Synchronous vs. asynchronous dynamics of diffusion-controlled reactions

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Abstract

An analytical method based on the classical ruin problem is developed to compute the mean reaction time between two walkers undergoing a generalized random walk on a 1d lattice. At each time step, either both walkers diffuse simultaneously with probability $p$ (synchronous event) or one of them diffuses while the other remains immobile with complementary probability (asynchronous event). Reaction takes place through same site occupation or position exchange. We study the influence of the degree of synchronicity $p$ of the walkers and the lattice size $N$ on the global reaction’s efficiency. For odd $N$, the purely synchronous case ($p = 1$) is always the most effective one, while for even $N$, the encounter time is minimized by a combination of synchronous and asynchronous events. This new parity effect is fully confirmed by Monte Carlo simulations on 1d lattices as well as for 2d and 3d lattices. In contrast, the 1d continuum approximation valid for sufficiently large lattices predicts a monotonic increase of the efficiency as a function of $p$. The relevance of the model for several research areas is briefly discussed.

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1. INTRODUCTION

Recently, the modelling of diffusion-controlled reactions on lattices has attracted renewed interest due to synergies with some research areas like e.g. heterogeneous catalysis, trapping problems, spin models, game theory, population dynamics or biological problems. An issue common to these systems is the important role played by the coexistence of different intrinsic time scales, the lattice characteristics (size and dimensionality) and many-body effects. The interplay of these ingredients may strongly affect the efficiency with which statistical processes such as front propagation on catalytic substrates, the spread of an infection, kink propagation in magnetic systems, or exciton trapping in photosynthetic cells take place. In order to obtain analytical insight for such systems, it is often necessary to make simplifying assumptions which nevertheless preserve their main generic features.

In this spirit, a prototypical diffusion-reaction system consists of two interacting walkers performing nearest neighbor jumps on a lattice. The walkers are assumed to react with each other whenever they meet at the same lattice site or attempt to exchange positions. Each of such “encounters” results in instantaneous reaction, the process therefore being diffusion-controlled. Regardless of the particular outcome of the reaction, a measure for its efficiency will be clearly given by the mean encounter time of both walkers.

In a pioneering work, Montroll investigated a simplified version of the problem in which one of the walkers is stationary, thereby playing the role of a fixed trap. In a recent article, Montroll’s results have been extended with the help of a Markovian method to account for the possibility of simultaneous displacement of the walkers. In the present work, the problem is further extended to the case in which the motion of the walkers consists of a random sequence of two different events: at each tick of the clock, a synchronous event takes place with probability \( p \), i.e., both walkers hop simultaneously to randomly chosen nearest neighbor sites. Alternatively, an asynchronous event takes place with probability \( 1 - p \), i.e. one of the walkers performs a nearest neighbor jump while the other remains immobile. Thus, the parameter \( p \) interpolates between the one walker plus trap case studied by Montroll (\( p = 0 \)) and the case of two simultaneously moving walkers (\( p = 1 \)). A central question we shall investigate here concerns the influence of the degree of synchronicity \( p \) of the walkers and the size \( N \) of the lattice in which they are embedded upon the reaction’s efficiency.

Our model may be of interest in several contexts. One can e.g. easily accomodate it to allow for events in which both walkers remain immobile in the original reference frame. Thus, three qualitative different joint events become possible for the two-walker system, which can e.g. be interpreted as resulting from a combination of two internal states for each of the walkers, namely a diffusing and an immobile state. Such two-state random walks are frequently used to model chromatographic or electrophoretic separation processes, in which the propagation of charged particles in an external field may be occasionally stopped by entanglement with the molecules of the substrate. Such systems, along with hopping models for transport and recombination of carriers in solids, might provide additional motivation for considering a generalized version of the random walk.

A different approach suggests to regard the fluctuations in the diffusivity of the walkers as a result of random fluctuations of lattice sites switching between a conducting and a stopping state, whereby the translational invariance of the lattice is preserved on average. An alternative formulation of the problem in terms of fluctuating dichotomous barriers between sites also seems possible. Such models for dynamic random media are relevant...
for the description of several physiochemical processes like e.g. ligand diffusion in proteins [19] or proton migration in water [20].

On the other hand, if one goes back to the original picture of two dissimilar walkers A and B, the model may be regarded as a schematized starting point for describing the dynamics of exciton absorption in biological light-harvesting systems [21]. In photosynthetic cells, a photon is absorbed by the pigment molecules (e.g. chlorophyll) in the cell and may give rise to an excited energy state. The exciton hops by resonant energy transfer through a network or lattice of 200-500 pigment molecules (antenna system) and can be eventually trapped at a reaction center [22], which is usually considered to be immobile within the time scale for trapping (a few hundred picoseconds). The exciton energy is then used to trigger a series of redox processes in the chain of chemical reactions leading to the production of sugars and carbohydrates. Thus, one of the time-limiting steps for the production of oxygen is precisely the absorption of the exciton by the trapping center. If we allow for a certain mobility of the reaction center (thereby generalizing Montröll’s approach for exciton trapping), we can identify the latter with a slowly hopping walker, say the A walker, while the propagating exciton would play the role of the B walker. As long as the hopping rate of the A walker remains small, the situation may be identified with the almost purely asynchronous case (small \( p \)); this is normally the case in \textit{in vivo} light-harvesting systems. However, a modification of the physical properties of the antenna system so as to make exciton propagation slower might, at least in principle, lead to interesting antiresonance phenomena as observed in our model.

The paper is organized as follows. In section 2, we define the two-walker system in detail and show how it can be recast into an equivalent one-walker system with absorbing sites. In section 3, we report analytic work on the 1\(d\) case and identify the principal differences between the purely asynchronous (\( p = 0 \)), the purely synchronous case (\( p = 1 \)) and the mixed case (\( 0 < p < 1 \)). These results are also supported by Monte Carlo simulations. In Section 4, similar results are found for the 2\(d\) and the 3\(d\) cases by means of simulations. In section 5, the results are compared with the predictions of the continuum approximation valid for large lattices. Finally, section 6 summarizes the main conclusions and discusses possible extensions.

2. FORMULATION OF THE PROBLEM: TWO-WALKER VS. ONE-WALKER PICTURE

The starting point is a 1\(d\) periodic lattice with \( N \) sites and discrete time dynamics (cf Fig. 1a). We place two walkers A and B on two distinct lattice sites and let them evolve at each time step as follows:

1. with probability \( p \), both walkers hop simultaneously to randomly chosen nearest neighbor sites (\textit{synchronous event}).

2. with probability \( 1 - p \), one of the walkers (no matter which one) remains at rest while the other performs a jump to a nearest neighbor site (\textit{asynchronous event}).

The walkers are assumed to be unbiased, i.e., their jumps are symmetric. We additionally assume that their jump directions are completely uncorrelated. An encounter takes place when both walkers ‘land’ on the same site or attempt to exchange positions. Each encounter
triggers instantaneously an irreversible reactive interaction, say the annihilation reaction \( A + B \rightarrow 0 \). The encounter time can thus be regarded as the characteristic reaction time governing the diffusion-controlled two-particle annihilation.

In principle, the mean encounter time can be computed for a single initial configuration of the walkers; in many practical situations, though, one has little knowledge about the initial conditions. We shall therefore give preference to a definition of the mean encounter time which contains an additional coarse graining over all possible initial configurations. In the sequel, we shall denote this quantity by \( \langle n \rangle \). The smaller \( \langle n \rangle \), the more efficient the reaction will be.

Note that, due to the translational invariance of the lattice, the physical distinguishability of the walkers is irrelevant for the computation of \( \langle n \rangle \): in other words, it does not matter which of the walkers \( A \) or \( B \) hops more often, since \( \langle n \rangle \) depends only on the relative motion of both walkers, the latter being fully characterized by \( p \). Therefore, we shall assume for simplicity and without loss of generality that \( A \) and \( B \) are physically identical walkers and drop the labels \( A \) and \( B \), as has been done in Fig. 1a.

For \( p = 0 \), only reactions through simultaneous site occupancy are possible. As far as \( \langle n \rangle \) is concerned, this case is equivalent to the one treated by Montroll [9]. However, if \( p > 0 \), reaction through position exchange becomes possible. This technical obstacle makes the analytical treatment of the problem more difficult.

A first step to circumvent this difficulty is to take advantage of the translational invariance of the lattice and reformulate the problem in terms of a single walker. To do so, we must switch over to a new comoving reference frame in which one of the walkers remains stationary, thereby playing the role of a fixed perfect trap \( T \) (Fig. 1b). Clearly, an asynchronous event in the original two-walker system is equivalent to nearest neighbor hopping in the single-walker system, while a synchronous event results either in a walker’s jump by two lattice sites (if both walkers hop in opposite directions in the original reference frame) or its remaining at rest (if they hop in the same direction). In this picture, reaction takes place any time the walker reaches or overreaches the trap \( T \).

We can now take advantage of the simple lattice geometry and the fact that the trap is perfect to unfold the \( N \)-site lattice into an equivalent one with \( N + 1 \) sites and two perfect traps \( T \) sitting at each end site, as shown in Fig. 2 for \( N = 7 \). This transformation does not of course affect the characteristics of the walk; a walker jump in anticlockwise direction will be equivalent to a jump to the left by the same number of sites in the transformed lattice. Next, we replace each trap \( T \) by two (fictitious) reactive sites \( r \) (Fig. 3). The random walk will instantaneously terminate when the walker lands on any of these \( r \)-sites. We shall therefore occasionally call the \( r \)-sites “absorbing” in what follows.

Let us assign the coordinates 1 to \( N - 1 \) to each of the non-absorbing sites, as shown in Fig. 3. Additionally, we term the \( r \)-sites at the left end \(-1\) and 0 and those at the right end \( N \) and \( N + 1 \). An attempt to overcome, say the left trap, triggered by a synchronous event will be equivalent to a jump from site 1 to site \(-1\). In contrast, the walker’s landing on the trap can be realized either by an asynchronous event (jump from site 1 to site 0) or by a synchronous event (jump from site 2 to site 0). If the dynamics is purely asynchronous, only one \( r \)-site at each end will be needed, since jumps by two sites are not possible in this case. Thus, events involving position exchange can be dealt with by going over to a one-walker picture and introducing fictitious absorbing sites. The mean duration of the walk averaged over the initial positions 1, \ldots , \( N - 1 \) of the walker plays the role of \( \langle n \rangle \) in the original two-walker system.
A standard approach for the calculation of \( \langle n \rangle \) is to formulate the problem for the restricted walk between the absorbing sites in terms of a conditional first passage problem for an unrestricted walk on an infinite 1d lattice \[23\]. The starting point is the Markovian master equation

\[
P_{n+1}(j) = \frac{P}{4} [P_n(j - 2) + 2P_n(j) + P_n(j + 2)] + \frac{1-P}{2} [P_n(j - 1) + P_n(j + 1)],
\]

where \( P_n(j) \) is the probability to find the walker at a given site \( j \) in the infinite lattice after \( n \) time steps. The first term on the right hand side of eq. (1) is the contribution due to the synchronous events, by which the walker either remains at rest or it moves (here) two lattice sites either to the left or to the right. The second term describes jumps by one lattice site as a consequence of asynchronous events. The mean time to absorption \( \langle n \rangle \) can now be viewed as a first-passage time and computed via a generating function approach \[23\]. Specifically, \( \langle n \rangle \) can be expressed in terms of the generating function for the probability of the walker arriving for the first time at a given \( r \)-site after a given number of steps without having been previously in neither of the other three \( r \)-sites. Unfortunately, the resulting expressions for \( \langle n \rangle \) are not very transparent and their analytical dependence on \( N \) and \( p \) is not easy to determine.

Another possibility is to make use of the single step probabilities appearing as coefficients in the right hand side of eq. (1) to compute the transition probabilities between the states of the underlying absorbing Markov chain. In this approach, \( \langle n \rangle \) can be related to the row sums over the elements of the fundamental matrix for the transition to the absorbing state or, alternatively, to its smallest eigenvalue \[24\]. The disadvantage of this method is that it requires the inversion of increasingly large matrices as \( N \) becomes large.

Finally, the method we shall further develop here exploits the analogy of our random walk problem with the classical ruin problem studied by Feller \[5\]. Even though this approach has the disadvantage of being difficult to generalize to higher dimensions, it provides an elegant solution for the 1d problem.

3. CONNECTION WITH RUIN PROBLEM AND ANALYTICAL SOLUTION

We first recall briefly the classical gambler’s ruin problem. Consider a single walker (in our setting, this would correspond to the limit \( p=0 \)), whose position \( z \) is viewed as the capital of a gambler playing against an adversary whose capital is \( N - z \). At each time step, a trial is made, as a result of which the gambler wins or loses one euro. Thus, the gambler’s winning corresponds to a nearest neighbor jump of the walker to the right, while losing the trial corresponds to a jump to the left. The game goes on until the gambler’s capital is reduced to zero or increases to \( N \) (absorption of the walker at sites 0 or \( N \)). One is interested in the mean duration of the game \( \langle n \rangle_z \) when the gambler starts with a given capital \( z \). This quantity can be shown to be finite as long as \( N < \infty \) and obeys the following difference equation \[5\]:

\[
\langle n \rangle_z = \frac{1}{2} \langle n \rangle_{z+1} + \frac{1}{2} \langle n \rangle_{z-1} + 1, \quad 0 < z < N
\]

with the boundary conditions

\[
\langle n \rangle_0 = 0 \quad \text{and} \quad \langle n \rangle_N = 0.
\]
Eq. (2) states that the walker has no memory of where it has been at earlier time steps; if it is initially at site \( z \), it will either jump to site \( z + 1 \) or to site \( z - 1 \) with probability 1/2. Once at any of these sites, the walker will continue his walk without remembering its previous position \( z \). It is as though the walker started a new walk from \( z + 1 \) or \( z - 1 \) with equal probability, except that the expected value of the mean time to absorption must be increased by one unit \([25]\). The boundary conditions (3) reflect the fact that, if the walker is initially placed at a \( r \)-site, it is immediately absorbed. In the original two-walker system, this is equivalent to placing both walkers at the same site.

Eqs. (2)-(3) can be solved by standard methods, e.g. by writing the general solution as the sum of the general solution of the corresponding homogeneous equation plus a particular solution \([26]\). One obtains in this way

\[
\langle n \rangle_z = z(N - z),
\]

(4)

and

\[
\langle n \rangle = \frac{1}{N} \sum_{z=1}^{N-1} \langle n \rangle_z = \frac{N(N+1)}{6}.
\]

(5)

The opposite limit of the above (\( p = 1 \)), corresponding in our setting to a purely synchronous motion of two walkers, is somewhat less standard. In this case, only jumps by zero or two lattice sites may occur. Depending on its initial position, the walker may land on any of the four \( r \)-sites depicted in Fig. 3. Therefore, two additional boundary conditions for the absorbing sites \(-1 \) and \( N + 1 \) are needed.

In the gambler’s jargon, a jump by two sites means doubling the stake of each trial, i.e., the player wins or loses two euros with probability 1/4. Besides, a tie occurs with probability 1/2 (no jump). The game terminates when either the player or his adversary reaches or overreaches a capital of \( N \) euros. Now, the difference equation for the duration of the game is a fourth-order one:

\[
\langle n \rangle_z = \frac{1}{4} \langle n \rangle_{z+2} + \frac{1}{2} \langle n \rangle_z + \frac{1}{4} \langle n \rangle_{z-2} + 1, \quad 0 < z < N.
\]

(6)

The solution of this equation requires four boundary conditions, namely

\[
\langle n \rangle_{-1} = 0, \quad \langle n \rangle_0 = 0, \quad \langle n \rangle_N = 0 \quad \text{and} \quad \langle n \rangle_{N+1} = 0.
\]

(7)

A particular solution of (6) is given by \(-\frac{1}{2}z^2\). The characteristic equation of the homogeneous equation has two double roots \( \lambda_{1,2} = \pm 1 \). Therefore, the full inhomogeneous solution reads

\[
\langle n \rangle_z = -\frac{1}{2}z^2 + c_1 + c_2 z + (c_3 + c_4 z)(-1)^z,
\]

(8)

Substituting into eq. (6) one obtains a system of equations for \( c_1 \) to \( c_4 \) whose solution yields

\[
\langle n \rangle_z = \frac{(z(N - 1 - z) + N)}{2} \quad \text{for } z \text{ odd, } N \text{ odd},
\]

\[
= \frac{z(N + 1 - z)}{2} \quad \text{for } z \text{ even, } N \text{ odd},
\]

\[
= \frac{(z(N - z) + (N + 1))}{2} \quad \text{for } z \text{ odd, } N \text{ even},
\]

\[
= \frac{z(N - z)}{2} \quad \text{for } z \text{ even, } N \text{ even}.
\]

(9)
The spatially averaged time to absorption $\langle n \rangle$ is again easily computed. One obtains

$$\langle n \rangle = N(N+1)(N+2)/12(N-1)$$  \hspace{1cm} \text{for } N \text{ even},

$$\langle n \rangle = (N+1)(N+3)/12$$  \hspace{1cm} \text{for } N \text{ odd.} \quad (10)$$

For notational convenience, let us rename the value of $\langle n \rangle$ obtained from eqs. (10) as $\langle n \rangle^{(1)}$, and the corresponding result of Montroll for the one-walker problem (eq. (5)) as $\langle n \rangle^{(0)}$. A comparison between $\langle n \rangle^{(0)}$ and $\langle n \rangle^{(1)}$ is shown in Fig. 4. As expected, the synchronous case becomes more efficient as soon as the lattice gets sufficiently large ($N \geq 5$). In the limit of a very large lattice, it is asymptotically twice as efficient as the asynchronous case [see Fig. 5].

It is also worth comparing the $z$-distribution of the encounter time for the case $p = 1$ (eq. (9)), with the earlier known result for $p = 0$ (eq. (4)). For odd $N$, the spatial profile in $z$ displays some qualitative similarities in both cases (cf. Figs. 6a and 6b). The highest value of $\langle n \rangle^{(z)}$ is attained at those sites $z$ that maximize the distance $d_z = \min(z, N-z)$ from the closest absorbing site. For $p = 0$, the encounter time always increases with increasing $d_z$, and it becomes maximum when $z = (N \pm 1)/2$. In contrast, the behavior is no longer strictly monotonic for $p = 1$, since $\langle n \rangle^{(z)}$ either increases or remains constant as $d_z$ becomes larger, giving rise to a “staircase” profile for high enough values of $N$ (Fig. 6b).

For even lattices, there are more marked differences between the cases $p = 0$ and $p = 1$. For $p = 0$, the discrete spatial profile resembles an inverted parabola like in the odd lattice case, the maximum now being located at $z = N/2$. However, if $p = 1$, one observes a series of alternating valleys and peaks in the distribution (cf Figs. 7a and 7b). There are two subcases here: if $N$ is divisible by 4, the highest values of $\langle n \rangle^{(z)}$ are attained for $z = (N \pm 2)/2$ (Fig. 7a). Otherwise, the maximum value corresponds again to $z = N/2$ (Fig. 7b).

Note that for $p = 0$ and even $N$ the time to absorption when the walker is started at sites 1 or $N-1$ is smaller than in the purely synchronous case. An intuitive argument points to the fact that, in the former case, the walker is absorbed one out of two times after the first time step, while absorption takes place only one out of four times if $p = 1$. However, this argument should be taken with care, since it fails for odd $N$. Besides, as we shall see later on, the minimum of $\langle n \rangle^{(0)} = \langle n \rangle^{(N-1)}$ corresponds to a process with $p > 0$.

We finally turn to the general case of a mixed walk. Assume that a given event is synchronous with probability $0 < p < 1$ and asynchronous with probability $1 - p$. The difference equation for $\langle n \rangle^{(z)}$ now reads:

$$\langle n \rangle^{(z)} = \frac{p}{4} \langle n \rangle^{(z+2)} + \frac{1-p}{2} \langle n \rangle^{(z+1)} + \frac{p}{2} \langle n \rangle^{(z)} + \frac{1-p}{2} \langle n \rangle^{(z-1)} + \frac{p}{4} \langle n \rangle^{(z-2)} + 1, \quad 0 < z < N. \quad (11)$$

The boundary conditions are again given by (4). A particular solution of eq. (11) is given by $-z^2/(1+p)$. The roots of the underlying characteristic equation are

$$\lambda_{1,2} = 1, \quad \lambda_{3,4} = \frac{-1 \pm \sqrt{1-p^2}}{p}. \quad (12)$$

The full solution reads

$$\langle n \rangle^{(z)} = -z^2/(1+p) + c_1 + c_2 z + c_3 \lambda_3^z + c_4 \lambda_4^z, \quad (13)$$
where the constants $c_1 - c_4$ are now given by the linear system

\[
\begin{align*}
-\frac{1}{1+p} + c_1 - c_2 + \lambda_3^{-1}c_3 + \lambda_4^{-1}c_4 &= 0, \\
c_1 + c_3 + c_4 &= 0, \\
-\frac{N^2}{1+p} + c_1 + Nc_2 + \lambda_3^Nc_3 + \lambda_4^Nc_4 &= 0, \\
-\frac{(N+1)^2}{1+p} + c_1 + (N+1)c_2 + \lambda_3^{N+1}c_3 + \lambda_4^{N+1}c_4 &= 0.
\end{align*}
\]

We prefer to omit the rather lengthy analytic form of the coefficients $c_1$-$c_4$. From the above equations, $\langle n \rangle_z$ and $\langle n \rangle$ can be explicitly computed. For $\langle n \rangle$ one has an expression of the form

\[
\langle n \rangle = -\frac{N(2N-1)}{6(1+p)} + c_1(N,p) + \frac{N c_2(N,p)}{2} + \frac{1}{N-1} \left( c_3(N,p) \left[ \lambda_3(p) \right]^{N-1} + c_4(N,p) \left[ \lambda_4(p) \right]^{N-1} \right).
\]

Table 1 displays the analytical expressions of $\langle n \rangle$ as a function of $p$ for increasing values of $N$. These are rational functions of $p$ whose complexity increases with $N$. For $N \geq 4$ and small $p$, one can obtain a first-order approximation to the exact solution by Taylor-expanding eq. (15):

\[
\langle n \rangle = \langle n \rangle^{(0)} \left[ 1 + \frac{N-3}{N} p + O(p^2) \right].
\]

Figs. 8a and 8b contain several numerical plots of $\langle n \rangle$, as a function of $p$ for different values of $N$. For $N = 2$, the purely asynchronous case is more effective than the purely synchronous case. As synchronicity is turned on, a monotonic increase of $\langle n \rangle$ as a function of $p$ is observed. For $N = 3$, $\langle n \rangle$ does not depend on $p$. At each individual time step, the probability of reaction is always $1/2$, regardless of whether both walkers hop or only one of them. In a sense, the cases $N = 2$ and $N = 3$ are non-generic, since they only involve a single symmetry-distinct initial condition. For $N \geq 4$, a new parity effect appears: if $N$ is even, the most effective process is observed for an intermediate value of $p$ associated to a minimum of the function $\langle n \rangle$ in the physically acceptable $p$-interval $[0,1]$; in contrast, for odd lattices, $\langle n \rangle$ is a monotonically decreasing function of $p$, i.e., the most effective process is always the purely synchronous one. For $N = 4$, any intermediate value of $p$ makes hopping more effective than in both limiting cases, and a minimum of $\langle n \rangle$ is obtained for $p_{\text{min}} = 2/3$. For higher, even values of $N$, the minimum is rapidly shifted to the right ($p_{\text{min}} \approx 0.86$ for $N = 6$) and the $p$-interval for which processes are more efficient than the purely synchronous case shrinks dramatically. For large $N$, $p_{\text{min}}$ gets arbitrarily close to 1 (see Table 2).

A series of Monte Carlo simulations for the periodic two-walker system has been carried out to confirm our analytic results based on the one-walker description. For two different lattice sizes, namely $N = 7$ and $N = 8$, we have performed a series of statistical runs to compute $\langle n \rangle$, each run thereby comprising a whole set of symmetric-distinct nonreactive

\[\text{1 Obviously, the purely asynchronous case has a maximum efficiency in this case, since the walker is always trapped after the first step.}\]
configurations. Due to the large variability \( \langle n^2 \rangle - \langle n \rangle^2 \) characteristic of first-passage problems, a relatively high number of runs was needed \( (10^6) \) to obtain an accurate value for \( \langle n \rangle \). The \( \langle n \rangle \)-values obtained from simulations (with an accuracy of three significant digits) are listed in Tables 3 and 4 for the cases \( N = 7 \) and \( N = 8 \), respectively. The agreement with the analytical predictions is good, the maximum observed deviation is off the theoretical value by about 1% only.

In order to obtain additional insight in the even-odd transition mechanism, we have studied qualitatively \( \langle n \rangle_z \) as a function of \( p \) and \( N \) for each single initial position \( z \) of the walker. Let us characterize each site \( z \) by its distance \( d_z \) to the closest \( r \)-site. For not too large values of \( p \), the behavior of the encounter time is roughly the same for all \( z \) values regardless of the parity of \( N \), i.e., a decrease of the encounter time is observed (Figs. 9a and 9b). However, the qualitative \( p \)-dependence of \( \langle n \rangle_z \) in the large \( p \) limit becomes different for initial positions with even or odd values of \( d_z \): for even values of \( N \) and initial positions with odd \( d_z \), \( \langle n \rangle_z \) begins to increase sharply, as a result of which a minimum of the curve is observed (cf Fig. 9a). Even though the contribution to the global efficiency \( \langle n \rangle \) arising from the \( (N/2) - 1 \) sites with even \( d_z \) decreases strongly in this regime, this effect is overcome by the increase of the contribution yielded by the \( N/2 \) sites with odd \( d_z \), thus giving rise to a net increase in \( \langle n \rangle \). In contrast, the sensitivity to the initial condition is less systematic and less important for odd values of \( N \) (Fig. 9b): again, a monotonic decrease is observed for even \( d_z \). Even though minima are still observed for \( d_z = 1 \), for all other odd values of \( d_z \), they are either absent \(^2\) or very flat (see curve for \( d_z = 3 \) in Fig. 9b).

4. MONTE CARLO RESULTS IN TWO AND THREE DIMENSIONS

To complement the analytic 1d results for the dependence of \( \langle n \rangle \) on the value of the parameter \( p \), we have also investigated how \( \langle n \rangle \) depends on \( p \) for dimensions 2d and 3d using Monte Carlo simulations. Figures 10 and 11 show the dependence of \( \langle n \rangle \) with respect to \( p \). As shown above for 1d, there is distinctively different behavior based on whether \( N \) is even or odd. In higher dimensions this even-odd effect becomes much more pronounced. It is clear that when \( N \) is an even number, the maximal efficiency is attained at some intermediate value between 0 and 1. Also, one notices that for the 6 \( \times \) 6 square lattice and for all 3d even lattices which we studied \( \langle n \rangle_z^{(0)} < \langle n \rangle_z^{(1)} \). This is a surprising result which we do not see in the 1d case for lattices with \( N > 4 \). This suggests the existence of a crossover effect in the large size limit when switching from 2d to 3d lattices, implying that in the former case the two simultaneously moving walkers are more effective than two asynchronous walkers, while in 3d the opposite holds. As in the 1d case, the value of \( p_{\text{min}} \) in 2d and 3d tends toward 1 in the limit of large lattice size, but it is interesting to note that in the largest 3d lattice which we studied \( (N = 1000) \), the difference between \( p = 0.999 \) and \( p = 1 \) is \( \sim 600 \), which is about 30% of \( \langle n \rangle^{(1)} \) in that case. This shows that for even lattices, a minute amount of asynchronicity allows for a much greater efficiency. Similar arguments to those given above for 1d exist for in 2d and 3d when attempting to determine why such even-odd behavior arises, and further analysis of this striking behavior is given in Ref. [27].

\(^2\) This is e.g. the case for \( N = 7 \) and \( d_z = 3 \) (not shown here).
5. COMPARISON WITH CONTINUUM APPROXIMATION

It is instructive to compare the above results in 1d with the continuum approximation valid for large \( N \). To do so, consider the one-walker system with absorbing sites and a fixed lattice length \( L = N\Delta x \), where \( \Delta x \) is the intersite distance (lattice constant). According to this definition, \( L \) is the distance between the inmost \( r \)-sites. The walker’s distance to site 0 is \( x = z \Delta x \). We perform the continuum limit by letting \( \Delta x \) and \( \Delta t \) simultaneously go to zero under the additional requirement that the diffusive combination \( (\Delta x)^2/\Delta t \) tend to a finite constant. Since \( L \) is fixed, this implies that one lets the number of sites \( N \) go to infinity while the spatial and temporal resolutions \( \Delta x \) and \( \Delta t \) are scaled as \( 1/N \) and \( 1/N^2 \), respectively. Let us next replace \( \langle n \rangle \) by a function \( \langle n \rangle \) varying smoothly in the space interval \([0, L]\). The mean elapsed time \( \langle t \rangle \) to absorption will then simply be the mean number of steps \( \langle n \rangle \) times the time unit \( \Delta t \). From eq. (11), we have:

\[
\frac{p}{4} [(t)_{x+2\Delta x} - 2<t>_x + (t)_{x-2\Delta x}] + \frac{1-p}{2} [(t)_{x+\Delta x} - 2<t>_x + (t)_{x-\Delta x}] + \Delta t = 0
\]

(17)

with the boundary conditions \(^3\)

\[
\langle t \rangle = \langle t \rangle_x = \langle t \rangle_L = \langle t \rangle_{L+\Delta x} = 0.
\]

We now divide eq. (17) by \( \Delta t \) and expand the expressions in the brackets in \( \Delta x \). Taking the diffusive limit in the resulting equation yields

\[
D \frac{d^2 \langle t \rangle_x}{dx^2} = -1,
\]

(19)

where the relative diffusion coefficient \( D \) is given by

\[
D = (1 + p) \lim_{\Delta x, \Delta t \to 0} \frac{(\Delta x)^2}{\Delta t} = (1 + p) D^{(0)}.
\]

(20)

In the rightmost equation, \( D^{(0)} \) is the value of the diffusion coefficient for \( p = 0 \). For \( p > 0 \), \( D^{(0)} \) is increased by the prefactor \( 1 + p \), i.e., the variance of the single-step probabilities of the random walk. In this limit, the four boundary conditions (18) coalesce into two distinct ones, namely \( \langle t \rangle_0 = 0 \) and \( \langle t \rangle_L = 0 \). The solution of (19) which fulfills these boundary conditions is

\[
\langle t \rangle_x = \frac{x(L-x)}{2D}.
\]

(21)

The spatially averaged reaction time \( \langle t \rangle \) is obtained by integrating over \( x \):

\[
\langle t \rangle = \frac{1}{L} \int_0^L \langle t \rangle_x dx = \frac{L^2}{12 D}.
\]

(22)

As expected, \( \langle t \rangle \) is proportional to the squared lattice length and inversely proportional to the relative diffusion coefficient \( D \). For the special cases \( p = 0 \) and \( p = 1 \), this result is

\(^3\) In the case \( p = 0 \), one only has two boundary conditions, namely \( \langle t \rangle_0 = \langle t \rangle_L = 0 \).
recovered by directly taking the diffusive limit in the discrete solutions (5) and (10). The relation (22) leads to the asymptotic law

\[
\frac{\langle t \rangle^{(0)}}{\langle t \rangle} = \lim_{N \to \infty} \frac{\langle n \rangle^{(0)}}{\langle n \rangle} = 1 + p,
\]

(23)

where \( \langle t \rangle^{(0)} = L^2/(12D^{(0)}) \) and \( \langle n \rangle \) is given by eq. (15). Eq. (23) shows that in the continuum limit, the efficiency of the reaction increases linearly with \( p \). The continuum approximation applies for sufficiently large \( N \), namely when the typical displacement of the walker \( \Delta l \equiv \sqrt{1 + p \Delta x} \) at each time step is small compared to the lattice length \( N \Delta x \). If this condition is not fulfilled, the approximation gets significantly worse at large values of \( p \) (cf Fig. 12).

A generalization of (19) for higher order moments \( \langle t^j \rangle_x \) can be obtained by writing down the difference equations for the discrete quantities \( \langle n^j \rangle_z \) and taking the diffusive limit thereof. One then gets the coupled set of equations

\[
D \frac{d^2 \langle t^{j+1} \rangle_x}{dx^2} = -(j + 1) \langle t^j \rangle_x,
\]

(24)

Eqs. (24), not to be further dealt with here, are well known from the theory of first-passage problems, where they are usually obtained from the adjoint Fokker-Planck equation for the underlying diffusion process [23, 28]. Again, deviations from the dynamics dictated by (24) are expected for small lattices.

6. CONCLUSIONS AND OUTLOOK

We have seen that the 1d problem of computing the mean reaction time between two diffusing co-reactants can be reduced to a trapping problem for a single walker. The latter can be viewed as a generalized ruin problem, the duration of the game plays thereby the role of the mean time to absorption.

In the diffusive limit, equivalent to the limit \( N \to \infty \) if the lattice length \( L \) is held fixed, the reaction efficiency increases linearly with \( p \), but important deviations are observed for not too large values of \( N \). Beyond the crossover size \( N = 4 \), a new parity effect is observed. For odd values of \( N \), the reaction time still increases monotonically (but no longer linearly) with \( p \), while for even values of \( N \), the efficiency is optimized for an intermediate value \( p_{\text{min}} < 1 \). In higher dimensions, this parity effect is even more pronounced, i.e. for even lattices there is a drastic increase in efficiency when a tiny amount of synchronicity is introduced. In contrast to the 1d case, the effect is enhanced with increasing \( N \).

Let us briefly comment on the 1d results from the perspective of the ruin problem. Assume that one of the gamblers is successively given an starting capital of 1, 2, ..., \( N - 1 \) euros at each round, while his adversary gets \( N - 1, N - 2, \ldots, 1 \) euros. Let us further suppose that the gamblers can choose between two kinds of trials: the stake for the first one is one euro and there is no tie. In the second trial, either nobody wins or one of the gamblers wins two euros. According to our results, for an odd capital \( N \), the gamblers minimize the average playing time if they always make a two-euro bet. However, if \( N \) is even, they should make a small amount of one-euro bets in order to finish the round as soon as possible.

Our work can be extended in many different ways. Perhaps the most straightforward one is the detailed characterization of the whole distribution \( P(n) \) in terms of \( p \) and \( N \).
A generalization of results such as equation (23) to higher dimensional integral and fractal lattices is also of interest, since it may further clarify the role of dimensionality and the lattice coordination number. According to our results, in one-dimension two synchronously moving walkers are asymptotically twice as efficient as when they hop one after the other. In a 2d square planar lattice, Kozak et al. have shown that the purely synchronous case is $\sqrt{2}$ times more efficient than the purely asynchronous one in the large $N$ limit for odd lattices [10]. The question is whether or not the relative efficiency of both processes in lattices with fractal dimension $1 < d_f < 2$ lies between 2 and $\sqrt{2}$. Preliminary calculations on a Sierpinski gasket (with fractal dimension $d_f = 1.585$) seem to indicate an asymptotic relative efficiency higher than 2 in this case, despite the fact that the lattice has (up to the three vertex sites) the same coordination number as a 2d square planar lattice [27]. The reason for this may be the important role played by the specific form of the lattice boundaries, even in the limit of a large lattice. This may motivate the study of boundary conditions other than periodic ones for the two-walker system. However, the analytical treatment of this case is considerably harder, at least in the framework of the method of difference equations, since the lattice is no longer translationally invariant.

As a further extension of our work, one can also consider more complex reactive schemes [29] involving more than two walkers to study the combined effect of synchronicity and many-body effects.

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Figure Captions

Figure 1: a) two-walker system on a seven-site periodic lattice (walkers represented by black circles). b) Equivalent one-walker system with trap. For convenience, the walker labels $A$ and $B$ in Fig. 1a have been left out. The arrows in Fig. 1a indicate that both walkers perform a synchronous step. In Fig. 1b this corresponds to a two-site jump of the walker.

Figure 2: Lattice transformation for the one-walker system displayed in Fig. 1b.

Figure 3: Replacement of the traps $T$ at each end site of the transformed lattice by two absorbing sites $r$.

Figure 4: Mean encounter time as a function of the lattice size for the purely synchronous case $\langle n \rangle = \langle n \rangle^{(1)}$ (circles) and the purely asynchronous case $\langle n \rangle = \langle n \rangle^{(0)}$ (crosses).

Figure 5: Ratio $\langle n \rangle^{(0)}/\langle n \rangle^{(1)}$ as a function of $N$. Note that the value of the ratio is the same for two consecutive odd and even values of $N$. The inset displays the behaviour for small $N$.

Figure 6: $z$-distribution of the encounter time in the cases $p = 0$ (dashed lines) and $p = 1$ (continuous lines) for a) $N = 3, 5, 7$ and b) $N = 9, 11$. For $N = 3$ both cases display the same flat distribution.

Figure 7: $z$-distribution of the encounter time for $p = 0$ (dashed lines) and $p = 1$ (continuous lines) for a) $N = 6, 10$ and b) $N = 4, 8$.

Figure 8: Mean encounter time as a function of $p$ for a) $N = 2, \ldots, 5$ and b) $N = 6, \ldots, 9$.

Figure 9: a) $p$-dependence of $\langle n \rangle_z$ for all possible values of $d_z$ on a lattice with a) 10 sites b) 9 sites.

Figure 10: Mean encounter time as a function of $p$ for two walkers on a $2d$ square planar lattice with periodic boundary conditions.

Figure 11: Mean encounter time as a function of $p$ for two walkers on a $3d$ cubic lattice with periodic boundary conditions.

Figure 12: Ratio $\langle n \rangle^{(0)}/\langle n \rangle$ as a function of $p$. 
FIG. 1:

FIG. 2:

FIG. 3:
FIG. 6:

FIG. 7:
FIG. 8:

FIG. 9:
FIG. 10:

FIG. 11:
FIG. 12:

\[
\langle n \rangle = \frac{2}{2 - p}
\]

\[
\langle n \rangle = \frac{10/3}{p^2 + 2p - 4}
\]

\[
\langle n \rangle = \frac{4(2p - 5)}{(p^2 - 4)}
\]

\[
\langle n \rangle = \frac{(28/5)(p^2 - 10p + 10)}{(p^3 - 4p^2 - 4p + 8)}
\]

\[
\langle n \rangle = \frac{(4/3)(p^2 + 8p - 14)}{(p^2 - 2)}
\]

\[
\langle n \rangle = \frac{(12/7)(13p^3 + 6p^2 - 126p + 112)}{(p^3 + 6p^2 - 8)}
\]

\[
\langle n \rangle = \frac{10(2p^3 - 5p^2 - 16p + 24)}{(p^2 + 2p - 4)(p^2 - 2p - 4)}
\]

\[
\langle n \rangle = \frac{(22/9)(7p^4 - 76p^3 + 16p^2 + 288p - 240)}{(p^5 - 6p^4 - 12p^3 + 32p^2 + 16p - 32)}
\]

TABLE 1: Analytic expressions for $\langle n \rangle$.

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

TABLE 2: Values of $p_{min}$ with 4-digit accuracy.

| $N$ | $p_{min}$ |
|-----|-----------|
| 2   | 0.0000    |
| 4   | 0.6667    |
| 6   | 0.8596    |
| 8   | 0.9204    |
| 10  | 0.9483    |
| 12  | 0.9636    |
| 14  | 0.9729    |
| 16  | 0.9791    |
| $p$ | $\langle n \rangle_{\text{sim}}$ | $\langle n \rangle_{\text{theo}}$ |
|-----|-----------------|-----------------|
| 0.2 | 8.410           | 8.408163        |
| 0.5 | 7.430           | 7.428571        |
| 0.8 | 6.826           | 6.823529        |
| 1   | 6.667           | 6.666667        |

**TABLE 3**: Theoretical vs. simulation value of $\langle n \rangle$ for $N = 7$.  

| $p$ | $\langle n \rangle_{\text{sim}}$ | $\langle n \rangle_{\text{theo}}$ |
|-----|-----------------|-----------------|
| 0.2 | 10.709          | 10.706177       |
| 0.5 | 9.345           | 9.344538        |
| 0.8 | 8.495           | 8.496241        |
| 1   | 8.572           | 8.571429        |

**TABLE 4**: Theoretical vs. simulation value of $\langle n \rangle$ for $N = 8$.  

