Models of hopping-controlled reactions with variable hopping range

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We propose two classes of models for hopping-controlled reactions in which one of the reactants forms a random distribution of static traps and the hopping distances of the other reactants (random walkers) are independent random variables with a preassigned distribution. Specifically, in the discrete model, at each step the random walkers are allowed to make hops of all possible lengths of integer units up to a preassigned maximum value L, all with equal probability. In one of the continuous models, the hopping distances are Gaussian-distributed independent random variables with a mean L. In the other continuous model, the distribution of the hopping distances r follow an exponential distribution, namely, $\exp(-|r|/L)$. We predict the L dependence as well as the time dependence of the reaction rates (the decay of the particle density as a function of time) for these models analytically. We also verify some of these predictions by Monte Carlo computer simulations.

I. INTRODUCTION

The prototypes of the diffusion-controlled reactions are (a) the unimolecular trapping reaction

$$A+B\rightarrow(1-\epsilon)A+B \quad (0<\epsilon\leq 1)\ ,$$

(b) the irreversible bimolecular reaction

$$A+B\rightarrow\text{inert}\ ,$$

multiparticle reactions, etc. These reactions have applications to a variety of phenomena of fundamental and technological importance in fields such as chemistry, biology, and surface science (including semiconductor and dielectric surfaces), one example being heterogeneous catalysis.[1] In the latter class of problems it is assumed that one of the reactants, say the A particles (by the term "particle" we mean an atom or a molecule or a cluster of molecules), wander diffusively in a medium in which the B particles are distributed randomly. For simplicity, the B particles are assumed to be immobile. It is also assumed that when any A particle comes in contact with a B particle the two particles react instantaneously. In other words, each of the A particles performs a random walk until it hits one of the "traps" formed by the B particles. For example, in the case of catalytic reactions on SiO_2, the so-called active centers, where the reactions take place, play the roles of the trap sites. We shall focus our attention on the unimolecular trapping reaction with $\epsilon=1$, so that each of the traps can react with an infinite number of A particles. For simplicity, we shall further assume that the random walkers (i.e., the A particles) are mutually noninteracting.

The problem of the random walk (diffusion) of particles in the presence of a random distribution of traps[2-11] has attracted much attention in the past. The fluctuations in the position of the traps give rise to trap-free regions of various sizes. This leads to a long tail in the decay of the particle density with time, viz., the particle density decays as $\exp(-\text{const}\times t^{x})$ where x depends on the space dimensionality d [$x=d/(d+2)$]. Such a "stretched exponential" decay is observed not only in the types of walks under consideration but also in many other disordered systems, e.g., in glasses and dielectrics as well as spin glasses.[12] However, so far in almost all the models of random walk with random trap distribution the particles are allowed to move only to one of the nearest-neighbor lattice sites at each step. Moreover, the problem of the long-ranged random walk without traps has been investigated quite extensively in the past.[13,14] Familiar examples of such long-ranged walks are the Levy flights, Levy walks[15] and the problem of random walks with unequal step sizes.[16] Because of long-ranged hoppings the particles sometimes run away from the nearby traps but at some other times run towards faraway traps. Recently, it has been shown[15] that in the presence of randomly distributed traps, the density of the Levy walkers decays as $\exp(-\text{const}\times t^{d/(d+1)})$ with time t. In this paper we propose a few models of hopping-controlled reactions where nature of the long-range hopping of the particles are different from those considered in the Levy flights and Levy walks.

We formulate the problems in the following way: on a d-dimensional lattice we have a density $\rho_p(\mathbf{r},t)$ of the particles at time t and a distribution $\rho_s(\mathbf{r})$ of traps; the traps are immobile and each of the traps can absorb an infinite number of particles. Then the three models are defined as follows.

Model I: in this discrete model, the maximum length of a step is L (with L much less than the linear size of the lattice) and the probability of a step of any length of integer unit r (with $1\leq r\leq L$) is $1/(2L)$, assuming the forward and the backward steps to be equally probable.

Model II: in this continuous model, the hopping lengths are Gaussian-distributed independent random variables with mean L.

Model III: in this continuous model, the hopping distances r follow an exponential distribution of the form $\exp(-|r|/L)$.

Our main aim is to calculate the L and t dependences of the density $n_p(r,t)=\langle\rho_p(r,t)\rangle$ (where $\langle\ \rangle$ denotes the sta-

tistical average over all trap configurations).

Model III is, probably, the most interesting because of its relevance in the motion of micro-organisms. It has been known for a long time that bacteria move on an approximately linear trajectory for some time and then choose a new direction along which they move again approximately linearly. Thus, the total trajectory of bacteria consists of a large number of linear segments, each connected to two others at its two ends. The real motion of bacteria is a little more complicated[13] because of the various biasing mechanisms. Besides, bacteria may remain immobile at a point for some time before resuming their motion. The lengths of the linear segments of such a trajectory of bacteria follow an exponential distribution.[17] Therefore, in model III, the random walkers can be assumed to be the models for the bacteria whereas the traps represent the randomly distributed bactericides.

For L much smaller than the linear size of the lattice, we propose a set of heuristic arguments for these models to estimate analytically a lower bound for the density $n_p(r,t)$. We then compare this estimate with the results as obtained by Monte Carlo (MC) computer simulation of model I.

II. ANALYTICAL RESULTS

Since the analytical treatment of the models I, II, and III will be restricted to $d=1$ in this paper, let us restate the model I, defined above, in the following way: the discrete-time Markovian jump process under consideration is described by

$$x_{n+1}=x_n+\xi_n \ , \tag{1}$$

where ξ_n is a sequence of independent random variables that determine the jump size at the nth step. The conditional jump probability

$$\text{Prob}(\xi_n=z \mid x_n=x)=W(z,x)$$

is assumed to be independent of x and is given by

$$W(z)=[1/(2L)][\,\delta(z-L)+\delta(z-L+1)+\cdots+\delta(z-1)+\delta(z+1)+\cdots+\delta(z+L)] \ . \tag{2}$$

This problem, as formulated through (1) and (2), is a special case of the general random walk studied by Donsker and Varadhan.[2] However, in Ref. 2 only the n dependence of the various relevant quantities was studied. Our work should be considered as complementary to that of Donsker and Varadhan in that we investigate the L dependence of relevant physical quantities which was not studied in Ref. 2. We address the following question: what is the probability that a particle starting from the origin (the origin being arbitrary) survives and arrives at a distance r after time t? We shall extend the argument for the nearest-neighbor hopping problem to our long-ranged hopping problem.

We first consider a line segment of length $2R$ centered around the origin and assume the two ends of this line segment to be totally absorbing (in the corresponding d-dimensional model one draws a sphere of radius R around the origin and imposes the constraint that the sphere is totally absorbing). That is, whenever a particle arrives at either of the two end points of this line segment it gets trapped. This approximation rules out the possibility of the return of particles from outside to the line segment, thereby underestimating the probability. Let us denote the probability with this constrained geometry as n_p' [where $n_p(r,t)>n_p'(r,t)$]. From the definition of configuration averaging, we have

$$n_p'(r,t)=\sum_{\{S\}} n_p'(r,t \mid \{S\})P(\{S\}) \ ,$$

where $P(\{S\})$ denotes the trap distribution probability and $n_p'(r,t \mid \{S\})$ is the conditional probability n_p' for a given distribution $\{S\}$ of the traps. Suppose $N_p(r,t)$ is the probability corresponding to the trap-free segment, viz., $\{S\}=0$, only. Since $N_p(r,t)<n_p'$, $N_p(r,t)$ represents only a lower bound. It is obvious that

$$N_p(r,t)=P_0(R)F(r,t) \ , \tag{3}$$

where $P_0(R)$ is the probability that there is no trap within a line segment of length $2R$ and $F(r,t)$ is the probability that a particle arrives, for the first time, at any of the endpoints of this line segment starting from the center. So far our approach is very similar to that of Grassberger and Procaccia[6] (GP). However, the main difference, as will be shown later, lies in the calculation of $F(r,t)$. Following GP we get

$$P_0=\exp(-n_s V_1) \ , \tag{4}$$

where $V_1=2R$ (for the corresponding d-dimensional problem V_1 must be replaced by $V_d=C_d R^d$, which is the volume of the d-dimensional sphere of radius R, with $C_d=\{2\pi^{d/2}/[d\Gamma(d/2)]\}$).

Next, we have to calculate the probability $F(r,t)$. The latter is the first-passage time distribution. We shall first estimate the dominant L dependence of $F(r,t)$ for the one-dimensional case. Suppose

$$p(x,y,n)=\text{Prob}(x(n)=y \mid x(0)=x)$$

denotes the transition probability. The latter satisfies the master equation

$$p(x,y,n+1)-p(x,y,n)=\int [p(x,y-z,n)W(z,y-z)-p(x,y,n)W(z,y)]dz \ . \tag{5}$$

The mean first-passage time $\tau(x)$, defined as

$$\tau(x)=\sum_n \int p(x,y,n)dy \ , \tag{6}$$

satisfies

$$\int [\tau(x+z)-\tau(x)]W(x,z)dz=-1 \quad \text{for } -R\le x\le R \tag{7}$$

and

$$\tau(x)=0 \quad \text{for } |x|>R \ .$$

Equation (7) is valid for all possible choices of W.[18] However, we shall present here a simple derivation which is valid only for the special form (2) of W. Since the W

in the problem under consideration is independent of x, we can rewrite Eq. (5) as

$$p(x,y,n+1)-p(x,y,n)=\int [p(x,y-z,n) -p(x,y,n)]W(z)dz \ . \quad (8)$$

Utilizing the homogeneity of space between $-R$ and $+R$, (8) further reduces to

$$p(x,y,n+1)-p(x,y,n)=\int [p(x+z,y,n) -p(x,y,n)]W(z)dz \ . \quad (9)$$

Finally, utilizing the definition (6) of τ we get (7). From (7) we get

$$\sum_k (m_k/k!)(\partial^k\tau/\partial x^k)_x=-1 \ , \quad (10)$$

where

$$m_k=\int z^k W(z)dz \ , \quad (11)$$

is the kth moment of W. Equation (10) is analogous to the Kramers-Moyal expansion. Using (2), (11) reduces to

$$m_k=\begin{cases}(1/L)(1+2^k+3^k+\cdots+L^k) & \text{for even } k \quad (12a)\\ 0 \quad \text{for odd } k \ . & (12b)\end{cases}$$

Since

$$\sum_{i=1}^{L} i^k \sim L^{k+1}+(\text{lower-order terms}) \ ,$$

we make the approximation that the dominant k dependence of m_k is given by

$$m_k \sim L^k \quad \text{for even } k \ . \quad (13)$$

Hence, in order to satisfy Eq. (10), given the form (13) for m_k, a plausible estimate of the dominant contribution to $\partial^k\tau/\partial x^k$ is

$$(\partial^k\tau/\partial x^k)_x \sim f_k(x)/L^k \ , \quad (14)$$

where the function $f_k(x)$ is independent of L. The form (14) indicates that

$$\tau \sim \exp[g(x)/L] \ , \quad (15)$$

where the function $g(x)$ is independent of L. [As we shall see later, our Monte Carlo results provide an *a posteriori* justification of (15).] The form (15) for the mean fast-passage time τ would be consistent with the first-passage time distribution

$$\exp\{-\text{const}\times[\exp(-1/L)]t/R^2\} \ , \quad (16)$$

where the negative sign in front of $1/L$ ensures smaller τ for longer L. We will explain the significance of the form (16) for the first-passage time distribution soon, but first let us justify the R dependence of (16). In order to get more insight into the problem, note that in the case of nearest-neighbor random walk the probability $F(r,t)$ is proportional to $\exp(-\text{const}\times t/r^2)$ where, as is well known, the mean-square distance traversed by the particle in time t is $\langle R^2\rangle \sim t$. On the other hand, in the case of Levy walks, where $\langle R^2\rangle \sim t^2$, the corresponding probability F is proportional to $\exp(-\text{const}\times t/R)$. It is difficult to calculate the true mean-square distance $\langle R^2\rangle$ for the long-range jump problem under consideration. However, the form of the t and R dependences in (16) should be taken in the spirit of a plausible ansatz. This ansatz is based on the assumption that the effect of the long-ranged hoppings is to enhance the diffusion constant, so that $\langle R^2\rangle \sim h(L)t$, where $h(L)$, a function of L, is independent of t. [The latter argument must not be confused with the behavior of $\langle R^2\rangle$ in the presence of traps; it is well known[6,11] in the latter case that for the special case $L=1$, $\langle R^2\rangle \sim t^\alpha$ where $\alpha=2/(d+2)$ for all finite d.] Now substituting (16) and (4) into (3) we get

$$n_p(r,t) > \exp\{-[C(e^{-1/L}t/R^2)+DR]\} \quad \text{for } d=1 \quad (17)$$

where C and D are constants independent of L and t. Finally, following GP, we optimize R so as to maximize the probability (17). This leads to

$$R_{\text{opt}}=(Ce^{-1/L}t/D)^{1/3} \quad (18)$$

for the optimum value of R and hence

$$n_p(r,t) > A\exp\{-B[\exp(-1/L)]t^{1/3}\} \quad \text{for } d=1 \quad (19)$$

in the long-time regime, where A and B are constants independent of L and t.

Next we shall extend these arguments to models II and III. In the case of model II,

$$W(z)=[1/(2\pi)^{1/2}\sigma]\exp[-(z-L)^2/(2\sigma^2)] \ ,$$

where we are mainly interested in the L dependence of $n_p(r,t)$. In this case the moments are given by

$$m_k=(\sqrt{2}\sigma)^k(2i)^{-k}H_k(iL/(\sqrt{2}\sigma)) \ ,$$

where H_k is the Hermite polynomial of order k. So far as the dominant dependence on L is concerned,

$$m_k \sim L^k \ ,$$

and hence, following the same arguments as those from Eqs. (12)–(18), we get

$$n_p(r,t) > A'\exp\{-B'[\exp(-1/L)]t^{1/3}\} \quad \text{for } d=1$$

which has the same t and L dependences as in expression (19) with L now standing for the mean of the Gaussian distribution. However, note that the nonuniversal constants A and B can differ in the two models.

In the case of model III,

$$W(z)=(1/L)\exp(-|z|/L) \ ,$$

so that

$$m_k \sim L^k \ ,$$

and hence the corresponding expression for $n_p(r,t)$ is given by

$$n_p(r,t) > A''\exp\{-B''[\exp(-1/L)]t^{1/3}\} \ ,$$

where the t and L dependences are identical with those in (19), but the nonuniversal constants A'' and B'' differ. Indeed, it is easy to convince oneself that the t and L dependences of $n_p(r,t)$, expressed by (19), hold for any type of random walk for which the moments are of the form (13) where L is the corresponding characteristic length scale associated with the jump sizes.

III. MONTE CARLO SIMULATION

In order to estimate the goodness of the lower bound (19), we have carried out a MC simulation of the discrete long-ranged model, defined by (2), in one dimension. A random trap configuration with average trap concentration c ($c \ll 1$) was created on a very long one-dimensional discrete lattice. A large number of particles, typically of the order of 10^3, were placed randomly on the remaining sites. The maximum step length L was chosen *a priori*. At each time step (one Monte Carlo step per particle) each particle was allowed to jump to any of the $2L$ lattice sites centered around its current position with equal probability $1/(2L)$. If the new position so chosen turns out to be a trap, the corresponding particle disappears. Then the number of particles which survived was monitored as a function of time. The same procedure was repeated for various values of L. The logarithm of the fraction of particles which survived after time t has been plotted against $t^{1/3}$ in Fig. 1(a) for different values of L. When L is small compared to the average distance between the traps, L_t (where L_t was about 200 in units of the lattice constant), there is a large number of trap-free regions with linear dimension larger than L, and therefore we expect to observe the stretched exponential decay for large enough t in our MC simulation. Indeed, the linear tails of the curves in Fig. 1(a) for small L and large t support the $\exp(\text{const}\times t^{1/3})$ behavior in (19). As L increases and becomes comparable to L_t, there are very few configurations sampled in our MC simulation that contain trap-free regions bigger than L. Thus, a fast decay of the particle density persists for a long time, as is evident from Fig. 1(a). The latter fast-decay law seems to be exponential, as suggested by Fig. 1(b) where we have plotted n_p against t on a logarithmic scale. Increasing the size of the system increases the probability of sampling very large trap-free regions. Therefore, in such big systems stretched exponential decay will be observed after a long time provided L is finite.

In principle, one can test the L dependence of n_p from a plot of the logarithm of the survival probability n_p against L for a given fixed large value of t. However, in order to smooth out the fluctuations in $n_p(L)$, we have first evaluated the slopes $K(L)$ of the curves in Fig. 1(a) and plotted $-\ln K(L)$ against $1/L$ in Fig. 2. The linearity of the curve in Fig. 2 for $L \ll L_t$ is consistent with the $\exp(-1/L)$ factor in (19). The latter figure also demonstrates the fast (exponential) decay dominates for long times in the case of larger L.

In the special case $L=1$ in one dimension, Weiss and Havlin[10] showed that the survival probability in the *short-time* (or more appropriately, intermediate-time) regime varies as $\exp(-\text{const}\times t^{1/2})$, in contrast with the $\exp(-\text{const}\times t^{1/3})$ behavior in the long-time regime. Plotting the logarithm of the survival probabilities as functions of $t^{1/2}$, we observed an approximately straight line in the intermediate-time regime (between about 400 and 1000 Monte Carlo steps per particle for $L \sim 10$) for different values of $L \ll L_t$. The linearity of the curves suggests that the prediction of Weiss and Havlin for the short-time behavior of the survival probability holds also for $L > 1$. However, for $L \sim L_t$, as mentioned before, a

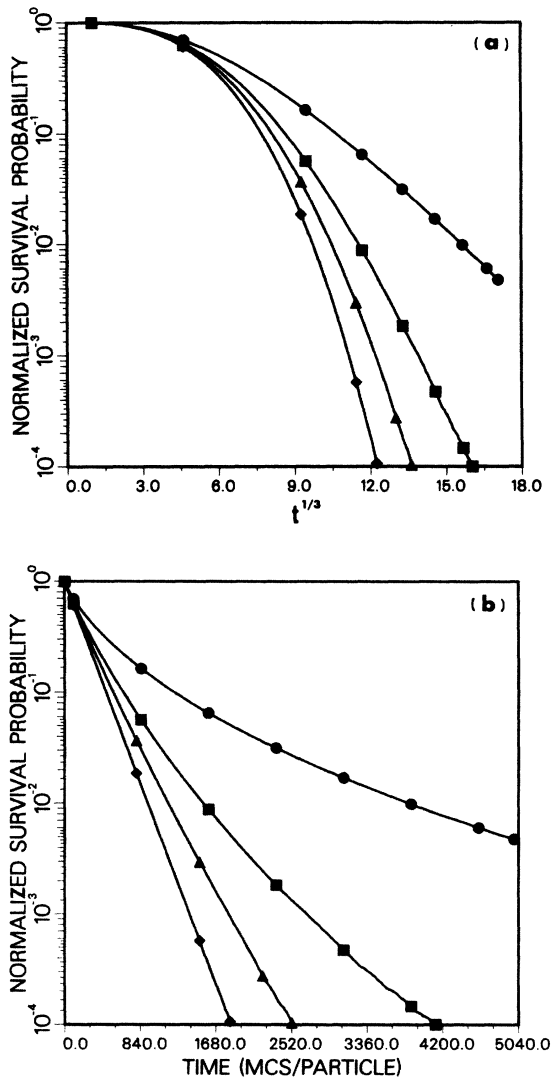

FIG. 1. Normalized survival probability $n_p(L,t)$ plotted against (a) $t^{1/3}$ and (b) t [units of Monte Carlo steps (MCS)] for different values of L; $L=20$ (circles), $L=50$ (squares), $L=100$ (triangles), and $L=1000$ (diamonds). The length of the lattice is 10^4 in the units of the lattice constant and there are 50 traps distributed randomly. The data for $L=20$ demonstrate the "stretched" exponential decay expressed by Eq. (19) whereas for $L=1000$ the particle density decays (exponentially) fast to a fraction 10^{-4} of the initial density for reasons explained in the text.

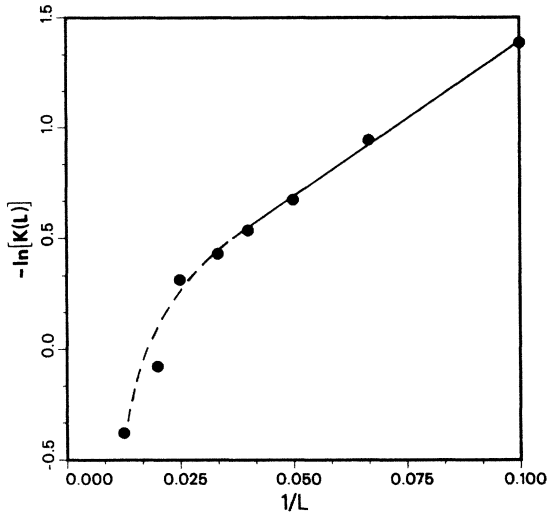

FIG. 2. $K(L)$ in the decay law $\exp[-\text{const}\times K(L)t^{1/3}]$, computed from the slope of the corresponding curves in Fig. 1(a), plotted against $1/L$. For not-too-large L the $K(L)$ data are consistent with the form (19) whereas an *apparent* deviation from (19) for large L is observed.

purely exponential decay dominates for a long time. Moreover, Weiss and Havlin argued that for $L=1$ in one dimension the magnitude of the correction terms to the asymptotic form (19) increases with decreasing n_s, and the asymptotic form (19) is followed after a longer t. However, such corrections become less significant for $L \gg 1$, because the trap density gets augmented by the factor $\exp(-1/L)$.

If the dimensionality of the space is d, the expression (16) is generalized to the form

$$\exp[-\alpha(L)t/R^2] , \tag{16'}$$

where $\alpha(L)$ might depend on d. However, it is difficult to determine the explicit form of the function $\alpha(L)$ by the method followed in deriving (16). Utilizing the well-known result that the $\langle R^2\rangle \sim t$ is "superuniversal" (i.e., independent of d) and making an ansatz, as before, that the role of the long-ranged hoppings is just to enhance the diffusion constant, we get the t dependence as well as the R dependence in the expression (16'). Using (16'), instead of (16), we get

$$n_p(r,t) \sim \exp[-\text{const}\times K(L)t^{d/(d+2)}] . \tag{20}$$

In other words, the exponent of t in $n_p(r,t)$ in d dimensions is expected to be the same as that in the case of nearest-neighbor hoppings, so long as L is finite. Thus, the difference between the long-range and the nearest-neighbor hoppings appears in the L-dependent multiplicative prefactor of the $t^{d/(d+2)}$ term.

IV. CONCLUSIONS

In summary, two classes of random-walk models are proposed in this paper as models for "hopping"-controlled reactions. In the first model each of the random walkers is allowed to hop up to a maximum distance L at every step at a medium with randomly distributed traps. Its properties are studied by (heuristic) analytical methods and by Monte Carlo computer simulations. In the second model the lengths of the hoppings are Gaussian-distributed random variables with mean L. In the third model, the hopping lengths are assumed to be random variables with exponential distribution. In all three cases we find a long-time tail in the decay of the particle density in agreement with an earlier work of Donsker and Varadhan.[2] We have mainly focused our attention on determining the L-dependent prefactor of $t^{1/3}$ in one dimension, as given by Eq. (19). Finally, we would like to emphasize that the result (19) should hold for any type of walk for which the kth moments m_k of the conditional jump probability W behave like L^k where L is the associated characteristic length scale determining the jump sizes.

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