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Competitive Trapping Effects in a Set of Partially Absorbing Traps

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This note contains a formalism for calculating properties of random walks in the presence of a set of partially absorbing traps. The properties that are considered are the probability of trapping at a specific point and the survival probability as a function of step number. The results are expressed in terms of determinants, but approximations to these can be found.

KEY WORDS: Random walks, trapping, reaction rates.

1. INTRODUCTION

A number of investigators have analyzed the problem of competitive effects for a particle diffusing in the presence of several absorbing surfaces.[1-11] Such models arise naturally when one tries to generalize the Smoluchowski theory[12] of diffusion-controlled reactions and the Onsager model[15] for ion recombination. Applications of these results can be made to radiation chemistry[14] and photogeneration.[15] In all of the cited analyses the assumption is made that the reaction centers, or trapping sites, are perfectly efficient. In the present note we consider the effects of imperfect trapping efficiencies on absorption probabilities of random walks on a lattice, thereby generalizing the theory of Watanabe[7] for perfect absorption. Sano[10] has shown that provided that the traps are separated by more than approximately five lattice spacings, one can get useful results from a continuum approximation, at least in the case of two traps. The results presented here are based on the work of Rubin and Weiss[16] who studied statistical properties of the number of visits of a random walker to a given

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set of points. The results of that work were presented in terms of a multiple generating function that will be shown to be exactly the quantity needed for the solution of the present problem.

2. DEVELOPMENT OF THE FORMALISM

We assume the existence of m traps located at $\mathbf{s}_1, \mathbf{s}_2,..., \mathbf{s}_m$, none of which are located at $\mathbf{r}=\mathbf{0}$, the initial position of the random walker. The possibility that $\mathbf{r}=\mathbf{0}$ is a trap can also be taken into account by the same techniques. The probability that a single encounter of the random walker with trap i leads to a trapping event will be denoted by α_i. In order to calculate the joint probability of trapping, at $\mathbf{s}_i$ at step n we need a set of probabilities defined on a trap-free lattice. These will be denoted by $P_n(\mathbf{r} \mid l_1,..., l_m)$ defined to be the probability that the random walker is at r at step n having visited $\mathbf{s}_1$ l_1 times, $\mathbf{s}_2$ l_2 times, and so forth. Let $\Gamma_{n,i}$ be the joint probability that the random walker is trapped at $\mathbf{s}_i$ at step n. This quantity can be expressed, in terms of the $P_n(\mathbf{r} \mid \mathbf{l})$ as

$$\Gamma_{n,i}=\alpha_i \sum_{l_1=0}^{\infty} \cdots \sum_{l_m=0}^{\infty} P_n(\mathbf{s}_i \mid \mathbf{l})(1-\alpha_1)^{l_1}(1-\alpha_2)^{l_2}\cdots(1-\alpha_m)^{l_m} \tag{1}$$

so that this joint probability is really a multiple generating function. Formal expressions for such generating functions have been found by Rubin and Weiss[16] and for related generating functions by Montroll[17] and den Hollander and Kasteleyn.[18] We simply apply these results to the present problem.

The statistical properties of a single step of the random walk are contained in the single-step transition probabilities, $\{p(\mathbf{j})\}$ or equivalently in the characteristic function

$$\lambda(\boldsymbol{\theta})=\sum_{\mathbf{j}} p(\mathbf{j}) \exp(i\mathbf{j}\cdot\boldsymbol{\theta}) \tag{2}$$

These will be used to generate the Green's functions required for the solution. In order to find the $\Gamma_{n,i}$ we need the following generating function

$$U(z, \mathbf{x}, \boldsymbol{\theta})=\sum_{n=0}^{\infty} z^n \sum_{\mathbf{l}} x_1^{l_1}x_2^{l_2}\cdots x_m^{l_m} \sum_{\mathbf{r}} P_n(\mathbf{r} \mid \mathbf{l}) \exp(i\mathbf{r}\cdot\boldsymbol{\theta}) \tag{3}$$

for $\mathbf{x}=(1-\alpha_1, 1-\alpha_2,..., 1-\alpha_m)$. The function U can be expressed in terms of generating functions of Green's functions

$$P(\mathbf{r}; z) \equiv \sum_{n=0}^{\infty} P_n(\mathbf{r})\, z^n=\frac{1}{(2\pi)^N}\int_{-\pi}^{\pi}\cdots\int \frac{\exp(-i\mathbf{r}\cdot\boldsymbol{\theta})\, d^N\boldsymbol{\theta}}{1-z\lambda(\boldsymbol{\theta})} \tag{4}$$

where N is the number of dimensions. Rubin and Weiss[16] have shown that

$$U(z, \mathbf{x}, \boldsymbol{\theta}) = [1 - z\lambda(\boldsymbol{\theta})]^{-1} \left\{1 - \sum_j (1 - x_j)(D_j/D) \exp(i\mathbf{s}_j \cdot \boldsymbol{\theta})\right] \qquad (5)$$

where D is the determinant whose ij element is

$$(D)_{ij} = x_{i,j} + (1 - x_j)\, P(\mathbf{s}_i - \mathbf{s}_j, z) \qquad (6)$$

and $D_j(z, \mathbf{x})$ is obtained from $D(z, \mathbf{x})$ by replacing its jth column by the vector

$$\begin{pmatrix} P(\mathbf{s}_1, z) \\ P(\mathbf{s}_2, z) \\ \vdots \\ P(\mathbf{s}_m, z) \end{pmatrix}$$

Equation (17b) of reference 16 can be used to show that $\Gamma_{n,j}$ is the coefficient of z in

$$\Gamma_j(z) = \alpha_j D_j(z, 1 - \alpha_1, 1 - \alpha_2, \ldots, 1 - \alpha_m)/D(z, 1 - \alpha_1, 1 - \alpha_2, \ldots, 1 - \alpha_m) \qquad (7)$$

Furthermore, the probability of being trapped at s_j can be expressed directly in terms of $\Gamma_j(z)$ as

$$\Gamma_j = \lim_{z \to 1-} \Gamma_j(z) \qquad (8)$$

3. SOME EXAMPLES

The simplest example of this formalism involves a single trap at s, in which case

$$\Gamma(z) = \alpha P(\mathbf{s}; z)/[1 - \alpha + \alpha P(\mathbf{0}; z)] \qquad (9)$$

If we introduce generating functions with respect to n for $F_n(\mathbf{s})$, the first passage time to s, it is known that[19]

$$\begin{aligned} F(\mathbf{0}; z) &= 1 - [P(\mathbf{0}; z)]^{-1} \\ F(\mathbf{s}; z) &= P(\mathbf{s}; z)/P(\mathbf{0}; z), \quad \mathbf{s} \neq \mathbf{0} \end{aligned} \qquad (10)$$

so that eq. (9) becomes

$$\Gamma(z) = \alpha F(\mathbf{s}; z)/[1 - (1 - \alpha)\, F(\mathbf{0}; z)] \qquad (11)$$

which has been derived earlier.[20] A second example for which results are readily obtained relates to the one-dimensional case with two partial traps. Let us set $s_1 = -s$, $s_2 = t$, where s, $t > 0$. It is readily verified that

$$\begin{aligned} D_1 &= (1-\alpha_2)\, P(-s; z) + \alpha_2[P(0; z)\, P(-s; z) - P(t; z)\, P(s+t; z)] \\ D &= (1-\alpha_1)(1-\alpha_2) + (\alpha_1+\alpha_2-2\alpha_1\alpha_2)\, P(0; z) \\ &\quad + \alpha_1\alpha_2\{P^2(0; z) - P(s+t; z)\, P[-(s+t); z]\} \end{aligned} \tag{12}$$

In particular, when the random walk is symmetric and

$$\sigma^2 = \sum_{j=-\infty}^{\infty} j^2 P(j) \tag{13}$$

is finite, the behavior of $P(r, z)$ as $z \to 1-$ and $r^2 \gg \sigma^2$ is known to be

$$P(r; z) \sim \exp[-(|r|/\sigma)\sqrt{2(1-z)}]/(\sigma\sqrt{2(1-z)}) \tag{14}$$

Under these conditions, eq. (7) implies that both D_1 and D are singular in the same limit so that Γ_1, the probability of trapping at s_1, is found in terms of the most singular terms in the numerator and denominator of D_1/D. After some algebra, one finds that

$$\Gamma_1 \sim \alpha_1 \left\{ \frac{2\alpha_2 t + \sigma^2(1-\alpha_2)}{2\alpha_1\alpha_2(s+t) + \sigma^2(\alpha_1+\alpha_2-2\alpha_1\alpha_2)} \right\} \qquad s, t \to \infty \tag{15}$$

Thus, when $\alpha_1 = \alpha_2 = 1$, $\Gamma_1 = t/(s+t)$, which is otherwise easy to find. When either or both α_1 and α_2 are less than 1 Γ_1 has the properties $\lim_{t\to\infty} \Gamma_1 = 1$, $\lim_{s\to\infty} \Gamma_1 = 0$, which are both intuitively reasonable. As the variance of a single step σ^2 increases without limit, Γ_1 becomes independent of s and t consistent with the idea that the random walker samples an increasingly larger part of space without remaining localized near one or the other trap. Finally, if $\alpha_1 = \alpha_2 = \alpha$ decreases to zero, then $\Gamma_1 \to \frac{1}{2}$, again because the random walker has a large amount of time in which to sample parts of the line, thereby allowing it to make many visits to both trapping sites. Notice that although we have assumed that the random walker initially lies between the two trapping points, this restriction can be dispensed with. An analysis similar to that given earlier shows that when the two traps are at $t > s > 0$, eq. (15) is to be replaced by

$$\Gamma_1 \sim \alpha_1 \left\{ \frac{2\alpha_2(t-s) + \sigma^2(1-\alpha_2)}{2\alpha_1\alpha_2(t-s) + \sigma^2(\alpha_1+\alpha_2-2\alpha_1\alpha_2)} \right\} \quad s, t, t-s \gg 1 \tag{16}$$

When $\alpha_2 = \alpha_1 = 1$, $\Gamma_1 = 1$ so that the random walker never gets beyond the closest trap to the origin. This result is obvious for nearest-neighbor walks.

When the number of dimensions is 3 or greater, the functions $P(\mathbf{r}; z)$ no longer diverge as $z \to 1$ and eventual trapping is no longer a certain event. Therefore, one can calculate trapping probabilities, but these no longer sum to 1. In this case the relative trapping probabilities defined by

$$\Omega_l = \alpha_l D_l \Big/ \sum_{i=1}^{m} \alpha_i D_i \tag{17}$$

are of interest.

As an example let us consider the case of two partially absorbing sites at $\mathbf{s}$ and $\mathbf{t}$ for a symmetric three-dimensional random walk. In addition, let us suppose that both s and t are far from the origin in the sense that $s^2, t^2 \gg 1$ and that they are far from each other so that $|\mathbf{t}-\mathbf{s}|^2 \gg 1$. These conditions suffice to allow the use of the asymptotic form for the various Green's function generating functions that appear in $D(z, \mathbf{x})$ and $D_j(z, \mathbf{x})$. If the random walk is such that in a neighborhood of the origin

$$\lambda(\theta) \sim 1 - (\sigma^2/2)(\theta_1^2 + \theta_2^2 + \theta_3^2) \tag{18}$$

as, for example, is valid for nearest-neighbor random walks on the simple cubic lattice then

$$P(\mathbf{r}; 1) \sim \frac{1}{2\pi\sigma^{3/2}} \cdot \frac{1}{r} \tag{19}$$

where $r = (\mathbf{r} \cdot \mathbf{r})^{1/2}$. Inserting this approximation into eq. (7) and keeping lowest-order terms we find

$$\Omega_1 = \frac{\alpha_1[1-\alpha_2+\alpha_2 P(\mathbf{0}; 1)]\, t}{\alpha_1[1-\alpha_2+\alpha_2 P(\mathbf{0}; 1)]\, t + \alpha_2[1-\alpha_1+\alpha_1 P(\mathbf{0}; 1)]\, s} \tag{20}$$

so that when $\alpha_1 = \alpha_2 = \alpha$, $\Omega_1 = t/(s+t)$ just as in one dimension. Higher-order terms in this expansion are readily calculated. It is interesting to note that details of the random walk contained in $P(\mathbf{0}; 1)$ are only important when the α's are unequal. To the order of approximation shown in eq. (20), one can also calculate Ω_1 for an arbitrary collection of trapping sites at $\mathbf{s}_1, \mathbf{s}_2, \ldots, \mathbf{s}_n$, provided that the distances between these sites are large. One finds that to lowest order

$$\Gamma_i \sim \frac{(\alpha_i/s_i)}{1-\alpha_i+\alpha_i P(\mathbf{0}; 1)} \tag{21}$$

with the relative probabilities being given by

$$\Omega_i = \Gamma_i \Big/ \sum_{j=1}^{m} \Gamma_j \tag{22}$$

When all of the traps are perfect ones, this equation reduces to

$$\Omega_i \sim (1/s_i) \Big/ \sum_{j=1}^{m} (1/s_j) \tag{23}$$

Thus far we have mainly focussed on the relative absorption probabilities for a set of imperfect traps, but the same formalism can also be used to discuss the survival probabilities as a function of n provided that we retain the dependence on z. For example, in three dimensions when the random walk is unbiassed and $\sigma^2 < \infty$

$$P(\mathbf{r}; z) \sim P(\mathbf{r}; 1) + a(\mathbf{r})(1-z)^{1/2} + \cdots \tag{24}$$

as $z \to 1-$. The function $a(\mathbf{r})$ is expressible as a triple integral.

In the case of trapping by a single imperfect trap

$$\Gamma(z) \sim \Gamma(1) \left\{ 1 + \left[\frac{a(\mathbf{s})}{P(\mathbf{s}; 1)} - \frac{\alpha a(\mathbf{0})}{1 - \alpha + \alpha P(\mathbf{0}; 1)} \right] (1-z)^{1/2} + \cdots \right\} \tag{25}$$

as $z \to 1$. But this implies that

$$\Gamma_{n,1} \sim \frac{2\Gamma(1)}{\sqrt{2\pi}} \left[\frac{a(\mathbf{s})}{P(\mathbf{s}; 1)} - \frac{\alpha a(\mathbf{0})}{1 - \alpha + \alpha P(\mathbf{0}; 1)} \right] \frac{1}{n^{3/2}} \tag{26}$$

It is obvious both from this and the last equation that the value of α has no influence on the form of the time dependence of survival, but only on the multiplicative constant. This proves to be true as well for any number of trapping sites, as can be verified by expanding $D(z, x)$ and $D_1(z, x)$ to lowest order in $(1-z)^{1/2}$. If one considers the multiple-site trapping problem on a finite lattice, then the Green's function generating functions in any number of dimensions takes the form of a rational fraction. In consequence, one can show that in any number of dimensions the probability of survival goes down exponentially at sufficently long times. A proof can be given along the lines taken by Weiss, Havlin, and Bunde[21] for a single trap or by den Hollander[22] for multiple traps. The calculation of constants will, of course, present difficulties of detail. Development of a similar theory for so-called non-Markovian traps[23] appears to be much more complicated than for the Markovian model developed here. However, when the average number of random walk-trap encounters necessary to produce a trapping event is finite we may expect that the asymptotic results for the survival probability are similar to those found in the present note.

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