

Monte Carlo Simulation Methods for External Field Effects on Diffusion-Influenced Reactions

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The external field effects including gravitational, magnetic, and electric effects on diffusion-reaction systems are ubiquitous in a broad range of chemical and biological systems. However, the theoretical approaches to study those effects have been relatively rare because of their complexities. The exact analytical results have been known only for simple systems, especially in one dimension¹⁻⁴ and three dimensions.⁵⁻⁷ On the other hand, the computer simulations can be applied to complicated systems more easily because of its flexibility. If we want to mimic the conditions in theories with simulations for external field effects, we first have to verify the consistency between theories and simulations rigorously. In this Note, we suggest the simulations methods dealing with the external field effects to predict the exact analytical results in one dimension.

Consider a pair of molecules diffusing under the influence of a potential field. Let $p(r,t)$ be the probability density function for observing the pair with a separation r at time t . The diffusion-reaction equation for the probability density function is given by

$$\frac{\partial p(r,t)}{\partial t} = Dr^{1-d} \frac{\partial}{\partial r} r^{d-1} e^{-U(r)} \frac{\partial}{\partial r} e^{U(r)} p(r,t), \quad (1)$$

where d is the dimensionality of the system, D is a relative diffusion constant, and $U(r)$ is a unit-dimensionless potential.

For the linear external potential, $U(x) = 2ax$, Eq. (1) simplifies to

$$\frac{\partial p(x,t)}{\partial t} = D \left[\frac{\partial^2}{\partial x^2} + 2a \frac{\partial}{\partial x} \right] p(x,t), \quad (2)$$

in one dimension. Here a determines the magnitude of the potential field and $x \equiv r - R$ with the reaction distance R . Without loss of generality, we can assume that one molecule is fixed at origin and the other is located at x ($x > 0$).¹ Note that for the positive value of a , the molecule tends to move toward the origin. The diffusion equation Eq. (2) can be reduced to the following field-free form,

$$\frac{\partial q(x,t)}{\partial t} = D \frac{\partial^2}{\partial x^2} q(x,t), \quad (3)$$

by the transformation of⁸⁻¹⁰

$$q(x,t) = \exp(ax + a^2Dt) p(x,t). \quad (4)$$

Then, we can solve Eq. (3) exactly for a variety of known

conditions. The probability density function for a free-diffusion can be obtained as

$$p(x,t|x_0) = \frac{1}{\sqrt{4\pi Dt}} \exp\left(-\frac{(x-x_0+2aDt)^2}{4Dt}\right), \quad (5)$$

where x_0 is the initial position ($x_0 \geq 0$). Then, the moments are

$$\langle x \rangle = x_0 - 2aDt, \quad (6)$$

$$\langle x^2 \rangle = x_0^2 + 2Dt(1-2ax_0) + (2aDt)^2. \quad (7)$$

For the Collins-Kimball boundary condition,¹¹

$$\left. \frac{\partial p(x,t)}{\partial r} + 2ap(x,t) \right|_{x=0} = \frac{k}{D} p(0,t), \quad (8)$$

where k is the intrinsic rate constant. Eq. (2) can be exactly solved to obtain

$$e^{a(x-x_0)+a^2Dt} p(x,t|x_0) = \frac{1}{\sqrt{4\pi Dt}} \left[\exp\left(-\frac{(x+x_0)^2}{4Dt}\right) + \exp\left(-\frac{(x-x_0)^2}{4Dt}\right) \right] - \frac{k-aD}{D} W\left(\frac{x+x_0}{\sqrt{4Dt}}, \frac{k-aD}{D} \sqrt{Dt}\right), \quad (9)$$

where $W(A,B) \equiv \exp(2AB+B^2) \operatorname{erfc}(A+B)$ with the complementary error function $\operatorname{erfc}(x)$.

For the Smoluchowski boundary condition ($k \rightarrow \infty$),⁸ we have

$$p(x,t|x_0) = \frac{e^{-a(x-x_0)-a^2Dt}}{\sqrt{4\pi Dt}} \left[\exp\left(-\frac{(x+x_0)^2}{4Dt}\right) - \exp\left(-\frac{(x-x_0)^2}{4Dt}\right) \right], \quad (10)$$

The survival probability for the initial separation x_0 is

$$S(t|x_0) = 1 - \frac{1}{2} \operatorname{erfc}\left(\frac{x_0}{\sqrt{4Dt}} - a\sqrt{Dt}\right) - \frac{1}{2} e^{2ax_0} \operatorname{erfc}\left(\frac{x_0}{\sqrt{4Dt}} + a\sqrt{Dt}\right), \quad (11)$$

One can see that Eq. (11) reduce to the field-free solutions of $S(t|x_0) = \operatorname{erf}(x_0/\sqrt{4Dt})$ when $a = 0$. In the long time limit, we have

$$\lim_{t \rightarrow \infty} S(t|x_0) = \begin{cases} 1 - e^{2ax_0} & (a < 0) \\ 0 & (a \geq 0) \end{cases} \quad (12)$$

Note that when the external field is against reaction, the ultimate escape probability has non-zero value even in one dimension.

For the reflecting boundary condition ($k = 0$), we have

$$e^{a(x-x_0)+a^2Dt} p(x,t|x_0) = \frac{1}{\sqrt{4\pi Dt}} \left[\exp\left(-\frac{(x+x_0)^2}{4Dt}\right) + \exp\left(-\frac{(x-x_0)^2}{4Dt}\right) \right] + aW\left(\frac{x+x_0}{\sqrt{4Dt}}, -a\sqrt{Dt}\right), \quad (13)$$

$$\lim_{t \rightarrow \infty} p(x,t|x_0) = \begin{cases} 2ae^{-2ax} & (a \geq 0) \\ \frac{e^{-a(x-x_0+aDt)}}{\sqrt{4\pi DtDt}} \left(xx_0 - \frac{x+x_0}{a} + \frac{1}{a^2} \right) & (a < 0) \end{cases} \quad (14)$$

For a positive value of a , we have an equilibrium distribution that is independent of the initial position in the long time limit.¹⁰

It is well known that the lattice-based Monte Carlo simulation can reproduce field-free solutions for Smoluchowski or absorbing boundary condition when the lattice constant or the distance between two neighboring lattice points, Δx is small enough.¹²⁻¹⁷ To study the field effects on diffusion-reaction systems, one should make the simulation methods produce consistent results with the known analytical ones of diffusion-reaction equations. The relation between the magnitude of the external field and the hopping probability can be found to utilize the energy difference between lattice points as in the conventional Metropolis method.¹⁸ For a positive value of a , the hopping to the left is always accepted, but the hopping to the right is only partially accepted. If the trial is rejected, the molecule will stay on the old position and will be retried in the next step. Therefore, in this case, the hopping probability to the left P_L is 0.5, the probability to the right P_R is $\exp(-2a\Delta x)/2$, and the probability of the stay P_S is $0.5 - \exp(-2a\Delta x)/2$ with $P_L + P_R + P_S = 1$.

The alternative method is that we eliminate P_S and rearrange P_L and P_R as $1/[1 + \exp(-2a\Delta x)]$ and $1 - P_L$, respectively. Then, we have the following simplified relation

$$P_L = 0.5 + \tanh(a\Delta x)/2. \quad (15)$$

One can see that this relation goes to $P_L \approx 0.5 + a\Delta x/2$ for small a , while $P_L \approx 1 - \exp(-2a\Delta x)$ for large a . This method is consistent with the field-free simulations in that the stay on the old position is not allowed.

To test which method describes the analytical results better, we compare simulation results adopting two methods for $a = 1$ and $a = 0.5$ with exact results in a one-dimensional reaction-free diffusion case in Figure 1. We perform the latticed-based random walk simulations. A molecule is initially implanted at $x_0 = 0$ and it starts moving in random directions. The hopping and stay probabilities are evaluated by above two methods. The lattice constant Δx is reduced until converged results are obtained. For these figures, we set $\Delta x = 0.1$ and the reaction distance $R = 1$ for unit-dimensionless parameters. In one dimensional lattice, $D = 1/2$. The magnitude of the slopes of $(\langle x^2 \rangle - 2Dt)^{1/2}$ and $\langle x \rangle$

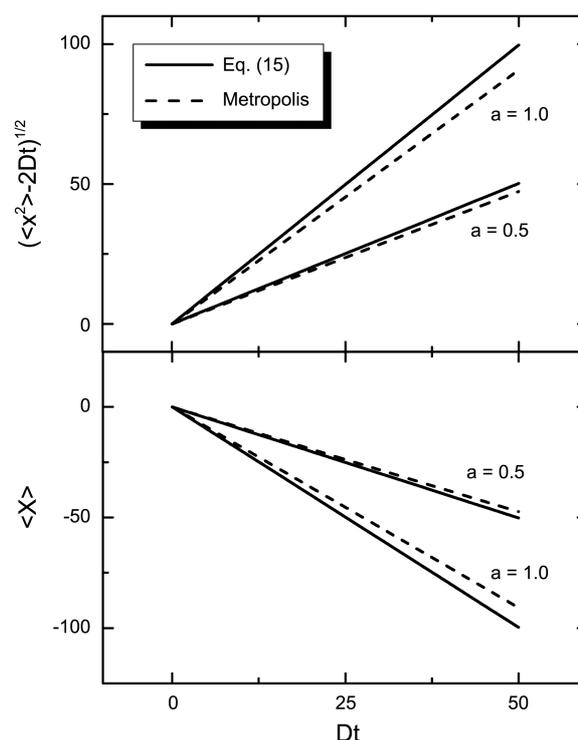


Figure 1. Comparison between two simulation methods: the Metropolis method and the methods adopting Eq. (15) in a one-dimensional free diffusion for two field strength parameters.

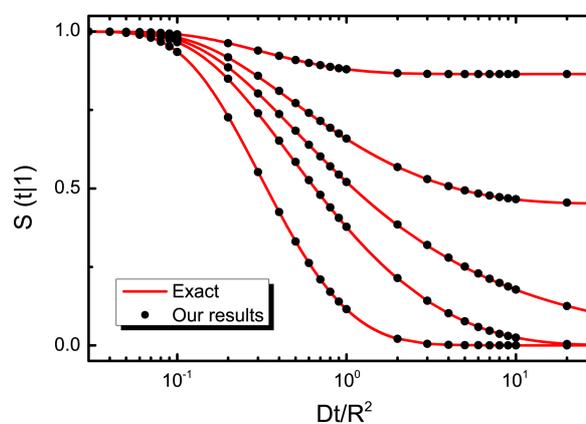


Figure 2. The survival probabilities in one dimension for $a = -1.0, -0.3, 0, 0.3, \text{ and } 1$ (from top to bottom).

against Dt in Eqs. (6) and (7) is $2a$. The method based on Eq. (15) is found to predict the correct slope values of 2.0 and 1.0 for $a = 1$ and $a = 0.5$, respectively. On the other hand, the Metropolis method¹⁸ is found to predict lower slopes of 1.8 and 0.9 and underestimates the field effects. Therefore, if one wants to use the Metropolis method, one should readjust the diffusion constants since the stay on the old position makes the slower diffusive motions.

With success in a free-diffusion case, we test whether our simulation adopting Eq. (15) can describe the reaction-diffusion systems rigorously or not. We implant a trap at origin and a molecule at $x_0 = r_0 - R = 1$. If the molecule encounters the trap within the reaction distance $R = 1$, the

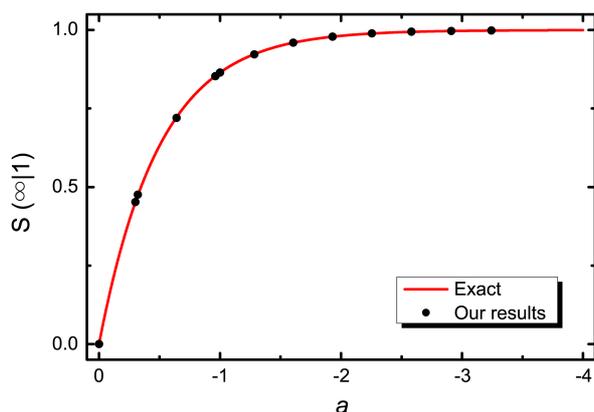


Figure 3. The survival probabilities in the long-time limit in one dimension for various negative values of a .

reaction occurs. In Figure 2, we plot survival probabilities to compare our simulation results adopting Eq. (15) with the exact analytical results of Eq. (11) for $a = -1.0, -0.3, 0, 0.3$, and 1.0 . A field-free result ($a = 0$) has been added as a reference. We set $\Delta x = 1/50$ here. We have virtually perfect agreement between simulation and theoretical results and we can confirm that our simulation results can rigorously reproduce the theoretical results of Eq. (11). Since the non-zero escape probability exists when $a < 0$, we plot the survival probabilities in the long time limit in Figure 3. One can see the long time simulation results also agree perfectly with the theoretical predictions of Eq. (12).

In summary, we have shown that the lattice-based Monte Carlo simulation methods can exactly reproduce the predic-

tions of the diffusion-influenced reaction theories with external field effects in one dimension by finding the rigorous relation between the field strength and the hopping probability. This method will be of great use since it can be easily extended to more complicated systems where no exact analytical results are known yet.

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