Single species diffusion-influenced reaction $A+A\rightarrow\alpha A$: Validity of the Smoluchowski approach

Hyojoon Kim and Kook Joe Shin*
Department of Chemistry and Center for Molecular Catalysis, Seoul National University, Seoul 151-742, Korea
(Received 30 June 1999; revised manuscript received 5 November 1999)

We investigate the single species diffusion-influenced reaction, $A+A\rightarrow\alpha A$ with a finite reactivity in all dimensions. The reaction model includes a pure coagulation ($\alpha=1$) or a pure annihilation ($\alpha=0$) model. We apply the hierarchical Smoluchowski approach to study the dimensional aspects of the fluctuation, reactivity, particle size, and $\alpha(0\leqslant\alpha\leqslant1)$. The theoretical results are compared with those of the Monte Carlo simulations in one, two, and three regular dimensions. The simulation results reveal that the classical Smoluchowski approach is exact in the short time limit in all dimensions and in the long time limit in three dimensions. The hierarchical Smoluchowski approach is found to be numerically exact at all times in two and three dimensions. A numerical method to obtain the exact result of the annihilation for a finite reactivity in one dimension is presented. We also propose a quite accurate analytic solution for an arbitrary α for the infinite reactivity in one dimension.

PACS number(s): 05.40.−a, 05.50.+q, 05.70.Ln, 82.35.+t

I. INTRODUCTION

The single species diffusion-influenced reaction $A+A\rightarrow\alpha A$ has been the subject of extensive theoretical, numerical, and experimental studies [1–30]. The reaction model includes an annihilation ($\alpha=0$) or a coagulation ($\alpha=1$) model. Besides the applicability to many experiments, these models have attracted much attention theoretically because they provide one of the simplest examples of many particle diffusion-influenced reactions. Moreover, the exact results known in one dimension (1D) [3–5] can be used to check the validity of various theories proposed by many workers.

In the classical kinetics, the rate coefficient is set to be a constant and we obtain the long time asymptotic behavior of the A species as $[A]\sim t^{-1}$ regardless of the dimensionality. However, it is now well known that the long-time asymptotic behavior, except for the exotic fractal distributions [26], is given by [2]

$$[A]\sim t^{-a} \quad \text{with} \quad a=\min(1,\, d/2), \tag{1}$$

where d is the dimensionality of the system.

Although some theories have been successful to obtain the exact results for the annihilation and coagulation models in 1D, the approaches in those studies are rather specific and have difficulties in generalizing to other systems. Among various theoretical approaches, those based on a hierarchy of Smoluchowski equations for the reduced distribution functions of the reactant particles are particularly useful. They not only predict the correct long time asymptotic power-law behavior but also provide a systematic and flexible theoretical framework for dealing with the system with a complicated reaction mechanism. This line of development was initiated by Waite [31] and Monchick *et al.* [32]. Lee and Karplus [33] reformulated the hierarchical Smoluchowski approach (HSA). The above HSA's, however, adopted the *reduced* superposition approximation reproducing the same result of the classical Smoluchowski approach (SM) [34] for the irreversible reaction system. The indirect correlation such as the correlation between the like particles can be considered by employing the Kirkwood superposition approximation (KSA) [1,11,13]. Kuzovkov and Kotomin [1] adopted the HSA with the KSA to investigate the two species system $A+B\rightarrow$inert and successfully attributed the long time asymptotic behavior of $[A]\sim t^{-d/4}$ to the microscopic fluctuation effect. However, they also found that the fluctuation effect in the single-species system is too weak to change the asymptotic power law exponent at long times.

It is very interesting that the SM, which is the oldest and the simplest theory in the diffusion influenced reaction field, predicts the correct long-time asymptotic power law decay as given by Eq. (1) [1,10,11]. Since the SM is a mean-field theory and it does not consider the fluctuation effect, the anomalous power law decay in the single species system results from the dimensional restriction rather than the microscopic fluctuation effect that changes the asymptotic power-law decay in the two species system.

The purpose of the present work is to investigate the dimensional aspects of the single species reaction system with the HSA with two types of superposition approximations; the reduced superposition approximation which leads to the SM and the KSA. We consider a general coagulation-annihilation model, $A+A\rightarrow\alpha A$ in which α is a real value within $0\leqslant\alpha\leqslant1$ and investigate the dimensional aspects of the fluctuation, reactivity, particle size, and α. Despite the usefulness of the HSA with the KSA, the results can only be obtained numerically. On the other hand, some general results of the SM can be obtained analytically. In this way, we find some simple explanations about many interesting results that were already reported by other complicated approaches. We also believe that some of the present results are newly revealed despite the long history of the SM.

The exact results in 1D have been reported only for the infinite reactivity. We find a numerical method to obtain the exact result of the annihilation ($\alpha=0$) for a finite reactivity case. We also propose an approximate solution for an arbi-

*Author to whom correspondence should be addressed. Electronic address: statchem@plaza.snu.ac.kr

trary value of α for the infinite reactivity. In higher dimensions, one has to rely on the simulation method to check the validity of the developed theories. In most lattice-based Monte Carlo (MC) simulations, the particle size is ignored even above two dimensions (2D) in which it affects the dynamics critically. We incorporate the particle size into the simulation and compare the results with those of the HSA quantitatively. Lin *et al.* [14] compared the results of the above two superposition approximations on the single species system in 1D. But they have never been compared in higher dimensions. We find that the HSA with the KSA gives the numerically exact results in higher dimensions and the results of the SM become exact at long times in three dimensions (3D).

The remains of this paper are organized as follows. In Sec. II, we extend the HSA to an arbitrary α and discuss the analytical results of the SM. Numerical and simulation methods are presented in Sec. III. Theoretical results are compared with those of simulations in Sec. IV followed by several concluding remarks in Sec. V.

II. THEORETICAL BACKGROUD

Kuzovkov and Kotomin [1] adopted the KSA in the HSA and obtained the corresponding kinetic equations that can be rewritten, for the general coagulation-annihilation model $A+A\rightarrow\alpha A$, as

$$\frac{d}{dt}[A]=-(1-\alpha/2)k(t)[A]^2, \tag{2}$$

$$k(t)\equiv\int dr\,\frac{2\pi^{d/2}r^{d-1}}{\Gamma(d/2)}S(r)\rho(r,t), \tag{3}$$

$$\frac{\partial}{\partial t}\rho(r,t)=[L_{AA}(r)-S(r)]\rho(r,t) + (2-\alpha)k(t)[A]\rho(r,t)[1-X(r,t)], \tag{4}$$

where $k(t)$ is the time-dependent rate coefficient and $\rho(r,t)$ the pair correlation function. The reactive sink function $S(r)$ and the nonreactive diffusive evolution operator $L_{AA}(r)$ are given, respectively, by

$$S(r)=\frac{k^0\Gamma(d/2)\,\delta(r-\sigma)}{2\pi^{d/2}\sigma^{d-1}}, \tag{5}$$

$$L_{AA}(r)=D\left(\frac{\partial^2}{\partial r^2}+\frac{d-1}{r}\frac{\partial}{\partial r}\right), \tag{6}$$

where $D(=2D_A)$ is the *relative* diffusion constant, k^0 the intrinsic reactivity, σ the reaction distance, $\Gamma(x)$ the gamma function, and $\delta(x)$ the Dirac delta function. For the regular dimensions, the expressions of $X(r,t)$ in Eq. (4) were given in Refs. [1] and [35].

Note that when the particle size is very small, $X(r,t)$ reduces to $\rho(r,t)$:

$$\lim_{\sigma\rightarrow 0}X(r,t)=\rho(r,t). \tag{7}$$

The physical meaning of $X(r,t)$ is similar to $\rho(r,t)$ averaged over the region covered by the reaction distance around r and, thus, one could use the point particle approximation of Eq. (7) in the small particle size limit. Since $\rho(r,t)$ is always smaller than unity in the present system, so is $X(r,t)$.

The last term of Eq. (4) disappears in adopting the reduced superposition approximation. In this way, the HSA can reproduce the result of the SM. In other words, the difference between the HSA with the KSA and the SM is the last term. From the derivation of the above results, one can know that the physical meaning of the last term is the difference between the global concentration decay $[(2-\alpha)k(t)[A]\rho(r,t)]$ and the competitive reaction $[(2-\alpha)k(t)[A]\rho(r,t)X(r,t)]$. The local concentration fluctuation due to reaction can make the particles aggregate as in the two species system but the aggregation in the single species system only leads to the reaction itself. This rather accelerates the global concentration change more than the competitive reaction. Consequently, the fluctuation effects are incorporated in the last term [1]. Although the SM considers some spatial inhomogeneities like the direct pair correlation, the SM is a mean-field theory and neglects the local fluctuation effect by setting the competitive reaction change equal to the bulk concentration decay or by neglecting the indirect pair correlation.

Unfortunately, it is impossible to solve the above coupled differential equations exactly and one has to solve them numerically as presented below. When the fluctuation term is neglected, we can obtain an analytical result which is a generalized version of the SM for the arbitrary reactivity (k^0), dimension (d), and α as

$$\frac{1}{[A]}-\frac{1}{[A]_0}=L^{-1}\left[\frac{(1-\alpha/2)k^0\sqrt{s/D}K_{d/2}(\sigma\sqrt{s/D})}{C_dk^0s^2K_{d/2-1}(\sigma\sqrt{s/D})+s^2\sqrt{s/D}K_{d/2}(\sigma\sqrt{s/D})}\right], \tag{8}$$

where $L^{-1}[\tilde{f}(s)]$ denotes the inverse Laplace transform of $\tilde{f}(s)$, $C_d\equiv\Gamma(d/2)/2\pi^{d/2}D\sigma^{d-1}$, and $K_v(x)$ the modified Bessel function of the second kind. The derivation of the above result is presented in Appendix A.

We now investigate the asymptotic expressions of Eq. (8) in the long and short time limits. The asymptotic long time results depend on d as

$$\lim_{t\rightarrow\infty}[A]=\frac{\Gamma(1-d/2)\Gamma(d/2)d}{(1-\alpha/2)2^{d+1}\pi^{d/2}D^{d/2}}t^{-d/2}\quad(d<2) \tag{9}$$

$$\lim_{t\to\infty}[A]=\frac{k^0\Gamma(d/2-1)+4\pi^{d/2}\sigma^{d-2}D}{(1-\alpha/2)k^0 4\pi^{d/2}\sigma^{d-2}D}t^{-1}\quad(d>2). \tag{10}$$

For the critical two dimensions (2D), the asymptotic expression contains the logarithmic corrections as $\lim_{t\to\infty}[A]\sim(\ln t)/t$ [7,36]. These results clearly show that the SM predicts the same well-known asymptotic power-law decay for any α and k^0. For the infinite reactivity, the long time asymptotic concentration is different from the finite reactivity case only for $d>2$ as

$$\lim_{\substack{k^0\to\infty\\ t\to\infty}}[A]=\frac{\Gamma(d/2-1)}{(1-\alpha/2)4\pi^{d/2}\sigma^{d-2}D}t^{-1}\quad(d>2). \tag{11}$$

It is interesting to note that while the rate coefficient converges to a constant as $t\to\infty$ for $d>2$, it goes to zero for $d<2$ as

$$\lim_{t\to\infty}k(t)=\frac{2^d\pi^{d/2}D^{d/2}}{\Gamma(1-d/2)\Gamma(d/2)}t^{(d/2)-1}\to 0\quad(d<2) \tag{12}$$

$$\lim_{t\to\infty}k(t)=\frac{k^0 4\pi^{d/2}\sigma^{d-2}D}{k^0\Gamma(d/2-1)+4\pi^{d/2}\sigma^{d-2}D}\quad(d>2). \tag{13}$$

This implies that the assumption of a constant rate coefficient in the classical kinetics fails and it gives incorrect results for $d<2$. The dependence on the dimensionality arises from the fact that diffusion is not an effective mixing mechanism for $d<2$ [15]. The restriction disappears in higher dimensions. Therefore, the failure of the classical kinetics in low dimensions can be explained better by the wrong assumption of a constant rate coefficient than by the neglect of the deviation of the spatial distribution from a random configuration since the latter effect is neglected also in 3D, for which the classical kinetics predicts the correct long time power-law exponent. Therefore, the argument that the anomalous kinetics cannot be accounted for in a mean-field reaction-diffusion model [5] is caused by the use of the constant rate coefficient.

The long time asymptotic rate coefficient in the critical dimension can be readily obtained from the general expression of the SM [37] as

$$\lim_{t\to\infty}k(t)=\frac{4\pi D}{\ln(4Dt/\sigma^2)-2\gamma+4\pi D/k^0}\quad(d=2), \tag{14}$$

where γ is the Euler constant. Note that the rate coefficient vanishes very slowly due to the logarithmic dependence in 2D but it does following the power-law behavior for $d<2$.

The fluctuation effect could be neglected in the low-concentration limit since the local fluctuation term is multiplied by the bulk concentration in Eq. (4). The SM is exact in this limit. This is not surprising since each pair of particles is implicitly assumed to be statistically independent in the SM. Note that the SM predicts that the concentration in the coagulation is twice as large as that in the annihilation not only at long times but at all times.

On the other hand, the short time dynamics depends only on k^0 for *all* dimensions:

$$\lim_{t\to 0}k(t)=k^0, \tag{15}$$

$$\lim_{t\to 0}\frac{1}{[A]}-\frac{1}{[A]_0}=(1-\alpha/2)k^0 t. \tag{16}$$

The above expressions have no dependence on the dimensionality. This tells us that the short time dynamics is reaction-limited and it can also be described by the classical kinetics. The relative magnitude of two terms in the denominator of Eq. (8) determines whether the dynamics is reaction limited or diffusion limited. As k^0 decreases, the second term dominates and the rate coefficient shows the reaction-limited behavior, while the diffusion-limited behavior prevails as k^0 increases. Interestingly, the reaction-limited behavior disappears for the infinite reactivity. The short time asymptotic expressions for infinite reactivity is given by

$$\lim_{\substack{k^0\to\infty\\ t\to 0}}\frac{1}{[A]}-\frac{1}{[A]_0}=\frac{(1-\alpha/2)4\pi^{(d-1)/2}\sigma^{d-1}\sqrt{D}}{\Gamma(d/2)}t^{1/2}. \tag{17}$$

Note that this expression shows not only the different power-law behavior from Eq. (16) but also the d dependence in the prefactor.

In the short time limit, the fluctuation term of Eq. (4) can be neglected for the random initial condition. This can be explained by the fact that the local fluctuation is not yet sufficiently developed. Therefore, the results of the SM, namely, Eqs. (16) and (17) are *exact* at short times. This can explain the finding of Argyrakis *et al.* [15] that the single species behavior appears at early times in the two species annihilation for which the SM predicts the same results as those in the single species model. One can expect that the SM is exact also for the two species system in the short time limit. Of course, it fails at long times because of the fluctuation effect.

If we define the survival probability $P(t)\equiv[A]/[A]_0$, one can see from Eqs. (2) and (4) that $P(t)$ is independent of α at all times when $[A]_0=1/(2-\alpha)$ [20–22]. It is well known, however, the concentration for the coagulation $[A]_c$ is twice as large as that for the annihilation $[A]_a$ in the long time limit without any restriction on $[A]_0$. This can be explained as follows. Since the long time power-law exponent is not affected by the fluctuation term, the asymptotic concentration is given by $[A]\sim b(\alpha)t^{-a}$, where $b(\alpha)$ is a certain constant depending on α. Then $\rho(r,t)$ and, thus, $k(t)$ are independent of α in the long time limit, which leads to the relation $[A]_c=2[A]_a$ without any restriction on the initial concentration. This result is, in fact, exact since the approximate nature of the HSA comes in only via $X(r,t)$ in Eq. (4) due to the truncation of the hierarchy by the KSA but the term including $X(r,t)$ vanishes in the long time limit. Remembering that the pair correlation function is always inde-

pendent of α in the SM, one can conclude that $\rho(r,t)$ depends less on α in the HSA as the concentration is decreased and/or the dimensionality is increased.

Recently, Molski [17] suggested an interesting argument that the long time result may be different from the exact result if the model allows the overlapping of particles at lattice points. In order to check this argument, we solve the problem for the overlapping initial condition for the infinite reactivity with the SM to give

$$\frac{1}{[A]}-\frac{1}{[A]_0}=L^{-1}\left\{\frac{1-\alpha/2}{C_d s\sqrt{sD}}\left[\frac{K_{d/2}(\sigma\sqrt{s/D})}{K_{d/2-1}(\sigma\sqrt{s/D})}+\frac{I_{d/2}(\sigma\sqrt{s/D})}{I_{d/2-1}(\sigma\sqrt{s/D})}\right]\right\}, \tag{18}$$

where $I_v(x)$ is the modified Bessel function of the first kind. In the long time limit, the overlapped particles disappear and Eq. (18) correctly reduces to Eq. (8) for the infinite k^0. This tells us that the overlapping initial condition does not affect the long time asymptotic behavior. It is also interesting to note that Eq. (18) reduces to Eq. (8) in the point particle limit $(\sigma\rightarrow 0)$ since it is impossible for the point particles to overlap. Consequently, the overlapping initial condition does not affect the long time dynamics.

III. NUMERICAL METHOD

Since there is no analytical result except for a few 1D systems, one should rely on the numerical method to obtain the correct results. It is not easy to solve the above coupled differential equations Eqs. (2)–(4) even numerically. We recently presented simple and efficient numerical methods for solving kinetic equations similar to the above equations [38]. 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.

The MC simulation method [39] that we employed in this paper is explained as follows. The diffusive motion of A molecules can be described as random walks consisting of a series of small steps. The average displacement $\mathbf{r}$ of random walks is given by the Einstein-Smoluchowski relation: $\langle \mathbf{r}^2\rangle = 2dD_A t$, where D_A is the self-diffusion constant of A molecules. This relation is used to define the displacement for one MC step as $\Delta r=\sqrt{2dD_A\Delta t}$, where Δr constitutes the lattice constant and Δt stands for the time taken in one MC step. This definition of the average displacement, along with a lattice model, provides a connection between the MC steps and the real times for the dynamics of the system. The optimum size of Δt and, therefore, Δr should be found since the small Δt increases the computational cost while the large Δt decreases the accuracy.

The size of the system should be increased until the edge effect can be nearly neglected. The number of particles is determined by the size of system to maintain the given concentration. This is the reason why the higher dimension is more difficult to carry out the simulation. The periodic boundary condition and the minimum image convention are used as usual to minimize the edge effect.

Initially, particles are randomly created on sites in a regular dimensional lattice. Each particle occupies several lattice points due to its size $\sigma(>\Delta r)$. For the point particle, it occupies only one site. When the tried site is already occupied by other particles, another unoccupied site is tried unless the overlap of particles is allowed. After all the particles are placed on the lattice, they start moving in random directions. If one particle moves within the reaction distance σ of the other, which is defined as a collision, a reaction may occur with the presumed reaction probability. If a reaction occurs, the particles are removed from the system according to the value of α. For example, only one particle is removed for the coagulation model and two particles for the annihilation. The microscopic reaction probability, p, which is the ratio of the number of reactive collisions to the number of total collisions in a system, is related to the intrinsic reactivity, k^0, appeared in the analytic theories. The relation is thought to be linear but the exact relation is yet to be clarified [29,40]. Unit reaction probability represents the case of infinite rate constant where every collision results in a reaction.

When one is interested in the long time dynamics, the computational cost for the simulation is very high since the edge effect becomes important at long times and the large system size or the large number of particles are needed, especially for 3D. The inclusion of the particle size effect further increases the computing time. The particle size is only tuned up by Δr and, therefore, Δt should be reduced to obtain the converged result. We have used several methods to reduce the computing time significantly. First, all programs of the simulations were coded for parallel processing. The present simulations are very well suited for the parallel processing since they can average the results of each independent ensemble, which can be easily parallelized into each CPU. We can obtain the gain in computational speed as many times as the number of CPU's. Our calculations were done on an IBM SP2 model MPP (Massively Parallel Processing) computer with 40 nodes. Secondly, one can use only integer operations for the main MC steps for the lattice model. Most computer architectures are well optimized for the integer calculation. The fact that all particles move by 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 the 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 simulation. The safe distance can be generated for no further cost in checking the collision. And, of course, it should be updated when the particle moves by that distance. Such safe distances allow the multiple jump method. If the minimum safe distance of all the particles is larger than the single step size, all particles

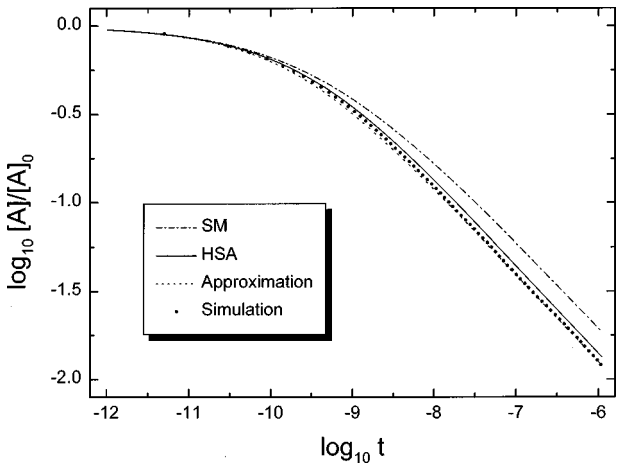

FIG. 1. The time dependence of the concentration for the coagulation reaction in 1D obtained from the SM, HSA, approximate, and simulation results. The simulation result almost coincides with the result of Eq. (19). Values of parameters used are: $D=2.0\times10^{-5}\,\mathrm{cm}^2\,\mathrm{s}^{-1}$, $[A]_0=1.0\times10^9\,\mathrm{m}^{-1}$, $\sigma=0$ m, $p=1$ ($k^0\to\infty$).

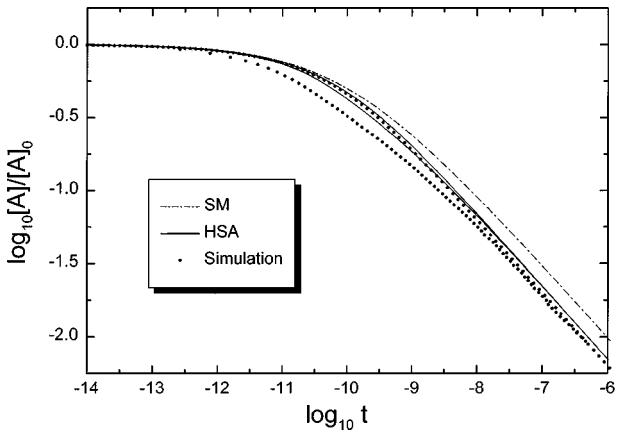

FIG. 2. The particle-size effect [$\sigma=0$ (the upper group) and 5×10^{-10} m (the lower group)] on the time dependence of the concentration for the annihilation in 1D obtained from the SM, HSA, and simulation results. Parameters are the same as in Fig. 1 except σ.

can move safely within the minimum distance. The speed gain is proportional to the square of the step size increase. The time saving by utilizing the safe distance method is larger at long times when the concentration is low and the safe distance is large. Therefore, the safe distance method is very efficient to investigate the long time dynamics.

IV. RESULTS AND DISCUSSION

For 1D systems, some exact results for the point particle and the infinite reactivity have been reported. Torney and McConnell [3] obtained the exact result for the annihilation model with the random initial condition. For the coagulation, Doering and ben-Avraham [5] obtained the exact result but, unfortunately, it is not a closed form for the random initial condition. For an arbitrary value of α, we generalize the exact result of Torney and McConnell approximately as given in Appendix B. The resulting approximate concentration in 1D for the infinite k^0 can now be used to obtain the accurate data for *all* times easily:

$$[A]\approx\frac{2[A]_0\Omega(2[A]_0\sqrt{Dt})}{\alpha\Omega(2[A]_0\sqrt{Dt})+2-\alpha}, \tag{19}$$

where $\Omega(x)\equiv\exp(x^2)\mathrm{erfc}(x)$, and $\mathrm{erfc}(x)$ is the complementary error function.

Doering and ben-Avraham also found a long time rate equation $d[A]/dt=-\pi(D/2)[A]^3$, which is different from the familiar form of Eq. (2). However, the exact long time asymptotic concentration can also be obtained from the familiar form of the rate equation, $d[A]/dt=-\sqrt{D\pi/4t}[A]^2$, once we know the exact rate coefficient given in Appendix B.

In Fig. 1, we compare the time evolution of the concentration predicted by the SM and the HSA with the simulation and we also test the accuracy of the above approximation [Eq. (19)] for $\alpha=1$ since the approximation is worst for the coagulation model. We set the parameters as follows: $D=2.0\times10^{-5}\,\mathrm{cm}^2\,\mathrm{s}^{-1}$, the random initial concentration $[A]_0=1.0\times10^9\,\mathrm{m}^{-1}$ (the number density of 0.1), the particle size $\sigma=0$ m (the point particle), and the reaction probability $p=1$ (which corresponds to $k^0\to\infty$). The approximate solution gives the nearly indistinguishable result from that of the simulation even for the relatively high initial density (0.1). Only at intermediate times it deviates slightly from the simulation result. It becomes more accurate for the lower value of α.

The SM and the HSA give qualitatively correct long time asymptotic behavior (the slope of $-1/2$), but the quantitative errors for the prefactors are 57% and 11%, respectively, as previously shown by Lin *et al.* [14]. We find an analytic expression of the asymptotic concentration which shows the best fit of the numerical results of the HSA as

$$\lim_{t\to\infty}[A]\sim\frac{1}{2-\alpha}\sqrt{\frac{\pi}{8Dt}}. \tag{20}$$

From Fig. 1, we can conclude that the HSA describes the fluctuation effect well but not completely, which is in agreement with the previous result for the two species system [35,38]. We have also performed the simulation where the overlap between particles is initially allowed. However, no distinguishable difference is found even at short times for the present parameter set.

The particle size (σ) effect depends on the dimensionality. The analytical results suggest that the rate coefficient vanishes as $\sigma\to0$ for $d>2$ and, therefore, the concentration does not decay. This can be explained by the fact that the reactive encounter of particles cannot occur since the collision cross section vanishes. Interestingly, the SM predicts that the σ-dependence disappears at all times in 1D. The size effect in 1D is related to the fluctuation effect described by the HSA. The fluctuation accelerates the reaction rate as σ gets larger. This can be easily understood since the reaction can occur faster at a larger reaction distance. Therefore, the σ dependence comes in only via $X(r,t)$ and it is expected to vanish at long times in 1D.

The particle size effect on the time evolution of the concentration in 1D is shown in Fig. 2 for the annihilation. The parameters are the same as before except the particle size

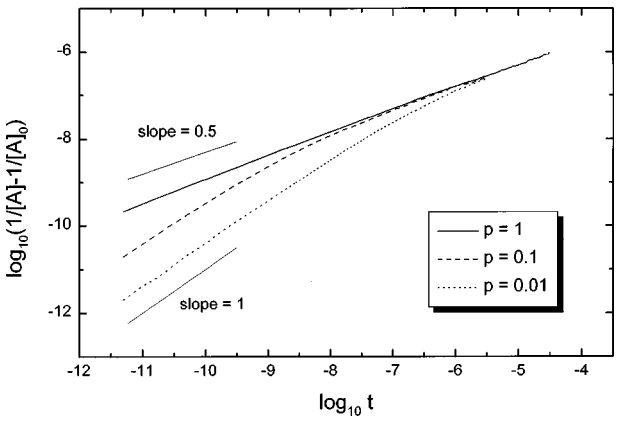

FIG. 3. The finite reactivity effect on the time dependence of the concentration for the annihilation in 1D obtained from the simulation result. Parameters are the same as in Fig. 1 except p.

($\sigma=0$ and 5×10^{-10} m). Since there is no exact result for a finite σ, we compare the SM and HSA results with the simulation. As previously shown, the SM predicts that the σ dependence disappears in 1D. However, the simulation results clearly show that the particle-size effect is important in the transient time region even in 1D. The HSA predicts the correct qualitative trends for the size effect. But it deviates from the simulation result more at the transient time region as σ increases. This is consistent with the fact that the HSA cannot describe the fluctuation effect completely. It can be estimated from the numerical calculations that the point particle approximation [Eq. (7)] is valid when $\sigma<1.0\times10^{-10}$ m. As expected, the particle size effect disappears at long times. We can conclude that as σ gets smaller, the long time asymptotic behavior appears at an earlier time. This can help to verify the universal behavior in higher dimensions with the experiments. For the investigation of the particle size effect by the simulation, one needs to be careful in checking the convergence of the result because a smaller size of the lattice spacing is required. For example, the data in Fig. 2 are obtained by using the size of the lattice spacing down to about 5×10^{-13} m.

The simulation results for the finite reactivity effect on the time evolution of the concentration for several values of the reaction probability in 1D are shown in Fig. 3 for the annihilation model. The parameters are the same as in Fig. 1 except the reaction probability. As the SM predicts, the behaviors at short times are different depending on whether k^0 is infinite (the slope of 1/2) or finite (the slope of 1). At long times, all the curves show the slope of 1/2, which is independent of the reactivity [24,25]. In fact, the slope for the infinite reactivity is 1/2 at both short and long time limits in 1D. This makes the curve nearly linear. For $d>2$, however, the long time slope becomes 1 for any reactivity but the amplitude depends slightly on the reactivity [see Eqs. (10) and (11)]. Lin *et al.* [23] showed by the 3D simulation for the infinite k^0 that, at early times, the slope is in the range 0.8~0.9 not unity. Since the slope changes from 1/2 at short times to 1 at long times in 3D, it appears that their simulation may not have reached sufficiently short times.

Some people introduced the crossover time t_c at which the reaction-limited behavior is changed to the diffusion-limited behavior [25,29,30]. Let us define the crossover time

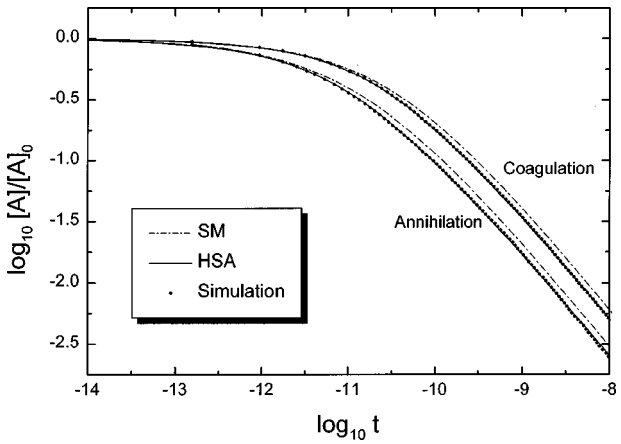

FIG. 4. The time dependence of the concentration for the annihilation and coagulation in 2D obtained from the SM, HSA, and simulation results. Parameters are the same as in Fig. 1 except $[A]_0=1.0\times10^{19}\,\mathrm{m}^{-2}$ and $\sigma=1.0\times10^{-10}$ m.

as the time at which the two asymptotic lines of the rate coefficient in both time limits meet. From the results of the SM results for the finite k^0, we find

$$t_c\sim\left[\frac{k^0\Gamma(1-d/2)\Gamma(d/2)}{2^d\pi^{d/2}D^{d/2}}\right]^{2/(d-2)} \qquad (d<2). \tag{21}$$

In 1D, the exact crossover time can be obtained as $t_c\sim D\pi/(k^0)^2$, which is larger than that of Eq. (21). Therefore, the slope change occurs earlier in the SM. It is worthwhile to note that there occur other changes of the slope of the rate coefficient for the infinite k^0. We find

$$t_c\sim\frac{\sigma^2}{4\pi D}\left[\frac{\Gamma(d/2-1)}{\Gamma(d/2)}\right]^2 \quad (d>2), \tag{22}$$

$$t_c\sim\frac{\sigma^2}{4D}\left[\frac{\Gamma(1-d/2)}{\pi^{1/2}}\right]^{2/(d-1)} \qquad (d<2,\ d\neq1). \tag{23}$$

In Figs. 4 and 5, we plot the time evolution of the concentration for the annihilation and the coagulation in 2D and

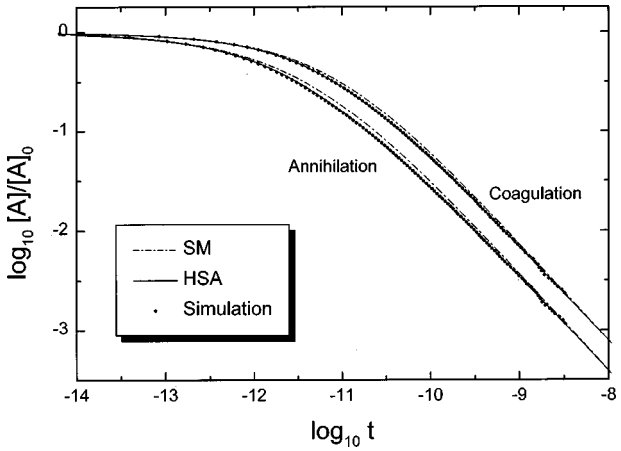

FIG. 5. The time dependence of the concentration for the annihilation and coagulation in 3D obtained from the SM, HSA, and simulation results. Parameters are the same as in Fig. 4 except $[A]_0=1.0\times10^{29}\,\mathrm{m}^{-3}$.

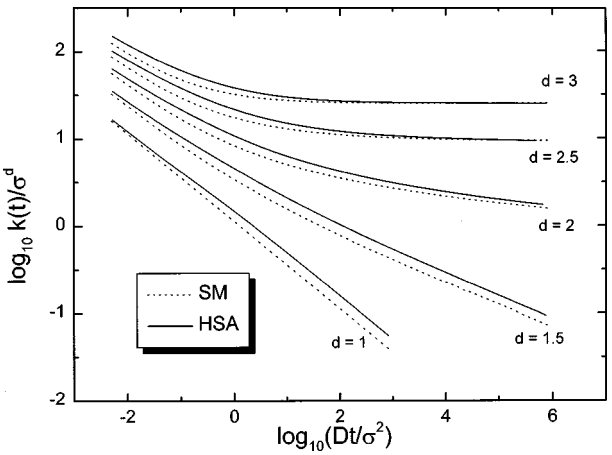

FIG. 6. The time dependence of the rate coefficient for the annihilation predicted in the SM and the HSA in several dimensions (d's) for $p=1$.

3D, respectively. We set the parameters as follows: $D=2.0\times10^{-5}\,\mathrm{cm}^{-2}\,\mathrm{s}^{-1}$, $[A]_0=1.0\times10^{19}\,\mathrm{m}^{-2}$(2D) and $1.0\times10^{29}\,\mathrm{m}^{-3}$ (3D) (the number density is 0.1 in both dimensions), $\sigma=1.0\times10^{-10}\,\mathrm{m}$, and $p=1$. In both dimensions the exact results have never been obtained. Therefore, the simulation results are expected to be useful to test the approximate theories. Surprisingly, the HSA gives nearly identical results with those of the simulation. This means that the HSA can describe many particle problem fairly well by incorporating the indirect pair correlation through the KSA. When one needs the accurate numerical data for the present system, the HSA for $d>2$ and the approximate solution Eq. (19) for $d=1$ are very useful. The computational cost for the simulation in 3D is very high [23].

It is very interesting that the SM also gives the numerically exact result at long times in 3D. To clarify the dimensional dependence, we plot the time evolution of the rate coefficient predicted in the SM and the HSA for several dimensions for the infinite reactivity in Fig. 6 in reduced units. For non-integer dimensions, we perform the inverse Laplace transform of Eq. (A6) for the SM and utilize the point particle approximation Eq. (7) for the HSA. It is clearly shown that the SM gives the exact rate coefficient at long times not only 3D but also above 2D since the HSA is numerically exact above 2D. For higher dimensions, the results are shown to coincide with each other earlier. The well-known fact that the SM becomes more accurate as the dimensionality increases is numerically confirmed. This result indicates that the fluctuation effect gets smaller since the diffusion becomes a more effective mixing mechanism in higher dimensions. Hence, we conclude that the fluctuation effect can be ignored and the SM becomes exact at long times for $d>2$. This is the reason why the SM has been so successful in 3D. We hope that this exact long time result could be a stimulus to finding an exact solution for all times in higher dimensions or at least a rigorous proof of the above fact.

For the critical 2D, the results of both theories in Fig. 6 converge slowly due to the logarithmic correction. Equation (14) reveals that the rate coefficient becomes independent of k^0 and σ at long times also in 2D but the dependence disappears slowly.

V. CONCLUDING REMARKS

We have discussed the kinetics of the single species reaction, $A+A\rightarrow\alpha A$. The long time asymptotic power law behavior results from the dimensional restriction rather than the microscopic fluctuation which, however, affects the dynamics significantly. The simulation results are compared with the various theoretical approaches. The main conclusions are as follows:

(1) The SM is exact in the short time and/or the low concentration limits for all dimensions. It also becomes exact in the long time limit for $d>2$.

(2) Regarding the reactivity effect, the SM predicts the correct behavior. The asymptotic short time behavior of $[A]^{-1}-[A]_0^{-1}$ is $\sim t$ for the finite k^0 and $\sim t^{1/2}$ for the infinite k^0 for all dimensions. At long times, $[A]\sim t^{-a}$ with $a=\min(1,d/2)$ but the concentration is independent of k^0 only for $d<2$.

(3) The SM predicts that the pair correlation function is always independent of α. However, the pair correlation function and, therefore, the rate coefficient are shown to be independent of α only in the short time, long time, and/or low concentration limits. In these cases, the concentration for the coagulation is simply related to that for the annihilation.

(4) The SM predicts that the particle size effect disappears in the long time limit for $d<2$ and at all times in 1D. However, the HSA and simulation results reveal that the particle-size effect becomes apparent in the transient time regime even in 1D. Of course, it becomes more important in higher dimensions.

(5) The HSA is found to give the numerically exact result for all times in 2D and 3D.

(6) A numerical method by which the exact result can be obtained for a finite reactivity in the annihilation model is suggested in 1D. We also present an approximate solution for an arbitrary α and for the infinite reactivity in 1D under the assumption that the rate coefficient is independent of α. This solution becomes exact in the short and long time limits.

ACKNOWLEDGMENTS

This work was supported by Grant No. 1998-015-D00148 from the Basic Science Research Program, Ministry of Education, and by the Korea Science and Engineering Foundation through the Center for Molecular Catalysis at Seoul National University.

APPENDIX A: GENERAL RESULT OF THE SMOLUCHOWSKI APPROACH

When the last term in the right hand side in Eq. (4) can be neglected, we can solve the results of HSA analytically for the following random initial condition and the radiation boundary condition.

$$\rho(r,0)=1, \tag{A1}$$

$$\left[\frac{d}{dr}\rho(r,t)\right]_{r=\sigma}=k^0C_d\rho(\sigma,t), \tag{A2}$$

$$\rho(r\rightarrow\infty,t)=1, \tag{A3}$$

where C_d is defined in Eq. (8). The solution in terms of the Laplace transform, $\tilde{f}(s) \equiv \int_0^\infty dt\ f(t)e^{-st}$, is given by

$$\tilde{\rho}(r,s) = \frac{1}{s}\left\{1 - \frac{C_d k^0 r^{-d/2+1} K_{d/2-1}(r\sqrt{s/D})}{\sigma^{-d/2+1}[C_d k^0 K_{d/2-1}(\sigma\sqrt{s/D}) + \sqrt{s/D} K_{d/2}(\sigma\sqrt{s/D})]}\right\}, \tag{A4}$$

where K_v is the modified Bessel function of the second kind. Using Eq. (3) or from the well known expression [41]

$$k(t) = \frac{1}{C_d}\left[\frac{d}{dr}\rho(r,t)\right]_{r=\sigma}, \tag{A5}$$

the rate coefficient can be obtained from the pair correlation function as [42,43]

$$\tilde{k}(s) = \frac{k^0\sqrt{s/D}K_{d/2}(\sigma\sqrt{s/D})}{C_d k^0 s K_{d/2-1}(\sigma\sqrt{s/D}) + s\sqrt{s/D}K_{d/2}(\sigma\sqrt{s/D})}. \tag{A6}$$

The concentration can be obtained from the following relation to give Eq. (8):

$$\frac{1}{[A]} - \frac{1}{[A]_0} = L^{-1}\left[\frac{(1-\alpha/2)\tilde{k}(s)}{s}\right], \tag{A7}$$

where $L^{-1}[\tilde{f}(s)]$ denotes the inverse Laplace transform of $\tilde{f}(s)$.

APPENDIX B: NUMERICALLY EXACT AND APPROXIMATE SOLUTIONS IN ONE DIMENSION

The exact rate coefficient for the infinite reactivity can be readily obtained from the result of Torney and McConnell [3] for $\alpha = 0$ as

$$k_{\text{exact}}(t) = \frac{\sqrt{4D/\pi t} - 4[A]_0 D\Omega(2[A]_0\sqrt{Dt})}{\Omega(2[A]_0\sqrt{Dt})^2}, \tag{B1}$$

where $\Omega(x) \equiv \exp(x^2)\text{erfc}(x)$ with $\text{erfc}(x)$ the complementary error function. For the finite reactivity case, no exact solution has been obtained. However, one can obtain the exact result *numerically* from Eqs. (A7) and (B1) with the well known relation [41] between rate coefficients with finite and infinite reactivities to give

$$\frac{1}{[A]} - \frac{1}{[A]_0} = L^{-1}\left[\frac{k^0\tilde{k}_{\text{exact}}(s,k^0\to\infty)}{s^2\tilde{k}_{\text{exact}}(s,k^0\to\infty) + sk^0}\right]. \tag{B2}$$

This numerical calculation is superior to the simulation method because it is free of stochastic noises. Note the concentration is independent of the reactivity in the long time limit ($s\to 0$) and Eq. (16) holds in the short time limit ($s\to\infty$).

If the rate coefficient is assumed to be independent of α, we can obtain the approximate solution for an arbitrary α using Eq. (B1) as

$$\frac{1}{[A]} - \frac{1}{[A]_0} \sim L^{-1}\left[\frac{(1-\alpha/2)k^0\tilde{k}_{\text{exact}}(s,k^0\to\infty)}{s^2\tilde{k}_{\text{exact}}(s,k^0\to\infty) + sk^0}\right]. \tag{B3}$$

For the infinite reactivity, this equation reduces to

$$\frac{1}{[A]} - \frac{1}{[A]_0} \sim \frac{(2-\alpha)(\Omega(2[A]_0\sqrt{Dt}) - 1)}{2[A]_0\Omega(2[A]_0\sqrt{Dt})}, \tag{B4}$$

which can be rearranged into Eq. (19). Equation (B3) becomes exact in the short and long time limits where the rate coefficient becomes independent of α. It is not only exact for the annihilation model but also in the low-concentration limit.

[1] V. N. Kuzovkov and E. A. Kotomin, Rep. Prog. Phys. **51**, 1479 (1988).
[2] D. Toussaint and F. Wilczek, J. Chem. Phys. **78**, 2642 (1983).
[3] D. C. Torney and H. M. McConnell, J. Phys. Chem. **87**, 1941 (1983); D. C. Torney, J. Chem. Phys. **79**, 3606 (1983).
[4] J. L. Spouge, Phys. Rev. Lett. **60**, 871 (1988).
[5] C. R. Doering and D. ben-Avraham, Phys. Rev. A **38**, 3035 (1988).
[6] R. Kroon, H. Fleurent, and R. Sprik, Phys. Rev. E **47**, 2462 (1993).
[7] L. Peliti, J. Phys. A **19**, L365 (1986).
[8] A. A. Ovchinnikov and Y. B. Zeldovich, Chem. Phys. **28**, 215 (1978).
[9] K. Kang and S. Redner, Phys. Rev. Lett. **52**, 955 (1984); Phys. Rev. A **32**, 435 (1985).
[10] G. Zumofen, A. Blumen, and J. Klafter, J. Chem. Phys. **82**, 3198 (1985); A. Blumen, J. Klafter, and G. Zumofen, in *Optical Spectroscopy of Glasses* (Reidel, Dordrecht, 1986), pp. 199–265.
[11] S. F. Burlatsky and G. S. Oshanin, J. Stat. Phys. **65**, 1095 (1991).
[12] E. A. Kotomin and V. N. Kuzovkov, Chem. Phys. **76**, 479 (1983); V. N. Kuzovkov and E. A. Kotomin, *ibid.* **81**, 335 (1983); *ibid.* **98**, 351 (1985).
[13] Y. B. Gaididei, A. I. Onipko, and I. V. Zozulenko, Chem. Phys. **117**, 367 (1987).
[14] J.-C. Lin, C. R. Doering, and D. ben-Avraham, Chem. Phys. **146**, 355 (1990).
[15] P. Argyrakis, R. Kopelman, and K. Lindenberg, Chem. Phys. **177**, 693 (1993).
[16] K. Lindenberg, P. Argyrakis, and R. Kopelman, J. Phys. Chem. **99**, 7542 (1995).
[17] A. Molski, Chem. Phys. Lett. **252**, 42 (1996).
[18] H. L. Martinez, J. Chem. Phys. **104**, 2692 (1996).

[19] M. Doi, J. Phys. A **9**, 1479 (1976).
[20] A. Molski and J. Keizer, J. Chem. Phys. **104**, 3567 (1996).
[21] J.-C. Lin, Phys. Rev. A **43**, 5714 (1991).
[22] V. Privman, Phys. Rev. E **50**, 50 (1994).
[23] A. Lin, R. Kopelman, and P. Argyrakis, Phys. Rev. E **53**, 1502 (1996).
[24] D. ben-Avraham, Mod. Phys. Lett. B **9**, 895 (1995).
[25] L. Braunstein, H. O. Martin, M. D. Grynberg, and H. E. Roman, J. Phys. A **25**, L255 (1992).
[26] P. A. Alemany, J. Phys. A **30**, 3299 (1997).
[27] D. ben-Avraham, Phys. Rev. Lett. **81**, 4756 (1998).
[28] J. Zhuo, Phys. Rev. A **43**, 5689 (1991).
[29] V. Privman, C. R. Doering, and H. L. Frisch, Phys. Rev. E **48**, 846 (1993).
[30] Z.-Y. Shi and R. Kopelman, J. Phys. Chem. **96**, 6858 (1992).
[31] T. R. Waite, Phys. Rev. **107**, 463 (1957).
[32] L. Monchick, J. L. Magee, and A. H. Samuel, J. Chem. Phys. **26**, 935 (1957).
[33] S. Lee and M. Karplus, J. Chem. Phys. **86**, 1883 (1987); Erratum, *ibid.* **96**, 1663 (1992)
[34] M. Smoluchowski, Z. Phys. Chem. (Leipzig) **92**, 129 (1917).
[35] E. Kotomin, V. Kuzovkov, W. Frank, and A. Seeger, J. Phys. A **27**, 1453 (1994).
[36] H. S. Carslaw and J. C. Jaeger, *Conduction of Heat in Solids* (Oxford University Press, New York, 1959).
[37] K. R. Naqvi, Chem. Phys. Lett. **28**, 280 (1974).
[38] H. Kim, S. Shin, and K. J. Shin, J. Chem. Phys. **108**, 5861 (1998); Chem. Phys. Lett. **291**, 341 (1998).
[39] H. Kim, S. Shin, S. Lee, and K. J. Shin, J. Chem. Phys. **105**, 7705 (1996).
[40] I. Dayan and G. H. Weiss, J. Chem. Phys. **92**, 5235 (1990).
[41] A. Szabo, J. Phys. Chem. **93**, 6929 (1989).
[42] A. V. Barzykin and M. Tachiya, J. Chem. Phys. **99**, 9591 (1993).
[43] G. Oshanin and A. Blumen, J. Chem. Phys. **108**, 1140 (1998).