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Localized Partial Traps in Diffusion Processes and Random Walks

Attila Szabo,[1] Gene Lamm,[1] and George H. Weiss[2]

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Reaction-diffusion equations, in which the reaction is described by a sink term consisting of a sum of delta functions, are studied. It is shown that the Laplace transform of the reactive Green's function can be analytically expressed in terms of the Green's function for diffusion in the absence of reaction. Moreover, a simple relation between the Green's functions satisfying the radiation boundary condition and the reflecting boundary condition is obtained. Several applications are presented and the formalism is used to establish the relationship between the time-dependent geminate recombination yield and the bimolecular reaction rate for diffusion-influenced reactions. Finally, an analogous development for lattice random walks is presented.

KEY WORDS: Diffusion-controlled reactions; first passage times; radiation boundary conditions; Green's functions; recombination rates; rate constants.

1. INTRODUCTION

The subject of trapping or absorption in both random walks and diffusion has a large literature. However, not a great deal of attention has been paid to comparable problems in which traps may be imperfect, i.e., in which random walkers who impinge on a trapping boundary are not necessarily absorbed (or "killed" in the mathematical terminology[1]). Funabashi was the first to discuss the kinetics of imperfect trapping in a lattice random

[1] Laboratory of Chemical Physics, National Institute of Arthritis, Diabetes, and Digestive and Kidney Diseases.

[2] Physical Sciences Laboratory, Division of Computer Research and Technology, National Institutes of Health, Bethesda, Maryland 20205.

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walk, in the context of impurity trapping of excitons and electrons.[2] Recently den Hollander and Kasteleyn[3] have analyzed random walks with a periodic distribution of imperfect traps, while Rubin and Weiss[4] treated a more general case in which there can be an arbitrary distribution of such traps. Comparable problems arise for diffusion processes and have been analyzed by the imposition of radiation (or partially reflecting) boundary conditions starting with Collins and Kimball[5] and discussed more recently by Mozumder,[6] and Szabo, Schulten, and Schulten.[7] Mozumder[6,8] was interested in the extension of Noyes'[9] theory of diffusion-controlled reactions. Shoup and Szabo[10] have also analyzed this class of problems as a model for ligand binding to macromolecules, while Weaver[11] used the imperfect absorption model to discuss localization of proteins on membrane surfaces. While the use of radiation boundary conditions for the relevant diffusion equation is a natural starting point for analyzing imperfect absorption problems, an alternative does exist. Wilemski and Fixman[12] treated diffusion-influenced reactions by introducing a position-dependent sink term in the diffusion equation itself. They pointed out that if the sink term is simply proportional to a delta function, then an appropriate solution of their reaction–diffusion equation yields results formally equivalent to using the radiation boundary condition. This has also been discussed by Northrup and Hynes.[13]

A purpose of this paper is to show that when the sink term is a sum of delta functions, then the Green's function describing the reaction can be simply expressed in terms of the Green's function for diffusion in the absence of reaction. Moreover, we show that one can easily construct the Green's function which satisfies the radiation boundary condition at a surface in terms of the simpler Green's function which satisfies reflecting boundary conditions at that surface. We use these results to solve several problems exactly both for diffusion and discrete random walks. The problem of obtaining approximate solutions to reaction–diffusion equations with more general sink terms will be considered in a companion paper.[14]

2. DIFFUSION PROCESSES

The evolution equation for $p(\mathbf{r}, t \mid \mathbf{r}_0, 0)$ will be written

$$\frac{\partial p}{\partial \tau} = Lp - k(\mathbf{r})p \tag{2.1}$$

where L is assumed to be a time-independent second-order conservative operator. That is to say, the solution to the equation

$$\frac{\partial G}{\partial \tau} = LG \tag{2.2}$$

has the property

$$\int G(\mathbf{r}, t \mid \mathbf{r}_0, 0)\, d\mathbf{r} = 1 \tag{2.3}$$

The solution to Eq. (2.2) can be regarded as a Green's function, allowing us to transform Eq. (2.1) into an integral equation in the form of Dyson's equation[15]

$$p(\mathbf{r}, \tau \mid \mathbf{r}_0, 0) = G(\mathbf{r}, \tau \mid \mathbf{r}_0, 0) - \int_0^\tau d\tau' \int G(\mathbf{r}, \tau - \tau' \mid \mathbf{r}', 0) k(\mathbf{r}') p(\mathbf{r}', \tau' \mid \mathbf{r}_0, 0)\, d\mathbf{r}' \tag{2.4}$$

where we have made use of the property $G(\mathbf{r}, t \mid \mathbf{r}', \tau) = G(\mathbf{r}, t - \tau \mid \mathbf{r}', 0)$ that follows from the time independence of L.

Equation (2.4) assumes that $p(\mathbf{r}, \tau \mid \mathbf{r}_0, 0)$ and $G(\mathbf{r}, \tau \mid \mathbf{r}_0, 0)$ obey identical time-independent boundary conditions. An analogous equation can be written down for random walks or other processes that occur in discrete time.[3] Notice also that G need not be taken to be a Green's function for propagation in free space (as has been generally assumed in the analysis of random walks) but may be that appropriate for diffusion in the presence of reflecting boundaries and/or in a potential. Equation (2.4) can be reduced to a much simpler form when the absorption term, $k(\mathbf{r})$, is a linear combination of delta functions. If we write

$$k(\mathbf{r}) = \sum_j \kappa_j \delta(\mathbf{r} - \mathbf{a}_j) \tag{2.5}$$

Eq. (2.4) takes the form

$$p(\mathbf{r}, t \mid \mathbf{r}_0, 0) = G(\mathbf{r}, t \mid \mathbf{r}_0, 0) - \sum_j \kappa_j \int_0^t d\tau\, G(\mathbf{r}, t - \tau \mid \mathbf{a}_j, 0) \times p(\mathbf{a}_j, \tau \mid \mathbf{r}_0, 0) \tag{2.6}$$

Thus $p(\mathbf{r}, t \mid \mathbf{r}_0, 0)$ depends only on its value at the special points $\mathbf{r} = \mathbf{a}_1$, $\mathbf{a}_2, \ldots, \mathbf{a}_n$. Before proceeding to the solution of this equation we remark that a term of the form $\kappa\delta(\mathbf{r} - \mathbf{a})$ represents a fully absorbing point at $\mathbf{a}$ in the limit $\kappa \to \infty$ and a partially absorbing point for finite κ.

To solve Eq. (2.6) we set $\mathbf{r} = \mathbf{a}_1, \mathbf{a}_2, \ldots, \mathbf{a}_n$ in turn which leads to the self-contained system of equations

$$p(\mathbf{a}_i, t \mid \mathbf{r}_0, 0) = G(\mathbf{a}_i, t \mid \mathbf{r}_0, 0) - \sum_{j=1}^{n} \kappa_j \int_0^t G(\mathbf{a}_i, t - \tau \mid \mathbf{a}_j, 0) p(\mathbf{a}_j, \tau \mid \mathbf{r}_0, 0)\, d\tau \tag{2.7}$$

These, in turn, can be converted into a set of n linear equations in the

Laplace transforms

$$\begin{aligned}\hat{p}(\mathbf{a}_i \mid \mathbf{r}_0) &= \int_0^\infty e^{-st} p(\mathbf{a}_i, t \mid \mathbf{r}_0, 0)\, dt \\ \hat{G}(\mathbf{a}_i \mid \mathbf{r}_0) &= \int_0^\infty e^{-st} G(\mathbf{a}_i, t \mid \mathbf{r}_0, 0)\, dt\end{aligned} \tag{2.8}$$

which can be written

$$\hat{p}(\mathbf{a}_i \mid \mathbf{r}_0) + \sum_{j=1}^{n} \kappa_j \hat{G}(\mathbf{a}_i \mid \mathbf{a}_j)\hat{p}(\mathbf{a}_j \mid \mathbf{r}_0) = \hat{G}(\mathbf{a}_i \mid \mathbf{r}_0) \tag{2.9}$$

Finally, the solution to this set of equations can be substituted into the Laplace-transformed version of Eq. (2.6):

$$\hat{p}(\mathbf{r} \mid \mathbf{r}_0) = \hat{G}(\mathbf{r} \mid \mathbf{r}_0) - \sum_{j=1}^{n} \kappa_j \hat{G}(\mathbf{r} \mid \mathbf{a}_j)\hat{p}(\mathbf{a}_j \mid \mathbf{r}_0) \tag{2.10}$$

Analogous equations for random walks in discrete time are to be found in Ref. 4. If we define the probability of survival to age t or greater to be

$$\Sigma(t; \mathbf{r}_0) = \int p(\mathbf{r}, t \mid \mathbf{r}_0, 0)\, d\mathbf{r} \tag{2.11}$$

then, since L is a conservative operator, it follows that the transform of $\Sigma(t; \mathbf{r}_0)$ is

$$\hat{\Sigma}(s; \mathbf{r}_0) = \frac{1}{s}\left\{1 - \sum_{j=1}^{n} \kappa_j \hat{p}(\mathbf{a}_j \mid \mathbf{r}_0)\right\} \tag{2.12}$$

When reaction occurs sufficiently quickly so that one can define an average reaction time τ, this parameter can be calculated directly from the Laplace transform

$$\tau(\mathbf{r}_0) = \int_0^\infty \Sigma(t; \mathbf{r}_0)\, dt = \hat{\Sigma}(0; \mathbf{r}_0) \tag{2.13}$$

However, we will see that in some simple examples $\tau(r_0)$ need not exist.

The simplest case that allows examination in detail is a system with a single partially absorbing point at $\mathbf{r} = \mathbf{a}$. In this case one can solve Eq. (2.6) explicitly, leading to the result

$$\hat{p}(\mathbf{r} \mid \mathbf{r}_0) = \hat{G}(\mathbf{r} \mid \mathbf{r}_0) - \frac{\kappa \hat{G}(\mathbf{r} \mid \mathbf{a})\hat{G}(\mathbf{a} \mid \mathbf{r}_0)}{1 + \kappa \hat{G}(\mathbf{a} \mid \mathbf{a})} \tag{2.14}$$

The corresponding equation for the survival probability is

$$\hat{\Sigma}(s; \mathbf{r}_0) = \frac{1}{s}\left[1 - \frac{\kappa \hat{G}(\mathbf{a} \mid \mathbf{r}_0)}{1 + \kappa \hat{G}(\mathbf{a} \mid \mathbf{a})}\right] \tag{2.15}$$

If we use the free space Green's function for $\hat{G}$, then Eqs. (2.14) and (2.15) give the Green's function and survival probability in the presence of a delta

function sink of strength κ at $\mathbf{r} = \mathbf{a}$. However, if we use a Green's function for $\hat{G}$ satisfying a purely reflecting boundary condition at $\mathbf{r} = \mathbf{a}$, then Eq. (2.14) yields the Green's function satisfying a radiation boundary condition at $\mathbf{r} = \mathbf{a}$ (see Appendix). This is a useful result because it is simpler to solve problems subject to reflecting boundary conditions than it is to solve the comparable equations with radiation boundary conditions.

Before presenting several applications of the above results, we consider the situation when the initial condition is taken to be the normalized equilibrium density associated with G. The equilibrium density, denoted by $\rho(\mathbf{r})$, has the property that

$$\int G(\mathbf{r}, t \mid \mathbf{r}_0, 0)\rho(\mathbf{r}_0)\, d\mathbf{r}_0 = \rho(\mathbf{r}) \tag{2.16}$$

so that

$$\int\int d\mathbf{r}\, d\mathbf{r}_0\, \hat{G}(\mathbf{r} \mid \mathbf{r}_0) = \frac{1}{s} \tag{2.17}$$

Therefore the Laplace transform of the survival probability, is found from Eq. (2.15) to be

$$\hat{\Sigma}(s) = \int dr_0\, \rho(\mathbf{r}_0)\Sigma(s; \mathbf{r}_0) = \frac{1}{s}\left\{1 - \frac{\kappa\rho(\mathbf{a})}{s\left[1 + \kappa\hat{G}(\mathbf{a} \mid \mathbf{a})\right]}\right\} \tag{2.18}$$

This expression is valid for diffusive motion in the presence of an arbitrary potential provided that the initial condition is chosen to be the equilibrium density. One can calculate the mean residence time from Eq. (2.18) provided the equilibrium density exists and $\hat{G}(\mathbf{a} \mid \mathbf{a})$ has the small s expansion of the form

$$\lim_{s \to 0} \hat{G}(\mathbf{a} \mid \mathbf{a}) = \frac{\rho(\mathbf{a})}{s} + \Gamma \tag{2.19}$$

where Γ is a constant. When this is the case the mean residence time is easily found to be

$$\tau = \hat{\Sigma}(0) = \frac{1 + \kappa\Gamma}{\kappa\rho(\mathbf{a})} \tag{2.20}$$

However, the solution for the residence moments can be found more directly using the algorithms given by Szabo *et al.*[7] and Deutch.[17]

We shall now present several applications of the above results. Consider the case of free diffusion along a line for which the operator $L = D\partial^2/\partial x^2$. The Laplace transform of the free Green's function is

$$\hat{G}_f(x \mid x_0) = \frac{1}{2}(Ds)^{-1/2}\exp\left\{-\left(\frac{s}{D}\right)^{1/2}|x - x_0|\right\} \tag{2.21}$$

while the Green's function which satisfies a reflecting boundary condition at $x = 0$ is

$$\hat{G}_r(x \mid x_0) = \hat{G}_f(x \mid x_0) + \hat{G}_f(x \mid -x_0), \qquad x > 0 \tag{2.22}$$

First, let us calculate the residence time for a situation when the delta function sink is located at $x = 0$. Using Eq. (2.21) in Eq. (2.15) we have

$$\hat{\Sigma}(s; x_0) = \frac{1}{s}\left[1 - \frac{\kappa \exp\left[-|x_0|(s/D)^{1/2}\right]}{\kappa + (4Ds)^{1/2}}\right] \tag{2.23}$$

the inverse transform of which is

$$\Sigma(t; x_0) = 1 - \operatorname{erfc}\left[\frac{|x_0|}{(4Dt)^{1/2}}\right] + \exp\left(\frac{\kappa|x_0|}{2D} + \frac{\kappa^2 t}{4D}\right)\operatorname{erfc}\left[\frac{|x_0|}{2(Dt)^{1/2}} + \left(\frac{\kappa^2 t}{4D}\right)^{1/2}\right] \tag{2.24}$$

At long times, the asymptotic behavior of $\Sigma(t; x_0)$ is

$$\Sigma(t; x_0) \sim \frac{1}{(\pi D t)^{1/2}}\left(\frac{2D}{\kappa} + |x_0|\right) \tag{2.25}$$

which shows that the effect of imperfect absorption is to change the coefficient, but not the asymptotic time dependence of the survival fraction. This type of result was remarked on by Funabashi[2] for lattice random walks. In higher dimensions one cannot talk about diffusion in the presence of absorbing points, but the problem of absorbing surfaces can be analyzed by this method as we will show in a later example. Random walks on discrete lattices do not have this same difficulty, and can be analyzed by the present formalism. An example will be given in a later section.

As a second example, let us calculate the Green's function which satisfies radiation boundary conditions at $x = 0$, i.e.,

$$D\left.\frac{\partial \hat{p}(x \mid x_0)}{\partial x}\right|_{x=0} = \kappa \hat{p}(0 \mid x_0) \tag{2.26}$$

Using Eq. (2.22) in (2.14) we immediately have when $a = 0$

$$\begin{aligned}\hat{p}(x \mid x_0) &= \hat{G}_r(x \mid x_0) - \frac{\kappa \hat{G}_r(x \mid 0)\hat{G}_r(0 \mid x_0)}{1 + \kappa \hat{G}_r(0 \mid 0)} \\ &= \frac{1}{2}(Ds)^{-1/2}\exp\left[-|x - x_0|(s/D)^{1/2}\right] \\ &\quad + \frac{1}{2}(Ds)^{-1/2}\exp\left[-(x + x_0)(s/D)^{1/2}\right] \\ &\quad - \frac{\kappa \exp\left[-(x + x_0)(s/D)^{1/2}\right]}{Ds + \kappa(Ds)^{1/2}}\end{aligned} \tag{2.27}$$

which is identical to the result derived by Carslaw and Jaeger[16] using a different argument.

As a somewhat less trivial example of the present formalism consider the case of diffusion in a harmonic potential centered at the origin in one dimension. For this problem G satisfies

$$\frac{\partial G}{\partial t} = D\frac{\partial}{\partial x}\left(\frac{\partial G}{\partial x} + \beta x G\right) \tag{2.28}$$

By rescaling length and time we can always choose $D = \beta = 1$. The free space propagator is

$$G_f(x, t \mid x_0, 0) = \left[2\pi(1 - e^{-2t})\right]^{-1/2} \exp\left[-\frac{(x - x_0 e^{-t})^2}{2(1 - e^{-2t})}\right] \tag{2.29}$$

We wish to obtain $\Sigma(t)$ for the situation that the reactivity is described by the radiation boundary condition at $x = 0$ with the initial condition being the normalized (in the region $0 \leqslant x \leqslant \infty$) equilibrium density

$$\rho(x) = \left(\frac{2}{\pi}\right)^{1/2} e^{-x^2/2}, \qquad x \geqslant 0 \tag{2.30}$$

To solve this problem using Eq. (2.18) we require the Laplace transform of the Green's function which satisfies a reflecting boundary condition at $x = 0$, as given in Eq. (2.22). Now

$$\begin{aligned}
\hat{G}_r(0 \mid 0) &= \left(\frac{2}{\pi}\right)^{1/2} \int_0^\infty \frac{e^{-st}}{(1 - e^{-2t})^{1/2}}\, dt \\
&= \left(\frac{2}{\pi}\right)^{1/2} \int_0^1 \frac{\rho^{s-1}\, d\rho}{(1 - \rho^2)^{1/2}} \\
&= \frac{1}{\sqrt{2}} \frac{\Gamma(s/2)}{\Gamma((s+1)/2)}
\end{aligned} \tag{2.31}$$

Thus, using Eq. (2.18) we have

$$\hat{\Sigma}(s) = \frac{1}{s}\left\{1 - \frac{\kappa(2/\pi)^{1/2}}{s\left[1 + \kappa/\sqrt{2}\,\Gamma(s/2)/\Gamma((s+1)/2)\right]}\right\} \tag{2.32}$$

Moreover, since

$$\lim_{s \to 0} \hat{G}_r(0 \mid 0) = \sqrt{\frac{2}{\pi}}\left(\frac{1}{s} + \ln 2\right) \tag{2.33}$$

it follows from Eq. (2.20) that the mean residence time is

$$\tau = \frac{1 + \kappa(2/\pi)^{1/2}\ln 2}{\kappa(2/\pi)^{1/2}} \tag{2.34}$$

In the special case that the boundary at $x = 0$ is perfectly absorbing (i.e., $\kappa \to \infty$), Eq. (2.32) reduces to

$$\hat{\Sigma}(s) = \frac{1}{s} - \frac{2}{\sqrt{\pi}\, s^2} \frac{\Gamma((s+1)/2)}{\Gamma(s/2)} \tag{2.35}$$

which can be inverted to yield

$$\Sigma(t) = \frac{2}{\pi} \sin^{-1}(e^{-t}) \tag{2.36}$$

This result has been previously obtained by Szabo *et al.*[7] using a completely different argument. Although these authors did not determine Σ for the partially reactive situation (i.e., $\kappa \neq \infty$), they did obtain the same mean residence time as in Eq. (2.34) by using the theory of first passage times.

3. THE RELATION BETWEEN BIMOLECULAR AND GEMINATE RECOMBINATION RATES

As the final example involving diffusion in a continuum, we discuss an application of the present methodology to diffusion-influenced reactions in a spherically symmetric field when the reactivity is described by the radiation boundary condition at contact. There are two physically distinct problems of interest. The first is the time-dependent bimolecular rate constant, $k(t)$. This is just the flux at contact given an initial equilibrium distribution. The second is the geminate recombination yield, $\phi(t)$. This is the fraction of molecules that have recombined at time t given that they were produced at contact at time $t = 0$. Berg[17] and Razi Naqvi *et al.*[18] have shown that, in the absence of a force field between the reactants there is a very simple relation between $k(t)$ and $\phi(t)$. Razi Naqvi *et al.*[18] discussed the relationship between this result, obtained within the framework of the radiation boundary condition, and the molecular pair approach of Noyes.[9] In this section we establish the relationship between $k(t)$ and $\phi(t)$ when the reactants interact via a spherically symmetric potential $V(r)$. The proof is almost immediate after the relevant quantities are defined.

To obtain the bimolecular rate constant, one must solve

$$\frac{\partial c}{\partial t} = \frac{D}{r^2} \frac{\partial}{\partial r}\left[r^2 e^{-\beta V(r)} \frac{\partial}{\partial r}\left(e^{\beta V(r)} c\right)\right] \tag{3.1}$$

where $\beta = (k_B T)^{-1}$, subject to the initial condition that

$$c(r,0) = e^{-\beta V(r)} \tag{3.2}$$

and the radiation boundary condition at $r = R$

$$4\pi D R^2 e^{-\beta V(R)} \left[\frac{\partial}{\partial r} e^{\beta V(r)} c(r,t) \right]_{r=R} = \kappa c(R,t) \tag{3.3}$$

The bimolecular rate is then just the flux at $r = R$, which by virtue of Eq. (3.3) is

$$k(t) = \kappa c(R,t) \tag{3.4}$$

Let $p(r,t \mid r_0,0)$ be the solution to Eq. (3.1) which satisfies Eq. (3.3). Then we have

$$c(R,t) = 4\pi \int_0^\infty r_0^2 p(R,t \mid r_0,0) e^{-\beta V(r_0)}\, dr_0 \tag{3.5}$$

Since

$$p(r,t \mid r_0,0) e^{-\beta V(r_0)} = p(r_0,t \mid r,0) e^{-\beta V(r)} \tag{3.6}$$

Eqs. (3.4) and (3.5) can be combined to give

$$k(t) = 4\pi\kappa e^{-\beta V(R)} \int_R^\infty r_0^2 p(r_0,t \mid R,0)\, dr_0 \tag{3.7}$$

Eq. (3.6) can be simply proved by transforming Eq. (3.1) to self-adjoint form and using the fact that the solution of the resulting equation is symmetric in r and r_0.

We now turn to the calculation of the geminate recombination yield, $\phi(t)$. We start with two molecules at contact so that $c(r,0)$ for this problem is $\delta(r - R)/(4\pi R^2)$. The recombination rate is

$$\dot{\phi}(t) = \kappa p(R,t \mid R,0) \tag{3.8}$$

and the yield is

$$\phi(t) = \kappa \int_0^t p(R,\tau \mid R,0)\, d\tau \tag{3.9}$$

since $\phi(0) = 0$.

To establish the relation between $k(t)$ and $\phi(t)$, we start with Eq. (2.6) specialized to a single delta function term located at $r = R$. We take G to be Green's function which satisfies a reflecting boundary condition at $r = R$. Integrating both sides with respect to r and setting $r_0 = R$, we have

$$4\pi \int_R^\infty r^2 p(r,t \mid R,0)\, dr = 1 - \kappa \int_0^t p(R,\tau \mid R,0)\, d\tau \tag{3.10}$$

where we have used Eq. (2.3). Finally, by comparing Eqs. (3.7), (3.9), and

(3.10), we have

$$k(t) = \kappa e^{-\beta V(R)}\left[1 - \phi(t)\right] \tag{3.11}$$

The free field result is obtained when $V = 0$. Note that in Eq. (3.11) the potential also appears implicitly in both k and ϕ. At steady state ($t \to \infty$), Eq. (3.11) is the same as Eqs. (29) and (30) of Shoup and Szabo[10] since our $k(\infty)$ is their k_{CKD} and our $\phi(\infty)$ is their capture probability $\gamma_{CKD}(R)$.

4. LATTICE RANDOM WALKS

Thus far we have discussed several problems related to continuous diffusion. We found that a mean residence time could be calculated in one dimension for a single reactive point, but that in higher dimensions one must have a reactive surface in order to have a properly posed problem. This distinction need not be made for random walks on a lattice. Rubin and Weiss[4] developed a formalism for counting the number of times a random walk visits a specified set of points. This theory can be applied directly to the problem of calculating statistical properties of residence time on a lattice with one or more partially absorbing points. The formalisms for both discrete and continuous diffusion are almost identical.

For simplicity we will consider a lattice random walk on a homogeneous lattice with a single partially reactive point at R. Let α be the probability that a random walker impinging on R will react (or be trapped). The probability that a random walker will react at R the jth time that it reaches that point is $(1 - \alpha)^{j-1}\alpha$. Let the random walk be characterized by a set of transition probabilities $\{p(\mathbf{j})\}$, where $p(\mathbf{j})$ is the probability that the random walker will make a transition equal to $\mathbf{j}$ at an arbitrary step, and define a structure function $\lambda(\boldsymbol{\theta})$ by

$$\lambda(\boldsymbol{\theta}) = \sum_{\{\mathbf{j}\}} p(\mathbf{j}) \exp(i\mathbf{j} \cdot \boldsymbol{\theta}) \tag{4.1}$$

Let $P_n(\mathbf{r})$ be the probability that the random walker is at $\mathbf{r}$ at step n having started at $\mathbf{0}$ ($= \mathbf{r}$) at step 0, and let $P(\mathbf{r}; z)$ be the generating function

$$P(\mathbf{r}; z) = \sum_{n=0}^{\infty} P_n(\mathbf{r}) z^n \tag{4.2}$$

which can be represented for homogeneous random walks as an integral:

$$P(\mathbf{r}; z) = \frac{1}{(2\pi)^D} \int_{-\pi}^{\pi} \cdots \int \frac{\exp(-i\mathbf{r} \cdot \boldsymbol{\theta})}{1 - z\lambda(\boldsymbol{\theta})} \, d^D\boldsymbol{\theta} \tag{4.3}$$

where D is the number of dimensions.[20] Let $Q_n(\mathbf{r}; l)$ be the probability that the random walk is at $\mathbf{r}$ at step n having visited the reactive point l

times without having reacted. The joint generating function for this quantity will be defined as

$$\zeta(\mathbf{r}; x, z) = \sum_{l=0}^{\infty} \sum_{n=0}^{\infty} Q_n(\mathbf{r}; l) x^l z^n \tag{4.4}$$

and is found to be[4]

$$\zeta(\mathbf{r}; x, z) = P(\mathbf{r}; z) - \frac{(1-x)P(\mathbf{r}-\mathbf{R}; z)P(\mathbf{R}; z)}{x + (1-x)P(\mathbf{0}; z)} \tag{4.5}$$

The resemblance of this expression to Eq. (2.14) is clear, with the identification $\kappa = (1-x)/x$ and replacement of the Laplace transform by a generating function.

The generating function for the probability of survival till step n or beyond will just be

$$S(z) = \sum_{n=0}^{\infty} S_n z^n = \sum_{\mathbf{r}} \zeta(\mathbf{r}; 1-\alpha, z) = \frac{1}{1-z}\left[1 - \frac{\alpha P(\mathbf{R}; z)}{1-\alpha+\alpha P(\mathbf{0}; z)}\right] \tag{4.6}$$

from which it is possible to derive asymptotic (in n) results by examining the behavior of $S(z)$ as $z \to 1$. For example, consider a symmetric random walk in two dimensions for which

$$\sum_{j_1} \sum_{j_2} j_1^2 p(j_1, j_2) = \sum_{j_1} \sum_{j_2} j_2^2 p(j_1, j_2) = \sigma^2 \tag{4.7}$$

It has been shown that in this case[20] as $z \to 1$,

$$\begin{aligned} P(R; z) &\sim \frac{1}{\pi\sigma^2} K_0\left[\frac{R}{\sigma}\sqrt{2(1-z)}\right], \qquad R \neq 0 \\ P(0; z) &\sim -\frac{1}{2\pi\sigma^2}\ln(1-z) \end{aligned} \tag{4.8}$$

where $K_0(u)$ is a Bessel function of the second kind. After expanding the expression for $P(R; z)$ in a neighborhood of $z = 1$, we find that the analytic behavior of $S(z)$ near this singularity is

$$S(z) \sim -\frac{2}{(1-z)\ln(1-z)}\left[\ln\left(\frac{R}{\sigma\sqrt{2}}\right) + \frac{2\pi\sigma^2(1-\alpha)}{\alpha}\right] \tag{4.9}$$

From this expression and a Tauberian theorem cited by Hardy,[21] we can infer that the probability of survival to step n or beyond is asymptotically

$$S_n \sim \frac{2}{\ln n}\left[\ln\left(\frac{R}{\sigma\sqrt{2}}\right) + \frac{2\pi\sigma^2(1-\alpha)}{\alpha}\right] \tag{4.10}$$

so that it is impossible to define a mean residence time. Notice that in this approximation the parameter α that measures the probability of reaction appears only as a multiplier of the time dependence, but does not affect the time dependence of S_n otherwise. This has also appeared in our treatment of the one-dimensional case [Eq. (2.25)]. When there are a finite number of imperfectly reactive sites the asymptotic n dependence of S_n will remain as in Eq. (4.10) but the coefficient will change from that shown. In three or more dimensions the functions $P(\mathbf{R}; 1)$ are all finite so that S_n approaches a constant in the limit of large n. This is consistent with the fact that the probability that a random walker will reach a given point in three or more dimensions is less than one.

While further theoretical developments along the lines of this paper are conceptually simple, the next order of interesting generalization involves the superposition of a continuum of reactive sites, which is to say, the complete solution to Eq. (2.1). Although one can write down a formal solution in terms of a Fredholm series this is not a computationally useful result. Hence, in the companion paper[14] we discuss perturbation schemes for the solution to Eq. (2.1) when $k(\mathbf{r})$ is small in some sense.

APPENDIX: EQUIVALENCE OF TWO FORMULATIONS OF BOUNDARY CONDITIONS

In this appendix we derive the relationship between the Green's function $p(\mathbf{r}, t \mid \mathbf{r}_0, 0)$ which satisfies the radiation boundary conditions at $\mathbf{r} = \mathbf{a}$ and the Green's function $G(\mathbf{r}, t \mid \mathbf{r}_0, 0)$ which satisfies a reflecting boundary condition at $\mathbf{r} = \mathbf{a}$. We then show that the resulting expression is identical to Eq. (2.4) when $k(\mathbf{r})$ is the delta function $\kappa\delta(\mathbf{r} - \mathbf{a})$. Since Eq. (2.14) is based on Eq. (2.4), it follows that when G satisfies a reflecting boundary condition at $\mathbf{r} = \mathbf{a}$, then p, as given by Eq. (2.14), satisfies a radiation boundary condition at $\mathbf{r} = \mathbf{a}$. In this proof we assume that L is the Smoluchowski operator describing diffusion in a potential $V(\mathbf{r})$.

The Green's function $p(\mathbf{r}, t \mid \mathbf{r}_0, 0)$ satisfies the equation

$$\frac{\partial p(\mathbf{r}, t \mid \mathbf{r}_0, 0)}{\partial t} = \nabla \cdot e^{-\beta V(\mathbf{r})} D(\mathbf{r}) \nabla \left[e^{\beta V(\mathbf{r})} p(\mathbf{r}, t \mid \mathbf{r}_0, 0) \right] \tag{A.1}$$

subject to the radiation boundary condition

$$D(\mathbf{r}) e^{-\beta V(\mathbf{r})} \mathbf{n} \cdot \nabla \left[e^{\beta V(\mathbf{r})} p(\mathbf{r}, t \mid \mathbf{r}_0, 0) \right] = \kappa p(\mathbf{r}, t \mid \mathbf{r}_0, 0) \qquad \text{at} \quad \mathbf{r} = \mathbf{a} \tag{A.2}$$

where $\mathbf{n}$ is a unit vector normal to the boundary at $\mathbf{r} = \mathbf{a}$ and directed towards the diffusion region. The Green's function $G(\mathbf{r}, t \mid \mathbf{r}_0, 0)$ also satisfies Eq. (A.1) but is subject to the reflecting boundary condition,

$$\mathbf{n} \cdot \nabla \left[e^{\beta V(\mathbf{r})} G(\mathbf{r}, t \mid \mathbf{r}_0, 0) \right] = 0 \qquad \text{at} \quad \mathbf{r} = \mathbf{a} \tag{A.3}$$

To express $p(\mathbf{r},t\,|\,\mathbf{r}_0,0)$ in terms of $G(\mathbf{r},t\,|\,\mathbf{r}_0,0)$, we start with the adjoint form of Eq. (A.1) for $G(\mathbf{r},t\,|\,\mathbf{r}_0,0)$,[7]

$$-\frac{\partial}{\partial t}G(\mathbf{R},T\,|\,\mathbf{r},t) = e^{\beta V(\mathbf{r})}\nabla\cdot e^{-\beta V(\mathbf{r})}D(\mathbf{r})\nabla G(\mathbf{R},T\,|\,\mathbf{r},t) \tag{A.4}$$

and the adjoint reflecting boundary condition[7]

$$\mathbf{n}\cdot\nabla G(\mathbf{R},T\,|\,\mathbf{r},t) = 0 \qquad \text{at} \quad \mathbf{r}=\mathbf{a} \tag{A.5}$$

If one multiplies Eq. (A.1) by $G(\mathbf{R},T\,|\,\mathbf{r},t)$ and Eq. (A.4) by $p(\mathbf{r},t\,|\,\mathbf{r}_0,0)$, subtraction of the resulting equations leads to

$$\begin{aligned}\frac{\partial}{\partial t}\left[G(\mathbf{R},T\,|\,\mathbf{r},t)p(\mathbf{r},t\,|\,\mathbf{r}_0,0)\right]&\\ = G(\mathbf{R},T\,|\,\mathbf{r},t)\nabla\cdot e^{-\beta V(\mathbf{r})}D(\mathbf{r})\nabla\left[e^{\beta V(\mathbf{r})}p(\mathbf{r},t\,|\,\mathbf{r}_0,0)\right]&\\ -p(\mathbf{r},t\,|\,\mathbf{r}_0,0)e^{\beta V(\mathbf{r})}\nabla\cdot\left[e^{-\beta V(\mathbf{r})}D(\mathbf{r})\nabla G(\mathbf{R},T\,|\,\mathbf{r},t)\right] &\quad\text{(A.6)}\\ = \nabla\cdot\Big\{G(\mathbf{R},T\,|\,\mathbf{r},t)e^{-\beta V(\mathbf{r})}D(\mathbf{r})\nabla\left[e^{\beta V(\mathbf{r})}p(\mathbf{r},t\,|\,\mathbf{r}_0,0)\right]&\\ -p(\mathbf{r},t\,|\,\mathbf{r}_0,0)D(\mathbf{r})\nabla G(\mathbf{R},T\,|\,\mathbf{r},t)\Big\} &\quad\text{(A.7)}\end{aligned}$$

Integration of Eq. (A.7) over r and t gives simply

$$\begin{aligned}p(\mathbf{R},T\,|\,\mathbf{r}_0,0) = G(\mathbf{R},T\,|\,\mathbf{r}_0,0) - \int_0^T dt\, G(\mathbf{R},T\,|\,\mathbf{a},t)&\\ \times\kappa p(\mathbf{a},t\,|\,\mathbf{r}_0,0)&\end{aligned} \tag{A.8}$$

The right-hand side of Eq. (A.7) leads to a surface contribution at $\mathbf{r}=\mathbf{a}$ that is evaluated using boundary conditions (A.3) and (A.5), while the contribution at infinity vanishes. Equation (A.8) is identical to Eq. (2.4) when $k(\mathbf{r}) = \kappa\delta(\mathbf{r}-\mathbf{a})$.

REFERENCES

1. S. Karlin and H. M. Taylor, *A Second Course in Stochastic Processes* (Academic Press, New York, 1981).
2. K. Funabashi, *J. Chem. Phys.* **72**:3123 (1980).
3. W. Th. F. den Hollander and P. W. Kasteleyn, *Physica* **112A**:523 (1982).
4. R. J. Rubin and G. H. Weiss, *J. Math. Phys.* **23**:250 (1982).
5. F. C. Collins and G. E. Kimball, *J. Coll. Sci.* **4**:425 (1949).
6. A. Mozumder, *J. Chem. Phys.* **69**:1384 (1978).
7. A. Szabo, A. K. Schulten, and Z. Schulten, *J. Chem. Phys.* **74**:4350 (1980).
8. A. Mozumder, *J. Chem. Phys.* **76**:5107 (1982).
9. R. M. Noyes, *Prog. React. Kinet.* **1**:129 (1961).
10. D. Shoup and A. Szabo, *Biophys. J.* **40**:33 (1982).
11. D. L. Weaver, *Biophys. J.* **40**:81 (1983).
12. G. Wilemski and M. Fixman, *J. Chem. Phys.* **58**:4009 (1973).

13. S. H. Northrup and J. T. Hynes, *J. Stat. Phys.* **18**:91 (1978).
14. G. H. Weiss, *J. Chem. Phys.* (to appear).
15. F. J. Dyson, *Phys. Rev.* **75**:486, 1736 (1949).
16. H. S. Carslaw and J. C. Jaeger, *Conduction of Heat in Solids* (Oxford University Press, Oxford, 1959), p. 358.
17. J. Deutch, *J. Chem. Phys.* **73**:4700 (1980).
18. O. G. Berg, *Chem. Phys.* **31**:47 (1978).
19. K. Razi Naqvi, K. J. Mork, and S. Waldenstrom, *J. Phys. Chem.* **84**, 1315 (1980).
20. E. W. Montroll and G. H. Weiss, *J. Math. Phys.* **6**:167 (1965).
21. G. H. Hardy, *Divergent Series* (Oxford University Press, Oxford, 1949).