

Diffusion-mediated geminate reactions under excluded volume interactions

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Abstract

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. The results interpolate between low and high concentrations of the inert particles. Excluded volume interactions by the inert particles hinder the diffusive motion of reactants. When the initial distribution of the inert particles is uniform, the excluded volume interactions slow the decay of the survival probability of a geminate pair in contrast to the acceleration of the decay found for the target problem under the presence of the excluded volume interactions among reactants. We also obtain the escape probability for a non-uniform initial distribution of the inert particles and 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.

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.

The diffusion of reactants can be hindered in the presence of inert macromolecules. The hindrance may reduce the diffusion coefficients of reactants compared to those in the absence of inert molecules while the diffusion processes still remain normal; the mean square displacements grow linear in time at long times. In some cases, subdiffusion is reported in crowded environments. [8–16] Subdiffusion is characterized by the time evolution of the mean square displacements, $\langle r^2(t) \rangle \sim t^\alpha$, with the exponent being $\alpha < 1$. Subdiffusion of molecules in crowded environments is observed and theoretically studied when molecules diffuse in gels or other compartmentalized systems. [8–15] In such systems, subdiffusion is found only at a transient time regime before a crossover to normal diffusion. Subdiffusion is also found even when the size of inert molecules is comparable to that of reactants but the mechanism behind it is unclear. [16] When the initial distribution of inert particles is uniform, the tracer exhibits essentially the normal diffusion at long times with reduced diffusion coefficients. [17] The subdiffusion kinetics can be caused by a nonuniform initial distribution of inert particles.

As a kind of reaction process, we consider reactions between a geminate pair of reactants generated simultaneously. 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.

In this paper, we study 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.

The excluded volume interactions has been theoretically treated by applying Nakazato-Kitahara's theory on tracer diffusion in a lattice. [18] Nakazato-Kitahara's 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. [18–21] By applying Nakazato-Kitahara's theory the survival probability of a geminate pair can be calculated analytically, which interpolates between low and high concentrations of inert particles.

For target reactions where a static reactive particle (target) is surrounded by many reactive counterparts (quenchers), Nakazato-Kitahara's theory was successfully applied to calculate the survival probability of a target with a constraint prohibiting the double occupancy of diffusing reactants. [22, 23] It turned out that the decay of the target survival probability is accelerated by prohibiting the double occupancy. [22, 23] Similar acceleration of the decay was obtained by other numerical and analytical approaches. [24–35] 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 prohibiting the double occupancy at each lattice site. [22, 23] Accordingly, the probability of reaction between a 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 should influence the kinetics of geminate reaction through different mechanism from that in the case of target reactions. Indeed, numerical simulations show that the reaction between a pair proceeds slowly by the crowding of inert particles and this result is supported by phenomenological argument. [36]

In this paper, we derive equations for the survival probability of a pair of reactants performing diffusion under site blocking effects in the presence of inert particles. Both homogeneous

and inhomogeneous initial distributions of inert particles are considered. On the basis of the equation derived, the mechanism of site blocking effects by inert particles in the geminate reactions is investigated in detail.

We formulate the problem and present the most simple mean field results in Sec. II. The higher order corrections to the mean field results are given in Sec. III. In Sec. IV, we compare the analytical results to simulation results. Continuous limit is taken in Sec. V and the influence of non-uniform initial distribution of inert particles is investigated in Sec. VI. In Sec. VII, we derive the escape probability when the initial distribution of the inert particles is non-uniform. Section VIII is devoted for 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 the origin of the coordinate system is taken to be its position. 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. [18] The diffusion of the tagged particle in the presence of site blocking by other particles has been studied. [18–21] 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 a 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, [18–20]

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

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 $k(\vec{r}_n)$, [37–39]

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

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 an 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,

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

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

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

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

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

The inverse transformation is given by applying the 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 finite, the right hand side of Eq. (9) can be calculated by applying the saddle point method, [18–20]

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

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, $\tilde{L}(\theta^*) = \tilde{L}_{\text{rw}} + L_{\text{rc}}$. Even after the transformation the term describing reaction is not changed, 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, [18–20]

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

and $\tilde{L}_{\text{rw}1}$ describes the transition where the number of particles is not conserved, [18–20]

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

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 nominator of Eq. (16) and we obtain,

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

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

$$s\hat{S}(\vec{m}, s) - 1 = \gamma_B(1-c) \sum_j \left(\hat{S}(\vec{m} + \vec{b}_j, s) - \hat{S}(\vec{m}, s) \right) - k(\vec{m}) \hat{S}(\vec{m}, s), \quad (18)$$

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

$$\frac{\partial}{\partial t} S(\vec{m}, t) = \gamma_B(1 - c) \sum_j \left(S(\vec{m} + \vec{b}_j, t) - S(\vec{m}, t) \right) - k(\vec{m}) S(\vec{m}, t). \quad (19)$$

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 the 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 the 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, [40]

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

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 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 the inert particles. The escape probability, $\lim_{t \rightarrow \infty} S(\vec{m}, t)$, which is 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 the concentration of the inert particles and the diffusion and the reaction do not interfere. In the subsequent section, we show that the diffusion and the reaction interfere in the presence of inert particles if we consider higher order correlations. The magnitude of the interference is assessed by comparison to simulations when the initial distribution of inert particles is uniform. We also examine the effect of nonuniform initial distribution of inert particles on the escape probability of a geminate pair.

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. [41] The Bardeen-Herring back correlation takes place when the reactant and the vacancy sites are exchanged by hopping; after the hopping the transition probability of the reactant back to the previously occupied site is higher than other sites. Suppose that a reactant occupies a reactive site after a hopping exchange by a vacant site. The rate of hopping back to the previous site competes with that of reaction. In this way, the reaction interferes 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.

In mathematical terms, we study the correction to the simple diffusion-reaction equation, Eq. (19), which is the inverse Laplace transform of Eq. (17). The exact relation, Eq. (16), can be rewritten as,

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

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,

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

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

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

When we substitute Eq. (27) into Eq. (26), we note Eq. (28) and the similar relations for the other terms. By using the relations, Eq. (26) can be expressed as,

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

$$= \sum_{\vec{n}} \hat{S}(\vec{n}, s) \langle \{\phi\} | \langle \vec{n}, \bullet | \tilde{L}_{\text{rw1}} \frac{1}{s - \tilde{L}_{\text{rw0}} - \tilde{L}_{\text{rc}}} \tilde{L}_{\text{rw1}} | \{\phi\} \rangle | \vec{m}, \bullet \rangle, \quad (30)$$

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,

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

where we define the four-point correlation function,

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

using the abbreviation,

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

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

where M'' denotes that the site \vec{r}_i and the site \vec{r}_j are excluded in the product. Eqs. (33)-(34) represent the state that all sites are vacant except at the site \vec{r}_i occupied by the reactant and the site \vec{r}_j occupied by an inert particle. By substituting Eq. (31) and rearranging the summation, Eq. (25) with Eq. (30) can be expressed as,

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

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

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

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

The time convolution represents the memory effect originated from the correlation between the mobile reactant and the inert particles. Reactant motion is correlated with the time dependent arrangements of the inert particles by prohibiting the double occupancy of the lattice sites. In particular, the site occupied by the reactant is 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 appeared by the

exchange of the reactant with a vacancy can be occupied by another inert particle. The time dependence of 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. Judging from the fact that Eq. (32) includes the operator describing reaction, \tilde{L}_{rc} , the diffusion memory kernel, $\hat{F}_c(\vec{n}, \vec{m}, s)$, depends on the reaction rate. In Appendix A, we show that the equation for $G(\vec{n}\bullet, \vec{n} + \vec{b}_r \circ | \vec{m}\bullet, \vec{m} + \vec{b}_q \circ, s)$ includes the reactive sink term. The interference between 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 reaction and correlated diffusion cannot be 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 reaction and the correlated diffusion violates the translational invariance and the resultant equation is hard to solve as shown in Appendix A. In the next section, we use numerical simulations to study the interference effect.

When we ignore the interference between reaction and correlated diffusion, the translation invariance is satisfied for the four-point correlation functions. We introduce the notation that explicitly shows the translational invariance,

$$G_{\vec{b}_r}(\vec{n} - \vec{m}, \vec{r}, s) = G_{\vec{n}, \vec{b}_r}(\vec{m}, \vec{r}, s). \quad (37)$$

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

$$\frac{\partial}{\partial t} S(\vec{k}, t) = \int_0^t dt_1 M(k, t - t_1) S(k, t_1) - \sum_{\vec{m}} \exp(i\vec{k} \cdot \vec{m}) k(\vec{m}) S(\vec{m}, t). \quad (38)$$

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

expressed as,

$$\hat{M}(\vec{k}, s) = -\Gamma_B(1-c) \left(1 - \lambda(\vec{k})\right) + \gamma_B^2 c(1-c) T_c(\vec{k}, s), \quad (39)$$

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

$$\hat{T}_c(\vec{k}, s) = \sum_q \sum_r \left(1 - \exp(-i\vec{k} \cdot \vec{b}_r)\right) G_{\vec{b}_r}(\vec{k}, \vec{b}_q, s) \left(1 - \exp(i\vec{k} \cdot \vec{b}_q)\right), \quad (40)$$

$$G_{\vec{b}_r}(\vec{k}, \vec{r}, s) = \sum_{\vec{\ell}} \exp(i\vec{k} \cdot \vec{\ell}) G_{\vec{b}_r}(\vec{\ell}, \vec{r}, s). \quad (41)$$

The same form of memory function expressed in terms of the four-point correlation function was derived by a different method. [42] Here, Eq. (41) is derived for $G_{\vec{b}_r}(\vec{k}, \vec{r}, s)$ and the equation for $G_{\vec{b}_r}(\vec{\ell}, \vec{r}, s)$ is explicitly shown in Appendix B.

In the limit of small wavelength, $k \rightarrow 0$, Eq. (39) leads to diffusion equation with a memory kernel and Eq. (38) can be expressed after the inverse Laplace transformation as,

$$\frac{\partial}{\partial t} S(\vec{m}, t) = \Gamma_B(1-c) \sum_j \int_0^t dt_1 f_c(t-t_1) \nabla^2 S(\vec{m}, t_1) - k(\vec{m}) S(\vec{m}, t), \quad (42)$$

where the correlation factor in the Laplace domain is given for the hypercubic lattices by,

$$\hat{f}_c(s) = 1 - \gamma_B c \sum_r \left[G_{\vec{b}_r}^{(a)}(\vec{b}_r, s) - G_{\vec{b}_r}^{(a)}(-\vec{b}_r, s) \right], \quad (43)$$

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

$$G_{\vec{b}_r}^{(a)}(\vec{b}_q, s) = \sum_{\vec{m}} \langle \{\phi\} | \langle \vec{n}, \bullet | \langle \vec{n} + \vec{b}_r, \circ | \frac{1}{s - \tilde{L}_{\text{rw}0}} | \{\phi\} | \vec{m}, \bullet | \vec{m} + \vec{b}_q, \circ \rangle, \quad (44)$$

which is independent of the choice of \vec{n} as shown in Appendix C. The equation for $G_{\vec{b}_r}^{(a)}(\vec{b}_q, s)$ was known and has been studied to obtain the tracer-diffusion coefficient. [18–20] It is shown in Appendix C. The solution is known and the correlation factor can be expressed as,

$$\hat{f}_c(s) = \frac{1 - \mu(s)}{1 - \mu(s) \frac{\gamma_w + \gamma_B(1-3c)}{\gamma_w + \gamma_B(1-c)}}, \quad (45)$$

where $\mu(s)$ is given by,

$$\mu(s) = \frac{1}{(2\pi)^d} \int \cdots \int_{-\pi}^{\pi} d^d \vec{k} \frac{2 \sin^2 k_1}{(s/\gamma_t) + 2d[1 - \lambda(\vec{k})]}, \quad (46)$$

and $\gamma_t = \gamma_w + \gamma_B(1 - c)$. 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 obtained respectively from Eq. (20) and Eq. (23) by introducing the correlation factor into the hopping frequency,

$$\gamma_B \rightarrow \gamma_B f_c, \quad (47)$$

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

$$f_c = \frac{1 - \mu}{1 - \mu \frac{\gamma_w + \gamma_B(1 - 3c)}{\gamma_w + \gamma_B(1 - c)}}, \quad (48)$$

and $\mu = \mu(s = 0)$ is known for some lattices. When the hopping frequency 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.

In summary of this section, we study 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 exchanges its position to vacancy, the reactant tends to jump back to its previously occupied empty site, which is called 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)-(36) and Eq. (A3). 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. (38)-(41) and Eq. (B9). By introducing further simplification of ignoring the memory effect, we obtain Eq. (19) with substitution shown by Eq. (47). In the below, these results will be compared with those obtained by numerical simulations.

IV. COMPARISON TO SIMULATION RESULTS

A. Simulation method

In order to see the interference of 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, it is allowed for both types of simulated particles 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. 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 as long as 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 $r_{\max} = 30$. 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 $r_{\max} = 60$ was about 2% higher than that calculated with $r_{\max} = 30$.

B. Simulation results

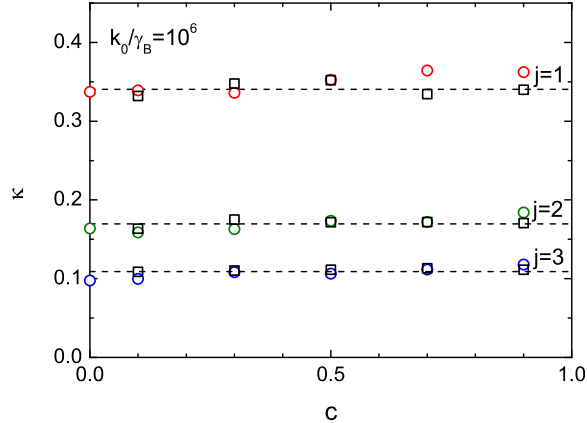
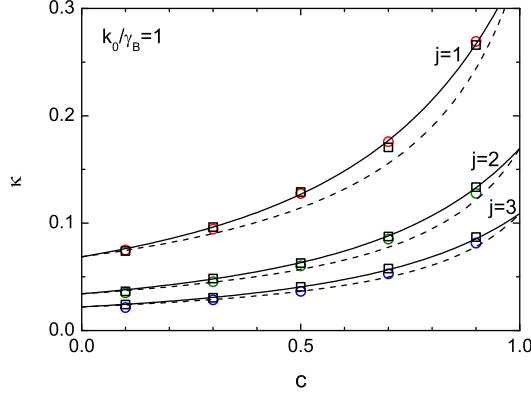
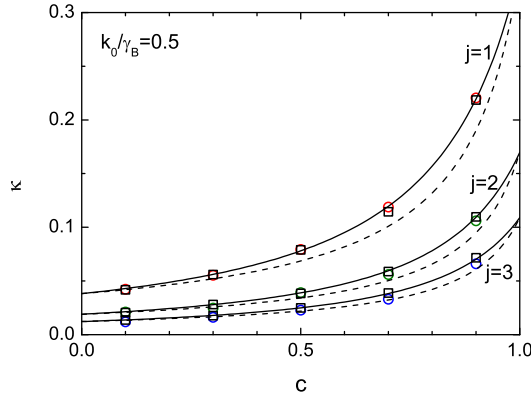


FIG. 1: Recombination probability of a geminate pair against concentration of inert particles, c , for $k_0 \rightarrow \infty$ (In the simulation, $k_0/\gamma_B = 10^6$) and $\gamma_w/\gamma_B = 1$. j indicates the initial separation of the geminate pair. Circles indicate the simulation results. Squares represent the solution of Eqs. (37)-(41) with Eq. (B9). Dashed lines indicate the mean field results of Eq. (23). The results of Eq. (23) with the substitution shown by Eq. (47) can be indicated by the same dashed lines.

We investigate quantitatively the factors ignored in deriving simple result, Eq. (19), by comparison to the more rigorous theoretical results and the simulation results.



(a)



(b)

FIG. 2: 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. Circles indicate the simulation results. Squares represent the solution of Eqs. (37)-(41) with Eq. (B9). The results of Eq. (23) with the substitution shown by Eq. (47) are indicated by the solid lines. Dashed lines indicate the mean field results of Eq. (23).

One of factors is the Bardeen-Herring back correlation. The Bardeen-Herring back correlation is described by the four-point correlation function given in the Appendix B. The Bardeen-Herring back correlation is taken into account fully by Eqs. (37)-(41) and partly by Eq.(48). Equation (48) is obtained from Eqs. (37)-(41) by taking the limit of small wave length,

$k \rightarrow 0$ and ignoring the memory effect. Equation (48) is much simpler than Eqs. (37)-(41) and the result can be easily obtained from that of Eq. (19) by the substitution shown by Eq. (47). The numerical way to solve Eqs. (37)-(41) with the additional set of equations are given in the Appendix B.

The other factor is the effect of the interference between 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. (37)-(41).

The recombination probability in the completely diffusion controlled limit, $k_0 \rightarrow \infty$, is shown in Fig. 1. The simulation results are compared to those obtained by the numerical evaluation of the analytical results based on Eqs. (37)-(41). In the theoretical results the influence of reaction on the four-point correlation function is ignored. As shown in Fig. 1, the influence of reaction on the four-point correlation function is very small for all concentrations of inert particles. In the completely diffusion controlled limit, $k_0 \rightarrow \infty$, the recombination probability obtained by the substitution shown by Eq. (48) is independent of the concentration of the inert particles. This is not a rigorous relation which is obtained by the oversimplification by taking the limit of small wave length, $k \rightarrow 0$, and ignoring the memory effect. However, the difference between the result of the simplified equation, Eq. (48), and that obtained without taking the limit of long-wave length, Eqs. (37)-(41), is also very small. Judging from Fig. 1, such approach is justified for the calculation of the recombination probability.

The presence of interference between reaction and the four-point correlation function is not restricted in the limit of $k_0 \rightarrow \infty$. Figure 2 shows the results when the reactivity is finite. The influence of reaction on the four-point correlation function can be shown as the difference between the simulation results and those based on Eqs. (37)-(41) and 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 by the substitution shown by Eq. (48) and the results of Eqs. (37)-(41) is again negligibly small.

In conclusion of this section, the mean field results of Eq. (19) 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 substitution shown by Eq. (47) into Eq. (19) to take into account the Bardeen-Herring back correlation. Generalization of Eq. (19) to the case of continuous diffusion and non-uniform distribution of inert particles is shown in the subsequent sections.

V. CONTINUOUS DIFFUSION

By taking the limit of zero lattice spacing, $b \rightarrow 0$, and introducing the volume fraction of inert particles, c_v , Eq. (19) can be expressed as,

$$\frac{\partial}{\partial t} S(r, t) = \vec{\nabla} \cdot D_B(1 - c_v)\vec{\nabla} S(r, t) - k(r) S(r, t), \quad (49)$$

where the diffusion constant is defined by, $D_B = b^2\Gamma_B$. If the reactants cannot penetrate each other, the perfectly reflecting boundary condition,

$$\left. \frac{\partial}{\partial r} S(r, t) \right|_{r=R} = 0. \quad (50)$$

is imposed at the contact distance R . For a localized reaction with the intrinsic rate k_0 given by,

$$k(r) = k_0 \frac{\delta(r - R)}{4\pi R^2}, \quad (51)$$

the recombination probability is obtained as,

$$\kappa(r) = \frac{\ell_R}{r}, \quad (52)$$

where the radius characterizing the escape of reactant is given by,

$$\ell_R = \frac{R}{1 + (4\pi R D_B(1 - c_v)/k_0)}. \quad (53)$$

For perfectly absorbing boundary conditions, ℓ_R , and accordingly the recombination probability become independent of the concentration of the inert particles. For finite reactivity, ℓ_R and the recombination probability increase as the concentration of the inert particles increases. The asymptotic decay of the survival probability is obtained as,

$$S(r, t) \sim \varphi(r) \left(1 + \frac{\ell_R}{\sqrt{\pi D_B(1 - c_v)t}} \right), \quad (54)$$

where the escape probability $\varphi(r)$ is given by $\varphi(r) = 1 - \kappa(r)$ as defined in the case of lattice random walks. The exponent of the power law asymptotic decay of survival probability is not influenced by the presence of the inert particles whose initial distribution is uniform in space.

VI. INHOMOGENEOUS DISTRIBUTION OF THE INERT PARTICLES

So far, we have assumed the homogeneous distribution of inert particles. Recently, the influence of inhomogeneous distributions of inert particles on catalytic reactions is taken into account by applying the theory of nonequilibrium thermodynamics. [43] In this chapter, we modify it to study geminate reactions in the sea of inert particles. The concentration of inert particles is denoted by c_v . In order to facilitate the thermodynamic argument, we introduce the pair distribution $p(r, t)$ of finding a pair of reactants at the separation distance r at time t instead of the survival probability of a pair of reactants at time t whose initial separation is r , $S(r, t)$. First, we rewrite Eq. (49) in terms of the current \vec{j} ,

$$\frac{\partial}{\partial t} p(r, t) + \text{div} \cdot \vec{j} = -k(r) p(r, t), \quad (55)$$

where the current is expressed by the chemical potential μ , the temperature T and the Onsager coefficient, L ,

$$\vec{j} = -L \vec{\nabla} \frac{\mu}{T}. \quad (56)$$

The chemical potential is defined by,

$$\mu = \frac{\delta F}{\delta p(r, t)}, \quad (57)$$

where the free energy is related to the entropy by the relation $F = -TS$ and the entropy is given by,

$$S = k_B \int d\vec{r} \{ -p(\vec{r}, t) \ln p(\vec{r}, t) - c_v \ln c_v - (1 - p(r, t) - c_v) \ln (1 - p(r, t) - c_v) \}, \quad (58)$$

where k_B is the Boltzmann's constant. By introducing Eq. (58) into Eq. (57), the chemical potential can be represented by,

$$\mu = k_B T \ln \{ p(\vec{r}, t) / (1 - p(r, t) - c_v) \}. \quad (59)$$

By substituting Eq. (59) into Eq. (56), Eq. (55) is consistent with Eq. (49) if and only if the Onsager coefficient is given by,

$$L = \frac{D_B}{k_B} p(\vec{r}, t) (1 - p(r, t) - c_v). \quad (60)$$

In general, the density of the inert particles depends on the position; the volume fraction of inert particles can be represented by $c_v(\vec{r}, t)$. The entropy given by Eq. (58) is generalized by substituting c_v by $c_v(\vec{r}, t)$. By the substitution, the chemical potential can be expressed by,

$$\mu = k_B T \ln \{p(\vec{r}, t) / [1 - p(r, t) - c_v(\vec{r}, t)]\}. \quad (61)$$

If the Onsager coefficient is defined in the same way as that defined for the homogeneous density of the inert particles, it can be written as

$$L = \frac{D_B}{k_B} p(\vec{r}, t) [1 - p(r, t) - c_v(\vec{r}, t)]. \quad (62)$$

By including the Onsager coefficient into Eq. (56) with the chemical potential, Eq. (61), Eq. (55) leads to

$$\frac{\partial}{\partial t} p(r, t) = \vec{\nabla} \cdot D_B \left[(1 - c_v(\vec{r}, t)) \vec{\nabla} p(r, t) + p(r, t) \vec{\nabla} c_v(\vec{r}, t) \right] - k(r) p(r, t), \quad (63)$$

where the perfectly reflecting boundary condition at R is imposed to express that the reactants cannot penetrate each other. Equation (63) includes the term which can be interpreted as the spurious drift. The drift is induced by the spurious potential defined by,

$$U = -k_B T \ln [1 - c_v(r, t)], \quad (64)$$

and Eq. (63) can be rewritten in terms of the potential as

$$\frac{\partial}{\partial t} p(r, t) = \vec{\nabla} \cdot D_B (1 - c_v(\vec{r}, t)) \left[\vec{\nabla} p(r, t) + p(r, t) \frac{\vec{\nabla} U}{k_B T} \right] - k(r) p(r, t). \quad (65)$$

As an illustrative example of inhomogeneous distribution of the inert particles, we consider a steady state where the inert particles are dilute in the vicinity of the immobile reactant. The degree of hindrance increases by increasing the distance from the immobile reactant. The simplest density profile of the inert particles may be given by, $c_v(r, t) = 1 - (R/r)$. In the

absence of the reaction term, Eq. (65) becomes formally equivalent to the diffusion equation for the fractal systems whose fractal dimension and spectral dimension are given by $d_f = 4$ and $d_s = 8/3$, respectively. [44–46] The mean square distance between a pair exhibits subdiffusion, $\langle r^2(t) \rangle \sim t^{2/3}$. [44–46] The subdiffusion kinetics is induced by the excluded volume interactions among the mobile reactant and the inert particles under the density gradient of the inert particles. Unfortunately, in the presence of the boundary conditions and the reaction terms, Eq. (65) is hard to solve analytically. In the following, we obtain the escape probability through the equation for the survival probability derived from that for the pair distribution $p(r, t)$.

VII. ESCAPE PROBABILITY UNDER THE NON-UNIFORM DENSITY OF THE INERT PARTICLES

We consider the case that the density of the inert particles is in the steady state 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. (65) by introducing the adjoint operator as, [47–49]

$$\frac{\partial}{\partial t} S(r, t) = \vec{\nabla} \cdot D_B(1 - c_v(r)) \vec{\nabla} S(r, t) - D_B \left[\vec{\nabla} c_v(r) \right] \cdot \vec{\nabla} S(r, t) - k(r) S(r, t), \quad (66)$$

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

$$\left. \frac{\partial}{\partial r} S(r, t) \right|_{r=R} = 0. \quad (67)$$

When the reaction takes place at the reaction radius, R , with the intrinsic rate, k_0 , [50] the equation for the escape probability defined by $\varphi(r) = \lim_{t \rightarrow \infty} S(r, t)$ in d -dimension is expressed as,

$$\frac{1}{r^{d-1}} \exp\left(\frac{U}{k_B T}\right) \frac{\partial}{\partial r} D_B(1 - c_v(r)) r^{d-1} \exp\left(-\frac{U}{k_B T}\right) \frac{\partial}{\partial r} \varphi(r) = 0, \quad (68)$$

using the potential defined by Eq. (64). The boundary conditions are given by $\lim_{r \rightarrow \infty} \varphi(r) = 1$ and

$$S_d D_B (1 - c_v(R)) \left. \frac{\partial}{\partial r} \varphi(r) \right|_{r=R} = k_0 \varphi(R), \quad (69)$$

where the surface area of the d -dimensional sphere is given by $S_d = d\pi^{d/2}/\Gamma((d/2) + 1)$. S_d reproduces $S_2 = 2\pi R$ and $S_3 = 4\pi R^2$. The solution of Eq. (68) subject to the above mentioned boundary conditions is obtained as,

$$\varphi(r) = \frac{\int_R^r dr_1 \frac{1}{D_B (1 - c_v(r_1))^2 r_1^{d-1}} + \frac{S_d}{k_0} \frac{1}{(1 - c_v(R)) R^{d-1}}}{\int_R^\infty dr_1 \frac{1}{D_B (1 - c_v(r_1))^2 r_1^{d-1}} + \frac{S_d}{k_0} \frac{1}{(1 - c_v(R)) R^{d-1}}}. \quad (70)$$

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

$$\varphi(r) = \int_R^r dr_1 \frac{1}{(1 - c_v(r_1))^2 r_1^{d-1}} / \int_R^\infty dr_1 \frac{1}{(1 - c_v(r_1))^2 r_1^{d-1}}. \quad (71)$$

According to Eq. (71), the escape probability is independent of the density of the inert particles when the density is homogeneous. The result is consistent with that obtained in the lattice system in Sec. IV. While, 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.

VIII. 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 taken into account

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 immediate jump of the diffusing particle back to the previously occupied empty site. We have shown that the Bardeen-Herring back correlation competes with reaction in deriving a reaction-diffusion equation. In the reaction-diffusion equation, the transition operator describing random walks is influenced by the reaction strength while leaving the reaction term unaltered. The reaction-diffusion equation is very complicated and cannot be solved analytically. By ignoring the interference between 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 by taking into account the Bardeen-Herring back correlation. The influence of the excluded volume interactions is taken into account solely by the tracer-diffusion constant. By comparison of the theoretical results with the results of numerical simulations the interference between reaction and the Bardeen-Herring back correlation is shown to be small. The tracer-diffusion constant decreases by increasing the concentration of the inert particles since the diffusive motion of reactive species is hindered by the presence of the inert particles. Site blocking effects slow the decay of the survival probability of a geminate pair in contrast to the acceleration of the decay found for the target problem under the presence of the excluded volume interactions among reactants. [22, 23]

Recently, the reaction in microfluid is investigated by the Monte-Carlo simulation. [36] 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 self-diffusion coefficient of a tagged particle in a sea of inert particles. [36] We have shown that the substitution is an approximation where the interference between reaction and the Bardeen-Herring back correlation is ignored. Although the slightly different expression of the self-diffusion coefficient is used in their equation and they study the mean first passage time instead of the survival probability, the use of the tracer-diffusion constant in the reaction-diffusion

equation of a geminate pair can be a good and a practical approximation to take into account the excluded volume interactions among the inert particles and the reactant.

The above conclusions are obtained by assuming the homogeneous distribution of the inert particles. We also formulate 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. Incidentally, the positive density gradient of the inert particles induces subdiffusion for the particular case we have studied. Although we need further investigation for the kinetics of the survival probability in the presence of the density gradient of the inert particles, we show by the escape probability that the crowding promotes reactions when the density of the inert particles increases by increasing the distance from the location of the immobile reactant.

Appendix A: Diffusion kernel

In order to obtain $F_c(\vec{n}, \vec{m}, t)$ we need to solve an equation for

$$G_{\vec{n}, \vec{b}_r}(\vec{m}, \vec{m} + \vec{r}, s) = G(\vec{n} \bullet, \vec{n} + \vec{b}_r \circ | \vec{m} \bullet, \vec{m} + \vec{r} \circ, s). \quad (\text{A1})$$

By applying the operator identity,

$$\frac{1}{s - \tilde{L}_{\text{rw0}} - \tilde{L}_{\text{rc}}} = \frac{1}{s} \left(1 + \frac{1}{s - \tilde{L}_{\text{rw0}} - \tilde{L}_{\text{rc}}} (\tilde{L}_{\text{rw0}} + \tilde{L}_{\text{rc}}) \right), \quad (\text{A2})$$

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

$$\begin{aligned} sG_{\vec{n}, \vec{b}_r}(\vec{m}, \vec{r}, s) - \delta_{\vec{r}, \vec{b}_r} \delta_{\vec{n}, \vec{m}} &= \sum_{\alpha} \left[\gamma_w G_{\vec{n}, \vec{b}_r}(\vec{m}, \vec{r} + \vec{b}_{\alpha}, s) + \gamma_B(1 - c) G_{\vec{n}, \vec{b}_r}(\vec{m} - \vec{b}_{\alpha}, \vec{r} + \vec{b}_{\alpha}, s) \right. \\ &\quad \left. - \gamma_t G_{\vec{n}, \vec{b}_r}(\vec{m}, \vec{r}, s) \right] - \delta_{\vec{r}, \vec{0}} \sum_{\alpha} \left[\gamma_w G_{\vec{n}, \vec{b}_r}(\vec{m}, \vec{b}_{\alpha}, s) + \gamma_B(1 - c) G_{\vec{n}, \vec{b}_r}(\vec{m} - \vec{b}_{\alpha}, \vec{b}_{\alpha}, s) \right] \\ &+ \sum_{\alpha} \delta_{\vec{r}, \vec{b}_{\alpha}} \left[\gamma_{BC} G_{\vec{n}, \vec{b}_r}(\vec{m} + \vec{b}_{\alpha}, -\vec{b}_{\alpha}, s) + (\gamma_t - \gamma_{BC}) G_{\vec{n}, \vec{b}_r}(\vec{m}, \vec{b}_{\alpha}, s) \right] - k(\vec{m}) G_{\vec{n}, \vec{b}_r}(\vec{m}, \vec{r}, s) \end{aligned} \quad (\text{A3})$$

where

$$\gamma_t = \gamma_w + \gamma_B(1 - c). \quad (\text{A4})$$

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

Appendix B: An equation for $G_{\vec{b}_r}(\vec{\ell}, \vec{r}, s)$

If we ignore $k(\vec{m})$ in the above equation, the translational invariance is satisfied. The equation for $G_{\vec{b}_r}(\vec{\ell}, \vec{r}, s)$ is given by,

$$\begin{aligned} sG_{\vec{b}_r}(\vec{\ell}, \vec{r}, s) - \delta_{\vec{r}, \vec{b}_r} \delta_{\vec{\ell}, \vec{0}} &= \sum_{\alpha} \left[\gamma_w G_{\vec{b}_r}(\vec{\ell}, \vec{r} + \vec{b}_{\alpha}, s) + \gamma_B(1 - c) G_{\vec{b}_r}(\vec{\ell} - \vec{b}_{\alpha}, \vec{r} + \vec{b}_{\alpha}, s) \right. \\ &\quad \left. - \gamma_t G_{\vec{b}_r}(\vec{\ell}, \vec{r}, s) \right] - \delta_{\vec{r}, \vec{0}} \sum_{\alpha} \left[\gamma_w G_{\vec{b}_r}(\vec{\ell}, \vec{b}_{\alpha}, s) + \gamma_B(1 - c) G_{\vec{b}_r}(\vec{\ell} - \vec{b}_{\alpha}, \vec{b}_{\alpha}, s) \right] \\ &\quad + \sum_{\alpha} \delta_{\vec{r}, \vec{b}_{\alpha}} \left[\gamma_B c G_{\vec{b}_r}(\vec{\ell} + \vec{b}_{\alpha}, -\vec{b}_{\alpha}, s) + (\gamma_t - \gamma_B c) G_{\vec{b}_r}(\vec{\ell}, \vec{b}_{\alpha}, s) \right]. \quad (\text{B1}) \end{aligned}$$

By applying Fourier transformation,

$$g_{\vec{b}_r}(\vec{k}, \vec{h}, s) = \sum_{\vec{\ell}} \sum_{\vec{r}} \exp \left[i(\vec{k} \cdot \vec{\ell} + \vec{h} \cdot \vec{r}) \right] G_{\vec{b}_r}(\vec{\ell}, \vec{r}, s) \quad (\text{B2})$$

$$\tilde{G}_{\vec{b}_r}(\vec{k}, \vec{r}, s) = \sum_{\vec{\ell}} \exp \left[i\vec{k} \cdot \vec{\ell} \right] G_{\vec{b}_r}(\vec{\ell}, \vec{r}, s) \quad (\text{B3})$$

we obtain,

$$\begin{aligned} sg_{\vec{b}_r}(\vec{k}, \vec{h}, s) &= \exp(i\vec{h} \cdot \vec{b}_r) + \sum_{\alpha} \left[\omega_t(\vec{b}_{\alpha}) \exp(-i\vec{h} \cdot \vec{b}_{\alpha}) - \gamma_t \right] g_{\vec{b}_r}(\vec{k}, \vec{h}, s) \\ &\quad + \sum_{\alpha} \left[\exp(-i\vec{h} \cdot \vec{b}_{\alpha}) \omega_B(\vec{b}_{\alpha}) c + \gamma_s \exp(i\vec{h} \cdot \vec{b}_{\alpha}) - \omega_t(\vec{b}_{\alpha}) \right] \tilde{G}_{\vec{b}_r}(\vec{k}, \vec{b}_{\alpha}, s), \quad (\text{B4}) \end{aligned}$$

where we define,

$$\gamma_s = \gamma_t - \gamma_B c, \quad (\text{B5})$$

$$\omega_B(\vec{r}) = \gamma_B \exp(i\vec{k} \cdot \vec{r}), \text{ and } \omega_t(\vec{r}) = \gamma_w + \gamma_B(1 - c) \exp(i\vec{k} \cdot \vec{r}). \quad (\text{B6})$$

It is convenient to introduce the function,

$$Q(\vec{k}, \vec{r}, s) = \frac{1}{(2\pi)^d} \int \cdots \int_{-\pi}^{\pi} d^d \vec{h} \frac{\exp(-i\vec{h} \cdot \vec{r})}{s + \Gamma_t - \Omega_t(\vec{k}, \vec{h})}, \quad (\text{B7})$$

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

$$\Omega_t(\vec{k}, \vec{h}) = 2d \left[\gamma_w \lambda(\vec{h}) + \gamma_B (1 - c) \lambda(\vec{k} - \vec{h}) \right]. \quad (\text{B8})$$

A closed set of equations can be obtained from,

$$\begin{aligned} \tilde{G}_{\vec{b}_r}(\vec{k}, \vec{b}_q, s) = Q(\vec{k}, \vec{b}_q - \vec{b}_r, s) + \sum_{\alpha} \left[\gamma_s Q(\vec{k}, \vec{b}_q - \vec{b}_{\alpha}, s) + \omega_B(\vec{b}_{\alpha}) c Q(\vec{k}, \vec{b}_q + \vec{b}_{\alpha}, s) - \right. \\ \left. \omega_t(\vec{b}_{\alpha}) Q(\vec{k}, \vec{b}_q, s) \right] \tilde{G}_{\vec{b}_r}(\vec{k}, \vec{b}_{\alpha}, s). \end{aligned} \quad (\text{B9})$$

The solution is independent of the position of the reactive sink in this approximation. By introducing the solution of Eq. (B9) into Eq. (40) and using Eq. (38) and Eq. (39) the survival probability is obtained after numerical inverse Laplace transformation and inverse Fourier transformation.

Appendix C: An equation for $G_{\vec{b}_r}^{(a)}(\vec{r}, s)$

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

$$\frac{1}{s - \tilde{L}_{\text{rw}0}} = \frac{1}{s} \left(1 + \frac{1}{s - \tilde{L}_{\text{rw}0}} \tilde{L}_{\text{rw}0} \right), \quad (\text{C1})$$

as [18–20]

$$\begin{aligned} s G_{\vec{b}_r}^{(a)}(\vec{r}, s) - \delta_{\vec{r}, \vec{b}_r} = \sum_{\alpha} \gamma_t \left[G_{\vec{b}_r}^{(a)}(\vec{r} + \vec{b}_{\alpha}, s) - G_{\vec{b}_r}^{(a)}(\vec{r}, s) \right] - \delta_{\vec{r}, \vec{0}} \sum_{\alpha} \gamma_t G_{\vec{b}_r}^{(a)}(\vec{b}_{\alpha}, s) + \\ \sum_{\alpha} \delta_{\vec{r}, \vec{b}_{\alpha}} \left[\gamma_{BC} G_{\vec{b}_r}^{(a)}(-\vec{b}_{\alpha}, s) + (\gamma_t - \gamma_{BC}) G_{\vec{b}_r}^{(a)}(\vec{b}_{\alpha}, s) \right]. \end{aligned} \quad (\text{C2})$$

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

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