Reaction under vacancy-assisted diffusion at high quencher concentration

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The theory of diffusion-mediated reactions is already established for the target problem in the dilute limit, where the immobile target is surrounded by many quenchers. For lattice random walks in the crowded situation, each quencher is surrounded by other quenchers differently. As a result, each quencher migrates differently in the presence of site blocking effects. However, in the conventional theory, such difference is ignored and quenchers are assumed to move independently of each other. In this paper, theory of diffusion-mediated reactions of target problem is developed by taking into account the site blocking effects for quencher migration and the difference in the configuration of quenchers around each quencher. Our result interpolates between those in high and low limits of quencher concentrations and is a lower bound of the survival probability. In the static limit, the exact result is reproduced for a localized sink. In the presence of diffusion, the approximation is better when intrinsic reaction rates are low.

I. INTRODUCTION

The theory of diffusion-mediated reactions is already established for the target problem in the dilute limit [1–5]. Consider reaction between excited probe A^* and quencher B, which deactivates excited probe. In ordinary experimental conditions, A^* is minority species and B is majority species. The case in which minority species are immobile and majority species are mobile is, in general, called the target problem. The opposite case is called the trapping problem. In this paper, we consider the target problem. We are interested in the decay of fraction of A^* after pulsed excitation or the fraction of A^* when A is continuously excited. In the dilute limit, movement of each quencher can be regarded as an independent event. When the target is surrounded by N quenchers on the lattice with M sites the survival probability of the target at time t denoted by $P_N(t)$ is expressed in terms of the pair survival probability at time t of a quencher starting from $\vec{r}_\ell$, $f(\vec{r}_\ell, t)$, by [4]

$$P_N(t) = \left(\sum_{\ell=1}^{M} f(\vec{r}_\ell, t) \right)^N = \left(1 - \frac{1}{M} \sum_{\ell=1}^{M} [1 - f(\vec{r}_\ell, t)] \right)^N$$

$$\simeq \exp\left(-c \sum_{\ell=1}^{\infty} [1 - f(\vec{r}_\ell, t)] \right), \quad (1)$$

where the infinite limit of all lattice points, M, is taken and the concentration is given by, $c = \lim_{M \to \infty} N/M$ in the thermodynamic limit. The theory is applicable even under the long-range reactions and the presence of electrostatic potential among reactants, which can be taken into account in $f(\vec{r}_\ell, t)$ as long as quencher concentration is dilute.

In the conventional theory, the decay of the survival probability by bulk reactions has been formulated in terms of the pair probability of the target and a quencher by ignoring the

excluded volume interactions among quenchers. However, in the crowded situation, each quencher is surrounded by other quenchers differently. As a result, each quencher migrates differently in the presence of site blocking effects. In the conventional theory, such difference is ignored and quenchers are assumed to move independently of each other. In this paper, we take into account the site blocking effects for quencher migration and the difference in the configuration of quenchers around each quencher by applying the tracer diffusion theory of Nakazato-Kitahara [6]. Excluded volume interactions are taken into account by prohibiting double occupancy of quenchers in site blocking effects. Quenchers can jump only to the empty neighbor sites. By noticing the success of the interpolating formula of Nakazato-Kitahara on the tracer diffusion coefficient between low and high concentrations of diffusing particles, we apply it to the target reaction on a lattice. Though site blocking is an aspect of many body interactions, rigorous results can be obtained by this method. In the continuous space, excluded volume interactions can be taken into account by introducing short range repulsive potentials and applying decoupling approximation of density correlations, as shown by Kuzovkov *et al.* [7]

II. STATIC QUENCHING WITHOUT DOUBLE OCCUPANCY

The simplest results that prohibit double occupancy of the same site are obtained in the absence of diffusion. Although the results are known, we rederive them to illustrate our method.

We consider the lattice with M sites. There are N quenchers on the lattice. We indicate the configuration of quenchers by the set of vectors denoting the lattice sites occupied by quenchers, $(\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_N)$. If quenchers are initially randomly distributed, the probability of taking an initial configuration $(\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_N)$ is given by,

$$P(\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_N; 0) = 1/(_M C_N). \quad (2)$$

The survival probability is obtained by applying the Cauchy's integral theorem [8],

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$$P_N(t) = \frac{1}{2\pi i} \int dx \frac{1}{x^{N+1}} \frac{1}{_M C_N} \prod_{\ell=1}^{M} \{1 + x \exp[-k(\vec{r}_\ell)t]\}, \quad (3)$$

where the path of integration encircles the origin on the complex plane and the right hand side of Eq. (3) represents the joint probability of independent quenching events at time t from all possible quencher configurations. Equation (3) can be rewritten as,

$$P_N(t) = \frac{1}{2\pi i} \int dx \frac{1}{x^{N+1}} \frac{1}{_M C_N} \exp\left[\sum_{\ell=1}^{M} \ln\{1 + x \exp[-k(\vec{r}_\ell)t]\}\right]. \quad (4)$$

In the thermodynamic limit, Eq. (4) is simplified by introducing Stirling formula $n! = \sqrt{2\pi n} \exp(-n) n^n$ and applying the steepest descent method,

$$P_N(t) = \frac{1}{2\pi i} \int dx \frac{(1+x)^M}{x^{N+1}} \frac{1}{_M C_N}$$

$$\times \exp\left[\sum_{\ell=1}^{M} \ln\left(1 + \frac{x}{1+x}\{\exp[-k(\vec{r}_\ell)t] - 1\}\right)\right] \quad (5)$$

$$= \exp\left[\sum_{\ell=1}^{M} \ln\{1 + c\{\exp[-k(\vec{r}_\ell)t] - 1\}\}\right], \quad (6)$$

where $c = N/M$ is the concentration. Equation (6) is the known expression for the static quenching obtained by Allinger and Blumen (AB) using a different method. [9] Our method is not simple but shows that Eq. (6) is correct in the thermodynamic limit for any concentration at all times and thus confirms the conclusion derived from the AB method, where the occupancy probability at each lattice site is assumed to be c instead of random occupancy of quencher sites among available lattice sites. In the AB method, the number of quenchers for a finite lattice with M sites is not necessarily equal to N since the occupancy probability of each lattice site is given for each realization of quencher configurations. For $c = 1$ we find the familiar result of,

$$P_N(t) = \exp\left(-\sum_{\ell=1}^{M} k(\vec{r}_\ell)t\right), \quad (7)$$

and its Laplace transform is given by,

$$\hat{P}_N(s) = 1/\left(s + \sum_{\ell=1}^{M} k(\vec{r}_\ell)t\right). \quad (8)$$

In the opposite limit, $c \sim 0$, Eq. (6) reduces to the well-known result [3,9]

$$P_N(t) \simeq \exp\left[-\sum_{\ell=1}^{M} c\{1 - \exp[-k(\vec{r}_\ell)t]\}\right]. \quad (9)$$

Equation (9) is the static limit of Eq. (1).

When reaction takes place only at a target site $\vec{r}_R$, $k(\vec{r}_\ell) = k_0 \delta_{\vec{r}_\ell, \vec{r}_R}$, the survival probability, Eq. (6), is simplified to,

$$P_N(t) = 1 - c + c \exp(-k_0 t), \quad (10)$$

and the Laplace transform, $\hat{P}_N(s) = \int_0^\infty dt \exp(-st) P_N(t)$, is expressed as,

$$\hat{P}_N(s) = \frac{s + (1-c)k_0}{s(s+k_0)}. \quad (11)$$

These trivial results will be used to check the results obtained under the presence of correlated diffusion. In this model, if a target site is not occupied by a quencher, the reaction never occurs there. However, in the presence of diffusion, even if a target site is not initially occupied by a quencher, a quencher may come to it by diffusion and react with it. In other words, the survival probability obtained under the condition of static quenching is always higher than that in the presence of diffusion.

Before closing this section, we comment on the natural decay. When the natural decay of the target with the time constant τ_0 is present, we multiply $P_N(t)$ by $\exp(-t/\tau_0)$ and s changes to $s + 1/\tau_0$ in $\hat{P}_N(s)$. The natural decay of the quencher with the time constant τ_{0q} is taken into account by replacing $k(\vec{r}_\ell)$ by $k(\vec{r}_\ell) + 1/\tau_{0q}$. The natural decay can be taken into account even under the presence of correlated diffusion in the same way.

III. QUENCHING UNDER DIFFUSION WITH EXCLUDED VOLUME INTERACTIONS

Quenchers perform random walk on a lattice under the condition that each site cannot be occupied by more than one quencher at the same time. Quenchers can jump only to the empty neighbor sites. The movement of quencher is influenced by the position of other quenchers through the site blocking effects. As a result, quencher diffusion is highly correlated at high concentrations. In addition to correlated diffusion, reaction takes place depending on the distance between the quencher and the target. Since the target is immobile, the reaction rate depends only on the configuration of quenchers.

As before, we consider the lattice with M quencher sites. An excited target is located at the origin. There are N quenchers on the lattice. If quenchers are initially randomly distributed over available sites, the probability of taking an initial configuration $(\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_N)$ is given by Eq. (2). The survival probability is given by,

$$P_N(t) = \sum_{\{\vec{r}_i\}} P(\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_N; t), \quad (12)$$

where the summation should be taken over all possible quencher configurations.

The self-diffusion of correlated random walk is studied by Nakazato and Kitahara in the absence of reaction [6]. Site blocking effects on the diffusion of tagged particle is calculated [6,10,11]. Following them, we introduce ket vectors for all accessible sites of quenchers. The ket vector $|\vec{r}, \bullet\rangle$ denotes the occupation of site $\vec{r}$ by a quencher particle, and $|\vec{r}, \phi\rangle$ represents that site $\vec{r}$ is an empty site. The probability of finding a configuration $(\vec{r}_1, \cdots \vec{r}_N)$, at time t averaged over all

possible initial configurations of random occupation is written as,

$$P(\vec{r}_1, \cdots, \vec{r}_N; t) = e^{-t/\tau_0} \left(\prod_{\ell=1}^{N} \langle \vec{r}_\ell, \bullet| \right)$$
$$\times \left(\prod_{k=N+1}^{M} \langle \vec{r}_k, \phi| \right) e^{Ht} \sum_{\{i\}} \frac{1}{{}_M C_N} \left(\prod_{\ell=1}^{N} |\vec{r}_\ell, \bullet\rangle \right)$$
$$\times \left(\prod_{k=N+1}^{M} |\vec{r}_k, \phi\rangle \right), \tag{13}$$

where the sum is taken over all possible configurations of N occupied sites on the M sites. H is given by $H = H_w + H_{rc}$, where H_w describes the diffusion of quenchers [6,10,11]

$$H_w = \sum_{\langle n,m \rangle} \Gamma/(2d)(|\vec{r}_n, \bullet\rangle\langle\vec{r}_n, \phi| \cdot |\vec{r}_m, \phi\rangle\langle\vec{r}_m, \bullet| - |\vec{r}_n, \bullet\rangle$$
$$\times \langle\vec{r}_n, \bullet| \cdot |\vec{r}_m, \phi\rangle\langle\vec{r}_m, \phi|), \tag{14}$$

where Γ is the jump frequency of quencher and the sum is taken over all nearest-neighbor pairs of accessible lattice sites by quenchers. Transition is possible from the state $|\vec{r}_m, \bullet\rangle|\vec{r}_n, \phi\rangle$ to the state $|\vec{r}_n, \bullet\rangle|\vec{r}_m, \phi\rangle$, which indicates that the site n must be empty to accept a quencher from an occupied neighboring site. Similarly, if the site n is occupied by a quencher, inverse transition is possible for the state, $|\vec{r}_n, \bullet\rangle|\vec{r}_m, \phi\rangle$, if at least one neighboring site is vacant. H_{rc} describes the reaction from an occupied site $\vec{r}_n$ with the rate $k(\vec{r}_n)$ [12–14],

$$H_{rc} = -\sum_{n=1}^{M} k(\vec{r}_n)|\vec{r}_n, \bullet\rangle\langle\vec{r}_n, \bullet|. \tag{15}$$

In order to calculate the survival probability, Eq. (12), from the configuration probability, it is convenient to introduce the generating function, [15]

$$G(x,t) = \sum_{N=0}^{M} \sum_{\{\vec{r}_i\}} x^N P(\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_N; t). \tag{16}$$

The survival probability is obtained from [15],

$$P_N(t) = e^{-t/\tau_0} \frac{1}{2\pi i} \int dx \frac{1}{x^{N+1}} G(x,t), \tag{17}$$

where the generating function is rewritten as [6],

$$G(x,t) = \frac{1}{{}_M C_N} \prod_{\ell=1}^{M} (\langle\vec{r}_\ell, \phi| + \sqrt{x}\langle\vec{r}_\ell, \bullet|) e^{Ht} \prod_{k=1}^{M} (|\vec{r}_k, \phi\rangle + \sqrt{x}|\vec{r}_k, \bullet\rangle). \tag{18}$$

Equation (17) with Eq. (18) generalizes Eq. (3) by including the effect of diffusion with excluded volume interactions.

In the thermodynamic limit in which M tends to infinity with the fraction of quenchers being fixed, $c = N/M$, we can apply a saddle point method to Eq. (17) as we have done to obtain Eq. (6). Originally, the method is introduced by Nakazato and Kitahara for the calculation of tracer diffusion constant of correlated random walk [6]. The same result as

theirs can be obtained by a different method [16]. The results of Nakazato and Kitahara is also confirmed by numerical simulation in two- and three-dimensional systems [10,11,17]. The method is based on the fact that the number of diffusing quenchers is conserved. In our case, the number of quenchers is conserved for the quencher configurations which survive reaction, and the correlated random walks are performed by exactly N quenchers. By applying a saddle point method, Eq. (17) becomes,

$$P_N(t) = e^{-t/\tau_0} \left(\prod_{\ell=1}^{M} \langle\vec{r}_\ell, \phi| \right) \exp(\widetilde{H}t) \left(\prod_{\ell=1}^{M} |\vec{r}_\ell, \phi\rangle \right), \tag{19}$$

where $\widetilde{H} = \exp(-\theta^* S) H \exp(\theta^* S)$, $S \equiv \sum_{\ell=1}^{M}(|\vec{r}_\ell, \bullet\rangle\langle\vec{r}_\ell, \phi| - |\vec{r}_\ell, \phi\rangle\langle\vec{r}_\ell, \bullet|)$, and $x = \tan^2\theta$, with $\tan\theta^* = \sqrt{c/(1-c)}$. $\widetilde{H}$ is obtained as $\widetilde{H} = \widetilde{H}_0 + \widetilde{H}_1$, where,

$$\widetilde{H}_0 = H_w - \sum_{n=1}^{M} k(\vec{r}_n)[(1-c)|\vec{r}_n, \bullet\rangle\langle\vec{r}_n, \bullet| + c|\vec{r}_n, \phi\rangle\langle\vec{r}_n, \phi|] \tag{20}$$

and

$$\widetilde{H}_1 = -\sum_{n=1}^{M} k(\vec{r}_n)\sqrt{c(1-c)}(|\vec{r}_n, \bullet\rangle\langle\vec{r}_n, \phi| + |\vec{r}_n, \phi\rangle\langle\vec{r}_n, \bullet|). \tag{21}$$

By making time differentiation of Eq. (19), we obtain the time evolution equation for the survival probability,

$$\frac{\partial}{\partial t} P_N(t) = -\frac{1}{\tau_0} P_N(t) - c\kappa P_N(t) - \sqrt{c(1-c)} \sum_{j=1}^{M} k(\vec{r}_j) q(\vec{r}_j, t), \tag{22}$$

where the sum of reaction rates is defined as,

$$\kappa = \sum_{j=1}^{M} k(\vec{r}_j). \tag{23}$$

$q(\vec{r}_j, t)$ is given by,

$$q(\vec{r}_j, t) \equiv e^{-t/\tau_0} \left(\prod_{\ell=1}^{M'} \langle\vec{r}_\ell, \phi|\langle\vec{r}_j, \bullet| \right) \exp(\widetilde{H}t) \left(\prod_{\ell=1}^{M} |\vec{r}_\ell, \phi\rangle \right), \tag{24}$$

where M' denotes that the site $\vec{r}_j$ is excluded in the product. The initial condition of Eq. (22) is $P(0) = 1$. After Laplace transformation, Eq. (22) leads to,

$$\hat{P}_N(s) = \frac{1}{s + 1/\tau_0 + \sum_{j=1}^{M} ck(\vec{r}_j)}$$
$$\times \left[1 - \sqrt{c(1-c)} \sum_{j=1}^{M} k(\vec{r}_j)\hat{q}(\vec{r}_j, s) \right], \tag{25}$$

where $\hat{q}(\vec{r}_j, s) = \int_0^\infty dt \exp(-st)q(\vec{r}_j, t)$.

$q(\vec{r}_j, t)$ is calculated by the perturbation expansion of $\exp(\tilde{H}t)$. $\tilde{H}_1$ is taken as the perturbation term. $\tilde{H}_0$ conserves the number of quenchers. On the other hand, $\tilde{H}_1$ defined by Eq. (21) changes the number of quenchers by the amount of one and only the odd powers of $\tilde{H}_1$ contribute in the perturbation expansion. The expansion parameter is proportional to $c(1-c)$ instead of $\sqrt{c(1-c)}$ given in the definition of $\tilde{H}_1$.

A simple expression is obtained by the Páde approximation,

$$\hat{q}(\vec{r}_j, s) = -\frac{\sum_{\ell=1}^{M} \hat{G}(\vec{r}_j, \vec{r}_\ell, s) k(\vec{r}_\ell) \sqrt{c(1-c)} \dfrac{1}{s + 1/\tau_0 + c\kappa}}{1 - c(1-c) \sum_{v=1}^{M} \sum_{w=1}^{M} \dfrac{k(\vec{r}_v) \hat{G}(\vec{r}_v, \vec{r}_w, s) k(\vec{r}_w)}{s + 1/\tau_0 + c\kappa}},$$

(26)

where κ is defined by Eq. (23) and $\hat{G}(\vec{r}_i, \vec{r}_j, s)$ is the Laplace transform of,

$$G(\vec{r}_i, \vec{r}_j, t) \equiv e^{-t/\tau_0} \left(\prod_{\ell=1}^{M'} \langle \vec{r}_\ell, \phi | \langle \vec{r}_i, \bullet | \right)$$
$$\times \exp(\tilde{H}_0 t) \left(\prod_{\ell=1}^{M'} |\vec{r}_\ell, \phi\rangle |\vec{r}_j, \bullet\rangle \right).$$

(27)

In the Páde approximation, higher-order Green's functions such as $\hat{G}(\vec{r}_1, \vec{r}_2, \vec{r}_3 | \vec{r}_4, \vec{r}_5, \vec{r}_6, s)$, defined similarly to Eq. (27), are ignored. As stated before, odd powers of $\tilde{H}_1$ should be left in the perturbation expansion. Since $\tilde{H}_1$ is a reaction term as shown in Eq. (21), the results gives minus contribution to the perturbation expansion. If we denote the complete solution including higher-order Green's functions by $q_T(\vec{r}_j, s)$, the approximate solution $q(\vec{r}_j, s)$ obeys, $q(\vec{r}_j, s) \geq q_T(\vec{r}_j, s) > 0$. By combining this inequality with Eq. (25), we find that the approximate expression is a lower bound of $P_N(t)$.

By making time differentiation of Eq. (27), we obtain,

$$\frac{\partial}{\partial t} G(\vec{r}_i, \vec{r}_j, t) = -\frac{1}{\tau_0} G(\vec{r}_i, \vec{r}_j, t) + \mathcal{L} G(\vec{r}_i, \vec{r}_j, t)$$
$$- (1 - 2c) k(\vec{r}_i) G(\vec{r}_i, \vec{r}_j, t) - c\kappa G(\vec{r}_i, \vec{r}_j, t),$$

(28)

where the initial condition is given by $G(\vec{r}_i, \vec{r}_j, 0) = \delta_{i,j}$. $\mathcal{L}$ represents the operator describing hopping transitions,

$$\mathcal{L} G(\vec{r}_i, \vec{r}_j, t) = \sum_{k=1}^{2d} \Gamma/(2d) [G(\vec{b}_k + \vec{r}_i, \vec{r}_j, t) - G(\vec{r}_i, \vec{r}_j, t)],$$

(29)

where d is the dimensionality of hypercubic lattice. $\vec{b}_k + \vec{r}_i$ denotes a nearest neighbor of the site $\vec{r}_i$ and the sum is taken over all nearest-neighbor sites.

By introducing Eq. (26) into Eq. (25) in the Laplace domain, the Laplace transform of the survival probability is expressed as,

$$\hat{P}_N(s) = \frac{1}{s + 1/\tau_0 + c\kappa - c(1-c) \sum_{v=1}^{M} \sum_{w=1}^{M} k(\vec{r}_v) \hat{G}(\vec{r}_v, \vec{r}_w, s) k(\vec{r}_w)}.$$

(30)

We can obtain the survival probability, $P_N(t)$, by introducing the solution of Eq. (28) into Eq. (30) and making the inverse Laplace transformation. The term with $c(1-c)$ represents the effect of correlated diffusion, which vanishes in the dilute limit, $c \to 0$. In the opposite limit of $c \to 1$, the factor $c(1-c)$ again vanishes corresponding to the absence of diffusion since every site is occupied by a quencher. In both limits, the survival probability is given by,

$$P_N(t) = \exp(-t/\tau_0 - c\kappa t).$$

(31)

Equation (31) reproduces Eq. (7) obtained for the static quenching when all sites are occupied by quenchers. In the dilute limit, $c \to 0$, Eq. (31) is also consistent with the known result of static quenching, Eq. (9), when the reaction rate is small. In the intermediate concentration, the survival probability is influenced by $G(\vec{r}_i, \vec{r}_j, t)$ defined by the probability of finding a quencher at position $\vec{r}_i$ at time t when it starts from $\vec{r}_j$ under the prohibition of double occupancy of a site.

IV. LOCALIZED REACTIONS

When reaction takes place only at a target site $\vec{r}_R$, $k(\vec{r}_\ell) = k_0 \delta_{\vec{r}_\ell, \vec{r}_R}$, the Laplace transform of the survival probability is expressed as,

$$\hat{P}_N(s) = \frac{1}{s + 1/\tau_0 + ck_0 - c(1-c)k_0 \hat{G}(\vec{r}_R, \vec{r}_R, s) k_0}. \quad (32)$$

In the absence of diffusion and natural decay, Eqs. (28) and (32) reproduce Eq. (11) derived by assuming the static quenching from the beginning.

In the presence of diffusion, Eq. (32) represents the approximate solution which interpolates between solutions in low and high limits of quencher concentrations. By substituting $k(\vec{r}_\ell) = k_0 \delta_{\vec{r}_\ell, \vec{r}_R}$, the solution of Eq. (28) in the Laplace space can be expressed as

$$\hat{G}(\vec{r}_R, \vec{r}_R, s) = \frac{\hat{G}_0(\vec{r}_R, \vec{r}_R, z)}{1 + (1 - 2c)k_0 \hat{G}_0(\vec{r}_R, \vec{r}_R, z)}. \quad (33)$$

$\hat{G}_0(\vec{r}_i, \vec{r}_j, s)$ is the Laplace transform of the Green's function satisfying,

$$\frac{\partial G_0(\vec{r}_i, \vec{r}_j, t)}{\partial t} = \mathcal{L} G_0(\vec{r}_i, \vec{r}_j, t) + \delta_{\vec{r}_i, \vec{r}_j} \delta(t), \quad (34)$$

where $\mathcal{L}$ represents the operator describing hopping transitions given by Eq. (29). $\hat{G}_0(\vec{r}_R, \vec{r}_R, z)$ in Eq. (33) is given in terms of the Green's function for free random walks, $\hat{G}_0(\vec{r}_R, \vec{r}_R, s)$, but the Laplace variable is modified as a result of the excluded volume interactions among quenchers and expressed in terms of the initial concentration of quenchers and the reaction rate, ck_0,

$$z = s + (1/\tau_0) + ck_0. \qquad (35)$$

When quenchers can migrate on all lattice sites including the target site, the Laplace transform of the Green's function in the absence of site blocking effects and the reaction can be written as

$$\hat{G}_0(\vec{r}_R, \vec{r}_R, s) = \frac{1 - \hat{\psi}(s)}{s} U(s) \qquad (36)$$

in terms of the Lattice Green's function $U(s)$ defined by

$$U(s) = \frac{1}{(2\pi)^d} \int \cdots \int_{-\pi}^{\pi} d^d\vec{k} \frac{1}{1 - \hat{\psi}(s)\widetilde{\lambda}(\vec{k})}, \qquad (37)$$

where $\hat{\psi}(s) = \Gamma/(s + \Gamma)$, and the structure factor is defined by $\widetilde{\lambda}(\vec{k}) \equiv \frac{1}{2d}\Sigma_{j=1}^{2d}\cos(\vec{k}\cdot\vec{b}_j/b)$. b denotes the lattice spacing. Equation (32) can be rewritten as,

$$\hat{P}_N(s) = \cfrac{1}{s + (1/\tau_0) + c\cfrac{1}{1/k_0 + (1-c)/(1/\hat{G}_0 - ck_0)}}, \qquad (38)$$

where we use the abbreviation, $\hat{G}_0 = \hat{G}_0(\vec{r}_R, \vec{r}_R, z)$ and z is defined by Eq. (35). Equation (38) is one of the most important results of this paper.

Equation (38) is simplified in the Smoluchowski limit which is given by $k_0 \to \infty$. In order to obtain the limit, we rewrite Eq. (38) as

$$\hat{P}_N(s) = \cfrac{1}{s + (1/\tau_0) + c\cfrac{1}{1/k_0 + (1-c)U(z)/\{s + (1/\tau_0) + \Gamma + ck_0[1 - U(z)]\}}}. \qquad (39)$$

By introducing the explicit expression of $U(z)$, we find,

$$\lim_{ck_0 \to \infty} U(z) = 1 \quad \text{and} \quad \lim_{ck_0 \to \infty} ck_0[1 - U(z)] = 0, \qquad (40)$$

for any spatial dimension. In the limit of $k_0 \to \infty$ (hopping-controlled limit), Eq. (39) is simplified into

$$\hat{P}_N(s) = \frac{1 - c}{s + 1/\tau_0 + c\Gamma}. \qquad (41)$$

Subsequent inverse Laplace transformation yields a single exponential decay,

$$P_N(t) = (1 - c)\exp[-(1/\tau_0 + c\Gamma)t]. \qquad (42)$$

In the limit of $c = 1$, the reaction site is occupied by a quencher at the initial time and the reaction takes place immediately in the limit of $k_0 \to \infty$. The probability that the reaction site is not occupied by a quencher is given by $1 - c$ and the reaction takes place with the rate $c\Gamma$ which is proportional to both the hopping rate and the quencher concentration. In the hopping-controlled limit, Eq. (42) is a lower bound of the survival probability.

In the Smoluchowski limit of $k_0 \to \infty$ for a localized sink in one-dimensional systems, the survival probability shows nonexponential decay if double occupancy of sites is allowed. The nonexponential decay in the presence of site blocking effects is also predicted by some theories. [18–23] However, our approximate results predict the exponential decay in the limit of $k_0 \to \infty$. Since our derivation involves the

steepest descent approximation of the theory of Nakazato-Kitahara and the Páde approximation of perturbation expansion, there should be a certain limitations on our theory. In the absence of diffusion our theory predicts the exact results of static quenching for localized reactions, regardless of the dimensionality of the systems. However, in the presence of diffusion, it gives only a lower bound of the survival probability. The accuracy of the approximation is worse in the limit of $k_0 \to \infty$ in the presence of diffusion. The accuracy also depends on the dimensionality of the systems. We conjecture that the perturbation term which appeared by applying the theory of Nakazato-Kitahara is large in the limit of $k_0 \to \infty$ in the presence of diffusion in one dimensional systems.

V. SIMPLIFICATION BY ADJOINT EQUATION

When the Green's function is not known, it is convenient to define the pair survival probability,

$$f(\vec{r}_\ell, t) = \sum_{i=1}^{M} G(\vec{r}_i, \vec{r}_\ell, t), \qquad (43)$$

which describes the survival probability of a pair whose initial separation is given by a vector $\vec{r}_\ell$. From the equation for $f(\vec{r}_\ell, t)$, the bulk survival probability can be obtained without knowing the Green's function. As shown below, the equation for $f(\vec{r}_\ell, t)$ is simpler than that for the Green's function. The initial condition is given by,

$$f(\vec{r}_\ell, t=0) = 1. \tag{44}$$

$f(r_\ell, t)$ satisfies the time evolution equation with the diffusional operator $\mathcal{L}^\dagger$ adjoint with $\mathcal{L}$,

$$\frac{\partial}{\partial t} f(\vec{r}_\ell, t) = -\frac{1}{\tau_0} f(\vec{r}_\ell, t) + \mathcal{L}^\dagger f(\vec{r}_\ell, t) - (1 - 2c)k(\vec{r}_\ell)f(\vec{r}_\ell, t)$$
$$- c\kappa f(\vec{r}_\ell, t). \tag{45}$$

This is a generalization of the time evolution equation of the pair survival probability derived by Sano and Tachiya. [24] In the absence of potential, $\mathcal{L}^\dagger$ and $\mathcal{L}$ are equal, $\mathcal{L}^\dagger = \mathcal{L}$. From Eq. (28), we obtain the following relation:

$$\frac{\partial}{\partial t} \sum_{i=1}^M \sum_{j=1}^M G(\vec{r}_i, \vec{r}_j, t)k(\vec{r}_j) = -(1-2c)\sum_{i=1}^M \sum_{j=1}^M k(\vec{r}_i)G(\vec{r}_i, \vec{r}_j, t)k(\vec{r}_j)$$
$$- c\kappa \sum_{i=1}^M \sum_{j=1}^M G(\vec{r}_i, \vec{r}_j, t)k(\vec{r}_j), \tag{46}$$

and after the Laplace transformation it leads to

$$\sum_{i=1}^M \sum_{j=1}^M k(\vec{r}_i)\hat{G}(\vec{r}_i, \vec{r}_j, s)k(\vec{r}_j) = \frac{\kappa - (s+c\kappa)\sum_{i=1}^M \sum_{j=1}^M \hat{G}(\vec{r}_i, \vec{r}_j, s)k(\vec{r}_j)}{1 - 2c}. \tag{47}$$

By substituting Eq. (47), Eq. (30) can be rewritten as,

$$\hat{P}_N(s)$$
$$= \frac{1}{s + 1/\tau_0 + \left(-c^2\kappa + c(1-c)z\sum_{\ell=1}^M k(\vec{r}_\ell)\hat{f}(\vec{r}_\ell, s)\right)/(1-2c)}, \tag{48}$$

where z is given by Eq. (35). This is a generalization of the equation for the survival probability derived by Tachiya, by taking into account the site blocking effects [4]. The expression for the reaction rate is known for localized reactions, which leads to [1,4,5],

$$z\sum_{\ell=1}^M k(\vec{r}_\ell)\hat{f}(\vec{r}_\ell, s) = \frac{1}{(1/k_0) + (1-2c)\hat{G}_0(\vec{r}_R, \vec{r}_R, z)}. \tag{49}$$

By substituting Eq. (49) into Eq. (48), we reproduce Eq. (32) with Eq. (33). For localized reactions, $G(\vec{r}_1, \vec{r}_2, t)$ is known and the adjoint equation may not be needed. However, for long-range reactions, calculation of $\hat{f}(\vec{r}_\ell, s)$ using the equilibrium initial condition can be easier than that of $\hat{G}(\vec{r}_R, \vec{r}_R, s)$ using the initial condition expressed by Kronecker's delta.

VI. STERN-VOLMER LAW

In this section, we study the site blocking effects of diffusion on Stern-Volmer law. A Stern-Volmer plot is obtained from the fluorescence intensity at different quencher concentrations. The relative fluorescence intensity against η_0 defined in the absence of quencher is given by [1,2],

$$\frac{\eta}{\eta_0} = \frac{\int_0^\infty dt P_N(t)}{\int_0^\infty dt P_0(t)} = \frac{1}{\tau_0}\hat{P}_N(s=0). \tag{50}$$

By substituting Eq. (30), η/η_0 is obtained as,

$$\frac{\eta}{\eta_0} = \frac{1}{\tau_0} \frac{1}{1/\tau_0 + c\kappa - c(1-c)\sum_{v=1}^M \sum_{w=1}^M k(\vec{r}_v)\hat{G}(\vec{r}_v, \vec{r}_w, 0)k(\vec{r}_w)}. \tag{51}$$

In the Stern-Volmer plot, $\eta_0/\eta - 1$ is plotted against the concentration, c,

$$\eta_0/\eta - 1 = c\kappa\tau_0 - c(1-c)\tau_0 \sum_{v=1}^M \sum_{w=1}^M k(\vec{r}_v)\hat{G}(\vec{r}_v, \vec{r}_w, 0)k(\vec{r}_w). \tag{52}$$

It increases linearly with c when quenchers are dilute. Deviation from linear concentration dependence of $\eta_0/\eta - 1$ is theoretically obtained by solving the equation for $\hat{G}(\vec{r}_1, \vec{r}_2, s)$ given by the Laplace transform of Eq. (28).

For the localized reactions, $k(\vec{r}_\ell) = k_0\delta_{\vec{r}_\ell, \vec{r}_R}$, we obtain the following equation by substituting $s \to 0$ limit of Eq. (33) into Eq. (52):

$$\eta_0/\eta - 1 = \frac{c\tau_0}{1/k_0 + \dfrac{1-c}{1/\hat{G}_0(\vec{r}_R, \vec{r}_R, z_0) - ck_0}} \tag{53}$$

$$= \frac{ck_0\tau_0}{1 + \dfrac{(1-c)U(z_0)}{c[1-U(z_0)] + (1/\tau_0 + \Gamma)/k_0}}, \tag{54}$$

where $s \to 0$ limit of z is introduced,

$$z_0 = 1/\tau_0 + ck_0. \tag{55}$$

The Laplace variable given by Eq. (55) includes the effect of initial concentration of quenchers and the reaction rate. This is a signature of the excluded volume interactions among quenchers. Equation (53) is positive since we can prove

$$1 > ck_0\hat{G}_0(\vec{r}_R, \vec{r}_R, z_0) > 0, \tag{56}$$

as shown in the Appendix. Equation (53) is an important result of this paper.

In the static limit, Eq. (53) reduces to the following equation by substituting $\hat{G}_0(\vec{r}_R, \vec{r}_R, z_0) = 1/z_0$:

$$\eta_0/\eta - 1 = \frac{c}{1 - c + 1/(\tau_0 k_0)}. \tag{57}$$

This is the exact result.

In the limit of $k_0 \to \infty$, the result in the hopping-controlled limit is obtained from Eq. (54) as,
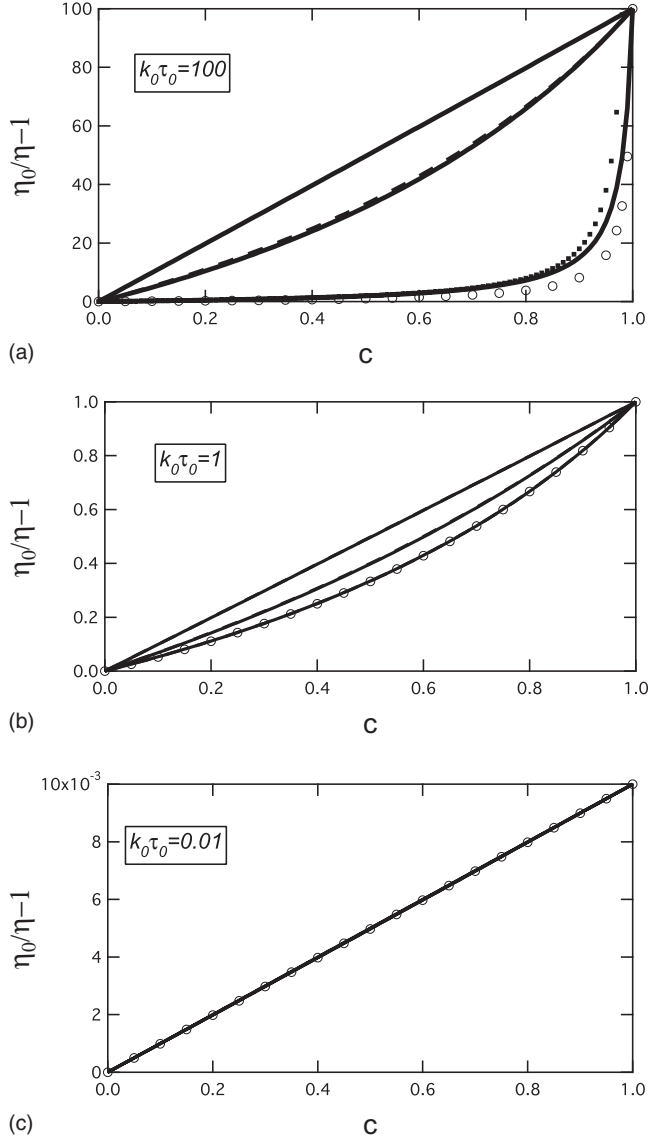
FIG. 1. $\eta_0/\eta - 1$ against concentration c. (a) $k_0\tau_0=100$; (b) $k_0\tau_0=1$; (c) $k_0\tau_0=0.01$. In all panels, curves correspond to $\Gamma/k_0 = 100$, $\Gamma/k_0=1$, and $\Gamma/k_0=0.01$ from top to bottom. The thick solid lines indicate the general results in the presence of site blocking effects, Eq. (53) with Eq. (59). In (c) they overlap. A dashed line in (a) indicates the approximate result of Eq. (61). The other dashed lines are not visible, since they overlap with the solid lines. A dotted line in (a) represents the results of hopping-controlled limit, Eq. (58), which is valid for $k_0 \to \infty$. Circles indicate the static solution, Eq. (57).

$$\eta_0/\eta - 1 = c \frac{1 + \Gamma\tau_0}{1 - c}. \quad (58)$$

The above expression shows that $\eta_0/\eta - 1$ increases linearly with increasing the hopping frequency, Γ, for any concentration. In the limit of $c=1$, the target site is occupied by a quencher at the initial time and reaction takes place with probability 1 when $k_0 \to \infty$. In the opposite limit of $c \to 0$, $\eta_0/\eta - 1$ is proportional to the concentration c. By time inte-

gration, we can show that Eq. (58) is consistent with Eq. (42).

For various lattices, the lattice Green's function, Eq. (37), is known. As an example, we consider random walks on the body-centered cubic (BCC) lattice. The reaction takes place at the site $\vec{r}_R$ with the rate k_0. Without loss of generality, the target site $\vec{r}_R$ can be taken at the origin of the lattice. Quenchers perform random walks on the lattice including the origin, and each site can be occupied at most by a single quencher. The lattice Green's function is known [25],

$$\hat{G}_0(\vec{r}_R, \vec{r}_R, s) = \left\{ {}_2F_1\left\{\frac{1}{4}, \frac{1}{4}; 1; [\Gamma/(s+\Gamma)]^2\right\} \right\}^2 /(s+\Gamma). \quad (59)$$

When $\Gamma < z_0$, we can approximate ${}_2F_1(\frac{1}{4}, \frac{1}{4}; 1; \xi^2) \sim 1 + \xi^2/16$, for $\xi \to 0$ [26] in Eq. (59), and Eq. (53) is expressed as,

$$\eta_0/\eta - 1 = \frac{c\tau_0}{\dfrac{1}{k_0} + \dfrac{1-c}{1/\tau_0 + \Gamma - (ck_0/8)\Gamma^2/(z_0+\Gamma)^2}}. \quad (60)$$

In the case of $ck_0 > \Gamma/8$, Eq. (60) is further simplified as,

$$\eta_0/\eta - 1 = \frac{c\tau_0}{\dfrac{1}{k_0} + \dfrac{1-c}{1/\tau_0 + \Gamma}}. \quad (61)$$

Equation (61) is the result valid irrespective of the lattice structure since it can be derived by introducing the approximation, $\hat{G}_0(\vec{r}_R, \vec{r}_R, z_0) \sim 1/(z_0+\Gamma)$, which is valid when $\Gamma < z_0$, into Eq. (53). In the reaction-controlled or static limit, we obtain Eq. (57), whereas, in the hopping-controlled limit, Eq. (58) is derived. Equation (61) interpolates between the static and hopping-controlled limits.

In Fig. 1, the general results of Eq. (53) with Eq. (59) are plotted for various values of k_0 and Γ. The simplified solutions of Eq. (60) overlap with those of Eq. (53) with Eq. (59) in Fig. 1. The further simplified solutions of Eq. (61) are also shown. The results of Eq. (61) reproduce the general results except for the case of $k_0\tau_0=100$ and $\Gamma/k_0=1$ where a small deviation is found. The results indicate that although Eq. (61) is derived under the condition of $8ck_0 > \Gamma$, it is applicable in practice over a wide range. The results in the hopping-controlled limit of $k_0 \to \infty$, Eq. (58), are also shown for comparison. The results in the static limit, Eq. (57), give the lower bound of η_0/η for a given value of $k_0\tau_0$.

VII. DECAY KINETICS

For localized reactions, the Laplace transform of the survival probability is obtained from Eq. (38). In BCC lattice, the lattice Green's function is given by Eq. (59). Therefore, when $\Gamma < 1/\tau_0 + ck_0$, Eq. (38) is expressed as,

$$\hat{P}_N(s) = \cfrac{1}{s + \cfrac{1}{\tau_0} + \cfrac{c}{1/k_0 + (1-c)/[s + 1/\tau_0 + \Gamma - (ck_0/8)\Gamma^2/(z+\Gamma)^2]}}, \tag{62}$$

where z is given by Eq. (35) and approximation of Eq. (59) using $_2F_1(\frac{1}{4},\frac{1}{4};1;\xi^2) \sim 1 + \xi^2/16$ as $\xi \rightarrow 0$ is introduced. In the case of $ck_0 > \Gamma/8$, Eq. (62) is simplified as,

$$\hat{P}_N(s) = \cfrac{1}{s + \cfrac{1}{\tau_0} + \cfrac{c}{1/k_0 + (1-c)/(s + 1/\tau_0 + \Gamma)}}. \tag{63}$$

The inverse Laplace transformation of Eq. (63) is obtained as,

$$P_N(t) = \frac{\exp(-t/\tau_0)}{s_+ - s_-}[(s_+ - ck_0)\exp(-s_-t) - (s_- - ck_0) \\ \times \exp(-s_+t)], \tag{64}$$

where

$$s_\pm = \frac{\Gamma + k_0 \pm \sqrt{(\Gamma+k_0)^2 - 4c\Gamma k_0}}{2}. \tag{65}$$

Equation (64) together with Eq. (65) is the result independent of the lattice structures. Equations (64) and (65) are derived under the condition $ck_0 > \Gamma/8$. Accordingly, the accuracy of the approximation decreases by decreasing the quencher concentration. The result in the hopping-controlled limit of $k_0 \rightarrow \infty$ reproduces Eq. (42).

In the reaction-controlled limit, Eq. (62) reduces to

$$\hat{P}_N(s) = \cfrac{1}{s + \cfrac{1}{\tau_0} + \cfrac{c}{1/k_0 + (1-c)/(s + 1/\tau_0)}}, \tag{66}$$

and its inverse Laplace transform is given by Eq. (10) when $1/\tau_0 = 0$.

For comparison, we present the conventional solution of the survival probability for target problem when site blocking effects among quenchers is completely ignored [4,5],

$$P_N(t) = \exp\left(-c\int_0^t dt_1 k_{cv}(t_1)\right), \tag{67}$$

where the Laplace transform of $k_{cv}(t)$ is obtained from,

$$s\hat{k}_{cv}(s) = \frac{k_0}{1 + k_0\hat{G}_0(\vec{r}_R,\vec{r}_R,s)}. \tag{68}$$

In Fig. 2, the numerically obtained inverse Laplace transform of Eq. (38) with Eq. (59) is compared with the conventional solution, Eqs. (67) and (68). Excluded volume interaction is considered in Eq. (38) with Eq. (59), whereas it is ignored and each quencher is assumed to migrate independently in the conventional solution. In all cases, our results indicate that the survival probability in the presence of site blocking effects decays faster than that of the conventional solution where the excluded volume interaction is absent.

In the dilute limit, $c \ll 1$, the difference between them is small regardless of the values of Γ/k_0. When the decay is mainly controlled by reaction, namely, $\Gamma/k_0 \gg 1$, the result of the conventional solution is close to that in the presence of site blocking effects even at high concentration of $c = 0.9$. In this case, the excluded volume interaction is not important. As Γ/k_0 decreases, the deviation of the conventional solution from the results in the presence of site blocking effects increases at high concentrations.

The initial decay of the solution of Eq. (38) with Eq. (59) follows the results of static quenching from the uniform distribution, Eq. (10), over a longer period than that of the conventional solution given by Eqs. (67) and (68) in the cases of (b) and (c). In the initial time range, the decay of the survival probability takes place from the configuration where a quencher is initially located in the vicinity of the target. In the presence of site blocking effects, the migration of quenchers is suppressed and the initial decay follows the results of static quenching over a longer period than that derived under the assumption of free migration in the absence of site blocking. It should also be noticed that the survival probability obtained by assuming static quenching is the upper bound of that in the presence of diffusion, whereas the solution of Eq. (38) with Eq. (59) is the lower bound. The exact solution should lie between them.

When $\Gamma/k_0 \ll 1$, the initial time regime is approximated by the static quenching, and is followed by the hopping-controlled regime approximately described by Eq. (42) as shown in Fig. 2.

VIII. CONCLUSIONS

We have investigated the target reaction problem in the presence of site blocking effects among quenchers. Quenchers migrate on any lattice sites until reaction takes place. Reaction rate depends on the distance between the quencher and the target. In the case of localized reactions, reaction takes place when a quencher comes to the target site. Once reaction occurs, the system becomes inert.

The probability of reaction event is high if the excited target is initially surrounded by quenchers in close vicinity. As time proceeds, quencher configurations in which the quencher concentration near the excited target is low is more likely to survive than other configurations in the ensemble.

In the conventional theory, excluded volume interactions among quenchers are ignored, i.e., quenchers are regarded as independent of one another. However, quencher migration is hindered by the presence of other quenchers; the migration of a quencher is influenced by the time-dependent positions
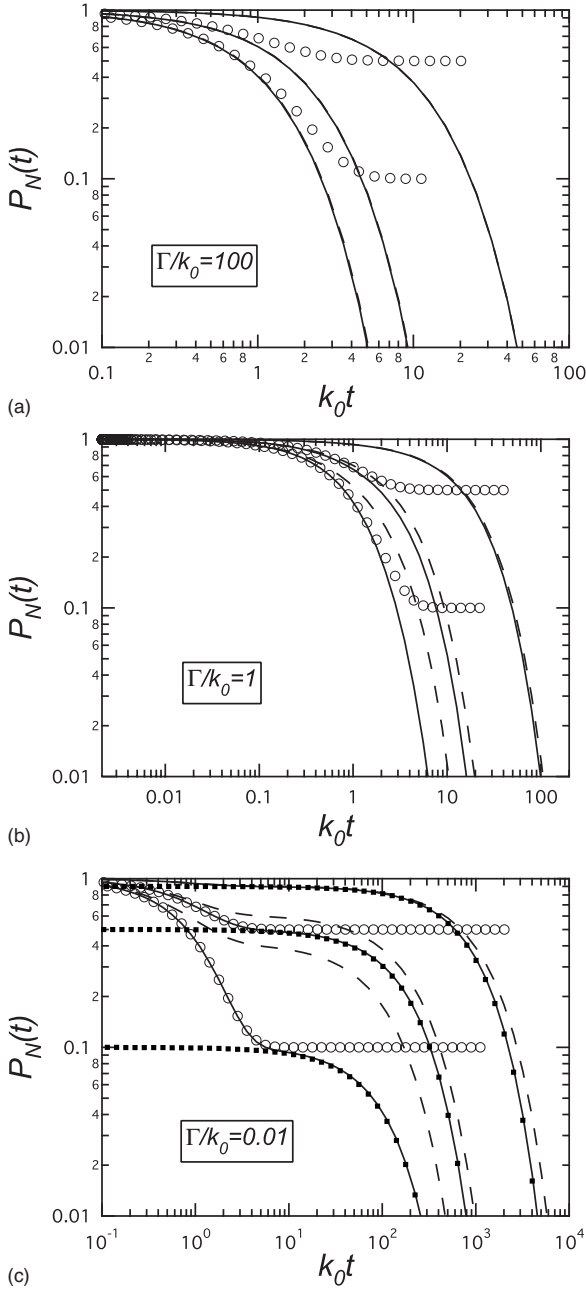
FIG. 2. The survival probability against normalized time, $k_0 t$. $1/\tau_0 = 0$. (a) $\Gamma/k_0 = 100$; (b) $\Gamma/k_0 = 1$; (c) $\Gamma/k_0 = 0.01$. In all panels, curves correspond to $c = 0.1$, $c = 0.5$, and $c = 0.9$ from right to left. The solid lines are obtained by the inverse Laplace transform of the general expression in the presence of site blocking effects, Eq. (38) with Eq. (59). Dashed lines are obtained by the conventional expression, Eqs. (67) and (68). In (a) the dashed lines are invisible because they overlap with the solid lines. Dotted lines in (c) represent the solution in the hopping-controlled limit given by Eq. (42). Circles indicate the solution in the static limit given by Eq. (10).

of other quenchers due to the site blocking effects. We take into account the excluded volume interactions among quenchers by applying the vacancy-assisted diffusion theory of Nakazato-Kitahara. Our analytical solutions of the survival probability interpolate between those in two limits of low and high quencher concentrations and the approximation

is good when the intrinsic reaction rate is low. When the intrinsic reaction rate is high and the condition for truncation of perturbation expansion, $c(1-c)k_0^2/(ck_0+\Gamma)^2 < 1$, is not satisfied, the higher-order terms in the expansion is only partly taken into account by the Páde approximation. In other words, the higher-order correlations originating from the diffusional collisions are not fully accounted for in the Páde approximation. In the presence of diffusion, our result is a lower bound of the survival probability. In the static limit, the exact results are reproduced from the Páde approximation.

The decay of the survival probability has been investigated for the target problem, where the target is excited by a pulse initially. The initial decay is well approximated by the static quenching. In particular, when the hopping frequency satisfies the relation, $\Gamma/k_0 < 1$, the initial decay of the survival probability at high quencher concentrations follows that of static quenching over a long period. The long time behavior of the general solution is approximated by the result in the hopping-controlled limit, Eq. (42), when $\Gamma/k_0 \ll 1$.

When the intrinsic reaction rate satisfies the relation, $\Gamma/k_0 \gg 1$, the conventional results in the absence of the site blocking effects reproduces those in the presence of the site blocking effects even at high quencher concentration of $c = 0.9$. In the reaction-controlled limit, the excluded volume interaction among quenchers is not so important as that in the hopping-controlled limit.

According to the Brownian dynamic simulation, the survival probability in the presence of excluded volume interaction decays faster than that in its absence [27,28]. Similar enhancement of deactivation was also found by numerical simulation of random walk model on one- and two-dimensional lattices [20–22,29]. Our results also suggest that the decay of the survival probability is accelerated by site blocking effects in the case of lattice random walk. The result can be understood as follows. Assume that there are N quenchers on the lattice. As time proceeds, quenchers hop from site to site. Therefore, individual sites occupied by quenchers change with time. As long as the target site remains outside the sites occupied by quenchers, reaction does not occur. Once the sites occupied by quenchers include the target site, reaction occurs. In the absence of site blocking effects, different quenchers are allowed to occupy the same site. Therefore, in this case the number of the sites occupied by quenchers is generally less than N. In the presence of site blocking effects, different quenchers are not allowed to occupy the same site. Therefore, in this case the number of the sites occupied by quenchers is N. In other words, the number of the sites occupied by quenchers is generally larger in the presence of site blocking effects than in its absence at any time. Accordingly, the probability that the sites occupied by quenchers will include the target site is higher in the presence of site blocking effects than in its absence at any time. As a result, the survival probability of the target decays faster in the presence of site blocking effects than in its absence.

It is interesting to note the quite opposite effect of site blocking on the survival probability of a geminate pair with a large initial separation. Recently, it has been shown that the pair survival probability decays slower in the presence of site

blocking effects by inert particles [30]. Here, the diffusion toward the target is just hindered by inert gases.

Finally, we comment on the excluded volume interaction between the target and a quencher. It is possible to exclude the origin occupied by the target for the random walk of quenchers by modifying the lattice Green's function of periodic lattice. The research in this direction is now undertaken.

APPENDIX: PROOF OF $1 > ck_0\hat{G}_0(\vec{r}_R,\vec{r}_R,z) > 0$

We first prove $1/\hat{G}_0(\vec{r}_R,\vec{r}_R,z) - ck_0 > 0$ which can be transformed into $1 > ck_0\hat{G}_0(\vec{r}_R,\vec{r}_R,z)$. By introducing

$$\hat{G}_0(\vec{r}_R,\vec{r}_R,z) = \frac{1 - \hat{\psi}(z)}{z}U(z),$$

we obtain

$$1/\hat{G}_0(\vec{r}_R,\vec{r}_R,z) - ck_0 = \frac{ck_0[1 - U(z)] + s + 1/\tau_0 + \Gamma}{U(z)}. \tag{A1}$$

From the definition of $U(s)$ given by Eq. (37), we can show $U(z) \geq 1$ since the denominator in the integrand of $U(s)$, 1

$-\hat{\psi}(z)\tilde{\lambda}(\vec{k})$, is smaller than 1. Since the denominator of Eq. (A1) is positive, we need to prove the positivity of the numerator, $ck_0[1 - U(z)] + (1/\tau_0) + \Gamma > 0$. By using

$$1 - U(z) = \frac{1}{(2\pi)^d}\int\cdots\int_{-\pi}^{\pi}d^d\vec{k}\frac{-\Gamma\tilde{\lambda}(\vec{k})}{z + \Gamma[1 - \tilde{\lambda}(\vec{k})]}, \tag{A2}$$

the numerator of Eq. (A1) can be rewritten as,

$$\Gamma + ck_0[1 - U(z)] = \frac{1}{(2\pi)^d}\int\cdots\int_{-\pi}^{\pi}d^d\vec{k}$$

$$\times\frac{\Gamma(s + 1/\tau_0) + \Gamma(ck_0 + \Gamma)[1 - \tilde{\lambda}(\vec{k})]}{s + 1/\tau_0 + ck_0 + \Gamma[1 - \tilde{\lambda}(\vec{k})]}. \tag{A3}$$

Since $\tilde{\lambda}(\vec{k}) \equiv \frac{1}{2d}\sum_{j=1}^{2d}\cos(\vec{k}\cdot\vec{b}_j/b) < 1$, Eq. (A3) is positive. Therefore, $ck_0[1 - U(z)] + (1/\tau_0) + \Gamma > 0$ and it leads to $1/\hat{G}_0(\vec{r}_R,\vec{r}_R,z) - ck_0 > 0$, which can be rewritten as,

$$1 > ck_0\hat{G}_0(\vec{r}_R,\vec{r}_R,z) > 0, \tag{A4}$$

where we have used the fact that both ck_0 and $\hat{G}_0(\vec{r}_R,\vec{r}_R,z)$ are positive. z in Eq. (A4) is given by $z = s + 1/\tau_0 + ck_0$. Therefore, if we take the limit of $s \to 0$ in Eq. (A4) we have Eq. (56).

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