

Point Particle Approximation for Single and Two Species Diffusion-Influenced Reactions

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Received February 8, 2013, Accepted February 16, 2013

The fluctuations in concentrations of reactants dominate the long-time dynamics of the single ($A + A \rightarrow 0$) and two species ($A + B \rightarrow 0$) diffusion-influenced annihilation reactions. Although hierarchical Smoluchowski approaches can provide a systematic and flexible framework to deal with the fluctuation effects, their results are too complicated to be analytically solved. For the efficient numerical calculation of the complicated fluctuation effect terms, we show that the presented point particle approximation is not only practical but also quite accurate for most conditions in diffusion-influenced reaction systems.

Key Words : Diffusion-reaction, Numerical solutions, Fluctuation effects, Kirkwood approximation

Introduction

The single and two species bimolecular diffusion-influenced annihilation reactions, which can be denoted as $A + A \rightarrow 0$ and $A + B \rightarrow 0$, respectively, are ubiquitous in biological and chemical reactions. It is natural that they attract increasing attention theoretically and experimentally. The well-known universal behavior of these reactions comes from the fluctuations in concentrations of reactants.¹⁻⁴ The long-time reaction rate laws have been known as $[A] \sim t^{-\min(1,d/2)}$ for the single species reactions and $[A] \sim t^{-\min(1,d/4)}$ for the two species reactions, where d is the spatial dimensionality of the system. Noting that the classical kinetics predicts the rate law as $[A] \sim t^{-1}$ for both reactions, the fluctuation effects make the reaction much slower at long times. Especially in a low dimension, the effects dominate the long time dynamics.

One of a systematic and flexible framework to deal with the fluctuation effects is the hierarchical Smoluchowski approaches (HSA).⁵⁻⁷ Their validity for single and two species reactions has been analyzed.⁸⁻¹¹ The result of HSA is usually a set of coupled partial differential equations which are not easy to evaluate even numerically.⁹⁻¹¹ The fluctuation effects make the numerical evaluation further complicated. Efficiency as well as accuracy is crucial for the long time dynamics. The point particle approximation (PPA) was suggested to make the numerical evaluation of the complicated fluctuation terms more tractable.^{8,11} However, the validity of PPA has never been analyzed rigorously. The main purpose of this article is to verify accuracy of this useful approximation.

Theory and Results

The classical Smoluchowski approach (SM),¹² which is the oldest and simplest theory in the diffusion-influenced reaction field, can measure a dimensional effect by predict-

$$\frac{1}{[A]} - \frac{1}{[A]_0} = L^{-1} \left[\frac{K_{d/2}(z)}{z^3 K_{d/2-1}(z)} \right], \quad (1)$$

for the absorbing or the Smoluchowski boundary condition.¹³ Here, $[A]_0$ is the initial density, $L^{-1}[f(s)]$ denotes the inverse Laplace transform of $f(s)$, $z = \sqrt{s}$, and $K_\nu(x)$ is the modified Bessel function of the second kind. It should be noted that all variables are made unit-dimensionless such as $s \leftarrow sR^2/D$ and $[A] \leftarrow [A]\gamma_d R^d$, where R is the reaction distance, D is the relative diffusion constant, and $\gamma_d = 2\pi^{d/2}/\Gamma(d/2)$ with Γ gamma function ($\gamma_1 = 2$, $\gamma_2 = 2\pi$, and $\gamma_3 = 4\pi$). The long-time asymptotic result of Eq. (1) gives $[A] \sim t^{-\min(1,d/2)}$. The validity of SM for the single and two species reactions was analyzed in detail.⁸ SM is qualitatively correct only for the single species reaction mainly because it is the mean-field theory.⁸

Among theories treating the fluctuation effects, HSAs⁵⁻⁷ can provide a systematic and flexible framework in a complicated reactive system, although they are not exact. The results can be obtained by solving the coupled diffusion-reaction equations numerically. For the single species reaction,

$$\frac{d[A]}{dt} = -k(t)[A]^2, \quad (2)$$

$$k(t) = k^0 \rho_{AA}(1,t), \quad (3)$$

$$\frac{\partial \rho_{AA}(r,t)}{\partial t} = \left(\frac{\partial^2}{\partial r^2} + \frac{d-1}{r} \frac{\partial}{\partial r} \right) \rho_{AA}(r,t) + F_d(\rho_{AA}) \rho_{AA}(r,t), \quad (4)$$

where k^0 is the intrinsic rate constant and the fluctuation factor is given by $F_d(\rho) = 2k(t)[A]\{1 - X_d(\rho)\}$.⁸ Note that the concentration $[A]$ can be obtained from the time-dependent rate coefficient $k(t)$, which can be obtained from the reduced distribution density function $\rho(r,t)$, which, in turn, can be obtained from the partial differential equation with diffusion and reaction terms. The expressions of $X_d(\rho)$ are known only in regular dimensions as¹⁴

$$X_1(\rho) = \{\rho(|r-1|, t) + \rho(r+1, t)\}/2, \quad (5)$$

$$X_2(\rho) = \frac{1}{\pi} \int_{-1}^1 dr' \frac{\rho(\sqrt{r^2 + 2rr' + 1}, t)}{\sqrt{1-r'^2}}, \quad (6)$$

$$X_3(\rho) = \frac{1}{2r} \int_{|r-1|}^{r+1} dr' \rho(r', t) r'. \quad (7)$$

Here, variables are made unit-dimensionless again as $r \leftarrow r/R$, $t \leftarrow Dt/R^2$, and $k^0 \leftarrow k^0/(\gamma_d DR^{d-2})$. The equations for the two species reaction are given by

$$\frac{d[A]}{dt} = -k(t)[A][B], \quad (8)$$

$$k(t) = k^0 \rho_{AB}(1, t), \quad (9)$$

$$\frac{\partial \rho_{AB}(r, t)}{\partial t} = \left(\frac{\partial^2}{\partial r^2} + \frac{d-1}{r} \frac{\partial}{\partial r} \right) \rho_{AB}(r, t) + F_d(\rho_{AA}) \rho_{AB}(r, t), \quad (10)$$

$$\frac{\partial \rho_{AA}(r, t)}{\partial t} = \left(\frac{\partial^2}{\partial r^2} + \frac{d-1}{r} \frac{\partial}{\partial r} \right) \rho_{AA}(r, t) + F_d(\rho_{AB}) \rho_{AA}(r, t), \quad (11)$$

For simplicity, we set $[A] = [B]$ and $\rho_{AA}(r, t) = \rho_{BB}(r, t)$ by assuming $R = R_{AB} = R_{AA}$, $D = D_{AB} = D_{AA}$, $[A]_0 = [B]_0$, $\rho_{AB}(r, 0) = \rho_{AA}(r, 0) = \rho_{BB}(r, 0)$.

The physical meaning of the last terms in Eqs. (4), (10), and (11) is the difference between the global concentration decay and the local competitive reaction. When these terms become negligible, namely, $F_d(\rho) = 0$, above coupled differential equations give the analytical result, which is the SM result [Eq. (1)]. Therefore, careful treatment of $F_d(\rho)$ term is critical to analyze the fluctuation effect. Previously, we suggested PPA for this term^{8,11}

$$X_d(\rho) \sim \rho(r, t), \quad (12)$$

by noting that this approximation becomes exact when $R \rightarrow 0$ as easily shown in Eqs. (5)-(7). PPA is quite practical since the additional numerical integration often increases the computing time drastically. For instance, using ten times larger number of spatial grids can cause hundred times larger computing time due to the direct integration of Eq. (7). PPA also makes the dimensional dependence of X_d disappear. This is a useful advantage for the study of reactions in fractal dimensions.¹¹ In this article, we will verify the accuracy of this useful approximation numerically.

As the density of reactants increases, the correlation effects between non-reactive reactants become non-negligible. Especially, the excluded volume effect increases.¹⁵⁻¹⁷ From Eq. (5), PPA including the excluded volume effect (PPA_EV) can be suggested as follows:

$$X_1(\rho) \sim \rho(r, t) \{1 + H(r-2)\}/2, \quad (13)$$

where $H(r)$ is the Heaviside step function. Note $r \geq 1$.

Results and Discussions

Since above coupled partial differential equations are not

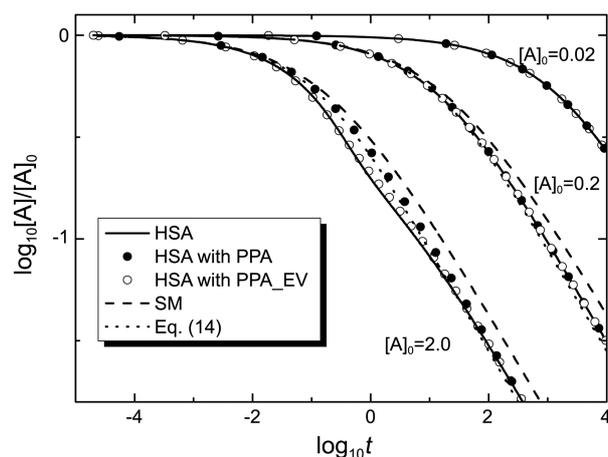


Figure 1. The time-dependent survival probability of $A + A \rightarrow 0$ reaction in one dimension for $[A]_0 = 0.02, 0.2$, and 2.0 . The solid, dashed, and dotted lines are obtained from the full numerical solution¹¹ of Eqs. (2)-(4), SM or Eq. (1), and Eq. (14), respectively. The closed and open circles are obtained from the approximations of Eq. (12) and Eq. (13), respectively.

analytically solvable except simple cases, we have to rely on the numerical methods to obtain results. Efficient numerical methods for solving above coupled diffusion-reaction equations have been suggested^{9,10} and recently generalized.¹¹ The methods are useful especially for the investigation of the long-time dynamics because of the adaptive size for both time steps and spatial grids.

In Figure 1, we plot the survival probability functions of the single species annihilation reaction in one dimension. Note that the fluctuation effects are stronger in a lower dimension. For comparison, we plot two additional results of SM and Torney and McConnell.¹⁸ The latter was given by,

$$[A] = [A]_0 \Omega([A]_0 \sqrt{t}), \quad (14)$$

where $\Omega(x) = \exp(x^2) \text{erfc}(x)$ with the complementary error function $\text{erfc}(x)$. It is well-known that SM predicts the correct slope but quantitatively erroneous results by neglecting the fluctuation effects in one dimension. While the Eq. (14) correctly treats the fluctuation effects but neglects the excluded volume effects, HSA can deal with the excluded volume effects straightforwardly but shows some deviations at long times due to its approximate treatment of the fluctuation effects.⁸

For relatively high initial densities of $[A]_0 = 0.02$ and 0.2 , (Remember that the dimensionless density is defined as $[A] \leftarrow 2[A]R$ in one dimension) our PPA results show nearly perfect agreement with the full numerical results of HSA. It is encouraging that the efficient PPA is shown to be quite accurate in severe conditions. The virtually no difference between PPA and PPA_EV means that the excluded volume effects are not significant at these densities. When we increase the initial density further up to a closely packed condition of $[A]_0 = 2.0$, the non-negligible excluded volume effects are found as the difference between PPA and PPA_EV at transient times. One can see that the effects are efficiently treated by PPA_EV and interestingly disappear in the long time

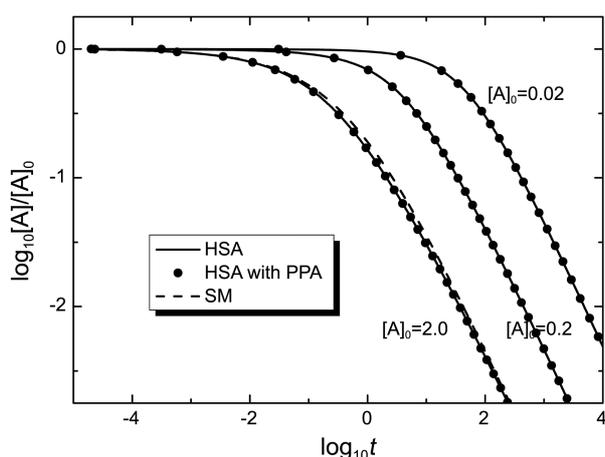


Figure 2. The time-dependent survival probability of $A + A \rightarrow 0$ reaction in three dimensions for $[A]_0 = 0.02, 0.2,$ and 2.0 . The solid and dashed lines are obtained from the full numerical solution¹¹ of Eqs. (2)-(4) and Eq. (1), respectively. The closed circles are obtained from the approximations of Eq. (12).

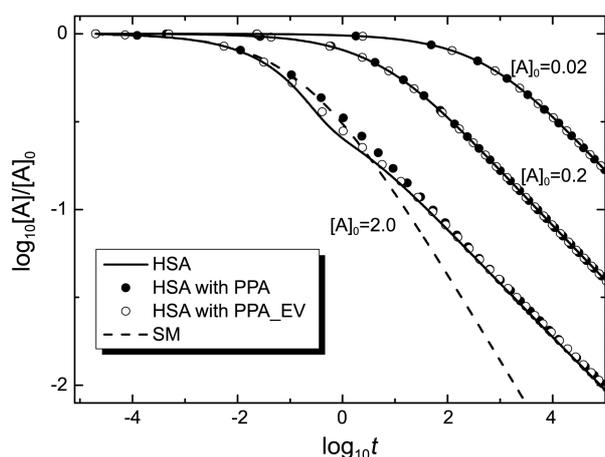


Figure 3. The time-dependent survival probability of $A + B \rightarrow 0$ reaction in one dimension for $[A]_0 = 0.02, 0.2,$ and 2.0 . The solid and dashed lines are obtained from the full numerical solution¹¹ of Eqs. (8)-(11) and Eq. (1), respectively. The closed and open circles are obtained from the approximations of Eq. (12) and Eq. (13), respectively.

limit.

To test PPA in a higher dimension, we plot the survival probabilities in three dimensions in Figure 2. Because of weaker fluctuation effects in a higher dimension, the overall accuracy of SM and HSA increases in three dimensions. Both approaches predict the correct results in the long time limit.⁸ As expected, the accuracy of PPA also increases. The three-dimensional results by PPA show nearly perfect agreement with those of HSA even for $[A]_0 = 2.0$, which means that the time-consuming numerical integral of Eq. (7) can be efficiently avoided for most cases.

In Figure 3, we plot the survival probability of the two species reaction in one dimension for $[A]_0 = 0.02, 0.2,$ and

2.0 . The fluctuation effects of the two species reaction are more dominant than those of the single species reaction.⁹ Note that SM is worse for $A + B \rightarrow 0$. Similarly to the results in the single species reaction, PPA is shown to be accurate for $[A]_0 = 0.02$ and 0.2 and PPA_EV can treat the excluded volume effects efficiently for $[A]_0 = 2.0$. We notice that the small difference between PPA result and the full numerical result does not disappear at long times for the case of $[A]_0 = 2.0$, which is thought to reflect the complicated nature of the fluctuation effects. Therefore, PPA is shown to be also reliable for the two species reaction.

Concluding Remarks

We have verified that the point particle approximation for the fluctuation effect terms in the hierarchical Smoluchowski approach is reliable for most conditions in diffusion-influenced single and two species reactions. The approximation is quite practical especially for high dimensional systems by reducing the computing time significantly. It is of use for the study of reactions in fractal dimensions by removing dimensional dependence. We also present the new approximation by including the excluded volume effects in one dimension, which is shown to be quite accurate even for the closely packed condition. The usefulness of the present approximation is not limited to the hierarchical Smoluchowski approach in diffusion-reaction systems. It can be applied to many theories based on the Kirkwood superposition approximation in the truncation of hierarchy.¹⁹

Acknowledgments. This work was supported by research funds from Dong-A University.

References

- Ovchinnikov, A. A.; Zeldovich, Y. B. *Chem. Phys.* **1978**, *28*, 215.
- Toussaint, D.; Wilczek, F. *J. Chem. Phys.* **1983**, *78*, 2642.
- Kang, K.; Redner, S. *Phys. Rev. Lett.* **1984**, *52*, 955.
- Monson, E.; Kopelman, R. *Phys. Rev. Lett.* **2000**, *85*, 666.
- Waite, T. R. *Phys. Rev.* **1957**, *107*, 463.
- Lee, S.; Karplus, M. *J. Chem. Phys.* **1987**, *86*, 1883.
- Kuzovkov, V.; Kotomin, E. *Rep. Prog. Phys.* **1988**, *51*, 1479.
- Kim, H.; Shin, K. *J. Phys. Rev. E* **2000**, *61*, 3426.
- Kim, H.; Shin, S.; Shin, K. *J. Chem. Phys.* **1998**, *108*, 5861.
- Kim, H.; Shin, S.; Shin, K. *J. Chem. Phys. Lett.* **1998**, *291*, 341.
- Kim, H. *Chem. Phys. Lett.* **2010**, *484*, 358.
- Smoluchowski, M. *Z. Phys. Chem. (Leipzig)* **1917**, *92*, 129.
- Carlsaw, H. S.; Jaeger, J. C. *Conduction of Heat in Solids*, 2nd ed.; Oxford University Press: New York, 1986.
- Kotomin, E.; Kuzovkov, V.; Frank, W.; Seeger, A. *J. Phys. A* **1994**, *27*, 1453.
- Lee, J.; Sung, J.; Lee, S. *J. Chem. Phys.* **2000**, *113*, 8686.
- Park, J.; Kim, H.; Shin, K. *J. Chem. Phys.* **2003**, *118*, 9697.
- Seki, K.; Wojcik, M.; Tachiya, M. *J. Chem. Phys.* **2011**, *134*, 094506.
- Torney, D. C.; McConnell, H. M. *J. Phys. Chem.* **1983**, *87*, 1941.
- McQuarrie, D. A. *Statistical Mechanics*; Harper and Row: New York, 1976.