Spectral theory of diffusion in partially absorbing media

P. C. Bressloff,
Department of Mathematics, University of Utah
155 South 1400 East, Salt Lake City, UT 84112

October 9, 2023

Abstract

A probabilistic framework for studying single-particle diffusion in partially absorbing media has recently been developed in terms of an encounter-based approach. The latter computes the joint probability density (generalized propagator) for particle position $\mathbf{X}_t$ and a Brownian functional $\mathcal{U}_t$ that specifies the amount of time the particle is in contact with a reactive component $\mathcal{M}$. Absorption occurs as soon as $\mathcal{U}_t$ crosses a randomly distributed threshold (stopping time). Laplace transforming the propagator with respect to $\mathcal{U}_t$ leads to a classical boundary value problem (BVP) in which the reactive component has a constant rate of absorption z, where z is the corresponding Laplace variable. Hence, a crucial step in the encounter-based approach is finding the inverse Laplace transform. In the case of a reactive boundary $\partial\mathcal{M}$, this can be achieved by solving a classical Robin BVP in terms of the spectral decomposition of a Dirichlet-to-Neumann (D-to-N) operator on $\partial\mathcal{M}$ In this paper we develop the analogous construction in the case of a reactive substrate $\mathcal{M}$. In particular, we show that the Laplace transformed propagator can be computed in terms of the spectral decomposition of a pair of D-to-N operators on $\partial\mathcal{M}$. However, inverting the Laplace transform with respect to z is considerably more involved. We illustrate the theory by considering the D-to-N operators for some simple geometries.

1 Introduction

The three classical boundary conditions for the diffusion equation $\partial u/\partial t = D\nabla^2 u$ in a bounded domain Ω are, respectively, Dirichlet ($u(\mathbf{x},t) = 0$), Neumann ($\nabla u(\mathbf{x},t)\cdot\mathbf{n}_1 = 0$) and Robin ($D\nabla u(\mathbf{x},t)\cdot\mathbf{n}_1 + \kappa_0 u(\mathbf{x},t) = 0$) for all $\mathbf{x}\in\partial\Omega$. Here u is particle concentration, D is the diffusivity, κ_0 is a positive reactivity constant, and $\mathbf{n}_1$ is the outward unit normal at a point on the boundary, see Fig. 1(a). However, implementing these boundary conditions at the level of a single diffusing particle is non-trivial. Individual trajectories of the particle are generated by a stochastic differential equation (SDE) that, in the case of

pure diffusion in $\mathbb{R}^d$ is given by a Wiener process. Although the evolution of the probability density $p(\mathbf{x},t)$ for the random position $\mathbf{X}_t$ in a bounded domain Ω is identical to the macroscopic diffusion equation for u, the effect of the boundary on the underlying SDE is more complicated. The simplest case is a totally absorbing boundary (Dirichlet), which can be handled by stopping the Brownian motion on the first encounter between particle and boundary. The random time at which this event occurs is known as the first passage time (FPT). On the other hand, it is necessary to modify the stochastic process itself in the case of a totally or partially reflecting boundary. For example, one can implement a Neumann boundary condition by introducing a Brownian functional known as the boundary local time [1, 2, 3, 4]. The latter determines the amount of time that a Brownian particle spends in the neighborhood of points on the boundary. Probabilistic versions of the Robin boundary condition can also be constructed [5, 6, 7, 8, 9].

One of the assumptions of the Robin boundary condition is that the surface reactivity is a constant. However, various surface-based reactions are better modeled in terms of a reactivity that is a function of the local time [10, 11]. That is, the surface may need to be progressively activated by repeated encounters with a diffusing particle, or an initially highly reactive surface may become less active due to multiple interactions with the particle (passivation). Recently, a theoretical framework for analyzing a more general class of partially absorbing boundary has been developed using a so-called encounter-based approach [12, 13, 14]. The basic idea is to consider the joint probability density or generalized propagator $P(\mathbf{x},\ell,t)$ for the pair $(\mathbf{X}_t,\ell_t)$ in the case of a perfectly reflecting boundary, where $\mathbf{X}_t$ and ℓ_t denote the particle position and local time, respectively. The effects of surface reactions are then incorporated by introducing the stopping time $\mathcal{T}=\inf\{t>0:\ \ell_t>\widehat{\ell}\}$, with $\widehat{\ell}$ a so-called stopping local time. Given the probability distribution $\Psi(\ell)=\mathbb{P}[\widehat{\ell}>\ell]$, the marginal probability density for particle position is defined according to $p(\mathbf{x},t)=\int_0^\infty \Psi(\ell)P(\mathbf{x},\ell,t)d\ell$. The classical Robin boundary condition for the diffusion equation corresponds to the exponential distribution $\Psi(\ell)=\mathrm{e}^{-\gamma\ell}$, where $\gamma=\kappa_0/D$. The crucial step in the encounter-based approach is computing the generalized propagator $P(\mathbf{x},\ell,t)$ by solving a corresponding boundary value problem (BVP) [13, 14]. Performing a double Laplace transform with respect to the time t and the local time ℓ,

$$\mathcal{P}(\mathbf{x},z,s)\equiv\int_0^\infty \mathrm{e}^{-z\ell}\int_0^\infty \mathrm{e}^{-st}P(\mathbf{x},\ell,t)dtd\ell, \tag{1.1}$$

one finds that $\mathcal{P}(\mathbf{x},z,s)$ satisfies a modified Helmholtz equation with a Robin boundary condition on $\partial\Omega$, in which the effective reactivity is proportional to the Laplace variable z. Hence, the calculation of the Laplace transformed propagator $\widetilde{P}(\mathbf{x},\ell,s)$ reduces to solving a classical Robin BVP and then inverting the solution with respect to the Laplace variable z,

$$\widetilde{P}(\mathbf{x},\ell,s)\equiv\int_0^\infty \mathrm{e}^{-st}P(\mathbf{x},\ell,t)dt=\mathcal{L}_\ell^{-1}[\mathcal{P}(\mathbf{x},z,s)]. \tag{1.2}$$

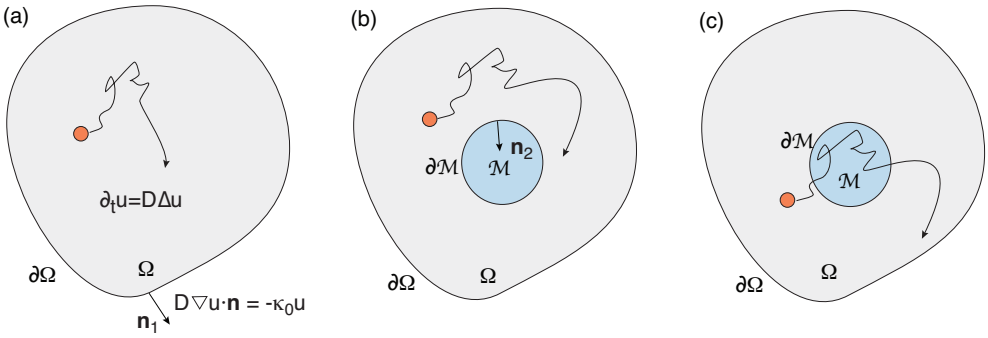


Figure 1: (a) Diffusion of a particle in a bounded domain Ω with a partially absorbing boundary $\partial\Omega$. The probability of particle absorption depends on the amount of time spent in a neighborhood of $\partial\Omega$, which is specified by the local accumulation time ℓ_t. (b) Diffusion in the bounded domain $\Omega\backslash\mathcal{M}$, with $\partial\mathcal{M}$ acting as a partially absorbing boundary. (c) A particle diffusing in Ω can freely enter and exit the substrate domain $\mathcal{M}$. The probability of particle absorption depends on the amount of time spent within $\mathcal{M}$, which is specified by the occupation time A_t. Note that the unit normal $\mathbf{n}_2$ is directed towards the interior of $\mathcal{M}$ in (b).

It turns out that solving the Robin BVP in terms of the spectrum of an associated Dirichlet-to-Neumann (D-to-N) operator on $\partial\Omega$ yields a series expansion that is easily inverted with respect to the Laplace variable z [13]. The corresponding marginal density $\widetilde{p}(\mathbf{x},s) = \int_0^\infty \Psi(\ell)\widetilde{P}(\mathbf{x},\ell,s)d\ell$ and the associated boundary flux generate various quantities of interest without having to transform back to the time domain, including the mean first passage time (MFPT) for absorption.

A simple generalization of diffusion in a bounded domain Ω is illustrated in Fig. 1(b), whereby a target domain $\mathcal{M}$ is inserted within the interior of Ω. There is now an exterior boundary $\partial\Omega$ and an interior boundary $\partial\mathcal{M}$, each of which has an associated boundary condition. A standard scenario at the single particle level is taking $\partial\Omega$ to be totally reflecting, or setting $\Omega = \mathbb{R}^d$, and calculating the statistics of the first absorption time in the case of a totally or partially absorbing target boundary $\partial\mathcal{M}$. However, the possibility of partial absorption naturally leads to another generalization, as illustrated in Fig. 1(c), in which $\mathcal{M}$ acts as a partially absorbing interior substrate or trap. Now the particle can freely enter and exit the domain $\mathcal{M}$, and the probability of being absorbed depends on the amount of time spent within $\mathcal{M}$. The latter is specified by another Brownian functional known as the occupation time A_t [4]. We have recently shown how to extend the encounter-based approach of Grebenkov to partially absorbing substrates by constructing the generalized propagator for the occupation time A_t rather than the local accumulation time ℓ_t [15]. In particular, we used a Feynman-Kac formula to derive the BVP for the occupation time propagator

and solved the resulting BVP in the special case of a spherically symmetric domain. However, more general aspects of the theory were not explored.

In this paper we develop the general analysis of the occupation time propagator BVP. In section 2 we construct the occupation time propagator BVPs along the lines of Ref. [15], and show how to incorporate partial absorption in terms of a stopping occupation time distribution $\Psi(a)$. We also briefly describe the analogous construction for the local time propagator. In section 3 we perform a double Laplace transform with respect to t and the occupation time A_t, and derive the analog of Robin boundary conditions for the occupation time BVP, namely, the particle can be absorbed at a constant rate z within $\mathcal{M}$, where z is the Laplace variable conjugate to the occupation time.

In section 4 we explore to what extent spectral methods used to solve the Robin BVP for the local time propagator [13] can be carried over to the occupation time propagator BVP. Our main results is to establish that the solution can be computed in terms of the spectral decomposition of a pair of D-to-N operators. defined on $\partial\mathcal{M}$. This doubling up of the number of operators means that inverting the Laplace transform in z is much more complicated than for the Robin BVP. In particular, assuming that $\partial\mathcal{M}$ is bounded, the eigenvalue expansion of the Laplace transformed occupation time propagator typically requires inverting an infinite-dimensional matrix equation, which means that the z-dependence is non-trivial. On the other hand, the eigenvalue expansion of the Laplace transformed local time propagator yields a meromorphic function of z with an infinite set of simple poles given by the eigenvalues of a single D-to-N operator on $\partial\mathcal{M}$. Finally, in section 5 we calculate the spectral decomposition for a few simple geometries, including a 1D substrate, where the D-to-N operators reduce to scalars, and a sphere. It is important to note that the spectral decomposition of the generalized propagator derived in this paper is independent of the choice of stopping time distribution Ψ. However, since the propagator typically takes the form of an infinite series, it has to be truncated when calculating quantities of interest such as the MFPT for absorption; the accuracy of any numerical truncation will thus depend on the particular choice of Ψ.

2 Brownian functionals and the generalized propagator BVP

Consider a particle diffusing in a bounded domain $\Omega \subset \mathbb{R}^d$ with a totally reflecting boundary $\partial\Omega$. Let $\mathbf{X}_t$ denote the position of the particle at time t. A Brownian functional over a fixed time interval $[0, T]$ is defined as a random variable $\mathcal{U}_t$ given by [4]

$$\mathcal{U}_t = \int_0^t F(\mathbf{X}_\tau) d\tau, \tag{2.3}$$

where $F(\mathbf{x})$ is some prescribed function or distribution such that $\mathcal{U}_t$ has positive support and $\mathbf{X}_0 = \mathbf{x}_0$ is fixed. We also assume that $\mathcal{U}_0 = 0$. Let $P(\mathbf{x}, u, t|\mathbf{x}_0)$

denote the joint probability density or propagator for the pair $(\mathbf{X}_t, \mathcal{U}_t)$. It follows that

$$P(\mathbf{x}, u, t|\mathbf{x}_0) = \left\langle \delta\left(u - \mathcal{U}_t\right) \right\rangle_{\mathbf{X}_0=\mathbf{x}_0}^{\mathbf{X}_t=\mathbf{x}}, \tag{2.4}$$

where expectation is taken with respect to all random paths realized by $\mathbf{X}_\tau$ between $\mathbf{X}_0 = \mathbf{x}_0$ and $\mathbf{X}_t = \mathbf{x}$. Using the Feynman-Kac formula, it can be shown that the propagator satisfies a BVP of the form [15]

$$\frac{\partial P(\mathbf{x}, u, t|\mathbf{x}_0)}{\partial t} = D\nabla^2 P(\mathbf{x}, u, t|\mathbf{x}_0) - F(\mathbf{x})\frac{\partial P}{\partial u}(\mathbf{x}, u, t|\mathbf{x}_0) \ - \delta(u)F(\mathbf{x})P(\mathbf{x}, 0, t|\mathbf{x}_0), \ \mathbf{x} \in \Omega, \tag{2.5a}$$

$$\nabla P(\mathbf{x}, u, t|\mathbf{x}_0) \cdot \mathbf{n}_1 = 0, \ \mathbf{x} \in \partial\Omega. \tag{2.5b}$$

Here $\mathbf{n}_1$ is the outward unit normal to a point on the boundary $\partial\Omega$. If Ω is unbounded then we replace the Neumann condition (2.5b) by $P(\mathbf{x}, u, t|\mathbf{x}_0) \to 0$ as $|\mathbf{x}| \to \infty$. The initial condition is $P(\mathbf{x}, u, 0|\mathbf{x}_0) = \delta(\mathbf{x} - \mathbf{x}_0)\delta(u)$.

2.0.1 Occupation time propagator

Suppose that a target domain $\mathcal{M}$ is introduced within the interior of Ω along the lines of Fig. 1(c), and that the particle can freely enter and exit $\mathcal{M}$. The amount of time the particle spends within $\mathcal{M}$ over the time interval $[0, t]$ is specified by a Brownian functional known as the occupation time A_t:

$$A_t = \int_0^t I_{\mathcal{M}}(\mathbf{X}_\tau) d\tau. \tag{2.6}$$

Here $I_{\mathcal{M}}(\mathbf{x})$ denotes the indicator function of the set $\mathcal{M} \subset \Omega$, that is, $I_{\mathcal{M}}(\mathbf{x}) = 1$ if $\mathbf{x} \in \mathcal{M}$ and is zero otherwise. It follows that

$$F(\mathbf{x}) = I_{\mathcal{M}}(\mathbf{x}) = \int_{\mathcal{M}} \delta(\mathbf{x} - \mathbf{x}') d\mathbf{x}'. \tag{2.7}$$

and equations (2.5) take the form

$$\begin{aligned} \frac{\partial P(\mathbf{x}, a, t|\mathbf{x}_0)}{\partial t} &= D\nabla^2 P(\mathbf{x}, a, t|\mathbf{x}_0) \\ &\quad - \int_{\mathcal{M}} \left(\frac{\partial P}{\partial a}(\mathbf{x}', a, t|\mathbf{x}_0) + \delta(a) P(\mathbf{x}', 0, t|\mathbf{x}_0) \right) \delta(\mathbf{x} - \mathbf{x}') d\mathbf{x}' \end{aligned} \tag{2.8}$$

for all $\mathbf{x} \in \Omega$, together with the Neumann boundary condition on $\partial\Omega$. That is,

$$\frac{\partial P(\mathbf{x}, a, t|\mathbf{x}_0)}{\partial t} = D\nabla^2 P(\mathbf{x}, a, t|\mathbf{x}_0), \ \mathbf{x} \in \Omega \backslash \mathcal{M}, \tag{2.9a}$$

$$\nabla P(\mathbf{x}, a, t|\mathbf{x}_0) \cdot \mathbf{n}_1 = 0, \ \mathbf{x} \in \partial\Omega, \tag{2.9b}$$

$$\frac{\partial Q(\mathbf{x}, a, t|\mathbf{x}_0)}{\partial t} = D\nabla^2 Q(\mathbf{x}, a, t|\mathbf{x}_0) - \left(\frac{\partial Q}{\partial a}(\mathbf{x}, a, t|\mathbf{x}_0) + \delta(a) Q(\mathbf{x}, 0, t|\mathbf{x}_0) \right) \tag{2.9c}$$

for $\mathbf{x} \in \mathcal{M}$, where the propagator within $\mathcal{M}$ is denoted by Q. We also have the continuity conditions

$$P(\mathbf{x}, a, t|\mathbf{x}_0) = Q(\mathbf{x}, a, t|\mathbf{x}_0), \quad \nabla Q(\mathbf{x}, a, t|\mathbf{x}_0)\cdot\mathbf{n}_2 = \nabla P(\mathbf{x}, a, t|\mathbf{x}_0)\cdot\mathbf{n}_2, \ \mathbf{x} \in \partial\mathcal{M}, \tag{2.9d}$$

and the initial conditions $P(\mathbf{x}, a, 0|\mathbf{x}_0) = \delta(\mathbf{x} - \mathbf{x}_0)\delta(a)$, $Q(\mathbf{x}, a, 0|\mathbf{x}_0) = 0$. The unit normal $\mathbf{n}_2$ on $\partial\mathcal{M}$ is directed towards the interior of $\mathcal{M}$, see Fig. 1(b). We assume that the particle starts out in the non-absorbing region. (The analysis is easily modified if $\mathbf{x}_0 \in \mathcal{M}$.)

Given the solution to the propagator BVP (2.9), we can introduce a probabilistic model of partial absorption by introduce the stopping time condition

$$\mathcal{T} = \inf\{t > 0 : \ A_t > \widehat{\mathcal{A}}\}, \tag{2.10}$$

where $\widehat{\mathcal{A}}$ is a random variable with probability distribution $\mathbb{P}[\widehat{\mathcal{A}} > a] = \Psi(a)$. Heuristically speaking, $\mathcal{T}$ is a random variable that specifies the time of absorption within $\mathcal{M}$, which is the event that $\mathcal{A}_t$ first crosses a randomly generated threshold $\widehat{\mathcal{A}}$. The marginal probability density for particle position $\mathbf{X}_t \in \Omega\backslash\mathcal{M}$ is then

$$p(\mathbf{x}, t|\mathbf{x}_0)d\mathbf{x} = \mathbb{P}[\mathbf{X}_t \in (\mathbf{x}, \mathbf{x} + d\mathbf{x}), \ t < \mathcal{T}|\mathbf{X}_0 = \mathbf{x}_0].$$

Given that $\mathcal{A}_t$ is a nondecreasing process, the condition $t < \mathcal{T}$ is equivalent to the condition $\mathcal{A}_t < \widehat{\mathcal{A}}$. This implies that

$$p(\mathbf{x}, t|\mathbf{x}_0)d\mathbf{x} = \mathbb{P}[\mathbf{X}_t \in (\mathbf{x}, \mathbf{x} + d\mathbf{x}), \ \mathcal{A}_t < \widehat{\mathcal{A}}|\mathbf{X}_0 = \mathbf{x}_0] = \int_0^\infty da \ \psi(a) \int_0^a da'[P(\mathbf{x}, a', t|\mathbf{x}_0)d\mathbf{x}],$$

where $\psi(a) = -d\Psi(a)/da$. Using the identity

$$\int_0^\infty du \ f(u) \int_0^u du' \ g(u') = \int_0^\infty du' \ g(u') \int_{u'}^\infty du \ f(u)$$

for arbitrary integrable functions f, g, it follows that

$$p(\mathbf{x}, t|\mathbf{x}_0) = \int_0^\infty \Psi(a)P(\mathbf{x}, a, t|\mathbf{x}_0)da, \quad \mathbf{x} \in \Omega\backslash\mathcal{M}. \tag{2.11}$$

Similarly,

$$q(\mathbf{x}, t|\mathbf{x}_0) = \int_0^\infty \Psi(a)Q(\mathbf{x}, a, t|\mathbf{x}_0)da, \quad \mathbf{x} \in \mathcal{M}. \tag{2.12}$$

One general quantity of interest is the survival probability $S(\mathbf{x}_0, t)$ that the particle hasn't been absorbed up to time t, given that it started at $\mathbf{x}_0$. In the case of a partially absorbing substrate $\mathcal{M}$,

$$S(\mathbf{x}_0, t) = \int_{\Omega\backslash\mathcal{M}} p(\mathbf{x}, t|\mathbf{x}_0)d\mathbf{x} + \int_{\mathcal{M}} q(\mathbf{x}, t|\mathbf{x}_0)d\mathbf{x}. \tag{2.13}$$

The probability density of the stopping time $\mathcal{T}$, equation (2.10), is given by $-\partial S/\partial t$ so that the MFPT (if it exists) is

$$T(\mathbf{x}_0) = -\int_0^\infty t\frac{\partial S(\mathbf{x}_0,t)}{\partial t}dt = \int_0^\infty S(\mathbf{x}_0,t)dt = \widetilde{S}(\mathbf{x}_0,0), \tag{2.14}$$

with $\widetilde{f}(s) \equiv \int_0^\infty f(t)\mathrm{e}^{-st}dt$. Similarly, higher order moments of the FPT density can be obtained in terms of s-derivatives of $\widetilde{S}(\mathbf{x}_0,s)$.

2.0.2 Local time propagator

As we showed in [15], the same mathematical framework can be applied to the case of a totally reflecting boundary ∂M, see Fig. 1(b). The relevant Brownian functional is now the boundary local time ℓ_t:

$$\ell_t = \lim_{h\to 0}\frac{D}{h}\int_0^t H(h-\mathrm{dist}(\mathbf{X}_\tau,\partial\mathcal{M}))d\tau, \tag{2.15}$$

where H is the Heaviside function. Note that although ℓ_t has units of length due to the additional factor of D, it essentially specifies the amount of time that the particle spends in an infinitesimal neighborhood of the surface $\partial\Omega$. In the case of the local time (2.15), the effective bounded domain is $\Omega\backslash\mathcal{M}$ and

$$F(\mathbf{x}) = \lim_{h\to 0}\frac{D}{h}\Theta(h-\mathrm{dist}(\mathbf{x},\partial\mathcal{M})) = D\int_{\partial\mathcal{M}}\delta(\mathbf{x}-\mathbf{x}')d\mathbf{x}'. \tag{2.16}$$

Equation (2.5a) becomes

$$\begin{aligned}\frac{\partial P(\mathbf{x},\ell,t|\mathbf{x}_0)}{\partial t} &= D\nabla^2 P(\mathbf{x},\ell,t|\mathbf{x}_0)\\ &\quad - D\int_{\partial\mathcal{M}}\left(\frac{\partial P}{\partial\ell}(\mathbf{x}',\ell,t|\mathbf{x}_0)+\delta(\ell)P(\mathbf{x}',0,t|\mathbf{x}_0)\right)\delta(\mathbf{x}-\mathbf{x}')d\mathbf{x}',\end{aligned} \tag{2.17}$$

which leads to the local time BVP previously derived in Ref. [13]:

$$\frac{\partial P(\mathbf{x},\ell,t|\mathbf{x}_0)}{\partial t} = D\nabla^2 P(\mathbf{x},\ell,t|\mathbf{x}_0),\ \mathbf{x}\in\Omega\backslash\mathcal{M},\ \nabla P(\mathbf{x},\ell,t|\mathbf{x}_0)\cdot\mathbf{n}_1 = 0,\ \mathbf{x}\in\partial\Omega, \tag{2.18a}$$

$$-D\nabla P(\mathbf{x},\ell,t|\mathbf{x}_0)\cdot\mathbf{n}_2 = DP(\mathbf{x},\ell=0,t|\mathbf{x}_0)\ \delta(\ell)+D\frac{\partial}{\partial\ell}P(\mathbf{x},\ell,t|\mathbf{x}_0),\mathbf{x}\in\partial\mathcal{M}. \tag{2.18b}$$

These equations are supplemented by the "initial conditions" $P(\mathbf{x},\ell,0|\mathbf{x}_0) = \delta(\mathbf{x}-\mathbf{x}_0)\delta(\ell)$ and

$$P(\mathbf{x},\ell=0,t|\mathbf{x}_0) = -\nabla p_\infty(\mathbf{x},t|\mathbf{x}_0)\cdot\mathbf{n}_2 \text{ for } \mathbf{x}\in\partial\mathcal{M}, \tag{2.18c}$$

where p_∞ is the probability density in the case of a totally absorbing surface $\partial\mathcal{M}$:

$$\frac{\partial p_\infty(\mathbf{x},t|\mathbf{x}_0)}{\partial t} = D\nabla^2 p_\infty(\mathbf{x},t|\mathbf{x}_0),\ \mathbf{x}\in\Omega\backslash\mathcal{M},\ \nabla p_\infty(\mathbf{x},t|\mathbf{x}_0)\cdot\mathbf{n}_1 = 0,\ \mathbf{x}\in\partial\Omega, \tag{2.19a}$$

$$p_\infty(\mathbf{x},t|\mathbf{x}_0) = 0,\ \mathbf{x}\in\partial\mathcal{M},\ p_\infty(\mathbf{x},0|\mathbf{x}_0) = \delta(\mathbf{x}-\mathbf{x}_0). \tag{2.19b}$$

One way to establish (2.18c) is to note that Laplace transforming equations (2.18a,b) with respect to ℓ leads to a Robin BVP, see section 3. Finally, given the solution to the local time propagator BVP, a partially absorbing surface $\partial\mathcal{M}$ can be implemented by introducing a stopping local time $\widehat{\ell}$ with distribution $\Psi(\ell)$ such that

$$p(\mathbf{x},t|\mathbf{x}_0) = \int_0^\infty \Psi(\ell)P(\mathbf{x},\ell,t|\mathbf{x}_0)d\ell, \quad \mathbf{x}\in\Omega\backslash\mathcal{M}. \tag{2.20}$$

3 Laplace transformed BVP

One of the difficulties of the above encounter-based model of absorption is that for general choices of the stopping time distribution Ψ, it is not possible to write down a closed BVP for the marginal probability densities. This means that we have to solve the BVP for the full propagator and then evaluate the integrals over Ψ. We now make the crucial observation that when $\Psi(a) = \mathrm{e}^{-za}$ in equation (2.11) or $\Psi(\ell) = \mathrm{e}^{-z\ell}$ in equation (2.20), the resulting marginal probability density is equivalent to the Laplace transform of the generalized propagator with respect to z. In particular, the Laplace transformed BVP reduces to the classical problem of a partially absorbing surface or substrate with constant reactivity z. The latter can be solved using classical methods such as spectral theory (see section 4), and then inverted to determine the original propagator.

3.0.1 Occupation time propagator

Laplace transforming the occupation time BVP (2.9) with respect to a and setting

$$\widetilde{P}(\mathbf{x},z,t|\mathbf{x}_0) = \int_0^\infty \mathrm{e}^{-za}P(\mathbf{x},a,t|\mathbf{x}_0)da, \quad \widetilde{Q}(\mathbf{x},z,t|\mathbf{x}_0) = \int_0^\infty \mathrm{e}^{-za}Q(\mathbf{x},a,t|\mathbf{x}_0)da, \tag{3.21}$$

yields

$$\frac{\partial \widetilde{P}(\mathbf{x},z,t|\mathbf{x}_0)}{\partial t} = D\nabla^2 \widetilde{P}(\mathbf{x},z,t|\mathbf{x}_0),\ \mathbf{x}\in\Omega\backslash\mathcal{M}, \tag{3.22a}$$

$$\nabla \widetilde{P}(\mathbf{x},z,t|\mathbf{x}_0)\cdot\mathbf{n}_1 = 0,\ \mathbf{x}\in\partial\Omega, \tag{3.22b}$$

$$\frac{\partial \widetilde{Q}(\mathbf{x},z,t|\mathbf{x}_0)}{\partial t} = D\nabla^2 \widetilde{Q}(\mathbf{x},z,t|\mathbf{x}_0) - z\widetilde{Q}(\mathbf{x},z,t|\mathbf{x}_0),\ \mathbf{x}\in\mathcal{M}, \tag{3.22c}$$

$$\widetilde{P}(\mathbf{x},z,t|\mathbf{x}_0) = \widetilde{Q}(\mathbf{x},z,t|\mathbf{x}_0),\quad \nabla \widetilde{P}(\mathbf{x},z,t|\mathbf{x}_0)\cdot\mathbf{n}_2 = \nabla \widetilde{Q}(\mathbf{x},z,t|\mathbf{x}_0)\cdot\mathbf{n}_2,\ \mathbf{x}\in\partial\mathcal{M}. \tag{3.22d}$$

This is a classical BVP for diffusion in a domain with a partially absorbing substrate $\mathcal{M}$ with a constant rate of absorption z. Note that z has units of inverse time. Equations (3.22) are the analog of a Robin BVP, in which a partially reactive surface $\partial\Omega$ is replaced by a partially absorbing substrate $\mathcal{M}$. Although specific examples of the BVP (3.22) for constant z have been solved elsewhere [22, 23], as far as we are aware, a general spectral decomposition in terms of D-to-N operators has not been performed. Moreover, an additional step in the encounter-based approach is having to invert the solution with respect to z.

It turns out that it is more convenient to perform a double Laplace transform with respect to both t and a by setting

$$\mathcal{P}(\mathbf{x},z,s|\mathbf{x}_0) = \int_0^\infty \mathrm{e}^{-za}\left[\int_0^\infty \mathrm{e}^{-st}P(\mathbf{x},a,t|\mathbf{x}_0)dt\right]da, \tag{3.23a}$$

$$\mathcal{Q}(\mathbf{x},z,s|\mathbf{x}_0) = \int_0^\infty \mathrm{e}^{-za}\left[\int_0^\infty \mathrm{e}^{-st}Q(\mathbf{x},a,t|\mathbf{x}_0)dt\right]da, \tag{3.23b}$$

This yields

$$D\nabla^2\mathcal{P}(\mathbf{x},z,s|\mathbf{x}_0) - s\mathcal{P}(\mathbf{x},z,s|\mathbf{x}_0) = -\delta(\mathbf{x}-\mathbf{x}_0),\ \mathbf{x}\in\Omega\backslash\mathcal{M}, \tag{3.24a}$$

$$-\nabla\mathcal{P}(\mathbf{x},z,s|\mathbf{x}_0)\cdot\mathbf{n}_1 = 0,\ \mathbf{x}\in\partial\Omega, \tag{3.24b}$$

$$D\nabla^2\mathcal{Q}(\mathbf{x},z,s|\mathbf{x}_0) - (s+z)\mathcal{Q}(\mathbf{x},z,s|\mathbf{x}_0) = 0,\ \mathbf{x}\in\mathcal{M}, \tag{3.24c}$$

$$\mathcal{P}(\mathbf{x},z,s|\mathbf{x}_0) = \mathcal{Q}(\mathbf{x},z,s|\mathbf{x}_0),\ \nabla\mathcal{P}(\mathbf{x},z,s|\mathbf{x}_0)\cdot\mathbf{n}_2 = \nabla\mathcal{Q}(\mathbf{x},z,s|\mathbf{x}_0)\cdot\mathbf{n}_2,\ \mathbf{x}\in\partial\mathcal{M}. \tag{3.24d}$$

Gven the solution to equations (3.24), we can then introduce a more general probability distribution $\Psi(a)$ for the stopping occupation time such that

$$\widetilde{p}(\mathbf{x},s|\mathbf{x}_0) = \int_0^\infty \Psi(a)\mathcal{L}_a^{-1}[\mathcal{P}(\mathbf{x},z,s|\mathbf{x}_0)]da,\ \mathbf{x}\in\Omega\backslash\mathcal{M}, \tag{3.25a}$$

$$\widetilde{q}(\mathbf{x},s|\mathbf{x}_0) = \int_0^\infty \Psi(a)\mathcal{L}_a^{-1}[\mathcal{Q}(\mathbf{x},z,s|\mathbf{x}_0)]da,\ \mathbf{x}\in\mathcal{M}. \tag{3.25b}$$

These can then be used to determine the MFPT for absorption within $\mathcal{M}$ according to equation (2.14) without the need to invert the Laplace transform with respect to s.

3.0.2 Local time propagator

Laplace transforming the local time BVP (2.18) with respect to ℓ and setting

$$\widetilde{P}(\mathbf{x}, z, t|\mathbf{x}_0) = \int_0^\infty \mathrm{e}^{-z\ell} P(\mathbf{x}, \ell, t|\mathbf{x}_0) d\ell \tag{3.26}$$

yields

$$\frac{\partial \widetilde{P}(\mathbf{x}, z, t|\mathbf{x}_0)}{\partial t} = D\nabla^2 \widetilde{P}(\mathbf{x}, z, t|\mathbf{x}_0), \ \mathbf{x} \in \Omega \backslash \mathcal{M}, \ \nabla \widetilde{P}(\mathbf{x}, z, t|\mathbf{x}_0) \cdot \mathbf{n}_1 = 0, \ \mathbf{x} \in \partial\Omega, \tag{3.27a}$$

$$-\nabla \widetilde{P}(\mathbf{x}, z, t|\mathbf{x}_0) \cdot \mathbf{n}_2 = z\widetilde{P}(\mathbf{x}, z, t|\mathbf{x}_0), \ \mathbf{x} \in \partial\mathcal{M}, \tag{3.27b}$$

and $\widetilde{P}(\mathbf{x}, z, 0|\mathbf{x}_0) = \delta(\mathbf{x} - \mathbf{x}_0)$. We see that equation (3.27b) is a classical Robin boundary condition on $\partial\mathcal{M}$ with an effective constant reactivity $\kappa_0 = zD$. (In contrast to the occupation time, z has units of inverse length.) Hence, as previously shown in Ref. [13], the Robin boundary condition is equivalent to an exponential law for the stopping local time $\widehat{\ell}_t$. Moreover, suppose that the Robin boundary condition is rewritten as

$$\nabla \widetilde{P}(\mathbf{x}, z, t|\mathbf{x}_0) \cdot \mathbf{n}_2 = -z\widetilde{P}(\mathbf{x}, z, t|\mathbf{x}_0) = -z \int_0^\infty \mathrm{e}^{-z\ell} P(\mathbf{x}, \ell, t|\mathbf{x}_0) d\ell, \ \mathbf{x} \in \partial\mathcal{M}. \tag{3.28}$$

Taking the limit $z \to \infty$ on both sides with $\widetilde{P}(\mathbf{x}, z, t|\mathbf{x}_0) \to p_\infty(\mathbf{x}, t|\mathbf{x}_0)$, and noting that $\lim_{z\to\infty} z\mathrm{e}^{-z\ell}$ is the Dirac delta function on the positive half-line, we obtain the supplementary condition (2.18c). Again, it is convenient to consider

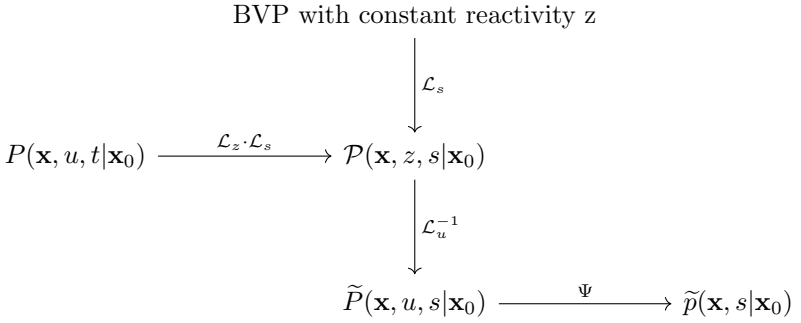


Figure 2: Commutative diagram illustrating how to incorporate the solution to a classical BVP with constant reactivity z into a more general theory of diffusion in partially absorbing media. This involves a propagator $P(\mathbf{x}, u, t|\mathbf{x}_0)$ and a stopping time distribution $\Psi(u)$, with u corresponding to an occupation time in the case of a partially reactive substrate $\partial\mathcal{M}$, and a local time in the case of a partially reactive surface $\partial\mathcal{M}$.

the BVP for the double Laplace transform (1.1), which in the case of the local time takes the form [13, 14]

$$D\nabla^2\mathcal{P}(\mathbf{x},z,s|\mathbf{x}_0)-s\mathcal{P}(\mathbf{x},z,s|\mathbf{x}_0)=-\delta(\mathbf{x}-\mathbf{x}_0),\ \mathbf{x}\in\Omega\backslash\mathcal{M},\ \nabla\mathcal{P}(\mathbf{x},z,s|\mathbf{x}_0)\cdot\mathbf{n}_1=0,\ \mathbf{x}\in\partial\Omega, \tag{3.29a}$$

$$-\nabla\mathcal{P}(\mathbf{x},z,s|\mathbf{x}_0)\cdot\mathbf{n}_2=z\mathcal{P}(\mathbf{x},z,s|\mathbf{x}_0),\ \mathbf{x}\in\partial\mathcal{M}. \tag{3.29b}$$

Finally, equation (2.20) implies that

$$\widetilde{p}(\mathbf{x},s|\mathbf{x}_0)=\int_0^\infty\Psi(\ell)\mathcal{L}_\ell^{-1}[\mathcal{P}(\mathbf{x},z,s|\mathbf{x}_0)]d\ell,\ \mathbf{x}\in\Omega\backslash\mathcal{M}. \tag{3.30}$$

The general probabilistic framework for analyzing single-particle diffusion in partially absorbing media is summarized in the commutative diagram of Fig. 2. One of the challenges of implementing this method is that solutions of the classical BVPs with a constant reactivity z tend to have a non-trivial parametric dependence on the Laplace variable z, which makes it difficult to calculate the inverse transform. In the case of reactive surfaces, solving the Robin BVP in terms of the spectrum of an associated D-to-N operator yields a series expansion that is easily inverted with respect to the Laplace variable z conjugate to the local time ℓ [13, 14]. In the next section we apply this approach to the occupation time propagator, and show that the analysis is considerably more involved.

4 Spectral decomposition of the occupation time propagator

It is well known from classical PDE theory that the solution of a general Robin BVP can be computed in terms of the spectrum of a D-to-N operator. This was applied to the single-particle local time propagator BVP in Ref. [13]. Here we carry out an analogous procedure for the occupation time BVP (3.22). The basic idea is to replace the matching conditions (3.22d) by the inhomogeneous Dirichlet condition $\mathcal{P}(\mathbf{x},s|\mathbf{x}_0)=\mathcal{Q}(\mathbf{x},s|\mathbf{x}_0)=f(\mathbf{x},s)$ for all $\mathbf{x}\in\partial\mathcal{M}$ and to find the function f for which $\mathcal{P}$ and $\mathcal{Q}$ are also the solution to the original BVP. (For the moment we drop the explicit dependence of the solutions on z.) Therefore, consider the modified BVP

$$D\nabla^2\mathcal{P}(\mathbf{x},s|\mathbf{x}_0)-s\mathcal{P}(\mathbf{x},s|\mathbf{x}_0)=-\delta(\mathbf{x}-\mathbf{x}_0),\ \mathbf{x}\in\Omega\backslash\mathcal{M}, \tag{4.31a}$$

$$-\nabla\mathcal{P}(\mathbf{x},s|\mathbf{x}_0)\cdot\mathbf{n}_1=0,\ \mathbf{x}\in\partial\Omega, \tag{4.31b}$$

$$D\nabla^2\mathcal{Q}(\mathbf{x},s|\mathbf{x}_0)-(s+z)\mathcal{Q}(\mathbf{x},s|\mathbf{x}_0)=0,\ \mathbf{x}\in\mathcal{M} \tag{4.31c}$$

$$\mathcal{P}(\mathbf{x},s|\mathbf{x}_0)=\mathcal{Q}(\mathbf{x},s|\mathbf{x}_0)=f(\mathbf{x},s),\ \mathbf{x}\in\partial\mathcal{M}. \tag{4.31d}$$

with the function $f(\mathbf{x},s)$ to be determined. This decouples the BVPs in the exterior and interior of $\mathcal{M}$. Given the solution to equations (4.31) we then determine the function f for which the solution also satisfies the original BVP (3.22).

The general solution of equations (4.31a,c) is of the form

$$\mathcal{P}(\mathbf{x}, s|\mathbf{x}_0) = \mathcal{F}_1(\mathbf{x}, s) + G_1(\mathbf{x}, s|\mathbf{x}_0),\ \mathbf{x} \in \Omega\backslash\mathcal{M}, \tag{4.32a}$$

$$\mathcal{Q}(\mathbf{x}, s|\mathbf{x}_0) = \mathcal{F}_2(\mathbf{x}, s),\ \mathbf{x} \in \mathcal{M}, \tag{4.32b}$$

where

$$\mathcal{F}_1(\mathbf{x}, s) = -D\int_{\partial\mathcal{M}} \partial_{\sigma'} G_1(\mathbf{x}', s|\mathbf{x}) f(\mathbf{x}', s) d\mathbf{x}', \quad \mathcal{F}_2(\mathbf{x}, s) = D\int_{\partial\mathcal{M}} \partial_{\sigma'} G_2(\mathbf{x}', s+z|\mathbf{x}) f(\mathbf{x}', s) d\mathbf{x}', \tag{4.33}$$

and $G_{1,2}$ are modified Helmholtz Green's functions:

$$D\nabla^2 G_1(\mathbf{x}, s|\mathbf{x}') - sG_1(\mathbf{x}, s|\mathbf{x}') = -\delta(\mathbf{x} - \mathbf{x}'),\ \mathbf{x}, \mathbf{x}' \in \Omega\backslash\mathcal{M}, \tag{4.34a}$$

$$G_1(\mathbf{x}, s|\mathbf{x}') = 0,\ \mathbf{x} \in \partial\mathcal{M}, \quad \nabla G_1(\mathbf{x}, s|\mathbf{x}') \cdot \mathbf{n}_1 = 0,\ \mathbf{x} \in \partial\Omega, \tag{4.34b}$$

and

$$D\nabla^2 G_2(\mathbf{x}, s|\mathbf{x}') - sG_2(\mathbf{x}, s|\mathbf{x}') = -\delta(\mathbf{x} - \mathbf{x}'),\ \mathbf{x}, \mathbf{x}' \in \mathcal{M}, \tag{4.34c}$$

$$G_2(\mathbf{x}, s|\mathbf{x}') = 0,\ \mathbf{x} \in \partial\mathcal{M}. \tag{4.34d}$$

The Green's functions have dimensions of [time]/[Length]^d The unknown function f is determined by substituting the solutions (4.32b) into equation (3.22b):

$$\mathbb{L}_s[f](\mathbf{x}, s) + \partial_\sigma G_1(\mathbf{x}, s|\mathbf{x}_0) = -\overline{\mathbb{L}}_{s+z}[f](\mathbf{x}, s), \quad \mathbf{x} \in \partial\mathcal{M}, \tag{4.35}$$

where $\mathbb{L}_s$ and $\overline{\mathbb{L}}_s$ are the D-to-N operators

$$\mathbb{L}_s[f](\mathbf{x}, s) = -D\partial_\sigma \int_{\partial\mathcal{M}} \partial_{\sigma'} G_1(\mathbf{x}', s|\mathbf{x}) f(\mathbf{x}', s) d\mathbf{x}', \tag{4.36a}$$

$$\overline{\mathbb{L}}_s[f](\mathbf{x}, s) = -D\partial_\sigma \int_{\partial\mathcal{M}} \partial_{\sigma'} G_2(\mathbf{x}', s|\mathbf{x}) f(\mathbf{x}', s) d\mathbf{x}'. \tag{4.36b}$$

acting on the space $L_2(\partial\mathcal{M})$. In the above equations we have set $\partial_\sigma = \mathbf{n}_2 \cdot \nabla_{\mathbf{x}}$ and $\partial_{\sigma'} = \mathbf{n}_2 \cdot \nabla_{\mathbf{x}'}$.

When the surface $\partial\mathcal{M}$ is bounded, the D-to-N operators $\mathbb{L}_s$ and $\overline{\mathbb{L}}_s$ have discrete spectra. That is, there exist countable sets of eigenvalues $\mu_n(s), \overline{\mu}_n(s)$ and eigenfunctions $v_n(\mathbf{x}, s), \overline{v}_n(s)$ satisfying (for fixed s)

$$\mathbb{L}_s v_n(\mathbf{x}, s) = \mu_n(s) v_n(\mathbf{x}, s), \quad \overline{\mathbb{L}}_s \overline{v}_n(\mathbf{x}, s) = \overline{\mu}_n(s) \overline{v}_n(\mathbf{x}, s). \tag{4.37}$$

It can be shown that the eigenvalues are non-negative and that the eigenfunctions form a complete orthonormal basis in $L_2(\partial\mathcal{M})$. We can now solve equation (4.35) by introducing an eigenfunction expansion of f with respect to one of the operators. For concreteness, we take

$$f(\mathbf{x}, s) = \sum_{m=0}^{\infty} f_m(s) v_m(\mathbf{x}, s). \tag{4.38}$$

Substituting equation (4.38) into (4.35) and taking the inner product with the adjoint eigenfunction $v_n^*(\mathbf{x}, s)$ yields the following matrix equations for the coefficients f_m:

$$\mu_n(s) f_n(s) = g_n(s) - \sum_{m \geq 1} H_{nm}(s+z) f_m(s), \tag{4.39}$$

where

$$g_n(s) = -\int_{\partial \mathcal{M}} v_n^*(\mathbf{x}, s) \partial_\sigma G_1(\mathbf{x}, s|\mathbf{x}_0) d\mathbf{x}, \tag{4.40}$$

$$H_{nm}(s) = -D \int_{\partial \mathcal{M}} v_n^*(\mathbf{x}, s) \partial_\sigma \left\{ \int_{\partial \mathcal{M}} v_m(\mathbf{x}', s) \partial_{\sigma'} G_2(\mathbf{x}', s|\mathbf{x}) d\mathbf{x}' \right\} d\mathbf{x}. \tag{4.41}$$

The orthogonality condition

$$\int_{\partial \mathcal{M}} v_n^*(\mathbf{x}, s) v_m(\mathbf{x}, s) d\mathbf{x} = \delta_{m,n} \tag{4.42}$$

means that v_n^* and v_m can each be taken to have dimensions of $[\text{Length}]^{-(d-1)/2}$. It also follows that $H_{nm}(s)$ has dimensions of inverse length.

Introducing the vectors $\mathbf{f}(s) = (f_n(s), n \geq 0)$ and $\mathbf{g}(s) = (g_n(s), n \geq 0)$, we can formally write the solution of equation (4.39) as

$$\mathbf{f}(s) = \left[\mathbf{M}(s) + \mathbf{H}(s+z)\right]^{-1} \mathbf{g}(s), \tag{4.43}$$

where $\mathbf{H}(s)$ is the matrix with elements $H_{nm}(s)$ and $\mathbf{M}(s) = \text{diag}(\mu_1(s), \mu_2(s) \ldots)$. Finally, substituting equation (4.43) into equations (4.32) gives

$$\mathcal{P}(\mathbf{x}, z, s|\mathbf{x}_0) = G_1(\mathbf{x}, s|\mathbf{x}_0) + \frac{1}{D} \sum_{n,m} \mathcal{V}_n(\mathbf{x}, s) \left[\mathbf{M}(s) + \mathbf{H}(s+z)\right]^{-1}_{nm} \mathcal{V}_m^*(\mathbf{x}_0, s), \ \mathbf{x} \in \Omega \backslash \mathcal{M}, \tag{4.44a}$$

$$\mathcal{Q}(\mathbf{x}, z, s|\mathbf{x}_0) = \frac{1}{D} \sum_{n,m} \widehat{\mathcal{V}}_n(\mathbf{x}, s+z) \left[\mathbf{M}(s) + \mathbf{H}(s+z)\right]^{-1}_{nm} \mathcal{V}_m^*(\mathbf{x}_0, s), \ \mathbf{x} \in \mathcal{M}, \tag{4.44b}$$

where

$$\mathcal{V}_n(\mathbf{x}, s) = -D \int_{\partial \mathcal{M}} v_n(\mathbf{x}', s) \partial_{\sigma'} G_1(\mathbf{x}', s|\mathbf{x}) d\mathbf{x}', \tag{4.45a}$$

$$\widehat{\mathcal{V}}_n(\mathbf{x}, s) = D \int_{\partial \mathcal{M}} v_n(\mathbf{x}', s) \partial_{\sigma'} G_2(\mathbf{x}', s|\mathbf{x}) d\mathbf{x}'. \tag{4.45b}$$

An analogous construction can be carried out for the local time BVP (3.29) by decomposing the generalized propagator as [13]

$$\mathcal{P}(\mathbf{x}, z, s|\mathbf{x}_0) = G_1(\mathbf{x}, s|\mathbf{x}_0) + \mathcal{F}(\mathbf{x}, z, s|\mathbf{x}_0), \tag{4.46}$$

with

$$D\nabla^2\mathcal{F}(\mathbf{x},z,s|\mathbf{x}_0)-s\mathcal{F}(\mathbf{x},z,s|\mathbf{x}_0)=0,\ \mathbf{x}\in\Omega\backslash\mathcal{M}, \tag{4.47a}$$

$$\nabla\mathcal{F}(\mathbf{x},z,s|\mathbf{x}_0)\cdot\mathbf{n}_2+z\mathcal{F}(\mathbf{x},z,s|\mathbf{x}_0)=-\nabla G_1(\mathbf{x},s|\mathbf{x}_0)\cdot\mathbf{n}_2 \text{ for } \mathbf{x}\in\partial\mathcal{M}, \tag{4.47b}$$

$$D\nabla\mathcal{F}(\mathbf{x},z,s|\mathbf{x}_0)\cdot\mathbf{n}_1=0 \text{ for } \mathbf{x}\in\partial\Omega. \tag{4.47c}$$

Replacing the Robin boundary condition by the Dirichlet condition $\mathcal{F}(\mathbf{x},z,s|\mathbf{x}_0)=f(\mathbf{x},s)$ leads to the equation

$$\mathbb{L}_s[f](\mathbf{x},s)+zf(\mathbf{x},s)=-\partial_\sigma G_1(\mathbf{x},s|\mathbf{x}_0), \tag{4.48}$$

where $\mathbb{L}_s$ is the D-to-N operator (4.36a). Again this can be solved by substituting for f using the eigenfunction expansion (4.38), which yields the result

$$\mathcal{P}(\mathbf{x},z,s|\mathbf{x}_0)=G_1(\mathbf{x},s|\mathbf{x}_0)+\frac{1}{D}\sum_{n=0}^{\infty}\frac{\mathcal{V}_n(\mathbf{x},s)\mathcal{V}_n^*(\mathbf{x}_0,s)}{\mu_n(s)+z}, \tag{4.49}$$

Comparison of equations (4.44) and (4.49), establishes that the occupation time propagator is a much more complicated function of the Laplace variable z. This means that, in general, the inverse Laplace transform has to be determined by computing a corresponding Bromwich integral. This, in turn, requires finding the roots of the characteristic equation $\det[\mathbf{M}(s)+\mathbf{H}(s+z)]=0$ in order to identify the poles in the complex z-plane. (An analogous issue arises in solving a classical Robin BVP with a space-dependent reactivity $\kappa(\mathbf{x})$, $\mathbf{x}\in\partial\mathcal{M}$ [12].) On the other hand, it is straightforward to obtain the inverse Laplace transform of equation (4.49), assuming that we can invert term-by-term in the infinite sum. In particular [13],

$$\widetilde{P}(\mathbf{x},\ell,s|\mathbf{x}_0)=G_1(\mathbf{x},s|\mathbf{x}_0)\delta(\ell)+\frac{1}{D}\sum_{n=0}^{\infty}\mathcal{V}_n^*(\mathbf{x}_0,s)\mathcal{V}_n(\mathbf{x},s)\mathrm{e}^{-\mu_n(s)\ell}. \tag{4.50}$$

Finally, note that when $\partial\mathcal{M}$ is bounded, both the local time and occupation time propagators in (z,s)-space are expressed in terms of infinite series. In order to invert the z-Laplace transforms term by term, we require these series to be uniformly convergent. Assuming that this is the case, one then has to determine how many terms in the series are required in order to obtain a given level of accuracy for quantities of interest such as the MFPT. After taking the $s\to 0$ limit, accuracy will depend on the choice of the stopping time distribution Ψ. That is, although the spectral decomposition of the propagator is independent of Ψ, the numerical truncation of the corresponding expansion of the MFPT will be Ψ-dependent.

5 Spectral decomposition for simple geometries

In order to illustrate the different levels of complexity of the spectral decomposition, we consider various simple geometries. In the case of a one-dimensional

(1D) substrate, the D-to-N operators for the occupation time propagator reduce to scalars, so that we do not have to invert an infinite-dimensional matrix. In addition, if the substrate is semi-infinite (unbounded) then exact expressions for the inverse z-transforms can be obtained using Laplace transform tables. This allows us to obtain exact expressions for quantities of interest such as the survival probability and MFPT for a given distribution $\Psi(a)$. On the other hand, for a bounded substrate, the inverse z-transform takes the form of an infinite series that is obtained using Bromwich contours. Finally, we consider a higher-dimensional geometry for which the spectral decompositions of the D-to-N operators $\mathbb{L}_s$ and $\overline{\mathbb{L}}_s$ are known exactly, namely a sphere.

5.1 Partially absorbing interval

Suppose that a particle diffuses in the interval $\Omega = [-L', L]$ with a partially absorbing subinterval $\mathcal{M} = [-L', 0]$, see Fig. 3. It follows that $\partial\Omega = \{-L', L\}$ and $\partial\mathcal{M} = \{0\}$. The 1D version of equations (3.22) takes the form

$$D\frac{\partial^2 \mathcal{P}(x,z,s|x_0)}{\partial x^2} - s\mathcal{P}(x,z,s|x_0) = -\delta(x-x_0),\ 0 < x < L, \tag{5.51a}$$

$$D\frac{\partial^2 \mathcal{Q}(x,z,s|x_0)}{\partial x^2} - (s+z)\mathcal{Q}(x,z,s|x_0) = 0,\ -L' < x < 0, \tag{5.51b}$$

$$\frac{\partial \mathcal{P}(x,z,s|x_0)}{\partial x} = 0,\ x = L, \quad \frac{\partial \mathcal{Q}(x,z,s|x_0)}{\partial x} = 0,\ x = -L'. \tag{5.51c}$$

These are supplemented by the matching conditions

$$\mathcal{P}(0,z,s|x_0) = \mathcal{Q}(0,z,s|x_0),\ \frac{\partial \mathcal{P}}{\partial x}(0,z,s|x_0) = \frac{\partial \mathcal{Q}}{\partial x}(0,z,s|x_0). \tag{5.51d}$$

Note that this particular BVP for fixed z and $L, L' \to \infty$ was previously considered within the context of so-called virtual traps [17]. The general solution of (5.51) is

$$\mathcal{P}(x,z,s|x_0) = A(z,s)\cosh\alpha(s)(L-x) + G_1(x,s|x_0),\ x \in [0,L] \tag{5.52a}$$

$$\mathcal{Q}(x,z,s|x_0) = B(z,s)\cosh\alpha(s+z)(L'+x),\ x \in [-L',0], \tag{5.52b}$$

where $\alpha(s) = \sqrt{s/D}$ and G_1 is the 1D Green's function that satisfies equation (5.51a) with a Dirichlet boundary condition at $x = 0$ and a Neumann boundary condition at $x = L$:

$$G_1(x,s|x_0) = \frac{H(x_0-x)g(x,s)\widehat{g}(x_0,s) + H(x-x_0)g(x_0,s)\widehat{g}(x,s)}{\sqrt{sD}\cosh(\sqrt{s/D}L)}, \tag{5.53}$$

where $H(x)$ is the Heaviside function and

$$g(x,s) = \sinh\sqrt{s/D}x, \quad \text{and} \quad \widehat{g}(x,s) = \cosh\sqrt{s/D}(L-x). \tag{5.54}$$

The unknown coefficients A, B are determined from the matching conditions at $x = 0$, which reduce to

$$A(z,s)\cosh\alpha(s)L = B(z,s)\cosh\alpha(s+z)L', \tag{5.55a}$$

$$-\alpha(s)A(z,s)\sinh\alpha(s)L = \alpha(s+z)B(z,s)\sinh\alpha(s+z)L' - \partial_x G_1(0,s|x_0). \tag{5.55b}$$

Substituting (5.55a) into (5.55b) gives

$$\{\alpha(s)\tanh\alpha(s)L\cosh\alpha(s+z)L' + \alpha(s+z)\sinh\alpha(s+z)L'\}\,B(z,s) = \frac{1}{D}\frac{\cosh\sqrt{s/D}(L-x_0)}{\cosh\sqrt{s/D}L} \tag{5.56}$$

Note that equation (5.56) could also be derived from the 1D version of equation (4.39), with $\partial\mathcal{M}$ corresponding to the single point $x = 0$ and $\partial_\sigma = -\partial_x$ etc. In particular, since $G_2(x,s|x_0)$ is the Dirichlet-Neumann Green's function on $(-L', 0]$, we find that

$$\mathbb{L}_s[f](L,s) \equiv -Df(L,s)\;\partial_x\partial_{x'}G_1(x',s|x)|_{x=x'=0} = f(0,s)\sqrt{\frac{s}{D}}\tanh(\sqrt{s/D}L), \tag{5.57}$$

and

$$\overline{\mathbb{L}}_s[f](L,s) \equiv -Df(L,s)\;\partial_x\partial_{x'}G_2(x',s|x)|_{x=x'=0} = f(0,s)\sqrt{\frac{s}{D}}\tanh(\sqrt{s/D}L'). \tag{5.58}$$

We deduce that for 1D diffusion, the D-to-N operators reduce to scalars with single eigenvalues $\mu(s) = \alpha(s)\tanh(\alpha(s)L)$ and $\overline{\mu}(s) = \alpha(s)\tanh(\alpha(s)L')$. In the specific case $x_0 = 0$, the solution has the particularly simple form

$$\mathcal{P}(x,z,s|0) = \frac{1}{\Phi(z,s)D}\frac{\cosh\alpha(s)(L-x)}{\cosh\alpha(s)L},\;\; x\in[0,L], \tag{5.59a}$$

$$\mathcal{Q}(x,z,s|0) = \frac{1}{\Phi(z,s)D}\frac{\cosh\alpha(s+z)(L'+x)}{\cosh\alpha(s+z)L'},\;\; x\in[-L',0], \tag{5.59b}$$

where

$$\Phi(z,s) \equiv \alpha(s)\tanh[\alpha(s)L] + \alpha(s+z)\tanh[\alpha(s+z)L']. \tag{5.60}$$

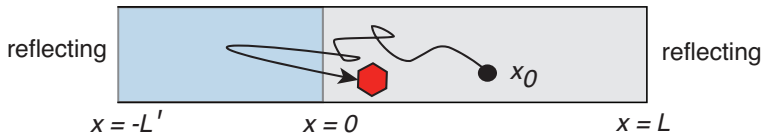


Figure 3: Partially absorbing substrate in 1D with $\mathcal{M} = [-L', 0]$ and $\Omega\backslash\mathcal{M} = [0, L]$.

For the sake of illustration, let us focus on the behavior of the solution at the interface $x = 0$ between the non-absorbing and absorbing regions, and the survival probability. Setting $x = x_0 = 0$ we have $\mathcal{P}(0, z, s|0) = \mathcal{Q}(0, z, s|0) \equiv C(z, s)$, where

$$C(z,s) = \frac{1}{\sqrt{D}} \frac{1}{\sqrt{s+z}\tanh(\sqrt{[s+z]/D}L') + \sqrt{s}\tanh(\sqrt{s/D}L)}. \tag{5.61}$$

The corresponding generalized survival probability is

$$\begin{aligned} S(z,s) &\equiv \int_{-L'}^{0} \mathcal{Q}(x,z,s|0)dx + \int_0^L \mathcal{P}(x,z,s|0)dx \\ &= \frac{1}{\Phi(z,s)D}\left(\frac{\tanh\alpha(s+z)L'}{\alpha(s+z)} + \frac{\tanh\alpha(s)L}{\alpha(s)}\right) \\ &= \frac{1}{\sqrt{s(s+z)}} \frac{\sqrt{s}\tanh(\sqrt{(s+z)/D}L') + \sqrt{s+z}\tanh(\sqrt{s/D}L)}{\sqrt{s+z}\tanh(\sqrt{(s+z)/D}L') + \sqrt{s}\tanh(\sqrt{s/D}L)}. \end{aligned} \tag{5.62}$$

In standard treatments of partial absorption [17], one simply identifies $C(\kappa_0, s)$ as the Laplace transformed probability density $\widetilde{p}(s)$ at the origin for a constant rate of absorption $z = \kappa_0$ within the domain $[-L', 0]$. Similarly $S(\kappa_0, s)$ is the Laplace transformed survival probability for a particle starting at $x_0 = 0$. It immediately follows from equations (2.14) and (5.62) that the corresponding MFPT for absorption is

$$T(0) = \lim_{s\to 0} S(\kappa_0, s) = \frac{L\tanh(\sqrt{\kappa_0/D}L')}{\sqrt{\kappa_0 D}} + \frac{1}{\kappa_0}. \tag{5.63}$$

Note that $T \to 0$ for a totally absorbing substrate ($\kappa_0 \to \infty$), since the particle starts at the interface. The novel feature of the encounter-based formalism is that one can construct a more general model of absorption within $\mathcal{M} = (-\infty, 0]$ by inverting with respect to z and introducing a stopping occupation time distribution $\Psi(a)$.

5.1.1 Unbounded partially absorbing substrate ($L' \to \infty$)

In the limit $L' \to \infty$ we have $\tanh(\sqrt{(s+z)/D}L') \to 1$ and the z-dependence of the solutions (5.59) simplifies greatly.

Limit $L \to \infty$. First, consider the limiting case $L \to \infty$ for which $\tanh(\sqrt{s/D}L) \to 1$. Using standard Laplace transform tables, we can invert with respect to s or z:

$$\widetilde{C}(z,t) = \frac{1}{2z\sqrt{\pi D t^3}}\left(1 - \mathrm{e}^{-zt}\right), \quad \widetilde{S}(z,t) = \mathrm{e}^{-zt/2} I_0(zt/2). \tag{5.64}$$

and

$$\widetilde{C}(a,s) = \frac{\mathrm{e}^{-sa}}{\sqrt{\pi a D}} - \sqrt{\frac{s}{D}}\mathrm{erfc}(\sqrt{sa}), \quad \widetilde{S}(a,s) = \frac{\mathrm{e}^{-sa}}{\sqrt{\pi s a}}, \tag{5.65}$$

where

$$\mathrm{erfc}(x) = \frac{2}{\sqrt{\pi}} \int_x^\infty \mathrm{e}^{-y^2} dy. \tag{5.66}$$

Moreover,

$$C(a,t) = \frac{1}{2\sqrt{\pi D t^3}} \left(H(a) - H(a-t) \right), \quad S(a,t) = \frac{1}{\pi \sqrt{a[t-a]}} H(t-a). \tag{5.67}$$

For a constant rate of absorption $z = \kappa_0$ (exponential distribution $\Psi(a) = \mathrm{e}^{-\kappa_0 a}$), we recover some of the results of Ref. [17]. For example, the density at the origin is $p(t) = \widetilde{C}(\kappa_0, t)$. Hence, at short times, $t \ll 1/\kappa_0$, the density is diffusion dominated with $p(t) \sim (4\pi D t)^{-1/2}$, whereas at large times $p(t) \sim t^{-3/2}$ such that $p(t) \to S(t)/\sqrt{D/\kappa_0}$, where $S(t)$ is the corresponding survival probability $\widetilde{S}(\kappa_0, t)$. On the other hand, for a non-exponential stopping occupation time distribution $\Psi(a)$, the marginal density at the origin becomes

$$p(t) = \int_0^\infty \Psi(a) C(a,t) da = \frac{1}{2\sqrt{\pi D t^3}} \int_t^\infty \Psi(a) da, \tag{5.68}$$

and the survival probability is now

$$S(t) = \int_0^\infty \Psi(a) S(a,t) da = \int_0^t \frac{\Psi(a)}{\pi \sqrt{a[t-a]}} da. \tag{5.69}$$

Since both the absorbing and non-absorbing intervals are unbounded, the MFPT is infinite.

Finite L. When L is finite, one has to invert the s-Laplace transforms using Bromwich integrals. However, the inverse z-Laplace transforms are more straightforward:

$$\widetilde{C}(a,s) = \frac{\mathrm{e}^{-sa}}{\sqrt{\pi a D}} - \sqrt{\frac{s}{D}} \tanh(\sqrt{s/D} L) \mathrm{e}^{-s \mathrm{sech}^2(\sqrt{s/D} L)} \mathrm{erfc}(\sqrt{sa} \tanh(\sqrt{s/D} L)). \tag{5.70}$$

and

$$\widetilde{S}(a,s) = \mathrm{e}^{-s \mathrm{sech}^2(\sqrt{s/D} L)} \mathrm{erfc}(\sqrt{sa} \tanh(\sqrt{s/D} L)) + \frac{\sqrt{D} \tanh(\sqrt{s/D} L)}{\sqrt{s}} \widetilde{C}(a,s). \tag{5.71}$$

Given a stopping occupation time distribution $\Psi(a)$, the corresponding MFPT is

$$T(0) = \lim_{s \to 0} \int_0^\infty \Psi(a) \widetilde{S}(a,s) da = \int_0^\infty \Psi(a) \left[\frac{L}{\sqrt{\pi a D}} + 1 \right] da. \tag{5.72}$$

Using integration by parts, we see that

$$\int_0^\infty \Psi(a) da = [a \Psi(a)]_0^\infty - \int_0^\infty a \Psi'(a) da = \int_0^\infty a \psi(a) da = -\widetilde{\psi}'(0).$$

Hence, a necessary condition for the existence of $T(0)$ is that $\psi(a)$ has a finite first moment.

One example of a non-exponential distribution that has finite moments is the gamma distribution:[1]

$$\psi_{\rm gam}(a) = \frac{\gamma(\gamma a)^{\mu-1}{\rm e}^{-\gamma a}}{\Gamma(\mu)}, \quad \Psi(a) = \frac{\Gamma(\mu,\gamma a)}{\Gamma(\mu)},\ \mu>0, \tag{5.73}$$

where $\Gamma(\mu)$ is the gamma function and $\Gamma(\mu,z)$ is the upper incomplete gamma function:

$$\Gamma(\mu) = \int_0^\infty {\rm e}^{-t}t^{\mu-1}dt, \quad \Gamma(\mu,z) = \int_z^\infty {\rm e}^{-t}t^{\mu-1}dt,\ \mu>0. \tag{5.74}$$

The corresponding Laplace transforms are

$$\widetilde{\psi}_{\rm gam}(z) = \left(\frac{\gamma}{\gamma+z}\right)^\mu, \quad \widetilde{\Psi}_{\rm gam}(z) = \frac{1-\widetilde{\psi}_{\rm gam}(z)}{z} \tag{5.75}$$

Here γ determines the effective absorption rate so that the substrate $\mathcal{M}$ is non-absorbing in the limit $\gamma\to 0$ and totally absorbing in the limit $\gamma\to\infty$. (In the latter case, if $x_0>0$ then the particle is absorbed as soon as it reaches $x=0$.) If $\mu=1$ then $\psi_{\rm gam}$ reduces to the exponential distribution with constant reactivity γ, that is, $\psi_{\rm gam}(a)|_{\mu=1} = \gamma{\rm e}^{-\gamma a}$. The parameter μ thus characterizes the deviation of $\psi_{\rm gam}(a)$ from the exponential case. If $\mu<1$ ($\mu>1$) then $\psi_{\rm gam}(a)$ decreases more rapidly (slowly) as a function of the occupation time a. In Fig 4 we plot the survival probability $S(t)$ of equation (5.69) as a a function of time for various parameter values of the gamma distribution. As expected, the survival probability at a given time t is larger for smaller γ or larger μ. In Fig. 5(a) we plot the corresponding MFPT $T(0)$ as a function of γ for various values of μ. It can be seen that as $\gamma\to\infty$ all the curves converge to zero. This is a consequence of the fact that the domain $\mathcal{M}=(-\infty,0]$ is totally absorbing in this limit and $x_0=0$. Fig. 5(b) shows that increasing μ increases the sensitivity of the MFPT to variations in the length of the non-absorbing domain. This is a particularly significant effect when the rate of absorption γ is small.

5.1.2 Bounded partially absorbing substrate ($L'<\infty$)

The z-dependence of the solutions (5.59) is more complicated when L' is finite. For the sake of illustration, let $L\to\infty$ so that the solutions (5.59) become (for

[1] See Ref. [13] for an extensive list of different distributions Ψ. Many of these have heavy tails and infinite first moments so that the corresponding MFPT does not exist. One example is the Pareto-II or Lomax distribution

$$\psi(\ell) = \frac{\gamma\mu}{(1+\gamma\ell)^{1+\mu}}, \quad 0<\mu<1.$$

A finite first moment does exist for. $\mu>1$ and one then finds qualitatively similar behavior to the gamma distribution for fixed μ.

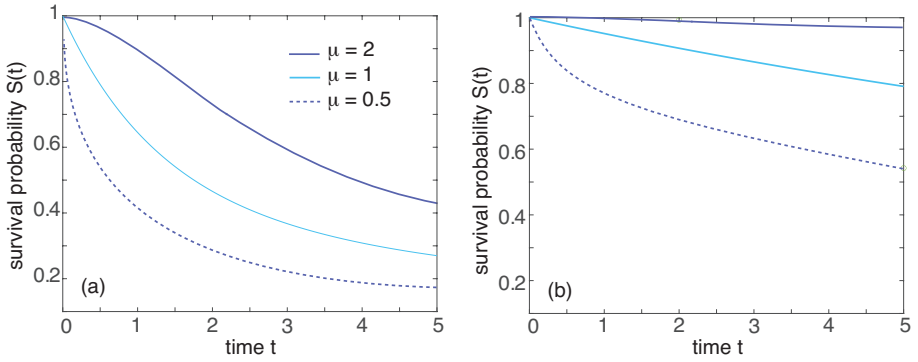


Figure 4: Plot of the survival probability $S(t)$ of equation (5.69) as a function of time t in the case of the gamma distribution. (a) $\gamma = 1$; (b) $\gamma = 0.1$. Other parameters are $L = D = 1$.

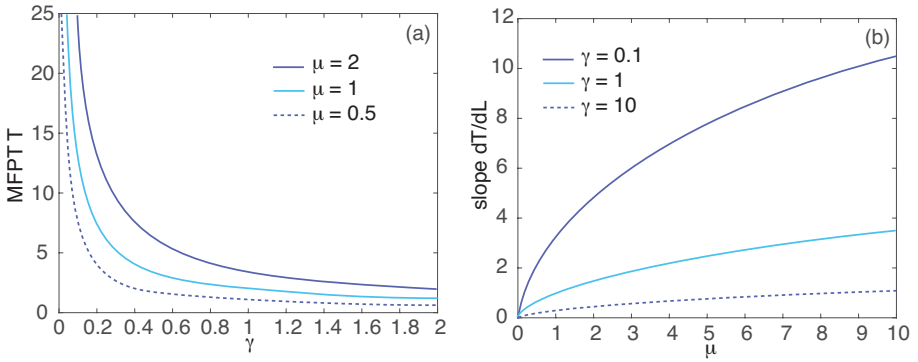


Figure 5: MFPT T of equation (5.72) for the gamma distribution in the case of a semi-infinite absorbing substrate and $L = 1$. (a) Plot of T as a function of γ for various values of μ. The case $\mu = 1$ corresponds to the exponential distribution (constant reactivity). (b) Corresponding plots of the slope dT/dL as a function of μ for various values of γ. Other parameters. are $L = D = 1$.

$x_0 = 0$)

$$\mathcal{P}(x,z,s|0) = \frac{\mathrm{e}^{-\alpha(s)x}}{\Phi(z,s)D},\ x \geq 0, \tag{5.76a}$$

$$\mathcal{Q}(x,z,s|0) = \frac{1}{\Phi(z,s)D}\frac{\cosh\alpha(s+z)(L'+x)}{\cosh\alpha(s+z)L'},\ x \in [-L',0], \tag{5.76b}$$

where

$$\Phi(z,s) \equiv \alpha(s) + \alpha(s+z)\tanh[\alpha(s+z)L']. \tag{5.77}$$

In order to find the inverse Laplace transforms we now use Bromwich integrals. For example, the inverse z-Laplace transform of $\mathcal{Q}(x,z,s|0)$ takes the form

$$\widetilde{Q}(x,a,s|0) = \frac{1}{2\pi i}\int_{c-i\infty}^{c+i\infty} \mathrm{e}^{za}\frac{1}{D\Phi(z,s)}\frac{\cosh\alpha(s+z)(L'+x)}{\cosh\alpha(s+z)L'}dz, \tag{5.78}$$

with c, $c>0$, chosen so that the Bromwich contour is to the right of all singularities of $\mathcal{Q}(x,z,s|0)$. The Bromwich integral (5.78) can be evaluated by closing the contour in the complex z-plane as illustrated in Fig. 6(a). The resulting contour encloses a countably infinite number of poles, which correspond to the zeros of the function $\Phi(z,s)$.[2] Setting $\Phi(z,s)=0$ in equation (5.77) and rearranging leads to the transcendental equation

$$\tanh y = -\sqrt{\frac{s}{s_0}}\frac{1}{y}, \quad s_0 = \frac{D}{L'^2}, \quad y = L'\sqrt{[s+z]/D}. \tag{5.79}$$

Clearly (5.79) does not have any real solutions. However, there exists a countably infinite number of pure imaginary solutions $y=i\omega_n$, $n\geq 1$, with ω_n real such that

$$\tan\omega_n = \sqrt{\frac{s}{s_0}}\frac{1}{\omega_n}. \tag{5.80}$$

The corresponding zeroes in the z-plane are real and lie to the left of $z=-s$ since $\omega_n\neq 0$:

$$z_n = -s - s_0\omega_n^2, \quad n\geq 1. \tag{5.81}$$

Example plots of the function $\Phi(z,s)/\alpha(s)$ are shown in Fig. 6(b). Since the roots are ordered on the negative real axis, there exists an integer $N=N(s)$ such that $\omega_n \gg \sqrt{s/s_0}$ for all $n\geq N(s)$. This implies that $\tan\omega_n \approx 0$ or $\omega_n \approx n\pi$ for all $n\geq N(s)$. In other words,

$$z_n \approx -s - s_0(n\pi)^2, \quad n\geq N(s). \tag{5.82}$$

Moreover, in the small-s regime ($s\ll s_0$), we have $N(s)=O(1)$.

Applying Cauchy's residue theorem to the Bromwich contour integral of Fig. 6(a), and noting that the contribution from the semi-circle C_R vanishes in the limit $R\to\infty$, we have

$$\widetilde{Q}(x,a,s|0) = \sum_{n\geq 1}\frac{1}{\Phi_n(s)}\mathrm{e}^{-(s+s_0\omega_n^2)a}\cos[\omega_n(L'+x)/L']. \tag{5.83}$$

We have used $\alpha(z_n+s)=i\omega_n/L'$,

$$\Phi(z_n,s)\cos\omega_n = -\frac{\omega_n}{L'}\sin\omega_n + \sqrt{\frac{s}{D}}\cos\omega_n. \tag{5.84}$$

[2]The dependence of $\mathcal{Q}(x,z,s|0)$ on $\alpha(s+z)=\sqrt{[s+z]/D}$ suggests that there is also a branch point at $z=-s$. However, $\cosh[\alpha(s+z)L']$ and $\alpha(s+z)\sinh[\alpha(s+z)L']$ are even functions of $\alpha(s+z)$, so $z=-s$ is a removable singularity and $\mathcal{Q}(x,z,s|0)$ is single-valued.

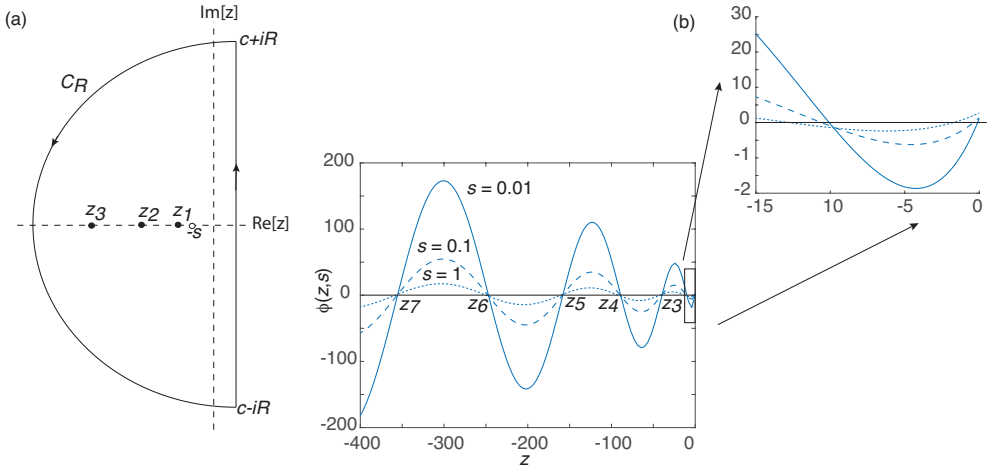


Figure 6: (a) Contour C for evaluating the Bromwich integral (5.78). The function $\mathcal{Q}(x, z, s|x_0)$ has a removable singularity at $z = -s$, and an infinite set of poles at $z = z_n < -s$ for $n \geq 1$ and $R \to \infty$. (b) Plot of the function $\phi(z, s) \equiv \Phi(z, s)/\alpha(s)$ against z for various values of s. Inset shows curves in a neighborhood of $z = 0$. We have also set $D = 1$ and $L' = 1$ so that $s_0 = 1$.

and

$$\partial_z[\Phi(z_n, s)\cos\omega_n] = \Phi_n(s) \equiv \frac{L'}{2D}\left(\cos\omega_n + \left[1 + L'\sqrt{\frac{s}{D}}\right]\frac{\sin\omega_n}{\omega_n}\right). \quad (5.85)$$

Assuming the series is uniformly convergent, the corresponding marginal density

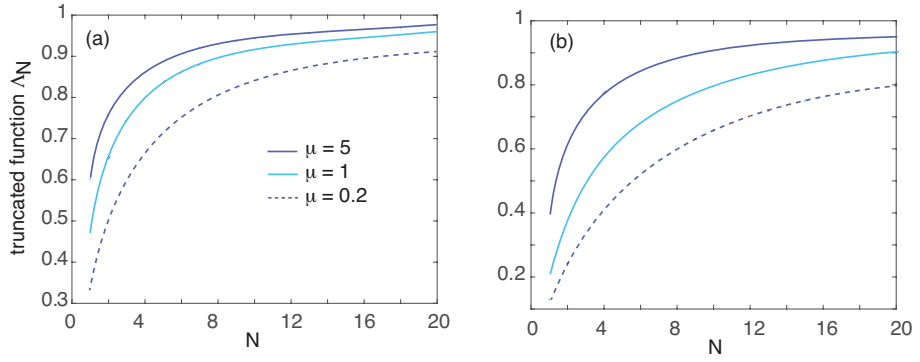


Figure 7: Plots of normalized truncated series $\Lambda_N(s_0)$ as a function of N and various μ for (a) $s_0 = 1$ and (b) $s_0 = 0.1$. We also set $\gamma = 1$.

(for $x_0 = 0$) is

$$\widetilde{q}(x,s) = \sum_{n\geq 1} \frac{\widetilde{\Psi}(s + s_0\omega_n^2)}{\Phi_n(s)} \cos[\omega_n(L' + x)/L']. \tag{5.86}$$

Analogous results holds for $\widetilde{P}(x,a,s|x_0)$ and $\widetilde{p}(\mathbf{x},s|\mathbf{x}_0)$. Hence, in contrast to the semi-infinite case, quantities of interest such as the survival probability and MFPT are expressed in terms of infinite series. Some form of numerical truncation is thus needed, whose accuracy will depend on the choice of distribution Ψ. As a simple illustration, consider the limit $s \to 0$, for which $\omega_n = n\pi$, and set $x = 0$:

$$\widetilde{q}(0,0) = 2L's_0 \sum_{n\geq 1} \widetilde{\Psi}(n^2\pi^2 s_0). \tag{5.87}$$

In fig. 7 we show plots of the truncated series $\Lambda_N(s_0) = \sum_{n=1}^{N} \widetilde{\Psi}(n^2\pi^2 s_0)$ as a function of N for the gamma distribution, normalized by $\Lambda_\infty(s_0)$. As expected, the rate of convergence depends on s_0 and the parameters (μ,γ) of the gamma distribution. Note that keeping only the first few terms leads to poor accuracy.

5.2 Partially absorbing sphere

One higher-dimensional example where the spectral decompositions of the D-to-N operators $\mathbb{L}_s$ and $\overline{\mathbb{L}}_s$ are known exactly is a partially absorbing sphere. Let $\Omega = \mathbb{R}^3$ and $\mathcal{M} = \{\mathbf{x} \in \mathbb{R}^3,\, 0 < |\mathbf{x}| < R\}$ so that $\partial\mathcal{M} = \{\mathbf{x} \in \mathbb{R}^3,\, |\mathbf{x}| = R\}$. (In the context of partially absorbing surfaces, $\mathbb{L}_s$ is the relevant operator for diffusion exterior to the sphere, whereas $\overline{\mathbb{L}}_s$ is the appropriate operator for diffusion within the sphere [12].) The rotational symmetry of $\mathcal{M}$ means that if $\mathbb{L}_s$ and $\overline{\mathbb{L}}_s$ are expressed in spherical polar coordinates (r,θ,ϕ), then the eigenfunctions are given by spherical harmonics, and are independent of the Laplace variable s and the radius r:

$$v_{nm}(\theta,\phi) = \overline{v}_{nm}(\theta,\phi) = \frac{1}{R} Y_n^m(\theta,\phi), \quad n \geq 0,\ |m| \leq n. \tag{5.88}$$

From orthogonality, it follows that the adjoint eigenfunctions are

$$v_{nm}^*(\theta,\phi) = \overline{v}_{nm}^*(\theta,\phi) = (-1)^m \frac{1}{R} Y_n^{-m}(\theta,\phi). \tag{5.89}$$

(Note that eigenfunctions are labeled by the pair of indices (nm).) The corresponding eigenvalues are [12]

$$\mu_n(s) = -\alpha(s)\frac{k_n'(\alpha(s)R)}{k_n(\alpha(s)R)}, \quad \overline{\mu}_n(s) = \alpha(s)\frac{i_n'(\alpha(s)R)}{i_n(\alpha(s)R)}, \tag{5.90}$$

where $\alpha(s) = \sqrt{s/D}$. Since the nth eigenvalue is independent of m, it has a multiplicity $2n+1$. It is also possible to compute the projections of the boundary

fluxes in (4.45) by using appropriate series expansions of the corresponding Green's functions. For example, one finds that [13]

$$-D\partial_\sigma G_1(\mathbf{x}', s|\mathbf{x}) = \sum_{n=0}^{\infty} \frac{2n+1}{4\pi R^2} P_n(\mathbf{x}' \cdot \mathbf{x}/(rR)) \frac{k_n(\alpha(s)r)}{k_n(\alpha(s)R)} \tag{5.91}$$

with $|\mathbf{x}'| = R$, $|\mathbf{x}| = r > R$, and $P_n(x)$ a Legendre polynomial. Hence, using $\partial_{\sigma'} = -\partial/\partial r'$, (see also. Ref. [16])

$$\mathcal{V}_{nm}(\mathbf{x}, s) \equiv D \int_{|\mathbf{x}'|=R_1} v_{nm}(\theta', \phi') \frac{\partial}{\partial r'} G_1(\mathbf{x}', s|r, \theta, \phi) d\mathbf{x}' = -v_{nm}(\theta, \phi) \frac{k_n(\alpha(s)r)}{k_n(\alpha(s)R)} \tag{5.92}$$

with $\mathbf{x} = (r, \theta, \phi)$ and $r > R$. Similarly, we have

$$\widehat{\mathcal{V}}_{nm}(\mathbf{x}, s) \equiv -D \int_{|\mathbf{x}'|=R_1} v_{nm}(\theta', \phi') \frac{\partial}{\partial r'} G_2(\mathbf{x}', s|r, \theta, \phi) d\mathbf{x}' = -v_{nm}(\theta, \phi) \frac{i_n(\alpha(s)r)}{i_n(\alpha(s)R)} \tag{5.93}$$

for $\mathbf{x} = (r, \theta, \phi)$ and $r < R$. Finally, the matrix $\mathbf{H}(s)$ in equation (4.41) becomes

$$\begin{aligned} H_{nm,n'm'}(s) &= -D \int_{\partial\mathcal{M}} v^*_{nm}(\theta, \phi) \frac{\partial}{\partial r} \left\{ \int_{\partial\mathcal{M}} v_{n'm'}(\theta', \phi') \frac{\partial}{\partial r'} G_2(\mathbf{x}', s|\mathbf{x}) d\mathbf{x}' \right\} d\mathbf{x} \\ &= \alpha(s) \frac{i'_{n'}(\alpha(s)R)}{i_{n'}(\alpha(s)R)} \left[\int_{\partial\mathcal{M}} v^*_{nm}(\theta, \phi) v_{n'm'}(\theta, \phi) d\mathbf{x} \right] \\ &= \overline{\mu}_n(s) \delta_{n,n'} \delta_{m,m'}. \end{aligned} \tag{5.94}$$

That is, $\mathbf{H}$ is a diagonal matrix. Finally, from equation (4.44) the generalized propagator within the sphere becomes

$$\mathcal{Q}(\mathbf{x}, z, s|\mathbf{x}_0) = \frac{1}{D} \sum_{n,m} \sum_{n',m'} \widehat{\mathcal{V}}_{nm}(\mathbf{x}, s+z) \left[\mathbf{M}(s) + \mathbf{H}(s+z)\right]^{-1}_{nm,n'm'} \mathcal{V}^*_{n'm'}(\mathbf{x}_0, s), \tag{5.95}$$

$$= \frac{1}{D} \sum_{n,m} v_{nm}(\theta, \phi) \frac{i_n(\alpha(s+z)r)}{i_n(\alpha(s+z)R)} \frac{1}{\mu_n(s) + \overline{\mu}_n(s+z)} \frac{k_n(\alpha(s)r_0)}{k_n(\alpha(s)R)} v^*_{nm}(\theta_0, \phi_0),$$

where $\mathbf{x} = (r, \theta, \phi)$ and $\mathbf{x}_0 = (r_0, \theta_0, \phi_0)$ with $r < R$ and $r_0 > R$. An analogous result holds for $\mathcal{P}(\mathbf{x}, s|\mathbf{x}_0)$. This higher-dimensional example shows that in addition to dealing with an infinite series, we now also have to invert an infinite-dimensional matrix. Again, the details of any numerical approximation scheme of quantities such as the MFPT will depend on Ψ.

6 Conclusion

In this paper we showed how transform methods and the spectral theory of D-to-N operators can be used to solve a general class of BVPs arising from

models of single-particle diffusion in partially absorbing media. In particular, we extended the encounter-based probabilistic framework for analyzing diffusion-mediated surface absorption [13, 14] to the case of partially absorbing interiors. Our main result was to establish that the solution can be computed in terms of the spectral decomposition of a pair of D-to-N operators. This doubling up of the number of operators means that inverting the Laplace transform in z is much more complicated than for surface absorption. The resulting infinite series representation of the propagator requires some form of efficient numerical truncation scheme. Incorporating the effects of absorption implies that the accuracy of any numerical truncation will depend on the particular choice of stopping time distribution Ψ.

There are a number of applications in neurobiology where partially absorbing interior substrates play an important role. One example concerns the lateral diffusion of neurotransmitter receptors within the plasma membrane of a dendrite, see Fig. 8. A typical dendrite is studded with thousands of synaptic contacts, each of which corresponds to a local trapping region that binds receptors to scaffolding proteins, followed by internalization of the receptors via endocytosis [18, 19, 20]. The interior of a synapse thus acts as a partially-absorbing domain $\mathcal{M}$ within the dendritic membrane Ω. A related example is the passive or active intracellular transport of a vesicle (particle) along the axon or dendrite of a neuron, with absorption within a trapping region corresponding to the transfer of the vesicle to a synapse within the surface membrane of the neuron [21]. (In the latter case, the synapse could also be treated as a 2D absorbing surface in a 3D model of a neuron.) Both of these examples motivate extending the analytical framework developed in this paper to investigate the competition for resources

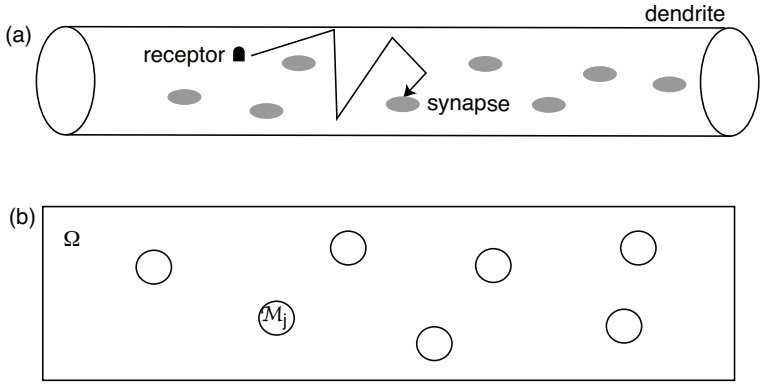


Figure 8: (a) Schematic illustration of a diffusion-trapping model for a protein receptor by synaptic targets distributed on surface of a dendritic cable. The receptor diffuses freely extrasynaptically, but can transiently bind to scaffolding proteins within each synapse, which thus acts as a trapping region. (b) The problem can be mapped to a 2D rectangular domain Ω with circular targets, say, with periodic boundary conditions imposed on the pair of horizontal edges.

between multiple partially absorbing targets. As we have shown elsewhere [15], it is relatively straightforward to extend the generalized propagator BVP of section 2 to multiple domains $\mathcal{M}_j$, $j = 1, \ldots, N$, each with its own local absorption scheme. Now one has a set of occupation times a_j and a corresponding set of Laplace variables z_j.

References

[1] Lévy P. 1939 Sur certains processus stochastiques homogènes. *Compos. Math.* **7**, 283

[2] McKean HP. 1975 Brownian local time. *Adv. Math.* **15**, 91-111

[3] Freidlin M. 1985 *Functional Integration and Partial Differential Equations* Annals of Mathematics Studies (Princeton University Press, Princeton New Jersey)

[4] Majumdar SN. 2005 Brownian functionals in physics and computer science. *Curr. Sci.* **89**, 2076

[5] Papanicolaou VG. 1990 The probabilistic solution of the third boundary value problem for second order elliptic equations *Probab. Th. Rel. Fields* **87**, 27-77

[6] Milshtein GN. 1995 The solving of boundary value problems by numerical integration of stochastic equations. *Math. Comp. Sim.* **38** 77-85

[7] Grebenkov DS. 2007 Residence times and other functionals of reflected Brownian motion, *Phys. Rev. E* **76** 041139

[8] Singer A, Schuss Z, Osipov A, Holcman D. 2008 Partially reflected diffusion. *SIAM J. Appl. Math.* **68**, 844-868

[9] Lawley SD, Keener JP 2015 A new derivation of Robin boundary conditions through homogenization of a stochastically switching boundary *SIAM J. Appl. Dyn. Syst.* **14** 1845-1867

[10] Bartholomew CH. 2001 Mechanisms of catalyst deactivation, *Appl. Catal. A: Gen.* **212**, 17-60

[11] Filoche M, Grebenkov DS, Andrade Jr JS, Sapoval B. 2008,Passivation of irregular surfaces accessed by diffusion. *Proc. Natl. Acad. Sci.* **105**, 7636-7640

[12] Grebenkov DS. 2019 Spectral theory of imperfect diffusion-controlled reactions on heterogeneous catalytic surfaces *J. Chem. Phys.* **151**, 104108

[13] Grebenkov DS. 2020 Paradigm shift in diffusion-mediated surface phenomena. *Phys. Rev. Lett.* **125**, 078102

[14] Grebenkov DS. 2022 An encounter-based approach for restricted diffusion with a gradient drift. *J. Phys. A.* **55** 045203

[15] Bressloff PC. 2022 Diffusion-mediated absorption by partially reactive targets: Brownian functionals and generalized propagators. *J. Phys. A.* **55** 205001

[16] Grebenkov DS. 2020 Surface hopping propagator: An alternative approach to diffusion-influenced reactions. *Phys. Rev. E* **102** 032125

[17] Ben-Naim E, Redner S, Weiss G. 1993 Partial absorption and virtual traps *J. Stat. Phys.* **71**, 75

[18] Bressloff PC, Earnshaw BA. 2006 A biophysical model of AMPA receptor trafficking and its regulation during LTP/LTD. *J. Neurosci.***26**, 12362-12373

[19] Holcman D, Triller A. 2006. Modeling synaptic dynamics driven by receptor lateral diffusion. *Biophys. J.* **91**, 2405-2415 (2006).

[20] Czondora K, Mondina M, Garciaa M, Heinec M, Frischknechtc R, Choquet D, Sibaritaa JB, Thoumine OR. 2012 A unified quantitative model of AMPA receptor trafficking at synapses. *Proc. Nat. Acad. Sci. USA* **109** 3522-3527

[21] Bressloff PC. 2021 Queuing model of axonal transport. *Brain Multiphysics* **2** 100042

[22] Schumm RD, Bressloff PC. 2021 Search processes with stochastic resetting and partially absorbing targets. *J. Phys. A* **54** 404004

[23] Guérin T, Dolgushev M, Bénichou O, Voituriez R. 2021 Universal kinetics of imperfect reactions in confinement. *Comm. Chem.* **4** 157.