

Chapter 1

Partially Reflected Brownian Motion: A Stochastic Approach to Transport Phenomena

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ABSTRACT

The transport phenomena are known to be important for various scientific domains: examples can be found in physics, electrochemistry, heterogeneous catalysis, physiology, etc. To obtain new information about diffusive or Laplacian transport towards a semi-permeable or resistive interface, one can study the random trajectories of diffusive particles modelled, in a first approximation, by the partially reflected Brownian motion. This stochastic process turns out to be a convenient mathematical foundation for discrete, semi-continuous and continuous theoretical descriptions of the diffusive transport.

This paper presents an overview on these topics with a special emphasis on the close relations between stochastic processes with partial reflections and the Laplacian transport phenomena. We give selected examples of these phenomena followed by a brief introduction to the partially reflected Brownian motion and related probabilistic objects (e.g., local time process and spread harmonic measure). A particular attention is paid to a useful relation to the Dirichlet-to-Neumann operator. Some practical consequences and further perspectives are discussed.

Keywords: Diffusion with Reflections; Mixed Boundary Value Problems; Laplacian Transport Phenomena.

Introduction

An erratic motion of pollens of *Clarkia* (primrose family) discovered by Robert Brown in 1827 and quantitatively described by Albert Einstein in 1905 gave a substantial impact for development of mathematical theory of stochastic processes, an important branch of modern mathematics. Supported by rigorous mathematical foundations, the Brownian motion and related stochastic processes found numerous applications in different scientific domains, from theoretical physics to biology and economics. To study the transport of species diffusing from a remote source towards and across semi-permeable or resistive interface (e.g., cellular membrane), one can employ either an averaged description in terms of an appropriate boundary value problem for the concentration of species, or stochastic analysis of its random trajectories. In the first case, a finite permeability of the interface leads to the mixed boundary condition, while in the second case it can be modelled by partial reflections on the boundary. Physical or chemical processes governed by the Laplace equation (stationary diffusion) with mixed boundary condition are generally called *Laplacian transport phenomena*. Its examples are found in physiology (oxygen diffusion towards and across alveolar membranes), in electrochemistry (electric transport through metallic electrodes), in heterogeneous catalysis (diffusion of reactive molecules towards catalytic surfaces). The theoretical or numerical analysis of these phenomena is generally complicated by an irregular geometry of the interface (e.g., microroughness of metallic electrodes, see Section 1.1). Studying random trajectories of diffusing species, one can extract a more subtle information about the system in question.

In this paper, we present a particular stochastic process, called *partially reflected Brownian motion* (PRBM), and its application to study the Laplacian transport phenomena. The main purpose we are standing for is to capture the attention to this motion for understanding the influence of a geometrical irregularity of the interface on transport properties of the whole system. Bearing in mind the particular role of the geometry, we would like to “bridge” theoretical, numerical and experimental studies of the Laplacian transport phenomena on the one side, and powerful mathematical methods of stochastic analysis on the other side. Since the extensive literature existing on both topics is generally difficult to get through for non-specialists, we prefer to use a descriptive style of writing in order to give the whole vision of the problem, without specifying particular details which can be easily found anywhere else (e.g., see references at the end of this paper).

In the first section, we present three examples of the Laplacian transport phenomena found in different scientific fields. Their mathematical description by the mixed boundary value problem opens encouraging possibilities to apply powerful tools of potential theory, variational analysis and probability theory. The second section is devoted to remind some basic definitions of stochastic process theory: stopping times, reflected Brownian motion, local time process, harmonic measure, etc. In the third section, we introduce the partially reflected Brownian motion and show its properties for a planar surface. An important relation to the Dirichlet-to-Neumann operator is revealed and then illustrated by several examples. The last section contains the stochastic descriptions of the Laplacian transport phenomena: recently developed continuous approach and two other approaches are described. In the conclusion, we summarize the essential aspects of the paper.

1.1 Laplacian transport phenomena

The transport of species between two distinct “regions” separated by an interface occurs in various biological systems: water and minerals are pumped by roots from the earth, ions and biological species penetrate through cellular membranes, oxygen molecules diffuse towards alveolar ducts, and so on. The transport processes are relevant for many other scientific domains,

for example, in heterogeneous catalysis (principal industrial process in petrochemistry) or in electrochemistry. In this section, we will give three important examples of particular transport process, called *Laplacian* or *diffusive transport*.

1.1.1 Stationary diffusion across semi-permeable membranes

Let us begin by considering the respiration process of mammals. Inbreathing a fresh air, one makes it flow from the mouth to the dichotomic bronchial tree of the lungs (Fig. 1.1). For humans, first fifteen generations of this tree serve for convective transport of the air towards pulmonary acini, terminal gas exchange units [1]. A gradual increase of the total cross-section of bronchiae leads to a decrease of air velocity. At the entrance of the acinus, it becomes lower than the characteristic diffusion velocity [2, 3]. As a consequence, one can describe the gas exchange into the acinus as stationary diffusion of oxygen molecules in air from the entrance (“source” with constant concentration C_0 during one cycle of respiration) to the alveolar membranes [4]. In the bulk, the flux density is proportional to the gradient of concentration (Fick’s law), $\mathbf{J} = -D\nabla C$, where D is the diffusion coefficient. The mass conservation law written locally as $\text{div } \mathbf{J} = 0$ leads to the Laplace equation $\Delta C = 0$ in the bulk. The flux density *towards* the interface is simply $J_n = D \partial C / \partial n$, where the normal derivative $\partial / \partial n$ is directed to the bulk. Arrived to the alveolar membrane, oxygen molecules can penetrate across the boundary for further absorption in blood, or to be “bounced” on it and to continue the motion. The “proportion” of absorbed and reflected molecules can be characterized by *permeability* W varying from 0 (perfectly reflecting boundary) to infinity (perfectly absorbing boundary). Thus, the flux density *across* the alveolar membrane is proportional to the concentration, $J_n = WC$. Equating these two densities, one obtains a mixed boundary condition, $D(\partial C / \partial n) = WC$, called also *Fourier* or *Robin* boundary condition. Resuming these relations, one provides the following mathematical description for the diffusion stage of human or, in general, mammalian respiration:

$$\Delta C = 0 \quad \text{in the bulk} \quad (1.1)$$

$$C = C_0 \quad \text{on the source} \quad (1.2)$$

$$\left[I - \Lambda \frac{\partial}{\partial n} \right] C = 0 \quad \text{on the alveolar membrane} \quad (1.3)$$

where the involved physics and physiology are characterized by a single parameter, $\Lambda = D/W$, being homogeneous to the length (I stands for the identity operator). Note also that the dependence on constant C_0 is irrelevant. In what follows, we address to this “classical” boundary value problem. The essential complication resides in a very irregular geometry of the pulmonary acinus which presents a branched structure of eight generations (for humans), “sticked” by alveolar ducts (Fig. 1.1). For small Λ , only a minor part of the boundary is involved to the transport process (so-called *Dirichlet active zone*), whereas the flux across the rest of the boundary is almost zero (this effect is called *diffusional screening* [4–10]). With an increase of Λ , larger and larger part of the boundary becomes active. As a result, the efficiency of human lungs depends on the parameter Λ in a non trivial manner that implies different physiological consequences. Considering the trajectory of a chosen oxygen molecule, one finds the Brownian motion from the source towards the alveolar membrane, with multiple bounces on the boundary and final absorption. One will see that such trajectories correspond to the partially reflected Brownian motion (Section 1.3). The profound study of the interplay between the irregular geometry of the acinus and erratic random motion of oxygen molecules inside should lead to a better understanding of the physiological functioning of human lungs.

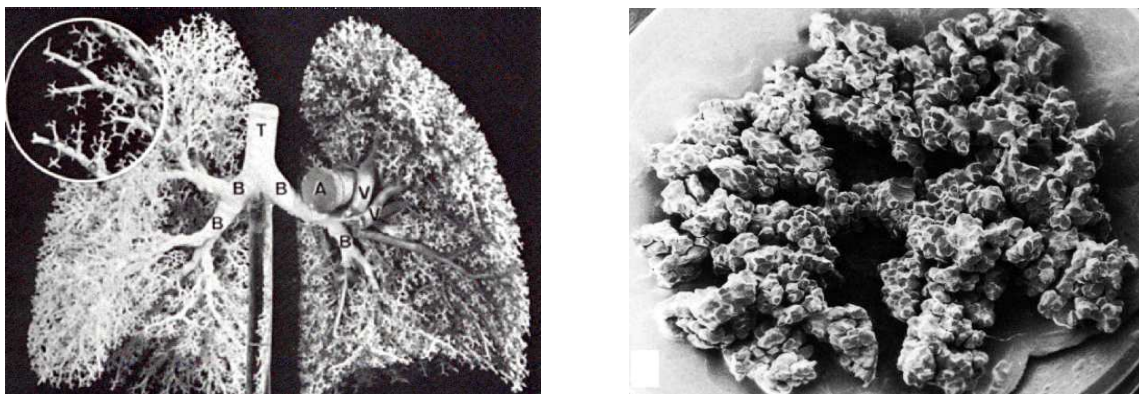


Figure 1.1: On the left, a cast of human lungs; on the right, a cast of pulmonary acinus [1, 11] (by E. Weibel).

1.1.2 Heterogeneous catalysis

The similar description can be brought to the heterogeneous catalysis omnipresent at petrochemistry. One considers reactive molecules A injected into a solvent and then diffusing towards a catalytic surface. Hitting this boundary, they can be transformed into other molecules A^* with a finite reaction rate K , or to be bounced for further diffusion. The new molecules diffuse from the catalytic surface and then they are collected with the help of appropriate physical or chemical technics. Assuming the presence of a remote source of reactive molecules A , one can model, in a first approximation¹, the heterogeneous catalysis by the mixed boundary value problem (1.1–1.3) with a characteristic length $\Lambda = D/K$ [12–16]. The keynote of this similitude is related to the fact that each reactive molecule arrived to the boundary terminates its motion after a number of successive reflections. The mechanism leading to their termination is different: for the oxygen diffusion, the molecules are absorbed by the alveolar membrane, whereas for the heterogeneous catalysis, the reactive molecules are transformed into other molecules which do not participate to further process. Since the overall production of new molecules A^* depends on the total surface area of the catalytic surface, one tries to design catalysts with the largest possible surface (for given volume), realizing porous and very irregular boundaries (Fig. 1.2). As a consequence, the diffusional screening becomes important for understanding numerous industrial processes in petrochemistry. Since random trajectories of reactive molecules correspond to the partially reflected Brownian motion, its study may allow to design more efficient catalysts.

1.1.3 Electric transport in electrochemistry

The other example of Laplacian transport phenomena can be found in electrochemistry: the electric transport between two metallic electrodes into an electrolyte is described by the same boundary value problem. Indeed, the electric potential V obeys the Laplace equation in the bulk since the electrolyte is locally neutral. Taking one electrode of very low resistance (*counter-electrode*), one writes the corresponding boundary condition as $V = V_0$, where V_0 is the applied tension. For the other electrode of surface resistance r (*working electrode*), one obtains the

¹This description is probably too simplified in order to model the heterogeneous catalysis *quantitatively*. First, the presence of other molecules A^* may obstruct the access to the catalytic surface. Second, certain parasite reactions happen on the boundary that implies a deactivation of the catalyst. Consequently, the reactivity K becomes dependent on the spatial position leading to an inhomogeneous boundary condition. Finally, the molecular diffusion can be applied if the mean free path of reactive molecules is lower than the geometrical features of the catalyst (in the opposite case, one deals with Knudsen diffusion [17]). Nevertheless, the simple description (1.1–1.3) permits to take into account many important features related to the catalytic process.

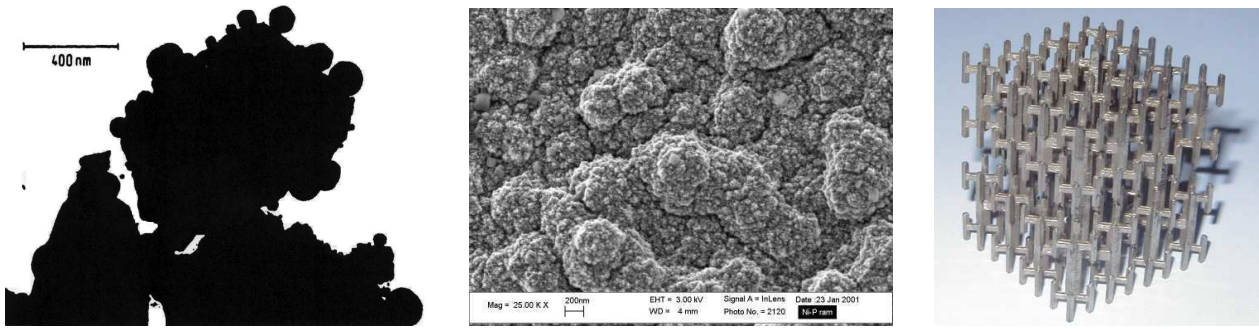


Figure 1.2: On the left, an example of an irregular catalytic surface (by J.S. Andrade jr.); at the center, photo of a rough metallic surface of nickel electrode (by E. Chassaing); on the right, photo of an irregular metallic electrode used to study the Laplacian transport phenomena experimentally (by B. Sapoval).

mixed boundary condition by equating the volume current density $-\rho^{-1}\nabla V$ (ρ is the electrolyte resistivity) and the surface current density V/r : $\Lambda \partial V/\partial n = V$, where $\Lambda = r/\rho$ is again the physical length of the problem. The similar description can be brought even in the case of an alternative tension [18, 19].

For electric transport, one cannot associate directly the mixed boundary value problem with the partially reflected Brownian motion since there is no diffusing particle. From this point of view, the electrochemical problem has only a formal analogy with two previous examples. At the same time, the electrochemistry provides a wide domain for experimental studies of the influence of the irregular geometry on the (average) transport properties. Taking different metallic electrodes with micro- or macro-roughness (Fig. 1.2), one can measure its *spectroscopic impedance* or *admittance* corresponding to the total flux across the boundary for diffusional problems [20]. The observation of anomalous impedance behavior in [21] had provoked numerous theoretical, numerical and experimental studies of the role of a geometrical irregularity in Laplacian transport phenomena [22–32] (for more information, see [33] and references therein).

1.1.4 Discrete and semi-continuous approaches

Between different theoretical approaches developed to study the Laplacian transport phenomena, one can distinguish semi-continuous and discrete approaches: the double layer theory of Halsey and Leibig [24, 25] and the formalism of the Brownian self-transport operator introduced by Filoche and Sapoval [20] respectively. In both cases, one involves the stochastic description of particle's motion corresponding to the mixed boundary value problem (1.1–1.3). Halsey and Leibig used the Green functions in order to account the number of jump-like reflections of the Brownian motion on the boundary (see Section 1.4.3), while Filoche and Sapoval considered random walks on a lattice with partial reflections (see Section 1.4.4). Although both approaches provide a complete description of the Laplacian transport phenomena (e.g., the explicit formula for the total flux across the boundary), their essential inconvenient resides in the dependence on an artificial length scale: jump distance a for the *semi-continuous* approach of Halsey and Leibig and lattice parameter a for the *discrete* approach of Filoche and Sapoval. A physical intuition suggests that, if the description is correct, there should exist a well defined continuous limit as a tends to 0. Certain substantial arguments to justify the existence of this limit are brought in [33], but a rigorous mathematical proof is still required. In this paper, we describe a different approach which can be called *continuous*, based on the partially reflected Brownian motion. It will integrate the advantages of previous ones, being a mathematical foundation for understanding the Laplacian transport phenomena. We will return to these questions in

Section 1.4.

1.2 Basic definitions

In this section, we recall the basic definitions related to the Brownian motion and reflected Brownian motion that can be found in extensive literature, e.g., [34–40]. The familiar reader may pass over this section.

1.2.1 Brownian motion and Dirichlet boundary value problem

The Brownian motion can be defined in different ways [34]. Throughout this paper, we use the following definition.

Definition 1.2.1 *A stochastic process W_t ($t \geq 0$) defined on the chosen probabilistic space is called one-dimensional Brownian motion (or Wiener process) started from the origin, if*

- *its trajectories are continuous almost surely (with probability 1);*
- *it starts from the origin almost surely, $\mathbb{P}\{W_0 = 0\} = 1$;*
- *its joint distribution is*

$$\mathbb{P}\{W_{t_1} \in \Gamma_1, \dots, W_{t_n} \in \Gamma_n\} = \int_{\Gamma_1} dx_1 \dots \int_{\Gamma_n} dx_n g(0, x_1; t_1) g(x_1, x_2; t_2 - t_1) \dots g(x_{n-1}, x_n; t_n - t_{n-1})$$

for any integer n , any real numbers $0 < t_1 < \dots < t_n$ and arbitrary intervals $\Gamma_1, \dots, \Gamma_n$, where $g(x, x'; t)$ is the Gaussian density

$$g(x, x'; t) = \frac{1}{\sqrt{2\pi t}} \exp\left[-\frac{(x - x')^2}{2t}\right] \quad x, x' \in \mathbb{R}, \quad t \in \mathbb{R}_+ \quad (1.4)$$

By definition, $g(0, x; t)dx$ is the probability to find the Brownian motion in dx vicinity of point x at time t :

$$\mathbb{P}\{W_t \in (x, x + dx)\} = g(0, x; t)dx$$

The collection $W_t = (W_t^1, \dots, W_t^d)$ of d independent one-dimensional Brownian motions W_t^k is called d -dimensional Brownian motion started from the origin (in the following, we will omit the pointing on the dimension). The translated stochastic process, $x + W_t$, is called Brownian motion started from the point $x \in \mathbb{R}^d$.

Various properties of the Brownian motion and its relations to other mathematical fields (like partially differential equations or potential theory) are well known and can be found in [34–40].

As one can see, the Brownian motion W_t is defined for the whole space \mathbb{R}^d , without any binding to a particular domain. However, the physical processes are usually confined into a certain domain $\Omega \subset \mathbb{R}^d$. The “presence” of its boundary $\partial\Omega$ can be introduced by a specific condition for a quantity we are looking for. To illustrate this notion, let us introduce the harmonic measure ω_x defined as the probability to hit the boundary $\partial\Omega$ on its different subsets for the first time.

Definition 1.2.2 Let $\Omega \subset \mathbb{R}^d$ be a domain with boundary $\partial\Omega$. For any $x \in \mathbb{R}^d$, a random variable $\mathbb{T}^x = \inf\{t > 0 : (x + W_t) \in \partial\Omega\}$ is called *stopping time on the boundary $\partial\Omega$* (it gives the first moment when the Brownian motion started from x hits the boundary). For any subset A from the Borel σ -algebra $\mathcal{B}(\partial\Omega)$, one defines its harmonic measure $\omega_x\{A\}$ (hitting probability) as:

$$\omega_x\{A\} = \mathbb{P}\{W_{\mathbb{T}^x} \in A, \mathbb{T}^x < \infty\}$$

(we remind that the Borel σ -algebra $\mathcal{B}(\partial\Omega)$ is generated by all open subsets of $\partial\Omega$).

We gave this classical definition of the harmonic measure in order to outline that the boundary $\partial\Omega$ is present in the problem through the stopping time \mathbb{T}^x . In other words, its introduction does not change the definition of the Brownian motion itself. This feature considerably simplifies the following analysis.

Up to this moment, we did not specify the domain Ω and its boundary $\partial\Omega$, since the harmonic measure can be well defined for very irregular domains [41–43]. However, the following definitions will require some restrictions on the boundary. Throughout this paper, we will consider a domain $\Omega \in \mathbb{R}^d$ ($d \geq 2$) with *bounded smooth boundary $\partial\Omega$* (twice continuous differentiable manifold). Note that this condition can be weakened in different ways, but it would require more sophisticated analysis overflowing the frames of this paper (e.g., see [59, 60]). Dealing with physical problems shown in Section 1.1, one can always *smooth* a given boundary $\partial\Omega$ whatever its original irregularity. Indeed, the physics provides a minimal cut-off ℓ (e.g., mean free path of diffusing or reacting molecules) which determines the “admissible” scales of the boundary. All geometrical features of the boundary smaller than ℓ should be irrelevant (otherwise, the proposed physical description would be invalid). Smoothing these geometrical elements, one obtains a boundary which is irregular on scales larger than ℓ and smooth on scales lower than ℓ . For a smooth boundary $\partial\Omega$, one can introduce the harmonic measure density $\omega_x(s)$ such that $\omega_x(s)ds$ is the probability that the Brownian motion hits the boundary in ds vicinity of the boundary point s .

The harmonic measure, generated by the Brownian motion, provides a general solution of the Dirichlet boundary value problem with a given function f on $\partial\Omega$:

$$\Delta u = 0 \quad (x \in \Omega), \quad u = f \quad (x \in \partial\Omega) \quad (1.5)$$

Since the harmonic measure density is equal to the normal derivative of the Green function for the Dirichlet problem (1.5), one writes the solution $u(x)$ explicitly [44]:

$$u(x) = \int_{\partial\Omega} f(s) \omega_x(s) ds$$

or as following expectation

$$u(x) = \mathbb{E}(f(W_{\mathbb{T}^x})) \quad (1.6)$$

One can give a physical interpretation of this mathematical relation. In order to calculate the expectation, one considers all possible trajectories of the Brownian motion started from the point $x \in \Omega$. For each trajectory terminated at boundary points s , one assigns the weight $f(s)$ and then averages over all these trajectories. Giving this interpretation, we do not discuss the mathematical realization of such average over all possible trajectories: to do this operation properly, one introduces the Wiener measure on the space of continuous functions and defines the corresponding functional integrals [34]. It is interesting to remark that this understanding traced to the Feynman integral’s description of quantum mechanics [45]. Note also that the relation (1.6) is the mathematical foundation for Monte-Carlo numerical tools to solve the Dirichlet problem (1.5): launching a large number of random walkers from the point x , for each trajectory one determines its hitting point s and assigns the corresponding weight $f(s)$. The

average over all random walkers gives an approximation to the value of the solution $u(x)$ at point x .

One concludes that the Brownian motion provides an efficient mathematical tool to study the Dirichlet boundary value problem. However, it becomes useless for other types of boundary conditions like, e.g., the Neumann condition. The simple physical reason is the following. As we have mentioned above, the Dirichlet boundary condition is introduced through the stopping time \mathbb{T}^x . It means that we are interested only in the Brownian motion W_t for times t between 0 and \mathbb{T}^x . Since the further motion (with $t > \mathbb{T}^x$) is completely irrelevant for this problem, one may think that the Brownian motion is *absorbed* on the boundary $\partial\Omega$ at the first hit. In other words, the Dirichlet condition corresponds to a *purely absorbing* boundary $\partial\Omega$. For the Neumann condition, the situation changes drastically. The normal derivative representing a flux leads to the notion of *reflection* on the boundary: if one would like to fix the flux density across the boundary, certain particles should be reflected. The probabilistic description of the Neumann boundary condition necessitates thus the introduction of other stochastic process called *reflected Brownian motion*.

1.2.2 Reflected Brownian motion

The fact of reflection on the boundary implies three essential distinctions with respect to the (simple) Brownian motion:

- the definition of the reflected Brownian motion will depend on the domain Ω (as a consequence, it will be more sophisticated than the definition of the Brownian motion);
- the type and direction of each reflection should be prescribed (e.g., right or oblique);
- some restrictions on the boundary $\partial\Omega$ should be introduced, e.g., the normal vector should be well defined at each point (as a consequence, the boundary cannot be very irregular).

It is not thus surprising that the definition of the reflected Brownian motion requires the study of *stochastic* differential equations. We do not pretend to reproduce the whole analysis leading to the reflected Brownian motion since one can find it in corresponding literature (e.g., see [34, 46–48]). Note that, in the case of smooth boundaries, this definition is quite classical. The situation becomes essentially more difficult when one tries to extend it for nonsmooth domains.

Definition 1.2.3 *Let Ω be a domain with boundary $\partial\Omega$, and $n(s)$ is a vector-valued function on $\partial\Omega$. For a given point $x \in \Omega$, one considers the stochastic equation in the following form:*

$$d\hat{W}_t = dW_t + n(\hat{W}_t)\mathbb{I}_{\partial\Omega}(\hat{W}_t)d\ell_t \quad \hat{W}_0 = x, \quad \ell_0 = 0 \quad (1.7)$$

where W_t is d -dimension Brownian motion and $\mathbb{I}_{\partial\Omega}$ is the indicator of the boundary $\partial\Omega$. By a solution of this equation, we mean a pair of almost surely continuous processes \hat{W}_t and ℓ_t , satisfying (1.7), adapted to the underlying family of σ -fields and satisfying, with probability 1, the following conditions:

- \hat{W}_t belongs to $\Omega \cup \partial\Omega$;
- ℓ_t is a nondecreasing process which increases only for $t \in \mathcal{T}$, $\mathcal{T} = \{t > 0 : \hat{W}_t \in \partial\Omega\}$ having Lebesgue measure zero almost surely.

The process \hat{W}_t is called *Brownian motion reflected on the boundary* or *reflected Brownian motion*, the process ℓ_t is called *local time on the boundary*.

The following theorem provides the existence and uniqueness of these stochastic processes in the case of smooth boundaries.

Theorem 1.2.4 *Let Ω be a bounded domain with twice continuous differentiable boundary $\partial\Omega$, $n(s)$ is the vector of the inward unit normal at boundary point s (orthogonal to the boundary at s and oriented towards the domain). For a given point $x \in \Omega \cup \partial\Omega$, the stochastic equation (1.7) possesses a unique solution, i.e., there exist the reflected Brownian motion \hat{W}_t and the local time on the boundary ℓ_t satisfying the above conditions, and they are unique.*

Proof can be found in [34, 46].

We should note that this theorem can be extended in different ways. For example, one can consider the Brownian motion, reflected on the boundary in the direction given by another vector-valued field than the field $n(s)$ of the inward unit normals. The assumption that the domain is bounded can be replaced by a more subtle hypothesis that allows to extend the definition of the reflected Brownian motion for some classes of unbounded domains. At last, one may define this motion for a general case of second order elliptic differential operators (with certain restrictions on their coefficients). The interested reader may consult the corresponding literature, e.g., [34, 38].

Although the rigorous mathematical definition of stochastic differential equations is more difficult than in the case of ordinary differential equations, an intuitive meaning of its elements remains qualitatively the same. For example, the stochastic equation (1.7) states that an infinitesimal variation $d\hat{W}_t$ of the reflected Brownian motion \hat{W}_t in the domain Ω is governed only by the variation dW_t of the (simple) Brownian motion W_t (the second term vanishes due to the indicator $\mathbb{I}_{\partial\Omega}$). When the motion hits the boundary, the second term does not allow to leave the domain leading to a variation directed along the inward unit normal $n(s)$ towards the interior of the domain. On the other hand, each hit of the boundary increases the local time ℓ_t . Consequently, the single stochastic equation (1.7) defines simultaneously two random processes, \hat{W}_t and ℓ_t , strongly dependent each of other.

As an example, one can consider the one-dimensional Brownian motion reflected at zero which can be written as mirror reflection of the (simple) Brownian motion: $\hat{W}_t = |x + W_t|$. Applying Itô's formula to this function, one obtains:

$$\hat{W}_t = |x + W_t| = x + \int_0^t \text{sign}(x + W_{t'}) dW_{t'} + \frac{1}{2} \int_0^t \delta(x + W_{t'}) dt'$$

One can show that the second term corresponds to a Brownian motion W'_t , whereas the third term, denoted as ℓ_t , is a continuous, nondecreasing random process which increases only on the set $\mathcal{T} = \{t > 0 : x + W_t = 0\}$ of the Lebesgue measure zero. The previous expression can be thus written as $\hat{W}_t = x + W'_t + \ell_t$ or, in differential form, as $d\hat{W}_t = dW'_t + d\ell_t$ which is the particular case of the stochastic equation (1.7). For the local time ℓ_t , Lévy proved the following representation [36, 37]:

$$\ell_t = \lim_{a \rightarrow 0} \frac{1}{2a} \int_0^t \mathbb{I}_{[0,a]}(\hat{W}_{t'}) dt' \quad (1.8)$$

This relation makes explicit the meaning of the local time ℓ_t : it shows how “many times” the reflected Brownian motion passed in an infinitesimal vicinity of zero up to the moment t . We give also the other useful representation for the local time (proposed also by Lévy):

$$\ell_t = \lim_{a \rightarrow 0} a \mathcal{N}_t(a) \quad (1.9)$$

where $\mathcal{N}_t(a)$ is the number of passages of the reflected Brownian motion through the interval $[0, a]$ up to the moment t . If one introduces a sequence of stopping times at points 0 and a ,

$$\begin{aligned} \tau_0^{(0)} &= \inf\{t > 0 : \hat{W}_t = 0\} & \tau_0^{(a)} &= \inf\{t > \tau_0^{(a)} : \hat{W}_t = a\} \\ \tau_n^{(0)} &= \inf\{t > \tau_{n-1}^{(a)} : \hat{W}_t = 0\} & \tau_n^{(a)} &= \inf\{t > \tau_{n-1}^{(0)} : \hat{W}_t = a\} \end{aligned}$$

the number of passages can be defined as

$$\mathcal{N}_t(a) = \sup\{n > 0 : \tau_n^{(0)} < t\}$$

Note that these representations can be extended for a general case of d -dimensional reflected Brownian motion.

1.3 Partially reflected Brownian motion

1.3.1 Definition and certain properties

Bearing in mind the description of the Laplacian transport phenomena, we would like to extend the reflected Brownian motion in order to be able to deal with the mixed boundary condition (1.3).

Definition 1.3.1 *For a given domain $\Omega \subset \mathbb{R}^d$ with smooth bounded boundary $\partial\Omega$, let \hat{W}_t be the reflected Brownian motion started from $x \in \Omega$ and ℓ_t be the related local time process. Let χ be the random variable, independent of \hat{W}_t and ℓ_t and distributed according to the exponential law with a positive parameter Λ :*

$$\mathbb{P}\{\chi \geq \lambda\} = \exp[-\lambda/\Lambda] \quad (\lambda \geq 0) \quad (1.10)$$

The stopping time

$$\mathbb{T}_\Lambda^x = \inf\{t > 0 : \ell_t \geq \chi\}$$

shows the first moment when the local time process ℓ_t exceeds the random variable χ . The process \hat{W}_t conditioned to stop at random moment $t = \mathbb{T}_\Lambda^x$ is called partially reflected Brownian motion (PRBM).

First of all, we stress that the partially reflected Brownian motion is not a *new* stochastic process: it reproduces completely the reflected Brownian motion \hat{W}_t up to the moment \mathbb{T}_Λ^x . The only difference between them resides in the fact that we are not interested in what happens after this moment. Consequently, the condition to stop at $t = \mathbb{T}_\Lambda^x$ may be thought as an absorption by the boundary $\partial\Omega$. It explains the term “partially reflected”: after multiple reflections, the process will be absorbed on the boundary (see Section 1.4 for further comments). Roughly speaking, the whole term “partially reflected Brownian motion” is a shorter version of the phrase “reflected Brownian motion conditioned to stop at random moment \mathbb{T}_Λ^x ”.

In the particular case $\Lambda = 0$, the exponential distribution (1.10) degenerates to $\mathbb{P}\{\chi = 0\} = 1$ and $\mathbb{P}\{\chi > 0\} = 0$. Consequently, the stopping time becomes: $\mathbb{T}_0^x = \inf\{t > 0 : \ell_t > 0\}$. Since the first moment of an increase of the local time process ℓ_t corresponds to the first hit of the boundary $\partial\Omega$, one obtains the stopping time of the (simple) Brownian motion: $\mathbb{T}_0^x = \mathbb{T}^x$. One concludes that, for $\Lambda = 0$, the partially reflected Brownian motion becomes the Brownian motion conditioned to stop at the first hit of the boundary.

The partially reflected Brownian motion allows to introduce a measure to quantify the absorption on different subsets of the boundary $\partial\Omega$.

Definition 1.3.2 *For any subset A from the Borel σ -algebra $\mathcal{B}(\partial\Omega)$, one defines its spread harmonic measure $\omega_{x,\Lambda}\{A\}$ as:*

$$\omega_{x,\Lambda}\{A\} = \mathbb{P}\{\hat{W}_{\mathbb{T}_\Lambda^x} \in A, \mathbb{T}_\Lambda^x < \infty\}$$

As for the harmonic measure, $\omega_{x,\Lambda}\{A\}$ satisfies the properties of a probabilistic measure, in particular, $\omega_{x,\Lambda}\{\partial\Omega\} = 1$. When Λ goes to 0, the spread harmonic measure tends to the harmonic measure: $\omega_{x,\Lambda}\{A\} \rightarrow \omega_x\{A\}$.

Since the definition of the PRBM requires the smoothness of the boundary, one can introduce the spread harmonic measure density $\omega_{x,\Lambda}(s)$.

Dealing with the Brownian motion, one could formally take the starting point x on the boundary $\partial\Omega$, but it would lead to trivial results: the stopping time \mathbb{T}^x becomes 0 and the harmonic measure ω_x is degenerated to the Dirac point measure: $\omega_x\{A\} = \mathbb{I}_A(x)$ (if $x \in \partial\Omega$). In the case of the partially reflected Brownian motion, the starting point x can belong to the domain Ω or to its boundary $\partial\Omega$: in both cases the spread harmonic measure has nontrivial properties.

It is convenient to separate each random trajectory of the PRBM in two parts, before and after the first hit of the boundary. The first part, $\hat{W}_{0 \leq t \leq \mathbb{T}^x}$, coincides with the (simple) Brownian motion started from x and conditioned to stop on the boundary, while the second part, $\hat{W}_{\mathbb{T}^x \leq t \leq \mathbb{T}_\Lambda^x}$, coincides with the reflected Brownian motion started on the boundary (at the first hitting point) and conditioned to stop on the same boundary at random moment \mathbb{T}_Λ^x . Since these two parts are independent, one can write the spread harmonic measure density as

$$\omega_{x,\Lambda}(s) = \int_{\partial\Omega} ds' \omega_x(s') T_\Lambda(s', s) \quad T_\Lambda(s', s) \equiv \omega_{s',\Lambda}(s) \quad (1.11)$$

The integral kernel $T_\Lambda(s, s')$ represents the probability density that the PRBM started from the boundary point s' is stopped (absorbed) in an infinitesimal vicinity of the boundary point s . Consequently, it is sufficient to determine the probabilities of displacements between two boundary points in order to reconstruct the whole spread harmonic measure density.

Lemma 1.3.3 *For any subset A from $\mathcal{B}(\partial\Omega)$ and fixed positive Λ , the spread harmonic measure $\omega_{x,\Lambda}\{A\}$, considered as function of x , solves the mixed boundary value problem:*

$$\Delta\omega_{x,\Lambda}\{A\} = 0 \quad (x \in \Omega), \quad \left[I - \Lambda \frac{\partial}{\partial n} \right] \omega_{x,\Lambda}\{A\} = \mathbb{I}_A(x) \quad (x \in \partial\Omega) \quad (1.12)$$

This lemma generalizes the Kakutani theorem for the harmonic measure (when $\Lambda = 0$) [49]. We do not reproduce the proof of this lemma since it would require many technical details. It can be also written for the spread harmonic measure density:

Lemma 1.3.4 *For any boundary point $s \in \partial\Omega$ and fixed positive Λ , the spread harmonic measure density $\omega_{x,\Lambda}(s)$, considered as function of x , satisfies the following conditions:*

$$\Delta\omega_{x,\Lambda}(s) = 0 \quad (x \in \Omega), \quad \left[I - \Lambda \frac{\partial}{\partial n} \right] \omega_{x,\Lambda}(s) = \delta(s - x) \quad (x \in \partial\Omega) \quad (1.13)$$

where $\delta(s - x)$ is the Dirac function (distribution) on the boundary.

According to this lemma, one can write the solution of a general mixed boundary value problem with a given function f on $\partial\Omega$ and fixed positive Λ ,

$$\Delta u = 0 \quad (x \in \Omega), \quad \left[I - \Lambda \frac{\partial}{\partial n} \right] u = f \quad (x \in \partial\Omega)$$

in two equivalent forms:

$$u(x) = \int_{\partial\Omega} f(s) \omega_{x,\Lambda}(s) ds = \mathbb{E}(f(\hat{W}_{\mathbb{T}_\Lambda^x}))$$

Again, one can give a physical interpretation of this relation: one averages the function f over all possible trajectories of the partially reflected Brownian motion started from the point x . Each trajectory is weighted by $f(s)$ according to the boundary point s of its final absorption.

1.3.2 Planar surface

We remind that the physical motivation of this study is a possibility to consider the partially reflected Brownian motion as the random trajectory of diffusing particles towards semi-permeable interfaces. Indeed, the boundary value problem (1.1–1.3) is an averaged description for the particle's concentration, while the stochastic description permits to “follow” the trajectory of each particle providing new information: typical or average distance between the first hitting point and the final absorption point; proportion of “flatten” trajectories, going near the interface, with respect to remote trajectories, moving away from the interface and then returning to it, etc. In this subsection, we briefly consider the particular case of the planar surface (boundary of a half space), when the partially reflected Brownian motion can be constructed in a simple way, without stochastic equations. Consequently, many related characteristics can be obtained explicitly. In addition, this construction for the half space provides an example of the PRBM for an unbounded domain.

Let Ω be the upper half space, $\Omega = \{x \in \mathbb{R}^d : x_d > 0\}$, with smooth boundary $\partial\Omega = \{x \in \mathbb{R}^d : x_d = 0\}$. Let W_t^k are d independent Brownian motions started from the origin. Then, the Brownian motion, started from a given point $x \in \Omega$ and reflected on the boundary $\partial\Omega$, can be written in a simple way as $(x_1 + W_t^1, \dots, x_{d-1} + W_t^{d-1}, |x_d + W_t^d|)$. The particular simplification is brought by the fact that reflections happen in a single direction, being involved through the one-dimensional reflected Brownian motion $|x_d + W_t^d|$. Without loss of generality, we can consider the reflected Brownian motion started from the origin ($x = 0$). The translational invariance along the hyperplane $\partial\Omega$ permits to move the starting point in $\partial\Omega$, whereas the convolution property (1.11) allows displacements in orthogonal direction. The local time process ℓ_t can be introduced either through the stochastic equations (1.7), or with the help of Lévy's formulae (1.8) or (1.9).

Lemma 1.3.5 *Let Ω be the upper half space, $\Omega = \{x \in \mathbb{R}^d : x_d > 0\}$. For any positive Λ , the stopping time \mathbb{T}_Λ^0 , defined in 1.3.1, is distributed according to*

$$\mathbb{P}\{\mathbb{T}_\Lambda^0 \in (t, t + dt)\} = \rho_\Lambda(t)dt, \quad \rho_\Lambda(t) = \int_0^\infty \frac{z e^{-z^2/2t} e^{-z/\Lambda}}{\Lambda\sqrt{2\pi} t^{3/2}} dz \quad (1.14)$$

Proof. Since the local time ℓ_t and the random variable χ are independent, one can write the probability $\mathbb{P}\{\mathbb{T}_\Lambda^0 \in (t, t + dt)\}$ as

$$\mathbb{P}\{\mathbb{T}_\Lambda^0 \in (t, t + dt)\} = \int_0^\infty \mathbb{P}\left\{ \inf\{\tau > 0 : \ell_\tau = z\} \in (t, t + dt) \right\} \mathbb{P}\{\chi \in (z, z + dz)\}$$

Then, the first factor is the well known density of the inverse local time process [35],

$$\mathbb{P}\left\{ \inf\{\tau > 0 : \ell_\tau = z\} \in (t, t + dt) \right\} = dt \frac{z e^{-z^2/2t}}{\sqrt{2\pi} t^{3/2}}$$

whereas the second factor is given by the exponential law density (1.10) that implies (1.14). \square

Note that the integral in (1.14) can be represented with the help of the Gaussian error function

$$\rho_\Lambda(t) = \frac{1}{2\Lambda^2} \left[\frac{1}{\sqrt{\pi}} \frac{1}{\sqrt{t/2\Lambda^2}} - \mathcal{K}\left(\sqrt{t/2\Lambda^2}\right) \right], \quad \mathcal{K}(z) = \frac{2}{\sqrt{\pi}} \int_z^\infty e^{z^2-x^2} dx$$

One finds the asymptotic behavior of the density $\rho_\Lambda(t)$:

$$\rho_\Lambda(t) \sim (\sqrt{2\pi}\Lambda)^{-1} t^{-1/2} \quad (t \rightarrow 0), \quad \rho_\Lambda(t) \sim (\sqrt{2\pi}/\Lambda)^{-1} t^{-3/2} \quad (t \rightarrow \infty)$$

Once the distribution of stopping time \mathbb{T}_Λ^0 is determined, one can calculate the spread harmonic measure density $\omega_{x,\Lambda}(s)$.

Lemma 1.3.6 *Let Ω be the upper half space, $\Omega = \{x \in \mathbb{R}^d : x_d > 0\}$. For any positive Λ , the spread harmonic measure density $\omega_{x,\Lambda}(s)$ is*

$$\omega_{x,\Lambda}(s_1, \dots, s_{d-1}) = \int_{-\infty}^{\infty} \dots \int_{-\infty}^{\infty} \frac{dk_1 \dots dk_{d-1}}{(2\pi)^{d-1}} \exp\left[-i \sum_{j=1}^{d-1} k_j (x_j - s_j)\right] \frac{e^{-x_d |k|}}{1 + \Lambda |k|} \quad (1.15)$$

where $|k| = \sqrt{k_1^2 + \dots + k_{d-1}^2}$.

Proof. First, the probability kernel $T_\Lambda(s, s')$, defined for two boundary points $s, s' \in \partial\Omega$, is translationally invariant in the hyperplane $\partial\Omega$, $T_\Lambda(s, s') = t_\Lambda(s - s')$, where

$$t_\Lambda(s_1, \dots, s_{d-1}) ds_1 \dots ds_{d-1} \equiv \mathbb{P} \left\{ W_{\mathbb{T}_\Lambda^0}^1 \in (s_1, s_1 + ds_1), \dots, W_{\mathbb{T}_\Lambda^0}^{d-1} \in (s_{d-1}, s_{d-1} + ds_{d-1}) \right\}$$

The stopping time \mathbb{T}_Λ^0 is related to the orthogonal motion and, consequently, independent of lateral motions W_t^1, \dots, W_t^{d-1} . Therefore, the previous probability can be written as

$$t_\Lambda(s_1, \dots, s_{d-1}) ds_1 \dots ds_{d-1} = \int_0^\infty \mathbb{P} \left\{ W_t^1 \in (s_1, s_1 + ds_1), \dots, W_t^{d-1} \in (s_{d-1}, s_{d-1} + ds_{d-1}) \right\} \rho_\Lambda(t) dt$$

Since the lateral motions are independent between themselves, the first factor is equal to the product of Gaussian densities (1.4):

$$t_\Lambda(s_1, \dots, s_{d-1}) = \int_0^\infty dt \rho_\Lambda(t) \prod_{j=1}^{d-1} \frac{e^{-s_j^2/2t}}{\sqrt{2\pi t}}$$

Using the integral representation (1.14), one finds

$$t_\Lambda(s_1, \dots, s_{d-1}) = \frac{\Gamma(d/2)}{\pi^{d/2} \Lambda} \int_0^\infty dz \frac{z e^{-z/\Lambda}}{[s_1^2 + \dots + s_{d-1}^2 + z^2]^{d/2}}$$

where $\Gamma(z)$ stands for Euler gamma function (see [33] for details).

Substituting the well known harmonic measure density $\omega_x(s)$ for the upper half space (generalized Cauchy distribution),

$$\omega_x(s_1, \dots, s_{d-1}) = \frac{\Gamma(d/2)}{\pi^{d/2}} \frac{x_d}{[(x_1 - s_1)^2 + \dots + (x_{d-1} - s_{d-1})^2 + (x_d)^2]^{d/2}}$$

into convolution (1.11), one finally obtains the expression (1.15) for the spread harmonic measure density. \square

One can easily verify that the spread harmonic measure density $\omega_{x,\Lambda}(s)$ and the probability kernel $T_\Lambda(s, s')$ satisfy the following conditions:

1. Normalization condition:

$$\int_{\partial\Omega} ds \omega_{x,\Lambda}(s) = 1 \qquad \int_{\partial\Omega} ds' T_\Lambda(s, s') = 1$$

2. Dirichlet limit ($\Lambda \rightarrow 0$):

$$\omega_{x,\Lambda}(s) \longrightarrow \omega_x(s) \qquad T_\Lambda(s, s') \longrightarrow \delta(s - s')$$

3. Translational invariance:

$$\omega_{x,\Lambda}(s) = \omega_{x-s,\Lambda}(0) \qquad T_\Lambda(s, s') = T_\Lambda(s - s', 0) \equiv t_\Lambda(s - s')$$

One can also deduce the asymptotic behavior of the function $t_\Lambda(s)$ as $|s| \rightarrow 0$ or $|s| \rightarrow \infty$. For these purposes, it is convenient to define the new function $\eta_d(z)$ by relation

$$t_\Lambda(s) = \eta_d(|s|/\Lambda) \omega_{(0,\dots,0,\Lambda)}(s)$$

where the second term is the harmonic measure density for the Brownian motion started from the point $\underbrace{(0, \dots, 0, \Lambda)}_{d-1}$. Using the explicit formulae for $t_\Lambda(s)$ and $\omega_{(0,\dots,0,\Lambda)}(s)$, one obtains:

$$\eta_d(z) = (1 + z^2)^{d/2} \int_0^\infty \frac{t e^{-t} dt}{(t^2 + z^2)^{d/2}} \quad (1.16)$$

Its asymptotic behavior for z going to infinity is

$$\eta_d(z) = 1 - \frac{5d}{2} z^{-2} + O(z^{-4}) \quad (1.17)$$

whereas for z going to 0, one has

$$\eta_d(z) \sim \frac{\Gamma(d/2)}{\pi^{d/2}} z^{2-d} \quad (d > 2), \qquad \eta_d(z) \sim \frac{1}{\pi} \ln z \quad (d = 2)$$

These relations can be used for qualitative study of the partially reflected Brownian motion. For instance, one identifies the parameter Λ as a characteristic length scale of the problem: the magnitude of any distance (e.g., $|s|$) has to be compared with Λ . Interestingly, the asymptotic behavior (1.17) for large z means that the function $t_\Lambda(s)$ is close to the harmonic measure density $\omega_{(0,\dots,0,\Lambda)}(s)$. Roughly speaking, for large $|s|/\Lambda$, the partially reflected Brownian motion started from the origin is qualitatively equivalent to the (simple) Brownian motion started from the point $(0, \dots, 0, \Lambda)$. In other words, the partial reflections on the boundary leads to a *spreading* of the harmonic measure with characteristic scale Λ (see also relation (1.11)).

The knowledge of the probability kernel $T_\Lambda(s, s')$ provides an important information about the partially reflected Brownian motion in the (upper) half space. As an example, we calculate the probability $\mathcal{P}_\Lambda(r)$ that the PRBM started from the origin is finally absorbed on the disk $B_r^{d-1} = \{ (x_1, \dots, x_d) \in \mathbb{R}^d : x_1^2 + \dots + x_{d-1}^2 \leq r^2, x_d = 0 \}$ of radius r centered at the origin:

$$\mathcal{P}_\Lambda(r) = \int_{B_r^{d-1}} ds t_\Lambda(s) = \frac{2 \Gamma(\frac{d}{2})}{\Gamma(\frac{d-1}{2}) \sqrt{\pi}} \int_0^\infty t e^{-t} dt \int_0^{r/\Lambda} \frac{x^{d-2} dx}{[x^2 + t^2]^{d/2}} \quad (1.18)$$

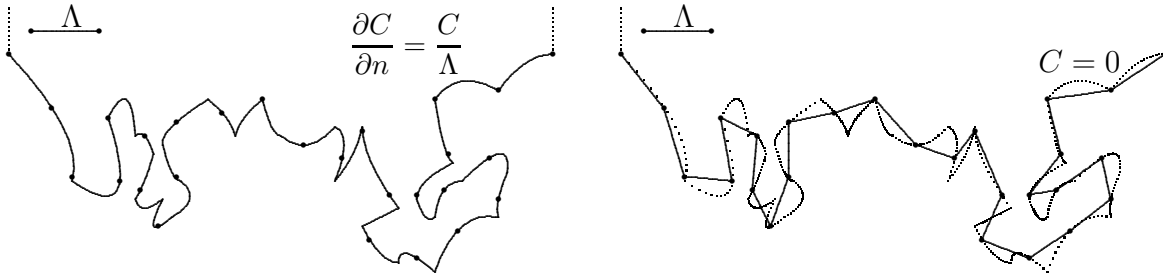


Figure 1.3: Land Surveyor Approximation: the total flux across the boundary can be approximately calculated when the mixed boundary condition $\partial C/\partial n = C/\Lambda$ on a given irregular curve (on the left) is replaced by the Dirichlet condition $C = 0$ on the coarse-grained boundary (on the right). The last one is obtained by replacing curvilinear intervals of length Λ by corresponding linear chords.

This probability shows how far the partially reflected Brownian motion can go away after the first hit of the boundary. One sees that this function depends only on the ratio r/Λ , going to 0 for small radii and to 1 for large radii. Again, the parameter Λ is the characteristic length scale of the problem. In two-dimensional case, $\mathcal{P}_\Lambda(\Lambda/2)$ is the probability that the PRBM is absorbed on the linear segment of length Λ , centered at the origin (the first hitting point). The numerical calculation gives $\mathcal{P}_\Lambda(\Lambda/2) \simeq 0.4521$, i.e., about half of the particles is absorbed on this region. In other words, the length of the characteristic absorption region (where half of the particles is absorbed) is equal approximately to Λ . It has been shown recently that this result is qualitatively valid for certain irregular boundaries [50]. Roughly speaking, if the one-dimensional boundary (curve) has no deep pores (fjords) and its perimeter is large with respect to the scale Λ , then the curvilinear interval of length Λ , centered on the first hitting point, absorbs approximately half of the diffusing particles.

This result can be considered as a first mathematical justification of the *Land Surveyor Approximation* (LSA) developed by Sapoval [18]. According to this approximation, one can coarse-grain a given one-dimensional interface (curve) with physical scale Λ in order to replace the mixed boundary condition $[I - \Lambda\partial/\partial n]C = 0$ by the Dirichlet condition $C = 0$ (see Fig. 1.3). Some heuristic physical arguments allow to state that the total flux across the irregular semi-permeable interface is equal approximately to the total flux across this coarse-grained boundary with Dirichlet condition. This statement provides a simple but powerful tool to study the Laplacian transport phenomena. The land surveyor approximation had been checked numerically [29, 30], but not mathematically. The study of the partially reflected Brownian motion provides its justification and further understanding. Actually, the coarse-grain procedure generates the regions of length Λ , where about half of the particles is absorbed. The LSA is based on two simplifications which can be clearly explained in terms of diffusing particles:

1. All particles arrived to the characteristic absorption region are absorbed (Dirichlet condition). This approximation does not take into account half of the particles which escapes this region.
2. The deterministic regions, generated by the coarse-grain procedure, cannot be centered on a random position of the first hit of the boundary.

Although these simplifications seem to be rough, the numerical simulations showed that the LSA reproduces the transport properties with relatively good accuracy. However, this approximation has no small parameter which would allow to control its applicability. More accurate approaches will be discussed below (see Section 1.4).

One can go further by extending the land surveyor approximation to the three-dimensional case, which remains still not well studied. Indeed, the numerical calculation leads to $\mathcal{P}_\Lambda(\Lambda) \simeq 0.4611$, i.e., about half of the particles is absorbed on the disk of radius Λ centered on the first hitting point. Consequently, if one finds a convenient cover of a semi-permeable irregular interface by disk-like sets of characteristic radius Λ , the LSA may be still valid, i.e., the total flux across a given interface can be approximated by the total flux across the perfectly absorbing coarse-grained interface (with Dirichlet condition). An accurate mathematical formulation of this extension and its numerical verification present still open problems.

1.3.3 Relation to the Dirichlet-to-Neumann operator

The construction of the partially reflected Brownian motion for a given domain Ω requires the resolution of the stochastic differential equation (1.7), a quite difficult problem. Fortunately, many characteristics of this process, e.g. the spread harmonic measure density $\omega_{x,\Lambda}(s)$, can be obtained in another way. This subsection is devoted to the Dirichlet-to-Neumann operator and its relation to the partially reflected Brownian motion.

Definition 1.3.7 *For a given domain $\Omega \subset \mathbb{R}^d$ ($d \geq 2$) with smooth bounded boundary $\partial\Omega$, let $u : \Omega \cup \partial\Omega \rightarrow \mathbb{R}$ be a harmonic function with Dirichlet condition $u = f$, a function f being from the Sobolev space $H^1(\partial\Omega)$ (in other words, u is the the solution of the boundary value problem (1.5)). Applying the normal derivative to u , one obtains a new function $g = \partial u / \partial n$ belonging to the square integrable functions space $L^2(\partial\Omega)$. Then the operator \mathcal{M} , acting from $H^1(\partial\Omega)$ to $L^2(\partial\Omega)$, which associates the new function g with a given function f , is called Dirichlet-to-Neumann operator.*

It is known that the Dirichlet-to-Neumann operator \mathcal{M} is self-adjoint pseudodifferential operator of the first order, with discrete positive spectrum $\{\mu_\alpha\}$ and smooth eigenfunctions forming a complete basis in $L^2(\partial\Omega)$ [51–60]. For this operator, one can define its resolvent operator $T_\Lambda = [I + \Lambda\mathcal{M}]^{-1}$, called *spreading operator*. This is an analytic operator function in the whole complex plane except a denumerable set of points, $\mathbb{C} \setminus \{-\mu_\alpha^{-1}\}$. In particular, T_Λ is well defined for any positive Λ .

Lemma 1.3.8 *For any strictly positive Λ , the spreading operator T_Λ acts from $L^2(\partial\Omega)$ to $L^2(\partial\Omega)$ as a compact integral operator,*

$$[T_\Lambda f](s) = \int_{\partial\Omega} ds' f(s') T_\Lambda(s', s)$$

where the kernel $T_\Lambda(s, s')$ is given by (1.11).

Proof. The probability kernel $T_\Lambda(s, s')$ is a positive function satisfying the normalization:

$$\int_{\partial\Omega} T_\Lambda(s, s') ds' = 1$$

since the partially reflected Brownian motion is conditioned to be finally absorbed on the boundary. Therefore, one obtains:

$$\int_{\partial\Omega} \int_{\partial\Omega} ds ds' |T_\Lambda(s, s')|^2 = S_{tot} < \infty$$

where S_{tot} is the total surface area of the boundary $\partial\Omega$. The integral operator T_Λ defined by the kernel $T_\Lambda(s, s')$ is a Hilbert-Schmidt operator and, consequently, a compact operator.

The boundary condition in lemma 1.3.4 can be written with the help of the Dirichlet-to-Neumann operator:

$$[I + \Lambda \mathcal{M}]T_\Lambda(s, s') = \delta(s - s')$$

that implies that the integral operator T_Λ coincides with the resolvent $[I + \Lambda \mathcal{M}]^{-1}$ of the Dirichlet-to-Neumann operator \mathcal{M} . \square

This simple lemma creates a “bridge” between the partially reflected Brownian motion and the Dirichlet-to-Neumann operator. In particular, the relation (1.11) for the spread harmonic measure density $\omega_{x,\Lambda}(s)$ can be now understood as application of the spreading operator T_Λ to the harmonic measure density $\omega_x(s)$. Consequently, once the Dirichlet-to-Neumann operator is constructed for a given domain, one can calculate the density $\omega_{x,\Lambda}(s)$ without solving the stochastic differential equations (1.7).

The self-adjointness of the Dirichlet-to-Neumann operator allows to involve efficient tools of the spectral theory. For example, one can rewrite the relation (1.11) as spectral decomposition of the harmonic measure density on eigenfunctions \mathbf{V}_α of the operator \mathcal{M} :

$$\omega_{x,\Lambda}(s) = \sum_\alpha \frac{(\omega_x \cdot \mathbf{V}_\alpha^*)_{L^2}}{1 + \Lambda \mu_\alpha} V_\alpha(s) \quad (\omega_x \cdot \mathbf{V}_\alpha^*)_{L^2} = \int_{\partial\Omega} \omega_x(s') \mathbf{V}_\alpha^*(s') ds' \quad (1.19)$$

where $(\cdot)_{L^2}$ denotes the scalar product in $L^2(\partial\Omega)$ space. The advantage of this relation is an explicit dependence on the physical parameter Λ .

1.3.4 Examples

In order to illustrate the underlying concepts, we consider several examples.

Two-dimensional disk

We are going to study the partially reflecting Brownian motion in a unit disk, $\Omega = \{x \in \mathbb{R}^2 : |x| < 1\}$ (its boundary is a unit circle, $\partial\Omega = \{x \in \mathbb{R}^2 : |x| = 1\}$).

In this case, the harmonic measure density $\omega_x(s) \equiv \omega(r, \theta)$ is a function of two real variables: the distance $0 \leq r < 1$ between the starting point $x \in \Omega$ and the origin, and the angle $0 \leq \theta < 2\pi$ between directions onto points x and $s \in \partial\Omega$ from the origin. The harmonic measure density is known as Poisson kernel:

$$\omega(r, \theta) = \frac{1 - r^2}{2\pi(1 - 2r \cos \theta + r^2)} \quad (1.20)$$

The rotational invariance of the domain Ω implies that the eigenbasis of the Dirichlet-to-Neumann operator \mathcal{M} is the Fourier basis,

$$\mathbf{V}_\alpha(\theta) = \frac{e^{i\alpha\theta}}{\sqrt{2\pi}} \quad (\alpha \in \mathbb{Z})$$

Taking a Fourier harmonics as boundary condition, $u(r = 1, \theta) = e^{i\alpha\theta}$, one finds the regular solution of the corresponding Dirichlet problem, $u(r, \theta) = r^{|\alpha|} e^{i\alpha\theta}$. Since the normal derivative coincides with the radius derivative, one obtains the eigenvalues of the Dirichlet-to-Neumann operator:

$$\mu_\alpha = |\alpha| \quad (\alpha \in \mathbb{Z})$$

These eigenvalues are doubly degenerated (except $\mu_0 = 0$).

The spread harmonic measure density is given by relation (1.19):

$$\omega_{x,\Lambda}(s) \equiv \omega_\Lambda(r, \theta) = \frac{1}{2\pi} \sum_{\alpha=-\infty}^{\infty} \frac{r^{|\alpha|} e^{i\alpha\theta}}{1 + \Lambda|\alpha|}$$

(the scalar product of the harmonic measure density $\omega_x(s)$ and eigenfunctions $\mathbf{V}_\alpha(\theta)$ is shown to be equal to $r^{|\alpha|}$, with $r = |x|$). In the case $\Lambda = 0$, one finds the Poisson representation for the harmonic measure density (1.20) just as required. The kernel of the resolvent operator T_Λ is

$$T_\Lambda(\theta, \theta') = \frac{1}{2\pi} \sum_{\alpha=-\infty}^{\infty} \frac{e^{i\alpha(\theta-\theta')}}{1 + \Lambda|\alpha|}$$

For the exterior problem, when $\Omega = \{x \in \mathbb{R}^2 : |x| > 1\}$, one obtains exactly the same results.

Three-dimensional ball

The similar arguments can be applied for higher dimensions. For example, in the three-dimensional case, one considers the unit ball $\Omega = \{x \in \mathbb{R}^3 : |x| < 1\}$. The harmonic measure density is known to be

$$\omega_x(s) \equiv \omega(r, \theta) \equiv \frac{1 - r^2}{4\pi(1 - 2r \cos \theta + r^2)^{3/2}} \quad (s \in \partial\Omega)$$

where $r = |x| < 1$ is the distance between the starting point $x \in \Omega$ and the origin, and θ is the angle between directions onto points x and $s \in \partial\Omega$ from the origin. The development of this function on spherical harmonics is

$$\omega_x(s) = \sum_{l=0}^{\infty} \sum_{m=-l}^l r^l Y_{l,m}(s) Y_{l,m}(x/r)$$

The rotational symmetry of the problem implies that the eigenbasis of the Dirichlet-to-Neumann operator is formed by spherical harmonics $Y_{l,m}$. A regular solution of the Dirichlet problem (1.5) in the unit ball can be written in spherical coordinates r , θ and φ as

$$u(r, \theta, \varphi) = \sum_{l=0}^{\infty} \sum_{m=-l}^l f_{l,m} r^l Y_{l,m}(\theta, \varphi)$$

where $f_{l,m}$ are coefficients of the development of a given function f (Dirichlet condition) on the complete basis of spherical harmonics. Since the normal derivative coincides with the radius derivative, one obtains

$$[\mathcal{M}f](\theta, \varphi) = \left(\frac{\partial u}{\partial n} \right)_{\partial\Omega} = \left(\frac{\partial u}{\partial r} \right)_{r=1} = \sum_{l=0}^{\infty} \sum_{m=-l}^l f_{l,m} l Y_{l,m}(\theta, \varphi)$$

i.e., the eigenvalues of the Dirichlet-to-Neumann operator \mathcal{M} are

$$\mu_l = l \quad (l \in \{0, 1, 2, \dots\}) \quad (1.21)$$

Note that the l -th eigenvalue is degenerated $n_l = (2l + 1)$ times.

Interestingly², the Dirichlet-to-Neumann operator \mathcal{M} for the unit ball $\Omega = \{x \in \mathbb{R}^3 : |x| < 1\}$ coincides with an operator introduced by Dirac in quantum mechanics [61]. It is known that

²The author thanks S. Schachine for valuable discussions on this relation.

the hydrogen atom is described by three quantum numbers: the main quantum number n , the orbital quantum number l and magnetic quantum number m . Two last numbers are associated with indices of spherical harmonics. Thus, the Dirichlet-to-Neumann operator for the ball is apparently the orbital quantum number operator for the hydrogen atom. In particular, the degeneracy of eigenvalues of this operator can be understood from the point of view of spin degeneracy.

The spread harmonic measure density $\omega_{x,\Lambda}(s)$ and the spreading operator kernel $T_\Lambda(s, s')$ can be written explicitly as spectral decompositions on the eigenbasis of the Dirichlet-to-Neumann operator \mathcal{M} as in the two-dimensional case.

The eigenvalues of the Dirichlet-to-Neumann operator for d -dimensional unit ball are still given by (1.21) with degeneracy

$$n_l = \frac{(2l + d - 2)}{(d - 2)} \frac{(l + d - 3)!}{(d - 3)! l!}$$

The exterior problem for $\Omega = \{x \in \mathbb{R}^3 : |x| > 1\}$ can be considered in the same manner. The harmonic measure density is given as $\tilde{\omega}_x(s) = (1/r) \omega(1/r, \theta)$, with $r = |x| > 1$. Using the same development on spherical harmonics, one obtains $\mu_l = l + 1$ with $l \in \{0, 1, 2, \dots\}$. In particular, the lowest eigenvalue $\mu_0 = 1$ is strictly positive. This difference with respect to the spectrum μ_l for the interior problem has a simple probabilistic origin: the Brownian motion in three dimensions is transient, i.e., there is a positive probability (equal to $1 - 1/r$) to never return to the ball. Another explication follows from the theory of boundary value problems for elliptic differential operators: the exterior Neumann problem has a unique solution, while the solution of the interior Neumann problem is defined up to a constant. Consequently, the Dirichlet-to-Neumann \mathcal{M} operator should be invertible for the exterior problem that implies a simple condition for its eigenvalues: $\mu_\alpha \neq 0$. On the contrary, \mathcal{M} is not invertible for the interior problem providing the condition that at least one eigenvalue is zero.

1.4 Stochastic approaches to Laplacian transport phenomena

In this section, we return to the Laplacian transport phenomena, discussed at the beginning. First, we are going to introduce the notion of source, diffusing particles started from. The definition of the partially reflected Brownian motion will require only a minor modification. After that, the recently developed continuous approach will be presented with a special emphasis on its physical importance. Finally, we will mention two other physical descriptions which can be now considered as useful approximations to the continuous approach.

1.4.1 Notion of source

The description of the partially reflected Brownian motion given in the previous section does not involve a source, an important element for the Laplacian transport phenomena. In this subsection, we are going to discuss the extension of previous definitions in order to introduce the source. As one will see, a minor modification will be sufficient.

Throughout this subsection, we consider a bounded domain Ω with twice continuous differentiable boundary composed of two disjoint parts, $\partial\Omega$ and $\partial\Omega_0$, referred as *working interface* and *source* respectively³. In practice, the working interface and the source are well separated in space, therefore one may think about a circular ring as generic domain.

³Previously, the whole boundary of the domain had been considered as the working interface. For this reason, we preserve the same notation $\partial\Omega$ for this object and hope that it will not lead to ambiguities.

As previously, one considers the reflected Brownian motion \hat{W}_t , started from any point $x \in \Omega \cup \partial\Omega \cup \partial\Omega_0$ and reflected on the whole boundary $\partial\Omega \cup \partial\Omega_0$, the corresponding local time process ℓ_t , and the stopping time \mathbb{T}_Λ^x defined in 1.3.1. Let us introduce a new stopping time τ as the first moment when the process \hat{W}_t hits the source $\partial\Omega_0$:

$$\tau = \inf\{t > 0 : \hat{W}_t \in \partial\Omega_0\}$$

Then, the spread harmonic measure can be defined for any subset A from Borel σ -algebra $\mathcal{B}(\partial\Omega)$ (defined on the working interface!) as

$$\omega_{x,\Lambda}\{A\} = \mathbb{P}\{\hat{W}_{\mathbb{T}_\Lambda^x} \in A, \mathbb{T}_\Lambda^x < \tau < \infty\} \quad (1.22)$$

We remark two distinctions with respect to the previous definition 1.3.2:

- The measure is considered on Borel subsets of the working interface $\partial\Omega$ only, whereas the reflected Brownian motion \hat{W}_t and the local time process ℓ_t are defined on the whole boundary $\partial\Omega \cup \partial\Omega_0$.
- There is a supplementary condition $\mathbb{T}_\Lambda^x < \tau$ providing that the process \hat{W}_t should be absorbed (killed) on the working interface before hitting the source.

Note that $1 - \omega_{x,\Lambda}\{\partial\Omega\}$ is the probability that the process \hat{W}_t started from a given point $x \in \Omega$ hits the source $\partial\Omega_0$ before its final absorption on the working interface $\partial\Omega$.

One can easily extend the lemma 1.3.3 to this spread harmonic measure:

Lemma 1.4.1 *For any subset A from $\mathcal{B}(\partial\Omega)$ and fixed positive Λ , the spread harmonic measure $\omega_{x,\Lambda}\{A\}$, considered as function of x , solves the boundary value problem:*

$$\Delta\omega_{x,\Lambda}\{A\} = 0 \quad (x \in \Omega), \quad \begin{cases} \left[I - \Lambda \frac{\partial}{\partial n} \right] \omega_{x,\Lambda}\{A\} = \mathbb{I}_A(x) & (x \in \partial\Omega) \\ \omega_{x,\Lambda}\{A\} = 0 & (x \in \partial\Omega_0) \end{cases} \quad (1.23)$$

Proof is similar to those of the lemma 1.3.3. The last condition holds since $x \in \partial\Omega_0$ implies $\tau = 0$. \square

Corollary 1.4.2 *Function $C_\Lambda(x) = C_0(1 - \omega_{x,\Lambda}\{\partial\Omega\})$ solves the boundary value problem (1.1–1.3).*

Proof is a direct verification. \square

Consequently, a simple introduction of the source allows to apply the previous description of the partially reflected Brownian motion to study the Laplacian transport phenomena. Due to reversibility of the Brownian motion, one may think that $(1 - \omega_{x,\Lambda}\{\partial\Omega\})dx$ gives also the probability to find the partially reflected Brownian motion, started from the absorbing source, in dx vicinity of the point $x \in \Omega$, under partially absorbing condition on the working interface $\partial\Omega$. Note that such way of reasoning, being intuitive and useful, is quite formal. In particular, the (simple) Brownian motion started from the source returns to it infinitely many times with probability 1. If one really needs to define such a process, the starting point should be taken slightly above the source.

Since the boundary $\partial\Omega$ is always supposed to be smooth, one can introduce the spread harmonic measure density $\omega_{x,\Lambda}(s)$. In turn, the kernel of the spreading operator is defined as previously, $T_\Lambda(s, s') \equiv \omega_{s,\Lambda}(s')$. In particular, one retrieves the relation (1.11):

$$\omega_{x,\Lambda}(s) = \int_{\partial\Omega} ds' \omega_{x,0}(s') T_\Lambda(s', s)$$

where the harmonic measure density $\omega_{x,0}(s)$ is defined by relation (1.22) with $\Lambda = 0$.

The definition of the Dirichlet-to-Neumann operator can be also extended to domains with a source. For a given function $f \in H^1(\partial\Omega)$, one solves the Dirichlet problem in the domain Ω :

$$\Delta u = 0 \quad (x \in \Omega), \quad u = f \quad (x \in \partial\Omega), \quad u = 0 \quad (x \in \partial\Omega_0)$$

In principle, one could consider another function on the source. For a given function f on $\partial\Omega$, the Dirichlet-to-Neumann operator \mathcal{M} , acting from $H^1(\partial\Omega)$ to $L^2(\partial\Omega)$, associates the new function $g = \partial u / \partial n$ on the working interface $\partial\Omega$. One demonstrates general properties of this operator and its relation to the partially reflected Brownian motion in a straight way. In particular, the spreading operator T_Λ , defined by its kernel $T_\Lambda(s, s')$, coincides with the resolvent operator $[I + \Lambda\mathcal{M}]^{-1}$. However, some normalization properties may be changed. In particular, for the probability kernel $T_\Lambda(s, s')$, one has

$$\int_{\partial\Omega} T_\Lambda(s, s') ds' < 1$$

since the PRBM started from the working interface $\partial\Omega$ can be absorbed on the source.

1.4.2 Continuous approach

The stochastic treatment by means of the partially reflected Brownian motion provides the solution of the problem (1.1–1.3) describing the Laplacian transport phenomena: $C_\Lambda(x) = C_0(1 - \omega_{x,\Lambda}\{\partial\Omega\})$ (see corollary 1.4.2). One can go further using the close relation to the Dirichlet-to-Neumann operator [33]. According to the lemma 1.4.1, the density $\omega_{x,\Lambda}\{\partial\Omega\}$, considered as function of x , solves the boundary value problem:

$$\Delta\omega_{x,\Lambda}\{\partial\Omega\} = 0 \quad (x \in \Omega), \quad \left[I - \Lambda \frac{\partial}{\partial n} \right] \omega_{x,\Lambda}\{\partial\Omega\} = 1 \quad (x \in \partial\Omega), \quad \omega_{x,\Lambda}\{\partial\Omega\} = 0 \quad (x \in \partial\Omega_0)$$

The restriction of the function $\omega_{x,\Lambda}\{\partial\Omega\}$ on $\partial\Omega$ can be written with the help of the Dirichlet-to-Neumann operator \mathcal{M} as

$$\omega_{x,\Lambda}\{\partial\Omega\} = [(I + \Lambda\mathcal{M})^{-1}1](s) = [T_\Lambda 1](s)$$

where $1(s)$ stands for a constant (unit) function on the working interface.

One defines then the flux density $\phi_\Lambda(s)$ across the working interface $\partial\Omega$:

$$\phi_\Lambda(s) = D \frac{\partial C_\Lambda}{\partial n}(s) = -D \frac{\partial \omega_{x,\Lambda}\{\partial\Omega\}}{\partial n}(s)$$

Since the normal derivative of a harmonic function can be represented as the application of the Dirichlet-to-Neumann operator to the restriction of this function on the boundary, one writes

$$\phi_\Lambda(s) = D \mathcal{M}\omega_{s,\Lambda}\{\partial\Omega\} = D \mathcal{M}[T_\Lambda 1](s)$$

(the sign is changed due to particular orientation of the normal derivative). Taking $\Lambda = 0$, one finds $\phi_0(s) = D [\mathcal{M}1](s)$ and finally

$$\phi_\Lambda(s) = [T_\Lambda \phi_0](s)$$

The transport properties of the working interface can be characterized by a physical quantity called *spectroscopic impedance*. We remind that the impedance of an electric scheme is defined as the tension applied between two external poles, divided by the total electric current passing

through. The formal analogy between the electric problem and the diffusive transport, discussed in section 1.1, leads to a natural definition of the impedance in our case as the concentration C_0 on the source $\partial\Omega_0$ divided by the total flux across the working interface $\partial\Omega$:

$$Z_{cell}(\Lambda) = \frac{C_0}{\int_{\partial\Omega} ds \phi_\Lambda(s)}$$

Taking $\Lambda = 0$, one deals with a purely absorbing interface $\partial\Omega$: any particle arrived to $\partial\Omega$ is immediately absorbed (without reflections). In other words, such interface has no resistance for passage across it. Consequently, the impedance $Z_{cell}(0)$ represents the ‘‘access resistance’’ by the volume: the possibility that the Brownian motion can return to the source without hitting the working interface. The resistance property of the working interface can be thus characterized by the difference between $Z_{cell}(\Lambda)$ and $Z_{cell}(0)$, called *spectroscopic impedance*:

$$Z_{sp}(\Lambda) = Z_{cell}(\Lambda) - Z_{cell}(0)$$

Using the simple identity

$$((\phi_\Lambda - \phi_0) \cdot 1)_{L^2} = \frac{\Lambda}{D} (\phi_\Lambda \cdot \phi_0)_{L^2} \quad (1.24)$$

one writes the spectroscopic impedance as

$$Z_{sp}(\Lambda) = \frac{\Lambda}{D} \frac{(\phi_\Lambda \cdot \phi_0)_{L^2}}{(\phi_\Lambda \cdot 1)_{L^2} (\phi_0 \cdot 1)_{L^2}}$$

Using again the identity (1.24), one finds a more convenient form:

$$Z_{sp}(\Lambda) = \frac{1}{\frac{1}{Z(\Lambda)} - \frac{1}{Z_{cell}(0)}}$$

The new function

$$Z(\Lambda) = \frac{\Lambda}{D} (T_\Lambda \phi_0^h \cdot \phi_0^h)_{L^2} \quad \phi_0^h(s) = \frac{\phi_0(s)}{(\phi_0 \cdot 1)_{L^2}}$$

can be called *effective impedance*, where $\phi_0^h(s)$ is the normalized flux density towards the perfectly absorbing working interface $\partial\Omega$. Finally, the spectral decomposition of the spreading operator T_Λ on the basis of eigenfunctions \mathbf{V}_α of the Dirichlet-to-Neumann operator \mathcal{M} leads to the important relation for the effective impedance:

$$Z(\Lambda) = \frac{\Lambda}{D} \sum_\alpha \frac{F_\alpha}{1 + \Lambda\mu_\alpha} \quad F_\alpha = (\phi_0^h \cdot \mathbf{V}_\alpha)_{L^2} (\phi_0^h \cdot \mathbf{V}_\alpha^*)_{L^2} \quad (1.25)$$

This relation presents the central result of the continuous approach developed in [33]. Let us briefly discuss its physical meaning. The spectroscopic impedance $Z_{sp}(\Lambda)$ or, equivalently, the effective impedance $Z(\Lambda)$, is a physical quantity which characterizes the transport properties of the whole working interface. More importantly, this quantity can be measured directly in experiment (e.g., in electrochemistry). On the other hand, the local transport properties of the working interface are described by the single physical parameter Λ , being related to the membrane’s permeability W , the electrode’s resistance r or the catalyst’s reactivity K (see Section 1.1). Varying the parameter Λ , one changes the local transport properties at each boundary point and, consequently, the whole linear response of the working interface. In a first sight, one may think that an increase of the local boundary resistance should imply a

proportional increase of the whole boundary resistance, i.e., $Z(\Lambda) \sim \Lambda$. This reasoning being true for a planar surface becomes invalid in a general case due to geometrical irregularities. In fact, an irregular geometry modifies considerably the linear response of the working interface [22–28]. The boundary value problem (1.1–1.3) describing the Laplacian transport phenomena on the average allows, in principle, to study such geometrical influence. Practically, however, this is a very difficult problem. The continuous approach provides an efficient tool to carry out these studies both in theoretical and numerical ways. In particular, the relation (1.25) makes explicit the impedance dependence on the local transport properties (parameter Λ) and allows to identify contributions due to the *physics* and due to the *geometry*, involved in the problem in a complex manner. In other words, whatever the physical problem (diffusion across semi-permeable membranes, heterogeneous catalysis or electric transport), the geometry enters *only* through the spectral characteristics of the Dirichlet-to-Neumann operator \mathcal{M} : its eigenvalues μ_α and the spectral components F_α of the normalized flux density $\phi_0^h(s)$ on the basis of its eigenfunctions $\mathbf{V}_\alpha(s)$.

The other important meaning of the relation (1.25) can be outlined if one considers the inverse problem [33]: what is the most available information that one can retrieve from a measurement of the spectroscopic impedance of an unknown working interface? The mathematical response can be given immediately if one rewrites (1.25) as Laplace transform of the new function $\zeta(\lambda)$:

$$Z(\Lambda) = \frac{1}{D} \int_0^\infty d\lambda e^{-\lambda/\Lambda} \zeta(\lambda), \quad \zeta(\lambda) \equiv \sum_\alpha F_\alpha e^{-\lambda\mu_\alpha}$$

Under assumption to be able to measure the impedance with an absolute precision, one can reconstruct the function $\zeta(\lambda)$ and, consequently, the set of characteristics $\{\mu_\alpha, F_\alpha\}$ which may be thus called *geometrical spectrum* of the working interface. In practice, however, the inverse problem is more difficult [62].

In two following subsections, we are going to discuss some aspects of the semi-continuous and the discrete descriptions of the Laplacian transport phenomena which can be referred as physical approaches based on the intuitive notion of partial reflections on the boundary. Since these descriptions turn out to be approximations to the continuous approach, we do not present the circumstantial details.

1.4.3 Semi-continuous approach

The semi-continuous approach, developed by Halsey and Leibig [25], is based on the following construction (for details, see [33]). For a given domain Ω with smooth bounded boundary $\partial\Omega$, one considers the Brownian motion started from a point $x \in \Omega$. When it hits the boundary at some point s , two complementary events may happen:

- with probability ε , the Brownian motion is reflected to the interior point $s + an(s)$, slightly above the boundary (here $n(s)$ is the unit normal vector to the boundary at point s , a is a small positive parameter); the Brownian motion continues from this point;
- or, with probability $1 - \varepsilon$, the Brownian motion is terminated at this point s (absorbed on the boundary).

This motion continues until the absorption on the boundary and can be called *Brownian motion reflected with jump*. Two new parameters, the jump distance a and the reflection probability ε , are related to the given physical parameter Λ [50]:

$$\varepsilon = \frac{1}{1 + (a/\Lambda)} \tag{1.26}$$

(one fixes Λ and takes $0 < a < \Lambda$ in order to have $0 < \varepsilon < 1$).

Now, one can calculate the probability $\omega_{x,\Lambda}^{(a)}(s)ds$ that this process is finally absorbed in ds vicinity of the boundary point s . Since the motions before and after each reflection are independent, this probability can be obtained as the sum of probabilities to be absorbed after 0, 1, 2, ... reflections:

$$\begin{aligned} \omega_{x,\Lambda}^{(a)}(s)ds &= [\omega_x(s)ds] (1 - \varepsilon) + \int_{\partial\Omega} [\omega_x(s_1)ds_1] \varepsilon [\omega_{s_1+an(s_1)}(s)ds] (1 - \varepsilon) + \\ &+ \int_{\partial\Omega} \int_{\partial\Omega} [\omega_x(s_1)ds_1] \varepsilon [\omega_{s_1+an(s_1)}(s_2)ds_2] \varepsilon [\omega_{s_2+an(s_2)}(s)ds] (1 - \varepsilon) + \dots \end{aligned}$$

For example, the third term represents the probability to hit the boundary in ds_1 vicinity of the point s_1 , to be reflected to the neighboring point $s_1 + an(s_1)$, to hit again the boundary in ds_2 vicinity of the point s_2 , to be reflected to the neighboring point $s_2 + an(s_2)$, to hit the boundary for the last time in ds vicinity of the point s , and to be finally absorbed. Introducing the integral operator $Q^{(a)}$, acting from $L^2(\partial\Omega)$ to $L^2(\partial\Omega)$ as

$$[Q^{(a)}f](s) = \int_{\partial\Omega} ds' f(s') \omega_{s'+an(s')}(s)$$

one rewrites the previous sum as the application of the new integral operator $T_\Lambda^{(a)}$ to the harmonic measure density $\omega_x(s)$:

$$\omega_{x,\Lambda}^{(a)}(s) = [T_\Lambda^{(a)}\omega_x](s) \quad T_\Lambda^{(a)} = (1 - \varepsilon) \sum_{k=0}^{\infty} (\varepsilon Q^{(a)})^k \quad (1.27)$$

What happens when the jump distance a goes to 0? Hitting the boundary, the Brownian motion will be reflected to interior points lying closer and closer to the boundary, i.e., displacements of the Brownian motion between two serial hits are getting smaller and smaller. At the same time, the reflection probability ε tends to 1 according to relation (1.26), i.e., the average number of reflections increases. Indeed, the distribution of the random number \mathcal{N} of reflections until the final absorption is simply

$$\mathbb{P}\{\mathcal{N} = n\} = (1 - \varepsilon) \varepsilon^n \quad (1.28)$$

implying that the average number $\langle \mathcal{N} \rangle = \varepsilon(1 - \varepsilon)^{-1}$ goes to infinity. Does the limiting process exist? The situation is complicated by the *local* choice between reflection and absorption: at each hitting point, the motion can be absorbed with vanishing probability $1 - \varepsilon$. In order to get round this difficulty, one can consider the process from a slightly different point of view. Actually, one can replace the local condition of the absorption (with probability $1 - \varepsilon$) by its *global* analog: the process is absorbed on the boundary when the number of reflections exceeds a random variable \mathcal{N} distributed according to the geometrical law (1.28). Evidently, this modification does not change at all the properties of the process. At the same time, we gain that the condition of the absorption is independent of the Brownian motion between serial hits. As a consequence, we can consider the corresponding limits (as $a \rightarrow 0$) separately. So, the Brownian motion reflected with jump should tend to the reflected Brownian motion as the jump distance a vanishes. This motion, however, is conditioned to stop when the number of reflections exceeds the random variable \mathcal{N} . Since the average number $\langle \mathcal{N} \rangle$ goes to infinity in the limit $a \rightarrow 0$, it is convenient to consider a normalized variable $\chi = a\mathcal{N}$ obeying the following distribution:

$$\mathbb{P}\{\chi \geq \lambda\} = \mathbb{P}\{\mathcal{N} \geq \lambda/a\} = \sum_{[\lambda/a]}^{\infty} \mathbb{P}\{\mathcal{N} = n\} \simeq \varepsilon^{[\lambda/a]} \simeq \exp[-\lambda/\Lambda] \quad (1.29)$$

(the last equality is written with the help of (1.26) when a goes to 0). Since the number of reflections on jump distance a , multiplied by a , tends to the local time process according to Lévy's formula (1.9), the previous condition of absorption can be reformulated: the motion is absorbed when its local time process exceeds a random variable distributed according to the exponential law (1.29). One thus concludes that the Brownian motion reflected with jump should tend to the partially reflected Brownian motion defined in 1.3.1.

The above analysis, presented as a sketch (without proofs), does not pretend to a mathematical rigour. It may be considered rather as a possible justification which can be brought for the semi-continuous approach if necessary. In particular, one can demonstrate that the density $\omega_{x,\Lambda}^{(a)}(s)$, given by relation (1.27), tends to the spread harmonic measure density as the jump distance a goes to 0:

$$\omega_{x,\Lambda}(s) = \lim_{a \rightarrow 0} \omega_{x,\Lambda}^{(a)}(s)$$

This relation may be useful for numerical computations. Similarly, the integral operator $T_{\Lambda}^{(a)}$ should converge to the spreading operator T_{Λ} as $a \rightarrow 0$. Calculating the geometrical series in (1.27) and representing $T_{\Lambda}^{(a)}$ as

$$T_{\Lambda}^{(a)} = (1 - \varepsilon)(I - \varepsilon Q^{(a)})^{-1} = \left(I + \Lambda \frac{I - Q^{(a)}}{a} \right)^{-1}$$

one obtains the following approximation for the Dirichlet-to-Neumann operator:

$$\mathcal{M} = \lim_{a \rightarrow 0} \frac{I - Q^{(a)}}{a}$$

Again, this relation may be useful for the numerical computation of the left hand side.

The advantages of the semi-continuous approach are based on an apparent intuitive meaning of partial reflections on the boundary. Moreover, this approach provides even a more realistic description of physico-chemical processes on microscopic level. For example, if one considers the partially reflected Brownian motion started from a boundary point, the number of hits of the boundary is infinite for any moment $t > 0$ that sounds impossible for real physical species. The keypoint is that, for diffusion across a semi-permeable membrane or heterogeneous reaction on a catalytic surface, the description by the boundary value problem (1.1–1.3) cannot be justified on scales less than the mean free path of diffusing particles. Since the continuous limit $a \rightarrow 0$ requires such *non-physical* scales, it is not surprising that the limiting process (the PRBM) presents some unrealistic properties from the physical point of view. The similar limitation happens for the electric transport problem when the smallest physical scale is given by the thickness of the double layer, being close to the Debye-Hückel length [24, 25]. Evidently, this remark does not devaluate the efficiency of the continuous approach based on the partially reflected Brownian motion. On the contrary, the mathematical rigour of this approach justifies the semi-continuous description and simplifies its study by introducing the Dirichlet-to-Neumann operator. However, dealing with a mathematical description of a physical problem, one should take care that deduced consequences do not go beyond the ranges of the model.

The capabilities of the semi-continuous approach are essentially limited by the fact that the central operator $Q^{(a)}$ is not self-adjoint (the function $\omega_{s+an(s)}(s')$ is not symmetric with respect to the permutation of s and s' except specific cases). As a consequence, one cannot develop the spectral decomposition (1.25) of the impedance, i.e., there is no possibility to distinguish contributions of different modes. Although the operator $Q^{(a)}$ is defined naturally by the harmonic measure density, it does not provide a proper description of the problem as it was done with the Dirichlet-to-Neumann operator.

1.4.4 Discrete approach

Another stochastic approach to Laplacian transport phenomena has been developed by Filoche and Sapoval [20]. The main idea is to model the partially reflected Brownian motion by random walks on a lattice with partial reflections on the boundary. Actually, one discretizes a given domain Ω by d -dimensional hypercubic lattice of mesh a and considers the following stochastic process: started from a remote source, a random walker jumps to a neighboring site at each step with probability $(2d)^{-1}$. When the walker arrives to a boundary site, it can be reflected to its neighboring site (belonging to the bulk) with probability ε (and the motion continues), or it can be absorbed with probability $(1 - \varepsilon)$. The motion continues until the final absorption on the boundary, or the return to the source. One can show [50] that the discrete parameters a and ε are related by the expression (1.26) involving the continuous physical parameter Λ .

In the discrete description, the harmonic measure density is replaced by the distribution of hitting probabilities $(\mathbf{P}_0)_j$ of boundary sites j , (simple) random walks being started from a remote source. Let $Q_{j,k}^{(a)}$ denote the probability to arrive to the boundary site k starting from the boundary site j by a random walk in the bulk without hitting the boundary or the source during the walk⁴. One can thus calculate the distribution of probabilities $(\mathbf{P}_\Lambda)_j$ to be finally absorbed on the boundary site j , when random walks with partial reflections are started from a remote source. Indeed, the Markov property of this process allows to calculate $(\mathbf{P}_\Lambda)_j$ as the sum of contributions provided by random trajectories with 0, 1, 2, ... reflections before the final absorption:

$$(\mathbf{P}_\Lambda)_j = (\mathbf{P}_0)_j(1 - \varepsilon) + \sum_{k_1} (\mathbf{P}_0)_{k_1} \varepsilon Q_{k_1,j}^{(a)} (1 - \varepsilon) + \sum_{k_1} \sum_{k_2} (\mathbf{P}_0)_{k_1} \varepsilon Q_{k_1,k_2}^{(a)} \varepsilon Q_{k_2,j}^{(a)} (1 - \varepsilon) + \dots$$

(we remind that $\varepsilon = (1 + a/\Lambda)^{-1}$). For example, the second term represents the product of the following probabilities: to hit a boundary site k_1 , to be reflected to its neighboring site, to arrive to the boundary site j , and to be finally absorbed on it. If one considers \mathbf{P}_0 and \mathbf{P}_Λ as vectors and $Q^{(a)}$ as matrix, the summation over intermediate sites k_1, k_2, \dots can be understood as matrix product:

$$\mathbf{P}_\Lambda = \left[(1 - \varepsilon) \sum_{n=0}^{\infty} (\varepsilon Q^{(a)})^n \right] \mathbf{P}_0$$

i.e., the distribution of absorption probabilities $(\mathbf{P}_\Lambda)_j$ is obtained as the application of a linear operator, depending on $Q^{(a)}$ and Λ (or ε), to the distribution of hitting probabilities $(\mathbf{P}_0)_j$. The symmetric matrix $Q^{(a)}$ represents a self-adjoint operator, called *Brownian self-transport operator*. Using the normalization property $|Q^{(a)}| \leq 1$ and relation (1.26) between Λ and ε , one obtains:

$$\mathbf{P}_\Lambda = T_\Lambda^{(a)} \mathbf{P}_0 \quad T_\Lambda^{(a)} = \left[I + \Lambda \frac{I - Q^{(a)}}{a} \right]^{-1}$$

The operator $T_\Lambda^{(a)}$, depending on the lattice parameter a , is called (*discrete*) *spreading operator*. The previous relation, written explicitly as

$$(\mathbf{P}_\Lambda)_j = \sum_k (\mathbf{P}_0)_k (T_\Lambda^{(a)})_{k,j}$$

allows to separate random trajectories in two independent parts:

- the random walker started from a remote source arrives to the boundary site k (first factor);

⁴We use the same notation $Q^{(a)}$ for the integral operator in semi-continuous approach and for the matrix of these probabilities since they have the same meaning and even may be used to approximate each other.

- it continues the motion with partial reflections until the final absorption on the boundary site j (second factor).

One concludes that the absorption probabilities $(\mathbf{P}_\Lambda)_j$ provide a discrete analog of the spread harmonic measure density, while the matrix $(T_\Lambda^{(a)})_{k,j}$ is a discrete analog of the kernel $T_\Lambda(s, s')$ of the spreading operator $T_\Lambda = [I + \Lambda\mathcal{M}]^{-1}$. In particular, the bounded operators $(I - Q^{(a)})/a$ can be understood as discrete approximations of the Dirichlet-to-Neumann operator \mathcal{M} (in resolvent sense). As for the semi-continuous approach, we do not furnish the corresponding proofs (see [33] for more details).

The advantage of the discrete description with respect to the semi-continuous approach is based on the fact that the Brownian self-transport operator $Q^{(a)}$ and, consequently, the (discrete) spreading operator $T_\Lambda^{(a)}$ are self-adjoint. This property allows to employ all the machinery of the spectral theory in order to express the physical characteristics of the Laplacian transport through eigenmodes of this operator in an explicit way. For example, the spectral decomposition (1.25) can be also written in the discrete case. Such decompositions have been used to study the Laplacian transport towards irregular geometries [33, 50]. Moreover, the discrete description provides at least two different ways to study the problem numerically: direct Monte Carlo simulations and discrete boundary elements method [63].

The discrete description, being intuitively the most simple and useful, may lead to mathematical difficulties when one tries to proceed the continuous limit a going to 0. Although the partially reflected Brownian motion is the natural limit of random walks with partial reflections, its rigorous demonstration, in our knowledge, is not yet realized in details. The interested reader can find more information on this topic in [64–69].

1.5 Conclusion

The application of stochastic processes to represent the solution of boundary value problems is well known and wide used. In particular, Monte Carlo simulations are generally based on this technique. In this paper, we gave an overview of the Laplacian transport phenomena found in different scientific domains (e.g., physics, electrochemistry, chemistry, physiology) and related stochastic approaches to describe them. The most attention has been paid to the recently developed continuous approach based on the partially reflected Brownian motion. This stochastic process can be thought as rigorous mathematical description for random trajectories of diffusing particles hitting a semi-permeable interface, in comparison with more intuitive physical descriptions by semi-continuous and discrete approaches. The partially reflected Brownian motion turns out to be the natural limit of the Brownian motion reflected with jump (semi-continuous approach) and of the random walks with partial reflections (discrete approach).

The profound relation between the partially reflected Brownian motion and spectral properties of the Dirichlet-to-Neumann operator \mathcal{M} are found to be useful for practical purposes. In particular, the kernel of the resolvent operator $T_\Lambda = [I + \Lambda\mathcal{M}]^{-1}$ provides the probability density $T_\Lambda(s, s')$ allowing to reconstruct the spread harmonic measure density $\omega_{x,\Lambda}(s)$. Moreover, the spectral decomposition on the complete basis of eigenfunctions of the Dirichlet-to-Neumann operator leads to the explicit analytical formula for this density. Consequently, the use of the operator \mathcal{M} gives an efficient way to study different probability distributions related to the partially reflected Brownian motion.

The spectral decomposition of the spectroscopic impedance, characterizing the linear response of the whole working interface, provides an explicit analytical dependence on the physical parameter Λ allowing to identify *physical* and *geometrical* contributions which were involved in a complex manner. The geometrical spectrum of the working interface contains the complete information about its transport properties. The combined use of stochastic characteristics of

the partially reflected Brownian motion and spectral properties of the Dirichlet-to-Neumann operator opens encouraging possibilities for further understanding of various physical and chemical transport processes in nature. In this light, a more profound mathematical analysis of these objects seems to be an important perspective for the present study.

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