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## Order statistics of the trapping problem

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When a large number N of independent diffusing particles are placed upon a site of a d-dimensional Euclidean lattice randomly occupied by a concentration c of traps, what is the mth moment  $\langle t_{j,N}^m \rangle$  of the time  $t_{j,N}$  elapsed until the first j are trapped? An exact answer is given in terms of the probability  $\Phi_M(t)$  that no particle of an initial set of  $M=N,N-1,\ldots,N-j$  particles is trapped by time t. The Rosenstock approximation is used to evaluate  $\Phi_M(t)$ , and it is found that for a large range of trap concentrations the mth moment of  $t_{j,N}$  goes as  $x^{-m}$  and its variance as  $x^{-2}$ , x being  $\ln^{2/d}(1-c)\ln N$ . A rigorous asymptotic expression (dominant and two corrective terms) is given for  $\langle t_{j,N}^m \rangle$  for the one-dimensional lattice.

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#### I. INTRODUCTION

Statistical problems related to the diffusion of a single random walker in a medium with traps have been subject of intense research during the last decades [1-8]. Usually it is assumed that the statistical properties of this single (N=1) random walker are representative of the statistical ensemble. However, there are multiparticle (N>1) problems that cannot be analyzed in terms of the single walker theory. An example is the number  $S_N(t)$  of distinct sites visited (or territory explored) up to time t by N independent random walkers all starting from the same origin [9-14]. Another multiparticle problem of interest, that as we will see is closely related to that of the territory explored, is the description of the order statistic of the diffusion processes, i.e., the estimate of the time at which the jth particle of an initial set of N particles all starting from the same origin is trapped.

The order-statistic problem when the traps are arranged on a (hyper) sphere (i.e., an absorbing boundary at a fixed distance) has been thoroughly studied [15–18]. In this paper we consider the more difficult problem in which the traps are arranged randomly ("the trapping problem") in a d-dimensional Euclidean medium. A related problem, in which the N particles are placed on the left of a one-sided random distribution of traps on a one-dimensional lattice, has been investigated in Ref. [19]. It is interesting to note that recent advances in optical spectroscopy [20] make it possible to monitor this kind of multiparticle dynamic process. Indeed, the simultaneous tracking of  $N \ge 1$  fluorescently labeled particles and the analysis of the diffusive motion of the particles individually is a useful recent technique for characterizing heterogeneous microenvironments (in particular, for samples dynamically changing in time such as biological samples) [21]. A useful feature of the order-statistics approach is that it allows one to infer properties of the diffusive system (diffusion constant, number of diffusing particles, concentration of traps, effective dimension of the diffusive substrate, ...) from only the analysis of the behavior of those particles that are first trapped. This could be an advantage when it is impractical or impossible to wait until all the reaction is over.

The order statistics of the trapping process will be described by means of the probability  $\Phi_{j,N}$  that j particles of the initial set of N diffusing particles have been trapped, and

the other N-j have survived, by time t. In this paper we consider that all the particles start from the same origin that is free of traps. The moments of the time  $t_{i,N}$  at which the jth particle of the initial set of N particles is trapped will be calculated from  $\Phi_{j,N}$ . This probability  $\Phi_{j,N}$  will be given in terms of the survival probability  $\Phi_M(t) \equiv \Phi_{0,M}(t)$  that no particle of an initial set of M  $(M=N,N-1,\ldots,N-j)$  has been absorbed by time t. This last quantity will be estimated by means of the Rosenstock approximation using expressions for  $S_N(t)$  calculated in Refs. [12–14]. It should be noted that our approach to the order statistics of the diffusion process in the presence of randomly placed traps is different from that used [15-18] for a fixed configuration of traps. What makes the two problems completely different, and hence the way of solving them, is that for the case with a given configuration of traps the probability that N particles are trapped by time t is simply the Nth power of the probability for a single particle. This simplifying result does not hold when many configurations of randomly placed traps are considered.

This paper is organized as follows. In Sec. II we deduce the main formulas that describe the order statistics of the trapping process: we relate  $\Phi_{j,N}$  to  $\Phi_N(t)$  and  $\langle t_{j,N}^m \rangle$  to  $\Phi_{j,N}(t)$ . In Sec. III we show that the ratio between the variance of  $S_N(t)$  and  $\langle S_N(t) \rangle^2$  goes roughly as  $(\ln N)^{-2}$  for large N. This suggests that the Rosenstock approximation for  $\Phi_N(t)$  can lead to good results even when N is large. This is checked in Sec. IV, where we also obtain asymptotic expressions (the main term) for  $\langle t_{j,N}^m \rangle$  and the variance. The procedure, based on the Rosenstock approximation, does not provide analytic asymptotic corrective terms for  $d \ge 2$ , although we show that numerical integration is feasible leading to excellent results. However, in Sec. V, for the onedimensional lattice we are able to find a rigorous asymptotic expression (up to the second-order corrective term) for  $\langle t_{i,N}^m \rangle$ for large N. Some remarks and the conclusions are presented in Sec. VI.

### II. ORDER STATISTICS OF THE TRAPPING PROCESS

Let us first show how to obtain  $\Phi_{j,N}(t)$  from  $\Phi_M(t)$  with  $M = N, N-1, \ldots, N-j$ . Let  $\Psi_{j,N}(t)$  be the probability that j random walkers of the initial set of N have been absorbed by

time t by a given configuration of traps and let  $\Psi(t) \equiv \Psi_{0,N}(t)$  be the probability that no single random walker has been absorbed by time t by this configuration of traps. Taking into account that  $\binom{N}{j}$  is the number of different groups of j particles that can be formed from a set of N, one finds

$$\Psi_{j,N}(t) = \binom{N}{j} (1 - \Psi)^j \Psi^{N-j},\tag{1}$$

or, using the binomial expansion,

$$\Psi_{j,N}(t) = \binom{N}{j} \sum_{m=0}^{j} (-1)^{j-m} \binom{j}{m} \Psi^{N-j+j-m}.$$
 (2)

Averaging over different configurations of traps and taking into account that  $\Phi_N(t) = \langle \Psi^N(t) \rangle$  and  $\Phi_{j,N}(t) = \langle \Psi_{j,N}(t) \rangle$ , we get

$$\Phi_{j,N}(t) = (-1)^j \binom{N}{j} \Delta^j \Phi_N(t), \tag{3}$$

where the backward difference formula for the jth derivative

$$\Delta^{j} \Phi_{N}(t) = \sum_{m=0}^{j} (-1)^{m} \binom{j}{m} \Phi_{N-m}(t), \tag{4}$$

has been used. The difference formula in Eq. (3) can be approximated by the derivative

$$\Phi_{j,N}(t) \simeq (-1)^j \binom{N}{j} \frac{d^j}{dN^j} \Phi_N(t), \tag{5}$$

when  $j \leq N$ . Let  $h_{j,N}(t)$  be the probability that the jth absorbed particle of the initial set of N disappears during the time interval (t,t+dt]. This quantity is related to  $\Phi_{i,N}(t)$  by

$$h_{j+1,N}(t) = h_{j,N} - \frac{d}{dt}\Phi_{j,N}(t) = -\frac{d}{dt}\sum_{m=0}^{j}\Phi_{m,N}(t),$$
 (6)

with  $h_{0,N}=0$ . Then, the *m*th moment of the time at which the *j*th particle is trapped is given by

$$\langle t_{j,N}^m \rangle = \int_0^\infty t^m h_{j,N}(t) dt, \tag{7}$$

or, using Eq. (6) and integrating by parts, by

$$\langle t_{j+1,N}^m \rangle = \langle t_{j,N}^m \rangle + m \int_0^\infty t^{m-1} \Phi_{j,N}(t) dt, \tag{8}$$

with

$$\langle t_{1,N}^m \rangle = m \int_0^\infty t^{m-1} \Phi_N(t) dt.$$
 (9) with

Using Eq. (3), Eq. (8) becomes

$$\langle t_{j+1,N}^m \rangle = \langle t_{j,N}^m \rangle + (-1)^j \binom{N}{j} \Delta^j \langle t_{1,N}^m \rangle. \tag{10}$$

Thus, the order statistics of the trapping problem is described from  $\langle t_{1,N}^m \rangle$  only. However, when N and j are large, Eq. (10) is hardly useful numerically because the quantities  $\langle t_{1,N-r}^m \rangle$ , that are added and subtracted (and almost cancelled) to obtain the jth difference derivative  $\Delta^j \langle t_{1,N}^m \rangle$  have to be calculated, then, with extraordinary accuracy (which is not easy; see Secs. IV and V) in order to get a reasonable estimate for the small quantity  $(-1)^j (\langle t_{j+1,N}^m \rangle - \langle t_{j,N}^m \rangle)$  from the multiplication of the tiny quantity  $\Delta^j \langle t_{1,N}^m \rangle$  by the huge binomial coefficient. In Sec. IV we will show how one can surmount, at least partially, this difficulty.

# III. MOMENTS OF THE NUMBER OF DISTINCT SITES VISITED BY N RANDOM WALKERS

The main purpose of this section is to show that for large N one can approximate  $\langle S_N^2(t) \rangle$  by  $\langle S_N(t) \rangle^2$ . In other words, we will show that the ratio  $\text{Var}(S_N)/\langle S_N \rangle^2$  is small for large N and that it decreases when N increases. In fact, we will show that the simulation results are compatible with the conjecture made in Ref. [19] that  $[\text{Var}(S_N)]^{1/2}/\langle S_N \rangle \sim 1/\ln N$ . These results make it very plausible that the Rosenstock approximation of order zero is a reliable method for estimating the survival probability  $\Phi_N(t)$  for not too long times and small concentrations. This will be analyzed in Sec. IV.

The problem of evaluating  $\langle S_N^m(t) \rangle$  for N=1 has been intensively studied since it was posed by Dvoretzky and Erdös [1,2,22]. In 1992, Larralde *et al.* [9,10] addressed the problem for  $N \ge 1$  and m = 1 on Euclidean media. They disclosed the existence of three time regimes: a very short-time regime  $[t \le t_{\times} \sim \ln(N)/\ln(d)]$ , or regime I, in which there are so many particles at every site that all the nearest neighbors of the already visited sites are reached at the next step, so that the number of distinct sites visited grows as the volume of an hypersphere of radius t,  $\langle S_N(t) \rangle \sim t^d$ ; a very long-time regime  $(t'_{\times} \leqslant t)$ , or regime III, that is the final stage in which the walkers move far away from each other so that their trails (almost) never overlap and  $\langle S_N(t) \rangle \sim N \langle S_1(t) \rangle$ ; and an intermediate regime  $(t_{\times} \ll t \ll t'_{\times})$ , or regime II, in which there exists a non-negligible probability of the trails of the particles overlapping. Of course, regime III does not exist for d=1  $(t'_{\times}=\infty)$ . For d=2,  $t'_{\times}=\exp(N)$ , and for  $d \ge 3$ ,  $t'_{\times}=N^{2/(d-2)}$ . In the simulations carried out in this paper and for the values of N we are interested in  $(N \ge 1)$ , the particles spend most of the time inside regime II, and regime III is never reached.

For regime II it has been found that [12,13]

$$\langle S_N(t)\rangle \approx \hat{S}_N(t)(1-\Delta),$$
 (11)

$$\hat{S}_N(t) = v_0 (4Dt \ln N)^{d/2}, \tag{12}$$

TABLE I. Parameters that appear in the asymptotic expression of  $S_N(t)$  [Eq. (11)] for the one-, two-, and three-dimensional simple hypercubic lattices. The parameter  $\tilde{p}$  is  $[2(6D\pi)^3/3]^{1/2}p(\mathbf{0},1)$  [23], where  $p(\mathbf{0},1) = \sqrt{6}/(32\pi^3)\Gamma(1/24)\Gamma(5/24)\Gamma(7/24)\Gamma(11/24) \approx 1.516386$  [1].

Case	A	μ	$h_1$
One-dimensional	$\sqrt{2/\pi}$	1/2	-1
Two-dimensional	1/ln <i>t</i>	1	-1
Three-dimensional	$1/(\widetilde{p}\sqrt{t})$	1	-1/3

$$\Delta = \Delta(N,t) = \frac{1}{2} \sum_{n=1}^{\infty} \ln^{-n} N \sum_{m=0}^{n} s_m^{(n)} \ln^m \ln N, \quad (13)$$

and where, up to second order (n=2),

$$s_0^{(1)} = -d\omega, \tag{14}$$

$$s_1^{(1)} = d\mu,$$
 (15)

$$s_0^{(2)} = d\left(1 - \frac{d}{2}\right)\left(\frac{\pi^2}{12} + \frac{\omega^2}{2}\right) - d\left(\frac{dh_1}{2} - \mu\omega\right),$$
 (16)

$$s_1^{(2)} = -d\left(1 - \frac{d}{2}\right)\mu\omega - d\mu^2,$$
 (17)

$$s_2^{(2)} = \frac{d}{2} \left( 1 - \frac{d}{2} \right) \mu^2. \tag{18}$$

Here  $\omega = \gamma + \ln A + \mu \ln(d/2)$ , where  $\gamma \approx 0.577215$  is the Euler constant,  $v_0$  is the volume of the hyphersphere with unit radius, and A,  $\mu$ , and  $h_1$  are given in Table I for d = 1, 2, and 3. The diffusion constant is defined by means of the Einstein relation

$$\langle r^2 \rangle \approx 2dDt,$$
 (19)

for large t, with  $\langle r^2 \rangle$  being the mean-square displacement of a single random walker. All the numerical results that appear in this paper are calculated using D = 1/(2d).

However, the calculation of higher-order moments of  $S_N(t)$  poses a problem of completely different order of magnitude that still remains unsolved. In Ref. [19], it was conjectured that the functional form of  $\langle S_N^m \rangle$  for Euclidean lattices has the same asymptotic structure for all m, namely, the asymptotic structure of Eq. (11). Moreover, it was conjectured that

$$\frac{\operatorname{Var}(S_{\mathrm{N}})}{\langle S_{\mathrm{N}} \rangle^{2}} \sim \frac{1}{\ln^{2} N} \left[ 1 + O\left(\frac{\ln^{3} \ln N}{\ln N}\right) \right],\tag{20}$$

for large N, where  $\operatorname{Var}(S_N) = \langle S_N^2 \rangle - \langle S_N \rangle^2$  is the variance of  $S_N(t)$ . Note that Eq. (20) implies  $\langle S_N^2 \rangle = \langle S_N \rangle^2$  up to the first-order asymptotic corrective term, as well as  $\operatorname{Var}(S_N) \sim t^d (\ln N)^{d-2}$  for large N.

Simulation data for  $\langle S_N^2(t) \rangle$  for the two-dimensional lattice are compared in Fig. 1 with results obtained from the

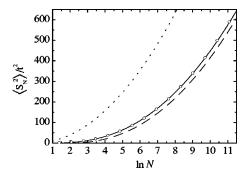


FIG. 1.  $\langle S_N^2 \rangle / t^2$  versus  $\ln N$  for the two-dimensional lattice when t=400. The circles are simulation results averaged over  $10^5$  configurations for  $N=2^2,\ldots,2^{12}$  and over  $10^4$  configurations for  $N=2^{13},\ldots,2^{16}$ . The lines represent  $\langle S_N(t) \rangle^2$  when the main term (dotted line), first-order approximation (dashed line), and second-order approximation (solid line) for  $\langle S_N(t) \rangle$  are used.

approximation  $\langle S_N^2(t) \rangle \simeq \langle S_N(t) \rangle^2$  in which the zeroth-, first-, and second-order asymptotic approximation for  $\langle S_N(t) \rangle$  given by Eq. (11) is used. The large difference between the performance of the three asymptotic approximations is quite noticeable as well as the excellent result obtained with the second-order approximation. Similar results (not shown) are found for d=1 and d=3. Figure 2 shows simulation data for the ratio  $\text{Var}(S_N)/\langle S_N \rangle^2$  for the two-dimensional lattice. We see that for large N this ratio decays roughly as predicted by Eq. (20).

# IV. ORDER STATISTICS OF THE TRAPPING PROCESS BY MEANS OF THE ROSENSTOCK APPROXIMATION

The extended Rosenstock approximation (or truncated cumulant expansion) first proposed by Zumofen and Blumen [7] is a well-known procedure [1–3] for solving the Rosenstock trapping problem for a single particle (N=1). Its generalization for estimating the (survival) probability  $\Phi_N(t)$  that no particle of the initial set of N diffusing particles has been trapped by time t is straightforward (details can be found in Ref. [19]) and we will only quote here those results that are useful for our objectives.

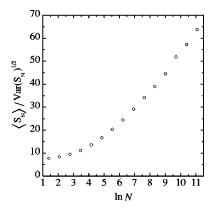


FIG. 2. Simulation results for the ratio  $\langle S_N \rangle / [Var(S_N)]^{1/2}$  for the two-dimensional lattice with  $N = 2^2, 2^3, \dots, 2^{16}$  and t = 400. The configurations employed were the same as in Fig. 1.

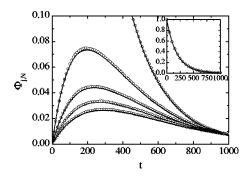


FIG. 3. The *j*th survival probability  $\Phi_{j,N}(t)$  versus time for (from top to bottom) j=0,1,2,3,4, with N=1000 and  $c=4\times 10^{-4}$  for the two-dimensional lattice. The lines represent  $\Phi_{j,N}^{(02)}(t)$ , i.e., the zeroth-order Rosenstock approximation with  $\langle S_N(t) \rangle$  given by the second-order asymptotic approximation. The circles are simulation results averaged over  $10^6$  configurations. Inset:  $\Phi_{0,N}(t)$ .

The zeroth-order Rosenstock approximation for estimating  $\Phi_N(t)$  is given by

$$\Phi_N^{(0)}(t) = e^{-\lambda \langle S_N(t) \rangle}, \tag{21}$$

where  $\lambda \equiv -\ln(1-c)$  and c is the concentration of traps. We will write  $\Phi_N^{(0n)}(t)$  to indicate that the nth-order approximation for  $\langle S_N(t) \rangle$  [see Eq. (11)] is used. The first-order Rosenstock approximation is

$$\Phi_N^{(1)}(t) = \exp\left[\langle S_N(t)\rangle \ln p \left(1 + \frac{\lambda}{2} \frac{\operatorname{Var}(S_N)}{\langle S_N(t)\rangle}\right)\right]. \tag{22}$$

Then, the error made by using the zeroth-order Rosenstock approximation can be estimated

$$\Phi_N(t) = \Phi_N^{(0)}(t) \{ 1 + O[\lambda^2 \text{Var}(S_N)] \}.$$
 (23)

Thus, the condition  $\lambda^2 \mathrm{Var}(S_N) \ll 1$  guarantees the good performance of the zeroth-order Rosenstock approximation. We have found in Sec. III that  $\mathrm{Var}(S_N) \sim t^d (\ln N)^{d-2}$  so that the zeroth-order Rosenstock approximation works well when  $\lambda^2 t^d (\ln N)^{d-2} \ll 1$ . This means that the approximation improves slightly for d=1 and worsens slightly for d=3 when N increases. For long times, the Rosentock approximation eventually breaks down, the Donsker-Varadhan regime settles in, and the survival probability decays in a distinct way known in the literature as Donsker-Varadhan behavior [5].

Figure 3 shows the survival probability  $\Phi_{j,N}$  for the two-dimensional lattice obtained from computer simulations and from Eq. (3) when the zeroth-order Rosenstock approximation  $\Phi_N^{(02)}(t)$  given by Eq. (21) is used. The agreement is excellent.

Now, we evaluate  $\langle t_{1,N}^m \rangle$  by means of Eq. (9) approximating the survival probability  $\Phi_N(t)$  by the zeroth-order Rosenstock approximation  $\Phi_N^{(0)}(t)$  for *all* times

$$\langle t_{1,N}^m \rangle \simeq m \int_0^\infty t^{m-1} \exp[-\lambda \langle S_N(t) \rangle] dt.$$
 (24)

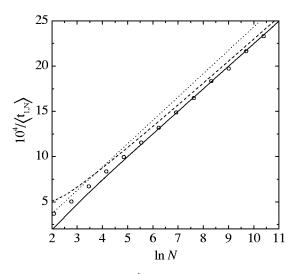


FIG. 4. The function  $10^4/\langle t_{1,N}\rangle$  versus  $\ln N$  for the one-dimensional lattice with concentration of traps  $c=8\times 10^{-3}$  and  $N=2^3,2^4,\ldots,2^{16}$ . We plot simulation results averaged over  $10^5$  configurations (circles) and the asymptotic approximations of order 0 (dotted line), order 1 (dashed line), and order 2 (solid line). The two last approximations are calculated by means of Eq. (36).

Notice that with this approximation we are assuming that, in the integration of Eq. (9) that leads to  $\langle t_{1N}^m \rangle$ , the relevant contribution comes from the time interval in which the Rosenstock approximation works. Next, the expression for  $\langle S_N(t) \rangle$  corresponding to the *intermediate* time regime is used in Eq. (24) for all times. This approximation is reasonable if the integrals of  $mt^{m-1}\Phi_N(t)$  on the intervals  $[0,t_{\times}]$ and  $[t'_{\times}, \infty]$  are negligible versus  $\langle t_{1,N}^m \rangle$ . As  $t_{\times} \sim \ln N$ , the approximation concerning the first interval is good as long as  $(\ln N)^m \le \langle t_{1,N}^m \rangle$ , i.e., [see Eq. (25) below], as long as  $\lambda$  $\ll (\ln N)^{-d}$ . For  $t \ge t_{\times}'$ , one has  $\langle S_N(t) \rangle \sim N \langle S_1(t) \rangle$ , so that the approximation regarding the interval  $[t'_{\times}, \infty]$  is good when  $\lambda \exp(N) \gg 1$  for d=2 and  $\lambda N^3 \gg 1$  for d=3. Inserting the main asymptotic term of  $\langle S_N(t) \rangle$ , namely,  $\langle S_N(t) \rangle$  $\approx v_0 (4Dt \ln N)^{d/2}$ , into Eq. (24) one gets, after a simple integration, a zeroth-order approximation for the mth moment of  $t_{1,N}$ ,

$$\langle t_{1,N}^m \rangle \simeq \frac{\Gamma(1 + 2m/d)}{(\lambda v_0)^{2m/d}} \frac{1}{(4D \ln N)^m}.$$
 (25)

The corrective terms of  $\langle S_N(t) \rangle$  are not used in Eq. (24) because their time dependence for the two- and three-dimensional cases impedes analytical integration.

In Figs. 4–6,  $\langle t_{1,N} \rangle$  calculated from Eq. (25) is compared with numerical simulation results. For the two- and three-dimensional lattices we also show the results obtained by means of the numerical integration of Eq. (24) when the first-and second-order asymptotic approximations for  $\langle S_N(t) \rangle$  [cf. Eq. (11) with n=1 and n=2, respectively] are used for  $t \ge t_\times \equiv (4/D) \ln N$ . For  $t \le t_\times$ , the expression  $\langle S_N(t) \rangle = v_0 t^d$  corresponding to the short-time regime is used. For d=1, the first- and second-order results are analytical (see Sec. V). Figures 4–6 illustrate the great importance of the asymptotic

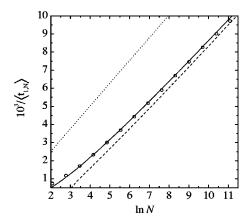


FIG. 5. The function  $10^3/\langle t_{1,N}\rangle$  versus  $\ln N$  for the two-dimensional lattice with  $c=4\times 10^{-4}$  and  $N=2^3,2^4,\ldots,2^{16}$ . The simulation results are averaged over  $10^5$  configurations (circles). The dotted line represents the asymptotic approximation of order 0. We also plot results obtained by means of the numerical integration of Eq. (24) when the first-order (dashed line) and second-order (solid line) asymptotic approximations for  $\langle S_N(t) \rangle$  are used.

corrective terms in the order-statistics quantities. The way in which the lines corresponding to the zeroth-order approximation run almost parallel to the simulation results indicates that the corrective term goes essentially as  $(\ln N)^{-1}$ . This is confirmed in Sec. V where it is found that the rigorous asymptotic expression for  $\langle t_{j,N}^m \rangle$  for the one-dimensional lattice exhibits corrective terms that decay logarithmically with N.

From Eq. (10) and approximating the difference operator  $\Delta^j$  by the derivative of order j, one finds

$$\langle t_{j+1,N}^{m} \rangle \simeq \langle t_{j,N}^{m} \rangle + m \frac{\Gamma(1+2m/d)}{(\lambda v_{0})^{2m/d} (4D)^{m}} \frac{(\ln N)^{-1-m}}{j},$$
(26)

for  $j \leq N$ , or, in terms of the psi (digamma) function [24]

$$\langle t_{j,N}^{m} \rangle \simeq \langle t_{1,N}^{m} \rangle + m \frac{\Gamma(1+2m/d)}{(\lambda v_{0})^{2m/d} (4D)^{m}} \frac{\psi(j) - \psi(1)}{(\ln N)^{1+m}}.$$
 (27)

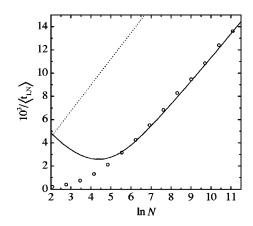


FIG. 6. The same as Fig. 5 but for the three-dimensional lattice with  $c = 4 \times 10^{-5}$ . The first-order approximation is out of scale. The simulation results are averaged over  $10^6$  configurations.

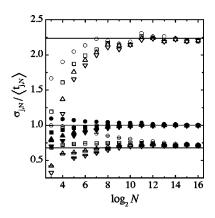


FIG. 7. The ratio  $\sigma_{j,N}/\langle t_{j,N}\rangle$ , j=1 (circles), j=2 (squares), j=3 (up triangles), j=4 (down triangles),  $N=2^3,2^4,\ldots,2^{16}$ , for d=1 with  $c=8\times 10^{-3}$  (hollow symbols at the top of the figure), d=2 with  $c=4\times 10^{-4}$  (filled symbols) and d=3 with  $c=4\times 10^{-5}$  (symbols with a bar at the bottom of the figure). The simulation results are averaged over  $10^5$  configurations for d=1 and d=2 and over  $10^4$  configurations for d=3. The lines represent the (main order) asymptotic theoretical results, namely,  $\sqrt{5}$  for d=1, 1 for d=2, and  $0.678\,968\cdots$  for d=3.

For  $1 \le j \le N$  one gets

$$\langle t_{j,N}^m \rangle \simeq \langle t_{1,N}^m \rangle + m \frac{\Gamma(1+2m/d)}{(\lambda v_0)^{2m/d} (4D)^m} \frac{\gamma + \ln j}{(\ln N)^{1+m}}, \quad (28)$$

because  $\psi(j) = \ln(j) + O(1/j)$  and  $\psi(1) = \gamma$  [24]. Therefore, the variance  $\sigma_{j,N}^2 = \langle t_{j,N}^2 \rangle - \langle t_{j,N} \rangle^2$  is given by

$$\sigma_{j,N}^2 \simeq \sigma_{1,N}^2 \simeq \frac{\Gamma(1+4/d) - [\Gamma(1+2/d)]^2}{(\lambda v_0)^{4/d} (4D \ln N)^2}.$$
 (29)

Thus, the main asymptotic term of the ratio  $\sigma_{j,N}/\langle t_{j,N}\rangle$  is independent of j and N for large N,

$$\frac{\sigma_{j,N}}{\langle t_{j,N} \rangle} \simeq \frac{\left[\Gamma(1+4/d) - \Gamma^2(1+2/d)\right]^{1/2}}{\Gamma(1+2/d)}.$$
 (30)

In Fig. 7 we plot this ratio for the one-, two-, and three-dimensional lattices for several values of j and N. The simulation results follow closely the theoretical predictions.

Finally, note that Eqs. (25)–(30) are valid for a given d when  $N \to \infty$ . For a given N and  $d \to \infty$ , time regimes I and II shrink, i.e.,  $t'_{\times} \to 0$ , so that  $\langle S_N(t) \rangle \sim Nt$  because  $\langle S_1(t) \rangle \sim t$  for  $d \ge 3$ . Introducing this relation into Eq. (24) one gets  $\langle t^m_{1:N} \rangle \sim (\lambda N)^{-m}$  for  $d \to \infty$ , as expected.

# V. ORDER STATISTICS OF THE ONE-DIMENSIONAL TRAPPING PROCESS. RIGOROUS RESULTS

In this section we obtain the order statistics of the trapping process for the one-dimensional lattice from the order statistics of the diffusion process in the presence of two fixed traps. Let  $\overline{t_{j,N}^m}(r)$  be the mth moment of the trapping time of the jth particle out of a total of N particles that were initially placed at distance r from a trap in a given direction and at a

distance greater than r from another trap in the other direction on a line. This quantity is given by [16]

$$\overline{t_{j,N}^m}(r) = \left(\frac{r^2}{4D\ln\kappa N}\right)^{2m} \tau_{j,N}(m),\tag{31}$$

where 
$$\tau_{i,N}(m) = \tau_{1,N}(m) + \delta_{i,N}(m)$$
,

$$\tau_{1,N}(m) = 1 + \frac{m}{\ln \kappa N} \left( \frac{1}{2} \ln \ln \kappa N - \gamma \right) + \frac{m}{2 \ln^2 \kappa N}$$

$$\times \left[ 1 + \gamma + (1+m) \left( \frac{\pi^2}{6} + \gamma^2 \right) - \left( \frac{1}{2} + (1+m) \gamma \right) \right]$$

$$\times \ln \ln \kappa N + \frac{1}{4} (1+m) \ln^2 \ln \kappa N$$

$$+O\left(\frac{\ln^3 \ln \kappa N}{\ln^3 \kappa N}\right),\tag{32}$$

$$\delta_{j,N}(m) = \frac{m}{\ln \kappa N} \sum_{n=1}^{j-1} \frac{\delta_n(m)}{n},\tag{33}$$

$$\delta_n(m) = 1 + \frac{m+1}{\ln \kappa N} \left[ (-1)^n \frac{S_n(2)}{(n-1)!} + \frac{1}{2} \ln \ln (\kappa N) \right]$$

$$-\frac{1}{2(m+1)} - \gamma \left] + O\left(\frac{\ln^2 \ln \kappa N}{\ln^2 \kappa N}\right), \tag{34}$$

and  $\kappa = 1/\sqrt{\pi}$ .

In order to get  $\langle t_{j,N}^m \rangle$ ,  $\overline{t_{j,N}^m}(r)$  is averaged over the different positions on which the *N* particles can be initially placed in an interval free of traps of size *L*,

$$\overline{t_{j,N}^{m}}(L) = \frac{2}{L} \int_{0}^{L/2} dr t_{j,N}^{m}(r)$$

$$= \frac{1}{2m+1} \left( \frac{1}{4D \ln \kappa N} \right)^{m} \left( \frac{L}{2} \right)^{2m} \tau_{j,N}(m).$$
(35)

Next, this quantity is averaged over the size distribution  $\eta(L) = \lambda^2 L \exp[-\lambda L]$  of the intervals that are free of traps (p. 217 of Ref. [2]) to get the final result

$$\langle t_{j,N}^{m}\rangle = \int_{0}^{\infty} dL \, \eta(L) \overline{t_{j,N}^{m}}(L) = \frac{\Gamma(1+2m)}{(2\lambda)^{2m}} \frac{\tau_{j,N}(m)}{(4D \ln \kappa N)^{m}}, \quad (36)$$

for large N and d=1. In Fig. 4, the theoretical results given by Eq. (36) are compared with simulation data. A behavior very close to that found for traps arranged over a (hyper) spherical surface [16] is found: the asymptotic corrective terms are not at all negligible even for very large values of N, and the second-order asymptotic expression is an excellent approximation even for not too large values of N (say, for  $N \gtrsim 100$ ).

Notice that the approximate result obtained in Eq. (25) agrees, for the one-dimensional case, with the main term of Eq. (36). This prompts us to investigate to what extent the approximate procedure of Sec. V is able to reproduce the results of the rigorous asymptotic approach. The answer is that the two approaches lead to the same main term (as we

have just discovered) and to almost the same first corrective term. For example, using Eq. (11) up to first-order corrective terms, one gets for j=1 and m=1 that

$$\langle t_{1,N} \rangle = \frac{1}{2\lambda^2 4D \ln \kappa N} \left( 1 + \frac{\ln \pi - 2\gamma + \alpha + \ln \ln N}{4 \ln N} + \dots \right), \tag{37}$$

with  $\alpha = 0$ . This expression differs from the rigorous asymptotic formula (36) in the value of  $\alpha$  only: the exact value is  $\alpha = \ln 2$ . Finally, from Eq. (36) one can also obtain for  $\langle t_{j+1,N}^m \rangle - \langle t_{j,N}^m \rangle$  the formula (26), which was obtained in Sec. IV for d-dimensional media.

Finally, from Eq. (36) one gets the variance

$$\sigma_{j,N}^2 = \frac{\Gamma(5)\tau_{j,N}(2) - \Gamma^2(3)\tau_{j,N}^2(1)}{(2\lambda)^4 (4D \ln \kappa N)^2},$$
 (38)

whose main-order asymptotic term reproduces Eq. (29) when d=1.

#### VI. CONCLUSIONS

The problem addressed in this paper is easy to formulate: When a set of  $N \gg 1$  diffusing particles are placed on a site of a d-dimensional Euclidean lattice occupied by a random distribution of static traps, how long is the survival time  $t_{j,N}$  of the jth trapped particle? The answer to this order-statistics problem is given in Eq. (8) in terms of the probability  $\Phi_{j,N}(t)$  that j particles have been trapped and N-j survive by time t, which, in turn, can be expressed [cf. Eq. (3)] exactly in terms of the survival probability  $\Phi_M = \Phi_{0,M}$  that no particle of an initial set of M ( $M = N, N-1, \ldots, N-j$ ) has been trapped by time t.

For the evaluation of  $\Phi_N(t)$  we resorted to the Rosenstock approximation generalized to the case of  $N \ge 1$  particles. This approximation is good for small concentrations of traps and small times. Its range of applicability depends logarithmically on N, improving slightly for d=1 and worsening slightly for d=3 when N increases. Analytical expressions for the main asymptotic term of mth moment of  $t_{i,N}$ and its variance  $\sigma_{i,N}^2$  for d-dimensional Euclidean media have been found by assuming that the density of traps is such that the contribution of  $\Phi_N(t)$  to  $\langle t_{i,N}^m \rangle$  is negligible in the time regimes I and III. It was found that  $\langle t_{1N}^m \rangle$  $\sim (\lambda^{2/d} \ln N)^{-m}$  and that the ratio  $\sigma_{j,N}/\langle t_{j,N} \rangle$  is not at all negligible. In fact  $\sigma_{i,N}$  is larger than the difference  $\langle t_{i+1,N} \rangle$  $-\langle t_{i,N}\rangle$ , which implies that it is not possible to infer with certainty the order j of a trapped particle from the time at which it is trapped. However, this ratio discriminates clearly the dimension of the Euclidean media in which the particles diffuse. This leads us to consider the possibility that this ratio could serve to estimate the dimension of fractal (disordered) media in a dynamical way.

For the one-dimensional lattice, the previous solution of the order-statistic diffusive problem for a given configuration (no randomly distributed) of traps has been used to obtain second-order asymptotic rigorous expressions for  $\langle t_{j,N}^m \rangle$  and the variance  $\sigma_{j,N}^2$ . For  $d \ge 2$  we resorted to numerical inte-

gration to obtain higher-order estimates. This numerical procedure leads to excellent results, but it is limited to not too large values of N and j because otherwise the binomial term that appears in Eq. (3) [or in Eq. (10)] becomes intractably large. In all the cases studied, there became clear the great importance of the corrective terms in the asymptotic expressions of the moments of the order-statistics quantities since the mth corrective term decay mildly as roughly the mth power of the logarithm of N. This characteristic behavior is shared with other cases with different configurations of traps (e.g., fixed traps) and substrates (e.g., fractal media).

We shall finish by mentioning some open problems. First, it would be very interesting to estimate the time  $t_{N,N}$  by which all the particles are eventually absorbed. Notice that the formulas of Secs. IV and V are not suitable for this purpose as they are valid for estimating  $t_{j,N}$  when  $j \leq N$  only. Also, it would be interesting to describe the order statistic of

the trapping problem for a trap concentration small enough for the trapping process to take place mainly inside the Donsker-Varandhan time regime. The recent analysis of Barkema *et al.* [6] on the crossover from the Rosenstock behavior to the Donsker-Varandhan behavior should facilitate this task. Finally, it would be desirable to extend the results of the present paper to fractal substrates. To this end, the recent results obtained in Ref. [14] on the territory explored by a set of random walkers in fractal media should be very useful.

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- B. H. Hughes, Random Walks and Random Environments, Random Walks Vol. 1 (Oxford, Clarendon Press, 1995); Random Walks and Random Environments, Random Environments Vol. 2 (Oxford, Clarendon Press, 1995).
- [2] G. H. Weiss, Aspects and Applications of the Random Walk (North-Holland, Amsterdam, 1994).
- [3] F. den Hollander and G. H. Weiss, *Contemporary Problems in Statistical Physics*, edited by G. H. Weiss (SIAM, Philadelphia, 1994), pp. 147–203; S. Havlin and D. Ben-Avraham, Adv. Phys. **36**, 695 (1987).
- [4] J. R. Beeler, Phys. Rev. 134, 1396 (1964); H. B. Rosenstock, *ibid.* 187, 1166 (1969); E. W. Montroll, J. Phys. Soc. Jpn. 26, 6 (1969); E. W. Montroll, J. Math. Phys. 10, 753 (1969); H. Miyagawa, Y. Hiwatari, B. Bernu, and J. P. Hansen, J. Chem. Phys. 88, 3879 (1988); T. Odagaki, J. Matsui, and Y. Hiwatari, Phys. Rev. E 49, 3150 (1994); J. K. Anlauf, Phys. Rev. Lett. 52, 1845 (1984); G. Oshanin, S. Nechaev, A. M. Cazabat, and M. Moreau, Phys. Rev. E 58, 6134 (1998); A. Blumen, J. Klafter, and G. Zumofen, in *Optical Spectroscopy of Glasses*, edited by I. Zschokke (Reidel, Dordrecht, 1986).
- [5] D. V. Donsker and S. R. S. Varadhan, Commun. Pure Appl. Math. 28, 525 (1975); A. A. Ovchinnikov, and Y. B. Zeldovich, Chem. Phys. 28, 215 (1978); P. Grassberger and I. Procaccia, J. Chem. Phys. 77, 6281 (1982); R. F. Kayser and J. B. Hubbard, Phys. Rev. Lett. 51, 79 (1983); L. K. Gallos, P. Argyrakis, and K. W. Kehr, Phys. Rev. E 63, 021104 (2001).
- [6] G. T. Barkema, P. Biswas, and H. van Beijeren, Phys. Rev. Lett. 87, 170601 (2001).
- [7] G. Zumofen and A. Blumen, Chem. Phys. Lett. 83, 372 (1981).
- [8] A. Blumen, J. Klafter, and G. Zumofen, Phys. Rev. B 28, 6112 (1983)
- [9] H. Larralde, P. Trunfio, S. Havlin, H. E. Stanley, and G. H. Weiss, Nature (London) 355, 423 (1992).
- [10] H. Larralde, P. Trunfio, S. Havlin, H. E. Stanley, and G. H. Weiss, Phys. Rev. A 45, 7128 (1992).
- [11] G. H. Weiss, I. Dayan, S. Havlin, J. E. Kiefer, H. Larralde, H. E. Stanley, and P. Trunfio, Physica A 191, 479 (1992); A. M. Berezhkovskii, J. Stat. Phys. 76, 1089 (1994); P. L. Krapivsky

- and S. Redner, J. Phys. A **29**, 5347 (1996); P. L. Krapivsky and S. Redner, Am. J. Phys. **67**, 1277 (1999); G. M. Sastry and N. Agmon, J. Chem. Phys. **104**, 3022 (1996); G. Berkolaiko, S. Havlin, H. Larralde, and G. H. Weiss, Phys. Rev. E **53**, 5774 (1996).
- [12] S. B. Yuste and L. Acedo, Phys. Rev. E 60, R3459 (1999).
- [13] S. B. Yuste and L. Acedo, Phys. Rev. E 61, 2340 (2000).
- [14] L. Acedo and S. B. Yuste, Phys. Rev. E 63, 011105 (2001).
- [15] K. Lindenberg, V. Seshadri, K. E. Shuler, and G. H. Weiss, J. Stat. Phys. 23, 11 (1980); G. H. Weiss, K. E. Shuler, and K. Lindenberg, *ibid.* 31, 255 (1983).
- [16] S. B. Yuste and K. Lindenberg, J. Stat. Phys. 85, 501 (1996); S. B. Yuste, Phys. Rev. Lett. 79, 3565 (1997); S. B. Yuste, Phys. Rev. E 57, 6327 (1998).
- [17] J. Dräger and J. Klafter, Phys. Rev. E 60, 6503 (1999); J. Mol. Liq. 86, 293 (2000).
- [18] S. B. Yuste, L. Acedo, and K. Lindenberg, Phys. Rev. E 64, 052102 (2001).
- [19] S. B. Yuste and L. Acedo, Physica A 297, 321 (2001).
- [20] For reviews, see T. Bache, W. E. Moerner, M. Orrit, and U. P. Wild, Single-Molecule Optical Detection, Imaging and Spectroscopy (VCH, Weinheim, 1996); X. S. Xie and J. K. Trautman, Annu. Rev. Phys. Chem. 49, 441 (1998); See also the section "Single Molecules" in Science 283, 1667 (1999).
- [21] M. T. Valentine, P. D. Kaplan, D. Thota, J. C. Crocker, T. Gisler, R. K. Prud'homme, M. Beck, and D. A. Weitz (preprint available at http://www.deas.harvard.edu/projects/weitzlab/papers/FINAL\_MPT.pdf)
- [22] A. Dvoretzky and P. Erdös, in *Proceedings of the Second Berkeley Symposium on Mathematical Statistics and Probability*, edited by J. Neyman (University of California Press, Berkeley, 1951), pp. 353–367.
- [23] Notice that in the value of  $\tilde{p}$  given in Ref. [13] there were two mistakes: 2 should be changed to 6 and the symbol t should be deleted. This symbol t should also be deleted from the expression for  $\tilde{p}$  given in Ref. [12].
- [24] *Handbook of Mathematical Functions*, edited by M. Abramowitz and I. Stegun (Dover, New York, 1972).