RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 28, NUMBER 10 15 NOVEMBER 1983

Trapping and reaction rates on fractals: A random-walk study

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(Received 8 August 1983)

In this Rapid Communication we study random walks on Sierpinski gaskets, which are fractal structures of simple geometry. We determine the probability of the walker to be captured by traps randomly distributed on the gaskets. The general reaction process is modeled through a kinetic approach. The decay laws which we find are smooth extensions to dimensionalities between one and two.

I. INTRODUCTION

Many aspects of solid-state physics and chemistry are related to random walks on periodic structures.[1–3] In the last few years processes of energy transfer and of carrier recombination in *disordered* materials have attracted considerable attention.[4–6] One way to introduce the disorder aspect has been the continuous-time random-walk approach, as discussed in previous works.[5–10] Another way of dealing with disorder is by realizing its self-similar nature, which then introduces the fractal concept.[11] A simple class of fractal structures are the Sierpinski gaskets. The gaskets are fairly regular: Their basic unit is the d-dimensional simplex from which the gasket is created by repeated dilatations.[11] In this Rapid Communication we deal with two- and three-dimensional gaskets ($d=2$ and 3) on which we perform random walks. We concentrate here on the decay laws and show, by comparison with former results,[12] that trapping on these fractals interpolates nicely between the decay laws found for one- and two-dimensional *regular* lattices.

II. THEORY

In this section we focus on the decay functions due to trapping and on the corresponding decay rates. For the evaluation of the decay laws we follow the procedure of Ref. 12: We take the traps to be randomly distributed on the gasket, occupying its sites with probability p. The microscopic transfer rates from a site to its neighboring sites are assumed to be equal, and the walker gets trapped at the first trap encounter.

For a particular realization of the random walk on the trap-free gasket, let R_n denote the number of distinct sites visited in n steps. Note, as is usual in disordered systems, the difference from the regular lattice: Here the stochastic variable R_n depends both on the starting point on the gasket and on the sequence of directions of the steps; for a regular lattice the starting point is irrelevant. For the same realization of the walk let F_n denote the probability that trapping has not occurred up to the nth step in the ensemble of lattices doped with traps. Thus F_n is also a stochastic variable, so that

$$F_n=(1-p)^{R_n-1} , \tag{1}$$

assuming the origin of the walk not to be a trap, and, in standard fashion,[7] having $R_0=1$. The measurable survival probability is Φ_n, the average of F_n over all realizations of the random walk[10,12,13]:

$$\Phi_n=F_n=\langle(1-p)^{R_n-1}\rangle . \tag{2}$$

As mentioned, the average in Eq. (2) also includes the average over starting points, and may be viewed as a double average; we encountered a similar situation for the continuous-time random-walk model.[10] Introducing $\lambda=-\ln(1-p)$, Eq. (2) allows a straightforward cumulant expansion

$$\Phi_n=e^{\lambda}\langle e^{-\lambda R_n}\rangle\equiv e^{\lambda}\tilde{\Phi}_n , \tag{3}$$

with

$$\tilde{\Phi}_n=\exp\left[\sum_{j=1}^{\infty}K_{j,n}(-\lambda)^j/j!\right] , \tag{4}$$

where the $K_{j,n}$ are the cumulants of the distribution of R_n. As an example, the first two cumulants are

$$K_{1,n}=\langle R_n\rangle\equiv S_n \tag{5}$$

and

$$K_{2,n}=\langle R_n^2\rangle-\langle R_n\rangle^2\equiv\sigma_n^2 , \tag{6}$$

where S_n and σ_n^2 are the mean and the variance of R_n.

The knowledge of all cumulants allows the exact determination of the decay function Φ_n via Eqs. (3) and (4). In general, however, one has to restrict oneself to the first cumulants, since the distribution of R_n is not known in great detail:

$$\tilde{\Phi}_{N,n}=\exp\left[\sum_{j=1}^{N}K_{j,n}(-\lambda)^j/j!\right] . \tag{7}$$

The expression for $N=1$,

$$\tilde{\Phi}_{1,n}=\exp(-\lambda S_n) , \tag{8}$$

has been advanced in many areas[14–17]; in the random-walk field it corresponds to the first-passage-time (FPT) approximation[15]; in the fractal field it was recently used by de Gennes.[16] For $N=2$ one obtains from Eq. (7) the

form[12]

$$\tilde{\Phi}_{2,n} = \exp(-\lambda S_n + \lambda^2 \sigma_n^2/2) \ , \tag{9}$$

which is akin to an approximate form advanced by Weiss.[13] Let us point out that for three-dimensional regular systems Eq. (8) was found to be a good approximation over the main portion of the decay, and that Eq. (9), which includes the variance, turned out to be very good both for three- and two-dimensional regular lattices. On the other hand, in the one-dimensional regular case the cumulant expansion, Eq. (7), is very slowly convergent, so that at least $N=4$ is needed in order to describe well the decay over the first two orders of magnitude.[12]

From the expressions for Φ_n one obtains the decay rates $k_n = (\Phi_{n-1} - \Phi_n)/\Phi_n$, the discrete analog of $k(t) = -\dot{\Phi}(t)/\Phi(t)$. From Eqs. (3) to (9) it is obvious that k_n is not exactly proportional to p, but that the proportionality gets better for lower p and higher dimensionalities. When this proportionality holds, one may proceed as in Refs. 5 and 17 and use the trapping results to determine, say, exciton fusion or electron-hole recombination in terms of the reaction scheme:

$$A + B \overset{k(t)}{\longrightarrow} AB \ , \tag{10}$$

whose solution for the initial condition $B(0) = A(0) + C$ is

$$r[A(t)] - r[A(0)] = \int_0^t k(t')dt' \ , \tag{11}$$

with $r(x) = C^{-1}\ln(1 + C/x)$ (see Ref. 5 for details). In how far the k_n vs p proportionality holds will become evident from the numerical results of the next Sec. III.

For an embedding Euclidean space of dimension d the Hausdorff fractal dimension of the Sierpinski gasket is[11] $\bar{d} = \ln(d+1)/\ln 2$ and its spectral dimension is $\tilde{d} = 2\ln(d+1)/\ln(d+3)$, so that $d \geq \bar{d} \geq \tilde{d}$.[18–20] Here, in the trapping problem, the fundamental quantity *(vide infra* and Refs. 18 to 20) is the spectral dimension $\tilde{d}$, which for any Sierpinski gasket is always less than 2. Sierpinski gaskets lie thus in the dimension range from one to two; this allows us to analyze the performance of the cumulant expansion in the region below $\tilde{d} = 2$.

III. SIMULATION RESULTS

We have simulated a series of different random walks on the Sierpinski gaskets of Euclidean dimensions $d=2$ and $d=3$, which correspond to the spectral dimensions $\tilde{d} = 1.365$ and $\tilde{d} = 1.547$, respectively.[11] The gaskets were generated iteratively, and were chosen to contain some 10 000 sites (being of eighth order of iteration for $d=2$ and of sixth order for $d=3$). Some 1000 to 5000 realizations of the walks were performed and both starting points and displacements were stochastically chosen using the random number generator RN1 of the Eidgenössische Technische Hochschule Computer Center. This routine has been extensively checked by us in the framework of random walks; it works very well even for the one-dimensional case, where the distributions in R_n are broadest, as we could show by comparison to the exact decay law.[12]

For regular lattices the first moment S_n is readily expressed as a (generally, nonanalytical) series in functions of n. One has (see Refs. 3, 7, and 21 for the correction terms)

$$S_n = an + \cdots \quad (d=3) \ , \tag{12a}$$

$$S_n = an/\ln(n) + \cdots \quad (d=2) \ , \tag{12b}$$

$$S_n = an^{1/2} + \cdots \quad (d=1) \ . \tag{12c}$$

For Sierpinski gaskets the asymptotic expansion depends on $\tilde{d}$ (Ref. 19):

$$S_n = an^{\tilde{d}/2} \ , \tag{13}$$

and thus Eq. (13) lies between Eqs. (12b) and (12c). We note that in two dimensions the asymptotic behavior of Eq. (12b) is reached very slowly; this contrasts with the situation in $d=1$ or in $d=3$, where the asymptotic regions of Eqs. (12a) and (12c) are quickly reached.[21]

In Fig. 1 we present our results for S_n in the range $0 \leq n \leq 1000$ for the two gaskets considered. For ease of reference, we have also included the S_n for the linear chain ($d=1$) and for the square lattice ($d=2$). As is evident, the gasket results are nicely bounded by the regular cases. The numerical results for S_n were fitted to Eq. (13), $S_n = an^{\alpha}$. On the scale of the figure the fit is excellent, and is indistinguishable from the numerical result, even for small n. Thus, for the gaskets, as in the one-dimensional regular case, the first term of the asymptotic expansion of S_n gives an adequate description for practically *all* n. The fit gives for the gaskets $a = 1.282$ and $\alpha = 0.686$ for $d=2$ and $a = 1.318$ and $\alpha = 0.753$ for $d=3$; the result for α for $d=2$ agrees with the result of Ref. 20. The difference between 2α and $\tilde{d}$ is very small, being 0.5% for $d=2$ and 3% for $d=3$.

For the second cumulant σ_n^2 the results are presented in

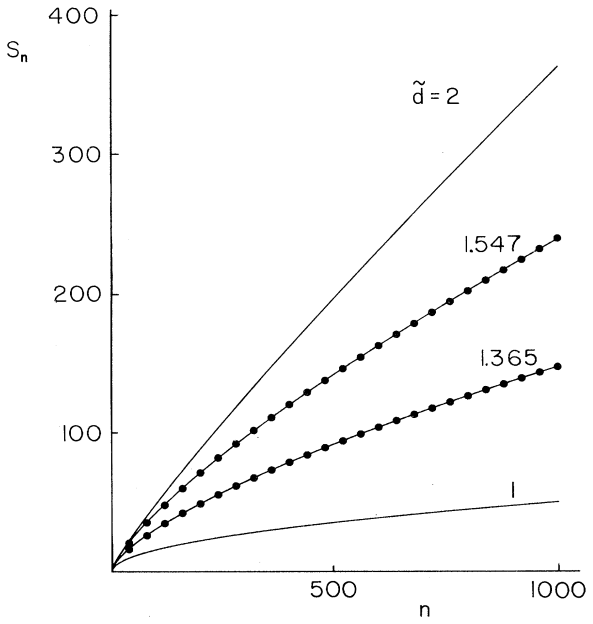

FIG. 1. Mean number S_n of distinct sites visited in n steps. Given are the results for two Sierpinski gaskets ($\tilde{d} = 1.365$ and $\tilde{d} = 1.547$) as well as for the linear chain ($\tilde{d} = 1$) and the square lattice ($\tilde{d} = 2$). The points are the simulation results, whereas the dashed lines are the fit to $S_n = an^{\alpha}$.

Fig. 2. We have fitted the numerical curves to the law

$$\sigma_n^2 = bn^\beta \ , \tag{14}$$

since there is strong evidence that this should be the leading term of the corresponding expansion, with β being $\beta = \tilde{d} = 2\alpha$.[20,22] This result is exact in one dimension; for a linear chain one has asymptotically[3]

$$\sigma_n^2 \sim 4(\ln 2 - 2/\pi)n \ . \tag{15a}$$

For two-dimensional regular lattices one has, for large n,[21,23]

$$\sigma_n^2 \sim bn^2/\ln^4 n \ , \tag{15b}$$

so that σ_n^2/S_n^2 differs from a constant only by a factor of the order $\ln^{-2} n$, a very slowly decaying function. Equations (13) and (14) imply that for fractals σ_n^2/S_n^2 should approach a constant b/a^2. As may be seen from Fig. 2 the fit, Eq. (14), is very satisfactory: We obtain $b = 0.106$ and $\beta = 1.356$ for the gasket in $d = 2$ and $b = 0.0445$ and $\beta = 1.579$ for $d = 3$. Comparison of β to $\tilde{d}$ shows agreement with 1% for $d = 2$ and within 2% for $d = 3$, lending strong support to the conjecture of Alexander.[22] The quotient b/a^2 equals 0.0645 for $d = 2$ and 0.0256 for $d = 3$; these values compare well with the exact result for the regular linear chain,[3] $\tilde{d} = 1$, where $\sigma_n^2/S_n^2 = 0.088$. Also they decrease monotonically with increasing $\tilde{d}$, which implies that the R_n distribution gets narrower for larger $\tilde{d}$. For three-dimensional regular lattices, on the other hand, $\sigma_n^2/S_n^2 \sim \ln(n)/n \to 0$ for n large.

The decay laws Φ_n are given in Figs. 3 and 4 for several values of the trap concentration ($p = 1\%$, 3%, 10%, and 30%) for the two gaskets considered. The Φ_n are plotted logarithmically versus n; the full curves correspond to the exact decay, whereas the broken lines are the approximating forms $\Phi_{1,n}$ and $\Phi_{2,n}$, Eqs. (8) and (9). For the plot the for-

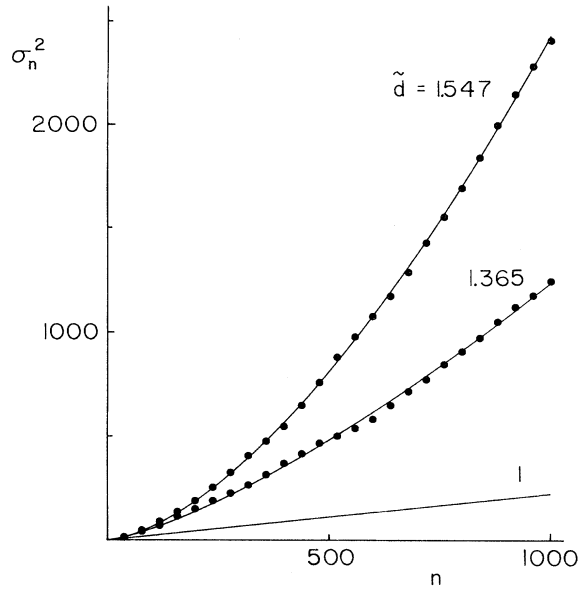

FIG. 2. Variance σ_n^2 of the distribution of distinct sites visited in n steps. All symbols are as in Fig. 1 and the results are fitted to $\sigma_n^2 = bn^\beta$. In the region plotted the results for the square lattice ($\tilde{d} = 2$) lie very near to those for the gasket with $\tilde{d} = 1.547$.

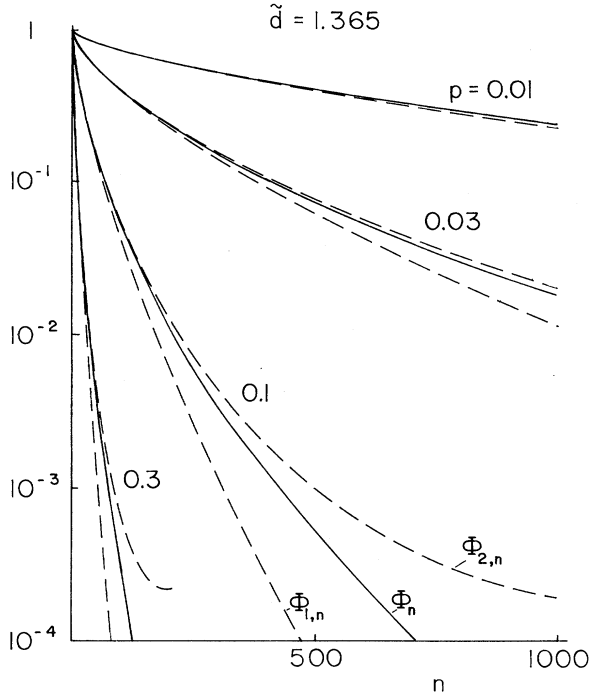

FIG. 3. Decay law Φ_n due to trapping for random walks on the $2d$ Sierpinski gasket ($\tilde{d} = 1.365$), where n is the number of steps. The full line denotes the simulated decay Φ_n, Eq. (3), whereas the dashed lines are the $\Phi_{1,n}$ and $\Phi_{2,n}$ approximations, Eqs. (8) and (9). The trap concentrations are $p = 0.01$, 0.03, 0.1, and 0.3, respectively.

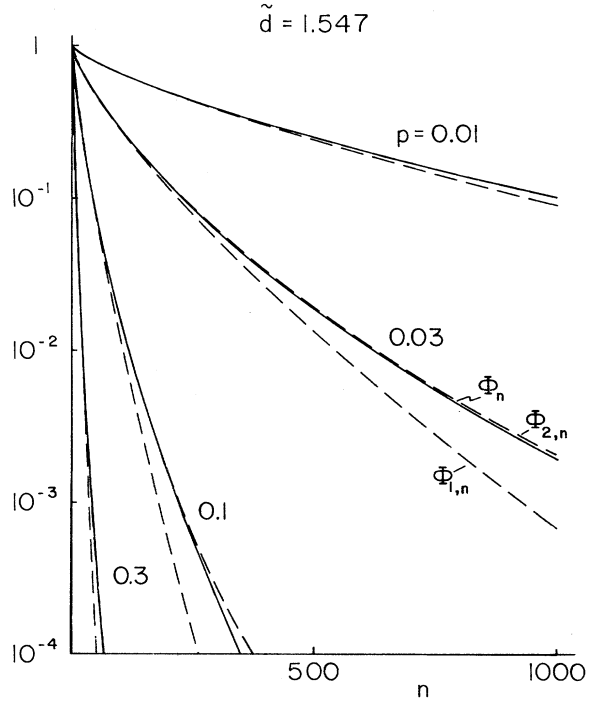

FIG. 4. Decay law Φ_n due to trapping for random walks on the $3d$ Sierpinski gasket ($\tilde{d} = 1.547$). The symbols are as in Fig. 3.

mulas Eqs. (13) and (14) for S_n and σ_n^2 were used, obtaining thus approximate expressions with a minimal number of parameters. For all trap concentrations the decays are clearly nonexponential. For both gaskets we find a behavior much reminiscent of the decay laws for the square lattice: The mean number of sites visited, S_n, does not describe the decay well, whereas inclusion of the variance σ_n^2 considerably improves the agreement.[12] We note that the agreement is better for the higher dimensional gasket, a fact not surprising when remembering the one-dimensional case, where four cumulants are necessary for a good description of the decay over two orders of magnitude.[12] Thus the decay laws for the gaskets interpolate nicely between the linear chain and the square lattice.

As in all cases considered, for fixed n the agreement between exact and approximate decays gets better for lower values of the trap concentration. Since in this region $\lambda = -\ln(1-p) \approx p$, one can directly read off from Figs. 3 and 4 the region in which k_n is proportional to p. Comparison of the exact form to $\Phi_{1,n}$ shows that this holds well for an order of magnitude in the decay, and that the agreement improves for larger $\tilde{d}$; in these regions the chemical analogs of Sec. II are valid.

IV. CONCLUSIONS

In this Rapid Communication we have presented the decay laws due to traps randomly distributed on Sierpinski gaskets, and analyzed it in terms of the statistics of the number of sites visited by a random walker. The dynamical quantities, such as the moments of the distribution of sites visited and also the decay, show a behavior which is situated between that which obtains for one- and two-dimensional regular lattices. The unifying aspect is the compact exploration of the geometrical structures by the walker, a concept stressed by de Gennes.[16] As in the one-dimensional case, this leads to relations between the moments of the distributions, relations which appear from our numerical simulations. A fundamental quantity which enters both the mean and the variance is the spectral dimension $\tilde{d}$, whose numerical evaluation agrees very well with the exact result. In the range of decay which may be of experimental importance the decay is well described by the first two cumulants. As found numerically, the domain of validity of their asymptotic forms is rapidly reached.

ACKNOWLEDGMENTS

The authors are thankful for stimulating discussions with Professor S. Alexander, Professor K. Dressler, and R. Hilfer. One of us (A.B.) gratefully acknowledges the hospitality of Exxon Corporation. The work was supported by a grant of computer time from the Computer Center of the Eidgenössische Technische Hochschule–Zürich, and by grants from the Fonds der Chemischen Industrie and the Deutsche Forschungsgemeinschaft.

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[1]M. N. Barber and B. W. Ninham, *Random and Restricted Walks; Theory and Applications* (Gordon and Breach, New York, 1970).

[2]E. W. Montroll and B. J. West, in *Fluctuation Phenomena,* edited by E. W. Montroll and J. L. Lebowitz (North-Holland, Amsterdam, 1979).

[3]G. H. Weiss and R. J. Rubin, Adv. Chem. Phys. 52, 363 (1983).

[4]For newer developments, see J. Phys. (Paris) Colloq. 42, C 4 (1981).

[5]A. Blumen, J. Klafter, and G. Zumofen, Phys. Rev. B 27, 3429 (1983).

[6]J. Klafter, A. Blumen, and G. Zumofen, J. Phys. Chem. 87, 191 (1983).

[7]E. W. Montroll and G. H. Weiss, J. Math. Phys. 6, 167 (1965).

[8]H. Scher and M. Lax, Phys. Rev. B 7, 4491, 4502 (1973).

[9]J. Klafter and R. Silbey, Phys. Rev. Lett. 44, 55 (1980).

[10]A. Blumen and G. Zumofen, J. Chem. Phys. 77, 5127 (1982).

[11]B. Mandelbrot, *The Fractal Geometry in Nature* (Freeman, San Francisco, 1982).

[12]G. Zumofen and A. Blumen, Chem. Phys. Lett. 88, 63 (1982).

[13]G. H. Weiss, Proc. Nat. Acad. Sci. U.S.A. 77, 4391 (1980).

[14]H. B. Rosenstock, Phys. Rev. 187, 1166 (1969); SIAM (Soc. Ind. Appl. Math.) J. Appl. Math. 27, 457 (1974).

[15]J. Klafter and R. Silbey, J. Chem. Phys. 74, 3510 (1981).

[16]P. G. de Gennes, C. R. Acad. Sci. Ser. II 296, 881 (1983).

[17]P. Evesque, J. Phys. (Paris) (in press).

[18]S. Alexander and R. Orbach, J. Phys. Lett. 43, L625 (1982).

[19]R. Rammal and G. Toulouse, J. Phys. Lett. 44, 13 (1983).

[20]R. Rammal, in *Common Trends in Particle and Condensed Matter Physics,* Proceedings of the Les Houches Summer School Session XXXVIII, edited by R. Stora and G. Grynberg (North-Holland, Amsterdam, in press).

[21]G. Zumofen and A. Blumen, J. Chem. Phys. 76, 3713 (1982).

[22]S. Alexander, in *Percolation Structures and Processes,* edited by G. Deutscher, R. Zahlen, and J. Adler [Ann. Isr. Phys. Soc. 5, 149 (1983)]; and private communication.

[23]N. C. Jain and W. E. Pruitt, in *Proceedings of the Sixth Berkeley Symposium on Mathematical Statistics and Probability* (Univ., California, Berkeley, 1973), Vol. III, p. 31.