotted in Fig. 3 for $\phi_B=0.1$. The EV effect becomes more pronounced as ρ_B increases in this figure just as the former does as ϕ_B increases in Fig. 2. This shows that the increased size of B molecules may correspond to the effective increase

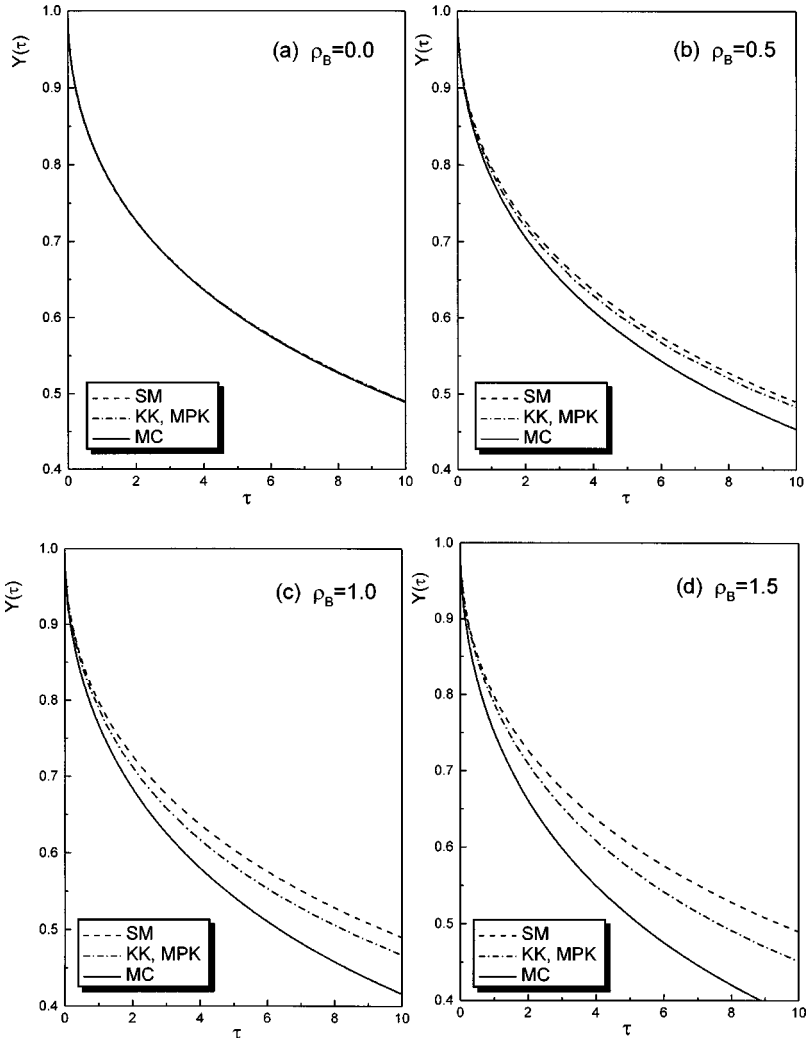

FIG. 3. The dependence of the time profiles of survival probabilities (with the EV effect) on the size of B molecules (ρ_B) from the MPK theory and MC simulations at $\phi_B=0.1$: (a) $\rho_B=0.0$, (b) $\rho_B=0.5$, (c) $\rho_B=1.0$, and (d) $\rho_B=1.5$.

of its concentration. Again, as in Fig. 2, the MC results show much lower values than the KK (or MPK) theory. It appears that the MC results are consistently lower than the present theoretical predictions as either the size or the concentration of B molecules is increased.

It is rather surprising to compare Fig. 3 with the similar figure in the 3D case of Lee *et al.*[17] Their Brownian dynamics (BD) simulations show very good agreement with the MPK theory except at large size of B molecules contrary to large discrepancy shown in 1D system. Since several ''coarse'' approximations were made in the MPK theory with the EV effect in 3D, it is not clear whether the good agreement between the MPK theory and their BD simulation is due to the dimensional effect or the approximations or, may be, some statistical errors in the simulation.

V. CONCLUDING REMARKS

We have investigated the EV effect on the pseudo-first-order irreversible diffusion-influenced reaction, $A+B\rightarrow C$, in 1D and the survival probability of A molecules is obtained by the Kuzovkov and Kotomin (KK) theory,[12] the many particle kernel (MPK) theory of Lee *et al.*,[17] and Monte Carlo (MC) simulations.

Contrary to the formulation of MPK theory in 3D, no additional coarse approximations are made in 1D formulation, thereby, the MPK results become more accurate in 1D than those of 3D. It is interesting to notice that, although formulations and resulting expressions are different, the MPK theory predicts almost identical results as those of the KK theory numerically. This may be due to the fact that the differences decrease in the pseudo-first-order limit and also for the irreversible system.

As in the previous investigation in 3D system, the EV effect becomes more pronounced as either the concentration or the size of the B molecules is increased. Although both the KK and MPK theories predict the EV effect successfully for limited parameter regions with small EV effect, these theories are shown to give very poor predictions for the system with large EV effects system. In fact, the MC results show much lower values compared to both theoretical predictions.

We believe that the EV effect is important due to two reasons. First, occupation of the finite volume affects the environment as if the concentration of B molecules is higher. As mentioned previously, the global concentration decay of A molecules is identical to the decrease by the competitive reaction when the B molecules have no correlation between them which corresponds to the Smoluchowski case. This oc-

cupation effect is considered in both the KK and MPK theories. The other reason is the cage effect due to the blocking of the outer shell structure of *B* molecules as well as to the diffusive movement toward the *A* molecule driven by the local concentration gradient produced by the reaction near the *A* molecule. This cage effect is not considered in both theories because the simple Smoluchowksi diffusion operator, in which the movement of *B* molecules is only dependent on the concentration gradient, is used. Both effects are included in MC simulations and this leads to a rather big difference from the theoretical predictions.

ACKNOWLEDGMENTS

This work was supported by Grant No. 2000-1-12100-003-1 from the Basic Research Program of the Korea Science and Engineering Foundation. J.P. thanks Juhyoek Lee for helpful discussions.

[1] M. Smoluchowski, Z. Phys. Chem., Stoechiom. Verwandtschaftsl. **92**, 129 (1917).
[2] A. Szabo, J. Phys. Chem. **93**, 6929 (1989).
[3] A. Blumen, G. Zumofen, and J. Klafter, Phys. Rev. B **30**, 5379 (1984).
[4] P. Grassberger and I. Procaccia, J. Chem. Phys. **77**, 6281 (1982).
[5] A. Szabo, R. Zwanzig, and N. Agmon, Phys. Rev. Lett. **61**, 2496 (1988).
[6] H. Kim and K. J. Shin, J. Chem. Phys. **112**, 8312 (2000).
[7] S. A. Rice, *Diffusion Limited Reaction, Comprehensive Chemical Kinetics, Vol. 25*, edited by C. H. Bamford, C. F. H. Tipper, and R. G. Compton (Elsevier, Amsterdam, 1985).
[8] E. Kotomin and V. Kuzovkov, *Modern Aspects of Diffusion-Controlled Reactions, Comprehensive Chemical Kinetics, Vol. 34*, edited by R. G. Compton and G. Hancock (Elsevier, Amsterdam, 1996).
[9] Yu. H. Kalnin, Phys. Status Solidi B **101**, K139 (1980).
[10] E. Kotomin and V. Kuzovkov, Chem. Phys. **76**, 479 (1983).
[11] V. Kuzovkov and E. Kotomin, Chem. Phys. **81**, 335 (1983); **98**, 351 (1985).
[12] V. Kuzovkov and E. Kotomin, Rep. Prog. Phys. **51**, 1479 (1988).
[13] S. F. Swallen, K. Weidemaier, and M. D. Fayer, J. Phys. Chem. **99**, 1856 (1995).
[14] S. F. Swallen and M. D. Fayer, J. Chem. Phys. **103**, 8864 (1995).
[15] A. Blumen and J. Manz, J. Chem. Phys. **71**, 4694 (1979).
[16] Y. Jung and S. Lee, J. Phys. Chem. **101**, 5255 (1997).
[17] J. Lee, J. Sung, and S. Lee, J. Chem. Phys. **113**, 8686 (2000).
[18] J. Sung and S. Lee, J. Chem. Phys. **111**, 796 (1999).
[19] V. Kuzovkov and E. Kotomin, Phys. Rev. Lett. **72**, 2105 (1994); S. F. Burlatsky, M. Moreau, G. Oshanin, and A. Blumen, *ibid.* **75**, 585 (1995); D. P. Bhatia, M. A. Prasad, and D. Arora, *ibid.* **75**, 586 (1995); V. Kuzovkov and E. Kotomin, *ibid.* **75**, 587 (1995).
[20] H. Kim, S. Shin, and K. J. Shin, J. Chem. Phys. **108**, 5861 (1998); Chem. Phys. Lett. **291**, 341 (1998).
[21] H. Kim, S. Shin, and K. J. Shin, J. Chem. Phys. **105**, 7705 (1996).
[22] S. Lee and M. Karplus, J. Chem. Phys. **86**, 1883 (1987).
[23] IMSL FORTRAN library version 1.1, Vol. 2-2 (IMSL, Houston, 1989).
[24] *Handbook of Mathematical Functions*, edited by M. Abramowitz and I. A. Stegun (Dover, New York, 1970).