First-passage method for the study of the efficiency of a two-channel reaction on a lattice

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We study the efficiency of a two-channel reaction between two walkers on a finite one-dimensional periodic lattice. The walkers perform a combination of synchronous and asynchronous jumps on the lattice and react instantaneously when they meet at the same site (first channel) or upon position exchange (second channel). We develop a method based on a conditional first-passage problem to obtain exact results for the mean number of time steps needed for the reaction to take place as well as for higher order moments. Previous results obtained in the framework of a difference equation approach are fully confirmed, including the existence of a parity effect. For even lattices the maximum efficiency corresponds to a mixture of synchronous events and a small amount of asynchronous events, while for odd lattices the reaction time is minimized by a purely synchronous process. We provide an intuitive explanation for this behavior. In addition, we give explicit expressions for the variance of the reaction time. The latter displays a similar even-odd behavior, suggesting that the parity effect extends to higher order moments.

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I. INTRODUCTION

In experimental systems there is always a finite discretization of the time window used for measurements. Thus, the degree of synchronicity for the dynamics of the different system constituents may vary when the size of the time window is changed, either intentionally or accidentally as a result of random fluctuations in the clock mechanism. But even for a fixed time resolution there may be intrinsic features of the experimental system that lead to the coexistence of synchronous and asynchronous events in the course of the evolution. Consider, e.g., diffusion of an ensemble of identical particles in a disordered or a randomly fluctuating medium [1,2]. The diffusivity of a particle will then be different depending on its location, and this will lead to the coexistence of different characteristic time scales in the system, resulting in partial desynchronization for the dynamics of its constituents.

Recently, the author and co-workers used a simplified lattice version of this problem to study the role of synchronicity on the efficiency of a diffusion-controlled two-channel reaction between two particles [3]. Here, the parameter chosen for the characterization of the reaction efficiency is the mean number of time steps to reaction. The effect of synchronicity was investigated by studying how this quantity is affected by the interplay between the transport dynamics and the geometric characteristics of the lattice, i.e., size, dimensionality, and boundary conditions. Finite size effects were found to play an important role, thus emphasizing the relevance of geometric constraints for systems with a small number of constituents. On the other hand, a variety of interesting problems in statistical physics may be recast in terms of a random walk in a lattice of a small size. An example thereof is a family of ruin problems where the capital of each gambler is typically a small number [3,4].

In Ref. [3] the analytic results for the one-dimensional (1D) case were based on a difference equation approach, whereas numerical simulations were used in higher dimensions. However, it is also instructive to compute the mean reaction time for this problem by other methods, e.g., approaches based on the theory of finite Markov processes [5–7] and on generating function techniques [8]. The first method has the advantage of being applicable in higher dimensions and to systems lacking translational invariance (e.g., with reflecting boundaries), while the second emphasizes the correspondence between diffusion-controlled reactions and first-passage problems [9]. In this paper, we shall apply the latter to determine the mean number of time steps necessary for the reaction to take place as well as the variance of this quantity. An important advantage of this approach is that the variance and higher order moments can be computed by a straightforward differentiation of the relevant generating function, as opposed to the method of difference equations, where moments are coupled to each other via a hierarchy of equations [3].

The work plan is as follows. In Sec. II we introduce the model and its reduced representation in a comoving reference frame. Section III introduces the generating function approach to compute the reaction time and higher order moments. For completeness, we first present the standard formalism to deal with some simple cases where only a single reaction channel is active. We then treat the general case, which is solved in two stages. First, we show that our model is equivalent to a model with a relaxed collision rule and then we solve for the latter. Section IV contains the main results for the reaction time and its variance. Finally, Sec. V summarizes the main conclusions.

II. THE MODEL

The system to be studied consists of two coreactants A and B performing symmetric nearest-neighbor random jumps on a N-site periodic lattice at discrete time steps. The reac-

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tants, also termed walkers in what follows, are assumed to react with each other whenever they meet at the same lattice site or attempt to exchange positions. Each of such "collisions" results in an instantaneous irreversible reaction. Regardless of the particular outcome of the reaction,[1] the mean reaction time can be identified with the mean number of time steps elapsed until the collision takes place; the larger this quantity, the less efficient the reaction will be. Each time step will be considered to be an elapsed time unit regardless of the lattice size. In the course of the dynamics, the following joint events may occur:

(1) With probability p both walkers hop simultaneously to randomly chosen nearest-neighbor sites (synchronous event).

(2) With probability $1-p$ one of the walkers (no matter whether A or B) hops to a nearest-neighbor site while the other one remains immobile (asynchronous event).

Thus, the characteristic parameter p interpolates between the asynchronous case ($p=0$) and the case of two simultaneously moving walkers ($p=1$). Occasionally, we shall refer to the limiting cases $p=0$ and $p=1$ as "the purely asynchronous case" and "the purely synchronous case," respectively. The purely asynchronous case was studied by Montroll [16,17] and Montroll and Weiss [18] in one, two, and three dimensions. For the particular case of a periodic 1D lattice they obtained

$$\langle n\rangle = \frac{N(N+1)}{6}, \tag{1}$$

where $\langle n\rangle$ is the initial-condition-averaged mean reaction time. Note that in this case the only active reaction channel is same site occupation (SSO), since reaction by position exchange of the walkers, i.e., by nearest-neighbor crossing (NNC) is not possible.

However, in the purely synchronous case, both reaction channels SSO and NNC will be active if the total number of sites N is odd, otherwise only one channel will be available, depending on the initial location of the walkers. A consequence is that the analytical expression for $\langle n\rangle$ in terms of the size of the 1D lattice depends on the parity of N [6,19]. This even-odd effect translates mathematically as follows [3]:

$$\langle n\rangle = \begin{cases} N(N+1)(N+2)/[12(N-1)] & \text{for } N \text{ even}, \\ (N+1)(N+3)/12 & \text{for } N \text{ odd}. \end{cases} \tag{2}$$

In contrast to the above cases, as soon as $0<p<1$, reaction by NNC becomes possible *regardless* of the value of N and the initial two-walker configuration.

Due to the translational invariance of the lattice, only the relative motion of both walkers is relevant for the computation of the collision time. This has two important consequences. First, it tell us that the physical distinguishability of the walkers is irrelevant for the solution of the problem. To emphasize this, the walker labels A and B have been left out in the scheme displayed in Fig. 1(a). The second consequence is that it is convenient to choose the reference frame

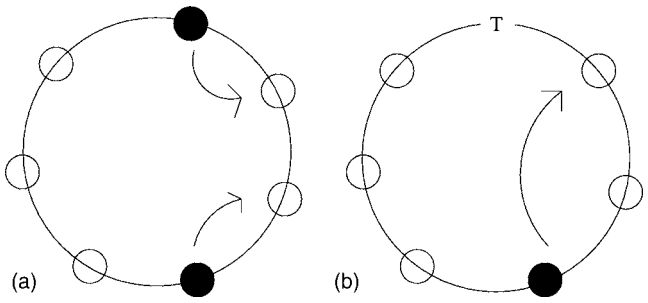

FIG. 1. (a) Two-walker system on a seven-site periodic lattice. Both walkers are represented by black circles. For convenience, the walker labels A and B have been left out (see text for explanation). (b) Equivalent one-walker plus trap system. The trapping site is denoted by "T." The arrows in Fig. 1(a) indicate that both walkers perform a synchronous step. In Fig. 1(b) this corresponds to a two-site jump of the walker.

in such a way that one of the walkers (say B) is at rest. In this comoving frame, walker A will either hop to a nearest neighbor (with probability $1-p$), hop to a next-to-nearest-neighbor site (with probability $p/2$), or remain immobile (again with probability $p/2$) as a result of the rules 1 and 2 prescribed above. In this one-walker representation, walker B plays the role of a stationary trap T, as indicated in Fig. 1(b); any time walker A reaches *or* attempts to overcome the site at which walker B is placed, the instantaneous reaction is triggered and the dynamics is stopped. In what follows, we shall therefore refer to walker B as "the trap" and to walker A as "the walker" when we work in the comoving frame.

For convenience, let us place the origin (site 0) of the comoving frame at the initial position of walker A and then number the remaining sites, say clockwise, from 1 to $N-1$. Denoting by j_T the coordinate of the site at which the trap is located, the distance in lattice spacings between both walkers will be $d=\min(j_T, N-j_T)$.

III. GENERATING FUNCTION APPROACH

Our next goal will be to derive an expression for the mean number of time steps $\langle n\rangle_{j_T}$ necessary for the reaction to take place for a given value of the coordinate j_T characterizing the initial condition. As a starting point, we take the equations that would govern the sojourn probabilities of an unrestricted walk *if* there were no interaction between the walker and the trap. These equations read

$$\mathcal{P}_{n+1}(j) = \frac{p}{4}[\mathcal{P}_n(j-2) + 2\mathcal{P}_n(j) + \mathcal{P}_n(j+2)] + \frac{1-p}{2}[\mathcal{P}_n(j-1) + \mathcal{P}_n(j+1)], \tag{3}$$

where $\mathcal{P}_n(j)$ is the probability to find the walker at a given site j after n time steps (j may take integer values from 0 and $N-1$ and the site addition and subtraction is performed modulo N). The first term in the right-hand side (RHS) of Eqs. (3) is the contribution due to the synchronous events, by which the walker either remains at rest or it moves two lat-

[1]The case $A+B\rightarrow$ inert is of great historical interest, see, e.g., Refs. [10–15].

tice sites clockwise or anticlockwise. The second term describes jumps by one lattice site yielded by the asynchronous events. In accordance with our definition for the origin, Eq. (3) must be solved using the deterministic initial condition $\mathbf{P}_0=[\mathcal{P}_0(0),\mathcal{P}_0(1),\ldots,\mathcal{P}_0(N-1)]^T=(1,0,\ldots,0)^T$.

A. A simple case

The next step is to incorporate the walker-trap interaction to the above formalism. Let us first consider the situation where reaction by NNC is precluded. This holds if and only if N and the walker-trap separation d are even integers. In this case site j_T can be viewed as a reactive site, also termed "r site" in what follows. Clearly, the mean reaction time will be given by the mean first-passage time $\langle n\rangle_{j_T}$ of the walker at site j_T:

$$\langle n\rangle_{j_T}=\sum_{n=1}^{\infty} n\mathcal{F}_n(j_T), \tag{4}$$

where $\mathcal{F}_n(j)$ is the probability of visiting a given site j for the *first* time after n time steps. Equation (4) can be expressed as

$$\langle n\rangle_{j_T}=\left.\frac{\partial}{\partial z}\mathcal{F}(j_T,z)\right|_{z=1}, \tag{5}$$

where $\mathcal{F}(j,z)\equiv\Sigma_{n=0}^{\infty}\mathcal{F}_n(j)z^n$ is the generating function of the first-passage probabilities $\mathcal{F}_n(j)$ and the limit $z\to 1$ is taken from below. On the other hand, this function can be directly related to the generating function $\mathcal{P}(j,z)\equiv\Sigma_{n=0}^{\infty}\mathcal{P}_n(j)z^n$. To do so, one uses the fact that the sets of probabilities $\mathcal{P}_n(j)$ and $\mathcal{F}_n(j)$ are linked to each other via the equation [8]

$$\mathcal{P}_n(j)=\sum_{k=1}^{n}\mathcal{F}_k(j)\mathcal{P}_{n-k}(0),\quad j\neq 0. \tag{6}$$

The discrete convolution on the RHS of Eq. (6) is equivalent to the product $\mathcal{P}(j,z)\mathcal{F}(j,z)$ in the reciprocal generating function space. Thus, we have

$$\mathcal{F}(j,z)=\sum_{n=0}^{\infty}\mathcal{F}_n(j)z^n=\frac{\mathcal{P}(j,z)}{\mathcal{P}(0,z)},\quad j\neq 0. \tag{7}$$

The collision time $\langle n\rangle_{j_T}$ then follows from Eqs. (5) and (7):

$$\langle n\rangle_{j_T}=\left.\frac{\partial}{\partial z}\frac{\mathcal{P}(j_T,z)}{\mathcal{P}(0,z)}\right|_{z=1}. \tag{8}$$

B. General case

Let us now extend these results to the general case where N, d and the synchronicity parameter p take arbitrary values. The strategy to tackle the problem will be as follows: we shall not deal with NNC events directly, but rather introduce a model with a relaxed definition of collision, show its equivalence to the original one by virtue of the topological restrictions imposed by the 1D lattice and then compute the reaction time for the relaxed model. For brevity, let us respectively refer to the original and the relaxed models as "model I" and "model II" in what follows.

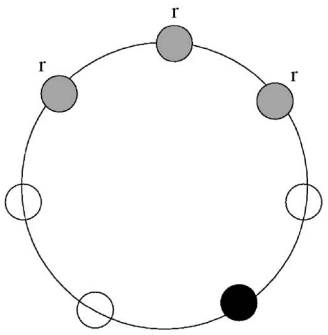

FIG. 2. Representation of model II in the comoving frame.

In model II, one assumes that the walkers react instantaneously by SSO *or* when they jump to nearest-neighbor sites, i.e., by nearest-neighbor occupation (NNO). The representation of the system in the comoving frame will consist of a walker in a lattice with three r sites, as shown in Fig. 2 for a seven-site system. According to the site numbering introduced in Sec. II, these three r sites will have the coordinates j_T (where the immobile reactant is located), j_T-1 and j_T+1. By definition, the walk will automatically terminate when the walker lands on any of the three r sites. For the purpose of computing $\langle n\rangle_{j_T}$, it is easy to realize that the system can be unfolded into an equivalent system with a nonperiodic lattice by introducing an additional fictitious r site, as shown in Fig. 3 for $N=7$.

On the other hand, let us again consider the walker-trap representation of model I depicted in Fig. 1(b) for $N=7$. Along the same lines as above, the system can be unfolded into an equivalent transformed lattice with two trapping sites T and $N-1=6$ nontrapping sites (see Fig. 4). Each site T can then be replaced with two fictitious r sites, as shown in Fig. 4.[2] Thus, we realize that model I embedded in a periodic lattice with N sites is equivalent to model II in a periodic lattice with $N+2$ sites.

Next, let us compute the reaction time $\langle n\rangle_{j_T}$ for model II. The situation is now more complex than the one described in the previous subsection, since we do not know *a priori* at which of the three r sites j_T-1, j_T, or j_T+1 the reaction will occur. Yet, it can still be formulated as a (conditional) first-passage problem. The key quantity in this case is $\mathcal{F}_n(s|s_1,n_1;s_2,n_2)$, i.e., the probability that a random walker arrives at site s for the *first* time at the nth time step after having visited the sites s_1 and s_2 exactly n_1 and n_2 times, respectively. For a given initial condition with a fixed value of j_T, the mean collision time is now

$$\langle n\rangle_{j_T}=\sum_{n=0}^{\infty} n\{\mathcal{F}_n(j_T|j_T-1,0;j_T+1,0)+\mathcal{F}_n(j_T-1|j_T,0;j_T+1,0)+\mathcal{F}_n(j_T+1|j_T-1,0;j_T,0)\}. \tag{9}$$

The RHS of Eq. (9) can again be expressed in terms of the generating functions

[2] If the dynamics is purely asynchronous ($p=0$), only one r site at each end will be needed, since jumps by two sites are not possible in this case

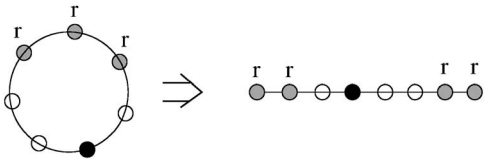

FIG. 3. Lattice transformation for model II in the comoving frame. A periodic lattice with three reactive sites is equivalent to a nonperiodic one with four r sites

$$\langle n\rangle_{j_T} = \frac{\partial}{\partial z}\{\mathcal{F}(j_T|j_T-1,0;j_T+1,0;z) + \mathcal{F}(j_T-1|j_T,0;j_T+1,0;z) + \mathcal{F}(j_T+1|j_T-1,0;j_T,0;z)\}|_{z=1}, \tag{10}$$

where

$$\mathcal{F}(s|s_1,n_1;s_2,n_2;z) = \sum_{n=0}^{\infty} \mathcal{F}_n(s|s_1,n_1;s_2,n_2)z^n. \tag{11}$$

To compute this generating function, let us first observe that

$$\mathcal{P}_n(s|s_1,0;s_2,0) = \sum_{k=1}^{n} \mathcal{F}_k(s|s_1,0;s_2,0)\mathcal{P}_{n-k}(0|s_1-s,0;s_2-s,0), \quad s \neq 0,s_1,s_2, \tag{12}$$

where $\mathcal{P}_n(s|s_1,0;s_2,0)$ is the probability that the walker is at site s at time n conditioned to its not having visited sites s_1 and s_2 but regardless of any previous visits to s. This probability must fulfil the initial condition $\mathcal{P}_0(0|s_1-s,0;s_2-s,0)=1$. A simple calculation shows that Eq. (12) leads to the relation

$$\mathcal{F}(s|s_1,0;s_2,0;z) = \frac{\mathcal{P}(s|s_1,0;s_2,0;z)}{\mathcal{P}(0|s_1-s,0;s_2-s,0;z)}, \tag{13}$$

where

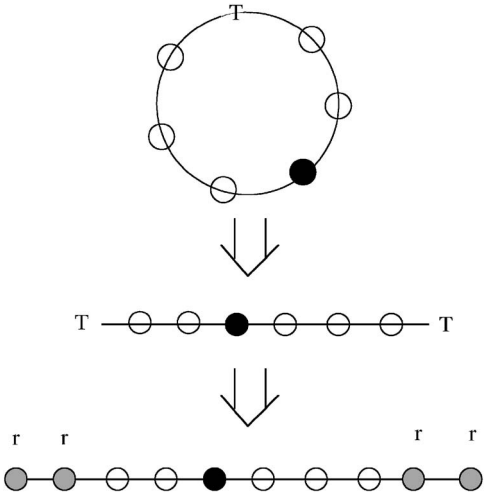

FIG. 4. Lattice transformation for the one-walker representation of model I displayed in Fig. 1(b).

$$\mathcal{P}(s|s_1,n_1;s_2,n_2;z) = \sum_{n=0}^{\infty} \mathcal{P}_n(s|s_1,n_1;s_2,n_2)z^n. \tag{14}$$

This generating function can be computed in terms of $\mathcal{P}(s,z)$. For details we refer to the book by Weiss (Ref. [8], Chap. 4). The result for $n_1=n_2=0$ is

$$\mathcal{P}(s|s_1,0;s_2,0;z) = \mathcal{P}(s,z) - \sum_{k=1}^{2} \frac{\mathcal{D}_k(0)}{\mathcal{D}(0)}\mathcal{P}(s-s_k,z), \quad s \neq s_1,s_2, \tag{15}$$

where $\mathcal{D}_k(0)$ and $\mathcal{D}(0)$ are the following determinants:

$$\mathcal{D}(0) = \begin{vmatrix} \mathcal{P}(0,z) & \mathcal{P}(s_2-s_1,z) \\ \mathcal{P}(s_1-s_2,z) & \mathcal{P}(0,z) \end{vmatrix}, \tag{16}$$

$$\mathcal{D}_1(0) = \begin{vmatrix} \mathcal{P}(s_1,z) & \mathcal{P}(s_2-s_1,z) \\ \mathcal{P}(s_2,z) & \mathcal{P}(0,z) \end{vmatrix}, \tag{17}$$

$$\mathcal{D}_2(0) = \begin{vmatrix} \mathcal{P}(0,z) & \mathcal{P}(s_1,z) \\ \mathcal{P}(s_1-s_2,z) & \mathcal{P}(s_2,z) \end{vmatrix}. \tag{18}$$

We can now use these expressions to compute explicitly the mean collision time $\langle n\rangle_{j_T}$. From Eqs. (10) and (13) we have

$$\langle n\rangle_{j_T} = \frac{\partial}{\partial z}\left\{ \frac{\mathcal{P}(j_T|j_T-1,0;j_T+1,0;z)}{\mathcal{P}(0|1,0;N-1,0;z)} + \frac{\mathcal{P}(j_T-1|j_T,0;j_T+1,0;z)}{\mathcal{P}(0|1,0;2,0;z)} + \frac{\mathcal{P}(j_T+1|j_T-1,0;j_T,0;z)}{\mathcal{P}(0|N-1,0;N-2,0;z)} \right\}\Bigg|_{z=1} \tag{19}$$

(recall that the arguments of the different generating functions are evaluated modulo N). Thus, the reaction time can again be expressed in terms of $\mathcal{P}(j,z)$. This quantity is easily computed from the relation

$$\mathcal{P}_{n+1}(j) = \sum_{j'=0}^{N-1} \mathcal{P}_n(j')\hat{p}(j-j'), \tag{20}$$

where the $\hat{p}(j)$'s are the single step probabilities for the random walk. Next, let us introduce the Fourier transform of the single step probabilities

$$\tilde{p}\left(\frac{2\pi l}{N}\right) = \sum_{k=0}^{N-1} \hat{p}(k)\exp\left(\frac{2\pi i k l}{N}\right). \tag{21}$$

This expression can be used to represent $\mathcal{P}(j,z)$ as follows [8]:

$$\mathcal{P}(j,z) = \frac{1}{N}\sum_{k=0}^{N-1} \frac{\exp(2\pi i k j/N)}{1-z\tilde{p}(2\pi k/N)}, \tag{22}$$

where $\tilde{p}(\cdots)$ is computed from the following single step probabilities:

$$\hat{p}(2)=\hat{p}(-2)=\frac{p}{4},\quad \hat{p}(1)=\hat{p}(-1)=\frac{1-p}{2},\quad \hat{p}(0)=\frac{p}{2}. \tag{23}$$

We now have the necessary ingredients to evaluate the functions $\mathcal{P}(j_1|j_2,0;j_3,0;z)$ explicitly and to compute $\langle n\rangle_{j_T}$ and $\langle n\rangle$ via the relations (15) and (19). The initial-condition-averaged reaction time $\langle n\rangle$ is obtained by averaging over a uniform ensemble of all possible nonreactive configurations characterized by distinct values of j_T, i.e.,

$$\langle n\rangle \equiv \frac{1}{N-3}\sum_{j_T=2}^{N-2}\langle n\rangle_{j_T}. \tag{24}$$

C. Higher order moments

An important advantage of our generating function approach is that once $\mathcal{F}(i|j,0;k,0;z)$ is known, the computation of higher order moments can be carried out straightforwardly by deriving with respect to z. Indeed, one has

$$\begin{aligned}\langle n^m\rangle_{j_T}=\left(z\frac{\partial}{\partial z}\right)^m \{&\mathcal{F}(j_T|j_T-1,0;j_T+1,0;z)\\&+\mathcal{F}(j_T-1|j_T,0;j_T+1,0;z)\\&+\mathcal{F}(j_T+1|j_T-1,0;j_T,0;z)\}|_{z=1}.\end{aligned} \tag{25}$$

In particular, the second-order moment

$$\begin{aligned}\langle n^2\rangle_{j_T}&\equiv\sum_{n=0}^{\infty}n^2\{\mathcal{F}_n(j_T|j_T-1,0;j_T+1,0)\\&\quad+\mathcal{F}_n(j_T-1|j_T,0;j_T+1,0)\\&\quad+\mathcal{F}_n(j_T+1|j_T-1,0;j_T,0)\}\\&=\left(z\frac{\partial}{\partial z}\right)^2\{\mathcal{F}(j_T|j_T-1,0;j_T+1,0;z)\\&\quad+\mathcal{F}(j_T-1|j_T,0;j_T+1,0;z)\\&\quad+\mathcal{F}(j_T+1|j_T-1,0;j_T,0;z)\}|_{z=1},\end{aligned} \tag{26}$$

the variance

$$\langle v\rangle_{j_T}\equiv\langle n^2\rangle_{j_T}-\langle n\rangle_{j_T}^2, \tag{27}$$

and its average over the different initial conditions

$$\langle v\rangle\equiv\frac{1}{N-3}\sum_{j_T=2}^{N-2}\langle v\rangle_{j_T} \tag{28}$$

are easily obtained.

IV. RESULTS

A. Behavior of the reaction time

In order to obtain the results for model I, the lattice size N must now be decreased by two units in the expressions for $\langle n\rangle$ and $\langle v\rangle$ obtained in the framework of the above formalism. The expressions for $\langle n\rangle$ as a function of p for small values of N are displayed in Table I.[3] It is seen that these are ratios of two polynomials whose complexity grows with increasing lattice size. These results are in full agreement with previous findings for $\langle n\rangle$ obtained in the framework of a difference equation approach by the author and co-workers [3]. Figure 5 displays the $\langle n\rangle$ plots computed from the ratios of polynomials given in Table I for small values of the lattice size N. Let us now summarize their main properties and provide an intuitive explanation for the observed behavior.

The plots confirm the validity of the expressions (1) and (2) for the two limiting cases $p=0$ and $p=1$. For a fixed value of p the collision time always increases with the lattice size. On the other hand, the behavior of $\langle n\rangle$ as a function of p is not always monotonic. For $N=2$ (the smallest physically interesting lattice) the most effective process is the purely asynchronous one, and $\langle n\rangle$ increases monotonically with p. For $N=3$ the reaction time does not depend on p. For $N=4,6,8$ the reaction time decreases with increasing p in a wide regime of p values, but it then increases again for a sufficiently large value of p. In contrast, for $N=5$, 7, and 9 $\langle n\rangle$ decreases monotonically with p.

These results as well as numerical simulations for larger lattices confirm the existence of an even-odd effect for $N>3$. For odd values of N, $\langle n\rangle$ decreases monotonically with p, whereas for even values of N it decreases up to a value $p_{\min}$ and it increases monotonically beyond this value. The value $p_{\min}$ is rapidly shifted to one as N increases, and the curves get closer and closer to the linear law $\langle n\rangle=\alpha(1+p)$ (with $\alpha>0$) predicted by the continuum approximation [3]. Deviations from this behavior for small lattices, where the purely synchronous process is not always the most efficient one, may thus be regarded as an indication of the important role played by finite-size effects as well as by the spatial discretization imposed by the lattice.

The even-odd effect described above is reminiscent of the one observed in the limiting case $p=1$ [6,19]. In the case $p=0$, only one of the reaction channels (SSO) will be open regardless of the value of N. In contrast, when $p=1$ one has two distinct behaviors depending on the parity of N. For odd values of N, both channels are open. However, for even values of N reactions occur via a single channel for a given initial condition, i.e., through SSO when the distance d is even or by NNC otherwise. Now, when p is no longer strictly equal to 1 but still close to this value, both reaction channels should be open, but the above parity effect still holds in a statistical sense, since NNC (SSO) reactions will be rare for an even (odd) value of d. Hence the parity-dependent behavior of the curves $\langle n\rangle(p)$ in this regime.

The nonmonotonic behavior of $\langle n\rangle$ for even values of N can be explained in terms of a competition between synchronous and asynchronous events. While synchronous transport is the most efficient mechanism to bring distant walkers in

[3]For large values of N, the evaluation of the generating function becomes rather time consuming, except in the limiting cases $p=0$ and $p=1$.

TABLE I. Analytic expressions for $\langle n \rangle$ for different lattice sizes in model I.

N	$\langle n \rangle$
2	$2/(2-p)$
3	2
4	$(10/3)(3p-4)/(p^2+2p-4)$
5	$4(2p-5)/(p^2-4)$
6	$(28/5)(p^2-10p+10)/(p^3-4p^2-4p+8)$
7	$(4/3)(p^2+8p-14)/(p^2-2)$
8	$(12/7)(13p^3+6p^2-126p+112)/((p-2)(p^3+6p^2-8))$
9	$10(2p^3-5p^2-16p+24)/((p^2+2p-4)(p^2-2p-4))$
10	$(22/9)(7p^4-76p^3+16p^2+288p-240)/(p^5-6p^4-12p^3+32p^2+16p-32)$

the vicinity of each other, it does not always maximize the efficiency of the reaction once the walkers are within the typical interaction radius. In a prereactive configuration with the walkers sitting at next to nearest-neighbor sites, reaction within the next step can only take place via a synchronous event. However, if they are at nearest neighbor sites, reaction through an asynchronous event becomes possible and it is then more efficient than reaction through a synchronous event (the reaction takes place 2 times out of 4 vs 1 time out of 4). Thus, if d and N are such that prereactive configurations with contiguous particles are favored, the resulting competition between synchronous and asynchronous dynamics will lead to an antiresonance of the reaction time (maximal efficiency) for a value $p_{\min}$ between 0 and 1. The statistical weight of such configurations is apparently stronger in the case of an even lattice, thus the antiresonance effect still prevails after averaging over the initial conditions, leading to the observed nonmonotonic behavior of $\langle n \rangle$. In the limit of large N, the role of diffusional transport becomes increasingly important for the efficiency, thus one has $p_{\min} \to 1$. On the other hand, one can also show that the parity effect is washed out in the diffusive limit, where the SSO and the NNC reaction channels become indistinguishable [3].

B. Behavior of the variance

The analytic expressions for $\langle v \rangle$ as a function of N in model I are given in Table II. The p behavior of these functions follows essentially the same law as $\langle n \rangle$ (see Fig. 6). For odd N the behavior is monotonically decreasing, while for even N a minimum is observed which rapidly shiftes to $p=1$ with increasing N. This suggests that the behavior observed for $\langle n \rangle$ extends to higher order moments; note, however, that the value $p_{\min}$ is slightly smaller than the one obtained from the $\langle n \rangle$ curves, except for $N=4$, where it turns out to be the same ($p_{\min}=2/3$). Thus, $\langle v \rangle$ and $\langle n \rangle$ cannot be simultaneously minimized except in this case.

In the limiting cases $p=0$ and $p=1$ it is possible to simplify the expressions of the relevant generating function and thereby obtain general expressions for $\langle v \rangle$ for arbitrary lattice sizes. In the purely asynchronous case one has

$$\langle v \rangle = \frac{N(N+1)(N-2)(N+2)}{30}. \tag{29}$$

This expression is also recovered by taking the average of Montroll's original result for the variance over all possible initial walker-trap separations d [17]. On the other hand, the case $p=1$ yields

$$\langle v \rangle = \begin{cases} N(N+1)(N+2)(N^2+2N+2)/[120(N-1)] & \text{for } N \text{ even}, \\ (N+1)(N+3)(N^2+2N-5)/120 & \text{for } N \text{ odd}. \end{cases} \tag{30}$$

The standard deviation $\sigma \equiv \sqrt{\langle v \rangle}$ thus turns out to be comparable to $\langle n \rangle$ in both cases. According to Eqs. (29) and (30), one has, respectively, $\sigma \propto N^2/\sqrt{30}$ and $\sigma \propto N^2/(2\sqrt{30})$ for large N, while Eqs. (1) and (2) give, respectively, $\langle n \rangle \propto N^2/6$ and $\langle n \rangle \propto N^2/12$. The standard deviation and the mean value remain comparable for intermediate values of p. This is not surprising in view of the large variability characteristic of first-passage problems.

V. CONCLUSIONS

We have used a generating function approach to compute the mean reaction time between two walkers performing a combination of synchronous and asynchronous jumps. The walkers react via two channels, i.e., same site occupation or position exchange. The reaction time and its variance display a different behavior for even and odd lattices, i.e., they behave monotonically as a function of the synchronicity pa-

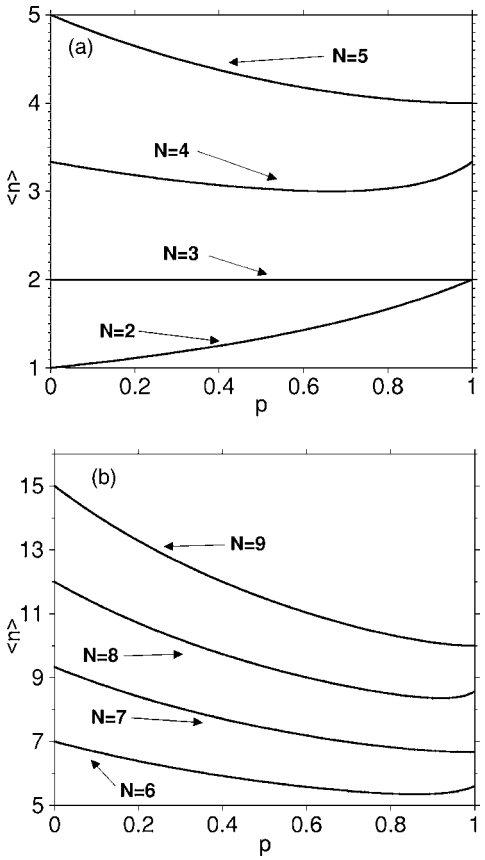

FIG. 5. Mean reaction time $\langle n \rangle$ as a function of p for (a) $N=2,\ldots,5$ and (b) $N=6,\ldots,9$.

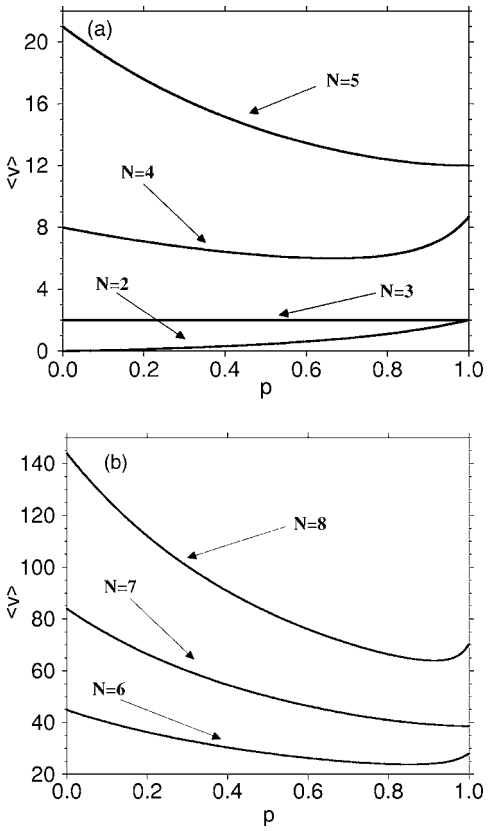

FIG. 6. Spatially averaged variance $\langle v \rangle$ of the encounter time as a function of p for (a) $N=2,\ldots,5$ and (b) $N=6,\ldots,8$.

rameter p for odd lattices and display antiresonances in the even-lattice case. This behavior has been explained in terms of a competition between synchronous and asynchronous dynamics. While the former favors diffusional transport over long distances, it may also lead to a decrease of the cross section once the particles are within the typical interaction radius, since they may avoid each other more easily when they hop simultaneously. The even-odd effect tends to vanish with increasing lattice size and in the continuum limit, since it is a signature of the discrete nature of the support.

As pointed out in the Introduction, the interest of considering the effect of synchronicity on the behavior of a given system arises in a variety of different contexts. A fundamental motivation is provided by the fact that, while free particles move simultaneously under the action of a natural law at the microscopic level of description, in many real systems the existence of geometric and energetic constraints (e.g., activation energies) results in an intrinsic nonzero degree of asynchrony in the dynamics of the constituents at mesoscopic time scales. Since in this context asynchronous dynamics can be understood as an expression of such constraints, it then becomes natural to ask how it affects the efficiency of a given physical process. In view of our results, the answer to this question cannot be considered to be straight-

TABLE II. Analytic expressions for $\langle v \rangle$ for lattice sizes up to $N=9$ in model I.

N	$\langle v \rangle$
2	$2p/(2-p)^2$
3	2
4	$(2/3)(192-316p+152p^2-15p^3)/(p^2+2p-4)^2$
5	$4(-2p^3+25p^2-80p+84)/(p^2-4)^2$
6	$(28/5)(-1096p+768p^2-206p^3+28p^4-p^5+512)/(8-4p+p^3-4p^2)^2$
7	$(4/3)(-320p+88p^2+8p^3+p^4+252)/(p^2-2)^2$
8	$(12/7)(-13p^7+252p^6+546p^5-4736p^4-2184p^3+35520p^2-50848p+21504)/((p^3+6p^2-8)^2(p-2)^2)$
9	$2(-10p^7+253p^6-816p^5-2748p^4+11872p^3+5552p^2-42496p+29568)/((p^2-2p-4)^2(p^2+2p-4)^2)$

forward. Moreover, it may turn out to be rather counterintuitive.

Admittedly, the results depend strongly on the specific definition of the collision rules. Yet, the equivalence between models I and II suggests that certain features of the observed behavior might be characteristic of a class of small systems. Similar antiresonance phenomena in the encounter time have, e.g., been recently observed in a model for target site localization of a protein on DNA [20]. On the other hand, the model shows that classical techniques inspired in first-passage problems can be successfully used to compute characteristic reaction times for complex processes involving more than one interaction channel.

Possible extensions of the model include the higher dimensional case,[4] the case of more complex media [21–23], and the evaluation of other quantities such as survival probabilities [24,25], nearest-neighbor distance to the trap [26] and concentration decays [27] in the framework of the many-particle problem [28,29] or more ellaborate reaction schemes [30,31].

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