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Occupation times of random walks in confined geometries: From random trap model to diffusion-limited reactions

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We consider a random walk in confined geometry, starting from a site and eventually reaching a target site. We calculate analytically the distribution of the occupation time on a third site, before reaching the target site. The obtained distribution is exact and completely explicit in the case or parallelepipedic confining domains. We discuss implications of these results in two different fields: The mean first passage time for the random trap model is computed in dimensions greater than 1 and is shown to display a nontrivial dependence with the source and target positions. The probability of reaction with a given imperfect center before being trapped by another one is also explicitly calculated, revealing a complex dependence both in geometrical and chemical parameters.

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How many times, up to an observation time t, has a given site i of a lattice been visited by a random walker? The study of the statistics of this general quantity, known in the random walk literature as the occupation time of this site, has been a subject of interest for a long time, both for mathematicians [1,2] and physicists [3–10]. As a matter of fact, the occupation time has proven to be a key quantity in various fields, ranging from astrophysics [11], transport in porous media [12], and diffusion limited reactions [13]. The point is that as soon as the sites of a system have different physical or chemical properties, it becomes crucial to know precisely how many times each site is visited by the random walker.

An especially important situation concerns the case when the observation time t up to which the occupation of site i is considered is itself random and generated by the random walker. To settle things and show how the occupation time $\mathbf{N_i}$ comes into play in various physical situations, we first give two different examples.

The first one concerns the case of the so-called random trap model (problem I), which is a very famous model of transport in quenched disordered media [12]. In this random trap model, a walker performs a symmetric lattice random walk, jumping toward neighboring sites. In addition, the time the walker spends at each site is a random variable τ_i, drawn once and for all from a probability distribution ψ, which is identical for all sites. A quantity which has proven to be especially important in transport properties is the first passage time, the time it takes to reach a given target site. It is the key property in many physical applications [14,15], ranging from diffusion-limited reactions [16–19] to search processes (e.g., animals searching for food) [20]. The mean first passage time (MFPT) for the random trap model has been studied [21,22] but, to our knowledge, these determinations have been strictly limited to the very specific one-dimensional (1D) case, and higher dimensional computations in confining geometries like in Fig. 1 are still lacking (see nevertheless [23] for a d-dimensional related problem). The relation with the occupation time is the following: The MFPT at the target r_T starting from site r_S can be written down as $\langle \mathbf{T} \rangle = \sum_{i=1}^{V} \langle \mathbf{N_i} \rangle \tau_i$, where V is the volume of the confining system, $\mathbf{N_i}$ is the number of times the site i has been visited before the target is reached, and $\langle \cdots \rangle$ stands for the average with respect to the random walk. Concerning the distribution of the MFPT with respect to the disorder, that is with respect to the τ_i's, we are finally back to summing a deterministic number V of independent random variables $\langle \mathbf{N_i} \rangle \tau_i$ but nonidentically distributed (because of the factor $\langle \mathbf{N_i} \rangle$), which requires the determination of the *mean* occupation times $\langle \mathbf{N_i} \rangle$ we introduced before.

The second situation has to deal with a very different problem (problem II), which is involved for diffusion limited reactions in confined media. We consider a free diffusing reactant A that enters in a cavity, and which can react with a given fixed center i. We assume that each time the walker reaches the reactive site i, it has a probability p to react, which schematically mimics an imperfect reaction in confined geometry. Actually, numerous chemical reactions, ranging from trapping in supermolecules [24] to activation processes of synaptic receptors [25,26] can be roughly rephrased by this generic scheme. The question we address here is the following: What is the probability for A to react with the center i before exiting the cavity? More generally, for a random walker starting from a site S, what is the probability Q

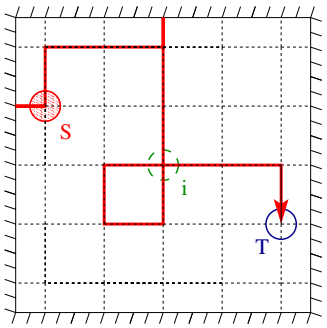

FIG. 1. (Color online) Schematic picture of the problem: the random walk begins at the site S, and the occupation time $\mathbf{N_i}$ is the number of times it visits the site i before reaching the target T. In this picture $\mathbf{N_i}=2$.

to react with i before reaching a target site T, possibly different from S. Partitioning over the number of times the reactive site i has been visited, we have

$$Q = 1 - \sum_{k=0}^{\infty} P(\mathbf{N_i} = k)(1-p)^k. \tag{1}$$

Once again, the random variable $\mathbf{N_i}$ is involved, but that time the determination of the *entire distribution* $P(\mathbf{N_i}=k)$ is needed.

In this Rapid Communication, we propose a method of computation of the statistics of $\mathbf{N_i}$ in confining geometry. In particular, we obtain explicitly the *exact distribution* in the case of parallelepipedic confining domains. Applications to the above-mentioned examples are discussed.

We start with the computation of the mean $\langle \mathbf{N_i} \rangle$, assuming for the time being that the starting and target sites are different ($S \neq T$). We note by w_{ij} the transition probabilities from site j to site i. We have $\Sigma_i w_{ij}=1$, and we take $w_{ij}=w_{ji}$. These general transition probabilities can take into account reflecting boundary conditions. We consider an outgoing flux J of particles in S. Since the domain is finite, all the particles are eventually absorbed in T, and, in the stationary regime, there is an incoming flux J of particles in T. The mean particle density ρ_i thus satisfies the following equation:

$$\rho_i = \sum_j w_{ij}\rho_j + J\delta_{iS} - J\delta_{iT}, \tag{2}$$

with the boundary condition $\rho_T=0$ (it is the absorbing site). To find the mean occupation time, we can simply notice that the mean particle density ρ_i is equal to $\langle \mathbf{N_i} \rangle J$. To solve this problem, we use the pseudo-Green function H [27,28], which satisfies

$$H(\mathbf{r}_i|\mathbf{r}_j) = \sum_k w_{ik} H(\mathbf{r}_k|\mathbf{r}_j) + \delta_{ij} - \frac{1}{V}, \tag{3}$$

where V is the total number of sites of the lattice. It is also symmetrical in its arguments, and the sum $\Sigma_i H(\mathbf{r}_i|\mathbf{r}_j)$ is a constant independent of j. Using the concise notation $H_{ij} = H(\mathbf{r}_i|\mathbf{r}_j)$, it can be seen by direct substitution that ρ_i is given by

$$\langle \mathbf{N_i} \rangle = \frac{\rho_i}{J} = H_{iS} - H_{iT} + H_{TT} - H_{ST}, \tag{4}$$

which satisfies Eq. (2) as well as the boundary condition $\rho_T=0$. Note that these results also give the mean occupation time of a subdomain, which is simply the sum of the mean occupation time of all the sites in the subdomain. In particular, we can check that the mean occupation time for the whole domain, $\Sigma_{i=1}^{V} \langle \mathbf{N_i} \rangle = V(H_{TT} - H_{ST})$, gives back the MFPT from S to T [28,29].

Before we go further, it is necessary to give a few elements on the evaluation of H for isotropic random walks. The following exact expression [28,30] is known in two dimensions for rectangles:

$$H(\mathbf{r}|\mathbf{r}') = \frac{4}{N}\sum_{m=1}^{X-1}\sum_{n=1}^{Y-1} \frac{\cos\dfrac{m\pi x'}{X}\cos\dfrac{n\pi y'}{Y}\cos\dfrac{m\pi x}{X}\cos\dfrac{n\pi y}{Y}}{1-\dfrac{1}{2}\left(\cos\dfrac{m\pi}{X}+\cos\dfrac{n\pi}{Y}\right)} + \frac{4}{N}\sum_{m=1}^{X-1} \frac{\cos\dfrac{m\pi x'}{X}\cos\dfrac{m\pi x}{X}}{1-\cos\dfrac{m\pi}{X}} + \frac{4}{N}\sum_{n=1}^{Y-1} \frac{\cos\dfrac{n\pi y'}{Y}\cos\dfrac{n\pi y}{Y}}{1-\cos\dfrac{n\pi}{Y}}, \tag{5}$$

where X and Y are the dimensions of the rectangle, and the coordinates x and y are half-integers going from $1/2$ to $X-1/2$ or $Y-1/2$. There is also a similar expression for parallelepipedic domains in three dimensions. In more general domains, the most basic approximation (which usually gives a good order of magnitude) is to approximate H by the infinite-space lattice Green function G_0 [27], G_0 being evaluated as $G_0(\mathbf{r}|\mathbf{r}')=3/(2\pi|\mathbf{r}-\mathbf{r}'|)$ for $\mathbf{r}\neq\mathbf{r}'$, and $G_0(\mathbf{r}|\mathbf{r})=1.516\ldots$ in three dimensions, and $G_0(\mathbf{r}|\mathbf{r}')=-(2/\pi)\ln|\mathbf{r}-\mathbf{r}'|$ for $\mathbf{r}\neq\mathbf{r}'$, and $G_0(\mathbf{r}|\mathbf{r})=1.029\ldots$ in two dimensions. More accurate approximations can be found [28], but the above approximations are good enough to capture the qualitative behavior of the pseudo-Green function and of the distribution of the occupation time.

It is indeed possible to obtain not only the mean, but also the entire distribution of the occupation time. The idea to tackle this *a priori* difficult problem is to use recent results concerning the so-called splitting probabilities [14,28,29]. In the presence of two targets T_1 and T_2, the splitting probability P_1 to reach T_1 before T_2 is [28,29]

$$P_1 = \frac{H_{1S} + H_{22} - H_{2S} - H_{12}}{H_{11} + H_{22} - 2H_{12}}. \tag{6}$$

Denoting here $P_{ij}(i|S)$ the splitting probability to reach i before j, starting from S, we have $P(\mathbf{N_i}=0)=P_{iT}(T|S)$, and for $k \geq 1$:

$$P(\mathbf{N_i}=k) = P_{iT}(i|S)\left[\sum_j w_{ji}P_{iT}(i|j)\right]^{k-1}\left[\sum_j w_{ji}P_{iT}(T|j)\right]. \tag{7}$$

The three terms of this last equation correspond, respectively, to the probability to reach i before T, starting from S, the probability to return to i before reaching T, starting from i, to

the power $k-1$, and the probability to reach T before returning to i. It can thus be written

$$P(\mathbf{N_i}=k)=AB(1-B)^{k-1} \quad \text{for } k\geq 1, \tag{8}$$

with

$$A\equiv P_{iT}(i|S)=\frac{H_{iS}+H_{TT}-H_{ST}-H_{iT}}{H_{ii}+H_{TT}-2H_{iT}}, \tag{9}$$

and

$$B\equiv \sum_j w_{ji}P_{iT}(T|j)=1-\sum w_{ji}P_{iT}(i|j) \tag{10}$$

$$=\frac{\sum_j w_{ji}H_{Tj}-H_{iT}-\sum_j w_{ji}H_{ji}+H_{ii}}{H_{ii}+H_{TT}-2H_{iT}} \tag{11}$$

$$=\frac{1}{H_{ii}+H_{TT}-2H_{iT}}, \tag{12}$$

using Eq. (3), and $\Sigma_i w_{ij}=1$. It can also be noted that $P(\mathbf{N}_i=0)=1-A$. The distribution of the occupation numbers given by Eqs. (8)–(12) is the main result of this Rapid Communication, and several comments are in order. (i) Expressions of H given in Eq. (5) make this result exact and completely explicit for parallelepipedic domains. (ii) Computing $\langle \mathbf{N_i}\rangle$ with this distribution gives back the expected result (4). (iii) It can be noted here that B, which characterizes the decay of the probability distribution of $\mathbf{N_i}$, is independent of the source. In addition, qualitatively, the basic evaluations of H following Eq. (5) (namely $H=G_0$) give for B the following order of magnitude, if i and T are at a distance R:

$$B\simeq \begin{cases} [2G_0(0)-3/(\pi R)]^{-1} & \text{in 3D}, \\ [2G_0(0)+(4/\pi)\ln R]^{-1} & \text{in 2D}, \end{cases} \tag{13}$$

where $G_0(0)=G_0(\mathbf{r}|\mathbf{r})$ is a dimension-dependant constant, given in the discussion on the evaluation of H. This shows that B decreases with the distance between i and T: a larger distance corresponds to a slower decay; but, while it tends towards 0 in two dimensions (which corresponds to a wide distribution of $\mathbf{N_i}$, and a large variance), it tends to a finite value in three dimensions. It can thus be said that the sites much further from the target than the source have, in three dimensions, a significant probability to be visited, but a low probability to be visited many times, whereas, in two dimensions, they have a low probability to be visited at all, but a comparatively high probability to be visited many times. This is connected with the transient or recurrent character of the free random walk in two or three dimensions. (iv) The results obtained here for different starting and target sites may easily be adapted to identical starting and target sites ($S=T$):

$$P(\mathbf{N_i}=0)=1-B; \quad P(\mathbf{N_i}=k)=B^2(1-B)^{k-1} \quad \text{for } k\geq 1. \tag{14}$$

Note that this gives in particular a mean occupation time of 1 for all sites, a result which could be derived from an extension of Kac's formula [1,28]. However, here, we obtain not only the mean occupation number but the entire distribution of this occupation number, which appears to vary from site to site: the further the site is from the target, the slower the probability distribution decays.

We now discuss the applications of these general results to the examples mentioned in the introduction. As for the random trap model (problem I), we focus here on the especially interesting case of a one-sided Levy stable distribution [2] $\psi(t)=f_\alpha[t,\tau_0\alpha\cos(\pi\alpha/2),1,0)]$ $(0<\alpha<1)$, which corresponds to an algebraic decay:

$$\psi(t)\sim \frac{\alpha\tau_0^\alpha}{\Gamma(1-\alpha)t^{1+\alpha}} \tag{15}$$

and whose Laplace transform is $\hat{\psi}(u)=\exp(-\tau_0^\alpha u^\alpha)$ (τ_0 can be seen as the typical waiting time). The Laplace transform $\hat{\pi}(u)$ of the distribution of the MFPT with respect to the disorder reads

$$\hat{\pi}(u)=\prod_{i=1}^{V}\hat{\psi}(\langle \mathbf{N_i}\rangle u)=\exp[-(T_{typ}u)^\alpha]. \tag{16}$$

The probability density of the MFPT is then as could have been expected a one-sided Levy stable law, but with a nontrivial typical time:

$$T_{typ}=\tau_0\left(\sum_{i=1}^{V}(H_{iS}-H_{iT}+H_{TT}-H_{ST})^\alpha\right)^{1/\alpha}. \tag{17}$$

For large size domain V, this result can be applied to any wide-tailed distribution of the waiting times satisfying Eq. (15) [12]. It can be shown that T_{typ} is bounded by $\tau_0 V^{1/\alpha}(H_{TT}-H_{ST})$, and tends towards this upper bound as V grows, which provides a simple estimation of T_{typ} and indicates that for large enough domains, the scaling of T_{typ} with the source and target positions is the same as for the discrete-time random walk (pure systems) [28,29]. We thus showed that the random trap problem in confined geometries, with a wide-tailed waiting time distribution, has a Levy distribution of mean first-passage times, with a nontrivial typical time. The scaling with the size V is $V^{1/\alpha}$. The scaling with the source and target positions is modified by the disorder in small confining domains, while it is the same as for pure systems in large enough domains.

Concerning the application to diffusion-limited reactions (problem II), the probability Q to have reacted with i before reaching T writes, using Eqs. (1) and (8):

$$Q=\frac{Ap}{1-(1-p)(1-B)}. \tag{18}$$

The expression (18) displays a subtle interplay between the geometrical factors, involved through the terms A and B, and the reactivity p. Focusing now on the specific case of identical starting and target points [meaning $A=B$, cf. Eq. (14)], we exhibit two interesting limiting regimes. In the "reactivity limited regime," defined by $p\ll B$, we have $Q\sim p$. In particular, in that regime Q does not depend on the reactive site i. In other words, for a fixed reactivity p, all sites i such that $p\ll B$ have the same probability of reaction Q, and the

detailed position of i does not come into play. On the contrary, the "geometrically limited regime" $p \gg B$ leads to $Q \sim B$, which no longer depends on p, but only on the geometry. Given the order of magnitude of B [cf. Eq. (13)], this can essentially happen in two dimensions, when $R \gg \exp[-\pi/(2p)]$. This can be explained by the recurrent character of the two-dimensional random walk: when the reacting site i is far enough from the target, if a random walker reaches it, it is likely to visit it many times before returning to T, and is thus almost sure to react whenever i is reached. The reaction probability Q then becomes the probability to reach the site i. Consequently, the position of the reacting site has a low influence on reactivity in three dimensions, or when the reacting site is within a disk of radius $R=\exp(-\pi/2p)$ around the target in two dimensions. If the reacting site is further, the geometrical effects become preeminent. We show in Fig. 2 a graph of Q, as a function of p, for different positions of i (near the target, in the middle of the domain, and at the opposite), the source and target point being identical. The limiting regimes can be well-identified.

To conclude, we have computed the distribution of the occupation time of a given site i, for a random walk in confined geometry, eventually trapped at a target. This distribution is exact and completely explicit in the case of parallelepipedic confining domains. While the mean occupation time, unsurprisingly, is higher when i is near the source and lower near the target (and uniform if the source and target are identical), the distribution of the occupation time is essentially exponential, with a slower decay when the point is far away from the target. We have also presented important applications of these results in two different fields. The first one is transport in quenched disorder media: The mean first passage time for the random trap model has been computed in dimensions greater than 1, and has been shown to display a nontrivial dependence with the source and target positions.

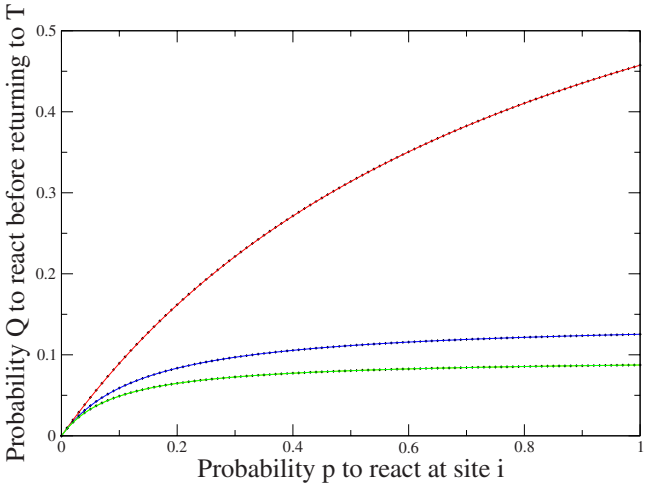

FIG. 2. (Color online) Simulations (symbols) versus analytical prediction (lines) Eq. (18) of the probability Q to react before returning to the target site as a function of the probability to react at site i. The confining domain is a square of side 51, and the target is at the middle of an edge, of coordinates (0,25), the site (0,0) being a corner site. The three curves correspond to different positions of site i: (1,25) (red, upper curve), (25,25) (blue, midcurve), and (50,25) (green, lower curve).

The second application is to diffusion limited reactions in confined geometry: The probability of reaction with a given imperfect center before being trapped by another one has been explicitly calculated and has proven to present a complex dependence both in the geometrical and chemical parameters. We believe that the results obtained in this Rapid Communication could be relevant to systems involving diffusion in confining domains, displaying inhomogeneous physical or chemical properties.

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