

## Lattice theory of trapping reactions with mobile species

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We present a stochastic lattice theory describing the kinetic behavior of trapping reactions  $A+B \rightarrow B$ , in which both the  $A$  and  $B$  particles perform an independent stochastic motion on a regular hypercubic lattice. Upon an encounter of an  $A$  particle with any of the  $B$  particles,  $A$  is annihilated with a finite probability; finite reaction rate is taken into account by introducing a set of two-state random variables—“gates,” imposed on each  $B$  particle, such that an open (closed) gate corresponds to a reactive (passive) state. We evaluate here a formal expression describing the time evolution of the  $A$  particle survival probability, which generalizes our previous results. We prove that for quite a general class of random motion of the species involved in the reaction process, for infinite or finite number of traps, and for any time  $t$ , the  $A$  particle survival probability is always larger in the case when  $A$  stays immobile, than in situations when it moves.

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### I. INTRODUCTION

Kinetics of chemical reactions involving diffusive species have attracted a great deal of scientific interest since the pioneering work by Smoluchowski [1]. Since then, many conceptually important results have been obtained [2–6]. In particular, it has been proved in specific cases that the classical, mean-field chemical kinetics does not apply, at least in low-dimensional systems [4–11].

Trapping  $A+B \rightarrow B$  reactions (TR), involving randomly moving  $A$  and  $B$  particles which react “when they meet” at a certain distance  $b$ , provide an example of chemical reactions showing a pronounced deviation from the textbook predictions.

For the TR two situations were most thoroughly studied: the case when  $A$ s diffuse while  $B$ s are static, and the situation in which the  $A$ s are immobile while  $B$ s diffuse—the so-called target annihilation problem (TAP). In the case of static, randomly placed (with mean density  $\rho$ ) traps the  $A$  particle survival probability  $P_A(t)$  shows a nontrivial, fluctuation-induced behavior [8,9,12–17]

$$\ln P_A(t) \sim -\rho^{2/(d+2)}(D_A t)^{d/(d+2)}, \quad t \rightarrow \infty, \quad (1)$$

which is intimately related to many fundamental problems of statistical physics [8,9,12–18].

Survival probability  $P_{\text{target}}(t)$  of an immobile target  $A$  of radius  $b$  in presence of pointlike diffusive traps  $B$  (TAP) can be calculated exactly for any  $d$  (see Refs. [21] and [4,8,19,20]),

$$P_{\text{target}}(t) = \exp(-\rho \phi_b^{(d)}(t)), \quad (2)$$

where  $\phi_b^{(d)}(t)$  obeys

$$\phi_b^{(d)}(t) = \int_0^t d\tau K_S(\tau) \sim \begin{cases} 4\sqrt{Dt/\pi}, & d=1 \\ \frac{4\pi Dt}{\ln(4Dt/b^2)}, & d=2 \\ 4\pi Dbt, & d=3, \end{cases} \quad (3)$$

where  $D=D_B$  and  $K_S(\tau)$  is the  $d$ -dimensional Smoluchowski-type “constant,” defined as the flux of diffusive particles through the surface of an immobile sphere of radius  $b$ . Decay forms in systems with hard-core interactions between  $B$ s [22] or with fluctuating chemical activity [23] have also been discussed.

On contrary, the physically most important case of TR when both  $A$ s and  $B$ s diffuse was not solved exactly. It has been proven [9] that here  $P_A(t)$  obeys

$$\ln P_A(t) = -\lambda_d(D_A, D_B) \begin{cases} t^{1/2}, & d=1 \\ \frac{t}{\ln(t)}, & d=2 \\ t, & d=3, \end{cases} \quad (4)$$

which equation defines its time dependence exactly. On the other hand, the factor  $\lambda_d(D_A, D_B)$  remained as yet an unknown function of the particles’ diffusivities and  $d$ . Since the time dependence of the function on the right-hand side of Eq. (4) follows precisely the behavior of  $\int^t d\tau K_S(\tau)$ , one might expect that the SA provides quite an accurate description for this situation and following its spirit to set  $D_A=0$  supposing that traps diffuse with the diffusion coefficient  $D=D_B+D_A$ . As a matter of fact, it has been often tacitly assumed that when both of species diffuse  $P_A(t)$  obeys Eq. (2) with  $\phi_b^{(d)}(t)$  defined by Eq. (3) and  $D=D_A+D_B$ . On the other hand, it has been shown that  $\lambda_d(D_A, D_B)$  is less than the corresponding prefactor in  $K_S(t)$  [31] and that it may be bounded by a nonanalytic function of  $D_A$  and  $D_B$  [24]. A perturbative approach for calculation of  $\lambda_d(D_A, D_B)$ , as well as corrections to the SA in one-dimensional systems were presented [20]. It has been also noted that  $\lambda_d(D_A, D_B)$  is not a function of the sum  $D=D_A+D_B$  only, since the diffusion-reaction equation are not separable [20]. This lack of knowledge of the precise form of  $\lambda_d(D_A, D_B)$ , of course, constitutes an annoying gap in the general understanding of the fluctuation phenomena in chemical kinetics.

Recently, some very interesting and unexpected results have been established for trapping  $A+B \rightarrow B$  reactions in-

volving randomly moving species [25,26], which have resolved, at least in part, this problem. It has been shown that in one or two dimensions [25], or more generally in systems, in which the fractal dimension of the  $B$  particle trajectories is greater than the dimension  $d$  of the embedding space [26], i.e., in case of the so-called “compact exploration” [27], the leading at long times kinetic behavior of perfect trapping is essentially independent of the  $A$  particle diffusion coefficient. In other words, it has been shown [25] that in such low dimensions, the leading long-time decay of the  $A$  particle survival probability in systems in which the  $A$  particle diffuses and the decay in systems in which it is fixed at the origin are exactly the same.

The derivation of this rather surprising result relies heavily on the assumption that the  $A$  particle has a larger probability to survive until a given time  $t$  (at least when  $t \rightarrow \infty$ ) if it stays immobile rather than when it moves randomly. In Ref. [25] some arguments have been proposed in favor of this conjecture, based on the analysis of the decay exponents in systems with a finite number of  $B$ s. Subsequently, it was shown rigorously in Ref. [28] that it is indeed the case in a one-dimensional continuum; on the other hand, the claim that Ref. [28] presents a rigorous proof of this conjecture for  $d=2$  does not seem to be justified; as a matter of fact, Eq. (2) of Ref. [28] does not make sense for  $d=2$  and the logarithmic correction does not follow from it, since particle’s radius is not taken explicitly into account within the approach of Ref. [28].

On the other hand, in a recent article [29], this conjecture has been examined rigorously within the context of reactions between the particles executing random walks on  $d$ -dimensional lattices; here, such a conjecture has been referred to as the “Pascal principle,” since it is reminiscent of a famous philosophical assertion of Blaise Pascal, who claimed that “all misfortune of man comes from the fact that he does not stay peacefully in his room” [30]. In Ref. [29], we showed that as  $t \rightarrow \infty$  the Pascal-principle-like inequality between the survival probabilities of a diffusive and of an immobile  $A$  particles is valid in any dimension, provided that the  $A$  particle performs some rather general continuous-time jump process on a hypercubic lattice, while the  $B$  particles perform independently a discrete time lattice jump process, which also satisfies some rather natural assumptions. The same conclusion was also obtained in Ref. [29] for a much more general case of stochastically gated reactions, which mimic situations with finite elementary reaction act constants.

We also emphasize that very similar Pascal-principle-like inequality has been proven earlier for the process of hopping transport of an excitation on a disordered array of immobile donor centers in presence of randomly placed, immobile quenchers [31]. We note, as well, that recent results obtained for the ballistic  $A + A \rightarrow 0$  annihilation process [32] are compatible with such a principle.

On the other hand, the analysis in Ref. [29] is rather condensed and moreover, some of the assumptions invoked, as well as some of the constraints imposed on particles’ random walks, seem to be unnecessary and thus can be safely relaxed. Consequently, our purpose here is to complete the

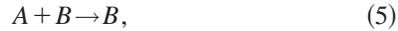
proof of the Pascal-principle-like inequality between the survival probabilities of the diffusive and immobile  $A$  particles and to extend it in several directions. In particular, we proceed to show that the Pascal-principle-like inequality holds at any finite time  $t$ , as well as for both infinite and finite number of traps. Moreover, we shall consider here the case when the chemical activity of the  $B$  particles fluctuates in time between active and inactive states. We set out to show that the Pascal principle also applies for this much more complex and realistic situation. As in our previous work [29], we will focus here solely on the lattice formulation of the model. The continuous-space case, which requires much more delicate analysis, will be studied elsewhere.

The paper is structured as follows. In Sec. II we formulate the model, introduce basic notations, and define the properties of reaction and random walks executed by the species involved. In Sec. III we will focus on the reaction kinetics in case of perfect trapping; that is, on the case when the  $A$  particle gets annihilated with probability 1 upon the first encounter with any of the traps  $B$ . Further on, in Sec. IV, the Pascal-principle-like inequality between the survival probabilities of a diffusive and immobile  $A$  particles will be extended to the case when the chemical activity of the  $B$  particle fluctuates randomly between active and inactive states, which mimics more realistic situations in which an annihilation of an  $A$  particle upon its encounter with any of the  $B$ s takes place with a finite probability. We consider here a rather general case when such activity fluctuations can be correlated in time. Some intermediate calculations, as well as analysis of the behavior in some special cases are relegated to the Appendixes A and B, in which, in particular, the special case of Polya random walks is considered.

## II. LATTICE MODEL OF TRAPPING REACTIONS BETWEEN MOBILE SPECIES

It is well known that lattice models of diffusion-controlled reactions yield, at least for sufficiently large times, the kinetic laws that are essentially the same as those obtained within the continuous-space descriptions. Thus in the present work we shall consider a *lattice model* of trapping reactions, which will simplify significantly our analysis. One of the advantages of such a consideration, apart of the fact that it allows for much more lucid analysis than in the continuous-space limit, is that we are not forced to attribute to particles a finite, nonzero radius, which allows to consider the behavior in systems of *any* spatial dimension. Finally, for the sake of simplicity, we will restrict our analysis here to hypercubic lattices; most of the results, of course, could be readily extended to other types of embedding lattices.

Consider  $N_A$  particles of type  $A$  and  $N_B$  particles of type  $B$ , which are initially placed at random at the sites of a  $d$ -dimensional hypercubic lattice, containing  $M$  sites. All particles perform independent jump processes on the nodes of the lattice. Each  $A$  particle can be destroyed (in the general case with a finite probability) as soon as this  $A$  particle appears on the same lattice site simultaneously with any of the  $B$  particles. The  $B$  particle remains unchanged after the reaction event, which corresponds to the annihilation mechanism



and represents the customary trappinglike reaction. One can also envisage a more general catalytic reaction process of the form:



where the catalyst  $B$  promotes the transformation of an  $A$  into some product molecule  $C$ , the product molecule  $C$  being immediately extracted from the system.

In regard to the reaction probability, we will distinguish between two situations: the one of perfect trapping or purely diffusion-controlled trapping, in which case any  $A$  gets annihilated with probability 1 upon the first encounter with any of  $B$ s, and that of imperfect trapping for which the annihilation of the  $A$  by any  $B$  takes place with a finite probability  $< 1$ . To mimic this condition, we will introduce a set of additional random variables, attached to each  $B$  particle, which will describe their instantaneous reactive activity. Finally, we will assume in what follows that collisions (simultaneous encounters) between two (or more)  $A$  particles are possible and do not affect these  $A$  particles or their random walks, and similarly, that collisions between the  $B$  particles are possible and do not lead to any reactions. In other words, neither  $A$  nor  $B$  particles have hard-core interactions and no single-species reactions may take place.

Now, as far as particle motions are concerned, we face here the following problem: on one hand, in regard to dynamics of  $A$  and  $B$  particles, we have to define two different random processes with different characteristics, e.g., diffusion coefficients, which may be used afterwards as tunable parameters. On the other hand, these random processes must allow a rigorous analysis, which is not always the case. If we choose, for example, that both species perform random hopping motion in discrete time, then it will be quite difficult to work out a rigorous formalism in which two random processes have different “waiting” times at lattice sites. If, on contrary, we choose that both processes evolve in continuous time, then we will face purely mathematical difficulties in treatment of the events in which the particles of different species appear simultaneously at the same lattice site. Not forsaking the generality, we thus choose here the “mixed” case, which seems to us most suitable for the rigorous description.

We thus assume that all  $A$  particles perform identical and independent continuous-time jump processes, so that they can jump at any time moment from one lattice site to any other site. No other hypothesis or additional constraints on their motions are required.

Further on, we suppose that all  $B$ s perform identical and independent discrete-time random walks; that is, at any integer time  $n \geq 0$ , any  $B$  particle can jump from a lattice site  $y$  to site  $y'$  with a given probability  $p(y'|y)$ , where  $y'$  can be identical to  $y$ , i.e.,  $B$  can remain at the site which it occupies at time moment  $n$ . Let  $Y_n$  denote the position of a given  $B$  particle at time moment  $n \geq 0$ . We assume that this random walk satisfies the following conditions.

(i) The random walk is homogeneous in space and in time: the probability  $p(y'|y)$  is independent of time and of the initial position, such that

$$p(y'|y) = p(y' - y). \quad (6)$$

(ii) The uniform distribution  $p(y) = 1/M$  is stationary for the  $B$  particles. We assume that it holds at time 0, and hence, it is realized at all times. This condition implies the bilateral normalization relation

$$\sum_y p(y'|y) = 1. \quad (7)$$

We remark that a stronger condition would be to assume that the probability  $p(y'|y)$  satisfies the detailed balance, i.e.,

$$p(y'|y) = p(y|y'),$$

which, together with the condition in Eq. (6), implies that

$$p(y - y') = p(y' - y). \quad (8)$$

However, the condition in Eq. (8), which clearly follows from Eq. (9), is sufficient for obtaining our main results.

(iii) At any time  $n$ , the conditional probability  $P(Y_n = y | Y_0 = 0)$  of finding a given  $B$  particle at an arbitrary position  $y$  at time moment  $n$ , provided that it started its random walk at the origin, does not exceed the return probability  $P(Y_n = 0 | Y_0 = 0)$ . That is,

$$P(Y_n = y | Y_0 = 0) \leq P(Y_n = 0 | Y_0 = 0) \equiv R_n. \quad (9)$$

This condition seems to be quite plausible for any symmetric random motion in a uniform medium if Eq. (8) holds, since here  $P(Y_n = y | y_0 = 0)$  is invariant upon reversal  $y$  into  $-y$ . Hence, this probability should always have an extremum for  $y = 0$ , which is likely to be a maximum. It should be noted, however, that inequality in Eq. (9) does not hold exactly for the usual Polya random walk, when the particle jumps at one of the neighboring sites at each integer time moment. For instance, on a one-dimensional lattice of unit spacing, the inequality in Eq. (9) is not satisfied if  $n$  and  $y$  are odd, since in this case the return probability  $R_n \equiv 0$ . Nevertheless, one easily obtains (without any significant lack of generality) random walks satisfying condition (iii): for instance, one may consider a modified Polya random walk on a  $d$ -dimensional hypercubic lattice, such that at each integer time moment a walker has a probability  $p_0$  to remain at the site it occupies, and a probability  $(1 - p_0)/2d$  to jump at one of the neighboring sites. In this case, it can be shown that the inequality in Eq. (9) is verified if  $p_0 \geq 1/2$ . More generally, Eq. (9) holds for any homogeneous and symmetric probability  $p(x|y)$  if  $p(x|x) \equiv p(0) \geq 1/2$  (see Appendix A). Furthermore, our conclusions can be extended to cover the case of the Polya random walks, as shown in Appendix B, where this special question is discussed in detail.

We finally remark that in the continuous-space case, in which the random walk is replaced by a Brownian motion, such a question does not arise at all, since here the probability density is always maximal and centered around the initial

position. Thus the inequality in Eq. (9) appears very naturally in unbiased diffusion problems, but it can also be verified for nonsymmetric jump probabilities.

We close this section by adopting some conventions on how to introduce reaction events into the model. We assume that a given  $B$  particle can only annihilate  $A$  at integer times  $n > 0$ . If at a noninteger time  $A$  jumps on a site which is occupied by a particle  $B$ , it will be only annihilated at the next integer time  $n$ . Finally, we remark that the probability that an  $A$  particle performs a jump exactly at an integer time is 0, which allows to neglect consideration of such events. Note also that all these assumptions would not change the global behavior of the system. They thus merely serve for convenience of exposition.

### III. PERFECT TRAPPING ON A LATTICE

We consider first the case of perfect trapping in which case an annihilation of an  $A$  particle takes place at the first encounter with any of  $B$  particles. Our aim here is to demonstrate, in a rigorous way, the Pascal-principle-like assertion that the survival probability of an  $A$  particle which moves randomly on a lattice is less or equal to the survival probability of an immobile  $A$  particle.

#### A. Mean-field kinetics of the trapping reaction

We start with a reminder on the predictions of a conventional mean-field approach [2]. One notices first that, clearly, the average number  $\langle N_A(n) \rangle$  of  $A$  particles surviving up to an integer time  $n$  is the sum of probabilities that a given  $A$  particle survives up to this time moment  $n$ . Since all of them have identical evolution laws, one has

$$\langle N_A(n) \rangle = N_A(0) \Psi(n),$$

where  $\Psi(n)$  denotes the survival probability of a single particle  $A$ . Since the particles  $B$  are completely insensitive (as far as their motions are concerned) to particles  $A$ ,  $\Psi(n)$  can be evaluated independently for each particle  $A$ . Thus, it is legitimate to consider only the survival of a single  $A$  particle in presence of  $N$  particles  $B$ .

In terms of the conventional mean-field kinetics [2], one obtains then an exponential decay form for  $\Psi(n)$ ,

$$\Psi(n) = \exp(-k\rho n), \quad (10)$$

which should hold in any dimension  $d$ . In the preceding equation  $k$  is the reaction constant and  $\rho$  stands for the mean density of the  $B$  particles.

Note that in case of perfect trapping Eq. (10) becomes senseless, since here  $k = \infty$ . Indeed, it has been well known for a long time, both for the continuous space and lattice models, that the decay law in Eq. (10) does not hold, at least for  $d = 1$  and  $d = 2$  [1,4,7–11], so that mean-field approach fails and a detailed stochastic theory is needed. Instead of it, one has either Eq. (1) or (4), depending on whether  $D_B = 0$ ,  $D_A = 0$  or not.

To illustrate the deviations from the mean-field behavior in Eq. (10) and the actual decay forms, let us consider the

case when one of the species only is moving [7,8]. In this illustration, we follow closely the methods outlined in Ref. [33].

#### B. Survival probability of an $A$ particle

Let us call  $\Gamma_A$  the  $A$  particle trajectory, and first suppose that it is given. Then, we denote as  $x_0 = 0, x_1, \dots, x_n$  the successive positions of the  $A$  particle at the integer times  $t_0 = 0, t_1, \dots, t_n$ .

We suppose next that the waiting time of  $A$  at each lattice site, i.e., the time which an  $A$  particle spends on this site between successive hops, is a stochastic variable, so that two successive positions are not necessarily different, and not necessarily nearest neighbors.

Further on, we denote the  $i$ th  $B$  particle,  $i = 1, \dots, N$ , as  $B_i$  and as  $\Gamma_{B_i}$ —the stochastic trajectory of this particle. Next, let  $Q_i(n|\Gamma_A)$  be the conditional probability that  $B_i$  does not destroy  $A$  up to time moment  $n$ , for a given trajectory  $\Gamma_A$  of  $A$ . Because all  $B_i$ s move and act independently of each other, the conditional probability  $\Psi(n|\Gamma_A)$  that the particle  $A$  survives up to time moment  $n$  for a given  $\Gamma_A$ , factorizes

$$\Psi(n|\Gamma_A) = \prod_{i=1}^N Q_i(n|\Gamma_A) \quad (11)$$

and hence, the overall  $A$  particle survival probability obeys

$$\Psi(n) = \langle \Psi(n|\Gamma_A) \rangle_{\Gamma_A}, \quad (12)$$

the average being taken over all possible trajectories of  $A$  from  $t = 0$  to  $t = n$ . Furthermore, since all  $B$  particles are identical, one has that  $Q_i(n|\Gamma_A) = Q(n|\Gamma_A)$  for all  $i$ , and hence

$$\Psi(n) = \langle Q(n|\Gamma_A)^N \rangle_{\Gamma_A}, \quad (13)$$

where, once again, the average is being taken over all possible trajectories  $\Gamma_A$  of the  $A$  particle.

#### C. The survival probability in the thermodynamic limit

Let us denote  $Y_0, Y_1, \dots, Y_n$  the successive positions of a given  $B$  particle at time moments  $0, 1, \dots, n$  and  $\Gamma_{y_0}$ —a trajectory starting from  $Y_0 = y_0$  at time 0. One can write then

$$Q(n|\Gamma_A) = \langle Q(n|\Gamma_A, y_0) \rangle_{y_0}, \quad (14)$$

where  $Q(n|\Gamma_A, y_0)$  stands for the conditional probability that a given  $B$  particle, starting its random walk from position  $y_0$  at time moment 0, does not destroy  $A$  until time moment  $n$  for a given trajectory  $\Gamma_A$ . The brackets  $\langle \dots \rangle_{y_0}$  in Eq. (14) denote averaging with respect to all possible initial positions  $y_0$  of a given  $B$  particle.

We now assume that the probability of the initial position  $Y_0$  is uniformly distributed among the  $M$  available sites. Then we have

$$\langle Q(n|\Gamma_A, y_0) \rangle_{y_0} = \frac{1}{M} \sum_{y_0} Q(n|\Gamma_A, y_0)$$

and Eq. (14) can be written as

$$\Psi(n) = \left\langle \left\{ 1 - \frac{1}{M} \sum_{y_0} [1 - Q(n|\Gamma_A, y_0)] \right\}^N \right\rangle_{\Gamma_A}. \quad (15)$$

Turning next to the thermodynamic limit, i.e., setting  $N \rightarrow \infty$  and  $M \rightarrow \infty$ , while keeping their ratio fixed,  $N/M \rightarrow \rho$ ,  $\rho$  being the concentration of the  $B$  particles, one obtains for the  $A$  particle survival probability at time  $n$  the following expression:

$$\Psi(n) = \left\langle \exp \left\{ -\rho \sum_{y_0} [1 - Q(n|\Gamma_A, y_0)] \right\} \right\rangle_{\Gamma_A}. \quad (16)$$

Hence, the survival probability  $\Psi(n)$  is simply related to the probability that a given  $B$ , starting from  $y_0$ , destroys  $A$  at some time  $t \leq n$ , for a given trajectory of  $A$ , which is

$$P(n|\Gamma_A, y_0) = 1 - Q(n|\Gamma_A, y_0). \quad (17)$$

Similar results were obtained [4,7–11,26,33] in the particular case when the  $A$  particle is immobile, i.e., for the so-called target annihilation problem. In this particular case there is no averaging over  $\Gamma_A$  as in the previous formulas, and the integral reaction rate is thus defined by

$$K(n|\Gamma_A) \equiv \sum_{y_0} P(n|\Gamma_A, y_0), \quad (18)$$

which replaces in this case the term “ $kn$ ” of the conventional kinetic law in Eq. (10). On contrary, in more realistic situations when  $A$  also moves, the average over the trajectories  $\Gamma_A$  makes the explicit calculation of the survival probability impossible in most cases.

#### D. A basic inequality

Let us define  $P^1(k|\Gamma_A, y_0)$  as the conditional probability that  $B$ , starting from  $y_0$  at time 0, meets  $A$  for the first time at time  $k$ , given the trajectory  $\Gamma_A$ . Then, the conditional probability  $P(n|\Gamma_A, y_0)$  that  $B$ , starting from  $y_0$ , destroys  $A$  at or before time moment  $n$  is given by

$$P(n|\Gamma_A, y_0) = \sum_{0 < k \leq n} P^1(k|\Gamma_A, y_0). \quad (19)$$

The conditional probability that the trajectory of  $B$  (extended after the possible annihilation of  $A$ ) meets  $\Gamma_A$  at time  $n$  (not necessarily for the first time) satisfies the equation

$$P(Y_n = x_n | Y_0 = y_0) = \sum_{0 \leq k < n} P(Y_n = x_n | Y_k = x_k) \times P^1(k|\Gamma_A, y_0), \quad (20)$$

where  $P(Y_n = x_n | Y_k = x_k) = \delta_{x_n, x_k}$  and  $P^1(0|\Gamma_A, y_0) = 0$ .

Summing both sides of the preceding equation over all initial positions  $y_0$  and using the relation in Eq. (7), which applies to  $P(Y_n = x_n | Y_0 = y_0)$ , we obtain

$$1 = \sum_{0 \leq k < n} P(Y_n = x_n | Y_k = x_k) S(k|\Gamma_A), \quad (21)$$

where we have used the notation

$$S(n|\Gamma_A) = \sum_{y_0} P^1(n|\Gamma_A, y_0). \quad (22)$$

Next, using the inequality in Eq. (9) we obtain from Eq. (21), the following basic inequality

$$1 \leq \sum_{0 \leq k < n} R_{n-k} S(k|\Gamma_A), \quad (23)$$

where  $R_{n-k}$  is the probability of return to the starting point in  $n-k$  steps, which is a well-known quantity for all classical random walks.

We note that if the  $A$  particle stays immobile, the inequality in Eq. (23) becomes the *equality*, since here  $x_k = 0$  for all times  $k$ .

Now, let  $\hat{F}(s)$  denote the generating function of some function  $F(n)$ ,

$$\hat{F}(s) = \sum_{n \geq 0} F(n) s^n. \quad (24)$$

Multiplying both sides of the inequality in Eq. (23) by  $s^n$  and performing summations, we have then

$$\left( \frac{1}{1-s} \right) \leq \hat{R}(s) \hat{S}(s|\Gamma_A), \quad (25)$$

where  $\hat{R}(s)$  is the generating function of the return probability  $R_n$ , while

$$\hat{S}(s|\Gamma_A) = \sum_{n \geq 0} \left( \sum_{y_0} P^1(n|\Gamma_A, y_0) \right) s^n. \quad (26)$$

Note that again, the inequality in Eq. (25) becomes the equality in the particular case when  $A$  is immobile, so that

$$\hat{S}(s|0) \leq \hat{S}(s|\Gamma_A), \quad (27)$$

where  $S(n|0)$  denotes the  $S(n|\Gamma_A)$  in the case when  $A$  is immobile.

On the other hand, one readily notices from Eqs. (16) to (18) and (22), that the  $A$  survival probability at time  $n$  is just

$$\Psi(n) = \langle \exp(-\rho K(n|\Gamma_A)) \rangle_{\Gamma_A}, \quad (28)$$

where

$$K(n|\Gamma_A) = \sum_{0 \leq k \leq n} S(k|\Gamma_A). \quad (29)$$

In the limit  $n \rightarrow \infty$  this expression coincides formally with the generating function of  $S(k|\Gamma_A)$ , if  $s \rightarrow 1$ , which suggests that inequality (27) corresponds, at least asymptotically, to the similar inequality

$$K(n|0) \leq K(n|\Gamma_A). \quad (30)$$

In this inequality the right-hand side corresponds to the case of an immobile particle  $A$ . Consequently, the inequality in Eq. (30) implies that the annihilation is faster if  $A$  moves than if it is immobile, in agreement with the Pascal principle.

However, the generating functions  $\hat{S}(s|0)$  and  $\hat{S}(s|\Gamma_A)$  tend to  $\infty$  when  $s \rightarrow 1$ , and the derivation of Eq. (30) requires a more careful analysis, which is the purpose of the following paragraph.

### E. General form of the Pascal principle

Let us turn back to the inequality in Eq. (23) and recall that it becomes an equality in the case when the  $A$  particle does not move. Then, we may formally rewrite the inequality in Eq. (23) in the following form:

$$0 \leq \sum_{0 \leq k \leq n} R_{n-k} [S(k|\Gamma_A) - S(k|0)]. \quad (31)$$

Next, let us introduce two auxiliary functions  $L_n$  and  $M_n$ , such that

$$L_n = S(k|\Gamma_A) - S(k|0) \quad (32)$$

and

$$M_n = \sum_{0 \leq k \leq n} L_k = K(n|\Gamma_A) - K(n|0). \quad (33)$$

By definition, we have  $R_0 = 1$  and  $L_0 = 0$ . Then, the inequality in Eq. (31) can be straightforwardly written as

$$M_n \geq \sum_{1 \leq k \leq n-1} (R_{n-1-k} - R_{n-k}) M_k. \quad (34)$$

Now, it can be shown (see Appendix A) that  $R_k$  is a decreasing function of  $k$ . Assuming that it has been proved that  $M_k \geq 0$  for all  $0 \leq k \leq n-1$ , it follows from Eq. (34) that  $M_n \geq 0$ , and inequality in Eq. (31) is proved by induction, since  $M_0 = 0$ .

Consequently, for any time  $n$ , the  $A$  particle survival probability  $\Psi(n)$ , defined by Eq. (28), in case when the  $A$  particle does not move is less than or equal to the survival probability in case when  $A$  is mobile. This result is much stronger than the asymptotic form of the Pascal principle obtained in Ref. [29].

We note also that this result holds for any finite system with a finite number of traps (i.e., not necessarily in the thermodynamic limit). Here, the survival probability is given by Eq. (13), in which equation  $Q(n|\Gamma_A)$  denotes the probability that a given  $B$  particle does not meet  $A$  before or at

time moment  $n$ . In fact, the probability  $P^1(n|\Gamma_A)$  that a given  $B$  particle meets  $A$  for the first time at time moment  $n$  obeys

$$P^1(n|\Gamma_A) = Q(n-1|\Gamma_A) - Q(n|\Gamma_A) \quad (35)$$

and we have

$$Q(n|\Gamma_A) = 1 - \sum_{0 \leq k \leq n} P^1(k|\Gamma_A). \quad (36)$$

In Sec. III C we introduced  $P^1(k|\Gamma_A)$  as the conditional probability that  $B$ , starting from  $y_0$  at time 0, meets  $A$  for the first time at time  $k$ . Particles  $B$  are uniformly distributed among the  $M$  lattice sites at time 0 (and at all time as well), so that, with the notations used in Eq. (22), we find that

$$P^1(k|\Gamma_A) = \frac{1}{M} \sum_{y_0} P^1(k|\Gamma_A, y_0) = \frac{1}{M} S(n|\Gamma_A), \quad (37)$$

while Eq. (36) reads

$$Q(n|\Gamma_A) = 1 - \frac{1}{M} K(n|\Gamma_A). \quad (38)$$

Thus, the inequality in Eq. (30) implies that, whatever may be the number of  $B$  particles, particle  $A$  has a higher probability to escape if it stays immobile, than if it moves. Note that this conclusion had been drawn previously by Bray and Blythe [25] for systems with a finite number of traps within the context of survival of a mobile prey  $A$  in presence of a finite number of predators  $B$ . Within this context, the Pascal-principle-like inequality in Eq. (30) appears to be even more sound.

To close this section we note that the inequality in Eq. (31) may be questioned for usual Polya random walks [34], since the condition in Eq. (10) is not strictly fulfilled. It is shown in Appendix B how our results can be extended to this case.

## IV. IMPERFECT TRAPPING

### A. Time-correlated chemical reactivity fluctuations

We now modify the model presented in Sec. II, assuming that the  $A$  particle has a finite probability (which may depend on time) to survive when encountered by a  $B$  particle. This case occurs if the reaction is not purely controlled by diffusion: at each encounter, another stochastic process arises and allows the reaction to be eventually completed, or to fail. This process is an elementary reaction act.

If there is a single  $A$  particle, it is physically plausible to assume that at each of its encounters with any of the  $B$ s, the latter can be either in a passive internal state with a (possibly time-dependent) probability  $p(t)$  ( $0 < p(t) < 1$ ), or in an active state with probability  $1 - p(t)$ . In the latter case, the  $A$  is destroyed, whereas it remains intact if  $B$  is passive and they may harmlessly coexist until the  $B$  changes its reactive state. In Ref. [29] we have already addressed this problem, assuming that this reaction probability was constant and independent of all prior events. In many circumstances, how-

ever, this assumption is not justified, and, in particular, the survival probability of the  $A$  particle during its encounter with any of the  $B$ s may itself depend on the trajectory of these particles. We will not treat this difficult problem in general, but only consider a special situation, in which the  $A$  particle survival probability depends on some internal, stochastic property of particle  $B$ . Then it is possible to take into account the time correlations of its fluctuations. This model can be justified as an approximation of certain phenomena, such as possible fluctuations in the activity of the catalyst in a chemical reaction [36].

More precisely, we assume [33,37] that each particle  $B$  can be in a passive state 0 or in an activated state 1, the waiting time  $T_i$  in state  $i$  being a stochastic variable independent of prior events, distributed following an exponential law

$$P(T_i > t) = \exp(-\lambda_i t) \quad (i=0 \text{ or } 1), \quad (39)$$

where  $\lambda_0$  and  $\lambda_1$  are given positive constants.

Now, the transition probability for the internal state  $I(t)$  of  $B$  is then given by the well-known ‘‘random telegraph’’ law [35]

$$P(I(t) = i | I(0) = j) = \alpha_i + (\delta_{ij} - \alpha_i) e^{-\lambda t} \quad (40)$$

with

$$\lambda = \lambda_0 + \lambda_1 \text{ and } \alpha_0 = \lambda_1 / \lambda, \quad \alpha_1 = \lambda_0 / \lambda. \quad (41)$$

Thus,  $\alpha_0 \equiv p$  is the asymptotic probability that  $A$  survives a collision with  $B$ , whereas  $\alpha_1 = 1 - p$  is the asymptotic reaction probability at each encounter. The elementary reaction act constant  $k$ , mentioned in the beginning of Sec. II, is just  $k \sim (1 - p)/p$ . We logically assume that the internal state of  $B$  is initially in its stationary probability distribution, as well as at the first encounter with  $A$ , but at the next encounter the law given by Eq. (40) should be used.

Extending Eq. (20) to the present situation with a stochastic elementary reaction act, we find

$$\begin{aligned} \alpha_1 P(Y_n = x_n | Y_0 = y_0) &= \underline{P}^1(n | \Gamma_A, y_0) + \sum_{0 \leq k \leq n-1} (\alpha_1 + \alpha_0 e^{-\lambda(n-k)}) \\ &\times P(Y_n = x_n | Y_k = x_k) \underline{P}^1(k | \Gamma_A, y_0). \end{aligned} \quad (42)$$

In fact,  $\alpha_1 P(Y_n = x_n | Y_0 = y_0)$  is the probability that  $B$  meets  $A$  at time  $n$ , while it is in its active state: the probability for  $B$  to be in its active state at time  $n$  is independent of the trajectories of  $B$  or  $A$ , and is given by the stationary value  $\alpha_1$ , since no value of the internal state is assigned before time  $n$ . Furthermore,  $\underline{P}^1(k | \Gamma_A, y_0)$  is the probability that  $B$  meets  $A$  in its active state at time  $k$  for the first time after 0, with  $\underline{P}^1(0 | \Gamma_A, y_0) = 0$ . If  $B$  meets  $A$  in its active state at time  $n$ , then necessarily the same situation occurred for the first time at some time  $k$ ,  $0 < k \leq n$ . If  $k < n$ , then the probability for  $B$  to be again in its active state is given by Eq. (40), which gives rise to the last term in the right-hand side of Eq. (42). Equation (42) can be written in a more compact form

$$\begin{aligned} \alpha_1 P(Y_n = x_n | Y_0 = y_0) &= \sum_{0 \leq k \leq n} (\alpha_1 + \alpha_0 e^{-\lambda(n-k)}) \\ &\times P(Y_n = x_n | Y_k = x_k) \underline{P}^1(k | \Gamma_A, y_0). \end{aligned} \quad (43)$$

Summing both sides of it over the initial position  $y_0$ , we then obtain

$$\begin{aligned} \alpha_1 &= \sum_{0 \leq k \leq n} (\alpha_1 + \alpha_0 e^{-\lambda(n-k)}) \\ &P(Y_n = x_n | Y_k = x_k) \underline{\mathcal{S}}(k | \Gamma_A), \end{aligned} \quad (44)$$

where  $\underline{\mathcal{S}}(k | \Gamma_A)$  is the probability that the annihilation of  $A$  occurs at time  $k$ , for a given trajectory of  $A$ .

Using next the inequality in Eq. (9), we find the following relation:

$$1 \leq \sum_{0 \leq k \leq n} \left( 1 + \frac{\alpha_0}{\alpha_1} e^{-\lambda(n-k)} \right) R_{n-k} \underline{\mathcal{S}}(k | \Gamma_A). \quad (45)$$

We now make use of the generating functions technique and obtain, returning to the notation  $p \equiv \alpha_0$ , that

$$\frac{1}{1-s} \leq \left[ \hat{R}(s) + \frac{p}{1-p} \hat{R}(s e^{-\lambda}) \right] \hat{\mathcal{S}}(s | \Gamma_A), \quad (46)$$

which becomes the equality in case  $A$  is immobile. The conclusions follow as previously: the generating function of the conditional reaction probability at time  $n$  is minimal if  $A$  is immobile, i.e.,

$$\hat{\mathcal{S}}(s | 0) \leq \hat{\mathcal{S}}(s | \Gamma_A). \quad (47)$$

Consequently, the integral reaction rate  $\underline{K}(n | \Gamma_A)$  is minimal if  $A$  stays immobile

$$\underline{K}(n | 0) \leq \underline{K}(n | \Gamma_A), \quad (48)$$

the left-hand sides of Eqs. (47) and (48) denoting the quantities corresponding to an immobile  $A$ , respectively.

The fact that Eq. (48) holds at any time  $n$  can be proved directly by using the inequality in Eq. (46) exactly in the same fashion as it has been done in Sec. III C [when all collisions are reactive ( $p = 0$ )].

## B. Asymptotic reaction kinetics

Let us first consider the special case when  $A$  is immobile. Then, the asymptotic kinetic behavior follows from Eq. (46),

$$(1-s) \hat{\mathcal{S}}(s | 0) = \left[ \hat{R}(s) + \frac{p}{1-p} \hat{R}(s e^{-\lambda}) \right]^{-1}. \quad (49)$$

In one and two dimensions,  $\hat{R}(s)$  tends to infinity when  $s \rightarrow 1$ , so that the terms due to the reactivity fluctuations in the right-hand side of Eq. (49) do not affect the kinetics, which proceeds exactly in the same way as in the case of perfect trapping reactions.

In three dimensions  $\hat{R}(s)$  tends to a finite limit  $1/S$  when  $s \rightarrow 1$ , where  $S$  is the probability that a given  $B$  particle never returns to its initial position (see Appendix A). Then, the left-hand side of Eq. (49) tends to an effective, apparent reaction constant  $\underline{k}$ , which satisfies the inverse addition relation

$$\frac{1}{\underline{k}} = \frac{1}{S} + \frac{p}{1-p} \hat{R}(e^{-\lambda}), \quad (50)$$

if  $A$  is immobile [33,37].

Equation (50) shows that if  $A$  is immobile, the reaction rate  $\underline{k}$  is an increasing function of the relaxation frequency  $\lambda$  of the activity fluctuations, so that the survival probability decreases with  $\lambda$ , if  $p$  is maintained constant. It can be shown that this remarkable property is more general and is also valid if both particles are mobile [37]. In the case of an infinite relaxation frequency or uncorrelated fluctuations Eq. (50) becomes

$$\frac{1}{\underline{K}} = \frac{1}{S} + \frac{p}{1-p}. \quad (51)$$

Equations (50) and (51) are particular cases of the ‘‘inverse addition law’’ which is well known in chemistry [11,36,38]. In fact, such a law is valid if the reaction can be considered as a succession of independent steps, which is the case for uncorrelated fluctuations. It was discussed in this context in our previous works [36].

We shall now partially extend these results for a mobile particle  $A$ . In fact, in one or two dimensions it has been shown [25,26] that when  $A$  is annihilated as soon as it meets any of  $B$  particles ( $p=0$ ), the survival probability does not depend on the motion of  $A$  in the limit  $n \rightarrow \infty$ ,

$$\Psi(n;p=0) \approx \Psi_0(n;p=0),$$

where  $\Psi_0$  is the survival probability in case of an immobile  $A$ .

If  $A$  has a finite probability to survive at each encounter, the overall survival probability  $\Psi(n;p,\lambda)$  is obviously larger than if  $p=0$ . However, we have shown in Eq. (47) that  $\Psi(n;p,\lambda)$  is smaller than the survival probability  $\Psi_0(n;p,\lambda)$  in the case of an immobile particle, and the latter is asymptotically independent of  $p$ . Thus, we can write

$$\begin{aligned} \Psi_0(n;p=0) &\approx \Psi(n;p=0) \leq \Psi(n;p,\lambda) \leq \Psi_0(n;p,\lambda) \\ &\approx \Psi_0(n;p=0) \end{aligned} \quad (52)$$

so that for large  $n$

$$\Psi(n;p,\lambda) \approx \Psi_0(n;p,\lambda) \approx \Psi_0(n;p=0), \quad (53)$$

which shows that in one and two dimensions the reactivity fluctuations of  $B$  as well as the motion of  $A$  do not affect the survival probability of  $A$  in the asymptotic limit  $n \rightarrow \infty$ , except if  $B$  is immobile, in which case the survival probability has a very different and unusual behavior [13].

In three dimensions, on the contrary, the fluctuations actually change the reaction kinetics. The survival probability

decreases exponentially and the overall reaction rate  $\underline{k}$  is given by the inverse addition law in Eq. (50). However, it is unclear if such a law still holds when both particles move, since then we have only proved inequality in Eq. (53). Thus, the first and the last approximate equalities in Eq. (51) do not hold in three dimensions, whereas the relations in Eq. (51) are valid. It is known [9] that for large  $n$ ,  $\Psi(n;p=0)$  decreases exponentially, as well as the survival probability of an immobile particle  $A$ ,  $\Psi_0(n;p,\lambda)$ , so that it may be assumed that  $\Psi(n;p,\lambda)$  also decreases exponentially with a constant larger than  $\underline{k}$  given by Eq. (50), but it is difficult to estimate this constant precisely.

## V. CONCLUSION

We have developed the stochastic lattice theory of the annihilation kinetics of a species  $A$  by another species  $B$ , in systems in which the  $A$  and  $B$  particles perform independent, stochastic motions which can be rather general. We obtained formal expressions for the survival probability of  $A$ . This probability cannot be evaluated exactly if  $A$  is actually mobile. However, we proved that the  $A$  particle survival probability is always larger in the case when  $A$  is immobile than when it moves. We have shown that this so-called Pascal principle holds for a large class of stochastic motions, provided  $B$  executes a random walk satisfying certain reasonable assumptions. This conclusion is of a special importance in view of its implications on chemical reactions or population dynamics. It also allows to demonstrate that in low dimensions the survival probability of the  $A$  particle is essentially insensitive to its motion and fluctuations of the reactivity, and does not obey the conventional mean-field laws of chemical kinetics. This result is extended to the case of stochastically gated reactions, including the case when the fluctuations of reactivity are time correlated. Furthermore, the method used here allows to obtain the chemical constant of a stochastically gated annihilation of immobile  $A$  particles in a straightforward manner.

The stochastic analysis of chemical reactions should be developed in different directions, in order to consider more realistic models. In particular, it would be interesting to address the case when the activity of  $A$  can also fluctuate. However, the most necessary improvement of the theory would be to extend it to the analysis of analogous reaction kinetics in continuous space and time.

## APPENDIX A: PROPERTIES OF THE RANDOM WALK OF PARTICLES $B$

*Stochastic motion of  $B$  particles.* The constraints imposed on this stochastic process are described in Sec. II A. We show here that the main condition in Eq. (9),

$$P(Y_n = y | Y_0 = 0) \leq P(Y_n = 0 | Y_0 = 0) \equiv R_n, \quad (A1)$$

is satisfied, if the elementary transition probability is symmetric and obeys

$$p(x|y) = p(x-y) = p(y-x) \text{ and } p(0) \geq 1/2.$$

To show this, it is expedient to use first the well-known formula for the propagator of a random walk on a  $d$ -dimensional regular lattice (see, e.g., Ref. [34]):

$$P(Y_n = y | Y_0 = 0) = \frac{1}{(2\pi)^d} \int_{\mathcal{B}} e^{-iz \cdot y} (\phi(z))^n d\mathbf{z}, \quad (\text{A2})$$

where  $\mathcal{B}$  is the first Brillouin zone of the lattice, while  $\phi(z)$  is the so-called structure function

$$\phi(z) = \sum_y e^{iz \cdot y} p(y) \quad (\text{A3})$$

in which equation  $z \cdot y$  stands for the scalar product of two  $d$ -dimensional vectors  $z$  and  $y$ , while  $d\mathbf{z}$  represents the differential element in a  $d$ -dimensional space.

Now, according to our assumption,  $p(y) = p(-y)$ , which implies that

$$\begin{aligned} \phi(z) &= \sum_y \cos(zy) p(y) \\ &= p(0) + [1 - p(0)] \sum_{y \neq 0} \cos(zy) p(y) / (1 - p(0)). \end{aligned} \quad (\text{A4})$$

Evidently, the second term in Eq. (A4) is bounded from above by unity if  $p(0) \geq 1 - p(0)$  or  $p(0) \geq 1/2$ . In this case,  $P(Y_n = y | Y_0 = 0) = (2\pi)^d \int_{\mathcal{B}} \cos(zy) (\phi(z))^n d\mathbf{z}$  is maximal for  $y = 0$ , which proves the inequality in Eq. (A1).

Furthermore, one readily notices that if this condition is fulfilled,  $R_n$  is a decreasing function of  $n$ .

*Relation with the first return time.* The probability  $R_n^1$  that the first return of  $B$  to its initial position occurs at time moment  $n$  is classically obtained from the relation

$$\begin{aligned} P(Y_n = 0 | Y_0 = 0) &\equiv R_n = R_n^1 + \sum_{1 \leq k \leq n-1} R_{n-k} R_k^1 \\ &= \sum_{0 \leq k \leq n-1} R_{n-k} R_k^1 \quad \text{for } n \geq 1, \end{aligned} \quad (\text{A5})$$

where  $R_0 \equiv 1$  and  $R_0^1 \equiv 0$ . Then, the generating functions of  $R_n$  and  $R_n^1$  satisfy

$$\hat{R}(s) - 1 = \hat{R}(s) \hat{R}^1(s), \quad (\text{A6})$$

which yields

$$\hat{R}(s) = [1 - \hat{R}^1(s)]^{-1} \rightarrow 1/S \quad \text{if } s \rightarrow 1, \quad (\text{A7})$$

$S$  being the probability that the  $B$  particle never returns to its initial position.

## APPENDIX B: THE CASE OF POLYA RANDOM WALKS

The assumptions of Sec. II exclude the Polya random walks, or any random walk such that there is a zero probability to stay immobile at each integer time:  $p(0) = 0$ , i.e., a

random walk in which a particle is forced to make a move at each integer time moment. In this case, the probability to return to the initial position is obviously zero at any odd time moment, and the inequality in Eq. (10), which plays a basic role in our reasonings, holds only at even moments of time. More precisely, possible displacements of the random walker in this case can be divided into two complementary subsets  $E_0$  and  $E_1$ , such that the total displacement during time  $n$  necessarily belongs to  $E_0$  if  $n$  is even, and to  $E_1$  if  $n$  is odd. Thus the Pascal principle cannot apply in a strict sense.

We can recover the Pascal principle for Polya random walks if we slightly change the rules of our model, imposing, for instance, that the  $A$  particle moves only on the lattice  $E_0$ , and that the  $B$  particles are distributed on  $E_0$  only. Thus no reaction can occur at odd times, and we only consider even times  $n = 2n'$ . Then, the inequality in Eq. (10) applies, as well as all previous calculations, and the Pascal principle holds.

However, it is interesting to discuss the case when  $B$  performs a Polya random walk, if the evolution of particles is not restricted on a sublattice. The Eq. (21),

$$\begin{aligned} P(Y_n = x_n | Y_0 = y_0) &= \sum_{0 \leq k < n} P(Y_n = x_n | Y_k = x_k) \\ &\quad \times P^1(k | \Gamma_A, y_0), \end{aligned} \quad (\text{B1})$$

is still valid (with possibly many vanishing terms), but the inequality in Eq. (24) cannot be deduced from it.

If, in Eq. (B1),  $n - k$  is even,  $x_n - x_k$  should belong to  $E_0$ , and inequality in Eq. (10) holds

$$P(Y_n = x_n | Y_k = x_k) \leq R_{n-k}. \quad (\text{B2})$$

On the contrary, if  $n - k$  is odd,  $R_{n-k} = 0$ , but we have

$$\begin{aligned} P(Y_n = x_n | Y_k = x_k) &= \sum_y p(x_n | y) P(Y_{n-1} = y | Y_k = x_k) \\ &\leq \sum_y p(x_n | y) R_{n-1-k} = R_{n-1-k}. \end{aligned} \quad (\text{B3})$$

Consequently, from Eq. (B1) we can deduce the inequality

$$P(Y_n = x_n | Y_0 = y_0) \leq \sum_{0 \leq k < n} R_{n-k}^* P^1(k | \Gamma_A, y_0), \quad (\text{B4})$$

where we have used the notation

$$R_k^* \equiv R_k + R_{k-1}^*. \quad (\text{B5})$$

Summing both sides of Eq. (B3) over  $y_0$  gives, with the same notations,

$$1 \leq \sum_{0 \leq k < n} R_{n-k}^* S(k | \Gamma_A). \quad (\text{B6})$$

Applying the generating functions technique, we find then

$$\frac{1}{1-s} \leq \hat{R}^*(s) \hat{S}(s|\Gamma_A), \quad (\text{B7})$$

where the generating function of  $R_k^*$ , Eq. (B5), is given by

$$\hat{R}^*(s) = (1+s) \sum_{0 \leq n < \infty} R_{2n} s^{2n} = (1+s) \hat{R}(s). \quad (\text{B8})$$

If now the  $A$  particle is fixed at the origin, Eq. (B1) becomes

$$\begin{aligned} P(Y_n=0|Y_0=y_0) &= \sum_{0 \leq k < n} P(Y_n=0|Y_k=0) P^1(k|0, y_0) \\ &= \sum_{0 \leq k < n} R_{n-k} P^1(k|0, y_0). \end{aligned} \quad (\text{B9})$$

Summing both sides of this equation over  $y_0$  and turning to the generating functions, we find, instead of Eq. (B7), the following equation:

$$\frac{1}{1-s} = \hat{R}(s) \hat{S}(s|0). \quad (\text{B10})$$

Now, on comparing it with Eq. (B7), we infer that

$$(1-s) \hat{S}(s|\Gamma_A) \geq \frac{1}{2} (1-s) \hat{S}(s|0), \quad (\text{B11})$$

which implies that, asymptotically, if  $A$  moves, the reaction integral for a given trajectory  $\Gamma_A$  is not smaller than half of the reaction integral when  $A$  is immobile.

This unexpected conclusion requires some comments. First, it can be noted that the equality in Eq. (B11) can be realized in a particular example. In fact, assume that  $B$  performs a classical Polya random walk on a  $d$ -dimensional lattice: at each step it can jump with an equal probability  $1/(2d)$  at one of the neighboring sites. Now, we choose a special trajectory  $\Gamma_A$  for  $A$ , consisting of jumps from the origin zero to one of its nearest neighbors, 1, and returns: thus, at each even time  $n$ ,  $A$  is at 0, whereas  $A$  is at 1 at each odd time.

For such a trajectory Eq. (B1) reads

$$P(Y_n=x_n|Y_0=y_0) = \sum_{0 \leq k < n} R_{n-k}^\circ P^1(k|\Gamma_A, y_0), \quad (\text{B12})$$

where

$$\begin{aligned} R_{n-k}^\circ &= R_{n-k} = P(Y_n=0|Y_k=0) = P(Y_n=1|Y_k=1) \\ &\quad \text{if } n-k \text{ is even} \\ &= R_{n-k+1} = P(Y_n=1|Y_k=0) = P(Y_n=0|Y_k=1) \\ &\quad \text{if } n-k \text{ is odd,} \end{aligned}$$

since

$$\begin{aligned} R_{2n} &= P(Y_{2n}=0|Y_0=0) = (2d)^{-1} \sum' P(Y_{2n-1}=y|Y_0=0) \\ &= P(Y_{2n-1}=1|Y_0=0), \end{aligned} \quad (\text{B13})$$

where the prime designates that we sum only over the nearest to the origin sites. Consequently, we can write

$$R_{n-k}^\circ = R_{n-k} + R_{n-k+1}. \quad (\text{B14})$$

Summing Eq. (B13) over  $y_0$  we obtain for the generating functions

$$\frac{1}{1-s} = \hat{R}^\circ(s) \hat{S}(s|\Gamma_A) \quad (\text{B15})$$

with

$$\hat{R}^\circ(s) = \frac{1+s}{s} \hat{R}(s). \quad (\text{B16})$$

Thus, for this special trajectory, we actually obtain

$$(1-s) \hat{S}(s|\Gamma_A) = \frac{1}{2} (1-s) \hat{S}(s|0) \text{ if } s \rightarrow 1, \quad (\text{B17})$$

which implies that the reaction is twice slower than that for an immobile  $A$ . For instance, in three dimensions, the expression in Eq. (B16) is bounded when  $s \rightarrow 1$ , which means that if  $A$  moves according to the previous rules, the reaction constant in the case of a mobile  $A$  is half of the reaction constant for an immobile  $A$ . If an average is taken over trajectories, the Pascal principle can be valid or not, depending on the probability weight of the different trajectories.

The physical reason for this conclusion may be understood if we consider the relative motion with respect to  $A$ . It is seen that at each integer time the relative displacement of  $B$  in the direction 0–1 can be 0 or 2 at odd times, and 0 or –2 at even times. On the other hand, the reaction integral at time  $n$  is related to the number of distinct sites visited by  $B$  up to time  $n$ . This number is clearly lower if  $A$  moves according to the foregoing rules, than if  $A$  is immobile, which explains that the reaction is slower in the first case. The same behavior can occur each time  $A$  and  $B$  are performing Polya walks with the same jump times.

However, it should be pointed out that when  $A$  and  $B$  both perform Polya random walks with the same jump times, it may well happen that they exchange their positions during simultaneous jumps. In this case, they do not react according to the rules we used here, but it can be relevant to adopt different rules, depending on the actual phenomenon to be modeled. Then, the results could depend very much on these rules.

- [1] M.V. Smoluchowski, *Phys. Z.* **17**, 585 (1916).
- [2] S. Rice, in *Diffusion-Limited Reactions*, edited by C. H. Bamford, C. F. H. Tipper, and R. G. Compton, *Chemical Kinetics Vol. 25* (Elsevier, Amsterdam, 1985).
- [3] D. Calef and J.M. Deutch, *Annu. Rev. Phys. Chem.* **34**, 493 (1983).
- [4] A. Blumen, G. Zumofen, and J. Klafter, *Phys. Rev. B* **30**, 5379 (1984); A. Blumen, J. Klafter, and G. Zumofen, in *Optical Spectroscopy of Glasses*, edited by I. Zschokke (Reidel, Dordrecht, 1986).
- [5] S.F. Burlatsky and G. Oshanin, *J. Stat. Phys.* **65**, 1095 (1991).
- [6] G. Oshanin, M. Moreau, and S.F. Burlatsky, *Adv. Colloid Interface Sci.* **49**, 1 (1994).
- [7] S. Redner and K. Kang, *J. Phys. A* **1**, 451 (1984).
- [8] S.F. Burlatsky and A.A. Ovchinnikov, *Zh. Éksp. Teor. Fiz.* **92**, 1618 (1987) [*Sov. Phys. JETP* **65**, 908 (1987)].
- [9] M. Bramson and J.L. Lebowitz, *Phys. Rev. Lett.* **61**, 2397 (1988).
- [10] A. Szabo, R. Zwanzig, and N. Agmon, *Phys. Rev. Lett.* **61**, 2496 (1989).
- [11] O. Bénichou, M. Moreau, and G. Oshanin, *Phys. Rev. E* **61**, 3388 (2000).
- [12] B.Ya. Balagurov and V.T. Vaks, *Zh. Éksp. Teor. Fiz.* **65**, 1939 (1973) [*Sov. Phys. JETP* **38**, 968 (1974)].
- [13] M.D. Donsker and S.R.S. Varadhan, *Commun. Pure Appl. Math.* **28**, 525 (1975).
- [14] L.A. Pastur, *Theor. Math. Phys.* **32**, 88 (1977).
- [15] P. Grassberger and I. Procaccia, *J. Chem. Phys.* **77**, 6281 (1982).
- [16] R.F. Kayser and J.B. Hubbard, *Phys. Rev. Lett.* **51**, 79 (1983).
- [17] T.C. Lubensky, *Phys. Rev. A* **30**, 2657 (1984); S.R. Renn, *Nucl. Phys. B* **275**, 273 (1986); Th.M. Nieuwenhuizen, *Phys. Rev. Lett.* **62**, 357 (1989).
- [18] C. Monthus, G. Oshanin, A. Comtet, and S.F. Burlatsky, *Phys. Rev. E* **54**, 231 (1996).
- [19] A. Blumen, G. Zumofen, and J. Klafter, *Phys. Rev. B* **30**, 5379 (1984).
- [20] A. Szabo, R. Zwanzig, and N. Agmon, *Phys. Rev. Lett.* **61**, 2496 (1988).
- [21] M. Tachiya, *Radiat. Phys. Chem.* **21**, 167 (1983).
- [22] S.F. Burlatsky, M. Moreau, G. Oshanin, and A. Blumen, *Phys. Rev. Lett.* **75**, 585 (1995); D.P. Bhatia, M.A. Prasad, and D. Arora, *ibid.* **75**, 586 (1995).
- [23] O. Bénichou, M. Moreau, and G. Oshanin, *Phys. Rev. E* **61**, 3388 (2000).
- [24] A.M. Berezhkovskii, Yu.A. Makhnovskii, and R.A. Suris, *J. Phys. A* **22**, L615 (1989).
- [25] A.J. Bray and R.A. Blythe, *Phys. Rev. Lett.* **89**, 150601 (2002).
- [26] G. Oshanin, O. Bénichou, M. Coppey, and M. Moreau, *Phys. Rev. E* **66**, 060101(R) (2002).
- [27] P.G. de Gennes, *J. Chem. Phys.* **76**, 3316 (1982).
- [28] A.J. Bray, S.N. Majumdar, and R.A. Blythe, *Phys. Rev. E* **67**, 060102(R) (2003).
- [29] M. Moreau, G. Oshanin, O. Bénichou, and M. Coppey, *Phys. Rev. E* **67**, 045104(R) (2003).
- [30] B. Pascal, *Pensées*, edited by Brunshvicg, Fragment Vol. 139, (Boutroux et Gazier, Paris, 1904).
- [31] S.F. Burlatsky, G. Oshanin, and A.A. Ovchinnikov, *Phys. Lett. A* **139**, 241 (1989).
- [32] F. Coppex, M. Droz, J. Piasecki, E. Trizac, and P. Wittwer, *Phys. Rev. E* **67**, 021103 (2003).
- [33] O. Bénichou, M. Moreau, and G. Oshanin, *Physica A* **306**, 187 (2002).
- [34] B. D. Hughes, *Random Walks and Random Environments* (Oxford Science Publishers, Oxford, 1995).
- [35] W. Feller, *An Introduction to Probability Theory and Its Applications* (Wiley, New York, 1966), Vol. 2, p. 447.
- [36] M. Moreau, B. Gaveau, M. Frankowicz, and A. Perera, in *Far from Equilibrium Dynamics of Chemical Systems*, edited by A. Popielawski and J. Gorecki (World Scientific, Singapore, 1993).
- [37] M. Moreau, G. Oshanin, O. Bénichou, and M. Coppey, *Physica A* **327**, 99 (2003).
- [38] F. Collins and K. Kimball, *J. Colloid Sci.* **4**, 425 (1949).