Decay Times in One-Dimensional Chains

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We calculate the average residence time τ for a particle performing a random walk over a chain of N neighboring sites $i = 1,..., N$, with decay rates λ_i depending on the location of the particle in the chain. Exact results are given for some particular cases, while bounds on τ are given for specific initial conditions. In the continuum limit, various results from the literature are recovered or improved upon.

1. INTRODUCTION

Survival probabilities in the trappings of random walks is a topic of con-siderable interest (see, e.g., Ref. 1). Another related subject which has received a lot of attention recently is the calculation of mean first passage times (see, e.g., Ref. 2). From still another, more engineering point of view, we mention the interest of obtaining the residence time distribution in a chemical reactor.[3]

In this paper, we derive results for average decay times in one-dimen-sional chains. Depending on the way of viewing this decay, these results apply to one of the three above-mentioned classes of problems. Sym-bolically, a decay can be represented as a chemical reaction:

$$X \to A \tag{1}$$
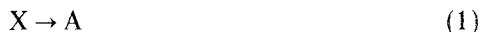
In the trapping problem, the occurence of a chemical reaction (1) will correspond to the trapping of the particle, changing its state from the free

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"X" to the trapped "A" state. In the first passage time problem, the average lifetime of a particle X is the average first passage time to the state A. Finally, in reactor theory, the symbolic reaction (1) can be regarded as a genuine chemical reaction in which the particle decays to an "inert" particle A or it can correspond to the exit of the particle out of the reaction volume in the case of a chemical reactor.

In the theory of radioactive decay or in chemical kinetics one usually defines a reaction rate λ as follows: $\lambda\,dt$ is the probability for a particle to change from the state X to the state A during a time interval dt. Note that we assume that this probability does not depend on the time that the particle has already been staying in the X state, i.e., the particle is not aging. In this case the average residence (or survival) time τ (mean first passage time to the state A) reads

$$\tau = \lambda^{-1} \tag{2}$$

In more complicated problems, such as those mentioned above, the decay rate λ is not a constant, but is a function of the position of the particle X in the system. As far as the geometry of the latter is concerned, we will mainly deal with a system formed by N adjacent sites or boxes i, $i = 1,..., N$ (see Fig. 1). The particles are performing a time-continuous Poisson random walk over these sites. A space-continuous one-dimensional system can be obtained in the appropriate limit. The decay rate is now a function of the cell i occupied by the particle, i.e., $\lambda = \lambda_i$. This dependence of λ on i can be due to the presence of inhomogeneities in a chemical system (e.g., temperature or concentration gradients) or due to the compartmentalization of the system (e.g., compartmentalized chemical reactors[3]). For the trapping problem, λ is nonzero only at the location of trapping centers, or the value of λ is changing from site to site if all the sites are trapping centers with different trapping activity. Note that the traps are imperfect, since trapping is not immediate. Finally, in the context of first passage time problems, we are dealing with the mean first passage time from a site in the one-dimensional chain to one or more sites on a neighboring chain.
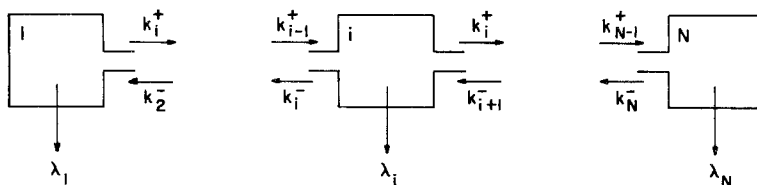

Fig. 1.   A one-dimensional chain of N adjacent sites, $k_i^{\pm}$ being the transition rates between sites i and $i \pm 1$ and λ_i being the decay rate in site 1.

Most of the papers in the literature deal with space-continuous models. However, it turns out that the calculations for the discrete model require very simple mathematics and the results for the space-continuous models are recovered in the appropriate limits.

The paper is organized as follows. In Section 2, we give general equations on the basis of which specific results will be derived in the subsequent sections. In Section 3, we give the mean first passage time τ from a given site in the N-dimensional chain to one of the sites on the neighboring chain, as well as the mean first passage time to the two sites at the extremity of the chain. In Section 4, we discuss the so-called weak and strong coupling limits. These limits correspond to letting the rate of exchange between adjacent boxes go to zero and to infinity, respectively. The corresponding residence times are τ^W and τ^S. It is shown that τ^W and τ^S are an upper bound and a lower bound, respectively, for the residence time τ for appropriate initial conditions. In Section 5, the first-order corrections to τ^W and τ^S are calculated. In Section 6, the continuum limit is discussed and we conclude the paper in Section 7 with some general remarks.

2. GENERAL FORMALISM

We will denote by $k_i^{\pm}\,dt$ the probability that a particle transfers from the site i to the adjacent site $i \pm 1$ (see Fig. 1) during a time interval of length dt. The exit or decay rates λ_i are nonnegative quantities and it will be supposed that at least one of them is different from zero. The probability $p(i, t)$, $i = 1,..., N$, that a particle is at site i at time t obeys the following gain–loss balance equation:

$$\frac{d}{dt}\, p(i, t) = k_{i+1}^- p(i + 1, t) + k_{i-1}^+ p(i - 1, t)$$

$$- (k_i^+ + k_i^-)\, p(i, t) - \lambda_i p(i, t), \qquad i = 1,..., N \qquad (3)$$

where, for convenience of notation, we have introduced the quantities $k_N^+ = k_1^- = 0$, i.e., we are considering the case of reflecting boundary conditions. The other quantities $k_i^{\pm}$ are supposed to be strictly positive. Note that the total probability $P(t)$ to be in one of the sites,

$$P(t) = \sum_{i=1}^{N} p(i, t) \qquad (4)$$

is decaying to zero in time

$$\frac{d}{dt} P(t) = - \sum_{i=1}^{N} \lambda_i p(i, t) < 0 \qquad (5)$$

expressing the obvious fact that a particle will ultimately decay. In fact $P(t)$ is the probability that a particle has a lifetime in the chain larger than t. The probability density $P_R(t)$ for a lifetime equal to t is given by

$$P_R(t) = -dP(t)/dt \tag{6}$$

and the average residence time reads

$$\tau = \int_0^\infty t P_R(t)\, dt = \int_0^\infty P(t)\, dt \tag{7}$$

For later convenience, we introduce the matrices K, Λ, and Q defined by their elements:

$$K_{ij} = k_{i+1}^- \delta_{j,i+1} + k_{i-1}^+ \delta_{j,i-1}$$
$$\qquad - (k_i^+ + k_i^-)\,\delta_{i,j}, \qquad i, j = 1,..., N \tag{8a}$$

$$\Lambda_{ij} = -\lambda_i \delta_{i,j} \tag{8b}$$

$$Q_{ij} = K_{ij} + \Lambda_{ij} \tag{8c}$$

The matrices K and Λ are nonpositive matrices, but the matrix Q is negative definite.[4] The solution of Eq. (3) can now be written in the form

$$p(i, t) = \sum_{j=1}^N (e^{Qt})_{ij}\, p_j^0 \tag{9}$$

where $p_j^0 = p(j, t = 0)$ is the initial condition. We will denote by X_{ir} and Y_{rj} the right and left eigenvectors of the matrix Q, corresponding to the eigenvalue μ_r, $r = 1,..., N$. For simplicity, we will suppose that the spectrum μ_r is nondegenerate. Equation (9) can thus be rewritten as follows:

$$p(i, t) = \sum_{j=1}^N \sum_{r=1}^N X_{ir} e^{\mu_r t} Y_{rj}\, p_j^0 \tag{10}$$

It is easily verified that the matrix Q can be symmetrized by a similarity transformation with the diagonal matrix S:

$$S_{ij} = \delta_{i,j}(p_i^{st})^{1/2} \tag{11}$$

where the p_i^{st}, $i = 1,..., N$, are the steady state distributions over the sites in the absence of a decay mechanism. The latter obey the detailed balance conditions:

$$k_i^+ p_i^{st} = k_{i+1}^- p_{i+1}^{st}, \qquad i = 1,..., N \tag{12}$$

More explicitly, we have

$$p_i^{\text{st}} = N k_i^+ \cdots k_{i-1}^+ k_{i+1}^- \cdots k_N^- \tag{13}$$

with N a normalization condition. As a consequence of the symmetrization property, we conclude that left and right eigenvectors of the matrix Q are related as follows:

$$X_{ir} = Y_{ri} p_i^{\text{st}} \tag{14}$$

Moreover, the eigenvalues μ_r are real and strictly negative. Taking these properties into account, we obtain by combining Eqs. (4), (7), (10), and (14)

$$\tau = -\sum_{i=1}^N \sum_{j=1}^N p_i^{\text{st}} G_{ij} p_j^0 \tag{15}$$

with the Green's function G_{ij} defined by

$$G_{ij} = \sum_{r=1}^N \frac{Y_{ri} Y_{rj}}{\mu_r} \tag{16}$$

Using the definition of an eigenvector, the detailed balance property (12), and the orthonormality of right and left eigenvectors, one can derive the following recurrence relation for $G_{i+1,j}$ in terms of $G_{l,j}$ with $l \leqslant i$, valid $\forall j$:

$$G_{i+1,j} - G_{i,j} = \frac{1}{k_i^+ p_i^{\text{st}}} \sum_{l=1}^i [\delta_{l,j} + \lambda_l p_l^{\text{st}} G_{lj}], \qquad i = 1, \dots, N-1 \tag{17}$$

For $i = N$, this relation has the following form:

$$\sum_{l=1}^N \lambda_l p_l^{\text{st}} G_{lj} = -1 \tag{18}$$

Equation (17) allows us in principle to determine $G_{i,j}$ in terms of $G_{1,j} = G_{j,1}$, hence in terms of G_{11}. The latter can be obtained from Eq. (18). Unfortunately, it seems to be impossible to obtain a simple compact solution of the recurrence relation (17) and (18). Nevertheless, they provide a good starting point to discuss particular cases, limits, and bounds on τ.

3. EXACT RESULTS FOR ONE, TWO, OR THREE TRAPPING CENTERS

We first consider the case in which only one of the decay rates is non-zero, i.e.,

$$\lambda_i = \lambda_{i*} \delta_{i,i*} \tag{19}$$

Consequently, we obtain from the identity (18)

$$G_{i*j} = -1/\lambda_{i*} p_{i*}^{st} \tag{20}$$

and the recurrence relation (17) becomes

$$G_{i+1,j} - G_{ij} = \frac{1}{k_i^+ p_i^{st}} \sum_{l=1}^{i} (\delta_{l,j} - \delta_{l,i*}) \tag{21}$$

From Eqs. (20) and (21), one obtains

$$G_{ij} = -\frac{1}{\lambda_{i*} p_{i*}^{st}} + \sum_{r=1}^{i-1} \frac{1}{k_r^+ p_r^{st}} \sum_{l=1}^{r} (\delta_{lj} - \delta_{li*})$$

$$- \sum_{r=1}^{i*-1} \frac{1}{k_r^+ p_r^{st}} \sum_{l=1}^{r} \delta_{lj}, \qquad i, j = 1,..., N \tag{22}$$

yielding for τ [cf. Eq. (15)]

$$\tau = \frac{1}{\lambda_{i*} p_{i*}^{st}} + \sum_{r=1}^{N-1} \frac{1}{k_r^+ p_r^{st}} \sum_{i=r+1}^{N} (p_i^{st} - \delta_{i,i*}) \sum_{j=r+1}^{N} (p_j^0 - \delta_{j,i*}) \tag{23}$$

Another case for which an exact solution can be obtained is for trapping centers at both extremities of the chain:

$$\lambda_i = \lambda_1 \delta_{i,1} + \lambda_N \delta_{i,N} \tag{24}$$

The discrete time version of this problem is the familiar gambler's ruin problem (for a more sophisticated discussion, see Ref. 1). Proceeding in a way analogous to the derivation of Eq. (23), we obtain

$$\tau = \left(\lambda_1 p_1^{st} + \lambda_N p_N^{st} + \lambda_1 p_1^{st} \lambda_N p_N^{st} \sum_{r=1}^{N-1} \frac{1}{k_r^+ p_r^{st}} \right)^{-1}$$

$$\times \left[1 + \frac{1}{2} \lambda_1 p_1^{st} \lambda_N p_N^{st} \sum_{r=1}^{N-1} \frac{1}{k_r^+ p_r^{st}} \sum_{q=1}^{N-1} \frac{1}{k_q^+ p_q^{st}} \right.$$

$$\times \left(\sum_{i=r+1}^{N} - \sum_{i=q+1}^{N} \right) p_i^{st} \left(\sum_{j=r+1}^{N} - \sum_{j=q+1}^{N} \right) p_j^0$$

$$\left. + \sum_{r=1}^{N-1} \frac{1}{k_r^+ p_r^{st}} \left(\lambda_1 p_1^{st} \sum_{i=r+1}^{N} p_i^{st} \sum_{j=r+1}^{N} p_j^0 + \lambda_N p_N^{st} \sum_{i=1}^{r} p_i^{st} \sum_{j=1}^{r} p_j^0 \right) \right] \tag{25}$$

The expressions (23) and (25) are complicated, but their generality allows us to investigate several interesting cases. For the particular case $i* = 1$ in

Eq. (23) or in the limit $\lambda_N \to 0$ in Eq. (25), we obtain the well-known result for the mean first passage time in the usual one-dimensional random walk to a fictitious box at zero[5,6]

$$\tau = \frac{1}{\lambda_1 p_1^{st}} + \sum_{r=1}^{N-1} \frac{1}{k_r^+ p_r^{st}} \sum_{i=r+1}^{N} p_i^{st} \sum_{j=r+1}^{N} p_j^0 \tag{26}$$

If all the rates are equal, $k_i^{\pm} = k$, and for initial conditions $p_i^0 = p_i^{st} = N^{-1}$, the results (23) and (25) simplify considerably. Equation (23) becomes

$$\tau = \frac{N}{\lambda_{i*}} + \frac{1}{k} \left[\frac{(N-1)(2N-1)}{6} + (i^* - 1)(i^* - N) \right] \tag{27}$$

For a trapping center with fixed activity $\lambda_{i*} = \lambda$, but positioned at random in the chain, $p(i^*) = N^{-1}$, we obtain for the doubly averaged residence time:

$$\langle \tau \rangle = \frac{N}{\lambda} + \frac{N^2 - 1}{6k} \tag{28}$$

For perfect trapping, $\lambda \to +\infty$, this result becomes

$$\langle \tau \rangle = \frac{N^2 - 1}{6k} \tag{29}$$

On the other hand, Eq. (25) reads for $k_i^{\pm} = k$ and $p_i^0 = p_i^{st} = N^{-1}$:

$$\tau = \frac{12Nk^2 + \lambda_1 \lambda_N (N-1)^2 (N-2) + 2k(\lambda_1 + \lambda_N)(N-1)(2N-1)}{12k[k(\lambda_1 + \lambda_N) + \lambda_1 \lambda_N (N-1)]} \tag{30}$$

and for perfect trapping (λ_1 and $\lambda_N \to +\infty$)

$$\tau = (N-1)(N-2)/12k \tag{31}$$

Note that for N large, the leading terms in the results for perfect and imperfect trapping are identical. For similar conclusions in a discrete time model, see Ref. (1).

Finally, we also mention the exact result for τ in the case of a chain with three sites, $N = 3$, under the simplified conditions $k_i^{\pm} \equiv k$ and $p_i^0 = p_i^{st} = \frac{1}{3}$:

$$\tau = \frac{9k^2 + 5k\lambda_1 + 5k\lambda_3 + 2k\lambda_2 + \lambda_1 \lambda_2 + \lambda_1 \lambda_3 + \lambda_2 \lambda_3}{3(k^2\lambda_1 + k^2\lambda_2 + k^2\lambda_3 + k\lambda_1\lambda_2 + k\lambda_2\lambda_3 + 2k\lambda_1\lambda_3 + \lambda_1\lambda_2\lambda_3)} \tag{32}$$

Further applications of Eqs. (23) and (25) will be given in Section 6, where the continuum limit is discussed.

4. BOUNDS ON τ

The stationary state distribution p_i^{st}, $i = 1,..., N$, is determined by detailed balance, Eq. (12), and by normalization. One can, without altering the values of these quantities, speed up or slow down the rates of exchange by replacing $k_i^{\pm}$ by $Ck_i^{\pm}$ with $C > 0$. Two extreme cases are worth considering.[7] In the so-called strong coupling limit, we let $C \to +\infty$. It is clear that in this case the initial probability distribution p_i^0 relaxes instantaneously to the stationary state distribution p_i^{st}. Due to the infinity frequent transitions between the sites, we expect that a particle will effectively see an average decay rate $\bar{\lambda}$:

$$\bar{\lambda} = \sum_{i=1}^{N} \lambda_i p_i^{st} \tag{33}$$

and its average residence time will be

$$\tau^S = 1 \left/ \sum_{i=1}^{N} \lambda_i p_i^{st} \right. \tag{34}$$

The other extreme case corresponds to taking the limit $C \to 0$, thereby virtually eliminating the exchanges between boxes. In this so-called weak coupling limit, the lifetime of a particle is the average decay time in the site that it is occupying at $t = 0$, hence

$$\tau^W = \sum_{i=1}^{N} \frac{p_i^0}{\lambda_i} \tag{35}$$

A rigorous derivation of Eqs. (34) and (35) will be given in the next section.

Generally speaking, it is clear that τ^W can be larger or smaller than τ^S, depending on the initial conditions. To obtain bounds on τ, we will specify further the initial conditions. A situation of practical interest is the case in which the initial probability distribution p_i^0 is equal to the steady state distribution p_i^{st} for all $i = 1,..., N$. Such a situation is realized, e.g., if the trapping mechanisms are activated after the steady state distribution has been reached or if excitations are produced at random places in a system with constant rates $k_i^+ \equiv k$ (hence $p_i^0 = p_i^{st} = N^{-1}$). In this case, the average residence time is given by [cf. Eq. (15)]

$$\tau = -\sum_{i=1}^{N} \sum_{j=1}^{N} p_i^{st} G_{ij} p_j^{st} \tag{36}$$

We will show that τ is now a monotonically decreasing function of the parameter C, starting from its upper limit τ^W at $C = 0$ and approaching its

lower limit τ^S when $C \to +\infty$. To prove this property, we will make use of the matrix notation introduced in Eq. (8). It can easily be seen that the Green's functions G_{ij} introduced in Eq. (16) are the matrix elements of the symmetric matrix

$$G = S^{-2} \frac{1}{K + \Lambda} \tag{37}$$

where S is the diagonal matrix (11). Introducing the parameter C adds a factor C to the matrix K, so that the corresponding $G(C)$ is given by

$$G(C) = S^{-2} \frac{1}{CK + \Lambda} \tag{38}$$

The matrices $G(C)$ are symmetric and negative definite when $C > 0$.

The expression (36) for the residence time has the form of a quantum mechanical "expectation value" of the positive-definite matrix $-G(C)$ in the "state vector" $\bar{p}^{st}$. Let us consider two values C_1 and C_2 of the parameter C with $0 \leqslant C_1 < C_2$. The difference of the corresponding residence times equals

$$\tau(C_2) - \tau(C_1) = -\bar{p}^{st} \cdot [G(C_2) - G(C_1)] \cdot \bar{p}^{st} \tag{39}$$

We will show that $\tau(C_2) \leqslant \tau(C_1)$. To prove this, it is sufficient to show that the matrix $G(C_2) - G(C_1)$ in (39) is a positive matrix. From

$$(C_1 K + \Lambda) S^2 - (C_2 K + \Lambda) S^2 = (C_1 - C_2) K S^2 \tag{40}$$

and the properties of K and S, it follows that the difference of the two operators on the left-hand side of Eq. (40) is a positive matrix.

We now use a theorem proven in Appendix B. From this theorem it follows that the difference of the inverse of these operators is a negative matrix. But the inverse operators are just $G(C_1)$ and $G(C_2)$. This shows that $G(C_1) - G(C_2)$ is a negative operator, from which it follows that $\tau(C_2) \leqslant \tau(C_1)$. From the derivation in Appendix B it can also be seen that the strict inequality sign $\tau(C_2) < \tau(C_2)$ will hold unless the diagonal matrix Λ is a constant matrix. In this case $\tau^W = \tau^S$ and τ is independent of C. This result is corroborated by calculating the difference between τ^W and τ^S from Eqs. (34) and (35). This yields

$$\tau^W - \tau^S = \tau^S \sum_{i=1}^{N} \sum_{j=1}^{N} p_i^{st} p_j^{st} \frac{(\lambda_i - \lambda_j)^2}{2\lambda_i \lambda_j} \tag{41}$$

which is always positive unless all λ_i are equal.

5. CORRECTIONS TO THE WEAK AND STRONG COUPLING LIMITS

In the strong coupling limit, we have to replace k_i^+ by Ck_i^+ in Eq. (17) and let C go to infinity. Since the matrix elements $\lambda_i p_i^{st} G_{ij}$ are all negative and have to satisfy Eq. (18), they are necessarily bounded. Hence in the limit $C \to +\infty$, the rhs of Eq. (17) goes to zero and we conclude that all the matrix elements G_{ij} are equal. From Eq. (18), we then find

$$G_{ij} \equiv G^S = -\frac{1}{\sum_{i=1}^{N} \lambda_i p_i^{st}} \tag{42}$$

yielding

$$\tau^S = -\sum_{i=1}^{N} \sum_{j=1}^{N} p_i^{st} G_{ij} p_j^{st} = \frac{1}{\sum_{i=1}^{N} \lambda_i p_i^{st}} = \frac{1}{\bar{\lambda}} \tag{43}$$

in accordance with the intuitive arguments given in the preceding section.

In order to obtain the first-order correction, we write

$$G_{ij} = G^S + \delta G_{ij} \tag{44}$$

Inserting this ansatz into Eqs. (17) and (18) and taking into account that the rhs of Eq. (17) is small (of order δ), we obtain

$$\delta G_{i+1,j} - \delta G_{i,j} = \frac{1}{k_i^+ p_i^{st}} \sum_{l=1}^{i} (\delta_{l,j} + \lambda_l p_l^{st} G^S) \tag{45}$$

$$\sum_{i=1}^{N} \lambda_i p_j^{st} \delta G_{ij} = 0 \tag{46}$$

These recurrence relations can be easily solved, leading to the following approximate result for the residence time close to strong coupling:

$$\tau \approx \tau^S + (\tau^S)^2 \sum_{r=1}^{N-1} \frac{1}{k_r^+ p_r^{st}} \sum_{i=r+1}^{N} (\bar{\lambda} - \lambda_i) p_i^{st} \sum_{j=r+1}^{N} (\bar{\lambda} p_j^0 - \lambda_j p_j^{st}) \tag{47}$$

Note that if $p_j^0 = p_j^{st}$, then the first-order correction to the strong coupling result τ^S is nonnegative, in accordance with the fact that τ^S is a lower bound on τ. The problem of calculating corrections to the strong coupling result for space-continuous systems has also been addressed in Refs. 8 and 9. The relation with our results is discussed in the next section.

Proceeding in an analogous way, we obtain the following first-order correction to the weak coupling limit:

$$G_{ij}^W = -\frac{\delta_{ij}^{Kr}}{\lambda_i p_i^{st}} \tag{48}$$

and

$$\tau \approx \tau^W - \sum_{r=2}^{N} \frac{\lambda_r - \lambda_{r-1}}{\lambda_r \lambda_{r-1}} \left(p_{r-1}^0 \frac{k_{r-1}^+}{\lambda_{r-1}} - p_r^0 \frac{k_r^-}{\lambda_r} \right) \tag{49}$$

Note that if $p_r^0 = p_r^{st}$, then the first-order correction is nonpositive, in accordance with the fact that τ^W is an upper bound on τ.

6. THE CONTINUUM LIMIT

Many results in the literature refer to the problem of trapping in space-continuous systems. In order to compare with these results, we take a continuum limit in the following way. We introduce an x axis along which the N boxes are lined up (see Fig. 2). Moreover, we call η the width of one box. We then take the limit $N \to \infty$, $\eta \to 0$ with $N\eta = L$ equal to the constant length of the entire system. The product $i\eta$ becomes a continuous variable $x \in [0, L]$. The transition rates will diverge, but the quantities

$$\tfrac{1}{2}(k_i^+ + k_i^-)\,\eta^2 = D(x), \qquad \tfrac{1}{2}(k_i^+ - k_i^-)\,\eta = w(x) \tag{50}$$

will be taken constant. $D(x)$ corresponds to the diffusion coefficient of the particle, and $v(x)$,

$$v(x) = 2w(x) - dD(x)/dx$$

to its systematic velocity. The decay rate λ_i becomes a continuous function $\lambda(x)$ of x. The probability density $P(x, t)$ to find a particle at position x,

$$P(x, t) = \lim_{\substack{\eta \to 0 \\ i\eta = x}} \frac{p(i, t)}{\eta} \tag{51}$$

obeys the following Fokker–Planck decay equation

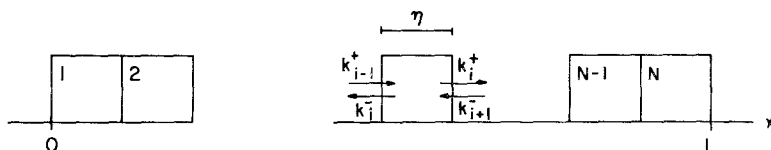$$\partial_t P(x, t) = -\frac{\partial}{\partial x} j(x, t) - \lambda(x)\, P(x, t) \tag{52}$$

Fig. 2. In the appropriate limit the discrete system of N cells goes over into a continuous system. In the same limit the random walk over the cells converges to a diffusion process.

with the probability flux $j(x, t)$ given by

$$j(x, t) = \left[v(x) - D(x) \frac{\partial}{\partial x} \right] P(x, t) \tag{53}$$

and with reflecting boundary conditions:

$$j(0, t) = j(L, t) = 0 \tag{54}$$

The average residence time for this space-continuous system can be obtained by carrying out the above-described limiting procedure on the results obtained in the previous sections. For example, the correction to the strong result, Eq. (47), becomes

$$\tau^S = \left[\int_0^L \lambda(x) \, P^{st}(x) \, dx \right]^{-1} = \frac{1}{\bar{\lambda}} \tag{55}$$

$$\tau = \tau^S + (\tau^S)^2 \int_0^L dy$$

$$\times \frac{\int_y^L dy' \, [\bar{\lambda} - \lambda(y')] \, P^{st}(y') \int_y^L dy'' \, [\bar{\lambda} P^0(y'') - \lambda(y'') \, P^{st}(y'')]}{D(y) \, P^{st}(y)} \tag{56}$$

with $P^{st}(x)$ given by (N is a normalization constant)

$$P^{st}(x) = N \exp \int^x dx' \frac{v(x')}{D(x')} \tag{57}$$

For initial conditions $P^0(x) = P^{st}(x)$, this result is identical to the one obtained by Wilemski and Fixman[8] [see also Eqs. (3.13) and (3.25) in Ref. 9]. In Ref. 9 a calculation procedure is outlined for general initial conditions, but no closed-form expression is given for the first-order correction to τ^S.

The weak coupling result, Eq. (49), reduces to

$$\tau^W = \int_0^L \frac{P^0(x)}{\lambda(x)} \, dx \tag{58}$$

$$\tau \approx \tau^W - \int_0^L dx \frac{\lambda'(x)}{\lambda^3(x)} \left\{ \left[v(x) - D(x) \frac{d}{dx} \right] P^0(x) \right.$$

$$\left. + D(x) \frac{\lambda'(x)}{\lambda(x)} P^0(x) \right\} \tag{59}$$

A prime stands for the derivative with respect to the argument.

The results (56) and (59) can, for instance, be used to fit the numerical results obtained by Agmen and Hopfield[7] for the special case of a harmonically bound particle and an exponential decay rate $\lambda(x)$. As another illustration of our results, we discuss an exactly solvable model in Appendix A.

In discussing the continuum limit of Eq. (23), two cases can be distinguished.

Case 1. $i^* = 1$. Setting $\lambda_1 \eta = \lambda$, combined with the above-described limit, we find that the probability density $P(x, t)$ obeys a Fokker–Planck equation:

$$\partial_t P(x, t) = -\frac{\partial}{\partial x} j(x, t) \tag{60}$$

with a reflecting boundary condition at $x = L$,

$$j(L, t) = 0 \tag{61a}$$

and a radiation boundary condition at $x = 0$,

$$j(0, t) = +\lambda P(0, t) \tag{61b}$$

The average survival time is obtained by applying the same limit procedure to Eq. (23):

$$\tau = \frac{1}{\lambda P^{st}(0)} + \int_0^L dy \, \frac{1}{D(y) \, P^{st}(y)} \int_y^L P^{st}(u) \, du \int_y^L P^0(v) \, dv \tag{62}$$

This result is identical with Eq. (6) in the paper by Deutch[9] (for dimension $d = 1$). The particular case $P^0 = P^{st}$ was obtained earlier by Szabo et al.[10] [Eq. (2.20) in Ref. 10].

Case 2. $i^* \neq 1$ and $i^* \neq N$. Noting that

$$\lambda_i = \lambda_{i^*} \delta_{ii^*}^{Kr} \xrightarrow[\eta \to 0]{} \lambda \delta(x - x_0) \qquad \text{with} \quad \lambda_{i^*} \eta = \lambda, \quad i^* \eta = x_0$$

we obtain for $P(x, t)$ the following Fokker–Planck equation with a delta-function sink with strength λ at $x = x_0$:

$$\partial_t P(x, t) = -\frac{\partial}{\partial x} j(x, t) - \lambda \delta(x - x_0) \tag{63}$$

The corresponding mean survival time reads

$$\tau = \frac{1}{\lambda P^{st}(x_0)} + \int_0^L dx \frac{1}{D(x)\,P^{st}(x)} \int_x^L du\, [P^{st}(u) - \delta(u - x_0)]$$

$$\times \int_x^L du\, [P^0(u) - \delta(u - x_0)] \tag{64}$$

Note that a nonexplicit result for τ was also given by Szabo et al.[11] for the particular case $P^0(x) = P^{st}(x)$.

The continuum limit of Eq. (25), with $\lambda_1 \eta = \lambda$ and $\lambda_N \eta = \lambda'$, provides us with the average survival time for a system obeying the Fokker–Planck equation (60) with radiation boundary conditions at $x = 0$ and $x = L$:

$$j(0, t) = \lambda P(0, t) \tag{65a}$$

$$j(L, t) = \lambda' P(L, t) \tag{65b}$$

One finds

$$\tau = \left[\lambda P^{st}(0) + \lambda' P^{st}(L) + \lambda P^{st}(0)\, \lambda' P^{st}(L) \int_0^L \frac{dy}{D(y)\,P^{st}(y)} \right]^{-1}$$

$$\times \left\{ 1 + \frac{1}{2} \lambda P^{st}(0)\, \lambda' P^{st}(L) \int_0^L \frac{dx}{D(x)\,P^{st}(x)} \int_0^L \frac{dy}{D(y)\,P^{st}(y)} \right.$$

$$\times \left(\int_x^L - \int_y^L \right) du\, P^{st}(u) \left(\int_x^L - \int_y^L \right) dv\, P^0(v)$$

$$+ \int_0^L \frac{dx}{D(x)\,P^{st}(x)} \left[\lambda P^{st}(0) \int_y^L du\, P^{st}(u) \int_y^L dv\, P^0(v) \right.$$

$$\left. \left. + \lambda' P^{st}(L) \int_0^y du\, P^{st}(u) \int_0^y dv\, P^0(v) \right] \right\} \tag{66}$$

As a simple example, we consider the case of free diffusion, $D(x) = D = $ const, and $P^{st}(x) = L^{-1}$, for the initial conditions $P^{st}(x) = P^0(x)$. One obtains [cf. Eq. (30)]

$$\tau = \frac{12D^2 L + 4DL^2(\lambda + \lambda') + \lambda\lambda' L^3}{12D[D(\lambda + \lambda') + \lambda\lambda' L]} \tag{67}$$

In the limit $\lambda' \to 0$, one recovers the simple result for one radiation boundary condition at $x = 0$ and one reflecting boundary condition at $x = L$ [cf. also Eqs. (27) and (62)]:

$$\tau = L/\lambda + L^2/3D \tag{68}$$

Finally, we note that the corresponding results for perfect absorbing (or Smoluchowski) boundary conditions are obtained by letting λ and λ' go to $+\infty$ in the above results.

7. DISCUSSION

We have calculated the average residence time τ in a one-dimensional finite chain for several particular cases and limits. In the space-continuous limit, several results obtained previously in the literature are recovered or improved upon. In the general case, no compact expression for τ could be derived, but for useful initial conditions one can show that τ^W is an upper bound on τ while τ^S is a lower bound. For general initial conditions, one can only state that λ_{max}^{-1} is a lower bound on τ, where λ_{max} is the maximum of the λ_i, $i = 1,..., N$, respectively.

APPENDIX A

As an example of an exactly solvable model, we consider the following situation [cf. Eqs. (52)–(54)]:

$$v(x) = 0$$

$$D(x) = D = \text{const}$$

$$\lambda(x) = \lambda_1 \quad \text{for} \quad x \in [0, l_1] \tag{A.1}$$

$$\lambda(x) = \lambda_2 \quad \text{for} \quad x \in [l_1, L]$$

$$P(x, t = 0) = 1/L$$

The solution of (52) subject to the conditions (54) is a standard heat conduction problem. From its solution, one can calculate the average residence time:

$$\tau = \int_0^\infty dt\, t \left[-\frac{d}{dt} \int_0^L dx\, P(x, t) \right]$$

$$= \int_0^\infty dt \int_0^L dx\, P(x, t) \tag{A.2}$$

One thus obtains $(L = l_1 + l_2)$

$$\tau = \frac{l_1}{\lambda_1 L} + \frac{l_2}{\lambda_2 L}$$

$$- \frac{D}{L} \left(\frac{1}{\lambda_1} - \frac{1}{\lambda_2} \right)^2 \frac{\omega_1 \omega_2}{\omega_2 \coth(\omega_1 l_1) + \omega_1 \coth(\omega_2 l_2)} \tag{A.3}$$

with

$$\omega_1^2 = \lambda_1/D, \qquad \omega_2^2 = \lambda_2/D \tag{A.4}$$

In the weak coupling result, $D \to 0$, one finds $\tau = \tau^W$. In the strong coupling result $(D \to \infty)$ one obtains, including the first-order correction term,

$$\tau = \left[\lambda_1 \frac{l_1}{L} + \lambda_2 \frac{l_2}{L} - \frac{(\lambda_1 - \lambda_2)^2\, l_1^2 l_2^2}{3DL^2} + O\left(\frac{1}{D^2}\right) \right]^{-1} \tag{A.5}$$

which is in agreement with the general result, Eq. (56).

It is obvious from (A.3) that $\tau \leqslant \tau^W$. On the other hand, one finds after some algebra that

$$\tau^S \leqslant \tau \rightleftarrows \omega_2 \left(\coth x_1 - \frac{1}{x_1} \right) + \omega_1 \left(\coth x_2 - \frac{1}{x_2} \right) \geqslant 0$$

with $x_1 = \omega_1 l_1$ and $x_2 = \omega_2 l_2$. Since

$$\coth x - \frac{1}{x} \geqslant 0, \qquad x \geqslant 0$$

we conclude that τ^S is a lower bound on τ.

APPENDIX B

We prove the following theorem. If A and B are symmetric and positive-definite matrices and $(A - B)$ is a positive matrix, then $(A^{-1} - B^{-1})$ is a negative matrix.

The proof is based on the well-known identity

$$\frac{1}{B} - \frac{1}{A} = \frac{1}{A}(A - B)\frac{1}{A} + \frac{1}{A}(A - B)\frac{1}{B}(A - B)\frac{1}{A}$$

The two operators on the right-hand side are positive operators. This is easily seen by taking their expectation value in an arbitrary vector and using the property that all occurring operators are symmetric and positive. Note that the operator $B^{-1} - A^{-1}$ is not necessarily positive definite: its expectation value will be zero in the vectors $A\bar{V}_0$, where $\bar{V}_0$ is an eigenvector of $(A - B)$ with eigenvalue zero.

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