

Diffusion-mediated geminate reactions under excluded volume interactionsKazuhiko Seki,¹ Mariusz Wojcik,² and M. Tachiya¹¹*National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba Central 5, Higashi 1-1-1, Tsukuba, Ibaraki, 305-8565 Japan*²*Institute of Applied Radiation Chemistry, Technical University of Lodz, Wroblewskiego 15, 93-590 Lodz, Poland*

(Received 3 June 2011; published 19 January 2012)

In this paper, influence of crowding by inert particles on the geminate reaction kinetics is theoretically investigated. Time evolution equations for the survival probability of a geminate pair are derived from the master equation taking into account the correlation among all diffusing particles, and the results are compared with those obtained by Monte Carlo simulations. In general, excluded volume interactions by the inert particles slow down the diffusive motion of reactants. However, when the initial concentration of the inert particles is uniform and high, we show that additional influence of interference between reaction and correlated diffusion accelerates the transient decay of the survival probability in the diffusion-controlled limit. We also study the escape probability for a nonuniform initial distribution of the inert particles by taking the continuous limit in space. We show that reaction yield is increased when the reaction proceeds in the presence of a positive density gradient of the inert particles which inhibits the escape of reactants. The effect can be interpreted as a cage effect.

DOI: [10.1103/PhysRevE.85.011131](https://doi.org/10.1103/PhysRevE.85.011131)

PACS number(s): 02.50.-r, 82.20.-w

I. INTRODUCTION

The importance of molecular crowding on chemical reactions has attracted great attention in connection with biochemical reactions in living cells [1–7]. Living cells contain a high volume fraction of macromolecules, in addition to reactants. Although these macromolecules are not reactive, the excluded volume interactions between reactants and macromolecules significantly affect transport properties of reactants, and therefore biochemical reactions.

In this paper, we consider a fundamental reaction process called a geminate reaction, which is observed in many systems including those encountered in biology. In a geminate reaction, a pair of reactants is generated simultaneously and subsequently diffuse and react when they encounter each other. Geminate reactions are influenced by spatial diffusion of a pair and the intrinsic recombination rates. The influence of many-body interactions between inert species and reactants on the geminate reaction kinetics can be very complicated and difficult to treat theoretically. The simplest model could be to assume that the reactants and the inert particles have the same size. Even under such simplification, the many-body nature of the problem remains since the migration of reactive species correlates with the time-dependent positions of inert species; the problem is still difficult to solve analytically.

To retain the many-body nature in the simplest situation, we study the geminate reaction between a static species and a diffusive species on a lattice. Reaction takes place according to the distance between one of the pair of reactants at the origin and the other. Inert particles perform random walks on a lattice. The transition to neighboring lattice sites is constrained by prohibiting the double occupancy; each lattice site can be occupied at most by a single diffusive particle regardless of whether it is reactive or inert. Particles are assumed to move randomly on vacancy sites of a lattice. However, the problem is still hard to solve analytically without approximations. Therefore, we perform Monte Carlo simulations to evaluate approximations and to elucidate effects which cannot be studied analytically. To facilitate comparisons

between theoretical results and those of simulations, the problem is further simplified; the origin is also allowed to be occupied at most by a single diffusive particle regardless of whether it is reactive or inert, and reaction takes place according to the intrinsic reaction rate when the origin is occupied by a reactant.

The excluded volume interactions were theoretically treated by Nakazato and Kitahara in tracer diffusion on a lattice [8]. The Nakazato-Kitahara formula of tracer diffusion constant interpolates between low and high concentrations of host particles and its accuracy is confirmed by comparison to the results of numerical simulations [8–11].

For target reactions where a static reactive particle (target) is surrounded by many reactive counterparts (quenchers), the Nakazato-Kitahara theory was successfully applied to calculate the survival probability of a target with a constraint of prohibited double occupancy of diffusing reactants [12,13]. It turned out that the decay of the target survival probability is accelerated by prohibiting the double occupancy [12,13]. Similar acceleration of the decay was obtained by other numerical and analytical approaches [14–25]. The acceleration of the decay is understood by noticing that the number of sites occupied by mobile reactants is generally larger at any time under the constraint of prohibited double occupancy at each lattice site [12,13]. Accordingly, the probability of reaction between the target and a quencher is higher at any time when multiple occupancy is not allowed.

Contrary to the target reaction, only a pair of reactants should be considered for geminate reaction. In other words, the number of sites occupied by reactants is not affected by prohibiting the double occupancy. However, the site blocking effects among diffusing particles influence the kinetics of the geminate reaction through different mechanism from that in the case of target reactions. First, crowding of inert particles slows down diffusion of reactive particles and retards the reaction between the pair. Indeed, numerical simulations show that the reaction between a pair proceeds slowly by the crowding of inert particles [26].

In this paper, we study more comprehensively the reaction of a pair of reactants performing diffusion under the constraint of prohibited double occupancy in the presence of inert particles. On the basis of results derived, the mechanism of site blocking effects by inert particles in the geminate reaction is investigated in detail when the initial distribution of inert particles is uniform. We show that reactions are influenced through excluded volume interactions not only through slowing down of diffusion of reactants but also by an interference between reaction and correlated diffusion in the diffusion-controlled limit. We also study the influence of inhomogeneous initial distributions of inert particles by taking the continuum limit in space. We show that the overall reaction yield is increased (decreased) from that assuming homogeneous initial distribution of inert particles by a positive (negative) density gradient of the inert particles.

In Sec. II we formulate the problem in the case when the initial distribution of inert particles is uniform and derive the solution within the mean-field approximation. In Sec. III higher order corrections to the mean-field results are presented. The calculation details are given in Appendix A. In Sec. IV, we compare the analytical results to simulation results. In Sec. V, the influence of nonuniform initial distribution of inert particles is investigated. The escape probability is derived for this case by using the continuous

limit derived in Appendix B. Section VI is devoted to conclusions.

II. GEMINATE PAIR REACTION UNDER THE PRESENCE OF INERT PARTICLES

For simplicity, we formulate the problem on a lattice where a reactive particle and inert particles perform random walks. The particles are assumed to move randomly on the vacant sites of a lattice. One of the reactants of the pair does not move and its position is taken as the origin of the coordinate system. The reactive particle undergoes reaction according to the distance from the origin, r . We denote the intrinsic reaction rate by $k(r)$.

The tracer diffusion in concentrated lattices was studied by Nakazato and Kitahara in the absence of reaction [8]. The diffusion of the tagged particle in the presence of site blocking by other particles has been studied [8–11]. Following them, we introduce ket vectors to show occupancy of a site by diffusing particles. The ket vector $|\vec{r}, \bullet\rangle$ denotes the occupation of site \vec{r} by a reactive particle, the ket vector $|\vec{r}, \circ\rangle$ denotes the occupation of site \vec{r} by an inert particle, and $|\vec{r}, \phi\rangle$ represents that site \vec{r} is empty. The conditional probability of finding inert particles at $(\vec{f}_1, \vec{f}_2, \dots, \vec{f}_N)$ and the reactant at \vec{n} at time t when the initial configuration of inert particles is $(\vec{i}_1, \vec{i}_2, \dots, \vec{i}_N)$ and that of the reactant is \vec{m} is written as

$$P(\vec{f}_1, \vec{f}_2, \dots, \vec{f}_N, \vec{n}, t; \vec{i}_1, \vec{i}_2, \dots, \vec{i}_N, \vec{m}) = \left(\prod_{\ell=1}^N \langle \vec{f}_\ell, \circ | \right) \left(\prod_{\ell=N+1}^M \langle \vec{f}_\ell, \phi | \right) \langle \vec{n}, \bullet | \exp(\mathcal{L}t) | \vec{m}, \bullet \rangle \left(\prod_{\ell=1}^N |\vec{i}_\ell, \circ \rangle \right) \left(\prod_{\ell=N+1}^M |\vec{i}_\ell, \phi \rangle \right), \quad (1)$$

where N and M denote the numbers of inert particles and lattice sites, respectively. \mathcal{L} is given by the sum of the term describing diffusion L_w and that describing reaction L_{rc} , $\mathcal{L} = L_w + L_{rc}$. L_w is explicitly expressed as [8–10]

$$L_w = \gamma_B \sum_{(n,m)} (|\vec{r}_n, \bullet\rangle \langle \vec{r}_n, \phi | \cdot |\vec{r}_m, \phi\rangle \langle \vec{r}_m, \bullet | - |\vec{r}_n, \bullet\rangle \langle \vec{r}_n, \bullet | \cdot |\vec{r}_m, \phi\rangle \langle \vec{r}_m, \phi |) \\ + \gamma_w \sum_{(n,m)} (|\vec{r}_n, \circ\rangle \langle \vec{r}_n, \phi | \cdot |\vec{r}_m, \phi\rangle \langle \vec{r}_m, \circ | - |\vec{r}_n, \circ\rangle \langle \vec{r}_n, \circ | \cdot |\vec{r}_m, \phi\rangle \langle \vec{r}_m, \phi |), \quad (2)$$

where the sum is taken over all nearest neighbor pairs of the accessible lattice sites by the diffusing particles. γ_B is given by $\gamma_B = \Gamma_B/(2d)$, where Γ_B is the jump frequency of a reactive particle and d denotes the lattice dimension. Similarly, we define $\gamma_w = \Gamma_w/(2d)$ where Γ_w is the jump frequency of inert particles. L_{rc} describes the reaction from an occupied site \vec{r}_n with the rate $k(\vec{r}_n)$ [27–29]

$$L_{rc} = - \sum_{n=1}^M k(\vec{r}_n) |\vec{r}_n, \bullet\rangle \langle \vec{r}_n, \bullet |. \quad (3)$$

The conditional probability $P_N(\vec{n}, t | \vec{m}, 0)$ that the reactant is at site \vec{n} at time t when it was initially at \vec{m} under the assumption of random initial occupation of inert particles is obtained from Eq. (1) by multiplying $1/(M C_N)$ and summing over all possible initial and final configurations of the inert particles. By defining the characteristic function by

$$\phi(\vec{n}, t | \vec{m}, 0; x) \equiv \sum_{N=0}^M P_N(\vec{n}, t | \vec{m}, 0) x^N, \quad (4)$$

it can be expressed as

$$\phi(\vec{n}, t | \vec{m}, 0; x) = \frac{(1+x)^M}{M C_N} g(\vec{n}, t | \vec{m}, 0; x), \quad (5)$$

where we define

$$g(\vec{n}, t | \vec{m}, 0; x) \equiv \langle \{\phi\} | \langle \vec{n}, \bullet | \exp[\tilde{L}(\theta)t] | \{\phi\} | \vec{m}, \bullet \rangle, \quad (6)$$

$\tilde{L}(\theta) = \exp(-\theta S) \mathcal{L} \exp(\theta S)$, $S \equiv \sum_{\ell=1}^M (|\vec{r}_\ell, \circ\rangle \langle \vec{r}_\ell, \phi | - |\vec{r}_\ell, \phi\rangle \langle \vec{r}_\ell, \circ |)$, and $x = \tan^2 \theta$. It is convenient to introduce the abbreviations

$$\langle \{\phi\} | \langle \vec{r}_j, \bullet | \equiv \left(\prod_{\ell=1}^{M'} \langle \vec{r}_\ell, \phi | \right) \langle \vec{r}_j, \bullet |, \quad (7)$$

$$| \{\phi\} | \vec{r}_j, \bullet \rangle \equiv \left(\prod_{\ell=1}^{M'} |\vec{r}_\ell, \phi \rangle \right) |\vec{r}_j, \bullet \rangle, \quad (8)$$

where M' denotes that the site \vec{r}_j is excluded in the product.

The inverse transformation is given by applying Cauchy's integral theorem,

$$P_N(\vec{n}, t | \vec{m}, 0) = \frac{1}{2\pi i} \int dx \frac{1}{x^{N+1}} \phi(\vec{n}, t | \vec{m}, 0; x), \quad (9)$$

where the path of integration encircles the origin on the complex plane.

In the thermodynamic limit of $M \rightarrow \infty$ with $c = N/M$ being constant, the right-hand side of Eq. (9) can be calculated by applying the saddle-point method [8–10]

$$P(\vec{n}, t | \vec{m}, 0) = g(\vec{n}, t | \vec{m}, 0; c/(1-c)). \quad (10)$$

The survival probability of a pair at time t whose initial separation is given by \vec{m} is defined by

$$S(\vec{m}, t) = \sum_{\vec{n}} P(\vec{n}, t | \vec{m}, 0). \quad (11)$$

From Eqs. (6) and (10) the Laplace transform of the survival probability, $\hat{S}(\vec{m}, s) = \int_0^\infty dt \exp(-st) S(\vec{m}, t)$, is expressed as

$$\hat{S}(\vec{m}, s) = \sum_{\vec{n}} \langle \{\phi\} | \langle \vec{n}, \bullet | \frac{1}{s - \tilde{L}(\theta^*)} | \{\phi\} \rangle | \vec{m}, \bullet \rangle, \quad (12)$$

where $\tan \theta^* = \sqrt{c/(1-c)}$. $\tilde{L}(\theta^*)$ can be expressed by the sum of the term describing diffusion and that describing reaction, $\tilde{L}(\theta^*) = \tilde{L}_{\text{rw}} + \tilde{L}_{\text{rc}}$. Even after the transformation the term describing reaction is not changed, $\tilde{L}_{\text{rc}} = L_{\text{rc}}$, while \tilde{L}_{rw} is given by the sum, $\tilde{L}_{\text{rw}} = \tilde{L}_{\text{rw}0} + \tilde{L}_{\text{rw}1}$, where $\tilde{L}_{\text{rw}0}$ describes the transition under the conservation constraint of the number of particles [8–10],

$$\begin{aligned} \tilde{L}_{\text{rw}0} = & (1-c)\gamma_B \sum_{(n,m)} (|\vec{r}_n, \bullet\rangle \langle \vec{r}_n, \phi | \cdot |\vec{r}_m, \phi\rangle \langle \vec{r}_m, \bullet | - |\vec{r}_n, \bullet\rangle \langle \vec{r}_n, \bullet | \cdot |\vec{r}_m, \phi\rangle \langle \vec{r}_m, \phi |) \\ & + c\gamma_B \sum_{(n,m)} (|\vec{r}_n, \bullet\rangle \langle \vec{r}_n, \circ | \cdot |\vec{r}_m, \circ\rangle \langle \vec{r}_m, \bullet | - |\vec{r}_n, \bullet\rangle \langle \vec{r}_n, \bullet | \cdot |\vec{r}_m, \circ\rangle \langle \vec{r}_m, \circ |) \\ & + \gamma_w \sum_{(n,m)} (|\vec{r}_n, \circ\rangle \langle \vec{r}_n, \phi | \cdot |\vec{r}_m, \phi\rangle \langle \vec{r}_m, \circ | - |\vec{r}_n, \circ\rangle \langle \vec{r}_n, \circ | \cdot |\vec{r}_m, \phi\rangle \langle \vec{r}_m, \phi |), \end{aligned} \quad (13)$$

and $\tilde{L}_{\text{rw}1}$ describes the transition where the number of particles is not conserved [8–10],

$$\begin{aligned} \tilde{L}_{\text{rw}1} = & \sqrt{c(1-c)}\gamma_B \sum_{(n,m)} (|\vec{r}_n, \bullet\rangle \langle \vec{r}_n, \bullet | \cdot |\vec{r}_m, \phi\rangle \langle \vec{r}_m, \circ | + |\vec{r}_n, \bullet\rangle \langle \vec{r}_n, \bullet | \cdot |\vec{r}_m, \circ\rangle \langle \vec{r}_m, \phi |) \\ & - |\vec{r}_n, \bullet\rangle \langle \vec{r}_n, \phi | \cdot |\vec{r}_m, \circ\rangle \langle \vec{r}_m, \bullet | - |\vec{r}_n, \bullet\rangle \langle \vec{r}_n, \circ | \cdot |\vec{r}_m, \phi\rangle \langle \vec{r}_m, \bullet |). \end{aligned} \quad (14)$$

By introducing the identity

$$\frac{1}{s - \tilde{L}(\theta^*)} = \frac{1}{s} \left(1 + \frac{1}{s - \tilde{L}(\theta^*)} \tilde{L}(\theta^*) \right), \quad (15)$$

Eq. (12) can be rewritten as

$$s\hat{S}(\vec{m}, s) = 1 + \sum_{\vec{n}} \langle \{\phi\} | \langle \vec{n}, \bullet | \frac{1}{s - \tilde{L}(\theta^*)} \tilde{L}(\theta^*) | \{\phi\} \rangle | \vec{m}, \bullet \rangle. \quad (16)$$

In the lowest order approximation, the perturbation term $\tilde{L}_{\text{rw}1}$ is ignored in the numerator of Eq. (16) and we obtain

$$\begin{aligned} s\hat{S}(\vec{m}, s) = & 1 + \sum_{\vec{n}} \langle \{\phi\} | \langle \vec{n}, \bullet | \\ & \times \frac{1}{s - \tilde{L}(\theta^*)} (\tilde{L}_{\text{rw}0} + \tilde{L}_{\text{rc}}) | \{\phi\} \rangle | \vec{m}, \bullet \rangle. \end{aligned} \quad (17)$$

By using Eq. (12) and the fact that the number of particles is conserved for both $\tilde{L}_{\text{rw}0}$ and \tilde{L}_{rc} , Eq. (17) leads to

$$\begin{aligned} s\hat{S}(\vec{m}, s) - 1 = & \gamma_B(1-c) \sum_j [\hat{S}(\vec{m} + \vec{b}_j, s) - \hat{S}(\vec{m}, s)] \\ & - k(\vec{m})\hat{S}(\vec{m}, s), \end{aligned} \quad (18)$$

where $\vec{m} + \vec{b}_j$ denotes a nearest neighbor of the site \vec{m} and the sum is taken over all nearest neighbor sites. By the

inverse Laplace transformation, the equation for the survival probability at time t of a pair with initial separation \vec{m} is obtained:

$$\begin{aligned} \frac{\partial}{\partial t} S(\vec{m}, t) = & \gamma_B(1-c) \sum_j [S(\vec{m} + \vec{b}_j, t) - S(\vec{m}, t)] \\ & - k(\vec{m})S(\vec{m}, t). \end{aligned} \quad (19)$$

In the lowest order approximation, the site blocking effects by inert particles reduces the transition rate. The transition rate is reduced since jump to a neighboring site is allowed only when the neighboring site is empty. The vacant probability is $1-c$ in the mean-field picture. Equation (19) is a mean-field result in the sense that the reduction factor is given by $1-c$. The transition rate of the reactant particle decreases linearly with increasing concentration of inert particles.

For localized reactions, $k(\vec{m}) = k_0 \delta_{\vec{m}, \vec{0}}$, the general solution after the Laplace transformation is obtained as

$$\hat{S}(\vec{m}, s) = \frac{1}{s} \left(1 - \frac{\hat{G}_0(\vec{m}, s) k_0}{1 + \hat{G}_0(\vec{0}, s) k_0} \right), \quad (20)$$

where Green's function

$$\hat{G}_0(\vec{j}, s) = \frac{1 - \hat{\psi}_B(s)}{s} U(\vec{j}, s) \quad (21)$$

is given in terms of the lattice Green's function [30]

$$U(\vec{j}, s) = \frac{1}{(2\pi)^d} \int \cdots \int_{-\pi}^{\pi} d^d \vec{k} \frac{\exp(-i\vec{k} \cdot \vec{j})}{1 - \hat{\psi}_B(s)\lambda(\vec{k})}, \quad (22)$$

where $\hat{\psi}_B(s)$ is given by $\hat{\psi}_B(s) = \Gamma_B(1-c)/[s + \Gamma_B(1-c)]$, the structure factor is defined by $\lambda(\vec{k}) \equiv \frac{1}{2d} \sum_{j=1}^{2d} \cos(\vec{k} \cdot \vec{b}_j/b)$, and b denotes the lattice spacing.

The recombination probability of a particle starting from \vec{m} , $\kappa(\vec{m}) = 1 - \lim_{t \rightarrow \infty} S(\vec{m}, t)$, is obtained as

$$\kappa(\vec{m}) = \frac{U(\vec{m}, 0)}{\frac{\Gamma_B(1-c)}{k_0} + U(\vec{0}, 0)}. \quad (23)$$

Note that $U(\vec{m}, 0)$ for any \vec{m} is independent of the concentration of the inert particles, c , in the mean-field result. In the limit of a perfectly absorbing boundary condition ($k_0 \rightarrow \infty$), the recombination probability is independent of the concentration of inert particles. For partially absorbing boundary conditions the recombination probability increases by increasing the concentration of inert particles. The escape probability, $\lim_{t \rightarrow \infty} S(\vec{m}, t)$, which is defined as the probability of a pair with initial separation \vec{m} surviving at infinite time, is given by

$$\varphi(\vec{m}) = 1 - \kappa(\vec{m}). \quad (24)$$

We have derived the simplest results on the survival probability of a geminate pair by ignoring correlations higher than the two-point correlation between the initial position and the position at an arbitrary time. In the reaction-diffusion equation thus derived, the presence of the inert particles only reduces the diffusion coefficient linearly with increasing concentration of inert particles, and the diffusion and the reaction do not interfere. In the subsequent section, we show that the diffusion and reaction interfere in the presence of inert particles if we consider higher order correlations.

III. CORRECTION TO THE MEAN-FIELD EQUATION

If we ignore correlations higher than two-point correlations, the Bardeen-Herring back correlation is not taken into account [31]. The Bardeen-Herring back correlation takes place when the reactant hops to a vacant site, leaving the previous occupied site vacant; after the hopping the transition probability of the reactant back to the previously occupied site is higher than other sites. The velocity autocorrelation function in a lattice gas shows a long time tail with a negative value due to the Bardeen-Herring back correlation [11]. Suppose that a reactant occupies a reactive site after a hopping. The rate of hopping back to the previous site competes with that of the reaction. In

this way, the reaction interferes with the correlated diffusion. Interference means that the reaction process and the diffusion are not statistically independent. In this section, we study the interference between the reaction and the correlated diffusion by taking into account the Bardeen-Herring back correlation. As in the previous section, we assume the initial uniform distribution for the inert particles.

The effect of the interference between the reaction and the correlated diffusions can be calculated as the correction to the simple diffusion-reaction equation (17). The exact relation, Eq. (16), can be rewritten as

$$s\hat{S}(\vec{m}, s) = 1 + \sum_{\vec{n}} \langle \{\phi\} | \langle \vec{n}, \bullet | \frac{1}{s - \tilde{L}(\theta^*)} \times (\tilde{L}_{\text{rw0}} + \tilde{L}_{\text{rc}}) | \{\phi\} \rangle | \vec{m}, \bullet \rangle + \hat{R}(\vec{m}, s), \quad (25)$$

where $\hat{R}(\vec{m}, s)$ represents the correction to Eq. (17) and is given by

$$\hat{R}(\vec{m}, s) = \sum_{\vec{n}} \langle \{\phi\} | \langle \vec{n}, \bullet | \frac{1}{s - \tilde{L}(\theta^*)} \tilde{L}_{\text{rw1}} | \{\phi\} \rangle | \vec{m}, \bullet \rangle. \quad (26)$$

By noticing $\tilde{L}_{\text{rw1}} = \tilde{L}(\theta^*) - \tilde{L}_{\text{rw0}} - \tilde{L}_{\text{rc}}$, we can prove the operator identity,

$$\frac{1}{s - \tilde{L}(\theta^*)} = \frac{1}{s - \tilde{L}(\theta^*)} \tilde{L}_{\text{rw1}} \frac{1}{s - \tilde{L}_{\text{rw0}} - \tilde{L}_{\text{rc}}} + \frac{1}{s - \tilde{L}_{\text{rw0}} - \tilde{L}_{\text{rc}}}. \quad (27)$$

\tilde{L}_{rw0} and \tilde{L}_{rc} conserve the number of \bullet in the bra and ket notations, while \tilde{L}_{rw1} does not, so we have

$$\langle \{\phi\} | \langle \vec{n}, \bullet | \frac{1}{s - \tilde{L}_{\text{rw0}} - \tilde{L}_{\text{rc}}} \tilde{L}_{\text{rw1}} | \{\phi\} \rangle | \vec{m}, \bullet \rangle = 0. \quad (28)$$

If we substitute Eq. (27) into Eq. (26) and use Eqs. (28) and (26) can be expressed as

$$\begin{aligned} \hat{R}(\vec{m}, s) &= \sum_{\vec{n}} \langle \{\phi\} | \langle \vec{n}, \bullet | \frac{1}{s - \tilde{L}(\theta^*)} \tilde{L}_{\text{rw1}} \\ &\quad \times \frac{1}{s - \tilde{L}_{\text{rw0}} - \tilde{L}_{\text{rc}}} \tilde{L}_{\text{rw1}} | \{\phi\} \rangle | \vec{m}, \bullet \rangle \\ &= \sum_{\vec{n}} \hat{S}(\vec{n}, s) \langle \{\phi\} | \langle \vec{n}, \bullet | \tilde{L}_{\text{rw1}} \\ &\quad \times \frac{1}{s - \tilde{L}_{\text{rw0}} - \tilde{L}_{\text{rc}}} \tilde{L}_{\text{rw1}} | \{\phi\} \rangle | \vec{m}, \bullet \rangle, \end{aligned} \quad (29)$$

$$\times \frac{1}{s - \tilde{L}_{\text{rw0}} - \tilde{L}_{\text{rc}}} \tilde{L}_{\text{rw1}} | \{\phi\} \rangle | \vec{m}, \bullet \rangle, \quad (30)$$

where the definition of $\hat{S}(\vec{n}, s)$ given by Eq. (12) is substituted. By introducing the explicit expression of \tilde{L}_{rw1} given by Eq. (14), we obtain

$$\begin{aligned} &\langle \{\phi\} | \langle \vec{n}, \bullet | \tilde{L}_{\text{rw1}} \frac{1}{s - \tilde{L}_{\text{rw0}} - \tilde{L}_{\text{rc}}} \tilde{L}_{\text{rw1}} | \{\phi\} \rangle | \vec{m}, \bullet \rangle \\ &= \gamma_B^2 c(1-c) \sum_r \sum_q [G(\vec{n}\bullet, \vec{n} + \vec{b}_r \circ | \vec{m}\bullet, \vec{m} + \vec{b}_q \circ, s) - G(\vec{n} + \vec{b}_r \bullet, \vec{n} \circ | \vec{m}\bullet, \vec{m} + \vec{b}_q \circ, s) \\ &\quad - G(\vec{n}\bullet, \vec{n} + \vec{b}_r \circ | \vec{m} + \vec{b}_q \bullet, \vec{m} \circ, s) + G(\vec{n} + \vec{b}_r \bullet, \vec{n} \circ | \vec{m} + \vec{b}_q \bullet, \vec{m} \circ, s)]. \end{aligned} \quad (31)$$

Here we define the four-point correlation function as

$$G(\vec{r}_i \bullet, \vec{r}_j \circ | \vec{r}_k \bullet, \vec{r}_\ell \circ, s) = \langle \{\phi\} | \langle \vec{r}_i, \bullet | \langle \vec{r}_j, \circ | \frac{1}{s - \tilde{L}_{\text{rw}0} - \tilde{L}_{\text{rc}}} | \{\phi\} \rangle | \vec{r}_k, \bullet \rangle | \vec{r}_\ell, \circ \rangle \rangle \quad (32)$$

using the abbreviations

$$\langle \{\phi\} | \langle \vec{r}_i, \bullet | \langle \vec{r}_j, \circ | \equiv \left(\prod_{\ell=1}^{M''} \langle \vec{r}_\ell, \phi | \right) \langle \vec{r}_i, \bullet | \langle \vec{r}_j, \circ |, \quad (33)$$

$$| \{\phi\} \rangle | \vec{r}_i, \bullet \rangle | \vec{r}_j, \circ \rangle \equiv \left(\prod_{\ell=1}^{M''} | \vec{r}_\ell, \phi \rangle \right) | \vec{r}_i, \bullet \rangle | \vec{r}_j, \circ \rangle, \quad (34)$$

where M'' denotes that the site \vec{r}_i and the site \vec{r}_j are excluded in the product. Equations (33) and (34) represent the state that all sites are vacant except the site \vec{r}_i occupied by the reactant and the site \vec{r}_j occupied by an inert particle. By substituting Eqs. (30) and (31) in Eq. (25), we have

$$s \hat{S}(\vec{m}, s) - 1 = \gamma_B (1 - c) \sum_{\vec{n}} \sum_r F_c(\vec{n}, \vec{m}, \vec{b}_r, s) \times [\hat{S}(\vec{n} + \vec{b}_r, s) - \hat{S}(\vec{n}, s)] - k(\vec{m}) \hat{S}(\vec{m}, s), \quad (35)$$

where the kernel $\hat{F}_c(\vec{n}, \vec{m}, \vec{b}_r, s)$ is given by

$$\hat{F}_c(\vec{n}, \vec{m}, \vec{b}_r, s) = \delta_{\vec{n}, \vec{m}} - \gamma_B c \sum_q [G(\vec{n} \bullet, \vec{n} + \vec{b}_r \circ | \vec{m} \bullet, \vec{m} + \vec{b}_q \circ, s) - G(\vec{n} \bullet, \vec{n} + \vec{b}_r \circ | \vec{m} + \vec{b}_q \bullet, \vec{m} \circ, s)]. \quad (36)$$

By the inverse Laplace transformation of Eq. (35), the survival probability is shown to satisfy the diffusion-reaction equation in which the diffusion term is expressed by the time convolution with the nonlocal kernel, $F_c(\vec{n}, \vec{m}, \vec{b}_r, t)$.

The time convolution represents the memory effect originating from the correlation between the mobile reactant and the inert particles. Reactant motion is correlated with the time-dependent arrangements of the inert particles through prohibited double occupancy of the lattice sites. In particular, the site occupied by the reactant becomes empty just after the hopping of the reactant and the chance of back transition to the previously occupied site is high. The back transition probability of the reactant decreases as time proceeds because the empty site generated by the hop of the reactant to a vacant site may be occupied by another inert particle. The time dependence of the back-jump correlation is the origin of the memory effect.

In principle, the back-jump correlation competes with reaction. Suppose that the reactant hops to the reactive site. The probability of jump back to the previously occupied site decreases as the reaction rate increases. Since Eq. (32) includes the operator describing reaction, \tilde{L}_{rc} , the diffusion memory kernel, $\hat{F}_c(\vec{n}, \vec{m}, \vec{b}_r, s)$, depends on the reaction rate. To obtain $\hat{F}_c(\vec{n}, \vec{m}, \vec{b}_r, s)$ we need to solve an equation for $G(\vec{n} \bullet, \vec{n} + \vec{b}_r \circ | \vec{m} \bullet, \vec{r} \circ, s)$.

In Eq. (A2) of Appendix A, we show that the equation for $G(\vec{n} \bullet, \vec{n} + \vec{b}_r \circ | \vec{m} \bullet, \vec{r} \circ, s)$ includes the reactive sink term. The

interference between the reaction and correlated diffusion is taken into account by the four-point correlation function. In the simplest theory given by the two-point function, Eq. (19), the interference between the reaction and correlated diffusion is not taken into account.

When the reactive sink strength changes according to the distance from the origin, the diffusion term given in terms of the four-point correlation function depends on the distance from the origin accordingly. In addition, the presence of the inert particles gives rise to correlation over distances as a result of the excluded volume interactions between the inert particles and the reactant. Interference between the reaction and the correlated diffusion breaks down the translational invariance as shown in Eq. (A2) of Appendix A, and the resultant equation is hard to solve. In the next section, we use numerical simulations to study the interference effect.

When we ignore the interference between the reaction and correlated diffusion, the translational invariance is satisfied for the four-point correlation functions. Under the translational invariance, $G(\vec{n} \bullet, \vec{n} + \vec{b}_r \circ | \vec{m} \bullet, \vec{r} \circ, s)$ depends only on relative vectors and satisfies

$$G(\vec{n} \bullet, \vec{n} + \vec{b}_r \circ | \vec{m} \bullet, \vec{r} \circ, s) = G(\vec{n}' \bullet, \vec{n}' + \vec{b}_r \circ | \vec{0} \bullet, \vec{r}' \circ, s), \quad (37)$$

where $\vec{n}' = \vec{n} - \vec{m}$ and $\vec{r}' = \vec{r} - \vec{m}$. Since the number of independent variables is reduced, it is convenient to introduce a new notation

$$G^{(T)}(\vec{n}' \bullet, \vec{b}_r \circ | \vec{r}' \circ, s) = G(\vec{n}' \bullet, \vec{n}' + \vec{b}_r \circ | \vec{0} \bullet, \vec{r}' \circ, s). \quad (38)$$

In this case, the time evolution equation for the survival probability is expressed after the spatial Fourier transform as

$$\frac{\partial}{\partial t} S(\vec{k}, t) = \int_0^t dt_1 M(\vec{k}, t - t_1) S(\vec{k}, t_1) - \sum_{\vec{m}} \exp(i\vec{k} \cdot \vec{m}) k(\vec{m}) S(\vec{m}, t). \quad (39)$$

In the Laplace domain, $\hat{M}(\vec{k}, s)$ can be regarded as a self-energy or memory function and is expressed as

$$\hat{M}(\vec{k}, s) = -\Gamma_B (1 - c) [1 - \lambda(\vec{k})] + \gamma_B^2 c (1 - c) \hat{T}_c(\vec{k}, s), \quad (40)$$

where the correlations among the inert particles and the reactant as a result of the excluded volume interactions are included in

$$\hat{T}_c(\vec{k}, s) = \sum_q \sum_r [1 - \exp(-i\vec{k} \cdot \vec{b}_r)] \tilde{G}(\vec{k}, \vec{b}_r | \vec{b}_q, s) \times [1 - \exp(i\vec{k} \cdot \vec{b}_q)], \quad (41)$$

$$\tilde{G}(\vec{k}, \vec{b}_r | \vec{r}, s) = \sum_{\vec{\ell}} \exp(i\vec{k} \cdot \vec{\ell}) G^{(T)}(\vec{\ell}, \vec{b}_r | \vec{r}, s). \quad (42)$$

The same form of memory function expressed in terms of the four-point correlation function was derived by a different method [32]. The equation for $\tilde{G}(\vec{k}, \vec{b}_r | \vec{r}, s)$ is explicitly shown in Eq. (A12) of Appendix A.

In the limit of small wavelength, $k \rightarrow 0$, Eq. (39) can be expressed after the inverse Laplace transformation as

$$\frac{\partial}{\partial t} S(\vec{m}, t) = D_B(1-c) \sum_j \int_0^t dt_1 f_c(t-t_1) \nabla^2 S(\vec{m}, t_1) - k(\vec{m}) S(\vec{m}, t), \quad (43)$$

where the diffusion constant is defined by $D_B = b^2 \gamma_B$, the correlation factor in the Laplace domain is given for the hypercubic lattices by

$$\hat{f}_c(s) = 1 - \gamma_B c \sum_r [G^{(a)}(\vec{b}_r | \vec{b}_r, s) - G^{(a)}(\vec{b}_r | -\vec{b}_r, s)], \quad (44)$$

and the initial condition is $S(\vec{m}, t=0) = 1$. $G^{(a)}(\vec{b}_r | \vec{b}_q, s)$ is defined by

$$G^{(a)}(\vec{b}_r | \vec{b}_q, s) = \sum_{\vec{m}} \langle \{ \phi \} | \vec{n}, \bullet | \langle \vec{n} + \vec{b}_r, \circ | \times \frac{1}{s - \tilde{L}_{\text{rw}0}} | \{ \phi \} | \vec{m}, \bullet | \vec{m} + \vec{b}_q, \circ \rangle, \quad (45)$$

which is independent of the choice of \vec{n} as shown in Eq. (A14) of Appendix A. The equation for $G^{(a)}(\vec{b}_r | \vec{b}_q, s)$ is known and has been studied to obtain the tracer-diffusion coefficient [8–10]. It is shown in Eq. (A14) of Appendix A. Its solution is known and the correlation factor can be expressed as

$$\hat{f}_c(s) = \frac{1 - \mu(s)}{1 - \mu(s) \frac{\gamma_w + \gamma_B(1-3c)}{\gamma_w + \gamma_B(1-c)}}, \quad (46)$$

where $\mu(s)$ is given by

$$\mu(s) = \frac{1}{(2\pi)^d} \int \dots \int_{-\pi}^{\pi} d^d \vec{k} \frac{2 \sin^2 k_1}{(s/\gamma_t) + 2d[1 - \lambda(k)]}, \quad (47)$$

and $\gamma_t = \gamma_w + \gamma_B(1-c)$. In the original derivation of the correlation factor $\hat{f}_c(s)$ and the tracer-diffusion coefficient by Nakazato and Kitahara, a projection operator method is applied. Here, a reaction-diffusion equation for the survival probability is derived directly without using the projection operator method.

To take into account the memory effect on the transient decay of the survival probability with reasonable simplicity, Eqs. (20)–(22) are used with

$$\hat{\psi}_B(s) = \frac{\Gamma_B \hat{f}_c(s)}{s + \Gamma_B \hat{f}_c(s)(1-c)}. \quad (48)$$

In this approximation, the lattice Green's function valid for finite wavelength is used together with the expression of $\hat{f}_c(s)$ derived in the limit of $k \rightarrow 0$. In the subsequent section, we show by comparison with simulation results that the approximation gives reasonable results as long as the interference between the reaction and the Bardeen-Herring back correlation is absent.

The equation can be further simplified by ignoring the memory in the diffusion kernel. In this approximation, the survival probability and the recombination probability for localized reactions can be calculated, respectively, from Eqs. (20) and (23) by introducing the correlation factor into

the hopping frequency,

$$\gamma_B \rightarrow \gamma_B f_c, \quad (49)$$

where the correlation factor $f_c = \hat{f}_c(s=0)$ is given by

$$f_c = \frac{1 - \mu}{1 - \mu \frac{\gamma_w + \gamma_B(1-3c)}{\gamma_w + \gamma_B(1-c)}}, \quad (50)$$

and $\mu = \mu(s=0)$ is known for some lattices. When the hopping frequencies are the same for the inert particles and the reactant, $\gamma_w = \gamma_B$, the value of μ is 0.20984 and $1 - (2/\pi) = 0.363$ for the cubic and the square lattice, respectively.

The summary of this section is as follows. We have studied the influence of back-jump correlations on the survival probability of a geminate pair when the initial distribution of inert particles is uniform. When the mobile reactant hops to a vacant site, the reactant tends to jump back to its previously occupied empty site (the Bardeen-Herring back correlation). In this way, the reactant motion is highly correlated with the time-dependent arrangements of the inert particles. The back-jump correlations interfere with reaction. In principle, the interference can be taken into account by Eqs. (35) and (36) with Eq. (A2). However, in practice these equations are hard to solve. If the interference is ignored, the influence of back-jump correlations is taken into account by Eqs. (39)–(42) with Eq. (A12). By introducing the further simplification of ignoring the memory effect, we obtain Eq. (19) with substitution given by Eq. (49). In the next section, these results will be compared with those obtained by numerical simulations.

IV. COMPARISON TO SIMULATION RESULTS

A. Simulation method

To see the interference of the reaction with the correlated diffusion, we perform Monte Carlo numerical simulations. We numerically obtain the probability of geminate reaction in the presence of site-blocking effects using a kinetic Monte Carlo method. The simulation is carried out on the simple cubic lattice. One reactant is placed at the lattice site (0,0,0) and assumed to be immobile. The other reactant is initially placed at (j,0,0), where j is an integer and the lattice constant is unity. Inert particles are randomly generated at lattice sites within the box (0, L-1)³, where L is the box length. The number of inert particles N is related to their concentration by $c = N/L^3$. Each lattice site may accommodate only one inert particle or the mobile reactant. We assume that the inert particles belonging to the box (0, L-1)³ are periodically replicated in three dimensions, so that the simulation volume is effectively unlimited. What should be noted is that the spatial periodicity is assumed only for the distribution of inert particles, and not for the reactants themselves. During the simulation, both the inert particles and the mobile reactant may perform hops to neighboring lattice sites. A hop is allowed only when the destination site is not occupied by another inert particle or the mobile reactant. However, both types of simulated particles are allowed to jump to (0,0,0). If the mobile reactant is staying at (0,0,0), its reaction with the other reactant is possible.

The procedure of selecting the event that actually takes place at a given simulation step is as follows. First, we

determine all possible hops for the mobile reactant and inert particles. We denote the numbers of such hops as K and K_{in} , respectively. If the mobile reactant is staying at a site other than $(0,0,0)$, the total rate of all possible events is calculated as $k_{\text{tot}} = K\gamma_B + K_{\text{in}}\gamma_w$. Otherwise, the total rate includes the rate of reaction and is calculated as $k_{\text{tot}} = K\gamma_B + K_{\text{in}}\gamma_w + k_0$. Now, we determine which event will actually take place. This is decided at random, taking the ratio of the rate of each possible event to the total rate k_{tot} as the event probability. The above procedure is repeated until either a reaction occurs or the mobile reactant separates to a large distance r_{max} from $(0,0,0)$. By repeating the simulation for a large number (at least 2×10^4) of independent runs, we can obtain the reaction probability. The accuracy of the simulation results depends on two parameters: L and r_{max} . They should be taken as large as possible within the practical limits imposed by the available computational time (the demand on computer time is especially high at large concentrations of inert particles). In the production runs of the simulation, we assumed $L = 10$ and $r_{\text{max}} = 30$. From test calculations carried out also for other values of these parameters, we found no significant effect of L on the obtained results. However, a weak dependence of the reaction probability on the value of r_{max} could be observed. For example, the reaction probability obtained for $j = 3$ and $c = 0$ with $r_{\text{max}} = 60$ was about 2% higher than that calculated with $r_{\text{max}} = 30$.

B. Simulation results

We investigate quantitatively the effects of the factors ignored in deriving a simple result, Eq. (19), by comparison to the more rigorous theoretical results and the simulation results. One of the factors ignored is the Bardeen-Herring back correlation, which is described by the four-point correlation function given in Appendix A. The Bardeen-Herring back correlation is taken into account fully by Eqs. (39)–(42) and partly by Eq. (19) with Eq. (49). Equation (49) is obtained from Eqs. (39)–(42) by taking the limit of the small wavelength $k \rightarrow 0$ and ignoring the memory effect. Equation (19) with Eq. (49) is much simpler than Eqs. (39)–(42). The numerical way to solve Eqs. (39)–(42) with Eq. (A12) is given in Appendix A.

Another factor ignored is the effect of the interference between the reaction and the Bardeen-Herring back correlation. The interference is taken into account in the results of numerical simulations but is ignored in any theoretical results including the most sophisticated one given by the solution of Eqs. (39)–(42).

The recombination probability in the completely diffusion-controlled limit, $k_0 \rightarrow \infty$, is shown in Fig. 1. The simulation results are compared to the numerical solutions of Eqs. (39)–(42). In the theoretical results the influence of the reaction on the four-point correlation function is ignored. As shown in Fig. 1, the reaction's influence on the four-point correlation function is relatively small for all concentrations of inert particles as far as the overall yield (recombination probability) is concerned. However, Fig. 1 shows small deviation at high concentration of inert particles for the initial separation of $j = 1$. The deviation is not an effect of statistical error of the simulation. We will discuss this point later when we study transient decay of the survival probability.

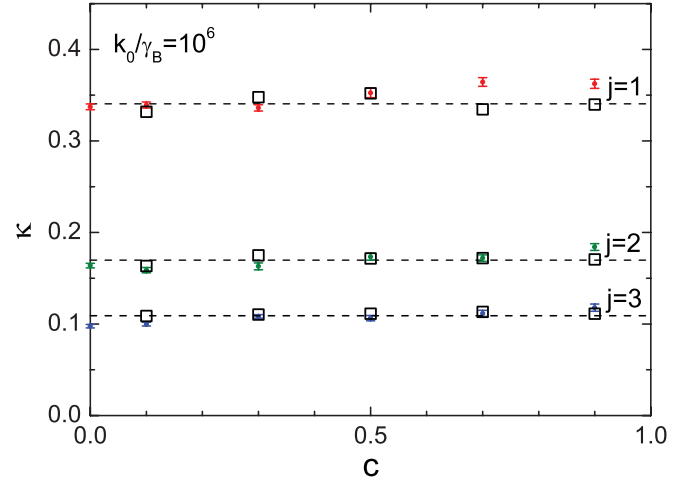


FIG. 1. (Color online) Recombination probability of a geminate pair against concentration of inert particles c for $k_0 \rightarrow \infty$ (in the simulation, $k_0/\gamma_B = 10^6$) and $\gamma_w/\gamma_B = 1$. j indicates the initial separation of the geminate pair. Dots with error bars indicate the simulation results. Squares represent the numerical solutions of Eqs. (39)–(42) with Eq. (A12). Dashed lines indicate the mean-field results of Eq. (23). The results of Eq. (23) with the substitution given by Eq. (49) practically coincide with those of Eq. (23).

In the completely diffusion-controlled limit, $k_0 \rightarrow \infty$, the recombination probability obtained from Eq. (23) with the substitution given by Eq. (49) is independent of the concentration of the inert particles. This result is not a rigorous relation. It is obtained by the oversimplification of taking the limit of small wavelength, $k \rightarrow 0$, and ignoring the interference between the reaction and the Bardeen-Herring back correlation. However, the difference between the result of the simplified equation, Eq. (23) with Eq. (49), and that obtained without taking the limit of the long wavelength, Eqs. (39)–(42), is also very small. Figure 1 indicates that the simplified approach which leads to Eq. (23) with Eq. (49) is justified for the calculation of the recombination probability in the diffusion-controlled limit.

The recombination probability in the case of finite reactivity is shown in Fig. 2. The influence of the reaction on the four-point correlation function can be seen as the difference between the simulation results and the numerical solutions of Eqs. (39)–(42). In the reaction-controlled limit, the difference is very small for all concentrations of the inert particles regardless of the initial distance of a geminate pair. The difference between the simplified results obtained in Eq. (23) with Eq. (49) and the solutions of Eqs. (39)–(42) is again negligibly small.

We also compare the transient decay of the survival probability obtained from simulations with theoretical results of Eqs. (20)–(22) with Eq. (48) to study the effect of interference between the reaction and the Bardeen-Herring back correlation. Figure 3(a) shows that the theoretical results reproduce the simulation results in the reaction-controlled limit ($k_0/\gamma_B = 1.0$) over the whole time range regardless of the concentration of inert particles. As we have theoretically shown in the previous section, the interference between the reaction and the Bardeen-Herring back correlation changes the diffusion term through four-point correlation functions, leaving the reaction term unaltered. The interference could be dominated in the diffusion-controlled limit but should be

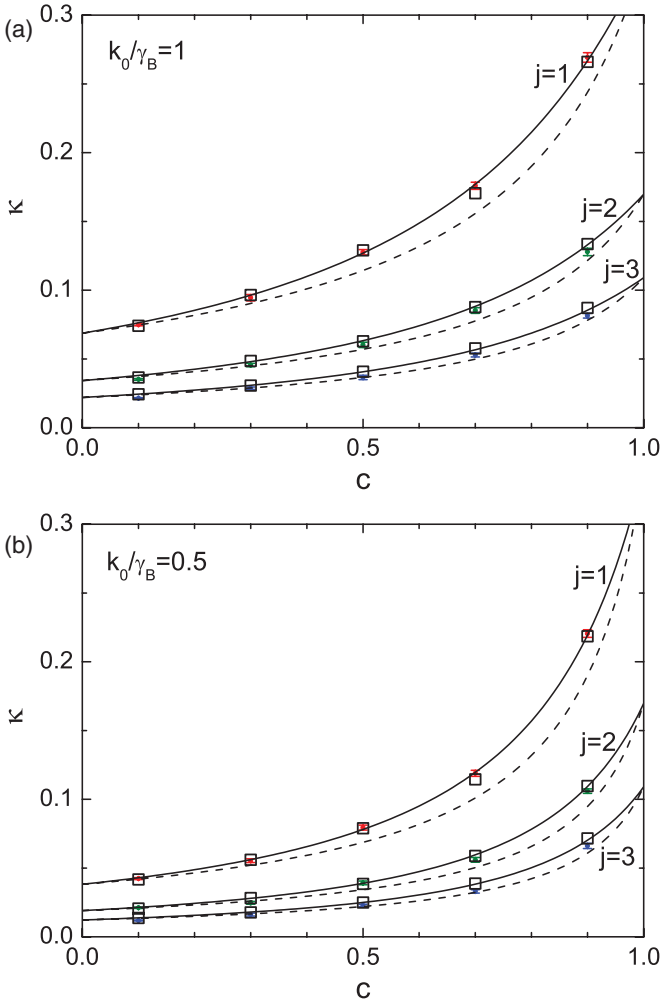


FIG. 2. (Color online) Recombination probability of a geminate pair against the concentration of the inert particles c when $\gamma_w/\gamma_B = 1$. (a) $k_0/\gamma_B = 1.0$ and (b) $k_0/\gamma_B = 0.5$. j indicates the initial separation of the geminate pair. Dots with error bars indicate the simulation results. Squares represent the numerical solutions of Eqs. (39)–(42) with Eq. (A12). The results of Eq. (23) with the substitution given by Eq. (49) are indicated by the solid lines. Dashed lines indicate the mean-field results of Eq. (23).

small in the reaction-controlled limit. Figure 3(a) indicates that the approximation used for finite k in Eqs. (20)–(22) and (48) is valid as long as interference between the reaction and the Bardeen-Herring back correlation can be ignored. Figure 3(b) shows that in the diffusion-controlled limit the theoretical results agree with the simulation results in the absence of inert particles. However, when the concentration of inert particles is high ($c > 0.5$), the survival probability obtained from simulation decays faster than that in the theoretical results. The acceleration of the decay should be attributed to the influence of the interference between the reaction and the Bardeen-Herring back correlation.

As the conclusion of this section, we point out that the interference between the reaction and the Bardeen-Herring back correlation is most pronounced in the transient decay of the survival probability in the diffusion-controlled limit at high concentration of inert particles. As far as the reaction yield is concerned, the mean-field results given by Eq. (19)

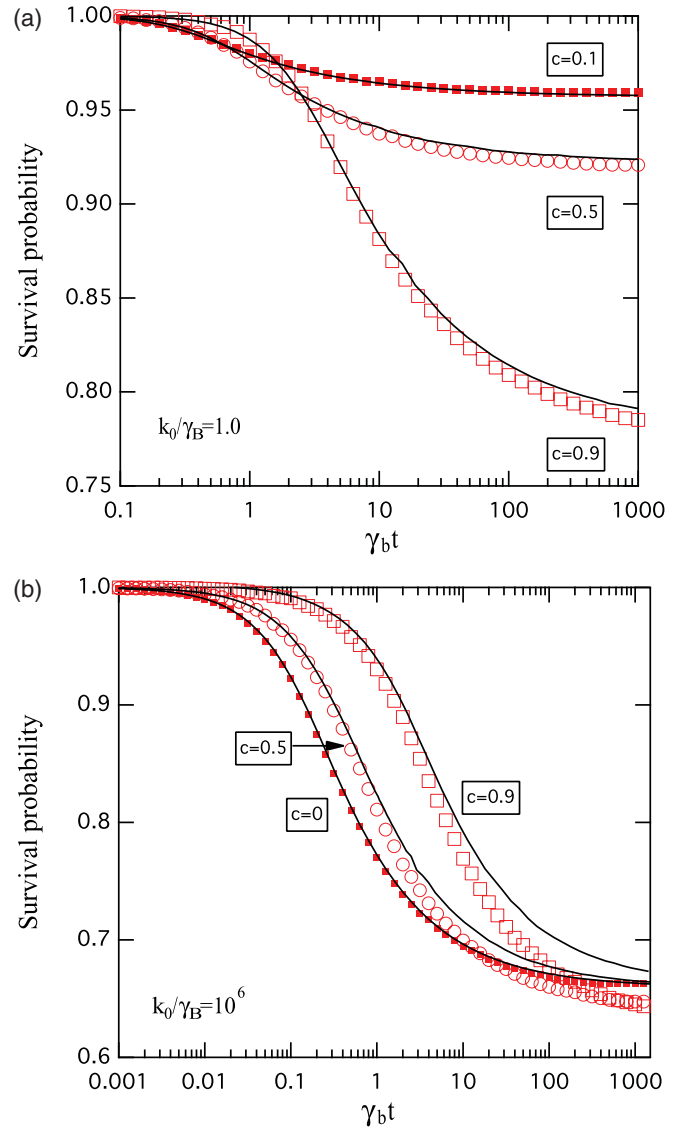


FIG. 3. (Color online) Survival probability as a function of $\gamma_B t$ for the initial separation of $j = 1$. (a) $k_0/\gamma_B = 1.0$ and (b) $k_0/\gamma_B = 10^6$. Concentrations of inert particles are shown in figures. Symbols represent the simulation results. Lines indicate the theoretical results of Eqs. (20)–(22) with Eq. (48).

reproduce the simulation results regardless of reaction strength and the concentration of the inert particles when the density of the inert particles is uniform. The result can be improved by introducing the substitution given by Eq. (49) into Eq. (19) to take into account the Bardeen-Herring back correlation. Generalization of Eq. (19) to the case of continuous diffusion and nonuniform distribution of inert particles is shown in the subsequent sections.

V. INHOMOGENEOUS DISTRIBUTION OF INERT PARTICLES

So far, we have assumed the homogeneous distribution of inert particles. Recently, the influence of inhomogeneous distributions of inert particles is taken into account to study catalytic surface reactions, in particular focusing on reaction front structures [33–38]. In this section, we study geminate

reactions under the inhomogeneous distribution of inert particles. Since we are not able to solve the lattice model for nonuniform initial distribution of inert particles with the same rigor as that under uniform distribution of inert particles, we study the results in the continuous limit by using the mean-field approximation. We consider the pair distribution $p(\vec{r}, t)$ of finding a pair of reactants at the separation \vec{r} at time t . As shown in Appendix B, the lattice model considered in this paper leads to

$$\frac{\partial}{\partial t} p(r, t) = \vec{\nabla} \cdot D_B \{ [1 - c_v(\vec{r}, t)] \vec{\nabla} p(r, t) + p(r, t) \vec{\nabla} c_v(\vec{r}, t) \} - k(r) p(r, t), \quad (51)$$

in the continuous limit, where the diffusion constant is defined by $D_B = b^2 \gamma_B$ and the concentration of inert particles is denoted by $c_v(\vec{r}, t)$. The first term on the right-hand side includes the diffusion term influenced by the concentration gradient of inert particles [33–38] and the drift term is induced by the spurious potential defined by

$$U = -k_B T \ln [1 - c_v(r, t)]. \quad (52)$$

Equation (51) can be rewritten in terms of the potential as

$$\frac{\partial}{\partial t} p(r, t) = \vec{\nabla} \cdot D_B [1 - c_v(\vec{r}, t)] \left[\vec{\nabla} p(r, t) + p(r, t) \frac{\vec{\nabla} U}{k_B T} \right] - k(r) p(r, t). \quad (53)$$

The perfectly reflecting boundary condition at R is imposed to express that the reactants cannot penetrate each other.

We calculate the escape probability on the basis of Eq. (53). We consider the case that the density of the inert particles is stationary and inhomogeneous. Both the intrinsic reaction rate and the density of the inert particles are assumed to be isotropic. The equation for the survival probability is obtained from Eq. (53) by introducing the adjoint operator as [39–41]

$$\frac{\partial}{\partial t} S(r, t) = \vec{\nabla} \cdot D_B [1 - c_v(r)] \vec{\nabla} S(r, t) - D_B [\vec{\nabla} c_v(r)] \cdot \vec{\nabla} S(r, t) - k(r) S(r, t), \quad (54)$$

where $\vec{\nabla}$ in the square brackets operates only on $c_v(r)$. The perfectly reflecting boundary condition at $r = R$ is represented by

$$\left. \frac{\partial}{\partial r} S(r, t) \right|_{r=R} = 0. \quad (55)$$

When the reaction takes place at the reaction radius R with the intrinsic rate k_0 [42], the equation for the escape probability defined by $\varphi(r) = \lim_{t \rightarrow \infty} S(r, t)$ in d dimensions satisfies

$$\frac{1}{r^{d-1}} \exp\left(\frac{U}{k_B T}\right) \frac{\partial}{\partial r} D_B [1 - c_v(r)] r^{d-1} \times \exp\left(-\frac{U}{k_B T}\right) \frac{\partial}{\partial r} \varphi(r) = 0, \quad (56)$$

using the potential defined by Eq. (52). The boundary conditions are given by $\lim_{r \rightarrow \infty} \varphi(r) = 1$ and

$$S_d D_B [1 - c_v(r)] \left. \frac{\partial}{\partial r} \varphi(r) \right|_{r=R} = k_0 \varphi(R), \quad (57)$$

where the surface area of the d -dimensional sphere is given by $S_d = d\pi^{d/2} / \Gamma[(d/2) + 1]$. For 2 and 3 dimensions, $S_2 = 2\pi R$ and $S_3 = 4\pi R^2$. The solution of Eq. (56) subject to the above mentioned boundary conditions is obtained as

$$\varphi(r) = \frac{\int_R^r dr_1 \frac{1}{D_B [1 - c_v(r_1)]^2 r_1^{d-1}} + \frac{S_d}{k_0} \frac{1}{[1 - c_v(r)] R^{d-1}}}{\int_R^\infty dr_1 \frac{1}{D_B [1 - c_v(r_1)]^2 r_1^{d-1}} + \frac{S_d}{k_0} \frac{1}{[1 - c_v(r)] R^{d-1}}}. \quad (58)$$

In the limit of perfectly absorbing boundary condition, the escape probability simplifies into,

$$\varphi(r) = \int_R^r dr_1 \frac{1}{[1 - c_v(r_1)]^2 r_1^{d-1}} \bigg/ \int_R^\infty dr_1 \frac{1}{[1 - c_v(r_1)]^2 r_1^{d-1}}. \quad (59)$$

According to Eq. (59), the escape probability is independent of the density of the inert particles when the density is homogeneous. This result is consistent with that obtained in the lattice system in Sec. IV. On the other hand, when the density of the inert particles is inhomogeneous, the escape probability in general depends on the density of the inert particles. The escape probability is lower than that for the homogeneous density of inert particles if $c_v(r)$ has a positive slope. The recombination reaction can be assisted by a positive density gradient of the inert particles. On the other hand, the recombination can be hindered by a negative density gradient of the inert particles.

VI. CONCLUSIONS

In this paper, the time evolution equations for the survival probability of a geminate pair under the presence of many inert particles are derived and the results are compared to the simulation results. If we ignore correlations higher than two-point correlations, Eq. (19) is derived. In this lowest order approximation, the influence of inert particles is described by using the mean-field expression of the tracer-diffusion constant in the reaction-diffusion equation.

In the lowest order approximation, the so-called Bardeen-Herring back correlation is not taken into account. The Bardeen-Herring back correlation is the tendency of the preferred jump of the diffusing particle back to the previously occupied empty site. We have shown that the reaction interferes with the Bardeen-Herring back correlation. In the reaction-diffusion equation, the transition operator describing diffusion is influenced by the reaction strength while leaving the reaction term unaltered. If the interference between the reaction and the Bardeen-Herring back correlation is taken into account, the reaction-diffusion equation becomes very complicated and cannot be solved analytically. By taking into account the Bardeen-Herring back correlation but ignoring the interference between the reaction and the Bardeen-Herring back correlation, we obtain the reaction-diffusion equation given in terms of the improved expression of the tracer-diffusion constant. The influence of the excluded volume interactions is taken into account solely by the tracer-diffusion constant. The tracer-diffusion constant decreases by increasing the concentration of the inert particles since the diffusive motion of the reactive species is hindered by the presence of the inert particles.

By comparison of the theoretical results with the results of numerical simulations, the interference between the reaction and the Bardeen-Herring back correlation is shown to be small as far as the overall reaction yield is concerned. The interference also influences the transient decay of the survival probability of a geminate pair in the diffusion-controlled limit. When the initial concentration of the inert particles is high, we show that interference between the reaction and the Bardeen-Herring back correlation accelerates the transient decay of the survival probability in the diffusion-controlled limit.

Recently, Schmit *et al.* studied the reaction in a microfluid by the Monte Carlo simulation [26]. The simulation results are well approximated by the survival probability of a pair of reactants obtained from the reaction-diffusion equation similar to Eq. (19): it is suggested to use the reaction-diffusion equation in which the mutual diffusion coefficient is substituted by the effective tracer-diffusion coefficient of a tagged particle in a sea of inert particles [26]. They calculated the mean first passage time instead of the survival probability. Since the mean first passage time can be given in terms of the inverse of the overall reaction rate, their results are consistent with our conclusion, although the slightly different expression of the effective tracer-diffusion coefficient is used in their equation. According to our work, the approximation would fail in the transient decay of the survival probability in the diffusion-controlled limit at high concentration of inert particles.

The above conclusions are obtained by assuming the homogeneous distribution of the inert particles. We have also formulated a way to obtain the survival probability of a geminate pair when the initial distribution of inert particles is inhomogeneous. The reaction yield is increased when the reaction proceeds in the presence of a positive density gradient of the inert particles which inhibits the escape of reactants. The effect can be interpreted as a cage effect. Although we need further investigation for the kinetics of the survival probability in the presence of the density gradient of the inert particles, our results on the escape probability indicate that the crowding promotes reactions when the density of the inert particles increases with the distance from the location of the immobile reactant.

Recently, the cage effect of crowding by inert particles was introduced by Kim and Yethiraj to interpret the increase of association rate constant with increasing the concentration of inert particles obtained by Brownian dynamic simulations when the intrinsic reaction rate constant was small [7]. The cage effect in this paper is similar to that introduced by them in the sense that the presence of inert particles surrounding a reactant pair promotes the reaction, but the mechanism is slightly different. In our case, the concentration gradient toward one of the reactant pair assists the recombination reaction, while the association rate in their case increases by the increase of the recollision probability due to the high concentration of inert particles rather than the concentration gradient.

APPENDIX A: DIFFUSION KERNEL

By introducing the operator identity

$$\frac{1}{s - \tilde{L}_{rw0} - \tilde{L}_{rc}} = \frac{1}{s} \left[1 + \frac{1}{s - \tilde{L}_{rw0} - \tilde{L}_{rc}} (\tilde{L}_{rw0} + \tilde{L}_{rc}) \right] \quad (\text{A1})$$

into Eq. (32) and from the definition given by Eq. (32), we derive

$$\begin{aligned} & sG(\vec{n}\bullet, \vec{n} + \vec{b}_r \circ | \vec{m}\bullet, \vec{r}\circ, s) - \delta_{\vec{r}, \vec{b}_r} \delta_{\vec{n}, \vec{m}} \\ &= \sum_{\alpha} [\gamma_w G(\vec{n}\bullet, \vec{n} + \vec{b}_r \circ | \vec{m}\bullet, \vec{r} + \vec{b}_{\alpha}\circ, s) + \gamma_B(1-c)G(\vec{n}\bullet, \vec{n} + \vec{b}_r \circ | \vec{m} - \vec{b}_{\alpha}\bullet, \vec{r} + \vec{b}_{\alpha}\circ, s) \\ & - \gamma_t G(\vec{n}\bullet, \vec{n} + \vec{b}_r \circ | \vec{m}\bullet, \vec{r}\circ, s)] - \delta_{\vec{r}, \vec{0}} \sum_{\alpha} [\gamma_w G(\vec{n}\bullet, \vec{n} + \vec{b}_r \circ | \vec{m}\bullet, \vec{b}_{\alpha}\circ, s) \\ & + \gamma_B(1-c)G(\vec{n}\bullet, \vec{n} + \vec{b}_r \circ | \vec{m} - \vec{b}_{\alpha}\bullet, \vec{b}_{\alpha}\circ, s)] + \sum_{\alpha} \delta_{\vec{r}, \vec{b}_{\alpha}} [\gamma_B c G(\vec{n}\bullet, \vec{n} + \vec{b}_r \circ | \vec{m} + \vec{b}_{\alpha}\bullet, -\vec{b}_{\alpha}\circ, s) \\ & + (\gamma_t - \gamma_B c)G(\vec{n}\bullet, \vec{n} + \vec{b}_r \circ | \vec{m}\bullet, \vec{b}_{\alpha}\circ, s)] - k(\vec{m})G(\vec{n}\bullet, \vec{n} + \vec{b}_r \circ | \vec{m}\bullet, \vec{r}\circ, s), \end{aligned} \quad (\text{A2})$$

where

$$\gamma_t = \gamma_w + \gamma_B(1-c). \quad (\text{A3})$$

In the presence of $k(\vec{m})$, $G(\vec{n}\bullet, \vec{n} + \vec{b}_r \circ | \vec{m}\bullet, \vec{r}\circ, s)$ does not satisfy the condition of translational invariance of \vec{m} against \vec{n} .

If we ignore $k(\vec{m})$ in Eq. (A2), the translational invariance is satisfied. The equation for $G^{(T)}(\vec{\ell}, \vec{b}_r | \vec{r}, s)$ introduced in Eq. (38) is given by

$$\begin{aligned} & sG^{(T)}(\vec{\ell}, \vec{b}_r | \vec{r}, s) - \delta_{\vec{r}, \vec{b}_r} \delta_{\vec{\ell}, \vec{0}} = \sum_{\alpha} [\gamma_w G^{(T)}(\vec{\ell}, \vec{b}_r | \vec{r} + \vec{b}_{\alpha}, s) + \gamma_B(1-c)G^{(T)}(\vec{\ell} - \vec{b}_{\alpha}, \vec{b}_r | \vec{r} + \vec{b}_{\alpha}, s) \\ & - \gamma_t G^{(T)}(\vec{\ell}, \vec{b}_r | \vec{r}, s)] - \delta_{\vec{r}, \vec{0}} \sum_{\alpha} [\gamma_w G^{(T)}(\vec{\ell}, \vec{b}_r | \vec{b}_{\alpha}, s) + \gamma_B(1-c)G^{(T)}(\vec{\ell} - \vec{b}_{\alpha}, \vec{b}_r | \vec{b}_{\alpha}, s)] \\ & + \sum_{\alpha} \delta_{\vec{r}, \vec{b}_{\alpha}} [\gamma_B c G^{(T)}(\vec{\ell} + \vec{b}_{\alpha}, \vec{b}_r | -\vec{b}_{\alpha}, s) + (\gamma_t - \gamma_B c)G^{(T)}(\vec{\ell}, \vec{b}_r | \vec{b}_{\alpha}, s)]. \end{aligned} \quad (\text{A4})$$

By applying Fourier transformation,

$$g(\vec{k}, \vec{b}_r | \vec{h}, s) = \sum_{\vec{\ell}} \sum_{\vec{r}} \exp[i(\vec{k} \cdot \vec{\ell} + \vec{h} \cdot \vec{r})] G^{(T)}(\vec{\ell}, \vec{b}_r | \vec{r}, s), \quad (\text{A5})$$

$$\tilde{G}(\vec{k}, \vec{b}_r | \vec{r}, s) = \sum_{\vec{\ell}} \exp[i\vec{k} \cdot \vec{\ell}] G^{(T)}(\vec{\ell}, \vec{b}_r | \vec{r}, s), \quad (\text{A6})$$

we obtain

$$\begin{aligned} sg(\vec{k}, \vec{b}_r | \vec{h}, s) &= \exp(i\vec{h} \cdot \vec{b}_r) + \sum_{\alpha} [\omega_t(\vec{b}_{\alpha}) \exp(-i\vec{h} \cdot \vec{b}_{\alpha}) - \gamma_t] g(\vec{k}, \vec{b}_r | \vec{h}, s) \\ &+ \sum_{\alpha} [\exp(-i\vec{h} \cdot \vec{b}_{\alpha}) \omega_B(\vec{b}_{\alpha}) c + \gamma_s \exp(i\vec{h} \cdot \vec{b}_{\alpha}) - \omega_t(\vec{b}_{\alpha})] \tilde{G}(\vec{k}, \vec{b}_r | \vec{b}_{\alpha}, s), \end{aligned} \quad (\text{A7})$$

where we define

$$\gamma_s = \gamma_t - \gamma_B c, \quad (\text{A8})$$

$$\omega_B(\vec{r}) = \gamma_B \exp(i\vec{k} \cdot \vec{r}), \quad \omega_t(\vec{r}) = \gamma_w + \gamma_B(1 - c) \exp(i\vec{k} \cdot \vec{r}). \quad (\text{A9})$$

It is convenient to introduce the function

$$Q(\vec{k}, \vec{r}, s) = \frac{1}{(2\pi)^d} \int \cdots \int_{-\pi}^{\pi} d^d \vec{h} \frac{\exp(-i\vec{h} \cdot \vec{r})}{s + \Gamma_t - \Omega_t(\vec{k}, \vec{h})}, \quad (\text{A10})$$

where $\Gamma_t = 2d\gamma_t$, and $\Omega_t(\vec{k}, \vec{h})$ is defined by

$$\Omega_t(\vec{k}, \vec{h}) = 2d[\gamma_w \lambda(\vec{h}) + \gamma_B(1 - c)\lambda(\vec{k} - \vec{h})]. \quad (\text{A11})$$

A closed set of equations can be obtained from Eq. (A7) as

$$\tilde{G}(\vec{k}, \vec{b}_r | \vec{b}_q, s) = Q(\vec{k}, \vec{b}_q - \vec{b}_r, s) + \sum_{\alpha} [\gamma_s Q(\vec{k}, \vec{b}_q - \vec{b}_{\alpha}, s) + \omega_B(\vec{b}_{\alpha}) c Q(\vec{k}, \vec{b}_q + \vec{b}_{\alpha}, s) - \omega_t(\vec{b}_{\alpha}) Q(\vec{k}, \vec{b}_q, s)] \tilde{G}(\vec{k}, \vec{b}_r | \vec{b}_{\alpha}, s). \quad (\text{A12})$$

The solution is independent of the position of the reactive sink in this approximation. By introducing the solution of Eq. (A12) into Eq. (41) and using Eqs. (39) and (40), the survival probability is obtained after numerical inverse Laplace transformation and inverse Fourier transformation.

An equation for $G^{(a)}(\vec{b}_r | \vec{r}, s)$ is obtained by applying the operator identity,

$$\frac{1}{s - \tilde{L}_{rw0}} = \frac{1}{s} \left(1 + \frac{1}{s - \tilde{L}_{rw0}} \tilde{L}_{rw0} \right), \quad (\text{A13})$$

as [8–10]

$$\begin{aligned} sG^{(a)}(\vec{b}_r | \vec{r}, s) - \delta_{\vec{r}, \vec{b}_r} &= \sum_{\alpha} \gamma_t [G^{(a)}(\vec{b}_r | \vec{r} + \vec{b}_{\alpha}, s) - G^{(a)}(\vec{b}_r | \vec{r}, s)] - \delta_{\vec{r}, \vec{0}} \sum_{\alpha} \gamma_t G^{(a)}(\vec{b}_r | \vec{b}_{\alpha}, s) \\ &+ \sum_{\alpha} \delta_{\vec{r}, \vec{b}_{\alpha}} [\gamma_B c G^{(a)}(\vec{b}_r | -\vec{b}_{\alpha}, s) + (\gamma_t - \gamma_B c) G^{(a)}(\vec{b}_r | \vec{b}_{\alpha}, s)]. \end{aligned} \quad (\text{A14})$$

The solution depends on a position of an inert particle through its relative vector against the initial position of a mobile reactant.

APPENDIX B: EXCLUDED VOLUME INTERACTIONS UNDER INHOMOGENEOUS DISTRIBUTION OF INERT PARTICLES

Since the particle jumps to a vacant site, $p(\vec{r}, t)$ obeys

$$\frac{\partial}{\partial t} p(\vec{r}, t) = \gamma_B \sum_j [p(\vec{r} + \vec{b}_j \bullet, \vec{r} \phi, t) - p(\vec{r} \bullet, \vec{r} + \vec{b}_j \phi, t)] - k(\vec{r}) p(\vec{r}, t), \quad (\text{B1})$$

where $p(\vec{r} \bullet, \vec{r}' \phi, t)$ denotes the joint probability at time t that the site \vec{r} is occupied by a reactive particle and the site \vec{r}' is empty. We note the relation [34,35,43]

$$p(\vec{r} \bullet, \vec{r}' \phi, t) = p(\vec{r}, t) - p(\vec{r} \bullet, \vec{r}' \circ, t) - p(\vec{r} \bullet, \vec{r}' \bullet, t), \quad (\text{B2})$$

where $p(\vec{r}\bullet, \vec{r}'\circ, t)$ and $p(\vec{r}\bullet, \vec{r}'\bullet, t)$ denote the joint probabilities at time t that the site \vec{r} is occupied by a reactive particle and the site \vec{r}' is occupied by an inert particle and that both sites are occupied by reactive particles, respectively. Equation (B1) can be rewritten as

$$\frac{\partial}{\partial t} p(\vec{r}, t) = \gamma_B \sum_j [p(\vec{r} + \vec{b}_j\bullet, \vec{r}\circ, t) - p(\vec{r}\bullet, t) - p(\vec{r} + \vec{b}_j\bullet, \vec{r}\circ, t) + p(\vec{r}\bullet, \vec{r} + \vec{b}_j\circ, t)] - k(\vec{r})p(\vec{r}, t). \quad (\text{B3})$$

By assuming that the pair correlation function depends on the distance vector between the reactant and the inert particle alone, the joint probability function can be written as [44]

$$p(\vec{r}\bullet, \vec{r}'\circ, t) = p(\vec{r}, t)c(\vec{r}', t)\sigma(\vec{r} - \vec{r}'), \quad (\text{B4})$$

where the occupation probability by an inert particle is denoted by $c(\vec{r}, t)$. When the spatial variation of $\sigma(\vec{r})$ is smaller than $p(\vec{r}, t)$ and $c(\vec{r}, t)$, we obtain in the limit of small lattice spacing,

$$\sum_j p(\vec{r} + \vec{b}_j\bullet, \vec{r}\circ, t) = [p(\vec{r}, t)c(\vec{r}, t) + b^2 c(\vec{r}, t)\nabla^2 p(\vec{r}, t)]\sigma(0), \quad (\text{B5})$$

$$\sum_j p(\vec{r}\bullet, \vec{r} + \vec{b}_j\circ, t) = [p(\vec{r}, t)c(\vec{r}, t) + b^2 p(\vec{r}, t)\nabla^2 c(\vec{r}, t)]\sigma(0), \quad (\text{B6})$$

where $\lim_{b \rightarrow 0} \sigma(\vec{b}_j) = \sigma(0)$. By introducing Eqs. (B5) and (B6), Eq. (B3) in the limit of $b \rightarrow 0$ becomes

$$\frac{\partial}{\partial t} p(\vec{r}, t) = \vec{\nabla} \cdot D_B \{ [1 - \sigma(0)c_v(\vec{r}, t)] \vec{\nabla} p(\vec{r}, t) + \sigma(0)p(\vec{r}, t) \vec{\nabla} c_v(\vec{r}, t) \} - k(\vec{r})p(\vec{r}, t), \quad (\text{B7})$$

where $D_B = b^2 \gamma_B$ and the concentration of inert particles is denoted by $c_v(\vec{r}, t)$ in the continuum limit. In the mean-field approximation in which $\sigma(0) = 1$, the derivation follows from that given previously [34,35]. Equation (B7) can be expressed in terms the correlation factor as

$$\frac{\partial}{\partial t} p(\vec{r}, t) = \vec{\nabla} \cdot D_B \{ [1 - c_v(\vec{r}, t)] f_c \vec{\nabla} p(\vec{r}, t) + \sigma(0)p(\vec{r}, t) \vec{\nabla} c_v(\vec{r}, t) \} - k(\vec{r})p(\vec{r}, t), \quad (\text{B8})$$

where $\sigma(0) = f_c + (1 - f_c)/c_v(r, t)$. f_c is given by Eq. (50), though, strictly speaking, the calculation of the correlation factor f_c is restricted to the homogeneous distribution of inert particles. In the mean-field approximation, we have $\sigma(0) = 1$ and Eq. (B7) leads to Eq. (51).

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