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Target annihilation by random walkers

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We study the target annihilation through random walkers on regular lattices, and for it we derive, based on the generating functions' formalism, an exact expression. Extensions to continuous time and to random walks on fractals are given. Using numerical simulations we compare the results to those which obtain for the trapping problem.

I. INTRODUCTION

Recently, much interest has been devoted to the study of diffusion-controlled reactions through random-walk models.[1–10] Here, the term *reaction* has to be understood in a very wide sense, since the applications range from chemical processes and their analogs, such as electron scavenging and recombination[6,9,11] and electronic and vibrational energy transfer in condensed media,[3–5,10,12] to models for the distribution of matter and antimatter (or of magnetic monopoles) in the universe.[7] Random-walk models are ideally suited for computer simulations, a practical way to obtain results, since for the vast majority of cases no purely analytical method exists. On the other hand, there is a strong challenge for solving special cases analytically; such solutions help in better understanding the models and are good testing grounds both for approximate solutions and for the numerical simulations.

In this Rapid Communication we report the exact solution for the target annihilation problem (also called the scavenging problem), in which randomly placed targets are annihilated by random walkers.[13–16] In a certain sense the problem is the dual of the trapping problem,[3–6,8–12,17–21] in which walkers (say, the A particles) are annihilated in reaching the traps (T particles); i.e., $A+T \rightarrow T$. For the target problem the analog reaction is $A+T \rightarrow A$. The trapping problem has been extensively studied by us and by other groups,[3–6,8–12,17–21] and for it, apart from the one-dimensional, nearest-neighbor, random-walk case,[1] no exact solutions are known. As pointed out, the difficulty of a general solution is that it is equivalent to knowing *exactly* the distribution R_n of the number of distinct sites visited in n steps by the walkers. However, the powerful method of the generating functions[1,22,23] allows one to determine only the average $S_n=\langle R_n\rangle$ exactly.

Interestingly, the target problem is amenable to a treatment in the framework of generating functions and, in this sense, exactly solvable. Applications of the target problem are the Williams-Watts dielectric relaxation in polymers and glasses[13–15] and also the poisoning of surface catalysts and of immobilized enzymes.[24] In the dielectric relaxation case Glarum proposed that a frozen-in dipole could relax when a mobile defect (particle A) reaches it; in glassy systems the defect may be a vacancy which upon reaching the dipole relieves the local strains.[25] Recent approximate analytical and numerical solutions to this problem have been obtained by Shlesinger and Montroll[14,15] and by Redner and Kang.[16]

In Sec. II we present our method and calculate, first for random walks on regular lattices, the decay of the number of targets as a function of the number of steps. We extend then this result to random walks in continuous time (CTRW) by including waiting-time distributions. Also, using another straightforward generalization we consider walks on fractal structures. From these expressions we derive directly the previously advanced approximate decay forms. In Sec. III we compare these to the exact forms; as a check we also present the results of computer simulations, and find for low dimensions ($d \leq 2$) that the decay forms due to trapping and to target annihilation behave differently at long times, the latter process leading to quicker decays.

II. THEORETICAL

We begin our considerations with a regular lattice and place with probability p walkers on the lattice sites. We focus on a target, assumed to be at the origin of the coordinate system. As will become evident in the following, the derivation carries through for an arbitrary number of targets, and therefore (distinct from the trapping problem) the validity of the final expression is not limited to low target densities. We let the walkers step from site to site according to a probability density $w(l)$, where $l=|\vec{l}|$ is the step length: Thus, the microscopic rates are symmetrical, and the walks are not necessarily restricted to nearest neighbors.

Let us denote by $F_m(\vec{r})$ the probability that a random walker starting from $\vec{r}$ reaches the origin $\vec{0}$ for the first time in the mth step. Because of the symmetry of the walk $F_m(\vec{r})$ is also the first-passage time from $\vec{0}$ to $\vec{r}$, as defined by Montroll and Weiss.[22] The probability $H_n(\vec{r})$ that a first passage from $\vec{r}$ and $\vec{0}$ occurred in the first n steps is

$$H_n(\vec{r}) \equiv \sum_{m=1}^{n} F_m(\vec{r}) \quad . \tag{1}$$

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Initially ($m=0$) one has a walker at $\vec{r}$ with probability p; hence, the probability $\Phi_n(\vec{r})$ that *no* particle from $\vec{r}$ visits the origin in the first n steps is

$$\Phi_n(\vec{r}) = 1 - pH_n(\vec{r}) \ . \tag{2}$$

We now take the target to be annihilated at the first visit of a walker. Furthermore, we assume the walkers to move independently of each other, their motion being also unaffected by target annihilation processes (the chemical analog being $A + T \rightarrow A$). The probability that the target at the origin survives the first n steps is then

$$\Phi_n = \prod_{\vec{r}}{}' \Phi_n(\vec{r}) = \prod_{\vec{r}}{}' [1 - pH_n(\vec{r})]$$

$$= \prod_{\vec{r}}{}' \left[1 - p \sum_{m=1}^{n} F_m(\vec{r}) \right] \ , \tag{3}$$

where the product extends over all sites of the lattice with the exception of the origin. We note that Eq. (3) holds for an uncorrelated motion of the walkers, so that during the walk, sites may be occupied by more than one walker.

Expression (3) forms the basis of our further analysis. We note that Φ_n involves $F_m(\vec{r})$, a quantity which can be evaluated via generating-function techniques[22] *(vide infra)*. Moreover, Φ_n is translationally invariant: for any distribution of N_T targets the ensemble averaged decay is $N_T\Phi_n$, an expression which holds for arbitrary target concentrations.

Taking logarithms we obtain from Eq. (3)

$$\ln\Phi_n = \sum_{\vec{r}}{}' \ln\Phi_n(\vec{r}) = \sum_{\vec{r}}{}' \ln[1 - pH_n(\vec{r})]$$

$$= -\sum_{j=1}^{\infty} (p^j/j) \sum_{\vec{r}}{}' [H_n(\vec{r})]^j \ , \tag{4}$$

where in the last line we remarked that both p and $H_n(\vec{r})$ lie between 0 and 1, so that the final series is absolutely convergent for all values of p and, thus, the order of summation can be exchanged. As a power series in p, Eq. (4) is particularly useful for obtaining approximate forms to the true decay Φ_n, by restricting the summation to a few j values.

As an example, we take only the first term $j=1$ and have

$$\ln\Phi_n \simeq -p \sum_{\vec{r}}{}' H_n(\vec{r}) = -p \sum_{m=1}^{n} \sum_{\vec{r}}{}' F_m(\vec{r}) \ . \tag{5}$$

Now, following Eqs. (III.2) and (III.3) of Ref. 22 one has

$$\sum_{\vec{r}}{}' F_m(\vec{r}) = S_m - S_{m-1} \quad (m \geq 1) \ , \tag{6}$$

where S_m is the mean number of distinct sites visited in m steps, $S_m = \langle R_m \rangle$, with $S_0 = 1$. Therefore, introducing Eq. (6) into Eq. (5) we get as a first-order (small p) approximation to Φ_n,

$$\Phi_n \simeq \exp[-p(S_n - 1)] \equiv \Phi_n^u \ . \tag{7}$$

This expression has beeen obtained using different methods by Shlesinger and Montroll[14,15] and by Redner and Kang[16] in the context of the *target* problem. We note that Eq. (7) is an *upper* bound to Φ_n, since all the terms discarded in Eq. (4) are negative. From Eq. (4) we also obtain a *lower* bound to Φ_n, by noticing that $H_n(\vec{r}) < 1$ and thus $[H_n(\vec{r})]^j < H_n(\vec{r})$. Thus,

$$\ln\Phi_n \geq -\sum_{j=1}^{\infty} (p^j/j) \sum_{\vec{r}}{}' H_n(\vec{r}) = -\lambda(S_n - 1) \ , \tag{8}$$

with $\lambda \equiv -\ln(1-p)$. Hence,

$$\Phi_n^l \equiv \exp[-\lambda(S_n - 1)] \leq \Phi_n \leq \exp[-p(S_n - 1)] \equiv \Phi_n^u \ . \tag{9}$$

Interestingly, Φ_n^l is also a lower bound for the *trapping* problem, when p denotes the density of traps (see Ref. 18 for details). However, the trapping and the target problems are different; the decay $\tilde{\Phi}_n$ in the trapping problem is[18]

$$\tilde{\Phi}_n = \exp\left[-\sum_{j=1}^{\infty} (-1)^j (\lambda^j/j!) K_{j,n} \right] \ , \tag{10}$$

where the $K_{j,n}$ are the cumulants of R_n, the number of distinct sites visited in n steps. The evaluation of higher cumulants ($j > 1$) is a very complex problems,[1,18] whereas, as we proceed to show, the higher terms in Eq. (4) are readily tractable.

Let us start from the generating function for the $H_n(\vec{r})$:

$$H(\vec{r};z) \equiv \sum_{n=1}^{\infty} z^n H_n(\vec{r}) \ . \tag{11}$$

After a few transformations, $H(\vec{r};z)$ may be expressed in terms of the generating function for the $F_n(\vec{r})$:

$$F(\vec{r};z) \equiv \sum_{n=1}^{\infty} z^n F_n(\vec{r}) = \sum_{n=1}^{\infty} z^n [H_n(\vec{r}) - H_{n-1}(\vec{r})]$$

$$= (1-z) H(\vec{r};z) \ , \tag{12}$$

where we used Eq. (1) and remarked that $H_0(\vec{r}) = 0$. On the other hand $F(\vec{r};z)$ is given directly in terms of the generating function $P(\vec{r};z)$ of the walk.[1,22,23,26,27] For primitive lattices (other cases are discussed in Refs. 26 and 27) one has

$$F(\vec{r};z) = [P(\vec{r};z) - \delta_{\vec{r},\vec{0}}]/P(\vec{0};z) \tag{13}$$

[Eq. (III.6) of Ref. 22], and thus

$$H(\vec{r};z) = [P(\vec{r};z) - \delta_{\vec{r},\vec{0}}]/[(1-z)P(\vec{0};z)] \ . \tag{14}$$

As an example, for simple hypercubic lattices in d dimensions one has

$$P(\vec{r};z)$$

$$= (2\pi)^{-d} \int \cdots \int_{d} d^d k \exp(-i\vec{r}\vec{k})/[1 - z\lambda(\vec{k})] \ , \tag{15}$$

where $\lambda(\vec{k})$, the structure function for nearest-neighbor walks, is

$$\lambda(\vec{k}) = \left(\frac{1}{d} \right) \sum_{i=1}^{d} \cos(k_i) \ , \tag{16}$$

k_i being the ith component of the d-dimensional vector $\vec{k}$.

Taken together, Eqs. (4), (14), and (15) are the (admittedly implicit) analytical solution of the target problem. For numerical purposes we found it more expedient to determine $H_n(\vec{r})$ in the n space by calculating iteratively $P_n(\vec{r})$ from $P_{n-1}(\vec{r})$ and by inverting then $P_n(\vec{r})$ to obtain $F_n(\vec{r})$. The method involves no random numbers and is straightforward (see Refs. 22 and 27 for details). To exemplify the ease with which the terms in Eq. (4) can be evaluated we give in Table I some typical results for walks in one and two dimensions, and we follow n over thousand steps: $1 \leq n \leq 1000$.

TABLE I. Values of the partial sums $\sum'_{\vec{r}} [H_n(\vec{r})]^j$ which determine the decay of the targets [Eq. (4)] for the linear chain ($d=1$) and for the square lattice ($d=2$).

	n	$j=1$	$j=2$	$j=3$
$d=1$	1	2.000 000	0.500 000	0.250 000
	10	5.167 969	2.111 858	1.295 327
	100	15.997 437	8.399 133	5.757 406
	1000	50.475 261	28.576 639	20.200 003
$d=2$	1	2.000 000	0.250 000	0.062 500
	10	7.881 383	1.423 142	0.439 911
	100	49.504 137	8.750 682	2.721 064
	1000	363.583 763	52.(6)	14.(1)

In Sec. III we compare the decay laws obtained from $P(\vec{r};z)$ with the results of numerical simulations, and there we also determine the domain of validity of approximate expressions such as Eq. (7). To close this section we show that the results obtained can be extended to the continuous-time domain (CTRW) and walks on fractal structures.

For walkers whose stepping times follow a distribution $\psi(t)$, the probability $\chi_n(t)$ of having performed exactly n steps during the time t obeys[4]

$$\chi_n(t) = L^{-1}\{[\psi(u)]^n[1-\psi(u)]/u\} , \tag{17}$$

where L denotes the Laplace transformation, L^{-1} its inverse, and $L[\psi(t)]=\psi(u)$. In continuous time Eq. (1) changes to

$$H(\vec{r},t) = \sum_{n=0}^{\infty} \chi_n(t) H_n(\vec{r}) , \tag{18}$$

with a corresponding change in the decay law:

$$\Phi(t) = \prod'_{\vec{r}} [1-pH(\vec{r},t)]$$

$$= \prod'_{\vec{r}} \left[1-p\sum_{n=0}^{\infty}\chi_n(t)\sum_{m=1}^{n} F_m(\vec{r})\right] . \tag{19}$$

The first-order approximation to Eq. (19) is

$$\ln\Phi(t) \simeq -p\sum_{n=0}^{\infty}\chi_n(t)(S_n-1) \equiv -p[S(t)-1] . \tag{20}$$

The methods of evaluating $S(t)$ are standard.[1,4,6] One should note, however, that the higher approximations to $\Phi(t)$ are more complex, since in them products of $\chi_n(t)$ functions appear, and thus the Laplace transformations get more involved.

For structures lacking translational symmetry, such as fractals, generating functions such as Eq. (15) are not available. One may still bypass the need of a complete numerical simulation of the full problem by determining the $F_m(\vec{r})$ through site enumerations on fractals *devoid* of targets, and then using Eq. (3) to compute Φ_n. As an example, in Ref. 28 we have determined S_n for several Sierpiski gaskets; these results can be directly inserted into Eq. (7) to obtain the first-order approximation for the decay of the targets.

Summarizing, for the model studied, we have obtained an exact expression for the target decay in an *infinite* volume, under the condition that at start the sites may be occupied with probability p by exactly one walker. For a fixed number M of walkers in a *finite* volume V, Shlesinger and Montroll[14] have given the target decay Φ_n^V for a possible multiple occupancy of sites by walkers. In our notation

$$\Phi_n^V = \left[1-N^{-1}\sum_{\vec{r}} H_n(\vec{r})\right]^M , \tag{21}$$

where N is the number of available starting sites in V. Owing to the different initial conditions, Eqs. (3) and (21) agree with each other only to leading order in M/N. Evidently, in the thermodynamic limit, which obtains for $V\to\infty$, such that $M/N\to p << 1$, Eq. (21) reverts to Eq. (7) and leads in the CTRW framework to Eq. (20).

III. RESULTS

In this section we present the decay laws for the targets, and compare the results to the trapping problem. We also use the exact decay laws in order to establish the domain of validity of the approximate expressoin [Eq. (7)].

For illustrative purposes we also display simulation results on one- and two-dimensional lattices. Such simulations provide an internal check, both of the theoretical approach and also of the numerical program, e.g., of the random-number generator.

To exemplify, we plot in Fig. 1 the decay of targets distributed on a one-dimensional chain. The *walkers* are placed randomly, with probability $p=0.5$ on a chain with $N=20\,000$ sites. All sites not occupied by walkers are viewed as targets, and their decay is monitored as a function of the steps of the walkers. Note that it is completely superfluous to distribute the *targets* at random on the lattice: the necessary configurational average wipes out the initial target distribution, a fact which we already encountered in the derivation of Φ_n [see the discussion following Eq. (3)].

In Fig. 1, the exact decay Φ_n is given as a solid line and the simulation results are indicated through black dots; the agreement is excellent. In the figure also Φ_n^u and Φ_n^l, the upper and lower bounds to Φ_n [see Eq. (9)], are given as dashed lines. Admittedly, because of the large p, none is a good approximation to Φ_n. For comparison we have also included in Fig. 1 the corresponding trapping decay $\tilde{\Phi}_n$ together with simulation results, indicated as open circles. As noticed[16] at longer times Φ_n decays quicker than $\tilde{\Phi}_n$.

In Fig. 2 we display the results obtained for a square lattice. Here, walkers are placed randomly with probability $p=0.5$ and 0.1 on the lattice. As in Fig. 1, we compare the simulated and exact decays for target annihilation and for trapping. As is evident upon inspection, for $p=0.5$ and for short times the target decay Φ_n is closer to the upper bound Φ_n^u while the trapping decay $\tilde{\Phi}_n$ follows more closely the lower bound Φ_n^l; i.e., at short times the trapping process is faster than the target annihilation. The situation is reversed at longer times, where trapping becomes slower, a behavior which agrees with the known asymptotics.[18–21] For the target problem we note that for small p values at not too long times the approximation Φ_n^u [Eq. (7)] works fairly well even in low ($d\leq 2$) dimensions. For trapping, on the other

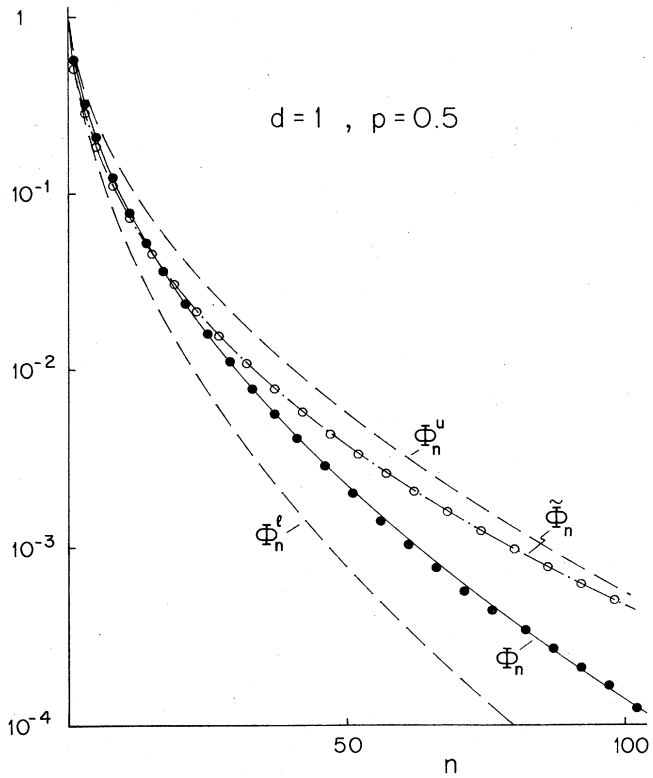

FIG. 1. Survival probability of the targets Φ_n for a linear chain ($d=1$). The density of the walkers is $p=0.5$. The dots are the simulation results and the solid line is the exact form [Eq. (4)]. The upper and lower bounds, Φ_n^u and Φ_n^l [Eq. (7)], are given as dashed lines. Included are also the simulation results (open circles) and the exact decay $\tilde{\Phi}_n$ of the trapping problem (dash-dotted line).

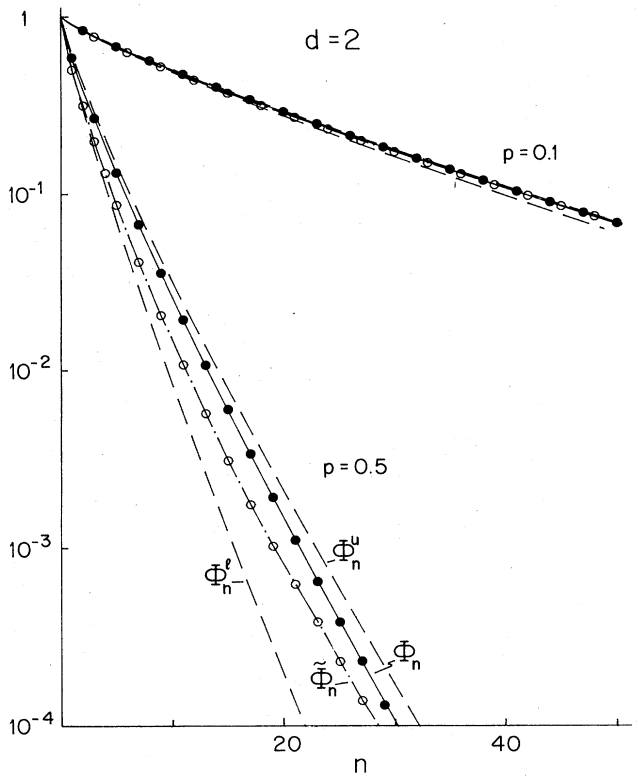

FIG. 2. Survival probability Φ_n of the targets for a square lattice ($d=2$). The density of walkers is $p=0.5$ and 0.1. The notation is as in Fig. 1.

hand, the form Φ_n^l approximates less successfully in low dimensions.[18] The results in three dimensions are similar to the two-dimensional case.

In summary, for random walks on regular lattices we have solved the target problem exactly. The solution may be readily extended to more complex cases such as CTRW's, or random walks on fractals; it can also be used as a test for simulation programs.

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