Journal of Statistical Physics, Vol. 69, Nos. 1/2, 1992

Random–Random Walk on an Asymmetric Chain with a Trapping Attractive Center

C. Aslangul,[1] N. Pottier,[1] P. Chvosta,[2] D. Saint-James,[3] and L. Skála[4]

Received November 6, 1991; final February 28, 1992

The random walk of a particle on an asymmetric chain in the presence of an attractive center, possibly trapping, is examined by means of the equivalent transfer rates technique. Both the situations of ordered and disordered hopping rates are studied. It is assumed that initially the particle is located on the attractive center. The (average) probability of presence of the particle at its initial point is computed as a function of time. In the ordered case this quantity decreases exponentially toward its limiting value (with in certain cases an inverse power-law prefactor), while in the presence of disorder it decreases according to a power law, with an exponent depending both on disorder and on asymmetry. When the possibility of trapping is taken into account, this model is relevant for the description of the transfer of energy in a photosynthetic system. The amount of energy conserved within the chain, as a function of time, and the average lifetime of the particle before it is captured by the trap are examined in both ordered and disordered situations.

KEY WORDS: Fluctuation phenomena; random walks; disordered media.

1. INTRODUCTION

In the present paper we consider the random walk of a particle on a Euclidean one-dimensional asymmetric lattice when an attractive center, possibly trapping, is present. By asymmetric we mean a lattice in which the two hopping rates corresponding to a given bond depend *a priori* on the direction. Both situations of ordered and disordered hopping rates are

[1] Groupe de Physique des Solides, Université Paris VII, 75251 Paris Cedex 05, France (Laboratory associated with CNRS, UA no. 17, and with Universités Paris VII et Paris VI).
[2] Institute of Physics of the Charles University, 121 16 Prague 2, Czechoslovakia.
[3] Laboratoire de Physique Statistique, Collège de France, 75231 Paris Cedex 05, France. Also at Université Paris VII, 75251 Paris Cedex 05, France.
[4] Faculty of Mathematics and Physics, Charles University, 121 16 Prague 2, Czechoslovakia.

0022-4715/92/1000-0017$06.50/0

considered. In the disordered case we are faced with a particular version of the so-called random–random walk problem.

Most of the previous studies of random–random walks have been devoted to the biased chain model in the presence of a local random force (e.g., ref. 1). There the questions of interest were the determination of the average probability of presence of the particle at its initial site and the study of its drift and diffusion properties, which in the presence of a local random force may be anomalous when the disorder is sufficiently strong.

However, other arrangements of the transfer rates may deserve study, for instance, systems with an attractive center.[2] We consider here such a system, more specifically, a chain in which the mean bias is directed toward a given fixed point. Moreover, we allow for the possibility for the particle to be trapped by this center.

This model is mathematically interesting and also relevant in the problem of photosynthesis. For example, in a photosynthetic molecule a typical arrangement is one trap (called a reaction center) surrounded by a number of sites (called antenna chlorophyll molecules).[3,4] The trap is at the center, and antenna molecules are around it in planar configurations. The transfer rates are larger for the transfer directed toward the trap. Linear geometries are also of interest.[3,4] We consider here a one-dimensional model in which, for the sites to the right of the trap, the hopping rates toward the left are larger than the ones toward the right, and the reverse is true for the sites to the left of the trap.

In the problem of photosynthesis, the first quantity of interest is the amount of energy conserved within the chain, as measured by the sum of probabilities of presence of the particle on the different sites, denoted $s(t) = \sum_{n=-\infty}^{\infty} p_n(t)$. This quantity is proportional to the measured fluorescence intensity. Because of the existence of the trap, $s(t)$ goes to zero as $t \to \infty$. The second quantity of interest is the lifetime of the particle before it is captured by the trap, denoted $\int_0^\infty s(t)\,dt$. We aim at studying the effect of disorder on these two quantities.

For practical purposes, it is simpler to treat the disordered case in the continuous limit. In both the ordered and disordered cases, we will use the equivalent transfer rates technique, as first introduced in refs. 6 and 7 (see also refs. 8 and 9). In the ordered case we shall compute the probability of presence of the particle at its initial site as a function of time, denoted $p(0, t)$. In the disordered case the same technique allows for the exact computation of the disorder average of the probability density of presence of the particle at its initial site, denoted $\langle p(0, t) \rangle$.

The paper is organized as follows. In Section 2 we describe the model in the ordered and disordered situations. In Section 3 we briefly recall how, in the disordered situation, the equivalent transfer rates technique allows for the computation of $\langle p(0, t) \rangle$. In Section 4 we determine the asymptotic behavior of $p(0, t)$ in the ordered case, successively without and with the possibility of trapping on the attractive center. Then, in Section 5, we calculate $\langle p(0, t) \rangle$ when a local random force is present. As a result, while in an ordered medium $p(0, t)$ decreases exponentially toward its limiting value (with in certain cases an inverse power-law prefactor), in the presence of disorder $\langle p(0, t) \rangle$ decreases according to a power law, with an exponent depending both on disorder and on asymmetry. This conclusion holds irrespective of the absence or of the presence of a trap on the attractive center. Disorder thus slows down the average motion. Finally, the consequences on $s(t)$ and on $\int_0^\infty s(t)\, dt$ are discussed in Section 6.

2. THE MODEL

2.1. Asymmetric Chain with an Attractive Center but with No Trap

The random walk of the particle on the Euclidean asymmetric chain is described by the usual master equation, which in the absence of trapping effects is written

$$\frac{dp_n(t)}{dt} = W_{n,n+1}\, p_{n+1}(t) + W_{n,n-1}\, p_{n-1}(t) - (W_{n+1,n} + W_{n-1,n})\, p_n(t) \qquad (1)$$

In Eq. (1), $p_n(t)$ denotes the probability of finding the particle on the site of index n at time $t \geqslant 0$. The hopping rates may be disordered or not. We assume that there exists on this chain an attractive center, which we take as site $n = 0$.

Let us first give the notations appropriate to the ordered chain. In this case all the hopping rates toward the attractive center $n = 0$ (from both sides) are equal and they assume the value W. All the hopping rates in the opposite direction, i.e., away from the attractive center, take the value w. Of course, since the center is attractive, one has $W > w$.

In the disordered case we assume that the hopping rates W_{ij} are random variables. They are not assumed to be symmetric, in other words, W_{ij} is not equal to W_{ji}. They are independent from one bond to another. We exclude the case where any W_{ij} vanishes. We adopt here the same notations as in a previous study of the random–random walk on a biased chain.[8,9] The hopping rates are chosen such that

$$\begin{aligned} W_{n,n+1} &= \frac{D_0}{a^2} \exp\left(-\frac{aF_{n+1}}{2D_0} \right) \\ W_{n+1,n} &= \frac{D_0}{a^2} \exp\left(\frac{aF_{n+1}}{2D_0} \right) \end{aligned} \qquad (2)$$

where D_0 is the diffusion coefficient, a is the spacing of the lattice, and F_{n+1} may be viewed as a random force between sites n and $n+1$. We assume that the F_n are distributed according to a Gaussian law, with

$$\langle F_n \rangle = F$$
$$\langle F_n F_m \rangle - F^2 = \frac{\sigma}{a}\,\delta_{n,m} \tag{3}$$

We make the following assumption (with obvious notations)

$$n \geqslant 0, \qquad \left\langle \log \frac{W_{\leftarrow}}{W_{\rightarrow}} \right\rangle > 0$$
$$n \leqslant 0, \qquad \left\langle \log \frac{W_{\rightarrow}}{W_{\leftarrow}} \right\rangle > 0 \tag{4}$$

which corresponds to the existence of an attractive center situated at the origin. In other words, the average value of the local random force is positive for the sites of negative index and negative for the sites of positive index.

It will turn out to be useful for the treatment of the disordered case to consider the continuous limit of the master equation (1). This will be done, essentially, in order to get exact analytical results in a completely explicit form.[5] As indicated in ref. 9, when the lattice spacing a becomes much smaller than $x_1 = 4D_0^2/\sigma$, the master equation (1) can be approximated by its continuous limit. This corresponds to a weak disorder on a lattice spacing scale. The probability density of the particle position at time t is defined by setting $p_n(t) = ap(x, t)$. The natural length and time units of the continuous model are x_1 and $2t_1$, where the diffusion time t_1 is linked to x_1 by $x_1^2 = 2D_0 t_1$. It is convenient to take as reduced variables $X = x/x_1$ and $T = t/2t_1$. The dimensionless quantity $x_1\, p(x, t)$, denoted for simplicity as $p(X, T)$, obeys for $X > 0$ the Fokker–Planck equation

$$\frac{\partial p(X, T)}{\partial T} = \frac{\partial^2 p(X, T)}{\partial X^2} - \frac{\partial}{\partial X}\,[2\psi(X)\, p(X, T)] \tag{5}$$

where $\psi(X) = (x_1/2D_0)\, F(x)$ is the dimensionless random force in the continuous limit. One sets

$$\langle \psi(X) \rangle = -\mu$$
$$\langle \psi(X)\, \psi(X') \rangle - \mu^2 = \delta(X - X') \tag{6}$$

[5] Actually, it can be proved that both discrete and continuous models belong to the same universality class, which means that only the prefactors, but not the exponents, of the asymptotic laws should depend on whether the calculation is done in a discrete or in a continuous medium.[9]

with $\mu = 2FD_0/\sigma > 0$ (average bias directed toward the origin). For $X < 0$, the same Fokker–Planck equation is obeyed by the probability density $p(X, T)$, but with μ changed into $-\mu$. The probability density $p(X, T)$ is continuous at $X = 0$.

2.2. Asymmetric Chain with a Trapping Attractive Center

If the attractive center situated at the origin is also a trapping center, then the master equation (1) has to be modified in order to include the trapping effect. It reads

$$\frac{dp_n(t)}{dt} = W_{n,n+1}\, p_{n+1}(t) + W_{n,n-1}\, p_{n-1}(t) - (W_{n+1,n} + W_{n-1,n})\, p_n(t) - c\delta_{n,0}\, p_n(t) \tag{7}$$

where c^{-1} is the trapping rate. Some caution will have to be taken in the disordered case when passing to the continuous limit. It will actually be necessary to take c of the form $c = x_1/a\tau_c$, τ_c being the characteristic time linked to the trap in the continuous medium, in order to keep in this limit a nonzero trapping effect.

3. THE EQUIVALENT TRANSFER RATES TECHNIQUE

One assumes that, at time $t = 0$, the particle is situated on site $n = 0$, which means that, initially, the particle is located *on* the attractive center. In an ordered lattice it is possible to avoid this assumption and to take any initial position for the particle. In a disordered medium such a calculation could probably be done along the same lines. In any case, one can think that the final regime in which we are interested is independent of the initial position of the particle.

Let us now recall the main lines of the equivalent transfer rates technique.[5-7] As usual, it is convenient to perform a Laplace transformation of the master equation (1) or (7), which are respectively rewritten as

$$zP_n(z) - \delta_{n,0} = W_{n,n+1} P_{n+1}(z) + W_{n,n-1} P_{n-1}(z) - (W_{n+1,n} + W_{n-1,n})\, P_n(z) \tag{8}$$

when no trap is present, and

$$zP_n(z) - \delta_{n,0} = W_{n,n+1} P_{n+1}(z) + W_{n,n-1} P_{n-1}(z) - (W_{n+1,n} + W_{n-1,n})\, P_n(z) - c\delta_{n,0} P_n(z) \tag{9}$$

when the origin acts as a trapping center. We have defined

$$P_n(z) = \int_0^\infty dt\, e^{-zt} p_n(t) \qquad (\mathrm{Re}\, z > 0) \tag{10}$$

From now on, for the sake of simplicity, we shall only consider Eq. (9), simply setting $c = 0$ when no trap is present. It can be rewritten as

$$\begin{aligned} zP_n(z) &= -G_n^+(z)\, P_n(z) + G_{n-1}^+(z)\, P_{n-1}(z) \\ zP_0(z) - 1 &= -G_0^+(z)\, P_0(z) - G_0^-(z)\, P_0(z) - cP_0(z) \\ zP_{-n}(z) &= -G_n^-(z)\, P_{-n}(z) + G_{n-1}^-(z)\, P_{-n+1}(z) \end{aligned} \tag{11}$$

($n = 1, 2,\ldots$), with the quantities $G_n^+(z)$ and $G_n^-(z)$ defined by

$$\begin{aligned} G_n^+(z)\, P_n(z) &= W_{n+1,n} P_n(z) - W_{n,n+1} P_{n+1}(z), \qquad n \geqslant 0 \\ G_n^-(z)\, P_{-n}(z) &= W_{-n-1,-n} P_{-n}(z) - W_{-n,-n-1} P_{-n-1}(z), \qquad n \geqslant 0 \end{aligned} \tag{12}$$

In this formulation, the quantities $G_n^+(z)$ and $G_n^-(z)$ play the role of energy-dependent effective transfer rates, toward the right of the sites of positive index or toward the left of the sites of negative index, respectively. Clearly, they can be used in the ordered as well as in the disordered case. In the ordered case, however, their use is not necessary, since any quantity of physical interest may be directly extracted from the master equations in their form (1) or (7). But in the disordered case for which they are random quantities, they provide the most natural way of calculating such a quantity as $\langle p(0, T) \rangle$.

The effective transfer rates obey the recursion relations

$$\begin{aligned} \frac{1}{G_n^+(z)} &= \frac{1}{W_{n+1,n}} + \frac{W_{n,n+1}}{W_{n+1,n}} \frac{1}{z + G_{n+1}^+(z)}, \qquad n \geqslant 0 \\ \frac{1}{G_n^-(z)} &= \frac{1}{W_{-n-1,-n}} + \frac{W_{-n,-n-1}}{W_{-n-1,-n}} \frac{1}{z + G_{n+1}^-(z)}, \qquad n \geqslant 0 \end{aligned} \tag{13}$$

Once they are known, the solution of the master equation can immediately be extracted from Eq. (11). For later use let us note that, due to the assumption (4), the quantities $G_n^+(z)$ and $G_n^-(z)$ behave proportionally to z at small z (this can most easily be seen along the lines developed in ref. 8).

4. EXACT SOLUTION FOR THE ORDERED CHAIN

It follows from the recursion relations (13) that in the ordered case the effective transfer rates do not depend on the site index, nor on the possible presence of the trap at the origin. More specifically, both recursion relations (13) reduce to

$$\frac{1}{G(z)}=\frac{1}{w}+\frac{W}{w}\frac{1}{z+G(z)} \tag{14}$$

which yields

$$G(z)=\frac{-(z+W-w)+[(z+W+w)^2-4Ww]^{1/2}}{2} \tag{15}$$

[The sign of the square root is clearly +, since $G(z)\to w$ as $z\to\infty$, which indeed gives the proper limiting values $p_n(t=0)=\delta_{n,0}$.] If $Z=(z+w+W)/2(wW)^{1/2}$, then we choose the cut for the function $(Z^2-1)^{1/2}$ as extending from $Z=-1$ to $Z=+1$ on the real axis.

Using the result (15), we can rewrite the Laplace transform $P_0(z)$ of $p_0(t)$, as given by Eq. (11), as

$$P_0(z)=\frac{1}{c+w-W+[(z+w+W)^2-4wW]^{1/2}} \tag{16}$$

It is possible to analyze the large-time behavior of the inverse Laplace transform of this function. By adding, as usual, the contributions of the residue and of the cut, one gets

$$\begin{aligned} p_0(t)=&\{\exp[-t(w+W)]\}\\ &\times\frac{|c+w-W|}{[4wW+(c+w-W)^2]^{1/2}}\\ &\times(\exp\{-t\,\mathrm{sgn}(c+w-W)[4wW+(c+w-W)^2]^{1/2}\}+\mathscr{L}(t)) \end{aligned} \tag{17}$$

where the cut contribution $\mathscr{L}(t)$ can be cast into the form of the following real integral:

$$\begin{aligned} \mathscr{L}(t)=&\frac{1}{\pi}\int_{-2(wW)^{1/2}}^{2(wW)^{1/2}}\frac{(1-x^2)^{1/2}}{[(c+w-W)/2(wW)^{1/2}]^2+1-x^2}\\ &\times\exp[x2(wW)^{1/2}t]\,dx \end{aligned} \tag{18}$$

This formula is valid for any value of the parameters c, w, and W (and it would even be valid if the center, instead of being an attractive one, were repulsive, that is, if one had $W<w$). In the special case $c+w-W=0$, one gets the exact closed formula

$$p_0(t)=e^{-t(w+W)}I_0(2(wW)^{1/2}t) \tag{19}$$

where I_0 is the modified Bessel function. Let us now analyze the large-time behavior of $p_0(t)$.

4.1. Ordered Chain without Trap

Let $c=0$. Since $w<W$ (attractive center), Eqs. (17) and (18) can be rewritten as

$$p_0(t)=\frac{W-w}{W+w}+\frac{1}{\pi}\int_{-2(wW)^{1/2}}^{2(wW)^{1/2}}\frac{(1-x^2)^{1/2}}{[(w-W)/2(wW)^{1/2}]^2+1-x^2}\times\exp[x2(wW)^{1/2}\,t]\,dx \tag{20}$$

It is easy to expand the cut contribution $\mathscr{L}(t)$ into the following asymptotic series of Bessel functions:

$$\mathscr{L}(t)\sim\frac{1}{\pi^{1/2}}\frac{1}{[(W-w)/2(wW)^{1/2}]^2}\times\sum_{n=0}^{\infty}(-1)^n\frac{1}{[(W-w)/2(wW)^{1/2}]^{2n}}\left(\frac{1}{(wW)^{1/2}\,t}\right)^{n+1}\times\Gamma\left(n+\frac{3}{2}\right)I_{n+1}(2(wW)^{1/2}\,t) \tag{21}$$

of which, as ordinarily, we retain only the first term when t is sufficiently large. [In Eq. (21), I_n is the modified Bessel function of order n.[10]] By adding the corresponding contribution to $p_0(t)$ and the contribution of the residue, one gets at large times

$$p_0(t)\sim\frac{W-w}{W+w}+\frac{(wW)^{1/4}}{(W-w)^2\sqrt{\pi}}\frac{1}{t^{3/2}}\exp[-(\sqrt{W}-\sqrt{w})^2\,t] \tag{22}$$

[Note that the same result can be obtained by other methods, e.g., by a saddle-point integration in formula (20).] Therefore $p_0(t)$ tends toward a constant and its asymptotic behavior is of the exponential type (with an inverse power-law prefactor). Since $w\neq 0$, the asymptotic value of $p_0(t)$ is smaller than one, and the probability to find the particle on the rest of the chain is equal to $2w/(W+w)$. A similar derivation yields the asymptotic values of the probabilities to find the particle at the sites $\pm n$, $n=1, 2,\ldots$, which are equal to

$$\frac{W-w}{W+w}\left(\frac{w}{W}\right)^n$$

Note that in the case of the symmetric chain ($w=W$) the large-time behavior of $p_0(t)$ is easily derived from Eq. (19). One gets a power-law decay

$$p_0(t)\sim\frac{1}{2(\pi t w)^{1/2}} \tag{23}$$

Correspondingly, in the limit $w \to W$, the exponentially decreasing term in Eq. (22) has a diverging coefficient, which indicates a crossover toward the power-law behavior (23).

4.2. Ordered Chain with Trap

If $c \neq 0$, then the trap pumps the energy (or probability) out of the chain, i.e., the energy flows toward the trap. Clearly, $W - w$ is a measure of the flux going toward the origin. Therefore $c + w - W$ is one of the relevant parameters. The asymptotic values of all the probabilities $p_n(t)$ are zero. According to the different possible values of the intensity of pumping c and of the bias due to the asymmetry of the transfer rates $W - w$, one can have the three regimes:

(i) If $c = W - w$, as indicated above, then the general formula (17) reduces to the simple form (19), which has the asymptotic behavior

$$p_0(t) \sim \frac{1}{2[\pi t(wW)^{1/2}]^{1/2}} \exp[-t(\sqrt{w} - \sqrt{W})^2] \tag{24}$$

This decay occurs with a single characteristic time $\tau_1 = (\sqrt{W} - \sqrt{w})^{-2}$.

(ii) If $c < W - w$, then the pumping is less efficient than the flow due to the asymmetry. The cut contribution $\mathscr{L}(t)$ can be expanded into an asymptotic series of Bessel functions similar to (21) with $w - W$ replaced by $c + w - W$,

$$\begin{aligned} \mathscr{L}(t) \sim & \frac{1}{\pi^{1/2}} \frac{1}{[(c+w-W)/2(wW)^{1/2}]^2} \\ & \times \sum_{n=0}^{\infty} (-1)^n \frac{1}{[(c+w-W)/2(wW)^{1/2}]^{2n}} \left(\frac{1}{(wW)^{1/2}\, t}\right)^{n+1} \\ & \times \Gamma\left(n + \frac{3}{2}\right) I_{n+1}(2(wW)^{1/2}\, t) \end{aligned} \tag{25}$$

Here, again, the term $n = 0$ yields the dominant contribution of the cut integral at large times. By adding this contribution to $p_0(t)$ and that of the residue, one gets at large times

$$\begin{aligned} p_0(t) \sim & \frac{W - w - c}{[4wW + (c+w-W)^2]^{1/2}} \\ & \times \exp(-t\{w + W - [4wW + (c+w-W)^2]^{1/2}\}) \\ & + \frac{(wW)^{1/4}}{(c+w-W)^2 \sqrt{\pi}} \frac{1}{t^{3/2}} \exp[-(\sqrt{W} - \sqrt{w})^2\, t] \end{aligned} \tag{26}$$

One observes here an additional relaxation time $\tau_2 > \tau_1$, which is given by

$$\tau_2 = \{w + W - [4wW + (c + w - W)^2]^{1/2}\}^{-1}$$

The first term in Eq. (26) is the dominant one at large times and the decay is thus of the exponential type.

(iii) Finally, if $c > W - w$, then the pumping is more efficient than the flow due to the asymmetry. The asymptotics of $p_0(t)$ is given by

$$\begin{aligned} p_0(t) \sim & \frac{c + w - W}{[4wW + (c + w - W)^2]^{1/2}} \\ & \times \exp(-t\{w + W + [4wW + (c + w - W)^2]^{1/2}\}) \\ & + \frac{(wW)^{1/4}}{(c + w - W)^2 \sqrt{\pi}} \frac{1}{t^{3/2}} \exp[-(\sqrt{W} - \sqrt{w})^2 t] \end{aligned} \tag{27}$$

where τ_1 and

$$\tau_2' = \{w + W + [4wW + (c + w - W)^2]^{1/2}\}^{-1} < \tau_1 < \tau_2$$

are now the two characteristic times. The second term in Eq. (27) is the dominant one at large times and the decay is thus of the exponential type with an inverse power-law prefactor.

5. RESULTS FOR A CHAIN WITH A LOCAL RANDOM FORCE

The effective transfer rates now are random variables. It has been shown in ref. 9 that they obey Riccati differential equations, which play the role of Langevin equations with a (spatially-dependent) multiplicative random noise. Their stationary (i.e., position-independent) probability densities Π^+ and Π^- can be determined. However, on a lattice this can only be done via the use of an asymptotic matching procedure, while in the continuous limit the distributions Π^+ and Π^- can be determined exactly. Of course, at large times the results are equivalent, both discrete and continuous models belonging to the same universality class. In order to have complete explicit results we shall therefore consider the continuous limit.

As a result, the normalized probability density of the transfer rates corresponding to the particle situated at the right of the origin can be obtained from ref. 9 provided that one takes into account the fact that now the bias is directed toward the origin (which amounts to changing μ into $-\mu$ in the result of ref. 9)

$$\Pi^+(G^+) = \frac{E^{\mu/2}}{2K_\mu(\sqrt{E})} \exp\left[-\frac{1}{2}\left(G^+ + \frac{E}{G^+}\right)\right](G^+)^{-\mu-1} \tag{28}$$

Here $E = 2t_1 z$ denotes the reduced variable associated with the Laplace variable z, and $\sqrt{E}$ is defined as usual with the cut on the semi-infinite negative real axis; the result involves the modified Bessel function of order μ, K_μ.[10] Similarly, the normalized probability density of the transfer rates corresponding to the particle situated at the left of the origin is obtained from[9]

$$\Pi^-(G^-) = \frac{E^{\mu/2}}{2K_\mu(\sqrt{E})} \exp\left[-\frac{1}{2}\left(G^- + \frac{E}{G^-}\right)\right](G^-)^{-\mu-1} \tag{29}$$

Note that the two distributions Π^+ and Π^- are here identical, in contradistinction with the biased chain case.

5.1. Disordered Chain without Trap

In the continuous medium the Laplace transform of $p(0, T)$ is simply, for a given configuration of the disordered medium,

$$P(0, E) = \int_0^\infty dE\, e^{-ET} p(0, T) = \frac{1}{G^+(0, E) + G^-(0, E)} \tag{30}$$

The average value of this quantity can be easily calculated since the probability densities of $G^+(0, E)$ and $G^-(0, E)$ are known. One has to compute

$$\langle P(0, E)\rangle = \int_0^\infty \int_0^\infty dx\, dy \frac{1}{x+y} \times \frac{\exp[-\frac{1}{2}(x + E/x)] \exp[-\frac{1}{2}(y + E/y)]}{4E^{-\mu} K_\mu^2(\sqrt{E})} x^{-\mu-1} y^{-\mu-1} \tag{31}$$

a formula which can be recast into the simple integral

$$\langle P(0, E)\rangle = \frac{1}{2}\int_1^\infty ds\, s^\mu \frac{K_\mu^2(\sqrt{Es})}{K_\mu^2(\sqrt{E})} \tag{32}$$

which in turn yields, for any value of E, the closed expression[11]

$$\langle P(0, E)\rangle = \frac{1}{4\mu + 2}\left[\frac{K_{\mu+1}^2(\sqrt{E})}{K_\mu^2(\sqrt{E})} - 1\right] \tag{33}$$

At small E one gets

$$\langle P(0, E)\rangle \simeq \frac{1}{E}\frac{2\mu^2}{2\mu+1} \tag{34}$$

Thus $\langle P(0, T)\rangle$ tends toward a constant at large times,

$$\langle P(0, T)\rangle \sim \frac{2\mu^2}{2\mu+1} \tag{35}$$

It is interesting to discuss the corresponding dynamics, that is, the way in which $\langle P(0, T)\rangle$ tends toward its limit (35). This can be done by properly looking at the analytical properties at small E of the ratio of Bessel functions

$$\frac{K_{\mu+1}(\sqrt{E})}{K_\mu(\sqrt{E})} \tag{36}$$

which is involved in formula (33). Note first that, since $K_\mu(z)$ has no zeros for $-\pi/2 \leqslant \operatorname{Arg} z \leqslant \pi/2$, $K_\mu(\sqrt{E})$ cannot vanish for $-\pi < \operatorname{Arg} E < \pi$. Therefore no pole contributes to the Laplace inversion and no exponential decay can occur. The ratio (36) is a multiple-valued function with the origin as a branch point, and gives rise to cut contributions introducing power-law time tails. Keeping only the leading one among the single-valued terms and the leading one among the multiform terms, one has

$$\frac{K^2_{\mu+1}(\sqrt{E})}{K^2_\mu(\sqrt{E})} \sim \frac{4\mu^2}{E}\left[1 + 2^{1-2\mu}\frac{\Gamma(1-\mu)}{\mu\Gamma(\mu)}E^\mu\right] \tag{37}$$

which yields for $\langle P(0, E)\rangle$ the expansion

$$\langle P(0, E)\rangle \sim \frac{2\mu^2}{2\mu+1}\frac{1}{E} + \frac{2\mu}{2\mu+1}2^{1-2\mu}\frac{\Gamma(1-\mu)}{\Gamma(\mu)}E^{\mu-1} + \cdots \tag{38}$$

One thus gets for $\langle P(0, T)\rangle$ the following asymptotic behavior[12]:

$$\langle P(0, T)\rangle \sim \frac{2\mu^2}{2\mu+1} + \frac{2\mu}{2\mu+1}2^{1-2\mu}\frac{T^{-\mu}}{\Gamma(\mu)} + \cdots \tag{39}$$

So $\langle P(0, T)\rangle$ decreases toward its final value following a power law of time, with an exponent $-\mu$ which is only a function of disorder and asymmetry.

Let us now compare the results (22) and (39), which respectively correspond to the ordered and to the disordered situations. First,

$\lim_{T \to \infty} \langle p(0, T) \rangle = 2\mu^2/(2\mu + 1)$ is an increasing function of μ; the largest possible value of this quantity is thus obtained in the ordered case (i.e., in the limit of infinite μ). More interesting is the comparison between the two dynamics. The dynamics is exponential (with an inverse power-law prefactor) in the ordered case, while it follows a power law of time in the disordered one. The characteristic duration of the attraction of the particle by the center is thus much larger in the presence of disorder. In other words, on the average the dynamics is slowed down by the disorder. One recovers here a result analogous to the one previously obtained on a biased chain.[9]

5.2. Disordered Chain with Trap

Taking the continuous limit of Eq. (11), one now has, for a given configuration of the disordered medium,

$$P(0, E) = \frac{1}{G^+(0, E) + G^-(0, E) + 2t_1/\tau_c} \tag{40}$$

where, as indicated after Eq. (7), $\tau_c = (x_1/a)\, c^{-1}$ is the characteristic time linked to the trap. Using the probability distributions of $G^+(0, E)$ and $G^-(0, E)$, one obtains the average value of $P(0, E)$ as

$$\langle P(0, E) \rangle = \int_0^\infty \int_0^\infty dx\, dy \frac{1}{x + y + 2t_1/\tau_c} \times \frac{\exp[-\frac{1}{2}(x + E/x)] \exp[-\frac{1}{2}(y + E/y)]}{4E^{-\mu} K_\mu^2(\sqrt{E})} x^{-\mu-1} y^{-\mu-1} \tag{41}$$

a formula which can be recast into the simple integral

$$\langle P(0, E) \rangle = \frac{1}{2} \int_1^\infty ds \exp\left[-(s-1)\frac{t_1}{\tau_c}\right] s^\mu \frac{K_\mu^2(\sqrt{Es})}{K_\mu^2(\sqrt{E})} \tag{42}$$

One first verifies that

$$\lim_{T \to \infty} \langle P(0, T) \rangle = \lim_{E \to 0} E \langle P(0, E) \rangle = 0 \tag{43}$$

as it should, since a trap is present. As before, since $K_\mu(\sqrt{E})$ has no zero for $-\pi < \operatorname{Arg} E < \pi$, the only contribution arises from the cut. The dynamics at large times is governed by the dominant multiform term, that is, by

$$2^{-2\mu} E^\mu \frac{\Gamma(1-\mu)}{\Gamma(\mu+1)} \left[\frac{\tau_c}{t_1} - \left(\frac{\tau_c}{t_1}\right)^{\mu+1} \exp\left(\frac{t_1}{\tau_c}\right) \Gamma\left(\mu+1, \frac{t_1}{\tau_c}\right)\right] \tag{44}$$

One thus gets for $\langle p(0, T)\rangle$ the following asymptotic behavior[12]

$$\langle p(0, T)\rangle \sim \frac{1}{2^{2\mu}\Gamma(\mu)}\left[\left(\frac{\tau_c}{t_1}\right)^{\mu+1} \exp\left(\frac{t_1}{\tau_c}\right)\Gamma\left(\mu+1, \frac{t_1}{\tau_c}\right) - \frac{\tau_c}{t_1}\right] T^{-(\mu+1)} \tag{45}$$

So $\langle p(0, T)\rangle$ decreases toward zero following a power law in time, with the exponent $-(\mu+1)$.

Let us now compare the results (24), (26), and (27) on the one hand, and (45) on the other hand, which respectively correspond to the ordered and disordered situations. Since there is a trap, $\lim_{t\to\infty} p_0(t)$ (in the ordered medium) and $\lim_{T\to\infty} \langle p(0, T)\rangle$ (in the disordered one) are zero, as should be the case. As for the dynamics, it is exponential for the ordered medium (with in certain cases an inverse power-law prefactor), while it follows a power law of time for the disordered one. In the presence of a trap the dynamics is also slowed down by the disorder. Note that this dynamics follows a $T^{-(\mu+1)}$ law in the presence of a trap, while it follows a $T^{-\mu}$ law in its absence. The presence of the trap speeds up the decay toward the final value. This behavior on a disordered chain with a trap may seem surprising at first sight. Indeed, in the limit $\tau_c \to 0$ one would have expected an exponentially decreasing law, since the particle, initially located at the origin, would be absorbed by the trap before having left it. But this is not the case. Among the possible configurations of the chain, there exist configurations for which the probability of leaving the origin is larger than the probability of being absorbed, whatever τ_c. The particle then can leave the origin and, as a result, the corresponding dynamics goes like $T^{-(\mu+1)}$. Since this variation is slower than an exponential, it governs the final dynamics. The coefficient of the $T^{-(\mu+1)}$ law may thus be viewed as a kind of measure of the number of chains allowing for some motion before complete absorption by the trap. Therefore, this coefficient has to vanish when $\tau_c \to 0$, which is indeed the case. Note that the time scale after which this regime appears diverges when $\tau_c \to 0$.

6. CONSEQUENCES ON THE TRANSFER OF ENERGY IN A PHOTOSYNTHETIC SYSTEM

As indicated in the introduction, the model with one trap is relevant in the problem of photosynthesis. The trapping site corresponds to the reaction center, and the other sites correspond to the antenna chlorophyll molecules.[3,4]

The amount of energy conserved within the chain, as measured by the sum of probabilities of presence of the particle on the different sites

$s(t)=\sum_{n=-\infty}^{\infty} p_n(t)$, is proportional to the measured fluorescence intensity. Because of the existence of the trap, $s(t)$ decays to zero as $t \to \infty$. Summing up the master equations (7) corresponding to the different probabilities $p_n(t)$, one gets

$$\frac{d}{dt} s(t) = -c p_0(t) \tag{46}$$

This equation shows that $s(t)$ always has a limit for $t \to \infty$. Indeed, $p_0(t)$ must tend to 0 and $s(t)$ is a bounded, decreasing function. One has

$$s(t) = 1 - c \int_0^t dt' \, p_0(t') \tag{47}$$

The Laplace transform of this quantity is

$$S(z) = \frac{1}{z} - c \frac{1}{z} P_0(z) \tag{48}$$

In the ordered case one easily verifies by looking at Eq. (16) that, since $W > w$,

$$\lim_{t \to \infty} s(t) = \lim_{z \to 0} zS(z) = 0 \tag{49}$$

In the disordered case (in the continuous limit), looking carefully at the exact formula (42), and keeping in the expansions at small E of the modified Bessel functions both the entire series in powers of E [let us call it $\Sigma(E)$] and the dominant multiform term, one gets

$$\langle P(0, E) \rangle \sim \Sigma(E) + \text{Cste} \cdot E^{\mu} \tag{50}$$

where

$$\Sigma(E) \sim \frac{\tau_c}{2t_1} + \cdots \tag{51}$$

Translating this result to a discrete lattice, one would obtain for $\langle P_0(z) \rangle$ the sum of an entire series in powers of z and of some multiform terms, the dominant one varying like z^{μ}. [Indeed, the exponents in the dominant multiform term, which determine the behavior at large times, are the same in the discrete and in the continuous models, which ensures the presence of the term proportional to z^{μ} in $\langle P_0(z) \rangle$.] As for the entire series, it begins by a constant term equal to $(1/c)$.[6] Now, looking at $S(z)$ as given by formula (49), one easily sees that the constant terms in the numerator

[6] This can also be seen by looking at the small-z behavior of $G_0^+(z)$ and $G_0^-(z)$, showing that for any sampling, $P_0(z=0) = 1/c$.

balance each other and that one is left with the sum of an entire series beginning with a constant and of a term proportional to $z^{\mu-1}$. Thus

$$\lim_{t\to\infty} s(t) = \lim_{z\to 0} zS(z) = 0 \tag{52}$$

Due to the presence of the trap, $s(t)$ tends here also toward zero, in spite of the fact that the motion of the particle toward the trap is slowed down by the disorder. At large times it follows from the result (45) that $s(t)$ behaves as $t^{-\mu}$.

The other quantity of interest in the problem of photosynthesis is the total average lifetime of the particle before it is captured by the trap. It is given by $\lim_{t\to\infty} \theta(t)$, where

$$\theta(t) = \int_0^t dt'\, s(t') \tag{53}$$

The asymptotic value of this integral is given by

$$\lim_{t\to\infty} \theta(t) = \lim_{z\to 0} S(z) \tag{54}$$

In the ordered case, this asymptotic value is equal to

$$\lim_{t\to\infty} \theta(t) = c^{-1}\frac{W+w}{W-w} \tag{55}$$

In the disordered case, taking into account the fact that $s(t)$ behaves as $t^{-\mu}$ at large times, one finds that $\theta(t)$ behaves as $t^{-\mu+1}$ (up to an additive constant). Its final value is thus either a constant (for $\mu > 1$, i.e., in situations of relatively weak disorder) or infinite (for $\mu < 1$, i.e., in situations of relatively strong disorder). It is interesting to note that the effect of disorder on $\theta(t)$ depends on the value of the parameter μ.

In closing this section, let us recall that, in modeling photosynthetic systems, one usually introduces additional deexcitation channels in order to describe various intramolecular processes at each site.[3,4] Thus, e.g., in the discrete case, one assumes an additional term $-kP_n(t)$ in Eq. (7), with k being a site-independent rate constant. The preceding discussion can easily be generalized to include this new possibility of deexcitation. Namely, it is sufficient to multiply our results for $p_n(t)$ by a factor e^{-kt} [which amounts to shifting z into $z+k$ in the Laplace transform $P_n(z)$]. Then, of course, the total probability for the excitation to escape through the trap site (quantum yield for this site) will be less than one, namely

$$\eta_0 = (c+k)\int_0^\infty p_0(t)\,dt = (c+k)\lim_{z\to 0} P_0(z+k) \tag{56}$$

with $P_0(z)$ as given by Eq. (16) or

$$\eta_0 = \frac{c+k}{c+w-W+[(k+w+W)^2-4wW]^{1/2}} \tag{57}$$

in the ordered case. As for the disordered case, when these channels are taken into account, the quantity $s(t)$ behaves at large times as $t^{-\mu}\exp(-kt)$. The integral (53) yielding the average lifetime of the particle before it is captured by the trap is then finite for any μ. The quantum yield η_0 for the trap site could be derived along similar lines using $\langle P(0, E)\rangle$ as given by Eq. (42), with $E = 2t_1/\tau_k$, $\tau_k = (x_1/a)\,k^{-1}$.

7. CONCLUSION

We have studied the random–random walk of a particle on a chain with an attractive center, possibly trapping. The hopping rates were taken either as ordered or disordered. The particle was assumed to be located on the attractive center at initial time. When the possibility of trapping is taken into account, this model is relevant for the description of the transfer of energy in a photosynthetic system. Using the equivalent transfer rates technique, we have determined the asymptotic behavior of the probability of the presence of the particle at its initial point, in both ordered and disordered situations, without the trap and with the trap. As a result, disorder slows down the motion, as in the previously studied case of a biased chain.

In the presence of a trap, the amount of energy conserved in the chain tends toward zero at infinite time, as it should, even in the presence of disorder. The slowing down of the motion induced by the disorder has a marked influence on the average lifetime of the particle before it is captured by the trap.

However, it must be emphasized that the preceding results have been derived for a *random force* model. Actually, the results could *a priori* be different in the presence of other types of disorder. This question deserves further investigation.

REFERENCES

1. J. P. Bouchaud and A. Georges, *Phys. Rep.* **195**:127 (1990), and references therein.
2. B. D. Hughes and M. Sahimi, *J. Stat. Phys.* **29**:781 (1982).
3. L. Skála and V. Kapsa, *Chem. Phys.* **137**:77 (1989).
4. L. Skála and P. Jungwirth, *Chem. Phys.* **137**:93 (1989).
5. L. Skála and O. Bílek, *Phys. Lett. A* **125**:262 (1987).
6. J. Bernasconi and W. R. Schneider, *J. Phys. A* **15**:L729 (1983).

7. J. Bernasconi and W. R. Schneider, *Phys. Acta* **58**:597 (1985).
8. C. Aslangul, N. Pottier, and D. Saint-James, *J. Phys.* (Paris) **50**:899 (1989); Erratum, **50**:1581 (1989).
9. C. Aslangul, N. Pottier, and D. Saint-James, *Physica A* **164**:52 (1990).
10. M. Abramowitz and I. A. Stegun, *Handbook of Mathematical Functions* (National Bureau of Standards, Washington, D.C., 1964).
11. G. N. Watson, *A Treatise on the Theory of Bessel Functions* (Cambridge University Press, Cambridge, 1966).
12. M. Lavrentiev and B. Chabat, *Méthodes de la théorie des fonctions d'une variable complexe* (Editions Mir, Moscow, 1951).