Non-Markovian reaction sites and trapping

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Most models of absorption sites for random walks or diffusion processes fall into one of two categories: (1) Perfect absorption, in which every encounter of a random walker with a trap produces a trapping event, and (2) imperfect absorption in which an encounter leads to a trapping event with probability $\alpha < 1$. We introduce the notion of a non-Markovian trap characterized by a set of probabilities $\{f_j\}$, where f_j is the probability that the jth encounter leads to a trapping event. Some consequences of this assumption are examined in the context of a one-dimensional trapping problem. It is shown that when the f_j have an associated finite first moment the asymptotic survivial probability goes like $n^{1/2} \exp(-an^{1/3})$ where n is the step number and a is a constant. This is equivalent to the results one would obtain with a Markovian model. However, when f_j is asymptotically proportional to $1/j^{1+\alpha}$ where $0 < \alpha < 1$ the survival probability falls off as $1/n^{\alpha}$.

I. INTRODUCTION

There has been considerable recent research on survival probabilities in the trapping of random walks.[1–27] Most analyses of this problem use the assumption of the perfectly absorbing trap, i.e., a single encounter of a random walker with a trap results in absorption. Many models of reaction rates starting from the analysis of Collins and Kimball[28] suggest that one needs to incorporate radiation boundary conditions to find physically realistic results for the Smoluchowski model.[29] This is equivalent, in random walk terminology, to imperfect trapping when a random walker encounters a trapping site. That is to say, the encounter of a random walker with a partial trap may or may not result in a trapping event. In this note we derive asymptotic results for the 1D model in which traps are partially absorbing and partially reflecting. Thus a random walker whose starting value lies within a given interval always remains within the same interval until it is finally trapped. The choice of reflection rather than transmission as an alternative to trapping allows us to derive a formal solution to the problem in closed form. It should be noted that if random walkers are allowed to pass through an absorbing point when they are not absorbed even the 1D problem presents great difficulties.

II. NON-MARKOVIAN TRAPPING

The nearly universal model for imperfect absorption is one in which an encounter of a random walker with a trap results in an absorption with some probability $\alpha < 1$ or survival with probability $1-\alpha$. More complicated models have recently been discussed by Monchick.[30] We will generalize this picture by defining f_j to be probability that absorption occurs at encounter j with a trap, conditional on survival until that encounter. Thus, for the random model described earlier, $f_j = \alpha(1-\alpha)^{j-1}$. However, more general cases can be considered, which allow us to model the possibility of energy changes due to collisions with absorbing points. These generally lead to what we might term non-Markovian absorption. To analyze the effects of such traps we will need the probabilities that more than j encounters are required for a trapping event. These will be denoted by F_j, where

$$F_j = \sum_{s=j+1}^{\infty} f_s. \tag{1}$$

For the random model characterized by a constant trapping probability $F_j = (1-\alpha)^j$. We will see later that important qualitative changes distinguish the cases in which the f_j have finite or infinite moments.

We will analyze a symmetric nearest neighbor random walk on a line in which the probability that a given site is a trap is equal to c. We calculate the asymptotic probability that a random walker placed uniformly on the line will survive for at least n steps. An initially randomly placed walker will find itself in an interval of $L = 1$ lattice points in which 0 and L are absorbing, with probability $p_L = c^2 L(1-c)^{L-1}$. Its starting point within the interval will be uniformly distributed and the random walker will remain in the same interval until its ultimate absorption at a trapping site. After a nonabsorbing encounter with a trapping site the random walker will either be at site 1 or $L-1$ depending on whether trapping site 0 or L has been visited. Let the survival probability of a random walker before an absorbing site encounter has occurred be denoted by S_n and let T_n be the probability that after a nonabsorbing encounter the random walker will survive at least n more steps. These probabilities are easily found to be

$$S_n = \frac{2}{L(L-1)} \sum_{j=0}^{[(L-1)/2]} \cos^n\left[\frac{\pi(2j+1)}{L}\right] \cot^2\left[\frac{\pi(2j+1)}{2L}\right], \tag{2}$$

$$T_n = \frac{4}{L} \sum_{j=0}^{[(L-1)/2]} \cos^n\left[\frac{\pi(2j+1)}{L}\right] \cos^2\left[\frac{\pi(2j+1)}{2L}\right],$$

where "[ ]" denotes "the largest integer contained in." These expressions can be derived from the Green's function for a random walk on an interval with two absorbing points. Let s_n be the probability that the first random walker-trap encounter takes place at step n and let t_n be the probability that the number of steps between two successive encounters

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is equal to n. These quantitites can be expressed in terms of S_n and T_n as

$$s_n = S_{n-1} - S_n, \quad t_n = T_{n-1} - T_n. \tag{3}$$

With the knowledge of these quantitites we can enumerate all possibilities that allow survival till step n. This quantity will be denoted by Ω_n and is given by

$$\Omega_n = S_n + F_1 \sum_{j=0}^{n} s_j T_{n-j} + F_2 \sum_{l=0}^{n} \sum_{j=0}^{l} s_j t_{l-j} T_{n-l} + \cdots . \tag{4}$$

The first term is the probability that no encounters have taken place by step n, the second is the probability that exactly one enounter has occurred without a trapping event, and so forth. Since the sums in Eq. (4) can be recognized as being in convolution form we can derive a relatively simple relation between the appropriate generating functions. Let $\Omega(z)$ be the generating function of the Ω_n, $S(z)$ that of the S_n, and so forth. Finally, let $F(z)$ be the generating function

$$F(z) = \sum_{n=1}^{\infty} F_n z^{n-1}. \tag{5}$$

Equation (4) implies that $\Omega(z)$ is given by

$$\Omega(z) = S(z) + s(z) T(z) F[t(z)] = S(z) + \beta(z), \tag{6}$$

where $\beta(z) = s(z)T(z)F[t(z)]$. Notice that because of Eq. (3), $s(z)$ and $t(z)$ are related to $S(z)$ and $T(z)$ by

$$s(z) = 1 - (1-z)S(z), \quad t(z) = 1 - (1-z)T(z). \tag{7}$$

Equation (6) is exact, and all terms in it contain L. The last step in our calculations will be to perform the integration (in the continuum limit) over L.

In deriving the contributions to the last term in Eq. (6) we will work in the limit of large L, since as was first observed by Grassberger and Procaccia[14] the asymptotic behavior is due to contributions from the large intervals. In the large L limit we can make the approximations

$$\begin{aligned}
&\cos^n\left[\frac{\pi(2j+1)}{L}\right] \\
&\quad\sim\left[1-\frac{\pi^2(2j+1)^2}{2L^2}\right]^n \sim \exp\left[-\frac{\pi^2(2j+1)^2 n}{2L^2}\right] \\
&\quad\times\cot^2\left[\frac{\pi(2j+1)}{2L}\right] \sim \frac{4L^2}{\pi^2}\cdot\frac{1}{(2j+1)^2} \\
&\quad\times\cos^2\left[\frac{\pi(2j+1)}{2L}\right] \sim 1,
\end{aligned} \tag{8}$$

so that

$$T_n \sim \frac{4}{L}\sum_{j=0}^{\infty} \exp\left\{-\frac{\pi^2(2j+1)^2 n}{2L^2}\right\}. \tag{9}$$

However, as only the large n behavior is of interest we can use the further approximation of neglecting all but the first term in this series. This allows us to write

$$T(z) \sim \frac{2}{L}\left(\frac{1+\rho}{1-z\rho}\right), \tag{10}$$

where

$$\rho = \exp\left(-\frac{\pi^2}{2L^2}\right). \tag{11}$$

In similar fashion we have

$$S(z) \sim \frac{8}{\pi^2}\cdot\frac{1}{(1-z\rho)} \tag{12}$$

while the remaining generating functions, $s(z)$ and $t(z)$ can be found from Eq. (7).

As a first case we consider the random encounter case for which the generating function $F(z)$ is

$$F(z) = \frac{1-\alpha}{1-(1-\alpha)z}. \tag{13}$$

Upon substituting the detailed expression for $S(z)$, $T(z)$, and $t(z)$ into the term $\beta(z)$ in Eq. (6) we find, after some algebra, that

$$\Omega(z) = \left[\frac{2(1-\alpha)(1+\rho)}{L\alpha + 2(1-\alpha)(1+\rho)} + \frac{8}{\pi^2}\frac{L\alpha}{L\alpha + 2(1-\alpha)(1+\rho)}\right]\cdot\frac{1}{1-z\rho'}, \tag{14}$$

in which

$$\rho' = \frac{L\alpha\rho + 2(1-\alpha)(1+\rho)}{L\alpha + 2(1-\alpha)(1+\rho)} \sim \rho + \frac{2(1-\alpha)(1-\rho^2)}{L\alpha} + \cdots . \tag{15}$$

Thus, to a very close approximation for large L we can take $\rho' = \rho$ and therefore

$$\Omega_n \sim \frac{\left[4\alpha(1-\alpha) + \dfrac{8L\alpha}{\pi^2}\right]}{L\alpha + 4(1-\alpha)}\rho^n. \tag{16}$$

Notice that this expression for Ω_n still contains L. As a final step we must perform the average over L. If we assume that the traps are randomly placed and c is the probability that a given site is a trap, then the probability that a random walker finds itself initially in a trap free interval of L is

$$p(L) = c^2 L(1-c)^{L-1}. \tag{17}$$

If we pass to the continuum limit then this distribution is to be replaced by the density

$$\varphi(L) = \lambda^2 L \exp(-\lambda L), \tag{18}$$

where λ is the reciprocal of the average spacing between traps. Thus $\langle\Omega_n\rangle$ is given by

$$\langle\Omega_n\rangle = \lambda^2 \int_0^{\infty} L\left[\frac{4\alpha(1-\alpha) + \dfrac{8L\alpha}{\pi^2}}{L\alpha + 4(1-\alpha)}\right] \times\exp\left(-\lambda L - \frac{n\pi^2}{2L^2}\right) \alpha L. \tag{19}$$

While this integral cannot be evaluated in closed form one can use the method of steepest descents, leading to the result

$$\langle\Omega_n\rangle \sim \lambda\left(\frac{128n}{3\pi}\right)^{1/2} \exp\left[-\tfrac{3}{2}(\pi^2\lambda^2 n)^{1/3}\right] \tag{20}$$

to lowest order in n which is the same as that for the perfectly efficient trap. The steepest descents method allows us to calculate corrections that are $O(n^{-1/3})$ to Eq. (20), that arise both from the retention of higher order terms of the exponential in Eq. (19) and from the term that multiplies the exponential. One can observe that Eq. (14) reduces to known results when $\alpha = 1$. The effects of imperfect traps, in this model, therefore do not differ from those predicted by

Donsker and Varadhan[4] for perfect traps. The result is also valid for more general models of imperfect traps. In particular if the F_j go to zero sufficiently quickly with j so that the average number of encounters required to produce an absorption is finite, then the Donsker–Varadhan result of Eq. (20) remains valid.

III. GROSSLY INEFFICIENT ABSORPTION

An alternative situation is one in which the average number of encounters to produce an absorption is infinite. In this case specific results for Ω_n will depend on the rate which F_n tends to zero. We will consider the case in which $F_n \sim A/n^\alpha$ for large n, where A is a constant and $0<\alpha<1$. In this case application of an Abelian theorem[31] for power series allows us to conclude that as $z \to 1$,

$$F(z) \sim B/(1-z)^{1-\alpha}, \tag{21}$$

where $B = \pi A/\sin(\pi\alpha)$. In this limit, the function of $\beta(z)$ in Eq. (6) is

$$\beta(z) \sim B\left[\frac{2(1+\rho)}{L(1-z\rho)}\right]^\alpha \frac{1}{(1-z)^{1-\alpha}}\left[1-\frac{8}{\pi^2}\left(\frac{1-z}{1-z\rho}\right)\right]. \tag{22}$$

On expanding this product into a Taylor series one sees that the radius of convergence is equal to 1 since the competing singularity occurs at $z=\rho^{-1}>1$. Hence we can determine the asymptotic behavior of the coefficients in the power series by appealing to a Tauberian theorem.[32] The results suffice to show that the coefficients of $\beta(z)$ have the asymptotic behavior

$$\beta_n(L) \sim \frac{B(2/L)^\alpha}{\Gamma(1-\alpha)} \coth\left(\frac{\pi^2}{4L^2}\right)\frac{1}{n^\alpha}, \tag{23}$$

so that the dependence on L and n factors. The n dependence of $\langle \beta_n \rangle$ is unrelated to the distribution of L, hence one cannot change the form of $\langle S_n \rangle$ by using correlated traps as in our earlier work.[18] We have not investigated the magnitude of n required for Eq. (23) to be valid hence we cannot rule out the possibility that n needs to be so large that Eq. (23) is useful only at unrealistically low values of the survival probability. Although the present calculation is one-dimensional we expect that the conclusions are valid more generally. That is, when the average number of encounters per collision is finite, the asymptotic averaged survival function has the Donsker–Varadhan[4] form

$$\ln \langle \Omega_n \rangle \sim -n^{D/(D+2)} \tag{24}$$

in D dimensions. However, when the average number of encounters per trapping event is infinite, it is that feature that determines the survival probability rather than the interaction between L and n. These conjectures remain to be tested.

In future work we hope to investigate the effects of the non-Markovian model for absorption probabilities on the boundary conditions required for the diffusion equation. It is known that in the Markovian case (constant probability of absorption at each encounter) the diffusion equation must be supplemented by the so-called radiation boundary condition. Whether the non-Markovian model can be incorporated into the diffusion picture by means of a simple boundary condition remains to be studied.

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