Diffusive motion in a fractal medium in the presence of a trap

Shlomo Havlin
National Institues of Health, Bethesda, Maryland 20892
*and Department of Physics, Bar-Ilan University, Ramat-Gan, 52100, Israel**

Raoul Kopelman and Rodney Schoonover
Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48109

George H. Weiss
National Institutes of Health, Bethesda, Maryland 20892
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There have been many studies of transport in an unbounded fractal medium. Here we discuss a number of quantities related to the concentration of reactants diffusing in fractal media in the presence of a trapping point. This investigation is suggested by an extension of the Smoluchowski model to calculate reaction rates in such media [M. von Smoluchowski, Phys. Z. **16**, 321 (1915); **17**, 557 (1917); **17**, 585 (1917)]. Results, some analytic and some based on a scaling argument, are given for the flux into the trap, which is the analog of the reaction rate, in addition to the concentration profile in the neighborhood of the trap and the time dependence of the distance between the trap and the nearest untrapped particle. The results of our theory are found to be in good agreement with Monte Carlo and exact enumeration calculations for the concentration profile on a Sierpinski gasket and on an infinite percolation cluster at criticality. Some scaling and numerical results are reported for the situation in which the traps move in the presence of fixed particles.

I. INTRODUCTION

The Smoluchowski model for diffusion-controlled reactions,[1,2] in spite of its extreme simplicity, still can be regarded as a useful visualization of microscopic events that are combined to produce a reaction rate used in ordinary chemical kinetics. The essence of this model can be framed in terms of the reaction scheme $A+B\rightarrow B$, where, in Smoluchowski's original analysis and almost all subsequent ones, many-body effects are ignored and replaced by the simplifying assumption that there is a single immobile B particle, surrounded by an initially uniformly distributed swarm of noninteracting point particles that are allowed to diffuse through an unbounded space. The B particle is then generally modeled as a sphere with an absorbing surface. In this picture the reaction rate is modeled as the flux of A particles into the B particle. Other applications of such an elementary picture include processes in which elementary excitation particles are trapped, quenched, or annihilated by another kind of excitation or particle in confined geometries. Physical examples of this possibility include electron trapping and recombination, exciton trapping, quenching or fusion, soliton-antisoliton recombination, phonon upconversion, and free-radical scavenging.[3-10] Furthermore, there are several examples of effectively one-dimensional systems, such as polydiacetalenes and other quasi-one-dimensional crystals, polymer chains in dilute blends, and crystals grown inside pores and microcapillaries. An interest in the reaction kinetics of such systems, in addition to a number of others, has motivated a number of recent studies of diffusion-controlled kinetics in such systems.[4,7,9-19]

One of the effects of a reaction in a confined geometry is a tendency for the reactants to self-segregate, that is, to form islands[20] in which one component or another tends to predominate, rather than having the complete mixing which underlies the classical chemical descriptions of reaction kinetics. A complete analysis of this tendency poses intractable physical and mathematical problems, which had led, in recent years, to a much simpler way of looking at the general phenomenon without entering into many of the complicated details. The model employed for this purpose is very much in the spirit of Smoluchowski's treatment of reaction kinetics. In it one considers local effects in the neighborhood of a single, isolated, immobile trap.[6,10,18-22] In the context of reaction kinetics in a confined geometry, the focus of interest is on the distance of the single B particle from the nearest untrapped A particle. This distance is a measure of the zone of depletion of A particles. A number of results have appeared in the literature for this simplified picture, for diffusion in a medium whose properties are strictly translationally invariant.[6,10,18-22] In this paper we present results for the same problem in the absence of translational invariance and when either the A or the B particles are allowed to move, the other component remaining fixed. Specifically, we consider some properties of an ensemble of initially uniformly distributed random walkers in an unbounded fractal medium containing a single trap. We will not delve into the much more complicated formulation in which *both* the A and B particles are allowed to diffuse, and for which, at the present time, only simulation results are available.[19] Some of the properties reported on here can be mimicked by those of a continuous-time random walk[23,24] (CTRW) whose pausing-time density is of stable law form, as reported elsewhere.[21]

The present study of nearest-neighbor distances on fractal media was tested numerically on two specific fractal media in which the diffusion is known to be anomalous. One is the deterministic Sierpinski gasket, and the second is a two-dimensional percolation cluster at criticality, exemplifying a random medium. In keeping with the Smoluchowski picture, we assume that the random walkers, the A particles, are initially randomly distributed on the fractal lattice, and that B is the trap. The theory clearly neglects many-body effects, and is expected to be applicable in those cases in which traps form a minority species.

II. ANALYSIS

We first define some of the exponents that characterize properties of the unbiased random walk in unbounded space. The exponent d_w characterizes anomalous diffusion in the sense that the mean-squared displacement after n steps satisfies the asymptotic relation

$$\langle r^2(n)\rangle \sim n^{2/d_w} , \tag{1}$$

where we have omitted a multiplicative constant. When the medium is rigorously translationally invariant, $d_w=2$, while on fractal media, $d_w>2$. The second exponent needed in our analysis is the fractal dimension d_f, which is a measure of the density of the medium, in the sense that the mass of the medium within a radius R scales as $M(R)\sim R^{d_f}$. Finally, the fracton dimension d_s is defined in terms of d_f and d_w by the relation $d_s=2d_f/d_w$.

Our initial results are presented for the reaction $A+B\rightarrow B$, where the trap is immobile. The first quantity of physical interest to us is the flux into the trap. The position of the trap is taken to be the origin of coordinates. The flux may be found in terms of the expected number of distinct sites visited by the random walker in n steps, a quantity which we denote by $\langle S(n)\rangle$. The flux into a trap at step n can be identified with the expected number of random walkers from the medium that first reach the origin at step n. Because of the assumed global symmetry of the random walk, the probability that a random walker initially at $\mathbf{r}_0$ first reaches the origin at step n is equal to the probability that a random walker at the origin first reaches $\mathbf{r}_0$ at step n. If this probability is denoted by $f_n(\mathbf{r}_0)$, then the flux into the trap at step n, $J(n)$, can be regarded over contributions from each individual site in the medium. That is, $J(n)$ is the sum of $f_n(\mathbf{r}_0)$ over all $\mathbf{r}_0$

$$J(n)=\sum_{\mathbf{r}_0}{}' f_n(\mathbf{r}_0) , \tag{2}$$

where the prime indicates that the sum excludes a contribution from $\mathbf{r}_0=\mathbf{0}$. To discuss the large n behavior of the flux, it is expedient to first form the generating function of the $J(n)$, a quantity that we denote by $\hat{J}(z)$,

$$\hat{J}(z)\equiv \sum_{n=0}^{\infty} z^n J(n)= \sum_{n=0}^{\infty} z^n \sum_{\mathbf{r}_0}{}' f_n(\mathbf{r}_0)=\sum_{\mathbf{r}_0}{}' \sum_{n=0}^{\infty} f_n(\mathbf{r}_0)z^n \equiv \sum_{\mathbf{r}_0}{}' f(\mathbf{r}_0;z) , \tag{3}$$

where $f(\mathbf{r}_0;z)$ is the generating function of the $f_n(\mathbf{r}_0)$ with respect to n. Let $p_n(\mathbf{r})$ be the propagator for the position of the random walk after n steps. It is known that when $\mathbf{r}_0\neq\mathbf{0}$ the function $f(\mathbf{r}_0;z)$ can be expressed in terms of the generating function of the free-space propagator of the random walk [i.e., $p(\mathbf{r};z)\equiv \sum_n p_n(\mathbf{r})z^n$] as[23]

$$f(\mathbf{r}_0;z)=p(\mathbf{r}_0;z)/p(\mathbf{0};z) . \tag{4}$$

Since, when $\mathbf{r}_0$ is allowed to range over the entire space, we have

$$\sum_{\mathbf{r}_0} p(\mathbf{r}_0;z)=1/(1-z) ,$$

it follows from the combination of Eqs. (3) and (4) that

$$\hat{J}(z)=\frac{1}{p(\mathbf{0};z)}\left[\frac{1}{1-z}-p(\mathbf{0};z)\right] . \tag{5}$$

The result given in this last equation is exact. To find the asymptotic behavior of $J(n)$, we can recast the results in terms of the expected number of distinct sites visited in n steps, $\langle S(n)\rangle$. The generating function for this quantity is known to be

$$\hat{S}(z)\equiv \sum_{n=0}^{\infty} z^n\langle S(n)\rangle=\frac{z}{(1-z)^2 p(\mathbf{0};z)} , \tag{6}$$

which allows us to express $\hat{J}(z)$ in terms of $\hat{S}(z)$ as

$$\hat{J}(z)=(1-z)\frac{\hat{S}(z)}{z}-1 . \tag{7}$$

The behavior of $J(n)$ in the limit $n\rightarrow\infty$ can, by an argument based on a Tauberian theorem for power series,[25] be related to singular behavior of $\hat{J}(z)$ in the limit $z\rightarrow 1$. This is equivalent to the assertion that Eq. (7) implies that as $n\rightarrow\infty$,

$$J(n)\sim\langle S(n)\rangle-\langle S(n-1)\rangle\sim\frac{d\langle S(n)\rangle}{dn} . \tag{8}$$

This relation has been also been suggested by a heuristic argument by Kopelman and Argyrakis.[26] The asymptotic dependence of $\langle S(n)\rangle$ on n for fractals has been found by Alexander and Orbach[27] to be

$$S(n)\sim n^{d_s/2} , \tag{9}$$

for $d_s\le 2$, with the result that $J(n)$ scales as

$$J(n)\sim\frac{1}{n^{1-d_s/2}} . \tag{10}$$

This prediction has been tested for a random walk on a two-dimensional infinite percolation cluster at criticality in a simulation based on the method of exact enumeration.[28] The result of this simulation is given in Fig. 1, which is a log-log plot of the cumulative number of ran-

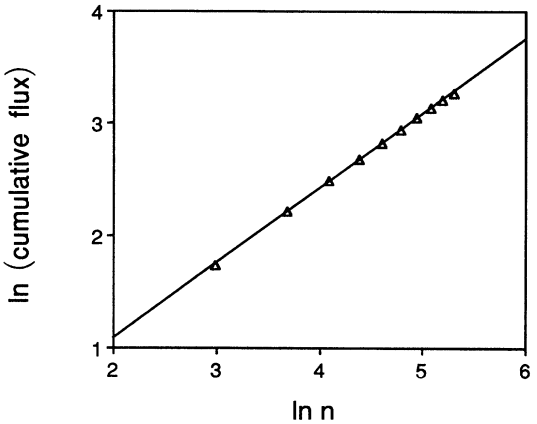

FIG. 1. A plot of the cumulative flux into the trap as a function of step number, for a random walk on an infinite percolation cluster at criticality in two dimensions. The data were obtained by the method of exact enumeration, and each point is an average of results obtained from 100 clusters.

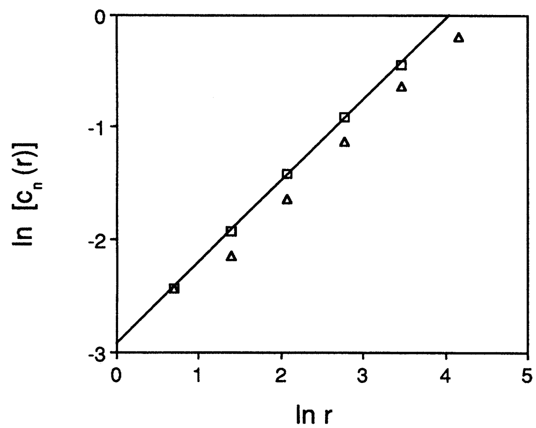

FIG. 2. Two sets of data for $c_n(r)$ on the Sierpinski gasket plotted as a function of $\ln r$ for $n=2000$. The upper line represents the profile along one side of the fractal and the second is for a line bisecting the fractal.

dom walkers trapped by step n. In this plot the expected value of the slope should be approximately equal to 0.66. Our simulated results are consistent with a slope equal to 0.67 ± 0.01. In contrast to the result shown in Eq. (10), the asymptotic form of the two-dimensional flux is inversely proportional to $\ln n$ and the three-dimensional flux is asymptotically a constant.

We next consider the effective repulsion of the random walkers due to the presence of a trap. One measure of this quantity is simply the form of the probability profile or, equivalently, the concentration in the neighborhood of the trap. A more specific measure of the depletion zone is the expected distance of the trap from the nearest untrapped random walker as a function of n. Let $c_n(\mathbf{r})$ be the concentration profile resulting from an initial uniform distribution of A particles and let $p_n(\mathbf{r}|\mathbf{r}_0)$ be the probability that a single random walker, initially at $\mathbf{r}_0$, is at $\mathbf{r}$ at step n, in the absence of any trapping boundaries. Because the medium is assumed to be isotropic $p_n(\mathbf{r}|\mathbf{r}_0)=p_n(r|r_0)$ and $c_n(\mathbf{r})=c_n(r)$; that is to say, only the radial dependence is required to describe diffusive motion in the fractal medium.

Let us assume that the concentration profile in the neighborhood of the trap is proportional to a power of r:

$$c_n(r)\sim A(n)r^{\alpha}\sim r^{\alpha}/n^{1-d_f/d_w}\ , \tag{11}$$

where the dependence on n is found by assuming that the flux $J(n)$ is proportional to the gradient of concentration at the trap. The dependence of $\langle r^2(n)\rangle$ on n given in Eq. (1) can be used to show that $\alpha=d_w-d_f$. Figure 2 shows some simulated data confirming the form of the profile suggested in Eq. (11).

A calculation of the expected distance from the trap to the nearest untrapped random walker, $\langle L(n)\rangle$, following the analysis of Ref. 6 requires that one first find a function $Q(L,n)$, defined to be the probability that the nearest-neighbor distance is greater than or equal to L at step n. This, in the continuum limit, is expressible in terms of $p_n(r|r_0)$ as[6]

$$Q(L,n)=\exp\left[-c\int_0^L dr\int_0^\infty dr_0 p_n(r|r_0)\right]\ , \tag{12}$$

where c is the initial uniform concentration. Substitution of the profile given in Eq. (11) into this equation suggests that $Q(L,n)$, at least for sufficiently small L, has the scaling form

$$Q(L,n)\sim\exp\left[-\frac{KL^{d_w}}{n^{1-d_s/2}}\right]\ , \tag{13}$$

where K is a constant. The function $\langle L(n)\rangle$ is found in terms of $Q(L,n)$ as

$$\langle L(n)\rangle=\int_0^\infty Q(L,n)dL\ . \tag{14}$$

On substituting Eq. (13) into Eq. (14), we find that the scaling behavior of $\langle L(n)\rangle$ is

$$\langle L(n)\rangle\sim n^{(1-d_s/2)/d_w}\ . \tag{15}$$

Figures 2 and 3 summarize data for $c_n(r)$ and $\langle L(n)\rangle$ on the Sierpinski gasket obtained by the method of exact enumeration. It is known[27] that the dimensions for the Sierpinski gasket are $d_f=\ln3/\ln2\sim1.58$, $d_w=\ln5/\ln2\sim2.32$, and $d_s=\ln3/\ln5\sim0.68$. The two sets of points in Fig. 2 correspond to the concentration profile taken along one side of the fractal medium and through a line bisecting the fractal medium. The slopes of both of these lines, except in the very close-in region, is found to be 0.73, which is to be compared to the value 0.737 predicted by the expression in Eq. (11) where the value of α is given in the text. The line in Fig. 3 has an estimated slope of 0.133 as opposed to the predicted 0.136. Results obtained from a Monte Carlo simulation yield an estimated slope of 0.142. All of these values are in excellent agreement with the scaling theory that we have developed.

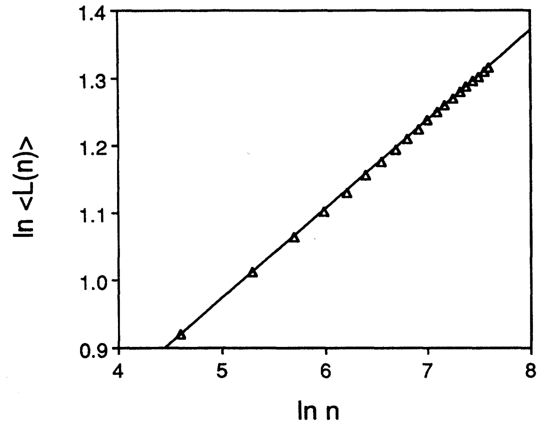

FIG. 3. A plot of $\ln\langle L(n)\rangle$ as a function of $\ln n$ for the Sierpinski gasket. The results were found by the method of exact enumeration.

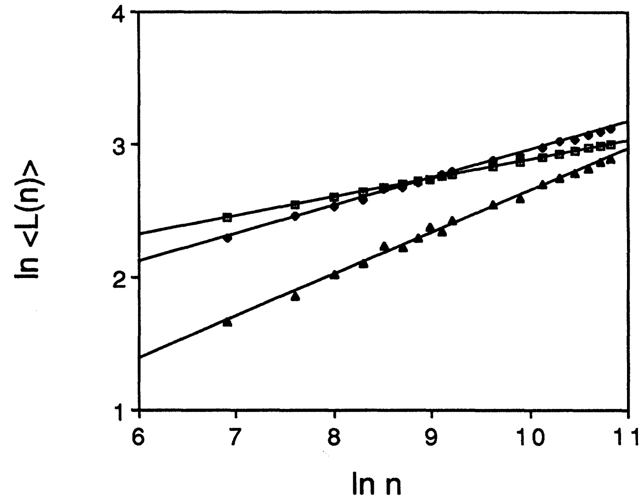

FIG. 4. Data for $\langle L(n)\rangle$ as a function of n on a log-log plot obtained by the simulation of a random walk on a Sierpinski gasket consisting of 9843 sites. Cyclic boundary conditions have been used. Each point represents an average of 1000 runs. The three sets of points are (▲), moving trap, fixed particles; (□), moving particles, fixed trap; (♦), moving particles and trap ($D_A = D_B$), where the diffusion constants are proportional to the probability that a particle moves on a given step. The associated estimates of the exponents are indicated in the text.

To this point we have been discussing a theory based on a stationary trap and a swarm of mobile particles. More generally, one should consider the case in which both the trap and the ambient random walkers are mobile, but such a theory is not presently available even for diffusion and reaction in a translationally invariant medium.[19] However, one can make some progress in discussing the case of a mobile trap and stationary swarm by resorting to a scaling argument. When the trap is mobile, we suggest that the property determining the principal kinetic features of the system is the efficiency of the trap in exploring unvisited sites. The efficiency will be identified with the quantity $d\langle S(n)\rangle/dn$. We will argue that $\langle L(n)\rangle$ is inversely proportional to the efficiency, so that the more new sites are visited, the smaller the distance to the closest unvisited walker. This leads to the prediction

$$\langle L(n)\rangle \sim (d\langle S(n)\rangle/dn)^{-1} \sim n^{(1-d_s/2)} . \tag{16}$$

Figure 4 shows a log-log plot of data obtained from Monte Carlo simulations of $\langle L(n)\rangle$ on a Sierpinski gasket, allowing for a fixed trap and moving particles, a moving trap and fixed particles, and a moving trap in the presence of moving particles. The exponent, which has been found numerically, for the case of the moving trap and stationary particles is 0.34 ± 0.02, to be compared with the exponent predicted by Eq. (16) to be equal to 0.32. When the trap is static, the exponent is found to be 0.142 ± 0.005, in agreement with the prediction of Eq. (15). Figure 4 also shows some data on $\langle L(n)\rangle$ when both the A particles and B trap are allowed to move with the same diffusion constant. It is evident from the figure that $\langle L(n)\rangle$ is proportional to a power of n, but there is no theory predicting what the exponent should be in this more complicated case.

We mention that our scaling theory for a single trap in the presence of a swarm of walkers gives a result for the flux that agrees with the prediction of a heuristic[21] theory based on the CTRW that incorporates a pausing-time density of fractal form $[\psi(t) \sim T^{\alpha}/t^{\alpha+1}]$ provided that the parameter d_w is set equal to $2/\alpha$. However, such a theory cannot predict all of the features found in the fractal picture, exemplified by the probability profile or $\langle L(n)\rangle$. This is not too surprising since the fractal behavior in the two types of models arises from different mechanisms. There is no analog of the anomalous pausing-time density at a single site in models of transport on a fractal medium. The concentration profile in this model in the neighborhood of the trap is given by the expression in Eq. (11), while the analogous result given by the CTRW in one dimension is proportional to x

In future work we will discuss the case of mobile particles in the presence of a trapping surface as suggested by applications of random-walk theory to phonon migration in a turbid medium.[29] Also, for this case it will be shown that some properties predicted by a pictured based on the CTRW differ from those obtained for fractal motion by simulation and scaling arguments.

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*Permanent address.

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