Spectral theory of diffusion in partially absorbing media

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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 $X_t$ and a Brownian functional $U_t$ that specifies the amount of time the particle is in contact with a reactive component $M$. Absorption occurs as soon as $U_t$ crosses a randomly distributed threshold (stopping time). Laplace transforming the propagator with respect to $U_t$ 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 $\partial M$, 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 $\partial M$. In this paper, we develop the analogous construction in the case of a reactive substrate $M$. 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 $\partial M$. 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 $\frac{\partial u}{\partial t} = D \nabla^2 u$ in a bounded domain $\Omega$ are, respectively, Dirichlet ($u(x, t) = 0$), Neumann ($\nabla u(x, t) \cdot \mathbf{n}_1 = 0$) and Robin ($D \nabla u(x, t) \cdot \mathbf{n}_1 + \kappa_0 u(x, t) = 0$) for all $x \in \partial \Omega$. Here $u$ is particle concentration, $D$ is the diffusivity, $\kappa_0$ is a positive reactivity constant, and $\mathbf{n}_1$ is the outward unit normal at a point on the boundary, see figure 1a. However, implementing these boundary conditions
A simple generalization of diffusion in a bounded domain is given by a Wiener process. Although the evolution of the probability density $p(x,t)$ for the random position $X_t$ in a bounded domain $\Omega$ 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 Robin boundary condition.

The effects of surface reactions are then incorporated by introducing the generalized propagator $\tilde{\Psi}(x,\ell,t)$ for the pair $(X_t, \ell_t)$ in the case of a perfectly reflecting boundary, where $X_t$ and $\ell_t$ denote the particle position and local time, respectively. The solutions of surface reactions are then incorporated by introducing a so-called stopping local time. Given the probability distribution $P(x,\ell,t)$ for the pair $(X_t, \ell_t)$ in the case of a perfectly reflecting boundary, where $X_t$ and $\ell_t$ denote the particle position and local time, respectively. The effects of surface reactions are then incorporated by introducing the stopping time $T = \inf\{t > 0 : \ell_t > \ell_0\}$, with $\ell_0$ a so-called stopping local time. Given the probability distribution $\Psi(\ell) = P(\ell > \ell_0)$, the marginal probability density for particle position is defined according to $p(x,t) = \int_0^\infty \Psi(\ell)P(x,\ell,t)\,d\ell$. The classical Robin boundary condition for the diffusion equation corresponds to the exponential distribution $\Psi(\ell) = e^{-\gamma \ell}$, where $\gamma = \kappa_0/D$. The crucial step in the encounter-based approach is computing the generalized propagator $P(x,\ell,t)$ 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 $\ell$, one finds that $P(x,z,s)$ 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 $\tilde{P}(x,\ell,s)$ reduces to solving a classical Robin BVP and then inverting the solution with respect to the Laplace variable $z$.

$$P(x,z,s) \equiv \int_0^\infty e^{-zt} \int_0^\infty e^{-st}P(x,\ell,t)\,dt\,d\ell,$$ (1.1)

$$\tilde{P}(x,\ell,s) \equiv \int_0^\infty e^{-st}P(x,\ell,t)\,dt = L_\ell^{-1}[P(x,z,s)].$$ (1.2)

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 $\tilde{p}(x,s) = \int_0^\infty \Psi(\ell)\tilde{P}(x,\ell,s)\,d\ell$ 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 $\Omega$ is illustrated in figure 1b, whereby a target domain $M$ is inserted within the interior of $\Omega$. There is now an exterior boundary $\partial M$ and an interior boundary $\partial \Omega$, each of which has an associated boundary condition. A standard scenario at the single particle level is taking $\partial M$ 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 $\partial M$. However, the possibility of partial absorption naturally leads to another generalization, as illustrated in figure 1c, in which $M$ 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 $\ell_t$ [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 §2, we construct the occupation time propagator BVPs along the lines of [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 §3, we perform a double Laplace transform with respect to $t$ and the occupation time $A_t$, and derive the analogue 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 §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 result 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 §5, we calculate the spectral decomposition for a few simple geometries, including a one-dimensional 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 $\Psi$. 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 $\Psi$. 

Figure 1. (a) Diffusion of a particle in a bounded domain $\Omega$ with a partially absorbing boundary $\partial \Omega$. The probability of particle absorption depends on the amount of time spent in a neighbourhood of $\partial \Omega$, which is specified by the local accumulation time $\ell_t$. (b) Diffusion in the bounded domain $\Omega \setminus \mathcal{M}$, with $\partial \mathcal{M}$ acting as a partially absorbing boundary. (c) A particle diffusing in $\Omega$ 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 $n_2$ is directed towards the interior of $\mathcal{M}$ in (b). (Online version in colour.)
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 $X_t$ 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 $U_t$ given by [4]

$$U_t = \int_0^t F(X_\tau) \, d\tau,$$  

(2.1)

where $F(x)$ is some prescribed function or distribution such that $U_t$ has positive support and $X_0 = x_0$ is fixed. We also assume that $U_0 = 0$. Let $P(x, u, t|x_0)$ denote the joint probability density or propagator for the pair $(X_t, U_t)$. It follows that

$$P(x, u, t|x_0) = \left[ \frac{\delta(u - U_t)}{\delta x_0} \right]_{x_0 = x_0}^{X_t = x},$$  

(2.2)

where expectation is taken with respect to all random paths realized by $X_t$ between $X_0 = x_0$ and $X_t = x$. Using the Feynman–Kac formula, it can be shown that the propagator satisfies a BVP of the form [15]

$$\frac{\partial P(x, u, t|x_0)}{\partial t} = D \nabla^2 P(x, u, t|x_0) - F(x) \frac{\partial P}{\partial u}(x, u, t|x_0) - \delta(u) F(x) P(x, 0, t|x_0), \quad x \in \Omega,$$  

(2.3a)

and

$$\nabla P(x, u, t|x_0) \cdot n_1 = 0, \quad x \in \partial \Omega.$$  

(2.3b)

Here $n_1$ is the outward unit normal to a point on the boundary $\partial \Omega$. If $\Omega$ is unbounded then we replace the Neumann condition (2.3b) by $P(x, u, t|x_0) \to 0$ as $|x| \to \infty$. The initial condition is $P(x, u, 0|x_0) = \delta(x - x_0)\delta(u)$.

(i) Occupation time propagator

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

$$A_t = \int_0^t I_M(X_\tau) \, d\tau.$$  

(2.4)

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

$$F(x) = I_M(x) = \int_M \delta(x - x') \, dx'.$$  

(2.5)

and equations (2.3) take the form

$$\frac{\partial P(x, a, t|x_0)}{\partial t} = D \nabla^2 P(x, a, t|x_0)$$

$$- \int_M \left( \frac{\partial F}{\partial a}(x', a, t|x_0) + \delta(a) P(x', 0, t|x_0) \right) \delta(x - x') \, dx'$$  

(2.6)

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

$$\frac{\partial P(x, a, t|x_0)}{\partial t} = D \nabla^2 P(x, a, t|x_0), \quad x \in \Omega \setminus M,$$  

(2.7a)

$$\nabla P(x, a, t|x_0) \cdot n_1 = 0, \quad x \in \partial \Omega,$$  

(2.7b)

and

$$\frac{\partial Q(x, a, t|x_0)}{\partial t} = D \nabla^2 Q(x, a, t|x_0) - \left( \frac{\partial Q}{\partial a}(x, a, t|x_0) + \delta(a) Q(x, 0, t|x_0) \right),$$  

(2.7c)

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

$$P(x, a, t|x_0) = Q(x, a, t|x_0), \quad \nabla Q(x, a, t|x_0) \cdot n_2 = \nabla P(x, a, t|x_0) \cdot n_2,$$  

(2.7d)
and the initial conditions \( P(x, a, 0 | x_0) = \delta(x - x_0) \delta(a), \) \( Q(x, a, 0 | x_0) = 0. \) The unit normal \( \mathbf{n}_2 \) on \( \partial M \) is directed towards the interior of \( M, \) see figure 1b. We assume that the particle starts out in the non-absorbing region. (The analysis is easily modified if \( x_0 \in M. \))

Given the solution to the propagator BVP (2.7), we can introduce a probabilistic model of partial absorption by introducing the stopping time condition

\[
T = \inf \{ t > 0 : A_t > \tilde{A} \},
\]

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

\[
p(x, t | x_0) \, dx = \mathbb{P} [X_t \in (x, x + dx), t < T | X_0 = x_0].
\]

Given that \( A_t \) is a non-decreasing process, the condition \( t < T \) is equivalent to the condition \( A_t < \tilde{A}. \) This implies that

\[
p(x, t | x_0) \, dx = \mathbb{P} [X_t \in (x, x + dx), A_t < \tilde{A} | X_0 = x_0] = \int_0^\infty da \, \Psi(a) \left[ \int_0^a \! \! \int_d \! \! \int u' [P(x, a', t | x_0) \, dx] \right],
\]

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

\[
\int_0^\infty du \, f(u) \left[ \int_0^u \! \! \int d\, g(u') \right] = \int_0^\infty du' \, g(u') \left[ \int_0^{\infty} u' \, du \, f(u) \right],
\]

for arbitrary integrable functions \( f, g, \) it follows that

\[
p(x, t | x_0) = \int_0^\infty \Psi(a)P(x, a, t | x_0) \, da, \quad x \in \Omega \setminus M.
\]

Similarly,

\[
q(x, t | x_0) = \int_0^\infty \Psi(a)Q(x, a, t | x_0) \, da, \quad x \in M.
\]

One general quantity of interest is the survival probability \( S(x_0, t) \) that the particle has not been absorbed up to time \( t, \) given that it started at \( x_0. \) In the case of a partially absorbing substrate \( M, \)

\[
S(x_0, t) = \int_{\Omega \setminus M} p(x, t | x_0) \, dx + \int_M q(x, t | x_0) \, dx.
\]

The probability density of the stopping time \( T, \) equation (2.8), is given by \(-\partial S/\partial t\) so that the MFPT (if it exists) is

\[
T(x_0) = - \int_0^\infty \frac{\partial S(x_0, t)}{\partial t} \, dt = \int_0^\infty S(x_0, t) \, dt = \tilde{S}(x_0, 0),
\]

with \( \tilde{S}(s) \equiv \int_0^\infty f(t) e^{-st} \, dt. \) Similarly, higher order moments of the FPT density can be obtained in terms of \( s \)-derivatives of \( \tilde{S}(x_0, s). \)

(ii) Local time propagator

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

\[
\ell_t = \lim_{h \to 0} \frac{D}{h} \int_0^t H(h - \text{dist}(X_t, \partial M)) \, dt,
\]

where \( H \) is the Heaviside function. Note that although \( \ell_t \) 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
neighbourhood of the surface \( \partial \Omega \). In the case of the local time (2.13), the effective bounded domain is \( \Omega \setminus \mathcal{M} \) and

\[
F(x) = \lim_{h \to 0} \frac{D}{h} \varphi(h - \text{dist}(x, \partial \mathcal{M})) = D \int_{\partial \mathcal{M}} \delta(x - x') \, dx'.
\]

(2.14)

Equation (2.3a) becomes

\[
\frac{\partial P(x, \ell, t|x_0)}{\partial t} = D \nabla^2 P(x, \ell, t|x_0) - D \int_{\partial \mathcal{M}} \left( \frac{\partial P}{\partial \ell}(x', \ell, t|x_0) + \delta(\ell)P(x', 0, t|x_0) \right) \delta(x - x') \, dx',
\]

(2.15)

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

\[
\frac{\partial P(x, \ell, t|x_0)}{\partial t} = D \nabla^2 P(x, \ell, t|x_0), \quad x \in \Omega \setminus \mathcal{M}, \quad \nabla P(x, \ell, t|x_0) \cdot \mathbf{n}_1 = 0, \quad x \in \partial \Omega
\]

(2.16a)

and

\[
- D \nabla P(x, \ell, t|x_0) \cdot \mathbf{n}_2 = DP(x, \ell = 0, t|x_0) \delta(\ell) + D \frac{\partial}{\partial \ell} P(x, \ell, t|x_0), \quad x \in \partial \mathcal{M}.
\]

(2.16b)

These equations are supplemented by the ‘initial conditions’ \( P(x, \ell, 0|x_0) = \delta(x - x_0)\delta(\ell) \) and

\[
P(x, \ell = 0, t|x_0) = - \nabla p_\infty(x, t|x_0) \cdot \mathbf{n}_2 \text{ for } x \in \partial \mathcal{M},
\]

(2.16c)

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

\[
\frac{\partial p_\infty(x, t|x_0)}{\partial t} = D \nabla^2 p_\infty(x, t|x_0), \quad x \in \Omega \setminus \mathcal{M}, \quad \nabla p_\infty(x, t|x_0) \cdot \mathbf{n}_1 = 0, \quad x \in \partial \Omega
\]

(2.17a)

and

\[
p_\infty(x, t|x_0) = 0, \quad x \in \partial \mathcal{M}, \quad p_\infty(x, 0|x_0) = \delta(x - x_0).
\]

(2.17b)

One way to establish (2.16c) is to note that Laplace transforming equations (2.16a), (2.16b) with respect to \( \ell \) leads to a Robin BVP, see §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 \( \ell \) with distribution \( \psi(\ell) \) such that

\[
p(x, t|x_0) = \int_0^\infty \psi(\ell)P(x, \ell, t|x_0) \, d\ell, \quad x \in \Omega \setminus \mathcal{M}.
\]

(2.18)

### 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 \( \psi \), 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 \( \psi \). We now make the crucial observation that when \( \psi(a) = e^{-2a} \) in equation (2.9) or \( \psi(\ell) = e^{-2\ell} \) in equation (2.18), 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 §4), and then inverted to determine the original propagator.
(iii) Occupation time propagator

Laplace transforming the occupation time BVP (2.7) with respect to \( t \) and setting

\[
\tilde{P}(x, z, t|x_0) = \int_0^\infty e^{-s t} P(x, a, t|x_0) \, da \quad \text{and} \quad \tilde{Q}(x, z, t|x_0) = \int_0^\infty e^{-s t} Q(x, a, t|x_0) \, da, \tag{3.1}
\]

yields

\[
\frac{\partial \tilde{P}(x, z, t|x_0)}{\partial t} = D \nabla^2 \tilde{P}(x, z, t|x_0), \quad x \in \Omega \setminus M, \tag{3.2a}
\]

\[
\nabla \tilde{P}(x, z, t|x_0) \cdot n_1 = 0, \quad x \in \partial \Omega, \tag{3.2b}
\]

\[
\frac{\partial \tilde{Q}(x, z, t|x_0)}{\partial t} = D \nabla^2 \tilde{Q}(x, z, t|x_0) - z \tilde{Q}(x, z, t|x_0), \quad x \in M \tag{3.2c}
\]

and

\[
\tilde{P}(x, z, t|x_0) = \tilde{Q}(x, z, t|x_0), \quad \nabla \tilde{P}(x, z, t|x_0) \cdot n_2 = \nabla \tilde{Q}(x, z, t|x_0) \cdot n_2, \quad x \in \partial M. \tag{3.2d}
\]

This is a classical BVP for diffusion in a domain with a partially absorbing substrate \( M \) with a constant rate of absorption \( z \). Note that \( z \) has units of inverse time. Equations (3.2) are the analogue of a Robin BVP, in which a partially reactive surface \( \partial \Omega \) is replaced by a partially absorbing substrate \( M \). Although specific examples of the BVP (3.2) for constant \( z \) have been solved elsewhere [16,17], 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 Laplace transform with respect to \( s \).

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

\[
P(x, z, s|x_0) = \int_0^\infty e^{-s a} \left[ \int_0^\infty e^{-s t} P(x, a, t|x_0) \, dt \right] \, da \tag{3.3a}
\]

and

\[
Q(x, z, s|x_0) = \int_0^\infty e^{-s a} \left[ \int_0^\infty e^{-s t} Q(x, a, t|x_0) \, dt \right] \, da, \tag{3.3b}
\]

This yields

\[
D \nabla^2 P(x, z, s|x_0) - s P(x, z, s|x_0) = -\delta(x - x_0), \quad x \in \Omega \setminus M, \tag{3.4a}
\]

\[
- \nabla P(x, z, s|x_0) \cdot n_1 = 0, \quad x \in \partial \Omega, \tag{3.4b}
\]

\[
D \nabla^2 Q(x, z, s|x_0) - (s + z) Q(x, z, s|x_0) = 0, \quad x \in M \tag{3.4c}
\]

and

\[
P(x, z, s|x_0) = Q(x, z, s|x_0), \quad \nabla P(x, z, s|x_0) \cdot n_2 = \nabla Q(x, z, s|x_0) \cdot n_2, \quad x \in \partial M. \tag{3.4d}
\]

Given the solution to equations (3.4), we can then introduce a more general probability distribution \( \Psi(a) \) for the stopping occupation time such that

\[
\tilde{p}(x, s|x_0) = \int_0^\infty \Psi(a) L^{-1}_a \{ P(x, z, s|x_0) \} \, da, \quad x \in \Omega \setminus M \tag{3.5a}
\]

and

\[
\tilde{q}(x, s|x_0) = \int_0^\infty \Psi(a) L^{-1}_a \{ Q(x, z, s|x_0) \} \, da, \quad x \in M. \tag{3.5b}
\]

These can then be used to determine the MFPT for absorption within \( M \) according to equation (2.12) without the need to invert the Laplace transform with respect to \( s \).
(iv) Local time propagator

Laplace transforming the local time BVP (2.16) with respect to $\ell$ and setting

$$\tilde{P}(x, z, t|x_0) = \int_0^\infty e^{-z\ell} P(x, \ell, t|x_0) \, d\ell,$$  

(3.6)

yields

$$\frac{\partial \tilde{P}(x, z, t|x_0)}{\partial t} = D\nabla^2 \tilde{P}(x, z, t|x_0), \quad x \in \Omega \setminus M, \quad \nabla \tilde{P}(x, z, t|x_0) \cdot \mathbf{n}_1 = 0, \quad x \in \partial \Omega$$  

(3.7a)

and

$$- \nabla \tilde{P}(x, z, t|x_0) \cdot \mathbf{n}_2 = z\tilde{P}(x, z, t|x_0), \quad x \in \partial M, \quad (3.7b)$$

and $\tilde{P}(x, z, 0|x_0) = \delta(x - x_0)$. We see that equation (3.7b) is a classical Robin boundary condition on $\partial M$ 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 [13], the Robin boundary condition is equivalent to an exponential law for the stopping local time $\hat{t}_i$. Moreover, suppose that the Robin boundary condition is rewritten as

$$\nabla \tilde{P}(x, z, t|x_0) \cdot \mathbf{n}_2 = -z\tilde{P}(x, z, t|x_0) = -z \int_0^\infty e^{-z\ell} P(x, \ell, t|x_0) \, d\ell, \quad x \in \partial M. \quad (3.8)$$

Taking the limit $z \to \infty$ on both sides with $\tilde{P}(x, z, t|x_0) \to p_\infty(x, t|x_0)$, and noting that $\lim_{z \to \infty} z e^{-z\ell}$ is the Dirac delta function on the positive half-line, we obtain the supplementary condition (2.16c).

Again, it is convenient to consider the BVP for the double Laplace transform (1.1), which in the case of the local time takes the form [13,14]

$$D\nabla^2 P(x, z, s|x_0) - sP(x, z, s|x_0) = -\delta(x - x_0), \quad x \in \Omega \setminus M, \quad \nabla P(x, z, s|x_0) \cdot \mathbf{n}_1 = 0, \quad x \in \partial \Omega \quad (3.9a)$$

and

$$- \nabla P(x, z, s|x_0) \cdot \mathbf{n}_2 = zP(x, z, s|x_0), \quad x \in \partial M. \quad (3.9b)$$

Finally, equation (2.18) implies that

$$\tilde{p}(x, s|x_0) = \int_0^\infty \Psi(\ell) \mathcal{L}_\ell^{-1} [P(x, z, s|x_0)] \, d\ell, \quad x \in \Omega \setminus M.$$

(3.10)

The general probabilistic framework for analysing single-particle diffusion in partially absorbing media is summarized in the commutative diagram of figure 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 $\ell$ [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 [13]. Here we carry out an analogous procedure for the occupation time BVP (3.2). The basic idea is to replace the matching conditions (3.2a) by the inhomogeneous Dirichlet condition $P(x, s|x_0) = Q(x, s|x_0) = f(x, s)$ for all $x \in \partial M$ and to find the function $f$ for which $P$ and $Q$ are also the solution to the original BVP. (For the moment we drop the explicit
BVP with constant reactivity $z$

$$P(x, u, t|x_0) \xrightarrow{\mathcal{L}_s} \mathcal{P}(x, s, s|x_0)$$

$$\mathcal{P}(x, s, s|x_0) \xrightarrow{\mathcal{L}_s^{-1}} \tilde{P}(x, u, s|x_0)$$

$$\tilde{P}(x, u, s|x_0) \xrightarrow{\Psi} \tilde{p}(x, s|x_0)$$

**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 $P(x, u, t|x_0)$ 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 $\mathcal{M}$.

The general solution of equations (4.1) is of the form

$$\mathcal{P}(x, s|x_0) = \mathcal{F}_1(x, s) + G_1(x, s|x_0), \quad x \in \Omega \setminus \mathcal{M}$$

(4.2a)

and

$$Q(x, s|x_0) = \mathcal{F}_2(x, s), \quad x \in \mathcal{M}$$

(4.2b)

where

$$\mathcal{F}_1(x, s) = -D \int_{\partial \mathcal{M}} \partial_{\nu'} G_1(x', s|x)f(x', s) \, dx'$$

and

$$\mathcal{F}_2(x, s) = D \int_{\partial \mathcal{M}} \partial_{\nu'} G_2(x', s + z|x)f(x', s) \, dx'$$

(4.3)

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

$$D \nabla^2 G_1(x, s|x') - s G_1(x, s|x') = -\delta(x - x'), \quad x, x' \in \Omega \setminus \mathcal{M}$$

(4.4a)

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

(4.4b)

and

$$D \nabla^2 G_2(x, s|x') - s G_2(x, s|x') = -\delta(x - x'), \quad x, x' \in \mathcal{M}$$

(4.4c)

$$G_2(x, s|x') = 0, \quad x \in \partial \mathcal{M}$$

(4.4d)

Green’s functions have dimensions of $[\text{time}]/[\text{Length}]^2$. The unknown function $f$ is determined by substituting the solutions (4.2b) into equation (3.2b):

$$\mathbb{L}_a[f](x, s) + \partial_\nu G_1(x, s|x_0) = -\mathbb{P}_{a+2}[f](x, s), \quad x \in \partial \mathcal{M}$$

(4.5)
where $L_s$ and $\Gamma_s$ are the D-to-N operators

$$L_s[f](x, s) = -D \partial_\sigma \int_{\partial M} \partial_\sigma G_1(x', s|x)f(x', s) \, dx'$$  

(4.6a)

and

$$\Gamma_s[f](x, s) = -D \partial_\sigma \int_{\partial M} \partial_\sigma G_2(x', s|x)f(x', s) \, dx'.$$  

(4.6b)

acting on the space $L_2(\partial M)$. In the above equations, we have set $\partial_\sigma = n_2 \cdot \nabla_x$ and $\partial_\sigma' = n_2 \cdot \nabla_{x'}$.

When the surface $\partial M$ is bounded, the D-to-N operators $L_s$ and $\Gamma_s$ have discrete spectra. That is, there exist countable sets of eigenvalues $\mu_n(s), \mu_n(s)$ and eigenfunctions $\nu_n(x, s), \nu_n(s)$ satisfying (for fixed $s$)

$$L_s \nu_n(x, s) = \mu_n(s) \nu_n(x, s), \quad \Gamma_s \nu_n(x, s) = \mu_n(s) \nu_n(x, s).$$  

(4.7)

It can be shown that the eigenvalues are non-negative and that the eigenfunctions form a complete orthonormal basis in $L_2(\partial M)$. We can now solve equation (4.5) by introducing an eigenfunction expansion of $f$ with respect to one of the operators. For concreteness, we take

$$f(x, s) = \sum_{n=0}^{\infty} f_n(s) \nu_m(x, s).$$  

(4.8)

Substituting equation (4.8) into (4.5) and taking the inner product with the adjoint eigenfunction $\nu_n^*(x, s)$ yields the following matrix equations for the coefficients $f_n$:

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

(4.9)

where

$$g_n(s) = -\int_{\partial M} \nu_n^*(x, s) \partial_\sigma G_1(x, s|x_0) \, dx$$  

(4.10)

and

$$H_{nn}(s) = -D \int_{\partial M} \nu_n^*(x, s) \partial_\sigma \left\{ \int_{\partial M} \nu_m(x', s) \partial_\sigma G_2(x', s|x) \, dx' \right\} \, dx.$$  

(4.11)

The orthogonality condition

$$\int_{\partial M} \nu_n^*(x, s) \nu_m(x, s) \, dx = \delta_{nm, n},$$  

(4.12)

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

Introducing the vectors $f(s) = (f_n(s), n \geq 0)$ and $g(s) = (g_n(s), n \geq 0)$, we can formally write the solution of equation (4.9) as

$$f(s) = [M(s) + H(s + z)]^{-1} g(s),$$  

(4.13)

where $H(s)$ is the matrix with elements $H_{nn}(s)$ and $M(s) = \text{diag}(\mu_1(s), \mu_2(s), \ldots)$. Finally, substituting equation (4.13) into equations (4.2) gives

$$P(x, z, s|x_0) = G_1(x, s|x_0) + \frac{1}{D} \sum_{n,m} V_n(x, s)[M(s) + H(s + z)]^{-1} \nu_n^*(x_0, s), \quad x \in \Omega \setminus M$$  

(4.14a)

and

$$Q(x, z, s|x_0) = \frac{1}{D} \sum_{n,m} \tilde{V}_n(x, s + z)[M(s) + H(s + z)]^{-1} \nu_n^*(x_0, s), \quad x \in M,$$  

(4.14b)

where

$$V_n(x, s) = -D \int_{\partial M} \nu_n(x', s) \partial_\sigma G_1(x', s|x) \, dx'$$  

(4.15a)

and

$$\tilde{V}_n(x, s) = D \int_{\partial M} \nu_n(x', s) \partial_\sigma G_2(x', s|x) \, dx'.$$  

(4.15b)
An analogous construction can be carried out for the local time BVP (3.9) by decomposing the generalized propagator as \[13\]

\[\mathcal{P}(x, z, s|x_0) = G_1(x, s|x_0) + \mathcal{F}(x, z, s|x_0), \tag{4.16}\]

with

\[D \nabla^2 \mathcal{F}(x, z, s|x_0) - s \mathcal{F}(x, z, s|x_0) = 0, \quad x \in \Omega \setminus M, \tag{4.17a}\]

\[\nabla \mathcal{F}(x, z, s|x_0) \cdot n_2 + z \mathcal{F}(x, z, s|x_0) = -\nabla G_1(x, s|x_0) \cdot n_2 \quad \text{for} \; x \in \partial M \tag{4.17b}\]

and

\[D \nabla \mathcal{F}(x, z, s|x_0) \cdot n_1 = 0 \quad \text{for} \; x \in \partial \Omega. \tag{4.17c}\]

Replacing the Robin boundary condition by the Dirichlet condition where

\[L \text{ is the D-to-N operator (4.6a).} \]

Again this can be solved by substituting for \(f\) using the eigenfunction expansion (4.8), which yields the result

\[\mathcal{P}(x, z, s|x_0) = G_1(x, s|x_0) + \frac{1}{D} \sum_{n=0}^{\infty} \frac{\mathcal{V}_n(x, s)}{\mu_n(s)} \mathcal{V}_n^*(x_0, s). \tag{4.19}\]

Comparison of equations (4.14) and (4.19) 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 \(\det[M(s) + H(s + z)] = 0\) 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 \(\kappa(x, x_0)\).) On the other hand, it is straightforward to obtain the inverse Laplace transform of equation (4.19), assuming that we can invert term-by-term in the infinite sum. In particular [13],

\[\tilde{\mathcal{P}}(x, \ell, s|x_0) = G_1(x, s|x_0) \delta(\ell) + \frac{1}{D} \sum_{n=0}^{\infty} \mathcal{V}_n^*(x_0, s) \mathcal{V}_n(x, s) e^{-\mu_n(s) \ell}. \tag{4.20}\]

Finally, note that when \(\partial M\) 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 \(\Psi\). That is, although the spectral decomposition of the propagator is independent of \(\Psi\), the numerical truncation of the corresponding expansion of the MFPT will be \(\Psi\)-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 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 \(L_s\) and \(\bar{L}_s\) are known exactly, namely a sphere.
and \( \partial \mathcal{M} = \{0, L\} \), \( \mathcal{M} \setminus \Omega = [-L', 0] \). (Online version in colour.)

(a) Partially absorbing interval

Suppose that a particle diffuses in the interval \( \Omega = [-L', L] \) with a partially absorbing subinterval \( \mathcal{M} = [-L', 0] \), see Figure 3. It follows that \( \partial \mathcal{M} = \{L, 0\} \) and \( \partial \Omega = \{-L', L\} \). The one-dimensional version of equations (3.2) takes the form

\[
\frac{D}{\partial x^2} \frac{D}{\partial x^2} P(x, z, s|x_0) - s P(x, z, s|x_0) = -\delta(x - x_0), \quad 0 < x < L,
\]

\[
\frac{D}{\partial x^2} Q(x, z, s|x_0) - (s + z) Q(x, z, s|x_0) = 0, \quad -L' < x < 0,
\]

and

\[
\frac{\partial P(x, z, s|x_0)}{\partial x} = 0, \quad x = L, \quad \frac{\partial Q(x, z, s|x_0)}{\partial x} = 0, \quad x = -L'.
\]

These are supplemented by the matching conditions

\[
P(0, z, s|x_0) = Q(0, z, s|x_0), \quad \frac{\partial P}{\partial x}(0, z, s|x_0) = \frac{\partial Q}{\partial x}(0, z, s|x_0).
\]

Note that this particular BVP for fixed \( z \) and \( L, L' \to \infty \) was previously considered within the context of the so-called virtual traps [18]. The general solution of (5.1) is

\[
P(x, z, s|x_0) = A(z, s) \cosh \alpha(s)(L - x) + G_1(x, s|x_0), \quad x \in [0, L]
\]

and

\[
Q(x, z, s|x_0) = B(z, s) \cosh \alpha(s + z)(L' + x), \quad x \in [-L', 0],
\]

where \( \alpha(s) = \sqrt{\frac{s}{D}} \) and \( G_1 \) is the one-dimensional Green’s function that satisfies equation (5.1a) with a Dirichlet boundary condition at \( x = 0 \) and a Neumann boundary condition at \( x = L \):

\[
G_1(x, s|x_0) = \frac{H(x_0 - x) \hat{g}(x, s|x_0) + H(x_0 - x) \hat{g}(x_0, s|x_0)}{\sqrt{s/D} \cosh(\sqrt{s/D}L)}
\]

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

\[
\hat{g}(x, s) = \sinh \sqrt{\frac{s}{D} x} \quad \text{and} \quad \hat{g}(x, s) = \cosh \sqrt{\frac{s}{D} (L - x)}.
\]

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

\[
A(z, s) \cosh \alpha(s)L = B(z, s) \cosh \alpha(s + z)L'
\]

and

\[
-\alpha(s)A(z, s) \sinh \alpha(s)L = \alpha(s + z)B(z, s) \sinh \alpha(s + z)L' - \partial_x G_1(0, s|x_0).
\]

Substituting (5.5a) into (5.5b) gives

\[
\{\alpha(s) \tanh \alpha(s)L \cosh (s + z)L' + \alpha(s + z) \sinh \alpha(s + z)L'\} B(z, s) = \frac{1}{D} \frac{\cosh \sqrt{s/D}(L_0 - x)}{\cosh \sqrt{s/D}L}
\]

Note that equation (5.6) could also be derived from the one-dimensional version of equation (4.9), with \( \partial \mathcal{M} \) corresponding to the single point \( x = 0 \) and \( \partial \mathcal{M} = \{0, L\} \). In particular, since \( G_2(x, s|x_0) \)
is the Dirichlet–Neumann Green’s function on \((-L', 0]\), we find that
\[
\mathbb{L}_s[f](L, s) \equiv -Df(L, s)\partial_x \partial_x G_1(x', s|x)\big|_{x'=0} = f(0, s)\sqrt{\frac{s}{D}} \tanh\left(\sqrt{\frac{s}{D}}L\right)
\] (5.7)
and
\[
\mathbb{L}_s[f](L, s) \equiv -Df(L, s)\partial_x \partial_x G_2(x', s|x)\big|_{x'=0} = f(0, s)\sqrt{\frac{s}{D}} \tanh\left(\sqrt{\frac{s}{D}}L'\right).
\] (5.8)

We deduce that for one-dimensional diffusion, the D-to-N operators reduce to scalars with single eigenvalues \(\mu(s) = \alpha(s)\tanh(\alpha(s)L)\) and \(\mathbb{P}(s) = \alpha(s)\tanh(\alpha(s)L')\). In the specific case \(x_0 = 0\), the solution has the particularly simple form
\[
\mathbb{P}(x, z, s|0) = \frac{1}{\Phi(z, s)\sqrt{D}} \cosh \frac{\alpha(s)(L - x)}{\alpha(s)L}, \quad x \in [0, L]
\] (5.9a)
and
\[
\mathbb{Q}(x, z, s|0) = \frac{1}{\Phi(z, s)\sqrt{D}} \cosh \frac{\alpha(s + z)(L' + x)}{\alpha(s)L'}, \quad x \in [-L', 0],
\] (5.9b)
where
\[
\Phi(z, s) \equiv \alpha(s)\tanh[\alpha(s)L] + \alpha(s + z)\tanh[\alpha(s + z)L'].
\] (5.10)

For the sake of illustration, let us focus on the behaviour 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 \(\mathbb{P}(0, z, s|0) = \mathbb{Q}(0, z, s|0) \equiv C(z, s)\), where
\[
C(z, s) = \frac{1}{\sqrt{D}} \frac{1}{\sqrt{\tanh(\sqrt{s}/DL')} + \sqrt{s} \tanh(\sqrt{s}/DL)}.
\] (5.11)

The corresponding generalized survival probability is
\[
S(z, s) \equiv \int_{-L'}^{0} \mathbb{Q}(x, z, s|0) \, dx + \int_{0}^{L} \mathbb{P}(x, z, s|0) \, dx
\]
\[
= \frac{1}{\Phi(z, s)\sqrt{D}} \left( \frac{\tanh \alpha(s + z)L'}{\alpha(s + z)} + \frac{\tanh \alpha(s)L}{\alpha(s)} \right)
\]
\[
= \frac{1}{\sqrt{s}} \frac{\sqrt{s} \tanh(\sqrt{s}/DL')} + \sqrt{s + z} \tanh(\sqrt{s}/DL') + \sqrt{s} \tanh(\sqrt{s}/DL')
\] (5.12)

In standard treatments of partial absorption [18], one simply identifies \(C(\kappa_0, s)\) as the Laplace transformed probability density \(\tilde{p}(s)\) 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 (2.12) and (5.12) that the corresponding MFPT for absorption is
\[
T(0) = \lim_{s \to 0} S(\kappa_0, s) = \frac{L \tanh(\sqrt{\kappa_0}/DL')} {\sqrt{\kappa_0}D} + \frac{1}{\kappa_0}.
\] (5.13)

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 \(\Psi(a)\).

(i) Unbounded partially absorbing substrate \((L' \to \infty)\)

In the limit \(L' \to \infty\) we have \(\tanh\left(\sqrt{(s + z)/DL}'\right) \to 1\) and the \(z\)-dependence of the solutions (5.9) 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 $z$:

$$
\tilde{C}(z, t) = \frac{1}{2z\sqrt{\piDt^3}}(1 - e^{-zt}), \quad \tilde{S}(z, t) = e^{-zt/2}I_0\left(\frac{zt}{2}\right),
$$

(5.14)

and

$$
\tilde{C}(a, s) = \frac{e^{-sa}}{\sqrt{\pi aD}} - \sqrt{\frac{s}{D}} \text{erfc}(\sqrt{sa}), \quad \tilde{S}(a, s) = \frac{e^{-sa}}{\sqrt{\pi sa}},
$$

(5.15)

where

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

(5.16)

Moreover,

$$
C(a, t) = \frac{1}{2\sqrt{\pi Dt^3}}(H(a) - H(a - t)), \quad S(a, t) = \frac{1}{\pi \sqrt{a(t - a)}}H(t - a).
$$

(5.17)

For a constant rate of absorption $z = \kappa_0$ (exponential distribution $\Psi(a) = e^{-\kappa_0 a}$), we recover some of the results of [18]. For example, the density at the origin is $p(t) = \tilde{C}(\kappa_0, t)$. Hence, at short times, $t \ll 1/\kappa_0$, the density is diffusion dominated with $p(t) \sim (4\pi Dt)^{-1/2}$, 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 $\tilde{S}(\kappa_0, t)$. On the other hand, for a non-exponential stopping occupation time distribution $\Psi(a)$, the marginal density at the origin becomes

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

(5.18)

and the survival probability is now

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

(5.19)

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:

$$
\tilde{C}(a, s) = \frac{e^{-sa}}{\sqrt{\pi aD}} - \sqrt{\frac{s}{D}} \tanh\left(\sqrt{\frac{s}{D}}L\right) \text{erfc}\left(\sqrt{sa} \tanh\left(\sqrt{\frac{s}{D}}L\right)\right),
$$

(5.20)

and

$$
\tilde{S}(a, s) = \text{sech}^2\left(\sqrt{s/D}L\right) \text{erfc}\left(\sqrt{sa} \tanh\left(\sqrt{\frac{s}{D}}L\right)\right) + \frac{\sqrt{D} \tanh(\sqrt{s/D}L)}{\sqrt{s}} \tilde{C}(a, s).
$$

(5.21)

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

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

(5.22)

Using integration by parts, we see that

$$
\int_0^\infty \Psi(a) \, da = \left[a\Psi(a)\right]_0^\infty - \int_0^\infty a\Psi'(a) \, da = \int_0^\infty a\psi(a) \, da = -\psi'(0).
$$

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:

\[ \psi_{\text{gam}}(a) = \frac{\gamma (\gamma a)^{\mu - 1} e^{-\gamma a}}{\Gamma(\mu)} \quad \text{and} \quad \Psi(a) = \frac{\Gamma(\mu, \gamma a)}{\Gamma(\mu)}, \quad \mu > 0, \]

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

\[ \Gamma(\mu) = \int_0^{\infty} e^{-t} t^{\mu - 1} \, dt \quad \text{and} \quad \Gamma(\mu, z) = \int_z^{\infty} e^{-t} t^{\mu - 1} \, dt, \quad \mu > 0. \]

The corresponding Laplace transforms are

\[ \tilde{\psi}_{\text{gam}}(z) = \left( \frac{\gamma}{\gamma + z} \right)^{\mu} \quad \text{and} \quad \tilde{\Psi}_{\text{gam}}(z) = \frac{1 - \tilde{\psi}_{\text{gam}}(z)}{z}. \]

Here \( \gamma \) determines the effective absorption rate so that the substrate \( M \) 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 \( \psi_{\text{gam}} \) reduces to the exponential distribution with constant reactivity \( \gamma \), that is, \( \psi_{\text{gam}}(a)_{\mu=1} = \gamma e^{-\gamma a} \). The parameter \( \mu \) thus characterizes the deviation of \( \psi_{\text{gam}}(a) \) from the exponential case. If \( \mu < 1 \) (\( \mu > 1 \)) then \( \psi_{\text{gam}}(a) \) decreases more rapidly (slowly) as a function of the occupation time \( a \). In figure 4, we plot the survival probability \( S(t) \) of equation (5.19) as 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 \( \gamma \) or larger \( \mu \). In figure 5a, we plot the corresponding MFPT \( T(0) \) as a function of \( \gamma \) for various values of \( \mu \). 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 \( M = (-\infty, 0] \) is totally absorbing in this limit and \( x_0 = 0 \). Figure 5b shows that increasing \( \mu \) 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 \( \gamma \) is small.

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1See [13] for an extensive list of different distributions \( \psi \). 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

\[ \psi(t) = \frac{\gamma \mu}{(1 + \gamma t)^{\mu+1}}, \quad 0 < \mu < 1. \]

A finite first moment does exist for \( \mu > 1 \) and one then finds qualitatively similar behaviour to the gamma distribution for fixed \( \mu \).
Figure 5. MFPT $T$ of equation (5.22) for the gamma distribution in the case of a semi-infinite absorbing substrate and $L = 1$. (a) Plot of $T$ as a function of $\gamma'$ for various values of $\mu$. The case $\mu = 1$ corresponds to the exponential distribution (constant reactivity). (b) Corresponding plots of the slope $dT/dL$ as a function of $\mu$ for various values of $\gamma$. Other parameters are $L = D = 1$. (Online version in colour.)

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

The $z$-dependence of the solutions (5.9) is more complicated when $L'$ is finite. For the sake of illustration, let $L \to \infty$ so that the solutions (5.9) become (for $x_0 = 0$)

$$P(x, z, s|0) = \frac{e^{-\alpha(s)x}}{\Phi(z, s)D}, \quad x \geq 0$$

(5.26a)

and

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

(5.26b)

where

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

(5.27)

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

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

(5.28)

with $c > 0$, chosen so that the Bromwich contour is to the right of all singularities of $Q(x, z, s|0)$. The Bromwich integral (5.28) can be evaluated by closing the contour in the complex $z$-plane as illustrated in figure 6a. The resulting contour encloses a countably infinite number of poles, which correspond to the zeros of the function $\Phi(z, s)$. Setting $\Phi(z, s) = 0$ in equation (5.27) and rearranging leads to the transcendental equation

$$\tanh y = -\sqrt{\frac{s}{s_0 - y}}, \quad s_0 = \frac{D}{L'^2}, \quad y = L' \sqrt{\frac{|s + z|}{D}}.$$  

(5.29)

Clearly (5.29) 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 $\omega_n$ real such that

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

(5.30)

The dependence of $Q(x, z, s|0)$ 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 $Q(x, z, s|0)$ is single-valued.

\footnote{The dependence of $Q(x, z, s|0)$ 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 $Q(x, z, s|0)$ is single-valued.}
The corresponding zeroes in the $z$-plane are real and lie to the left of $z = -s$ since $\omega_n \neq 0$:

$$z_n = -s - s_0 \omega_n^2, \quad n \geq 1. \quad (5.31)$$

Example plots of the function $\Phi(z, s)/\alpha(s)$ are shown in figure 6b. 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,

$$z_n \approx -s - s_0 (n\pi)^2, \quad n \geq N(s). \quad (5.32)$$

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 figure 6a, and noting that the contribution from the semi-circle $C_R$ vanishes in the limit $R \to \infty$, we have

$$\tilde{Q}(x, a, s | 0) = \sum_{n \geq 1} \frac{1}{\Phi_n(s)} e^{-(s+s_0 \omega_n^2)at} \cos[\omega_n(L' + x)/L']. \quad (5.33)$$

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

$$\Phi(z_n, s) \cos \omega_n = -\frac{\omega_n}{L'} \sin \omega_n + \sqrt{\frac{s}{D}} \cos \omega_n \quad (5.34)$$

and

$$\partial_z[\Phi(z_n, s) \cos \omega_n] = \Phi_n(s) \equiv \frac{L'}{2D} \left( \cos \omega_n + \left[ 1 + \frac{L'}{D} \sqrt{s/s_0} \right] \frac{\sin \omega_n}{\omega_n} \right). \quad (5.35)$$

Assuming the series is uniformly convergent, the corresponding marginal density (for $x_0 = 0$) is

$$\tilde{q}(x, s) = \sum_{n \geq 1} \frac{\tilde{\Psi}(s + s_0 \omega_n^2)}{\Phi_n(s)} \cos[\omega_n(L' + x)/L']. \quad (5.36)$$

Analogous results holds for $\tilde{P}(x, a, s | x_0)$ and $\tilde{p}(x, s | x_0)$. 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
Figure 7. Plots of normalized truncated series $\Lambda_N(s_0)$ as a function of $N$ and various $\mu$ for (a) $s_0 = 1$ and (b) $s_0 = 0.1$. We also set $\gamma = 1$. (Online version in colour.)

choice of distribution $\Psi$. As a simple illustration, consider the limit $s \to 0$, for which $\omega_n = n\pi$, and set $x = 0$:

$$\tilde{q}(0, 0) = 2L's_0 \sum_{n \geq 1} \tilde{\Psi}(n^2\pi^2s_0). \quad (5.37)$$

In figure 7, we show plots of the truncated series $\Lambda_N(s_0) = \sum_{n=1}^{N} \tilde{\Psi}(n^2\pi^2s_0)$ 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 ($\mu, \gamma$) of the gamma distribution. Note that keeping only the first few terms leads to poor accuracy.

(b) Partially absorbing sphere

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

$$v_{nm}(\theta, \phi) = \tau_{nm}(\theta, \phi) = \frac{1}{R} Y_n^m(\theta, \phi), \quad n \geq 0, \ |m| \leq n. \quad (5.38)$$

From orthogonality, it follows that the adjoint eigenfunctions are

$$v_{nm}^*(\theta, \phi) = \tau_{nm}^*(\theta, \phi) = (-1)^{m} \frac{1}{R} Y_n^{-m}(\theta, \phi). \quad (5.39)$$

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

$$\mu_n(s) = -\alpha(s) \frac{k_n'(s_0R)}{k_n(s_0R)} \quad \text{and} \quad \overline{\mu}_n(s) = \alpha(s) \frac{j_n'(s_0R)}{j_n(s_0R)} \quad (5.40)$$

where $\alpha(s) = \sqrt{s/D}$. Since the $n$th eigenvalue is independent of $m$, it has a multiplicity $2n + 1$. It is also possible to compute the projections of the boundary fluxes in (4.15) by using appropriate
series expansions of the corresponding Green’s functions. For example, one finds that [13]

\[-D \partial_{\alpha} G_1(\mathbf{x'}, \mathbf{s}|x) = \sum_{n=0}^{\infty} \frac{2n + 1}{4\pi R^2} P_n \left( \frac{\mathbf{x'} \cdot \mathbf{x}}{(rR)} \right) k_n(\alpha(s)r) \frac{k_n(\alpha(s)R)}{k_n(\alpha(s)R)} (5.41)\]

with \(|\mathbf{x'}| = R, |\mathbf{x}| = r > R\) and \(P_n(x)\) a Legendre polynomial. Hence, using \(\partial_{\alpha'} = -\partial/\partial r'\) (see also [19])

\[
V_{nm}(x, s) \equiv D \int_{|\mathbf{x'}| = R} v_{nm}(\theta', \phi') \frac{\partial}{\partial r'} G_1(x', s|r, \theta, \phi) d\mathbf{x'} = -v_{nm}(\theta, \phi) \frac{k_n(\alpha(s)r)}{k_n(\alpha(s)R)} (5.42)
\]

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

\[
\hat{V}_{nm}(x, s) \equiv -D \int_{|\mathbf{x'}| = R} v_{nm}(\theta', \phi') \frac{\partial}{\partial r'} G_2(x', s|r, \theta, \phi) d\mathbf{x'} = -v_{nm}(\theta, \phi) \frac{i_n(\alpha(s)r)}{i_n(\alpha(s)R)} (5.43)
\]

for \(x = (r, \theta, \phi)\) and \(r < R\). Finally, the matrix \(H(s)\) in equation (4.11) becomes

\[
H_{nm,n'm'}(s) = -D \int_{\partial M} v_{nm}^*(\theta, \phi) \frac{\partial}{\partial r} \left[ \int_{\partial M} v_{n'm'}(\theta', \phi') \frac{\partial}{\partial r'} G_2(x', s|x) d\mathbf{x'} \right] dx
= a(s) \frac{i_{n'}(\alpha(s)R)}{i_n(\alpha(s)R)} \left[ \int_{\partial M} v_{nm}^*(\theta, \phi) v_{n'm'}(\theta, \phi) d\mathbf{x} \right]
= \overline{\mu}_n(s) \delta_{n,n'} \delta_{m,m'}. (5.44)
\]

That is, \(H\) is a diagonal matrix. Finally, from equation (4.14) the generalized propagator within the sphere becomes

\[
Q(x, z|s_0) = \frac{1}{D} \sum_{n,m,n',m'} \hat{V}_{nm}(x, s + z|M(s) + H(s + z)]^{-1} v_{n'm'}^*(x_0, s),
\]

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

where \(x = (r, \theta, \phi)\) and \(x_0 = (r_0, \theta_0, \phi_0)\) with \(r < R\) and \(r_0 > R\). An analogous result holds for \(P(x, s|x_0)\). 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 \(\psi\).

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 analysing 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 \(\psi\).

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 (figure 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 [20–22]. The interior of a synapse thus acts as a partially absorbing domain \(M\) within the
**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 two-dimensional rectangular domain $\Omega$ with circular targets, say, with periodic boundary conditions imposed on the pair of horizontal edges.

dendritic membrane $\Omega$. 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 [23]. (In the latter case, the synapse could also be treated as a two-dimensional absorbing surface in a three-dimensional model of a neuron.) Both of these examples motivate extending the analytical framework developed in this paper to investigate the competition for resources between multiple partially absorbing targets. As we have shown elsewhere [15], it is relatively straightforward to extend the generalized propagator BVP of §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 $z_j$.

**Data accessibility.** This article has no additional data.

**Authors’ contributions.** All authors contributed to the writing and revision of the manuscript.

**Conflict of interest declaration.** We declare we have no competing interest.

**Funding.** No funding has been received for this article.

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