Kinetics of stochastically gated diffusion-limited reactions and geometry of random walk trajectories

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In this paper we study the kinetics of diffusion-limited, pseudo-first-order $A+B\rightarrow B$ reactions in situations in which the particles' intrinsic reactivities are not constant but vary randomly in time. That is, we suppose that the particles are bearing ''gates'' which fluctuate in time, randomly and independently of each other, between two states—an active state, when the reaction may take place between A and B particles appearing in close contact; and a blocked state, when the reaction is completely inhibited. We focus here on two customary limiting cases of pseudo-first-order reactions—the so-called target annihilation and the Rosenstock trapping model—and consider four different particular models, such that the A particle can be either mobile or immobile or gated or ungated, and ungated or gated B particles can be fixed at random positions or move randomly. All models are formulated on a d-dimensional regular lattice, and we suppose that the mobile species perform independent, homogeneous, discrete-time lattice random walks. The model involving a single, immobile, ungated target A and a concentration of mobile, gated B particles is solved exactly. For the remaining three models we determine exactly, in the form of rigorous lower and upper bounds showing the same N dependence, the large-N asymptotical behavior of the probability that the A particle survives until the Nth step. We also realize that for all four models studied here the A particle survival probability can be interpreted as the moment generating function of some functionals of random walk trajectories, such as, e.g., the number of self-intersections, the number of sites visited exactly a given number of times, the ''residence time'' on a random array of lattice sites, etc. Our results thus apply to the asymptotic behavior of corresponding generating functions which are not known as yet.

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I. INTRODUCTION

Many naturally occurring chemical reactions, or reactions used in various technological and material processing operations, involve molecules with a rather complex internal structure. For such reactions the geometrical complexity of the molecules appears to be a significant rate-controlling factor, in addition to the transport limitations and constraints imposed by the elementary reaction act; that is, the chemically active groups of complex molecules involved may be effectively screened by their inactive parts, which thus impedes the access of the reactive species and inhibits the reaction. For instance, geometrical restrictions are crucial for ligand binding to proteins, such as, e.g., myoglobin or hemoglobin [1]. Here, in the static x-ray structure of myoglobin there is no hole for the ligand to enter, and it is believed that binding of the ligand occurs when the side chains blocking the entrance swing out in the course of their thermal motion (Figs. 1 and 2). Similarly, intercalation of drugs by DNA may be controlled by breathing motions that involve the unstacking of adjacent pairs of bases. In some cases, the ligands themselves can possess a complicated internal structure (as exemplified, for instance, by peptides), such that their reactivity may be influenced significantly by conformational changes. Last but not least, geometrical restrictions do manifest themselves in such contexts, as, e.g., certain chemical reactions occurring within biomembranes [2], incoherent exciton trapping by substitutional traps on aromatic vinyl polymers [3], molecular transport inside proteins [4–7], and in some medical therapies [8]. Clearly, an understanding of the impact of the geometrical limitations on the reaction kinetics constitutes an important challenge for the theoretical analysis.

A physically plausible approach to account for the influence of the geometrical restrictions on the reactivity of complex molecules is to assume that the reaction in question, say a generic pseudo-first-order reaction of the form

$$A+B\rightarrow B, \tag{1}$$

is modulated by the side reactions of the form $A\leftrightarrow A^*$ or $B\leftrightarrow B^*$, where A (B) stands for an active state, and A^* (B^*) for an inactive, blocked state, in which case the reaction in Eq. (1) is complete inhibited. In other words, one says that one or both species involved in the reaction are gated, the gates changing their states in time according to some prescribed rules.

The kinetics of gated diffusion-limited reactions has been studied analytically for nearly two decades. Following the seminal work of McCammon and Northrup [9], who analyzed a simple case of a two-state gating described by an arbitrary deterministic function of time, several important advancements have been made. In particular, a classical Smoluchowski approach [10] was generalized in Refs. [11–13] to describe the kinetics of *stochastically* gated (SG) pseudo-first-order reactions in Eq. (1) for both cases when the gate is imposed on the traps B or on the A particles. It has

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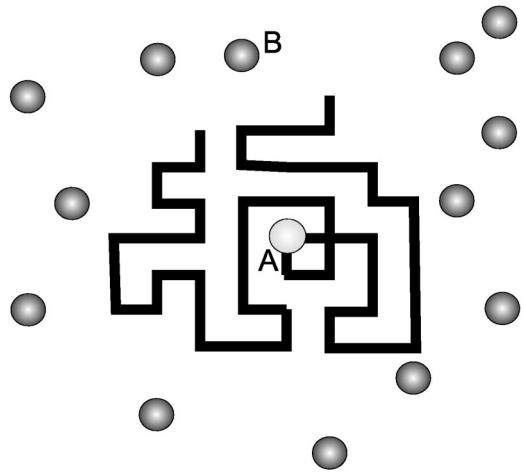

FIG. 1. A schematic illustration of the effective geometric screening of an active A particle by inactive parts of a complex (polymer) molecule. In the situation depicted in this figure the A particle, which is attached to a polymer, is completely inaccessible to the B species, and the reaction between them is inhibited due solely to the geometrical restrictions.

been realized that no symmetry exists between these two situations; as a matter of fact, the kinetic behavior appears to be rather different depending on which of the species precisely is being gated. Furthermore, Spouge *et al.* [14] studied the SG reactions with more general mechanisms, including a non-Markovian case, while Berezhkovski and co-workers discussed the impact of the many-particle effects on the SG reactions kinetics [13,15,16]. However, the available theoretical analysis is either based on uncontrollable assumptions, akin to the Smoluchowski-type approaches (see, e.g., Refs. [17,18], and references therein), or employs exact formalisms, which do not always allow for explicit calculation of the corresponding decay patterns and become tractable only when some simplifying assumptions are made. Consequently, except for a relatively simple model involving an immobile ungated target A and a concentration of mobile SG B particles (see, e.g., Refs. [11–14]), temporal evolution of the SG reactions remains incompletely understood. This is,

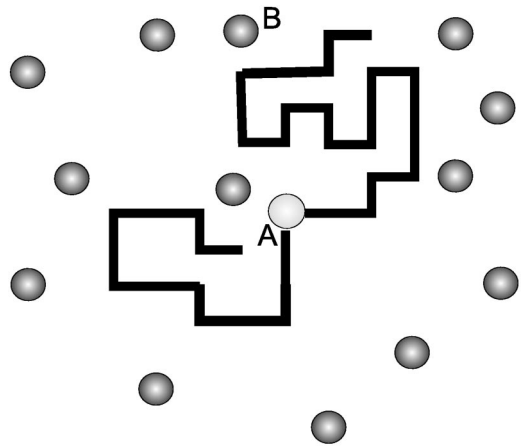

FIG. 2. In the situation depicted in this figure the B's may diffuse through the hole opened in the course of the polymer's thermal motion, and hence, may enter into a reaction with the chemically active A particle.

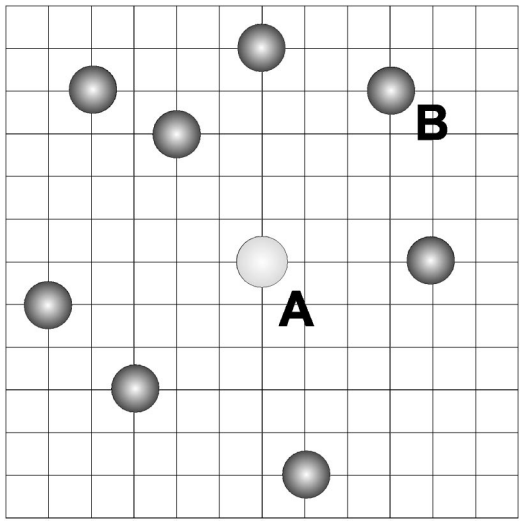

FIG. 3. Pseudo-first-order $A+B\rightarrow B$ reaction involving a single mobile (immobile) A particle and a concentration of fixed (mobile) B particles taking place on a two-dimensional lattice. The gate may be imposed on either A or B particles.

of course, not at all surprising, since diffusion-limited reactions with stochastic reactivity clearly pose more complex technical problems to the theoretical analysis than their ungated counterparts, which themselves are not solvable exactly and often exhibit spectacular, essentially many-particle behavior.

In this paper we study in detail the kinetics of the SG pseudo-first-order reactions in Eq. (1), involving a single A particle and a concentration of B particles. We focus here on two limiting cases—the so-called target annihilation [19–23] and the Rosenstock trapping model [24]—and consider four different models such that an A particle can be either mobile or immobile, gated or ungated, and ungated or gated B particles can be fixed at random positions or move randomly (Fig. 3). For computational convenience, all models are formulated on a d-dimensional regular lattice, and we suppose that mobile species perform independent, homogeneous, discrete-time lattice random walks. Further on, in regard to reactivity fluctuations, we restrict ourselves to the two-state Poisson gating model of Ref. [14], in which each gate is supposed to be in either of two states, active on blocked, and to update its state at each tick of the clock. The updating process is assumed to proceed completely at random, without memory in time and without correlations with the gates imposed on the other particles.

For such a gating model we analyze the time evolution of the A particle survival probability P_N, i.e., the probability that a single mobile or immobile, gated or ungated A particle is not annihilated up to the Nth time step by a concentration of immobile or mobile, ungated or gated B particles. For a model involving a single immobile, ungated target A and a concentration of SG mobile B particles, the complete temporal evolution of P_N is calculated exactly. For the remaining three models we determine exactly the form of the large-N asymptotical decay of P_N by deriving rigorous lower and upper bounds, which both show the same N dependence but slightly differ in prefactors.

An interesting by-product of our analysis, which appears in especially lucid fashion within the discrete-space descrip-

tion, is that for any particular model the A particle survival probability P_N can be interpreted as a moment generating function of certain functionals, which mirror the internal geometry of random walks trajectories—an issue which has recently gained renewed attention in view of many important applications [25–28]. As a matter of fact, it has been known for a long time that for ungated trapping reactions taking place on a d-dimensional lattice the survival probability P_N can be thought off as the moment generating function of the number $\mathcal{S}(\{\mathbf{r}_N\})$ of distinct sites visited by a given trajectory $\{\mathbf{r}_N\}$ of an N-step lattice random walk [24]; in addition, for Brownian motion in a d-dimensional continuum, P_N can be interpreted as the generating function of the volume of the so-called Wiener sausage, i.e., the volume swept by a spherical particle during time t [30]. We realize that for the SG pseudo-first-order reactions some other characteristic functionals of random walk trajectories come into play, which probe some interesting aspects of the geometrical structure of a single or of a collection of lattice random walks. Depending on the particular model, P_N then appears as the generating function of such characteristic functionals of random walk trajectories such as, e.g., the number of self-intersections, the number of sites visited exactly a given number of times, the ''residence time'' on a random array of lattice sites, and some others. Consequently, our results also apply to the asymptotical behavior of the corresponding generating functions, which is not yet known in many cases.

The paper is structured as follows. In Sec. II we discuss two customary limiting cases of the pseudo-first-order reactions in Eq. (1)—the so-called target annihilation model and the Rosenstock trapping model—and present a brief outline of different results concerning their kinetic behavior in the ungated case. In Sec. III we consider a gated target problem, focusing on the survival probability P_N of an immobile ungated target in the presence of randomly moving, stochastically gated B particles. Here we derive an exact temporal evolution of the probability that none of mobile particles hits the target within an N-step walk. In Sec. IV we study the survival of an immobile *gated* target in the presence of a concentration of mobile particles. The corresponding survival probability is found here in the form of rigorous lower and upper bounds, which both display the same N dependence and thus determine the temporal evolution of P_N exactly. Next, in Secs. V and VI, we consider two models of stochastically gated trapping reactions; in the first case these are the immobile traps B that are supposed to be stochastically gated, while the mobile A particle is always assumed to be in a reactive state (ungated); in the second case the mobile A particle is assumed to bear a stochastic gate, while the immobile traps B are considered as perfect, nonfluctuating traps. For both cases the A particle survival probability is determined exactly, in the form of rigorous lower and upper bounds showing the same N dependence. Finally, we conclude in Sec. VII with a brief summary of our results.

II. A REMINDER ON THE KINETICS OF UNGATED PSEUDO-FIRST-ORDER REACTIONS: TARGET ANNIHILATION AND THE ROSENSTOCK TRAPPING MODELS

To fix the ideas, we first present a brief summary of results concerning the kinetics of ungated, diffusion-limited pseudo-first-order reactions in Eq. (1) taking place on d-dimensional regular lattices. We will focus here and in the remainder of the paper on two particular cases—the so-called target annihilation model, involving a single, immobile A particle and a concentration of randomly moving B particles; and the Rosenstock trapping model involving a single mobile A particle performing lattice random walk in the presence of a concentration of immobile, randomly placed B particles: the traps. In subsequent sections of our work we will study how the kinetics in these two models will be modified if one imposes a stochastic gate on either of two species; consequently, the results of this section will serve us in what follows as an important point of reference.

A. Target annihilation

We start with the target annihilation model, which allows for an exact solution [19–22]. Consider an immobile A particle, located at the lattice origin, and B particles, which are initially all placed at random positions on a d-dimensional regular lattice and after that are allowed to move by performing independent, homogeneous, discrete-time random walks. As soon as any of the B's appears at the lattice origin, the A particle is instantaneously annihilated. Thus, following the terminology earlier introduced, the A particle will be called the ''target,'' while the B particles will be referred to as the ''scavengers'' [23]. The property whose temporal evolution we wish to study is the probability $P_N = \exp[-cQ_N^{(tar)}]$ that the target particle ''survives'' until time N; here and henceforth c will denote the number density of the B particles, while $Q_N^{(tar)}$, in view of the pseudo-first-order of the reaction in Eq. (1), can be interpreted as the integral effective reaction rate.

Now we define the model more precisely. We first suppose that the lattice is of a finite extent and contains M sites, whereas the number of the scavengers is also fixed and equal to K. In what follows we will turn to the limit $M,K\to\infty$, while keeping the ratio K/M fixed: $K/M=c$.

Further on, let $\mathbf{S}_n^{(k)}$ denote the position at which the kth scavenger appears on the nth step $(n=0,1,\ldots,N)$ for a given realization of its trajectory. Then, we construct a function Ψ_N of the form

$$\Psi_N = \lim_{\beta\to\infty} \exp\left[-\beta \sum_{n=0}^{N}\sum_{k=1}^{K} \mathcal{I}(\mathbf{S}_n^{(k)})\right] = \prod_{n=0}^{N}\prod_{k=1}^{K} \lim_{\beta\to\infty} \exp[-\beta \mathcal{I}(\mathbf{S}_n^{(k)})], \tag{2}$$

where $\mathcal{I}(\mathbf{S}_n^{(k)})$ is the indicator function,

$$\mathcal{I}(\mathbf{X}) = \begin{cases} 1, & \mathbf{X}=\mathbf{0} \\ 0, & \mathbf{X}\neq\mathbf{0}, \end{cases} \tag{3}$$

which shows whether the kth scavenger is at the lattice origin 0 at the nth step, or elsewhere.

Note that the function Ψ_N serves as the indicator of the reaction event; it is equal to 1 if within an N-step walk none of the K scavengers has visited the origin (i.e., the target),

and becomes 0 when within the ''time'' interval $[0,N]$ at least one of the scavengers has visited the origin at least once.

The property one is generally interested in computing is not, however, the realization-dependent function Ψ_N, but rather its averaged value $P_N=\langle\Psi_N\rangle$, the average being taken over different realizations of scavengers' random walks and their initial positions. Below we will briefly outline an exact computation of $\langle\Psi_N\rangle$ (see also Refs. [19–23]).

Noticing first that all $\mathbf{S}_n^{(k)}$'s with different values of k are independent of each other, we have that the target survival probability can be written in the factorized form

$$P_N=\left(\lim_{\beta\to\infty}\frac{1}{M}\sum_{\mathbf{S}_0}E_{\mathbf{S}_0}\left\{\exp\left[-\beta\sum_{n=0}^{N}\mathcal{I}(\mathbf{S}_n)\right]\right\}\right)^K, \quad (4)$$

where the summation extends over all sites of a d-dimensional lattice, while the symbol $E_{\mathbf{S}_0}\{\cdots\}$ denotes the expectation on the set of different random walk trajectories starting at the site $\mathbf{S}_0$. Note next that

$$E_{\mathbf{S}_0}\left\{\lim_{\beta\to\infty}\exp\left[-\beta\sum_{n=0}^{N}\mathcal{I}(\mathbf{S}_n)\right]\right\} \equiv \mathrm{Prob}(\mathbf{S}_n\neq\mathbf{0} \ \text{ for any } \ n\in[0,N]|\mathbf{S}_0), \quad (5)$$

i.e., is equal to the probability that a random walker starting at the site $\mathbf{S}_0$ does not visit the origin within first N steps. Turning now to the infinite-space limit, i.e., letting $K,M\to\infty$ while keeping their ratio fixed, $K/M=c$, we then find that Eq. (4) attains the form

$$P_N=\lim_{K,M\to\infty|K/M=c}\left(1-\frac{1}{M}\sum_{\mathbf{S}_0}\times[1-\mathrm{Prob}(\mathbf{S}_n\neq\mathbf{0} \ \text{ for any } \ n\in[0,N]|\mathbf{S}_0)]\right)^K =\exp\left[-c\sum_{\mathbf{S}_0}\mathrm{Prob}_N(0|\mathbf{S}_0)\right], \quad (6)$$

where $\mathrm{Prob}_N(0|\mathbf{S}_0)$ stands for the probability that a first passage from the site $\mathbf{S}_0$ to the origin did actually occur within the first N steps.

The probability $\mathrm{Prob}_N(0|\mathbf{S}_0)$ is known exactly (see, e.g., Ref. [25]); being summed over all possible starting points it defines another important characteristic property of random walks—the expectation of the number $\mathcal{S}(\{\mathbf{S}_N\})$ of *distinct* sites visited by a given trajectory $\{\mathbf{S}_N\}$ of an N-step walk starting at the origin, i.e.,

$$\sum_{\mathbf{S}_0}\mathrm{Prob}_N(0|\mathbf{S}_0)=E_0\{\mathcal{S}(\{\mathbf{S}_N\})\}. \quad (7)$$

The expected number of distinct sites visited by an N-step walk shows different asymptotical behavior depending on the dimensionality d and on the type of the lattice [25]. In particular, for d-dimensional Polya random walks, one has

$$E_0\{\mathcal{S}(\{\mathbf{S}_N\})\}=\left(\frac{8N}{\pi}\right)^{1/2}+O\left(\frac{1}{\sqrt{N}}\right), \quad d=1,$$

$$E_0\{\mathcal{S}(\{\mathbf{S}_N\})\}=\frac{\pi C_2 N}{\ln(N)}+O\left(\frac{N}{\ln^2(N)}\right), \quad d=2, \quad (8)$$

$$E_0\{\mathcal{S}(\{\mathbf{S}_N\})\}=\frac{N}{P(0|0;1^-)}+O(\sqrt{N}), \quad d=3,$$

where $C_2=4/3\sqrt{3}$, 1, and $2/\sqrt{3}$ for hexagonal, square and triangular two-dimensional lattices, respectively. The constant $P(0|0;1^-)$ determines the probability R of eventual return to the origin, $P(0|0;1^-)=(1-R)^{-1}$, and is defined as the limit $\xi\to1^-$ of the generating function $P(0|0;\xi)=\sum_{N=0}^{\infty}P_N(0|0)\xi^N$, $P_N(0|0)$ being the probability of finding a random walker at the origin at the Nth step, provided that the walk has started at the origin. The exact values of $P(0|0;1^-)$ are $12\Gamma^6(\frac{1}{3})/(2^{4/3}\pi^4)$, $\sqrt{6}\Gamma(\frac{1}{24})\Gamma(\frac{5}{24})\Gamma(\frac{7}{24})\Gamma(\frac{11}{24})/(284\pi^3)$, $\Gamma^4(\frac{1}{4})/(4\pi^3)$, and $\Gamma^6(\frac{1}{3})/(2^{14/3}\pi^4)$ for diamond, simple cubic, body-centered-cubic and face-centered-cubic lattices, respectively [25].

Therefore, for the target annihilation model the decay law can be computed exactly and the integral effective reaction rate $Q_N^{(tar)}$ is simply equal to the expected number of distinct sites visited by an N-step walk [19–22]. Note also that the decay form appears to be essentially dependent on the dimensionality of the embedding lattice; it is characterized by a stretched-exponential dependence for low-dimensional lattices, on which the Polya walks are recurrent [$R=1, P(0|0;1^-)=\infty$], and shows a purely exponential behavior for lattices of spatial dimension $d>2$, where $R<1$ and $P(0|0;1^-)$ is well defined.

B. Rosenstock trapping model

We turn next to the so-called Rosenstock trapping problem, in which one focuses on the fate of a single A particle performing a random walk over the lattice in the presence of immobile, perfect, randomly placed traps B. We start by assuming again that the lattice is finite and contains M sites. The K traps B are placed completely at random and their positions are determined by the lattice vectors $\mathbf{S}^{(k)}, k=1,2,\ldots,K$. Denoting the lattice position of the A particle at the nth step as $\mathbf{r}_n$, we can now write down the indicator function of the reaction event as

$$\Psi_N=\lim_{\beta\to\infty}\exp\left[-\beta\sum_{n=0}^{N}\sum_{k=1}^{K}\mathcal{I}(\mathbf{r}_n-\mathbf{S}^{(k)})\right], \quad (9)$$

where $\mathcal{I}(\mathbf{X})$ is the indicator function defined in Eq. (3). The function in Eq. (9) is equal to one for such N-step trajectories which avoid passing through any of the sites $\mathbf{S}^{(k)}$ and turns to zero for those trajectories which visit at least once at least one of these sites.

Now, we pass to averaging the function in Eq. (9) over the traps' placement. Since all $\mathbf{S}^{(k)}$'s are mutually independent, one can write down such an the average in the factorized form

$$\langle \Psi_N \rangle = E_0 \left\{ \prod_{k=1}^{K} \left(\frac{1}{M} \sum_{\mathbf{S}^{(k)}} \lim_{\beta \to \infty} \times \exp\left[-\beta \sum_{n=0}^{N} \mathcal{I}(\mathbf{r}_n - \mathbf{S}^{(k)}) \right] \right) \right\} \tag{10}$$

Next, in the limit $K, M \to \infty$, one has that

$$\begin{aligned} \langle \Psi_N \rangle &= E_0 \left\{ \left(\frac{1}{M} \sum_{\mathbf{S}} \lim_{\beta \to \infty} \exp\left[-\beta \sum_{n=0}^{N} \mathcal{I}(\mathbf{r}_n - \mathbf{S}) \right] \right)^K \right\} \\ &= E_0 \left\{ \exp\left(-c \sum_{\mathbf{S}} \left[1 - \lim_{\beta \to \infty} \times \exp\left(-\beta \sum_{n=0}^{N} \mathcal{I}(\mathbf{r}_n - \mathbf{S}) \right) \right] \right) \right\} \\ &= E_0 \left\{ \exp\left(-c \sum_{\mathbf{S}} \left[1 - \mathcal{I}\left(\sum_{n=0}^{N} \mathcal{I}(\mathbf{r}_n - \mathbf{S}) \right) \right] \right) \right\}, \end{aligned} \tag{11}$$

where

$$\sum_{\mathbf{S}} \left[1 - \mathcal{I}\left(\sum_{n=0}^{N} \mathcal{I}(\mathbf{r}_n - \mathbf{S}) \right) \right] \equiv \mathcal{S}(\{\mathbf{r}_N\}) \tag{12}$$

is the number of distinct sites visited by a given trajectory $\{\mathbf{r}_N\}$. Consequently, the A particle survival probability obeys

$$\langle \Psi_N \rangle = E_0\{\exp[-c\mathcal{S}(\{\mathbf{r}_N\})]\} = \exp[-cQ_N^{(tr)}], \tag{13}$$

and hence, appears here as the moment generating function of the number of distinct sites visited by an N-step random walk.

Therefore, the major difference between the target annihilation model and the trapping model is exactly that in the former the survival probability is the exponential of the expected number of distinct sites, while in the latter case it involves a fairly more complex property—its moment generating function. As a consequence, the trapping problem turns out to be essentially more difficult than the target one and hence, shows a richer behavior.

To display the time evolution of P_N in the trapping problem, we will first outline the predictions of a certain heuristic approach—the so-called Rosenstock approximation [24]—and then write down the results of a rigorous analysis by Donsker and Varadhan, which concerns the large-N asymptotical behavior [30].

1. Rosenstock approximation

This approximation was first applied by Rosenstock [24] in his studies of luminescence quenching kinetics and amounts, in essence, to the mere replacement of the average of an exponential of the number of sites visited by an exponential of the expected number,

$$\langle \Psi_N \rangle \approx \exp[-cE_0\{\mathcal{S}(\{\mathbf{r}_N\})\}]. \tag{14}$$

As one may readily notice, this heuristic procedure yields exactly the behavior found for the target annihilation problem, and, consequently, within the framework of this approximation one finds that $Q_N^{(tr)} \equiv Q_N^{(tar)}$.

As a matter of fact, numerical simulations demonstrate that a rather crude and uncontrollable approximation in Eq. (14) provides quite a fair description of the decay for the trapping problem for intermediate values of N [20], until at very large N some deviations emerge. The reason why the Rosenstock approximation works at intermediate N can be apparently explained as follows: As a matter of fact, the Rosenstock approximation represents a rigorous lower bound on P_N, since replacement of the average of an exponential of the number of distinct sites visited by an exponential of the expected number is tantamount to the application of the Jensen inequality, $\langle \exp[-cQ_N] \rangle \geqslant \exp[-c\langle Q_N \rangle]$. On the other hand, this inequality can be rewritten as

$$\langle \Psi_N \rangle = \langle \exp[\ln(\Psi_N)] \rangle \geqslant \exp[\langle \ln(\Psi_N) \rangle], \tag{15}$$

which signifies that in such an approach the average of the idicator function is approximated by the exponential of the averaged logarithm of this function. Since the logarithm is a slowly varying function, it is generally believed that its average value is supported by typical realizations of random walk trajectories which are representative at moderate values of N.

2. Fluctuation-induced large-N tails of the survival probability

In the large-N limit, however, the kinetics of the trapping reactions proceeds somewhat slower than that predicted by Eq. (14). This happens due to some fluctuation effects, which a mean-field-type approximation in Eq. (14) cannot capture. It has been first predicted in Ref. [29], and subsequently proven by Donsker and Varadhan [30], that for arbitrary d the decay follows

$$P_N \sim \exp[-a_d c^{2/(d+2)} N^{d/(d+2)}], \quad N \to \infty, \tag{16}$$

where a_d is a constant, dependent on the lattice dimensionality [30].

The physical origin of such an anomalous decay law can be illustrated by the following heuristic derivation. Consider first the function in Eq. (13), and suppose that for some given realization of the N-step A particle trajectory $\{\mathbf{r}_N\}$ the maximal excursion from the origin is equal to R_{max}. Consequently, for this realization the number $\mathcal{S}(\{\mathbf{r}_N\})$ of distinct sites visited by this realization of random walk trajectory can be majorized as $\mathcal{S}(\{\mathbf{r}_N\}) \leqslant R_{max}^d$, and the overall decay function can be bounded from below by

$$P_N \geqslant \int d^d R_{max} \exp[-cR_{max}^d] \mathrm{Prob}(\max\{\mathbf{r}_N\} = R_{max}), \tag{17}$$

where $\mathrm{Prob}(\max\{\mathbf{r}_N\} = R_{max})$ is the probability that for a d-dimensional, N-step random walk the maximal displacement from the starting point is exactly equal to R_{max}. For sufficiently large N, the leading behavior of this probability follows $\sim \exp[-\gamma_d N/R_{max}^2]$, where γ_d is a dimension-dependent constant. Substituting the latter form to Eq. (17) and noticing that the integrand is a bell-shaped function, we thus perform the integration in terms of the saddle-point method. In doing so one finds that the value of R_{max} which

provides the maximum to the integrand is given by $R^*_{max}=(2\gamma_d N/cd)^{1/(d+2)}$. Consequently, the overall decay function obeys

$$P_N \geqslant \exp[-\text{const}\times c^{2/(d+2)}N^{d/(d+2)}], \tag{18}$$

which bound displays exactly the same N dependence as the result in Eq. (16).

Another illustrative derivation can be performed starting directly from the definition of the indicator function of the reaction event Ψ_N in Eq. (9). To do this, suppose first that for a given realization of traps' placement the nearest to the origin trap B appears at a certain distance L. For such a realization, evidently, $\Psi_N=1$ for those trajectories $\{\mathbf{r}_N\}$ which do not leave within N first steps the volume L^d. Consequently, here the overall decay function can be bounded from below by

$$P_N \geqslant \max_L\{\exp[-cL^d] \times \text{Prob}(|\mathbf{r}_n|\leqslant L \quad \text{for any} \quad n\in[0,N]|0)\}, \tag{19}$$

where the first multiplier gives the probability of having a trap-free void of volume L^d, while the second one stands for the probability that a random walk starting at the origin does not leave this volume within first N steps. For N sufficiently large, the latter probability follows $\exp[-\gamma_d N/L^2]$, and hence, maximizing the right-hand side of Eq. (19) with respect to L, i.e., searching for the maximal lower bound, one ends up with the dependence of essentially the same form as that given by Eq. (18). Consequently, these bounds demonstrate that the long-time behavior of the survival probability in Eq. (16) is supported, first, by the presence of sufficiently large trap-free voids of typical size $\sim N^{1/(d+2)}$, and second, by realizations of random walks constrained not to leave these voids within time N, i.e., atypical, spatially confined realizations for which $|\mathbf{r}_N|$ grows in proportion to $N^{1/(d+2)}$ only.

To conclude this section, we emphasize that the long-time behaviors of the trapping and target annihilation problems are different. Whereas the integral effective rate constant for the target annihilation follows the behavior of the expected number of distinct sites visited, the trapping decay contains all the higher moments of this characteristic property and tends at very long times toward the asymptotic form in Eq. (16), i.e., $Q_N^{(tr)}\sim(N/c)^{d/(d+2)}$ as $N\to\infty$. Thus the decay patterns differ, depending on which of the two species in Eq. (1) is the mobile one. One consequently has a counterexample to the view that in reaction kinetics only the relative motion of the species, but not the individual movements, is important. In what follows we intend to analyze how the reaction kinetics will differ depending on which of the species precisely is being gated.

III. MODEL I: AN IMMOBILE TARGET *A* AND RANDOMLY MOVING STOCHASTICALLY GATED SCAVENGERS *B*

We start our analysis of stochastically gated pseudo-first-order reactions considering first survival of an immobile target in the presence of a concentration of mobile gated scavengers B—the model which again admits an exact solution. We suppose here that each gate can be in either of two states, one active and the other blocked. In the active state the B particles are reactive, whereas the blocked or inactive state inhibits the reaction. The gate on any B particle is supposed to update its state at each moment of time, at random, and independently of the gates imposed on the other particles. The A particle is ''annihilated'' at the very moment when any of the B particles visits it for the first time in the reactive state. Conversely, if any of the B's visits the A particle in the blocked state, both particles can harmlessly coexist with each other.

More precisely, we specify the reactive ability of the kth scavenger ($k=1,\ldots,K$) at the nth step, $n=0,1,\ldots,N$, by assigning to each of the B particles a random variable $\eta_n^{(k)}$. This random variable may assume two values: 0, with probability p, in which case the scavenger is neutral with respect to the reaction; and 1, with probability $1-p$, which corresponds to the reactive state. In all the models to be studied here, we will suppose that the reactivities of gated particles follow independent Poisson processes [14], such that all $\eta_n^{(k)}$ are independent, randomly distributed variables δ correlated with respect to n and k. The average with respect to the distribution of $\eta_n^{(k)}$ will be denoted by the overbar.

Further on, denoting as $\mathbf{S}_n^{(k)}$ the position at which the kth scavenger appears at the nth step for a given realization of its N-step trajectory $\{\mathbf{S}_N^{(k)}\}$, we construct the reaction event indicator function Ψ_N, which now takes the form

$$\Psi_N=\lim_{\beta\to\infty}\exp\left[-\beta\sum_{n=0}^{N}\sum_{k=1}^{K}\mathcal{I}(\mathbf{S}_n^{(k)})\,\eta_n^{(k)}\right] =\prod_{n=0}^{N}\prod_{k=1}^{K}\lim_{\beta\to\infty}\exp[-\beta\mathcal{I}(\mathbf{S}_n^{(k)})\,\eta_n^{(k)}], \tag{20}$$

where $\mathcal{I}(X)$ is the indicator function showing whether the kth scavenger is at the lattice origin at the nth step, or elsewhere [Eq. (3)].

The indicator function Ψ_N is equal to 1 if within the N-step random walk none of the K scavengers has visited the origin in the reactive state, and turns to zero otherwise; i.e. in the case when, within the interval $[0,N]$, at least one of the scavengers has once visited the origin in the reactive state. Its average over the reactivity fluctuations, i.e., the states of the gates $\eta_n^{(k)}$, can be performed very directly, since for the Poisson gating model under study all terms in the double product in Eq. (20) are statistically independent of each other. Consequently, we have that

$$\overline{\Psi}_N=\prod_{n=0}^{N}\prod_{k=1}^{K}\overline{\lim_{\beta\to\infty}\exp[-\beta\mathcal{I}(\mathbf{S}_n^{(k)})\,\eta_n^{(k)}]} =\prod_{n=0}^{N}\prod_{k=1}^{K}\{(1-p)\lim_{\beta\to\infty}\exp[-\beta\mathcal{I}(\mathbf{S}_n^{(k)})]+p\}. \tag{21}$$

Further on, noticing that

$$\lim_{\beta\to\infty}\exp[-\beta\mathcal{I}(\mathbf{S}_n^{(k)})]=1-\mathcal{I}(\mathbf{S}_n^{(k)}), \tag{22}$$

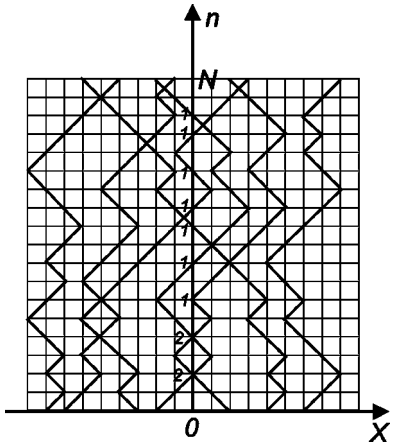

FIG. 4. Representation of the B particles' trajectories in the form of ''directed polymers.'' Numbers on the n axis denote the total number of crossings of different points on this axis by different trajectories.

and, hence, that

$$(1-p)\lim_{\beta\to\infty}\exp[-\beta\mathcal{I}(\mathbf{S}_n^{(k)})]+p=\exp[-\alpha_p\mathcal{I}(\mathbf{S}_n^{(k)})],$$

$$\alpha_p=-\ln(p), \tag{23}$$

we find that the indicator function of the reaction event Ψ_N, averaged over the reactivity fluctuations, takes the form

$$\overline{\Psi}_N=\exp[-\alpha_p\mathcal{N}(\{\mathbf{S}_N^{(k)}\})], \tag{24}$$

where

$$\mathcal{N}(\{\mathbf{S}_N^{(k)}\})=\sum_{n=0}^{N}\sum_{k=1}^{K}\mathcal{I}(\mathbf{S}_n^{(k)}). \tag{25}$$

Note now that the functional $\mathcal{N}(\{\mathbf{S}_N^{(k)}\})$ determines the number of times that K given N-step random walk trajectories $\{\mathbf{S}_N^{(k)}\}$, with their starting points at fixed positions $\mathbf{S}_0^{(k)}$, pass through the origin. Note also that here all walks contribute independently, which means that the simultaneous visit of k walkers is counted k times, and hence, $\mathcal{N}(\{\mathbf{S}_N^{(k)}\})$ can be interpreted as the ''residence time'' at the origin for K independent random walkers.

As a matter of fact, the number $\mathcal{N}(\{\mathbf{S}_N^{(k)}\})$ can be also viewed from a different perspective, which turns to be rather useful for illustration of the distinction between different models. In Fig. 4 we depict, for a one-dimensional case, a given realization of several random walks trajectories in form of ''directed polymers'' in $1+1$ dimensions, the Y-axis being the time n; in this language $\mathcal{N}(\{\mathbf{S}_N^{(k)}\})$ appears as the total number of times that an n axis is intersected on a segment $[0,N]$ by a brush of K phantom directed polymers with their ends fixed on a d-dimensional substrate. The survival probability P_N can then be thought of as the generating function of the moments of the number of visits rendered by K independent walkers to the origin during ''time'' N, or of the number of intersections of the n axis on the segment $[0,N]$ by a brush of directed polymers. In the infinite space limit P_N is hence the generating function of moments of the number of visits to the origin by random walkers which are initially uniformly distributed with a given number density c on an infinite d-dimensional lattice.

We next pass to averaging over the scavengers' trajectories. Noticing that all multipliers in Eq. (25) with the same index k are again statistically independent of the multipliers with a different k, we may write this average as

$$\begin{aligned}P_N=\langle\overline{\Psi}_N\rangle&=\left\langle\prod_{k=1}^{K}\exp\left[-\alpha_p\sum_{n=0}^{N}\mathcal{I}(\mathbf{S}_n^{(k)})\right]\right\rangle\\&=\prod_{k=1}^{K}\left\langle\exp\left[-\alpha_p\sum_{n=0}^{N}\mathcal{I}(\mathbf{S}_n^{(k)})\right]\right\rangle\\&=\left(\frac{1}{M}\sum_{\mathbf{S}_0}E_{\mathbf{S}_0}\left\{\exp\left[-\alpha_p\sum_{n=0}^{N}\mathcal{I}(\mathbf{S}_n)\right]\right\}\right)^K.\end{aligned} \tag{26}$$

Turning to the infinite space limit, we find from Eq. (26) that the survival probability P_N follows

$$\begin{aligned}P_N&=\left(1-\frac{1}{M}\sum_{\mathbf{S}_0}\left(1-E_{\mathbf{S}_0}\left\{\exp\left[-\alpha_p\sum_{n=0}^{N}\mathcal{I}(\mathbf{S}_n)\right]\right\}\right)\right)^K\\&=\exp\left[-c\sum_{\mathbf{S}_0}E_{\mathbf{S}_0}\{\mathcal{M}_{\{0\}}(\{\mathbf{S}_N\})\}\right],\end{aligned} \tag{27}$$

where $\mathcal{M}_{\{0\}}(\{\mathbf{S}_N\})$ is a functional of a given N-step random walk trajectory, which is defined by

$$\mathcal{M}_{\{0\}}(\{\mathbf{S}_N\})=\left[1-\exp\left(-\alpha_p\sum_{n=0}^{N}\mathcal{I}(\mathbf{S}_n)\right)\right]. \tag{28}$$

One notices now that $\mathcal{M}_{\{0\}}(\{\mathbf{S}_N\})$ again counts a number of visits to the origin by a given N-step random walk trajectory with its starting point being fixed at $\mathbf{S}_0$. That is, $\mathcal{M}_{\{0\}}(\{\mathbf{S}_N\})=0$ for such N-step trajectories, which never pass through the origin, equals $1-p$ for such trajectories which visit the origin only once, and $1-p^j$ for those trajectories which do it exactly j times. Consequently, the expected value of the functional $\mathcal{M}_{\{0\}}(\{\mathbf{S}_N\})$, which enters the exponential in Eq. (27), can be written down as the following polynomial in powers of the gating probability p:

$$E_{\mathbf{S}_0}\{\mathcal{M}_{\{0\}}(\{\mathbf{S}_N\})\}=\sum_{j=0}^{N}\beta_N^{(j)}(0|\mathbf{S}_0)(1-p^{j+\delta_{\mathbf{S}_0,0}}), \tag{29}$$

where $\delta_{\mathbf{S}_0,0}$ is the Kronecker δ and $\beta_N^{(j)}(0|\mathbf{S}_0)$ is the probability that a simple random walk starting from the site $\mathbf{S}_0$ visits the origin in the first N steps exactly j times [25]. We adhere here to the definition for $\beta_N^{(j)}(0|\mathbf{S}_0)$ presented in Ref. [25], and adopt the convention that the initial moment $n=0$ is regarded as the zeroth visit to the site $\mathbf{S}_0$.

We turn next to the analysis of the N-dependence of the integral effective reaction rate for the model I, $Q_N^{(I)}$. It follows from Eq. (29) that $Q_N^{(I)}$ is defined as the polynomial of the form

$$Q_N^{(I)}=\sum_{\mathbf{S}_0}\sum_{j=0}^{N}\beta_N^{(j)}(0|\mathbf{S}_0)(1-p^{j+\delta_{\mathbf{S}_0,0}}). \tag{30}$$

To compute $Q_N^{(I)}$ for any N, we introduce the generating function

$$\begin{aligned}Q^{(I)}(\xi)&\equiv\sum_{N=0}^{\infty}Q_N^{(I)}\xi^N\\&=(1-p)\sum_{N=0}^{\infty}\beta_N^{(0)}(0|0)\xi^N\\&\quad+\sum_{j=1}^{\infty}(1-p^{j+1})\sum_{N=1}^{\infty}\beta_N^{(j)}(0|0)\xi^N\\&\quad+\sum_{\mathbf{S}_0,\mathbf{S}_0\neq\mathbf{0}}\sum_{j=1}^{\infty}(1-p^j)\sum_{N=1}^{\infty}\beta_N^{(j)}(0|\mathbf{S}_0)\xi^N,\end{aligned} \tag{31}$$

where we have made use of an evident fact that all $\beta_N^{(j)}(0|\mathbf{S}_0)$ vanish for $j>N$.

Now, to evaluate the generating function $Q^{(I)}(\xi)$ explicitly, we calculate three different sums entering Eq. (31). First of all, we find that

$$\begin{aligned}&(1-p)\sum_{N=0}^{\infty}\beta_N^{(0)}(0|0)\xi^N\\&=(1-p)\left\{1+\sum_{N=1}^{\infty}\left(1-\sum_{n=1}^{N}F_n(0|0)\right)\xi^N\right\}\\&=(1-p)\left\{1+\frac{\xi}{1-\xi}-\sum_{n=1}^{\infty}F_n(0|0)\sum_{N=n}^{\infty}\xi^N\right\}\\&=\frac{1-p}{1-\xi}(1-F(0|0;\xi)),\end{aligned} \tag{32}$$

where $F(0|0;\xi)$ is the generating function of $F_n(0|0)$—the average probability that a random walk trajectory starting at the origin returns to the origin for the first time exactly on the nth step [25]. Further on, we have

$$\begin{aligned}&\sum_{j=1}^{\infty}(1-p^{j+1})\sum_{N=1}^{\infty}\beta_N^{(j)}(0|0)\xi^N\\&=\frac{1}{1-\xi}(1-F(0|0;\xi))\sum_{j=1}^{\infty}(1-p^{j+1})F(0|0;\xi)^j\\&=\frac{1-p}{1-\xi}\,\frac{F(0|0;\xi)[1+p(1-F(0|0;\xi))]}{1-pF(0|0;\xi)},\end{aligned} \tag{33}$$

and, eventually,

$$\begin{aligned}&\sum_{\mathbf{S}_0\neq\mathbf{0}}\sum_{j=1}^{\infty}(1-p^j)\sum_{N=1}^{\infty}\beta_N^{(j)}(0|\mathbf{S}_0)\xi^N\\&=\frac{1-F(0|0;\xi)}{1-\xi}\left[\sum_{j=1}^{\infty}(1-p^j)F(0|0;\xi)^{j-1}\right]\\&\quad\times\left[\sum_{\mathbf{S}_0\neq\mathbf{0}}F(0|S_0;\xi)\right]\\&=\frac{1-F(0|0;\xi)}{1-\xi}\,\frac{1-p}{(1-F(0|0;\xi))(1-pF(0|0;\xi))}\\&\quad\times(1-F(0|0;\xi))\left[\frac{1}{1-\xi}-P(0|0;\xi)\right]\\&=\frac{1-p}{1-\xi}\,\frac{1-F(0|0;\xi)}{1-pF(0|0;\xi)}\left[\frac{1}{1-\xi}-P(0|0;\xi)\right],\end{aligned} \tag{34}$$

where $P(0|0;\xi)$, as usual, stands for the generating function of the probability $P_N(0|0)$ of having a walker at the origin on the Nth step, provided that the walker started his random walk at the origin. Consequently, summing up the results in Eqs. (32)–(34), we obtain the following exact expression for the generating function:

$$\begin{aligned}Q^{(I)}(\xi)&=\frac{(1-p)}{(1-\xi)^2}\,\frac{1-F(0|0;\xi)}{1-pF(0|0;\xi)}\\&=\frac{1}{(1-\xi)^2}\,\frac{(1-p)}{p+(1-p)P(0|0;\xi)}\\&=S(\xi)\left[1+\frac{p}{(1-p)P(0|0;\xi)}\right]^{-1},\end{aligned} \tag{35}$$

$S(\xi)$ being the generating function of the expected number of distinct sites visited by an N-step random walk [25], $S(\xi)=\Sigma_{N=0}^{\infty}E_0\{S(\{\mathbf{S}_N\})\}\xi^N$. In principle, the integral effective reaction rate for model I valid for any N can be obtained now by inverting the result in Eq. (35), which will require, however, computation of very complex integrals.

We now turn to an analysis of the large-N behavior of the reaction rate $Q_N^{(I)}$. However, before doing this, it may be expedient to make first the following observation, which might seem to be quite surprising at the first glance:

The result in Eq. (35) reveals that for *recurrent* random walks the leading large-N behavior of the integral reaction rate $Q_N^{(I)}$ should be *independent* of the gating probability. It happens actually because for recurrent walks $P(0|0;\xi)\to+\infty$ as $\xi\to1^-$ ($N\to\infty$), and hence, the expression on the right-hand side of Eq. (35) appears to be independent of p. In virtue of the Tauberian theorem, it implies that the effective integral reaction rate $Q_N^{(I)}$ is independent of p when $N\to\infty$. Moreover, the result in Eq. (35) shows that for recurrent walks the leading at $N\to\infty$ behavior of $Q_N^{(I)}$ is defined exactly by the expected number of distinct sites visited by an N-step random walk. Consequently, for recurrent walks and $N\to\infty$ the target survival probability P_N is not influenced by fluctuating gates imposed on the scavengers, and has exactly

the same form for reactions which are subject to stochastic gating or reactions in which the scavengers are always in the reactive state [20–22].

On the other hand, such a behavior is not counterintuitive and agrees with our previous knowledge of the diffusion-limited reactions kinetics. The point is that imposing a fluctuating gate on otherwise perfect scavengers is in a way similar to imposing the constraint that annihilation of the target by a scavenger may happen with some finite probability, or at a finite rate prescribed by certain elementary reaction act constant K_{el} ($K_{el}<\infty$). Following the seminal mean-field analysis of Collins and Kimball [31] (see also Refs. [18] and [33] for more details), the overall reaction constant taking into account both the constraints imposed by the elementary reaction act (finite K_{el}) and the transport limitations (in order to react, particles have first to find each other in the course of their random motions) follows

$$(\partial Q_N/\partial N)^{-1}=\frac{1}{K_{el}}+\frac{1}{K_{Smol}}, \tag{36}$$

where K_{Smol} is the so-called Smoluchowski constant which equals the diffusive current through the surface of an immobile, perfectly adsorbing sphere. Now, it is well-known (see, e.g., Ref. [18] for more discussion) that for low-dimensional systems the Smoluchowski constant is not a real constant but rather a time-dependent coefficient which vanishes as time evolves. This means that in low dimensions random transport of particles offers progressively higher resistance with respect to the overall reaction rate than the constraints imposed by the elementary reaction rate, which results ultimately in a kinetics which is totally controlled by random transport of particles toward each other and is independent of K_{el}. This is precisely the effect which we observe in case of low-dimensional stochastically gated target annihilation problem.

We note also parenthetically that a similar effect was recently predicted for low-dimensional catalytically activated binary reactions, in which case the particles' reactivity does not fluctuate in time but is rather a random function of the space variables [32]. It has been shown here that the long-time kinetics is also insensitive to the concentration of the catalytic sites which promote reactions between randomly moving A particles and is independent of K_{el}. Of course, in higher-dimensional space (such that d is greater than the fractal dimension of the random walk) the effective reaction rate does depend on the density of catalytic sites and K_{el}. Similarly, for stochastically gated target annihilation reactions, $P(0|0;1^-)$ is well defined for $d>2$, which implies, by virtue of Eq. (35), that the leading at $N\to\infty$ terms in the integral effective reaction rate should depend on the gating probability p.

We focus next on the special case of Polya random walks and proceed to determine the long-time behavior of the reaction rate in Eq. (35) explicitly, first for one- and two-dimensional lattices, in which case the Polya walks are recurrent, and then for d-dimensional lattices with $d>2$, for which the walks are nonrecurrent.

A. Polya walks on one-dimensional lattices

For Polya random walks on one-dimensional lattices the generating function of the first-visit probability is known exactly and has a particularly simple form (see, e.g., Ref. [25]), $F(0|0;\xi)=1-\sqrt{1-\xi^2}$. Consequently, in this case the generating function $Q^{(I)}(\xi)$ of the integral effective reaction rate obeys

$$Q^{(I)}(\xi)=\frac{(2\xi-1)(1-p)}{(1-\xi)^{3/2}}\,\frac{\sqrt{1+\xi}}{1-p+p\sqrt{1-\xi^2}}. \tag{37}$$

In the asymptotical limit $\xi\to1^-$ (or equivalently, when $N\to\infty$) we find then from Eq. (37) that

$$Q^{(I)}(\xi)=\frac{\sqrt{2}}{(1-\xi)^{3/2}}-2\frac{p}{(1-p)(1-\xi)}+O(1/\sqrt{(1-\xi)}). \tag{38}$$

Hence, by virtue of a Tauberian theorem, we have that, in the limit $N\to\infty$, the effective reaction rate follows

$$Q_N^{(I)}=\left(\frac{8N}{\pi}\right)^{1/2}-2\frac{p}{1-p}+O\left(\frac{1}{\sqrt{N}}\right), \tag{39}$$

i.e., as we have already remarked, the leading behavior as $N\to\infty$ in case of the target annihilation problem with stochastic gates imposed on the scavengers is exactly the same as in the case of its ungated counterpart [Eq. (8)]. The first correction term, however, does depend on the gating probability p and diverges when $p\to1$, i.e., in the limit when scavengers are being completely inert with respect to the reaction. A simple comparison of the first two terms in Eq. (39) shows that the universal, p-independent behavior is established when N exceeds a certain crossover value N^*, such that $N^*\approx\pi p^2/2(1-p)^2$. Note also that a similar behavior has been predicted earlier in Ref. [13] within the framework of a continuous-space description.

B. Polya walks on two-dimensional lattices

The generating function $P(0,0|\xi)$ is not known explicitly for Polya walks on two-dimensional lattices. However, its asymptotical behavior as $\xi\to1^-$ (or, equivalently, when $N\to\infty$) is well documented (see, e.g., Ref. [25]), and is given by

$$P(0|0;\xi)=\frac{1}{\pi C_2}\ln\left(\frac{K}{1-\xi}\right)[1+O(1-\xi)], \tag{40}$$

where the constant C_2 has been defined in the text after Eq. (8), while the constant K equals 4, 8, and 12 for hexagonal, square, and triangular lattices, respectively.

From the latter equation we find then that the leading asymptotical behavior of $Q^{(I)}(\xi)$ as $\xi\to1^-$ follows

$$Q^{(I)}(\xi)=-\frac{\pi C_2}{(1-\xi)^2\ln(1-\xi)}-\pi^2\left(p+\frac{(1-p)\ln(K)}{\pi C_2}\right)\times\frac{C_2^2}{(1-p)(1-\xi)^2\ln^2(1-\xi)}+O\left(\frac{1}{\ln^3(1-\xi)(1-\xi)^2}\right). \tag{41}$$

Hence, by applying the Tauberian theorem we find that for two-dimensional target annihilation with stochastically-gated scavengers the integral effective reaction rate obeys

$$Q_N^{(I)} = \pi C_2 \frac{N}{\ln(N)} + \pi C_2[1-\gamma-\ln(K)-p\,\pi/C_2(1-p)] \times \frac{N}{\ln^2(N)} + O\left(\frac{N}{\ln^3(N)}\right), \tag{42}$$

where γ denotes the Euler constant. Note that again, in accord with our earlier prediction, the leading large-N behavior appears to be independent of the gating probability and proceeds exactly in the same way as for the ungated target problem. This long-time regime can be observed, however, at considerably longer times than that for the one-dimensional systems; on comparing the first two terms on the right-hand side of Eq. (42) we infer that the corresponding crossover time N^* is given by

$$N^* \approx \exp\left[\frac{\pi C_2 p}{1-p}\right], \tag{43}$$

i.e., is *exponentially* large when $p \to 1$, while in one-dimensional systems this dependence is only algebraic.

C. Polya walks on d-dimesional lattices, $d>2$

Finally, we turn to the case of recurrent Polya walks, which case is realized, namely, for lattices with spatial dimension $d>2$. Here the probability R of eventual return to the origin is finite, and consequently, we find from Eq. (35) that

$$Q^{(I)}(\xi) = \frac{1-p}{(1-p)P(0|0;1^-)+p}\,\frac{1}{(1-\xi)^2} + O\left(\frac{1}{(1-\xi)^{3/2}}\right), \tag{44}$$

which yields, in the large-N limit, the result

$$Q_N^{(I)} = \frac{1-p}{(1-p)P(0|0;1^-)+p} N + O(\sqrt{N}) \tag{45}$$

Hence, for lattices with $d>2$, the decay of the survival probability is purely exponential in all dimensions. Note also that the exact result in Eq. (45) confirms in a way the mean-field result by Collins and Kimball [Eq. (36)]; as a matter of fact, it appears that Eq. (45) can be cast exactly into the form of Eq. (36) if we set $K_{el}=(1-p)/p$ and $K_{smol} = 1/P(0|0;1^-)$. Note also that our Eq. (45) confirms the conclusion of Szabo *et al.* [11] concerning the possibility of the calculation of the steady-state stochastically gated rate constant in terms of an appropriately defined ungated model.

IV. MODEL II: AN IMMOBILE FLUCTUATING TARGET AND RANDOMLY MOVING UNGATED SCAVENGERS

We turn next to the survival of a *stochastically* gated, immobile A particle—a target, in the presence of ungated scavengers B, which perform independent random walks on a d-dimensional lattice. For this model the indicator function of the reaction event can be written down as

$$\Psi_N = \lim_{\beta\to\infty} \exp\left[-\beta \sum_{n=0}^{N} \eta_n \sum_{k=1}^{K} \mathcal{I}(\mathbf{S}_n^{(k)})\right], \tag{46}$$

where η_n is the indicator variable of the gate imposed on the target, while $\mathbf{S}_n^{(k)}$ defines the lattice positions of the kth scavenger at the nth step, $n=0,1,\ldots,N$. We again suppose that the target reactivity assumes at random two values -1 and 0 with probabilities $1-p$ and p, respectively. In the state $\eta_n = 1$ the target is accessible for reaction and can be annihilated by any of the scavengers arriving at the origin, while in the state $\eta_n = 0$ reaction cannot take place.

Averaging first Ψ_N in Eq. (46) with respect to the fluctuations of the reactivity, we obtain

$$\overline{\Psi}_N = \overline{\prod_{n=0}^{N} \lim_{\beta\to\infty} \exp\left[-\beta\eta_n \sum_{k=1}^{K} \mathcal{I}(\mathbf{S}_n^{(k)})\right]} = \prod_{n=0}^{N} \left\{(1-p)\lim_{\beta\to\infty}\exp\left[-\beta\sum_{k=1}^{K}\mathcal{I}(\mathbf{S}_n^{(k)})\right]+p\right\}. \tag{47}$$

Further on, noticing that

$$(1-p)\lim_{\beta\to\infty}\exp\left[-\beta\sum_{k=1}^{K}\mathcal{I}(\mathbf{S}_n^{(k)})\right]+p = \begin{cases} 1, & \sum_{k=1}^{K}\mathcal{I}(\mathbf{S}_n^{(k)})=0 \\ p, & \sum_{k=1}^{K}\mathcal{I}(\mathbf{S}_n^{(k)})>0, \end{cases} \tag{48}$$

and hence, rewriting this expression as

$$(1-p)\lim_{\beta\to\infty}\exp\left[-\beta\sum_{k=1}^{K}\mathcal{I}(\mathbf{S}_n^{(k)})\right]+p = \exp\left\{-\alpha_p\left[1-\mathcal{I}\left(\sum_{k=1}^{K}\mathcal{I}(\mathbf{S}_n^{(k)})\right)\right]\right\}, \tag{49}$$

we find that the indicator function of the reaction event, averaged over the fluctuations of the target reactivity, attains the form

$$\overline{\Psi}_N = \exp[-\alpha_p \mathcal{N}^*(\{\mathbf{S}_N^{(k)}\})], \tag{50}$$

where $\mathcal{N}^*(\{\mathbf{S}_N^{(k)}\})$ is given by

$$\mathcal{N}^*(\{\mathbf{S}_N^{(k)}\}) = \sum_{n=0}^{N}\left[1-\mathcal{I}\left(\sum_{k=1}^{K}\mathcal{I}(\mathbf{S}_n^{(k)})\right)\right] \tag{51}$$

Note now that the functional $(1-\mathcal{I}[\Sigma_{k=1}^{K}\mathcal{I}(\mathbf{S}_n^{(k)})])$ measures the occupancy of the origin at time moment n. It equals zero if none of K walkers is present at the origin at the time moment n and equals 1 if one or several scavengers appear at the origin at the nth step. In this regard, $\mathcal{N}^*(\{\mathbf{S}_N^{(k)}\})$ is similar to the earlier defined functional $\mathcal{N}(\{\mathbf{S}_N^{(k)}\})$ appearing in the analysis of model I. An important difference, however, is that a simultaneous visit of the origin by several walkers is counted as a single visit, and consequently, $\mathcal{N}^*(\{\mathbf{S}_N^{(k)}\})$ describes *collective* behavior of all K walkers, which cannot be factorized, as it appears in model I. This substantial distinction between the models involving ungated and gated targets was noticed already by Szabo *et al.* in Ref. [12] (see, also Ref. [13] for more details), who stated that the crucial difference between the case when the gates are imposed on B's or on the A particle is that in the latter case the ''switching of the A from the reactive conformation to a nonreactive one is felt simulateneously by all scavengers.'' This means, in particular that, if we define the functional $\mathcal{N}^*(\{\mathbf{S}_N^{(k)}\})$ using the ''directed'' polymer representation in Fig. 4, then it would count all sites on the n axis visited simultaneously by two, three, etc., walkers as singly visited sites. In this regard, $\mathcal{N}^*(\{\mathbf{S}_N^{(k)}\})$ determines the number of *distinct* visits to the origin by K independent walkers.

We notice next that an upper bound on the integral effective reaction rate $Q_N^{(II)}$ for model II can be found very straightforwardly. To do this, it suffices merely to observe that

$$1-\mathcal{I}\left(\sum_{k=1}^{K}\mathcal{I}(\mathbf{S}_n^{(k)})\right)\leqslant\sum_{k=1}^{K}\mathcal{I}(\mathbf{S}_n^{(k)}), \tag{52}$$

and hence, that $\mathcal{N}^*(\{\mathbf{S}_N^{(k)}\})\leqslant\mathcal{N}(\{\mathbf{S}_N^{(k)}\})$. This implies, in turn, that the survival probability P_N for model II is greater than the survival probability obtained for model I, and the integral effective reaction rate $Q_N^{(II)}$ obeys

$$Q_N^{(II)}\leqslant Q_N^{(I)}, \tag{53}$$

which inequality sets a rigorous upper bound on $Q_N^{(II)}$. Note that the inequality in Eq. (53) was established earlier using different type of arguments in Ref. [15].

It may be worthy to remark that the inequality in Eq. (52) holds as an equality when all $\mathbf{S}_n^{(k)}$ are different at a given n, which happens when the scavengers do obey a hard-core exclusion and no two scavengers can simultaneously occupy the same lattice site. Given that the scavegers are indistinguishable, we may thus expect that for model II with hard-core scavengers, the A particle survival probability will be determined exactly by Eqs. (39)–(45) at sufficiently large times.

We next proceed to calculate the upper bound on the survival probability for model II, which requires a slightly more complicated analysis. To do this, we return to the indicator function of the reaction event in Eq. (47) and perform a first averaging with respect to the trajectories and the initial positions of the scavengers. The steps involved in the averaging procedure in this case are as follows:

$$\begin{aligned}\langle\Psi_N\rangle&=\left\langle\prod_{k=1}^{K}\lim_{\beta\to\infty}\exp\left\{-\beta\sum_{n=0}^{N}\eta_n\mathcal{I}(\mathbf{S}_n^{(k)})\right\}\right\rangle\\&=\prod_{k=1}^{K}\left\langle\lim_{\beta\to\infty}\exp\left\{-\beta\sum_{n=0}^{N}\eta_n\mathcal{I}(\mathbf{S}_n^{(k)})\right\}\right\rangle\\&=\prod_{k=1}^{K}\left(\frac{1}{M}\sum_{\mathbf{S}_0}\mathrm{E}_{\mathbf{S}_0}\left\{\lim_{\beta\to\infty}\exp\left(-\beta\sum_{n=0}^{N}\eta_n\mathcal{I}(\mathbf{S}_n^{(k)})\right)\right\}\right)\\&=\left(\frac{1}{M}\sum_{\mathbf{S}_0}\mathrm{Prob}\,\{\eta_n\mathcal{I}(\mathbf{S}_n)=0\right.\\&\qquad\left.\text{for any}\quad n\in[0,N]|\mathbf{S}_0\}\right)^K,\end{aligned} \tag{54}$$

where $\mathrm{Prob}(\eta_n\mathcal{I}(\mathbf{S}_n)=0\ \text{ for any }\ n\in[0,N]|\mathbf{S}_0)$ is the probability that an N-step random walk, starting at $\mathbf{S}_0$ and characterized by internal two-state variable η_n, has never visited the origin being in the reactive state $\eta_n=1$. Next, turning to the infinite-space limit, we find

$$\begin{aligned}\langle\Psi_N\rangle&=\left(1-\frac{1}{M}\sum_{\mathbf{S}_0}\{1-\mathrm{Prob}[\,\eta_n\mathcal{I}(\mathbf{S}_n)=0\right.\\&\qquad\left.\text{for any}\quad n\in[0,\,N]|\mathbf{S}_0]\}\right)^K\\&=\exp\left[-c\sum_{\mathbf{S}_0}\{1-\mathrm{Prob}[\,\eta_n\mathcal{I}(\mathbf{S}_n)=0\right.\\&\qquad\left.\text{for any}\quad n\in[0,\,N]|\mathbf{S}_0]\}\right].\end{aligned} \tag{55}$$

Evidently,

$$\begin{aligned}&1-\mathrm{Prob}[\,\eta_n\mathcal{I}(\mathbf{S}_n)=0\ \text{ for any }\ n\in[0,\,N]|\mathbf{S}_0]\\&\qquad=\mathrm{Prob}\left(\sum_{n=0}^{N}\eta_n\mathcal{I}(\mathbf{S}_n)\geqslant1\,\middle|\,\mathbf{S}_0\right),\end{aligned} \tag{56}$$

where $\mathrm{Prob}[\Sigma_{n=0}^{N}\eta_n\mathcal{I}(\mathbf{S}_n)\geqslant1|\mathbf{S}_0]$ is the probability that an N-step random walk starting at site $\mathbf{S}_0$ has at least once visited the origin being in the reactive state.

Note that $\mathrm{Prob}[\Sigma_{n=0}^{N}\eta_n\mathcal{I}(\mathbf{S}_n)\geqslant1|\mathbf{S}_0]$ is not constrained in the sense that it provides no information at which of the visits to the origin precisely the reactive state has appeared; that is, the particle could visit the origin many times until it arrived eventually at the reactive state. Keeping this in mind, we now realize how the sum in the exponent in the last line of Eq. (55) can be bounded from below, which will result in the desired upper bound on the target survival probability in model II. To do this, we will proceed as follows: Suppose first that the starting point of the trajectory $\{\mathbf{S}_N\}$ is not the origin. Then we notice that, for $\mathbf{S}_0\neq\mathbf{0}$, one has

$$\mathrm{Prob}\left(\sum_{n=0}^{N}\eta_n\mathcal{I}(\mathbf{S}_n)\geqslant 1\,\middle|\,\mathbf{S}_0\right) \geqslant \sum_{n=0}^{N}\mathrm{Prob}\left(\eta_n\mathcal{I}(\mathbf{S}_n)=1 \text{ and } \sum_{l=0}^{n-1}\eta_l\mathcal{I}(\mathbf{S}_l)=0\,\middle|\,\mathbf{S}_0\right), \tag{57}$$

where $\mathrm{Prob}[\eta_n\mathcal{I}(\mathbf{S}_n)=1 \text{ and } \Sigma_{l=0}^{n-1}\eta_l\mathcal{I}(\mathbf{S}_l)=0|\mathbf{S}_0]$ stands for the probability that the origin has been visited for the first time exactly at the nth step (has not been visited prior to the nth step), and the particle at this very step was in the reactive state, i.e., such that $\eta_n=1$. Hence the right-hand side of Eq. (57) is the constrained probability that within an N-step walk starting at the site $\mathbf{S}_0\neq\mathbf{0}$ the particle happened to be in the reactive state at its first visit to the origin. Summing next both sides of the inequality in Eq. (57) over all starting points, we obtain

$$\begin{aligned}\sum_{\mathbf{S}_0}\mathrm{Prob}\left(\sum_{n=0}^{N}\eta_n\mathcal{I}(\mathbf{S}_n)\geqslant 1\,\middle|\,\mathbf{S}_0\right) &\geqslant \sum_{\mathbf{S}_0,\mathbf{S}_0\neq\mathbf{0}}\mathrm{Prob}\left(\sum_{n=0}^{N}\eta_n\mathcal{I}(\mathbf{S}_n)\geqslant 1\,\middle|\,\mathbf{S}_0\right)\\ &\geqslant \sum_{\mathbf{S}_0,\mathbf{S}_0\neq\mathbf{0}}\sum_{n=0}^{N}\times\mathrm{Prob}\left(\eta_n\mathcal{I}(\mathbf{S}_n)=1 \text{ and } \sum_{l=0}^{n-1}\eta_l\mathcal{I}(\mathbf{S}_l)=0\,\middle|\,\mathbf{S}_0\right)\\ &= \sum_{\mathbf{S}_0,\mathbf{S}_0\neq\mathbf{0}}\sum_{n=0}^{N}\eta_n F_n(0|\mathbf{S}_0)=\sum_{n=0}^{N}\eta_n\sum_{\mathbf{S}_0,\mathbf{S}_0\neq\mathbf{0}}F_n(0|\mathbf{S}_0)\\ &= \sum_{n=0}^{N}\eta_n\sum_{\mathbf{S}_0}F_n(\mathbf{S}_0|0)=\sum_{n=0}^{N}\eta_n E_0\{\Delta(\{\mathbf{S}_n\})\},\end{aligned} \tag{58}$$

where $\Delta(\{\mathbf{S}_n\})$ is an auxiliary random variable, defined to be the number of $virgin$ sites visited on the nth step by a given particle trajectory $\{\mathbf{S}_n\}$ [25],

$$\Delta(\{\mathbf{S}_n\})=\mathcal{S}(\{\mathbf{S}_n\})-\mathcal{S}(\{\mathbf{S}_{n-1}\}). \tag{59}$$

Consequently, we can bound the right-hand side of Eq. (55) as

$$\begin{aligned}P_N &\leqslant \overline{\exp\left[-c\sum_{n=0}^{N}\eta_n E_0\{\Delta(\{\mathbf{S}_n\})\}\right]}\\ &= \prod_{n=0}^{N}\overline{\exp[-c\,\eta_n E_0\{\Delta(\{\mathbf{S}_n\})\}]}\\ &= \prod_{n=0}^{N}\{(1-p)\exp[-cE_0\{\Delta(\{\mathbf{S}_n\})\}]+p\}.\end{aligned} \tag{60}$$

Further on, following the Dvoretzky-Erdös Lemma, $E_0\{\Delta(\{\mathbf{S}_n\})\}$ is a monotonic decreasing sequence of time n (see, e.g., Ref. [25]), i.e.,

$$\begin{aligned}1\geqslant E_0\{\Delta(\{\mathbf{S}_1\})\}\geqslant E_0\{\Delta(\{\mathbf{S}_2\})\}\geqslant\cdots\geqslant E_0\{\Delta(\{\mathbf{S}_n\})\}\geqslant\cdots\\ \geqslant E_0\{\Delta(\{\mathbf{S}_N\})\},\end{aligned} \tag{61}$$

such that

$$\lim_{n\to\infty}E_0\{\Delta(\{\mathbf{S}_n\})\}=\frac{1}{P(0|0;1^-)}; \tag{62}$$

we can majorize the terms in the curly brackets on the right-hand side of Eq. (60) by replacing $E_0\{\Delta(\{\mathbf{S}_n\})\}$ by its minimal value $E_0\{\Delta(\{\mathbf{S}_N\})\}$. Enhancing in such a way the bound in Eq. (60), we have that

$$\begin{aligned}P_N &\leqslant \prod_{n=0}^{N}[(1-p)\exp[-cE_0\{\Delta(\{\mathbf{S}_N\})\}]+p]\\ &= [(1-p)\exp[-cE_0\{\Delta(\{\mathbf{S}_N\})\}]+p]^{N+1}\\ &= \exp\{-(N+1)\ln[1/((1-p)\\ &\quad\times\exp[-cE_0\{\Delta(\{\mathbf{S}_N\})\}]+p)]\}\end{aligned} \tag{63}$$

and hence, the integral effective rate constant obeys

$$Q_N^{(II)}\geqslant\frac{(N+1)}{c}\ln[1/((1-p)\exp[-cE_0\{\Delta(\{\mathbf{S}_N\})\}]+p)]. \tag{64}$$

For d-dimesnional Polya walks, in particular, from Eq. (64) we find the following explicit lower bounds on the integral effective rate constant in the model II:

$$\begin{aligned}d=1,&\quad Q_N^{(II)}\geqslant(1-p)\left(\frac{2N}{\pi}\right)^{1/2}[1+O(1/\sqrt{N})],\\ d=2,&\quad Q_N^{(II)}\geqslant(1-p)\frac{\pi C_2 N}{\ln(N)}[1+O(1/\ln(N))],\\ d>2,&\quad Q_N^{(II)}\geqslant\frac{N}{c}\ln[1/((1-p)\\ &\qquad\times\exp[-c/P(0|0;1^-)]+p)]\\ &\qquad\times[1+O(1/\sqrt{N})],\end{aligned} \tag{65}$$

which hold in the limit $N\to\infty$.

On comparing the results in Eqs. (53) and (65), we notice that both lower and upper bounds display the same N dependence, but differ slightly in numerical factors. This means, in turn, that the N dependence of the integral effective reaction rate $Q_N^{(II)}$ is determined here exactly by Eqs. (53) and (65). Consequently, at sufficiently large times the decay laws in the models I and II of gated target annihilation are essentially the same (up to a possible difference in characteristic decay times), and coincide with the decay law predicted for the ungated model of Sec. II.

Note also that the time evolution of the A particle survival probability for the model II defined in a one-dimensional continuum was considered earlier in Ref. [13]. Within the framework of the heuristic Smoluchowski-type approach, it

was predicted that the long-time decay of P_N should follow the decay law in the first line in Eq. (8), i.e., should proceed at long times exactly in the same fashion as that for the model I and, consequently, should be essentially the same as in the ungated target problem. While intuitively such a behavior seems to be quite plausible for low-dimensional systems [see the discussion following the Collins-Kimball result in Eq. (36)] and, as a matter of fact, agrees with our prediction in Eq. (53), one still cannot, in principle, rule out the possibility that the integral effective reaction rates for models I and II may have different numerical factors even in low dimensions. The point is that the Smoluchowski approach in Ref. [13], which is a continuous-space counterpart of the Rosenstock approximation, here allows one to determine only a lower bound on the target survival probability and thus cannot produce exact numerical factors.

V. MODEL III: AN UNGATED, MOBILE *A* PARTICLE AND IMMOBILE, RANDOMLY PLACED, STOCHASTICALLY GATED TRAPS *B*

We turn next to the case of stochastically gated trapping reactions, focusing first on the situation involving an ungated *A* particle, which performs a discrete-time, homogeneous random walk on a *d*-dimensional lattice starting from the origin at $n=0$, in the presence of immobile, randomly placed, stochastically gated *B* particles. The properties of the gates are the same as defined in model I.

For this model, the indicator function of the reaction event can be written down

$$\Psi_N = \lim_{\beta\to\infty} \exp\left[-\beta \sum_{n=0}^{N} \sum_{k=1}^{K} \mathcal{I}(\mathbf{r}_n - \mathbf{S}^{(k)})\, \eta_n^{(k)} \right] = \prod_{n=0}^{N} \prod_{k=1}^{K} \lim_{\beta\to\infty} \exp[-\beta \mathcal{I}(\mathbf{r}_n - \mathbf{S}^{(k)})\, \eta_n^{(k)}], \qquad (66)$$

where $\mathbf{S}^{(k)}$ are *d*-dimensional lattice vectors denoting positions of *K* traps *B*, while $\mathbf{r}_n$ defines the lattice position of the *A* particle at the *n*th step.

Averaging first over the reactivity of the traps, we readily find

$$\overline{\Psi}_N = \prod_{n=0}^{N} \prod_{k=1}^{K} \overline{\lim_{\beta\to\infty} \exp[-\beta \mathcal{I}(\mathbf{r}_n - \mathbf{S}^{(k)})\, \eta_n^{(k)}]} = \prod_{n=0}^{N} \prod_{k=1}^{K} \{(1-p) \lim_{\beta\to\infty} \exp[-\beta \mathcal{I}(\mathbf{r}_n - \mathbf{S}^{(k)})] + p\}. \qquad (67)$$

Further on, noticing that

$$(1-p) \lim_{\beta\to\infty} \exp[-\beta \mathcal{I}(\mathbf{r}_n - \mathbf{S}^{(k)})] + p = \begin{cases} p, & \mathbf{r}_n = \mathbf{S}^{(k)} \\ 1, & \mathbf{r}_n \neq \mathbf{S}^{(k)}, \end{cases} \qquad (68)$$

and hence, rewriting this expression as

$$(1-p) \lim_{\beta\to\infty} \exp[-\beta \mathcal{I}(\mathbf{r}_n - \mathbf{S}^{k})] + p = \exp[-\alpha_p \mathcal{I}(\mathbf{r}_n - \mathbf{S}^{k})], \qquad (69)$$

we have that the indicator function of the reaction event, averaged over the reactivity fluctuations, takes the following form:

$$\overline{\Psi}_N = \exp\left[-\alpha_p \sum_{n=0}^{N} \sum_{k=1}^{K} \mathcal{I}(\mathbf{r}_n - \mathbf{S}^{(k)}) \right]. \qquad (70)$$

Note that the averaged indicator function $\overline{\Psi}_N$ is now an exponential of the factor α_p times the number of times a given random walk trajectory starting at $n=0$ at the origin visits a given array of lattice sites $\{\mathbf{S}^{(k)}\}$, i.e., can be thought of as the moment generating function of the ''residence time'' of a single random walker on a given array $\{\mathbf{S}^{(k)}\}$. From a different perspective, Ψ_N can be viewed as the partition function of a phantom polymer chain on a lattice with randomly placed energetic barriers of finite height: the limit $\alpha_p \to \infty$ $(p \to 0)$, then corresponding to the case of randomly placed, impenetrable obstacles [28].

Now the double average over the trajectories of the *A* particle and over the positions of the traps can be written down as follows:

$$\begin{aligned} P_N = \langle \overline{\Psi}_N \rangle &= E_0\left\{ \left\langle \prod_{k=1}^{K} \exp\left[-\alpha_p \sum_{n=0}^{N} \mathcal{I}(\mathbf{r}_n - \mathbf{S}^{(k)}) \right] \right\rangle \right\} \\ &= E_0\left\{ \prod_{k=1}^{K} \left\langle \exp\left[-\alpha_p \sum_{n=0}^{N} \mathcal{I}(\mathbf{r}_n - \mathbf{S}^{(k)}) \right] \right\rangle \right\} \\ &= E_0\left\{ \left(\frac{1}{M} \sum_{\mathbf{S}} \exp\left[-\alpha_p \sum_{n=0}^{N} \mathcal{I}(\mathbf{r}_n - \mathbf{S}) \right] \right)^K \right\}. \end{aligned} \qquad (71)$$

Turning next to the infinite-space limit, i.e., letting $M, K \to \infty$, while keeping their ratio fixed, we have that

$$\begin{aligned} P_N &= E_0\left\{ \left(1 - \frac{1}{M} \sum_{\mathbf{S}} \left[1 - \exp\left(-\alpha_p \sum_{n=0}^{N} \mathcal{I}(\mathbf{r}_n - \mathbf{S}) \right) \right] \right)^K \right\} \\ &= E_0\left\{ \exp\left[-c \sum_{\mathbf{S}} \mathcal{M}_{\{\mathbf{S}\}}(\{\mathbf{r}_N\}) \right] \right\}, \end{aligned} \qquad (72)$$

where $\mathcal{M}_{\{\mathbf{S}\}}(\{\mathbf{r}_N\})$ is defined by

$$\mathcal{M}_{\{\mathbf{S}\}}(\mathbf{r}_n) = \left(1 - \exp\left[-\alpha_p \sum_{n=0}^{N} \mathcal{I}(\mathbf{r}_n - \mathbf{S}) \right] \right). \qquad (73)$$

Note that $\mathcal{M}_{\{\mathbf{S}\}}(\{\mathbf{r}_N\})$ is quite similar to the functional defined in Eq. (28), with the only minor difference being that the latter is associated with the multiple visits to some given site $\mathbf{S}$; that is, $\mathcal{M}_{\{\mathbf{S}\}}(\{\mathbf{r}_N\}) = 1 - p^j$ if the site $\mathbf{S}$ is visited exactly *j* times by an *N*-step walk starting at the site $\mathbf{r}_0 = \mathbf{0}$. Consequently, the sum $\Sigma_{\mathbf{S}} \mathcal{M}_{\{\mathbf{S}\}}(\{\mathbf{r}_N\})$ probes the occupancy of the sites visited by a given realization of a random walk trajectory (see Fig. 5).

However, an important difference with the previously considered model, which makes the computation of P_N for

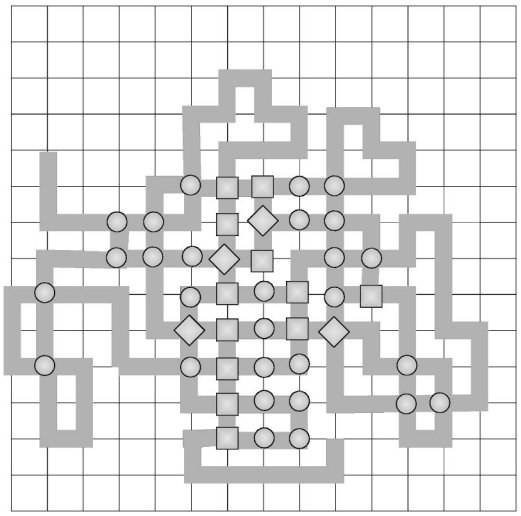

FIG. 5. A realization of the $N=130$ step random walk trajectory $\{\mathbf{r}_N\}$ on a two-dimensional square lattice. The sites visited two times are marked by circles, the sites visited three times by squares, and the sites visited four times by diamonds. For this particular realization $\Sigma_S \mathcal{M}_{\{\mathbf{S}\}}(\{\mathbf{r}_N\})$ is a fourth-order polynomial with respect to the gating probability p of the form $\Sigma_S \mathcal{M}_{\{\mathbf{S}\}}(\{\mathbf{r}_N\}) = 113 - 69p - 28p^2 - 12p^3 - 4p^4$. The coefficients in this polynomial are random, correlated variables dependent on the particular realization of trajectory $\{\mathbf{r}_N\}$.

model III to be a fairly complex problem, is that here we have to deal with a moment-generating function of $\mathcal{M}_{\{\mathbf{S}\}}(\{\mathbf{r}_N\})$, compared to a much easier problem of computation of an expected value of $\mathcal{M}_{\{\mathbf{S}\}}(\{\mathbf{r}_N\})$, encountered in the model I. Below we consider first predictions based on some approximate approach—the Rosenstock approximation—and next derive rigorous lower and upper bounds, which both have the same dependence on the time N but differ in the prefactors.

A. Rosenstock approximation. Decay pattern at intermediate times N

We start our analysis of the N dependence of the survival probability in Eq. (72) by first considering the predictions of the Rosenstock approximation. Applying the Jensen inequality, we may bound P_N in Eq. (72) as follows:

$$P_N \geqslant \exp\left[-cE_0\left\{ \sum_{\mathbf{S}} \mathcal{M}_{\{\mathbf{S}\}}(\{\mathbf{r}_N\}) \right\} \right]. \tag{74}$$

To proceed further, we note that the sum $\Sigma_{\mathbf{S}} \mathcal{M}_{\{\mathbf{S}\}}(\{\mathbf{r}_N\})$ can be written down formally (see Fig. 5) as a polynomial with random coefficients,

$$\sum_{\mathbf{S}} \mathcal{M}_{\{\mathbf{S}\}}(\{\mathbf{r}_N\}) = \sum_{j=1}^{N} \mathcal{V}^{(j)}(\{\mathbf{r}_N\})(1-p^j)$$

$$= \mathcal{S}(\{\mathbf{r}_N\}) - \sum_{j=1}^{N} \mathcal{V}^{(j)}(\{\mathbf{r}_N\}) p^j, \tag{75}$$

where each $\mathcal{V}^{(j)}(\{\mathbf{r}_N\})$, $j=1,\ldots,N$, is a random variable, which equals the number of sites in a given N-step random walk trajectory $\{\mathbf{r}_N\}$ visited exactly j times. Note that $\mathcal{V}^{(j)}(\{\mathbf{r}_N\})$ are not independent; this can be readily seen if one notices that the combination $\Sigma_{j=1}^{N} j\mathcal{V}^{(j)}(\{\mathbf{r}_N\})$ is a nonfluctuating quantity and equals the total number of sites visited by an N-step walk, i.e., N. Lastly, the random function $\mathcal{S}(\{\mathbf{r}_N\})$ in Eq. (75) denotes, as previously defined, the number of *distinct* sites visited by an N-step random walk trajectory $\{\mathbf{r}_N\}, \mathcal{S}(\{\mathbf{r}_N\}) = \Sigma_{j=1}^{N} \mathcal{V}^{(j)}(\{\mathbf{r}_N\})$.

Consequently, we find that Eq. (74) attains the following form:

$$P_N \geqslant \exp\left[-cE_0\{\mathcal{S}(\{\mathbf{r}_N\})\} + c\sum_{j=1}^{N} E_0\{\mathcal{V}^{(j)}(\{\mathbf{r}_N\})\} p^j \right]. \tag{76}$$

The averaging in the exponent in Eq. (76) can be performed directly using the results obtained in Ref. [25] for the generating function of the expectation $E_0\{\mathcal{V}^{(j)}(\{\mathbf{r}_N\})\}$. On the other hand, it is evident that for homogeneous random walks

$$E_0\left\{ \sum_{\mathbf{S}} \mathcal{M}_{\{\mathbf{S}\}}(\{\mathbf{r}_N\}) \right\} \equiv \sum_{\mathbf{r}_0} E_{\mathbf{r}_0}\{\mathcal{M}_{\{0\}}(\{\mathbf{r}_N\})\}, \tag{77}$$

which implies, in turn, that in terms of the Rosenstock approximation the integral effective reaction rate for model III, $Q_N^{(III)}$, has exactly the same form as that obtained for model I. As a matter of fact, this does not seem to be surprising since the mean-field-type Rosenstock approximation is not sensitive to the fact which of the reactive species precisely is mobile and which is fixed [see Eqs. (74) and (77)]. However, a profound difference between these two models does exist and below we will show that the large-N decay of P_N proceeds slower than it is predicted by Eqs. (39), (42), and (45).

B. Large-N decay of the survival probability

First of all, we note that in virtue of Eq. (75) and of an evident observation that for any given random walk trajectory $\{\mathbf{r}_N\}$ all $\mathcal{V}^{(j)}(\{\mathbf{r}_N\})$ are non-negative, one finds that

$$\mathcal{M}_{\{\mathbf{S}\}}(\{\mathbf{r}_N\}) \leqslant \mathcal{S}(\{\mathbf{r}_N\}), \tag{78}$$

which implies that, quite trivially, P_N is bounded from below by

$$P_N \geqslant E_0\{\exp[-c\mathcal{S}(\{\mathbf{r}_N\})]\}. \tag{79}$$

On the other hand, for any $p \leqslant 1$ and any $j > 0$, the difference $1-p^j \geqslant 1-p$. Consequently, the survival probability is always bounded from above by

$$P_N \leqslant E_0\{\exp[-c(1-p)\mathcal{S}(\{\mathbf{r}_N\})]\}, \tag{80}$$

i.e., large-N decay of P_N in model III proceeds slower than the decay in the ungated trapping problem (Sec. II), with the concentration of traps equal to $c(1-p)$. This inequality, however, does not seem to be trivial at first glance, since for model III the factor $c(1-p)$ represents only the average value of the active traps concentration, which does fluctuate in time and may exceed $c(1-p)$ at certain time moments.

Finally, taking advantage of the analysis in Ref. [30], we infer from two latter inequalities that the integral effective reaction rate for the model III obeys the two-sided inequality

$$a_d(1-p)^{2/(d+2)}\left(\frac{N}{c}\right)^{d/(d+2)} \leqslant Q_N^{(III)} \leqslant a_d\left(\frac{N}{c}\right)^{d/(d+2)}. \tag{81}$$

Note now that both lower and upper bounds show the same dependence on N (but have slightly different prefactors), which insures that in the large-N limit the integral effective reaction rate $Q_N^{(III)}$ grows in proportion to $N^{d/(d+2)}$ and consequently, the decay of the survival probability for model III is described by the dependence $\ln(P_N) \sim -N^{d/(d+2)}$, i.e., the same N dependence as in the ungated case [29,30].

VI. MODEL IV: A MOBILE, GATED *A* PARTICLE AND RANDOMLY PLACED FIXED TRAPS

Consider, finally, a trapping model involving an A particle bearing a *stochastic* gate and performing a lattice random walk in the presence of randomly placed, immobile ungated traps. For such a model the indicator function of the reaction event can be written as

$$\Psi_N = \lim_{\beta\to\infty} \exp\left[-\beta \sum_{n=0}^{N} \eta_n \sum_{k=1}^{K} \mathcal{I}(\mathbf{r}_n - \mathbf{S}^{(k)})\right], \tag{82}$$

which equals unity if an N-step trajectory $\{\mathbf{r}_N\}$ does not visit any site from a given array $\{\mathbf{S}^{(k)}\}$ in the reactive state, and turns to zero if any of $\mathbf{r}_n$, $n=0,1,\ldots,N$, coincides with any $\mathbf{S}^{(k)}$ when $\eta_n = 1$.

We turn first to averaging the indicator function of the reaction event [Eq. (82)] over the traps' placement on the lattice. First rewriting Ψ_N in Eq. (82) in the factorized form

$$\Psi_N = \prod_{k=1}^{K} \lim_{\beta\to\infty} \exp\left[-\beta \sum_{n=0}^{N} \eta_n \mathcal{I}(\mathbf{r}_n - \mathbf{S}^{(k)})\right], \tag{83}$$

and noticing that since all traps are placed independently of each other, all multipliers in Eq. (83) appear to be statistically independent, we have that the indicator function averaged over the traps' placement reads

$$\langle \Psi_N \rangle_{\{\mathbf{S}^{(k)}\}} = \left(\frac{1}{M}\sum_{\mathbf{S}} \lim_{\beta\to\infty} \exp\left[-\beta \sum_{n=0}^{N} \eta_n \mathcal{I}(\mathbf{r}_n - \mathbf{S})\right]\right)^K, \tag{84}$$

where the brackets with the subscript $\{\mathbf{S}^{(k)}\}$ stand for the averaging with respect to the positions of the traps. Next, turning to the infinite-space limit, we find that $\langle \Psi_N \rangle_{\{\mathbf{S}^{(k)}\}}$ is given explicitly by

$$\langle \Psi_N \rangle_{\{\mathbf{S}^{(k)}\}} = \exp\{-c\mathcal{S}(\{\mathbf{r}_N\}|\{\eta_n = 1\})\}, \tag{85}$$

where the functional

$$\mathcal{S}(\{\mathbf{r}_N\}|\{\eta_n = 1\}) = \sum_{\mathbf{S}} \left[1 - \mathcal{I}\left(\sum_{n=0}^{N} \eta_n \mathcal{I}(\mathbf{r}_n - \mathbf{S})\right)\right] \tag{86}$$

determines the number of *distinct* sites visited in the $\eta_n = 1$ state by a given N-step trajectory $\{\mathbf{r}_N\}$, or, in other words, the number of distinct sites visited by the A particle being in the reactive state within a given realization of its N-step random walk. Below we will study the temporal evolution of the function in Eq. (85), averaged over the reactivity fluctuations and trajectories $\{\mathbf{r}_N\}$, first using the Rosenstock approximation and then evaluating rigorous lower and upper bounds.

A. Rosenstock approximation. An intermediate time decay

Now consider the prediction of the Rosenstock-type approximation for the A particle survival probability in model IV. Applying the Jensen inequality, we have that the particle survival probability in model IV is bounded by

$$P_N \geqslant \exp[-c\overline{E_0\{\mathcal{S}(\{\mathbf{r}_N\}|\{\eta_n = 1\})\}}]. \tag{87}$$

The average of $\mathcal{S}(\{\mathbf{r}_N\}|\{\eta_n = 1\})$ over the reactivity fluctuations can be performed straightforwardly. First of all, we rewrite Eq. (86) as

$$\begin{aligned}\mathcal{S}(\{\mathbf{r}_N\}|\{\eta_n = 1\}) &= \sum_{\mathbf{S}} \left[1 - \mathcal{I}\left(\sum_{n=0}^{N} \eta_n \mathcal{I}(\mathbf{r}_n - \mathbf{S})\right)\right] \\ &= \sum_{\mathbf{S}} \left(1 - \frac{1}{2\pi}\int_0^{2\pi} dZ \prod_{n=0}^{N} \right. \\ &\quad \left. \times \exp[iZ\eta_n \mathcal{I}(\mathbf{r}_n - \mathbf{S})]\right).\end{aligned} \tag{88}$$

Next, averaging the latter equation with respect to the distribution of the variables $\{\eta_n\}$, we have that

$$\begin{aligned}\overline{\mathcal{S}(\{\mathbf{r}_N\}|\{\eta_n = 1\})} &= \sum_{\mathbf{S}} \left(1 - \frac{1}{2\pi}\int_0^{2\pi} dZ\{p \right. \\ &\quad \left. + (1-p)\exp[iZ]\}^{\sum_{n=0}^{N} \mathcal{I}(\mathbf{r}_n - \mathbf{S})}\right) \\ &\equiv \sum_{\mathbf{S}} \mathcal{M}_{\mathbf{S}}(\{\mathbf{r}_N\}),\end{aligned} \tag{89}$$

where the functional $\mathcal{M}_{\mathbf{S}}(\{\mathbf{r}_N\})$ was defined previously in Eq. (73).

On comparing the result in Eq. (89) with Eqs. (74) and (77), we notice that within the Rosenstock approximation the integral effective rate constant for model IV appears to be exactly the same as the one previously found for model III and coincides, as well, with the result obtained for the integral effective rate constant in model I. Hence this approximation predicts that the decay of the survival probability in model III proceeds exactly in the same fashion as the decay laws obtained for models I and III. In other words, the Rosenstock approximation appears to be completely insensitive to the fact of precisely which of the reactive species is mobile, and precisely which of them is stochastically gated.

B. Large-*N* decay of the survival probability

We start with the derivation of a rigorous lower bound on the A particle survival probability. Here an averaging of the indicator function of the reaction event in Eq. (82) with respect to the reactive state of the mobile A particle can be performed as follows:

$$\overline{\Psi}_N = \overline{\lim_{\beta\to\infty} \exp\left[-\beta \sum_{n=0}^{N} \eta_n \sum_{k=1}^{K} \mathcal{I}(\mathbf{r}_n - \mathbf{S}^{(k)}) \right]} = \prod_{n=0}^{N} \overline{\lim_{\beta\to\infty} \exp\left[-\beta \eta_n \sum_{k=1}^{K} \mathcal{I}(\mathbf{r}_n - \mathbf{S}^{(k)}) \right]} = \prod_{n=0}^{N} \left\{ (1-p) \lim_{\beta\to\infty} \exp\left[-\beta \sum_{k=1}^{K} \mathcal{I}(\mathbf{r}_n - \mathbf{S}^{(k)}) \right] + p \right\}. \tag{90}$$

Next, noticing that

$$(1-p) \lim_{\beta\to\infty} \exp\left[-\beta \sum_{k=1}^{K} \mathcal{I}(\mathbf{r}_n - \mathbf{S}^{(k)}) \right] + p = \begin{cases} 1, & \sum_{k=1}^{K} \mathcal{I}(\mathbf{r}_n - \mathbf{S}^{(k)}) = 0 \\ p, & \text{otherwise,} \end{cases} \tag{91}$$

and hence, that

$$(1-p) \lim_{\beta\to\infty} \exp\left[-\beta \sum_{k=1}^{K} \mathcal{I}(\mathbf{r}_n - \mathbf{S}^{(k)}) \right] + p = \exp\left\{ -\alpha_p \left[1 - \mathcal{I}\left(\sum_{k=1}^{K} \mathcal{I}(\mathbf{r}_n - \mathbf{S}^{(k)}) \right) \right] \right\}, \tag{92}$$

we find that the averaged indicator function of the reaction event obeys

$$\overline{\Psi}_N = \exp[-\alpha_p \mathcal{N}_{\{\mathbf{S}^{(k)}\}}(\{\mathbf{r}_N\})], \tag{93}$$

where

$$\mathcal{N}_{\{\mathbf{S}^{(k)}\}}(\{\mathbf{r}_N\}) = \sum_{n=0}^{N} \left[1 - \mathcal{I}\left(\sum_{k=1}^{K} \mathcal{I}(\mathbf{r}_n - \mathbf{S}^{(k)}) \right) \right] \tag{94}$$

is the ''residence time'' of a given N-step random walk trajectory on the subset of ''distinct,'' i.e., noncoinciding sites from the set $\{\mathbf{S}^{(k)}\}$, $k=1,\ldots,K$. This means that if any two (three, etc.) sites from $\{\mathbf{S}^{(k)}\}$ coincide, i.e., the traps overlap, a visit of $\{\mathbf{r}_N\}$ to such a multiply covered site singly contributes to $\mathcal{N}_{\{\mathbf{S}^{(k)}\}}(\{\mathbf{r}_N\})$. A rigorous lower bound on $\overline{\Psi}_N$ follows then from an evident inequality,

$$\sum_{n=0}^{N} \left[1 - \mathcal{I}\left(\sum_{k=1}^{K} \mathcal{I}(\mathbf{r}_n - \mathbf{S}^{(k)}) \right) \right] \leqslant \sum_{n=0}^{N} \sum_{k=1}^{K} I(\mathbf{r}_n - \mathbf{S}^{(k)}), \tag{95}$$

where the right-hand side determines the unconstrained ''residence time'' of the same N-step random walk trajectory on the set of all sites from $\{\mathbf{S}^{(k)}\}$. Clearly, the inequality in Eq. (95) becomes an equality if all sites $\{\mathbf{S}^{(k)}\}$ are distinct, e.g., when the traps obey a hard-core exclusion. Consequently, in virtue of the inequality in Eq. (95), we have that

$$\overline{\Psi}_N \geqslant \exp\left[-\alpha_p \sum_{n=0}^{N} \sum_{k=1}^{K} \mathcal{I}(\mathbf{r}_n - \mathbf{S}^{(k)}) \right], \tag{96}$$

where the right-hand side, as one can readily see, is exactly the indicator function of the reaction event for model III, averaged over the reactivity fluctuations. This implies the inequality

$$Q_N^{(IV)} \leqslant Q_N^{(III)} \leqslant a_d \left(\frac{N}{c} \right)^{d/(d+2)}, \tag{97}$$

which signifies, in particular, that similarly to the relation between two Q_N's, describing survival of gated and ungated targets (models II and I), the integral effective reaction rate for the model involving a mobile *gated A* particle in the presence of immobile ungated traps is generally less than or equal to the corresponding rate for the model, with the *ungated A* particle performing random walk in presence of gated traps.

We finally proceed to the derivation of a rigorous upper bound on the A particle survival probability in model IV. To do this, let us turn back to the functional $\mathcal{S}(\{\mathbf{r}_N\}|\{\eta_n=1\})$ in Eq. (86), and recall that it determines the number of *distinct* sites visited by a particle appearing in the *reactive* state within its N-step random walk $\{\mathbf{r}_N\}$. Note that similarly to the situation encountered in the derivation of the analogous bound in model II, here there is no restriction as to at precisely which visit the particle appears in the reactive state; that is, each site $\mathbf{S}$ can be visited many times by an inactive particle until it eventually reappears at this site in the reactive state, which event contributes to the overall value of the functional $\mathcal{S}(\{\mathbf{r}_N\}|\{\eta_n=1\})$. Hence, to find a lower bound on $\mathcal{S}(\{\mathbf{r}_N\}|\{\eta_n=1\})$ in Eq. (86) we will pursue the strategy employed already in Sec. IV, i.e., we will try to restrict the order of the reactive visit to site $\mathbf{S}$. Here, however, this appears to be a slightly more delicate problem, since we have to deal with the realization-dependent functional in Eq. (86), rather than with its expected value.

To find a lower bound on $\mathcal{S}(\{\mathbf{r}_N\}|\{\eta_n=1\})$, we thus proceed as follows: First, we constrain the summation in Eq. (86), supposing that it runs not over all sites of an *infinite* lattice, but only over some *finite* subset $\{\mathbf{S}^*\}$. Clearly, since the functional $[1-\mathcal{I}(\Sigma_{n=0}^{N} \eta_n \mathcal{I}(\mathbf{r}_n - \mathbf{S}))]$ is positive definite, such an operation will result in a lower bound on $\mathcal{S}(\{\mathbf{r}_N\}|\{\eta_n=1\})$. Next we define the subset $\{\mathbf{S}^*\}$; we stipulate that for a given realization of a particle's trajectory, the subset $\{\mathbf{S}^*\}$ is just a collection of such lattice sites $\mathbf{S}$ on which the particle appeared for the first time in the reactive state, i.e., sites which remained ''virgin'' until the first visit in the $\eta_n=1$ state.

More formally, a derivation of such a lower bound on $\mathcal{S}(\{\mathbf{r}_N\}|\{\eta_n=1\})$ can be based on the evident inequality between the following two indicator functions:

$$\mathcal{I}_{\mathbf{S}}(\{\mathbf{r}_N\}|\{\eta_n=1\})=\left[1-\mathcal{I}\left(\sum_{n=0}^{N}\eta_n\mathcal{I}(\mathbf{r}_n-\mathbf{S})\right)\right]$$

$$\geqslant\Delta_{\mathbf{S}}(\{\mathbf{r}_N\}|\{\eta_n=1\})$$
$$=\sum_{n=0}^{N}\eta_n\left\{\mathcal{I}\left(\sum_{l=0}^{n-1}\mathcal{I}(\mathbf{r}_l-\mathbf{S})\right)-\mathcal{I}\left(\sum_{l=0}^{n}\mathcal{I}(\mathbf{r}_l-\mathbf{S})\right)\right\}, \quad (98)$$

where the indicator function on the left-hand side of Eq. (98) equals 1 if **S** has been visited at least once by the particle in the reactive state within a given realization $\{\mathbf{r}_N\}$ of its N-step walk, and equals 0 otherwise. Meanwhile, $\Delta_{\mathbf{S}}(\{\mathbf{r}_N\}|\{\eta_n=1\})$ equals 1 if, within an N-step walk, the particle appeared for the first time on site **S** in the reactive state, not having visited this site before; otherwise it is equal to 0.

Summing both sides of the inequality in Eq. (98) over all lattice sites **S**, we have, consequently, that

$$\mathcal{S}(\{\mathbf{r}_N\}|\{\eta_n=1\})$$
$$=\sum_{\mathbf{S}}\mathcal{I}_{\mathbf{S}}(\{\mathbf{r}_N\}|\{\eta_n=1\})$$
$$\geqslant\sum_{\mathbf{S}}\sum_{n=0}^{N}\eta_n\left\{\mathcal{I}\left(\sum_{l=0}^{n-1}\mathcal{I}(\mathbf{r}_l-\mathbf{S})\right)-\mathcal{I}\left(\sum_{l=0}^{n}\mathcal{I}(\mathbf{r}_l-\mathbf{S})\right)\right\}$$
$$=\sum_{n=0}^{N}\eta_n\sum_{\mathbf{S}}\left\{\left[1-\mathcal{I}\left(\sum_{l=0}^{n}\mathcal{I}(\mathbf{r}_l-\mathbf{S})\right)\right]-\left[1-\mathcal{I}\left(\sum_{l=0}^{n-1}\mathcal{I}(\mathbf{r}_l-\mathbf{S})\right)\right]\right\}, \quad (99)$$

which yields, by virtue of the definition in Eq. (59), a desired lower bound of the form

$$\mathcal{S}(\{\mathbf{r}_N\}|\{\eta_n=1\})\geqslant\sum_{n=0}^{N}\eta_n\Delta(\{\mathbf{r}_n\}), \quad (100)$$

where the right-hand side of Eq. (100) determines the number of ''virgin'' sites visited by an N-step random walk in the reactive state. Equation (100) implies, in turn, that the function $\langle\Psi_N\rangle_{\{\mathbf{S}^{(k)}\}}$ in Eq. (85) is bounded from above by

$$\langle\Psi_N\rangle_{\{\mathbf{S}^{(k)}\}}\leqslant\prod_{n=0}^{N}\exp[-c\,\eta_n\Delta(\{\mathbf{r}_n\})]. \quad (101)$$

Now, averaging both sides of the latter equation over the fluctuations of the reactivity, we find

$$\overline{\langle\Psi_N\rangle}_{\{\mathbf{S}^{(k)}\}}\leqslant\overline{\prod_{n=0}^{N}\exp[-c\,\eta_n\Delta(\{\mathbf{r}_n\})]}$$
$$=\prod_{n=0}^{N}\overline{\exp[-c\,\eta_n\Delta(\{\mathbf{r}_n\})]}$$
$$=\prod_{n=0}^{N}\{(1-p)\exp[-c\Delta(\{\mathbf{r}_n\})]+p\}. \quad (102)$$

Recollecting next that the realization-dependent property $\Delta(\{\mathbf{r}_n\})$ assumes only two values -1 or 0, and hence, that

$$(1-p)\exp[-c\Delta(\{\mathbf{r}_n\})]+p=\begin{cases}\{(1-p)\exp[-c]+p\}, & \Delta(\{\mathbf{r}_n\})=1\\ 1, & \Delta(\{\mathbf{r}_n\})=0,\end{cases} \quad (103)$$

we may rewrite quite formally the bound in Eq. (102) as

$$\overline{\langle\Psi_N\rangle}_{\{\mathbf{S}^{(k)}\}}\leqslant\prod_{n=0}^{N}\{(1-p)\exp[-c\Delta(\{\mathbf{r}_n\})]+p\}$$
$$=\exp\left[-\ln\left(\frac{1}{(1-p)\exp[-c]+p}\right)\sum_{n=0}^{N}\Delta(\{\mathbf{r}_n\})\right]. \quad (104)$$

Finally, noting that $\Sigma_{n=0}^{N}\Delta(\{\mathbf{r}_n\})=\mathcal{S}(\{\mathbf{r}_N\})$, we find that the A particle survival probability obeys

$$P_N=E_0\{\overline{\langle\Psi_N\rangle}_{\{\mathbf{S}^{(k)}\}}\}$$
$$\leqslant E_0\left\{\exp\left[-\ln\left(\frac{1}{(1-p)\exp[-c]+p}\right)\mathcal{S}(\{\mathbf{r}_N\})\right]\right\}, \quad (105)$$

and hence, by taking the lower bound in Eq. (97) into account, we arrive at the following two-sided inequality for the integral effective rate constant in model IV:

$$\frac{a_d}{c}\left[\ln\left(\frac{1}{(1-p)\exp[-c]+p}\right)\right]^{2/(d+2)}N^{d/(d+2)}$$
$$\leqslant Q_N^{(IV)}$$
$$\leqslant a_d\left(\frac{N}{c}\right)^{d/(d+2)}. \quad (106)$$

Note that again, both sides of the inequality in Eq. (106) show the same dependence on the time N and consequently, exactly determine the N dependence of the integral effective rate constant in model IV. We also remark that in the limit $c\ll 1$ one has that $\ln[1/((1-p)\exp[-c]+p)]\approx(1-p)c$, and, hence, in this limit the lower bound on the integral effective reaction rate for model IV [Eq. (106)], coincides with the lower bound on $Q_N^{(III)}$ in Eq. (81).

C. Conclusion

To conclude, we have studied the time evolution of the A particle survival probability in four models of stochastically gated, diffusion-limited pseudo-first-order reactions of the form $A+B\rightarrow B$. We have considered two different models of targetlike annihilation reactions, where the first one concerns the survival of a single, immobile A particle (the target) in the presence of randomly moving gated scavengers B (model I), and the second focuses on the fate of a gated immobile A particle in the presence of randomly moving ungated scavengers B (model II). Two other examples of stochastically gated pseudo-first-order reactions are furnished here by trapping reactions between a mobile, ungated A particle and a concentration of randomly placed, immobile, gated traps B (model III); and the reverse situation with a mobile gated A particle and randomly placed, immobile, ungated traps B (model IV). In all the models studied we have supposed that mobile species perform symmetric lattice random walks. In addition, we have adopted the two-state Poisson gating model of Ref. [14], in which each of the gates is supposed to be in either an active state on a blocked one, and to update its state at each tick of the clock at random, independently of the previous history as well as of the gates imposed on other particles.

We have demonstrated that model I allows for an exact solution, and derived explicit asymptotic decay forms for lattices of different spatial dimensionalities. Curiously enough, it appeared that for low-dimensional lattices ($d \leqslant 2$), for which lattice random walks are recurrent, the long-time behavior is independent of the presence of stochastic gates (as soon as the gating probability $p<1$) and proceeds exactly in the same fashion as for reactions with well-defined, nonfluctuating reaction rates (Sec. II). Correction terms do, however, depend on the gating probability p and may be important for reactions in which the species are blocked most of the time. Next, we have found that for model I in higher dimensions the decay is described by a purely exponential function of time with a characteristic time dependent on both the gating probability and on the probability of the eventual return to the origin. A physical explanation of the predicted behavior has also been provided.

Further on, for model II the decay pattern has been determined exactly in the form of rigorous lower and upper bounds showing the same dependence on the time N but having slightly different prefactors. We have demonstated that the decay of the A particle survival probability in this model is characterized by essentially the same time dependence as that for model I, i.e., the integral effective reaction rate follows the behavior of the expected number of distinct sites visited by an N-step random walk, but may have a different numerical factor.

Next, for models III and IV, we have presented some approximate results, based on the so-called Rosenstock approximation, which may provide a plausible description of the kinetic behavior at intermediate times, as well as exact results concerning the long-time evolution of the A particle survival probability. We have demonstrated that within the Rosenstock approach no difference exists between the kinetic behavior in models III and IV. Moreover, we have shown that the decay forms coincide with the exact result obtained for model I. The long-time evolution of the decay functions in models III and IV has been determined in the form of rigorous lower and upper bounds characterized by the same dependence on the time N. We have also realized that in the case of stochastically gated trapping reactions the long-time decay of the A particle survival probability has essentially the same form as that describing the kinetic behavior of their ungated counterparts (Sec. II); however, the characteristic times might be renormalized to include the dependence on the reaction probability.

As an interesting by-product of our analysis, we have also shown that the survival probability in all four models under study can be interpreted as a moment generating function of some refined characteristics of random walk trajectories. In particular, we have demonstrated that for model I the survival probability is the moment generating function for the number of visits rendered by a concentration of independent random walkers to the origin. In other models this survival probability appears as the moment generating function of the number of self-intersections of random walk trajectories, the residence time on a disordered array of marked sites, the number of sites visited exactly a given number of times, and so on. Consequently, our results also apply to the asymptotical behavior of the above mentioned generating functions, which in many cases is not known yet.

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