Mathematical basis for a general theory of Laplacian transport towards irregular interfaces

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The theory of Laplacian transport towards and across irregular surfaces is reformulated in terms of the Dirichlet-to-Neumann operator and its spectral characteristics. This permits us to obtain an exact equivalent circuit for the impedance of a working interface of arbitrary shape. The important result is that only very few eigenmodes of this operator do govern the entire response of a macroscopic system. This property drastically simplifies the understanding of irregular or prefractal interfaces. The results can be applied in electrochemistry, physiology and chemical engineering, fields where exchange processes across surfaces with complex geometry are ubiquitous.

I. INTRODUCTION

Irregular interfaces are ubiquitous in nature and industry, and the understanding of their role in macroscopic transport is a long standing question. In many systems the transport towards and across such surfaces is driven by Laplacian fields. Examples can be found in domains such as electrochemistry, heterogeneous catalysis, NMR relaxation in porous media, and transfer across biological membranes [1]. For instance, a highly irregular geometry of the mammalian lungs is required to provide a sufficient alveolar surface, confined into a relatively small volume of the rib cage [2]. In this light, the geometrical irregularity is not only a common feature of biological or industrial systems, but the indispensable element of their functioning. A long standing problem is thus, "How does the irregular geometry of the semipermeable interface influence the net response of the whole system?" [3–15].

The net flux across such a system is in general the result of a competition between the following two physical or chemical mechanisms [15]:

(i) The transport in the bulk towards the interface which is limited by an "access resistance." This volume effect is determined by a diffusion coefficient D (or electrolyte conductivity ρ^{-1}).

(ii) The transfer across the "semipermeable" surface (or the chemical reaction on this interface). It is characterized by the permeability W (or the reaction rate K, or the electrode surface conductivity $1/r$) that can vary from 0 (perfectly reflecting interface) up to infinity (perfectly absorbing interface).

In the case of the transport across an irregular surface, some parts of the surface are more accessible to diffusing particles than others. Hence, the current density across the surface may strongly vary from one place to another. This phenomenon is known as diffusional screening [15–17]. The overall transport of particles across the semipermeable interface then depends on the particular geometry of the interface.

In other words, the transport properties of the system (through the bulk and across the interface) interplay in a complicated way with the geometrical features of the interface, to give rise to a nontrivial macroscopic response. For instance, the constant phase angle behavior, often observed in electrochemical measurements, may be caused by the roughness of metallic electrodes [3,4]. Similar effects are observed in heterogeneous catalysis [18].

The above Laplacian transport phenomena can be modeled in the following mathematical frame: "species" characterized by their concentration C diffuses in the bulk from a distant source towards a semipermeable interface, on which it disappears at a given rate (either by transferring across the interface, or by reacting in the case of a catalytic cell). The steady state concentration field obeys the following equations:

$$\Delta C = 0 \text{ in the bulk,}$$
$$C = C_0 \text{ at the source,} \tag{1}$$
$$\frac{\partial C}{\partial n} = \frac{C}{\Lambda} \text{ on the surface.}$$

The length $\Lambda = D/W$ characterizes the balance between the two competitive transport mechanisms [15]. It has a simple physical meaning: it represents typically the perimeter of a region of an irregular interface which works uniformly. It can be visually observed by electrochemical direct decoration technique [19].

If one knows the surface geometry, the question of the transport is in principle simple. For a given geometry, one can solve the boundary value problem (1) numerically and determine the total flux Φ_Λ for any value of Λ or D:

$$\Phi_\Lambda = \int_{\partial\Omega} \phi_\Lambda(s)ds, \qquad \phi_\Lambda(s) = D\frac{\partial C}{\partial n}(s), \tag{2}$$

where $\partial/\partial n$ denotes the normal derivative at the interface $\partial\Omega$ directed towards the bulk. Of course, the real situation is often the opposite: one measures the flux, or needs a given flux for some practical reasons. One may thus wonder what

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are the respective roles of the transport parameters and the geometry. This question is of particular importance in electrochemistry, where it is related to finding of the "second current distribution."

Among several approaches, Halsey first proposed to map the electrochemical phenomena to the study of random walks nearby the working electrodes [10]. In a seminal paper, he introduced the operator H called "matrix of periods of the harmonic measure" whose elements $H_{\mu\nu}$ are the probabilities for a random walker emitted from the μth element of the surface first returning to the surface within the νth element. Later, Halsey and Leibig essentially used Green function's representation to describe the secondary current distribution in an electrolytic cell [11–14]. Within their description, the original physical problem has been reduced to a numerical analysis of Green functions. Further probabilistic interpretation permitted to predict scaling exponents of fractal electrodes [11,12]. In that approach, the geometry is characterized by the whole Green function, limiting practical implementation of this description for complex morphologies. Second, the representation of the admittance through series expansion requires the knowledge of all its coefficients (see Ref. [20] for details). Finally, the assumption about the finite thickness of the double layer makes the application of the above theory difficult to other transport phenomena (such as, for example, the oxygen diffusion in the human lungs [21]), which, however, lead finally to analog conclusions if one uses the correct transposition of physical quantities.

In this paper, we reformulate the classical Laplacian description (1) of transport phenomena by introducing the Dirichlet-to-Neumann operator in such a way that the contribution of the geometry can be identified explicitly. Thanks to the use of the spectral theory, it is shown that one can reduce the relevant information on the system geometry to a set of real-valued quantities having a rigorous mathematical definition and clear physical interpretation. More precisely, we shall show that, for the original continuous problem (1), there exists a self-adjoint mathematical operator called the Dirichlet-to-Neumann operator whose spectral characteristics contain all the geometrical information on the boundary that is relevant to the Laplacian transport. In particular, an analytical representation of the total flux Φ_Λ as a function of the physical parameter Λ will be deduced. First, we briefly remind the reader of the discrete approach in Sec. II that provides an intuitive thinking about the Laplacian transport phenomena. We shall then describe in Sec. III the continuous approach, the central subject of this paper. In Sec. IV, we discuss its physical and probabilistic interpretations that help to present the practical applications of this approach.

II. THE DISCRETE APPROACH

The original Halsey idea about the governing operator H was further developed by Filoche and Sapoval [22], introducing a finite absorption probability on the working surface. This absorption probability has a simple physical meaning. For instance, it is the reaction probability in the case of heterogeneous catalysis. In this section, we briefly recall the discrete approach that provides an intuitive thinking about the Laplacian transport phenomena.

Here the diffusion source, the diffusive bulk and the semipermeable interface are discretized into a finite number of sites. The Brownian motion of diffusing particles is then modeled by random walks on a regular d-dimensional lattice with mesh a and jump time τ. A finite permeability of the interface can be interpreted via *partial* absorptions on the boundary: a particle arriving on an interface site is reflected to the neighboring bulk site with a reflection probability ε, or absorbed with a sticking probability $1-\varepsilon$. The particle then resumes its Brownian motion until it is absorbed either by the interface or the source. The two macroscopic physical quantities D and W are related to three microscopic discrete parameters a, τ, and ε as [23]

$$D = \frac{a^2}{2d\tau}, \qquad W = \frac{a(1-\varepsilon)}{2d\tau\varepsilon}, \qquad (3)$$

whence one gets

$$\Lambda = a\frac{\varepsilon}{1-\varepsilon}. \qquad (4)$$

The total flux density $\phi_\Lambda(s)$ is represented by a finite number of fluxes $\phi^a_{\Lambda,k}$ across each interface site k, where the superscript a points out the dependence on the discretization. In a probabilistic view, these fluxes are proportional to the probabilities $(\mathbf{P}^a_\Lambda)_k$ for a random walker coming from the diffusion source to be finally absorbed on the site k of the interface (given the fact that it can be reflected with probability ε against this interface):

$$\phi^a_{\Lambda,k} = C_0 D a^{d-2}(\mathbf{P}^a_\Lambda)_k.$$

For convenience, the probabilities $(\mathbf{P}^a_\Lambda)_k$ can be considered as components of a N-dimensional vector $\mathbf{P}^a_\Lambda$, where N stands for the number of sites discretizing the interface. The key point of the discrete approach [22] is that the probabilities $(\mathbf{P}^a_\Lambda)_k$ can be expressed through the Brownian self-transport operator that only depends on the (discretized) geometry of the system. This operator is represented by the $(N\times N)$-dimensional matrix Q^a which is composed of the probabilities $Q^a_{j,k}$ for a random walker to reach at first hit the site k on the interface when starting at the site j of the same interface, without hitting the source during the walk.

For a perfectly absorbing interface ($\varepsilon=0$ and $\Lambda=0$), the probabilities $(\mathbf{P}^a_0)_k$ are given by the normalization condition for matrix Q^a:

$$(\mathbf{P}^a_0)_k = 1 - \sum_j Q^a_{k,j} \qquad \text{or} \qquad \mathbf{P}^a_0 = [I - Q^a]\mathbf{1},$$

where I stands for the identity operator and $\mathbf{1}=(1,1,\ldots,1)^T$. These are the probabilities for a random walker to reach *at first hit* the site k on the interface when starting at the diffusion source.

For a strictly positive Λ, the Markovian property of the random walks allows to express the probability $(\mathbf{P}^a_\Lambda)_k$ as the sum of probabilities to cross the interface after $0,1,2,\ldots$, intermediate hits. First, the probability to cross the interface at first hit is simply $(1-\varepsilon)(\mathbf{P}^a_0)_k$. Then, the probability to cross the interface after one intermediate hit is

$(1-\varepsilon)\Sigma_{k_1}(\mathbf{P}_0^a)_{k_1}\varepsilon Q_{k_1,k}^a$. A similar expression can be written for the contribution of trajectories with $2,3,\ldots,$ intermediate hits. The probability $(\mathbf{P}_\Lambda^a)_k$ is then

$$(\mathbf{P}_\Lambda^a)_k = (1-\varepsilon)(\mathbf{P}_0^a)_k + (1-\varepsilon)\sum_{k_1}(\mathbf{P}_0^a)_{k_1}\varepsilon Q_{k_1,k}^a + \cdots$$

$$+ (1-\varepsilon)\sum_{k_1,\ldots,k_n}(\mathbf{P}_0^a)_{k_1}\varepsilon Q_{k_1,k_2}^a\varepsilon\cdots Q_{k_n,k}^a + \cdots.$$

Being written in a matrix form

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

this formula gives the distribution of absorption probabilities $(\mathbf{P}_\Lambda^a)_k$ as the application of the (discrete) spreading operator T_Λ^a to the distribution of hitting probabilities $(\mathbf{P}_0^a)_k$. Using relation (4), one finally writes

$$\mathbf{P}_\Lambda^a = \left(I + \Lambda\frac{I-Q^a}{a}\right)^{-1}\mathbf{P}_0^a. \qquad (5)$$

This expression shows how the geometrical irregularity represented by the operator $(I-Q^a)/a$ spreads the hitting probability distribution $\mathbf{P}_0^a$ with the physical length scale Λ.

The stationary flux Φ_Λ^a across the system can be expressed as the sum of all fluxes passing through each site of the interface:

$$\Phi_\Lambda^a = C_0 D a^{d-2}\sum_k(\mathbf{P}_\Lambda^a)_k.$$

This relation provides an explicit dependency of the total flux Φ_Λ^a on the physical parameter Λ and identifies the contribution of the geometry of the interface.

In order to return to the original *continuous* description, one has to go to the limit where three discrete parameters a, τ, and $1-\varepsilon$ vanish. Since the macroscopic parameters D and W have to be independent of the discretization, one discrete parameter (e.g., the lattice mesh a) goes to zero in an arbitrary way, while two other parameters vanish in such a way that relations (3) still remain valid. In this limit, the mathematical difficulty is to show the existence of $\lim_{a\to 0}(I-Q^a)/a$ and to identify its meaning. In this paper, we present a different approach which solves directly the continuous problem represented by Eq. (1).

III. THE CONTINUOUS APPROACH

The continuous approach is based on the spectral properties of the Dirichlet-to-Neumann operator which is known as a natural mathematical tool for describing fixed and moving boundary value problems in electromagnetism, fluid dynamics and solid mechanics [24–27] or inverse conductivity problems [28]. A recent development of efficient numerical techniques allow one to compute this operator for different interfaces in order to apply it in practice [29,30].

A. The Dirichlet-to-Neumann operator

Consider a bounded domain $\Omega \subset \mathbb{R}^d (d \geq 2)$ of a smooth (twice continuously differentiable) boundary that is com-
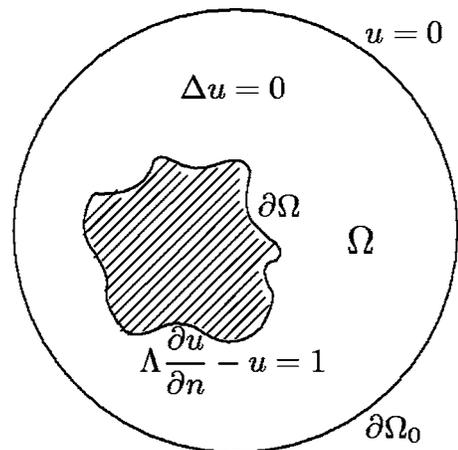
FIG. 1. In a typical diffusional cell, "species" diffuses in a bulk Ω from a distant source $\partial\Omega_0$ towards an irregular working interface $\partial\Omega$. This transport phenomena can be written as the mixed boundary value problem for the function u related to the concentration of species C as $C=C_0(1-u)$.

posed of two disjoint parts, $\partial\Omega$ and $\partial\Omega_0$, respectively, called the "working interface" and the "source" (Fig. 1). For a given function f on $\partial\Omega$, one can solve the following Laplace-Dirichlet problem:

$$\Delta u = 0 \ (x \in \Omega), \qquad \begin{cases} u = f & (x \in \partial\Omega), \\ u = 0 & (x \in \partial\Omega_0). \end{cases} \qquad (6)$$

The application of the normal derivative to the solution u leads to a new function g defined on the working interface $\partial\Omega : g = \partial u/\partial n$. This procedure, allowing one to associate for a given function f on $\partial\Omega$ the new function g on $\partial\Omega$, introduces a mathematical operator $\mathcal{M}$ called the Dirichlet-to-Neumann operator. It can be shown that this operator, acting from $H^1(\partial\Omega)$ (particular Sobolev space) to $L^2(\partial\Omega)$ (space of measurable and square integrable functions), is a pseudodifferential self-adjoint operator with discrete positive spectrum and smooth eigenfunctions forming a complete basis of $L^2(\partial\Omega)$ [31,32]. By definition, this operator only depends on the geometry of the domain Ω since no physical or chemical parameter was introduced up to this moment.

For diffusional problems, the function f can be thought as a given distribution of "species" on the working interface that have been sent to diffuse in the bulk Ω and then comes back to this interface. Its flux density is proportional to the function g and can be thus written as an application of the Dirichlet-to-Neumann operator $\mathcal{M}$ to the initial distribution f. In the electrochemical frame, one can consider the working interface $\partial\Omega$ with a given electric charge distribution f, and the application of the operator $\mathcal{M}$ to f provides the density of the induced electric field on the working interface.

B. Flux density

Once the Dirichlet-to-Neumann operator is defined for a given domain Ω, it can be applied to study the mixed boundary value problem (1). Searching concentration C in the form $C=C_0(1-u)$, one rewrites this problem as

$$\Delta u = 0 \ (x \in \Omega), \qquad \begin{cases} \left[I - \Lambda \dfrac{\partial}{\partial n} \right] u = 1 & (x \in \partial\Omega), \\ u = 0 & (x \in \partial\Omega_0). \end{cases}$$

The normal derivative of the harmonic function u on $\partial\Omega$ can be written as the image of its boundary restriction $u_{|\partial\Omega}$ by the operator $\mathcal{M}$, therefore the first boundary condition becomes $(I + \Lambda\mathcal{M}) u_{|\partial\Omega} = \mathbf{1}$. The sign is changed according to the definition of the normal derivative directed towards the bulk. Consequently, if one looks for the boundary values of the function u, it is sufficient to apply the operator $(I + \Lambda\mathcal{M})^{-1}$ to the constant function $\mathbf{1}$ on the working interface (the existence of the inverse operator is provided by the positivity of the spectrum of $\mathcal{M}$ and the natural inequality $\Lambda \geqslant 0$). According to the definition (2), the total flux density $\phi_\Lambda(s)$ of particles diffusing from the source $\partial\Omega_0$ towards the working interface $\partial\Omega$ can be thus calculated as

$$\phi_\Lambda(s) = DC_0\left(-\frac{\partial u}{\partial n} \right)(s) = DC_0[\mathcal{M}(I + \Lambda\mathcal{M})^{-1}\mathbf{1}](s).$$

For a purely absorbing interface ($\Lambda = 0$), the flux density is simply

$$\phi_0 = DC_0[\mathcal{M}\mathbf{1}] \qquad (7)$$

that implies the following important relation:

$$\phi_\Lambda = (I + \Lambda\mathcal{M})^{-1}\phi_0. \qquad (8)$$

It means that the finite permeability of the working interface ($\Lambda > 0$) leads to a spreading of the flux density $\phi_0(s)$ by the operator $T_\Lambda = (I + \Lambda\mathcal{M})^{-1}$, which is called the (continuous) spreading operator. The comparison of relations (5) and (8) suggests that T_Λ is the continuous analog of the discrete spreading operator T_Λ^a. In this light, the Dirichlet-to-Neumann operator $\mathcal{M}$ naturally appears as a limit of the sequences $(I - Q^a)/a$ as a goes to 0. Although the Dirichlet-to-Neumann operator has no simple probabilistic interpretation as the Brownian self-transport operator Q^a does, it provides a direct and continuous description of the Laplacian transport phenomena, without any auxiliary discretization of the initially *continuous* mixed boundary value problem (1) and difficulties related to further continuous limit of the discrete approach.

C. Macroscopic response: A general case

The total flux Φ_Λ across the working interface is obtained by the integration of the flux density $\phi_\Lambda(s)$ over the working interface $\partial\Omega$:

$$\Phi_\Lambda = \int_{\partial\Omega} ds\, \phi_\Lambda(s) = (\phi_\Lambda \cdot \mathbf{1})$$

which can be considered as the scalar product in $L^2(\partial\Omega)$ space. Using relations (7) and (8), one obtains a simple representation for the total flux

$$\Phi_\Lambda = DC_0\big([I + \Lambda\mathcal{M}]^{-1}\mathcal{M}\mathbf{1} \cdot \mathbf{1}\big). \qquad (9)$$

This expression shows explicitly how the experimentally measurable macroscopic response of the system (e.g., the

electric current through electrochemical cell) depends both on the transport parameters (D, C_0, and Λ), and on the geometry of the system. The last one is entirely represented via the Dirichlet-to-Neumann operator $\mathcal{M}$.

Since the operator $\mathcal{M}$ is self-adjoint, one can define its eigenmodes $\mathcal{M}\mathbf{V}_\alpha = \mu_\alpha \mathbf{V}_\alpha$ satisfying the normalization condition

$$(\mathbf{V}_\alpha \cdot \mathbf{V}_\beta) = \delta_{\alpha,\beta}. \qquad (10)$$

Whatever the bounded domain Ω, the eigenvalues μ_α are strictly positive and discrete:

$$0 < \mu_0 \leqslant \mu_1 \leqslant \mu_2 \leqslant \cdots.$$

For a smooth boundary, the eigenfunctions $\mathbf{V}_\alpha$ are also smooth (twice differentiable) and they form a complete basis of $L^2(\partial\Omega)$. Using these properties, one can represent the total flux Φ_Λ as the spectral decomposition of the constant function $\mathbf{1}$ on the eigenbasis $\{\mathbf{V}_\alpha\}$:

$$\Phi_\Lambda = DC_0 \sum_\alpha \frac{\mu_\alpha \widetilde{F}_\alpha}{1 + \Lambda\mu_\alpha}, \qquad (11)$$

where

$$\widetilde{F}_\alpha = (\mathbf{1} \cdot \mathbf{V}_\alpha)(\mathbf{1} \cdot \mathbf{V}_\alpha^*). \qquad (12)$$

In this expression, all the relevant information on the geometry of the system is entirely represented via the eigenvalues μ_α and the squared scalar products $\widetilde{F}_\alpha$ between $\mathbf{V}_\alpha$ and $\mathbf{1}$. Moreover, it provides an explicit dependency of the total flux on Λ, the only physical characteristics of the interface.

D. Effective impedance: A distant source at infinity

Since the Dirichlet-to-Neumann operator depends on the geometry of the whole domain Ω, the spectral decomposition (11) is sensitive not only to the geometry of the working interface, but also to the geometry of the source, and to their mutual arrangement. In many practical applications, the source is placed far from the working interface, therefore one may expect to separate the proper contribution of the working interface. Starting from a distant source, a diffusing particle "forgets" its geometrical details during a long stochastic motion. It allows us to simplify the problem by considering sources of planar or spherical shapes.

Moving away the source, one makes more difficult the access of the working interface since only a few diffusing particles can reach this interface before returning to the source. Consequently, the bulk access resistance $R = C_0/\Phi_0$ grows, and the total flux Φ_Λ decreases whatever the physical transport properties of the working interface. These qualitative arguments are supported by the following analysis of the spectral decomposition (11). If one considers a source going to infinity, the lowest eigenvalue μ_0 vanishes, while the corresponding eigenvector $\mathbf{V}_0$ tends to a constant function $S_{\text{tot}}^{-1/2}$ [44], where the value $S_{\text{tot}}^{-1/2}$ appears from the normalization condition (10), S_{tot} being the total surface area. Consequently, all the numerators in (11) vanish, either thanks to $\mu_0 \to 0$, or due to the orthogonality of eigenvectors $\mathbf{V}_\alpha$ to $\mathbf{V}_0 \propto \mathbf{1}$.

In order to characterize the macroscopic response of the working interface *alone*, one has to subtract the bulk contribution from the total flux Φ_Λ, and to use a convenient normalization

$$Z(\Lambda) = C_0 \frac{\Phi_0 - \Phi_\Lambda}{\Phi_0^2}. \tag{13}$$

This quantity represents the effective impedance of the working interface. The substitution of the spectral decomposition (11) into this relation gives

$$Z(\Lambda) = \frac{\Lambda}{D} \sum_\alpha \frac{F_\alpha}{1 + \Lambda \mu_\alpha}, \tag{14}$$

where the new coefficients have been introduced:

$$F_\alpha = \widetilde{F}_\alpha \mu_\alpha^2 \left(\frac{DC_0}{\Phi_0}\right)^2. \tag{15}$$

As shown below, these new coefficients F_α turn out to be the intrinsic geometrical characteristics of the interface. For this purpose, one first expresses the constant function **1** in definition (12) by inverting the relation (7) that leads to

$$\widetilde{F}_\alpha = \left(\frac{1}{DC_0}\right)^2 (\mathcal{M}^{-1} \phi_0 \cdot \mathbf{V}_\alpha)(\mathcal{M}^{-1} \phi_0 \cdot \mathbf{V}_\alpha^*).$$

Since the Dirichlet-to-Neumann operator is self-adjoint, one can simply move $\mathcal{M}^{-1}$ to the eigenvector $\mathbf{V}_\alpha$. Finally, one normalizes the flux density $\phi_0(s)$ by the total flux Φ_0:

$$\phi_0^N(s) = \frac{\phi_0(s)}{\Phi_0},$$

whence one gets

$$\widetilde{F}_\alpha = \left(\frac{\Phi_0}{DC_0}\right)^2 \mu_\alpha^{-2} (\phi_0^N \cdot \mathbf{V}_\alpha)(\phi_0^N \cdot \mathbf{V}_\alpha^*).$$

Comparing this expression with formal definition (15), one concludes that

$$F_\alpha = (\phi_0^N \cdot \mathbf{V}_\alpha)(\phi_0^N \cdot \mathbf{V}_\alpha^*). \tag{16}$$

The normalized flux density $\phi_0^N(s)$ can be also written with the help of the Dirichlet-to-Neumann operator as

$$\phi_0^N(s) = \frac{[\mathcal{M}\mathbf{1}](s)}{(\mathcal{M}\mathbf{1} \cdot \mathbf{1})}.$$

In the limit of an infinitely distant source, this density is still well defined, converging to the harmonic measure density. It means that, for a sufficiently large distance between the source and the working interface, the function $\phi_0^N(s)$ is essentially independent of this distance. Consequently, the coefficients F_α and the whole spectral decomposition (14) appropriately describe the macroscopic response of the working interface. One sees that, in the case of a distant source, the transport properties of the working interface are entirely characterized by a set of positive real numbers $\{\mu_\alpha, F_\alpha\}$ determined by the Dirichlet-to-Neumann operator, where μ_α are homogeneous to an inverse length and F_α are homogeneous to an inverse area (in particular, $F_0 = 1/S_{tot}$).

E. Spectroscopic impedance: A distant source at finite distance

The fact that the spectral components F_α are weakly dependent on the distance to the source suggests to use them even in the case of a finite distant source instead of previously defined coefficients $\widetilde{F}_\alpha$. In particular, one can rewrite the spectral decomposition (11) as

$$\Phi_\Lambda = \frac{\Phi_0^2}{DC_0} \sum_\alpha \frac{F_\alpha}{\mu_\alpha(1 + \Lambda \mu_\alpha)}. \tag{17}$$

In particular, this expression for $\Lambda = 0$ gives Φ_0 and allows one to calculate the access resistance R of the bulk:

$$\Phi_0 = DC_0 \left(\sum_\alpha \frac{F_\alpha}{\mu_\alpha}\right)^{-1} \quad \text{and} \quad R = \frac{1}{D} \sum_\alpha \frac{F_\alpha}{\mu_\alpha}. \tag{18}$$

Finally, it is convenient to represent the total working surface area S_{tot} as a similar spectral decomposition:

$$S_{tot} = \left(\frac{\Phi_0}{DC_0}\right)^2 \sum_\alpha \frac{F_\alpha}{\mu_\alpha^2}. \tag{19}$$

By analogy with electric problems, one can also define the spectroscopic impedance $Z_{sp}(\Lambda)$ of the working interface risen due to its surface resistance:

$$Z_{sp}(\Lambda) = \frac{C_0}{\Phi_\Lambda} - \frac{C_0}{\Phi_0}.$$

Using the definition (13) of the effective impedance, one simply rewrites this expression as

$$Z_{sp}(\Lambda) = \frac{Z(\Lambda)}{1 - R^{-1}Z(\Lambda)}. \tag{20}$$

When the distance between the source and the working interface is sufficiently high, the access resistance R is large, and the spectroscopic impedance is close to $Z(\Lambda)$. In what follows, we focus our attention on the effective impedance $Z(\Lambda)$, bearing in mind that one can always relate this quantity to the physically measured characteristics $Z_{sp}(\Lambda)$ according to Eq. (20).

The spectral decompositions (14) and (17) are the main relations in the present theoretical description of the Laplacian transport phenomena. Whatever the geometry of the diffusional or electrolytic cell (domain Ω), the macroscopic response of the working interface can be decomposed into a sum of simple elementary contributions defined by the spectral characteristics μ_α and F_α. Since these quantities are only determined by the geometry of the system, the decomposition (14) allows one to separate the physics and the geometry of the problem in an explicit way. Whatever the nature of the Laplacian transport phenomena (oxygen diffusion, electric transport, heterogeneous catalysis,...), the geometrical irregularity of the interface can be taken into account through a set of real positive numbers μ_α and F_α which can be thus called the "harmonic geometrical spectrum" of the interface.

Since this spectrum can be thought as "identity" of the working interface with respect to the Laplacian transport, its thorough study for several surfaces with "canonical" irregular geometry would certainly be useful. The examples of

interest would be a single pore, a pore lattice in 2D or 3D, deterministic self-affine or self-similar interfaces, a branched tree with diffusion and reaction on the surface as the pulmonary acinus. The importance of such "canonical" cases is related to the fact that random and deterministic fractal surfaces with the same dimension transfer the diffusing particles very much in a similar way [33].

F. Spectral characteristics

As we mentioned above, the normalized flux density $\phi_0^N(s)$ converges to the density of the harmonic measure on the working interface $\partial\Omega$, when the source goes to infinity. It means that $\phi_0^N(s)ds$ is the conditional probability that the Brownian motion started from the source $\partial\Omega_0$ hits the working interface for the first time in ds vicinity of the boundary point s, without returning to the source. Consequently, the coefficients F_α can be called the "spectral components" of the harmonic measure density since they describe the spectral decomposition of this density on the eigenbasis $\{\mathbf{V}_\alpha\}$ of the Dirichlet-to-Neumann operator. In other words, F_α is the weight of the corresponding eigenfunction $\mathbf{V}_\alpha$ projected onto the harmonic measure density ("compared" with ϕ_0^N).

The Perron-Frobenius theorem allows one to show that the eigenfunction $\mathbf{V}_0(s)$ (corresponding to the lowest eigenvalue μ_0) is a positive function. For instance, if the source is at infinity, it is a constant. The orthogonality of eigenmodes implies that the other eigenfunctions $\mathbf{V}_\alpha(s)$ (with $\alpha > 0$) must oscillate around zero along the working interface $\partial\Omega$ (for the source at infinity, the integral of the other eigenfunctions over the working interface is strictly zero). Roughly speaking, the Dirichlet-to-Neumann operator has "oscillating" eigenmodes of "spatial frequencies" increasing with α (or μ_α). For example, if one considers a circular ring $\Omega = \{x \in \mathbb{R}^2 : 1 < |x| < 1+h\}$ (with $h \gg 1$), the eigenfunctions of the Dirichlet-to-Neumann operator are Fourier harmonics $e^{i\alpha s}$, and the spatial frequencies are equal to α and very close to μ_α [20]. In the general case, one can say that the eigenvalues μ_α, being homogeneous to an inverse length, provide the information about the "spatial frequencies" of corresponding eigenmodes. An apparent similarity to Fourier harmonics suggests that we think of the eigenmodes of the Dirichlet-to-Neumann operator as the "pseudo-Fourier-basis." In other words, each interface "generates" its own eigenbasis of $L^2(\partial\Omega)$, particularly adapted to describe the Laplacian transport phenomena.

Since the Dirichlet-to-Neumann operator is unbounded, the spectral decompositions (14) and (17) contain, in general, an infinitely large number of terms. However, these terms are *weighted* by the spectral components $\{F_\alpha\}$, i.e., different eigenmodes bring different contributions to the effective impedance $Z(\Lambda)$ or the total flux Φ_Λ. The fact that $\{F_\alpha\}$ correspond to the projections of the harmonic measure density onto *oscillating* eigenfunctions $\mathbf{V}_\alpha$ implies that the contributions of eigenmodes with high spatial frequencies vanish. Quantitatively, if ℓ is the smallest geometrical feature of the boundary, the harmonic measure density varies slowly on scales smaller than ℓ, and there is almost no contribution of eigenmodes with $\mu_\alpha \gg \ell^{-1}$. Consequently, the Laplacian transport towards arbitrarily irregular surface with a finite minimal cutoff ℓ can mostly be described by a *finite* number of contributing terms. More generally, since the characteristic scales of an irregular boundary are represented in the behavior of the harmonic measure density, one may think about certain type of "resonant" effect at spatial frequencies corresponding to the geometrical scales of the working electrode.

G. Link with the discrete approach

An important feature of the present approach is that the use of the Dirichlet-to-Neumann operator allows one to study the originally continuous problem (1) without auxiliary intermediate steps (discretization and passage to continuous limit). It allows one to avoid difficult mathematical problems of the continuous limit that had been risen for the discrete approach. Moreover, apparent similarities between the discrete and continuous descriptions indicate that the Dirichlet-to-Neumann operator $\mathcal{M}$ is the continuous limit of a sequence of the discrete operators $(I-Q^a)/a$.

At the same time, it should be stressed that the probabilistic vision of diffusing particles becomes mathematically more difficult. Intuitively, one can think about a limiting stochastic process of partially reflected random walks on the lattice with vanishing mesh a. The sticking probability $(1-\varepsilon)$ decreases linearly with a being proportional to $1/\Lambda$ according to Eq. (4). Consequently, the displacements of random walks become smaller and smaller, but the average number of reflections grows. One may expect that these effects are mutually compensated leading to a well defined stochastic process in the limit $a \to 0$. A rigorous definition of this so-called "partially reflected Brownian motion" (PRBM) is given in Refs. [20,34]. Although this probabilistic picture is not so transparent as for the discrete case, the study of the PRBM provides a subtle information about stochastic trajectories of diffusing particles [35].

IV. THE ELECTROCHEMICAL PROBLEM: AN EXACT EQUIVALENT CIRCUIT

Although the notion of diffusing "species" has no more sense for the secondary current distribution in electrochemistry, the above results shed a new light in this field. Please note that we are not considering here the problem known as that of the diffusion impedance in electrochemistry [36,37], but we use the formal mathematical analogy between the diffusional and electrochemical problems.

Here, one has to replace the "diffusional" quantities by "electrochemical" ones: the concentration of particles C on the source becomes the amplitude V_0 of the applied electric potential, the diffusion coefficient D is replaced by the inverse of the electrolyte resistivity ρ, while the membrane permeability W is replaced by the inverse of the surface impedance ζ. In particular, one obtains $\Lambda = \zeta/\rho$. The total electric current Φ_Λ is conventionally normalized by the applied potential V_0 to give the admittance (or conductance) of the electrolytic cell

$$Y(\Lambda) = \frac{\rho}{R^2} \sum_\alpha \frac{F_\alpha}{\mu_\alpha(1 + \Lambda\mu_\alpha)}, \qquad (21)$$

where $R = V_0/\Phi_0$ stands for the access resistance of the electrolyte. At the same time, one could simply rewrite the spectral decomposition (14) for the effective impedance by replacing D by ρ^{-1}:

$$Z(\Lambda) = \rho\Lambda \sum_\alpha \frac{F_\alpha}{1 + \Lambda\mu_\alpha}. \qquad (22)$$

The surface impedance ζ characterizes the local transport properties of the electrolyte double layer near the working electrode. Often, these properties can be described by a surface capacitance γ and surface resistance r connected in parallel, whence $\zeta = (-i\omega\gamma + 1/r)^{-1}$, where ω is the frequency of the applied potential. Note that such form of the surface impedance leads to a complex-valued parameter Λ (being still homogeneous to a length). For the static problem ($\omega = 0$), one simply has $\zeta = r$. In general, whatever the dependence of the surface impedance ζ with respect to ω, one can still use the spectral decomposition (21) for the admittance in order to take into account the geometrical irregularity of the working electrode.

An experimental study of the impedance spectroscopy of macroscopically irregular electrodes has been recently undertaken to validate this approach [38]. For this purpose, we measured the following physical quantities: the electrolyte resistivity ρ, the surface impedance $\zeta(\omega)$ of a flat brass electrode, and the spectroscopic impedance $Z_{\exp}(\omega)$ of the studied brass electrodes (first generations of the Von Koch surface). This last one was then compared to its theoretical prediction by Eq. (22) in which the harmonic geometrical spectrum $\{\mu_\alpha, F_\alpha\}$ was calculated numerically for the considered macroscopic geometries [20]. The preliminary results showing a good agreement between the theory and experiment was announced in Ref. [38] and will be published in detail in a forthcoming paper.

An important practical consequence of the spectral decomposition (21) is the possibility to derive an *exact* equivalent electric scheme for an electrolytic cell of arbitrary geometry of electrodes. By introducing a set of resistances R_α and areas S_α according to

$$R_\alpha = \rho\left(\frac{R}{\rho}\right)^2 \frac{\mu_\alpha}{F_\alpha}, \qquad S_\alpha = \left(\frac{\rho}{R}\right)^2 \frac{F_\alpha}{\mu_\alpha^2} \qquad (23)$$

one can rewrite Eq. (21) as

$$Y(\omega) = \sum_\alpha \frac{1}{R_\alpha + \zeta(\omega)/S_\alpha}, \qquad (24)$$

i.e., the admittance $Y(\omega)$ is represented as a sum of admittances

$$Y_\alpha(\omega) = \frac{1}{R_\alpha + \zeta(\omega)/S_\alpha}$$

connected between them in parallel. Consequently, the electrolytic cell has exactly the same macroscopic response as the electric circuit composed of a parallel connection of the
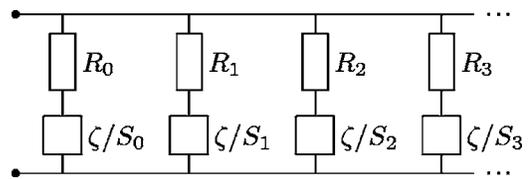
FIG. 2. Equivalent electric scheme for an electrolytic cell constitutes a parallel connection of transmission lines "resistance R_α + linear element ζ/S_α" (characterized by the surface impedance ζ). Depending on the local transport properties of the electrolyte double layer near the working electrode, the linear element can be purely resistive ($\zeta = r$), purely capacitive [$\zeta = (i\gamma\omega)^{-1}$], their combination [$\zeta = (i\gamma\omega + 1/r)^{-1}$] or a more complex electrochemical element.

following transmission lines: the resistance R_α in series with the linear element $\zeta(\omega)/S_\alpha$ characterized by the surface impedance $\zeta(\omega)$ (see Fig. 2). For the static problem (if $\zeta = r$), this linear element is simply another resistance. Since the electrochemical cell, as a two-pole electric circuit, can be represented by an electric network of resistances and capacitors [39,40], our approach permits to compute exactly the constitutive elements of such equivalent circuit.

Writing relations (18) and (19) in terms of R_α and S_α, one obtains

$$R^{-1} = \sum_\alpha R_\alpha^{-1}, \qquad S_{\text{tot}} = \sum_\alpha S_\alpha. \qquad (25)$$

It means that the Dirichlet-to-Neumann operator provides a specific *partition* of the total electrolyte resistance R into a set of resistances R_α connected in parallel, and of the total surface area S_{tot} of the working electrode into a set of areas S_α.

In order to give a physical interpretation of this partition, we first consider a flat working interface when the harmonic geometrical spectrum can be calculated explicitly. In this case, the only contributing eigenmode is the lowest one ($\alpha = 0$), with $\mu_0 = 1/h$ and $F_0 = 1/S_{\text{tot}}$, where h is the distance between the source (counter-electrode) and the working interface. Since the other spectral components F_α are equal to 0, one obtains $R_\alpha^{-1} = 0$ and $S_\alpha = 0$ for $\alpha > 0$. The relations (25) lead then to $R_0 = R$ and $S_0 = S_{\text{tot}}$. In particular, one retrieves the classical relation for the bulk resistance of a conducting material between two flat boundaries: $R = \rho h/S_{\text{tot}}$. This result is related to the fact that the equipotential surfaces of the electric potential inside the electrolytic cell are parallel to both flat boundaries. The admittance $Y(\omega)$ of this electrolytic cell can be thus written as

$$Y_{\text{flat}}(\omega) = \frac{S_{\text{tot}}}{\rho h + \zeta(\omega)},$$

i.e., each surface element ds gives the same contribution $ds[\rho h + \zeta(\omega)]^{-1}$ to the admittance.

In a general case, the equipotential surfaces are not parallel to the working interface and the source, and the contributions of different surface elements are not equal as they are dependent on their locations on the working interface. In order to calculate the admittance of the electrolytic cell, one

may think to gather uniformly working surface elements into "groups." The surface area of each "group" would measure its relative contribution to the admittance. This way of thinking leads us directly to the partition of the total surface area S_{tot} into specific areas S_α determined by the Dirichlet-to-Neumann operator. The spectral decomposition (24) of the admittance is then understood as a parallel connection of different "groups" characterized by their admittances

$$Y_\alpha(\omega) = \frac{1}{R_\alpha + \zeta(\omega)/S_\alpha}.$$

Using the definitions (23), it is convenient to write the resistances R_α in the form of the classical relation for the bulk resistance for flat boundaries

$$R_\alpha = \rho \mu_\alpha^{-1}/S_\alpha,$$

where $\{\mu_\alpha^{-1}\}$ correspond to different length scales of the working interface. One obtains

$$Y_\alpha(\omega) = \frac{S_\alpha}{\rho\mu_\alpha^{-1} + \zeta(\omega)}.$$

Qualitatively, one may think that the electrolytic cell is composed of a number of simple "blocks" of height μ_α^{-1} and area S_α, with surface resistance $\zeta(\omega)$. The harmonic geometrical spectrum determines the corresponding partition of the total surface area in a *unique* way. At the same time, it does not provide a means to locate the positions of the specific areas S_α onto the working interface.

We would like to mention another curious remark. For an irregular interface, one may intuitively expect to have a contribution from each length varying continuously. In this case, the admittance of the electrolytic cell would be the integral of these contributions. In reality, however, there is only a discrete set $\{\mu_\alpha^{-1}\}$ of lengths contributing to the macroscopic response according to Eq. (24).

In the particular case of a source at infinite distance, one has to use the spectroscopic or effective impedance instead of the admittance. A similar analysis for the effective impedance $Z(\Lambda)$ provides an equivalent electric scheme corresponding to the following representation:

$$Z(\omega) = \sum_\alpha \frac{1}{\dfrac{1}{\tilde{R}_\alpha} + \dfrac{1}{\zeta(\omega)/\tilde{S}_\alpha}},$$

where a new set of resistances $\tilde{R}_\alpha$ and areas $\tilde{S}_\alpha$ is introduced:

$$\tilde{R}_\alpha = \rho\frac{F_\alpha}{\mu_\alpha}, \qquad \tilde{S}_\alpha = \frac{1}{F_\alpha}.$$

As expected, these quantities do not depend on the access resistance R, being intrinsic characteristics of the working interface. They obey the following relations:

$$R = \sum_\alpha \tilde{R}_\alpha, \qquad S_{tot}^{-1} = \sum_\alpha \tilde{S}_\alpha^{-1}.$$

The corresponding electric scheme is shown on Fig. 3. Since the *infinitely* distant source is merely a convenient theoretical
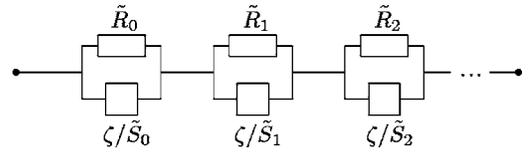
FIG. 3. Equivalent electric scheme for the working interface constitutes a series connection of transmission lines "resistance $\tilde{R}_\alpha$+linear element $\zeta/\tilde{S}_\alpha$" (characterized by the surface impedance ζ). Depending on the local transport properties of the electrolyte double layer near the working electrode, the linear element can be purely resistive ($\zeta=r$), purely capacitive [$\zeta=(i\gamma\omega)^{-1}$], their combination [$\zeta=(i\gamma\omega+1/r)^{-1}$], or a more complex electrochemical element.

abstraction, we do not discuss in details a potential physical interpretation of this scheme.

The present approach resolves thus the long standing problem of finding an equivalent electric scheme to describe the behavior of a given electrochemical cell. It may be also seen as a mathematical basis for developing approximate schemes which are used to predict the electrochemical response of some irregular electrodes [9,41], or to fit the experimental data in electrochemical measurements (e.g., Voigt model) [42,43].

V. CONCLUSION

In this paper, we have addressed the transport processes governed by Laplacian fields in the vicinity of irregular interfaces. This problem is known to be crucial in physiology, electrochemistry, and heterogeneous catalysis. The Dirichlet-to-Neumann operator is introduced to properly identify the influence of a geometrical irregularity on the physical properties of the system. The spectral characteristics μ_α and F_α of this operator contain all the information about the system geometry that is needed to reconstruct its transport properties. As a practical consequence, an exact equivalent electric circuit is associated to an electrolytic or diffusional cell of a given geometry. The eigenvalues μ_α correspond to "spatial frequencies" of eigenmodes, while the spectral components F_α of the harmonic measure density stand to weigh the contributions of each eigenmode α to the total flux or effective impedance. The important point is that as the harmonic measure density behaves relatively smoothly on irregular or even prefractal boundaries (presenting only integrable singularities), the scalar product with the eigenfunctions of high spatial frequencies rapidly vanishes. The consequence is that only a few eigenmodes contribute to the macroscopic response and the equivalent circuit. This is a drastic simplification of the problem.

Its practical application in electrochemistry would be a promising perspective to disentangle the respective roles of geometry and intrinsic electrochemical characteristics of the working electrode. This approach has been recently validated by impedance spectroscopy of prefractal electrodes [38]. The knowledge of the geometrical influence on transport properties seems to be helpful for an optimal design of efficient

catalysts in chemical engineering.

The very fact that only few eigenmodes determine entirely the exchange properties of an irregular surface opens for the future an interesting field of study. It would certainly be useful to list the first eigenmodes for several surfaces with "canonical" irregular geometry. The examples of interest would be a single pore, a pore lattice in 2D or 3D, deterministic self-affine or self-similar interfaces, a branched tree with diffusion and reaction on the surface as the pulmonary acinus.

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[1] B. Sapoval, in *Fractals and Disordered Systems*, edited by A. Bunde and S. Havlin (Springer, Berlin, 1996), p. 233.

[2] E. R. Weibel, *The Pathway for Oxygen. Structure and Function in the Mammalian Respiratory System* (Harvard University Press, Cambridge, MA, 1984).

[3] R. de Levie, Electrochim. Acta **10**, 113 (1965).

[4] R. D. Armstrong and R. A. Burnham, J. Electroanal. Chem. Interfacial Electrochem. **72**, 257 (1976).

[5] A. Le Méhauté and G. Crepy, C. R. Seances Acad. Sci., Ser. 2 **294**, 685 (1982).

[6] L. Nyikos and T. Pajkossy, Electrochim. Acta **30**, 1533 (1985).

[7] S. H. Liu, Phys. Rev. Lett. **55**, 529 (1985).

[8] B. Sapoval, Solid State Ionics **23**, 253 (1987).

[9] M. Keddam and H. Takenouti, Electrochim. Acta **33**, 445 (1988).

[10] T. C. Halsey, Phys. Rev. A **35**, 3512 (1987).

[11] T. C. Halsey and M. Leibig, Europhys. Lett. **14**, 815 (1991).

[12] T. C. Halsey and M. Leibig, Electrochim. Acta **36**, 1699 (1991).

[13] T. C. Halsey and M. Leibig, Ann. Phys. (N.Y.) **219**, 109 (1992).

[14] M. Leibig and T. C. Halsey, J. Electroanal. Chem. **358**, 77 (1993).

[15] B. Sapoval, Phys. Rev. Lett. **73**, 3314 (1994).

[16] B. Sapoval, M. Filoche, and E. R. Weibel, Proc. Natl. Acad. Sci. U.S.A. **99**(16), 10411 (2002).

[17] M. Felici, M. Filoche, and B. Sapoval, J. Appl. Physiol. **94**, 2010 (2003).

[18] M. -O. Coppens, Catal. Today **53**, 225 (1999).

[19] M. Rosso, Y. Huttel, E. Chassaing, B. Sapoval, and R. Gutfraind, J. Electrochem. Soc. **144**, 1713-1717 (1997).

[20] D. S. Grebenkov, Ph.D. thesis, Ecole Polytechnique, France, 2004, http://pmc.polytechnique.fr/pagesperso/dg/phd/these.pdf

[21] M. Felici, M. Filoche, C. Straus, T. Similowski, and B. Sapoval, Respir. Physiol. **145**, 279 (2005).

[22] M. Filoche and B. Sapoval, Eur. Phys. J. B **9**, 755 (1999).

[23] D. S. Grebenkov, M. Filoche, and B. Sapoval, Eur. Phys. J. B **36**, 221 (2003).

[24] A. Kirsch, *An Introduction to the Mathematical Theory of Inverse Problems*, Vol. 120 of Applied Mathematical Sciences (Springer, New York, 1996).

[25] W. Craig and S. Sulem, J. Comput. Phys. **108**, 73 (1993).

[26] D. M. Milder, Radio Sci. **31**, 1369 (1996).

[27] T. Y. Hou, J. S. Lowengrub, and M. J. Shelly, J. Comput. Phys. **169**, 302 (2001).

[28] A. Friedman and V. Isakov, Indiana Univ. Math. J. **38**, 563 (1989).

[29] D. P. Nicholls and F. Reitich, J. Comput. Phys. **170**, 276 (2001).

[30] P. Guidotti, J. Comput. Phys. **190**, 325 (2003).

[31] M. S. Agranovich, in *Partial Differential Equations IX*, edited by M. S. Agranovich, Yu. V. Egorov, and M. S. Shubin, EMS 79 (Springer, Berlin, 1997).

[32] M. S. Birman, M. Z. Solomyak, *Spectral Theory of Self-Adjoint Operators in Hilbert Space* (Reidel, Dordrecht, 1987).

[33] M. Filoche and B. Sapoval, Phys. Rev. Lett. **84**, 5776 (2000).

[34] D. S. Grebenkov, Fractals (in press).

[35] B. Sapoval, J. S. Andrade Jr, A. Baldassari, A. Desolneux, F. Devreux, M. Filoche, D. S. Grebenkov, and S. Russ, Physica A **357**, 1 (2005).

[36] L. Nyikos and T. Pajkossy, Electrochim. Acta **31**, 1347 (1986).

[37] B. Sapoval, J. -N. Chazalviel, and J. Peyrière Phys. Rev. A **38**, 5867 (1988).

[38] D. S. Grebenkov, E. Chassaing, M. Filoche, and B. Sapoval, in Proceedings of the 17th Forum of Electrochemical Impedances (Paris, 2005).

[39] A. Lasia, in *Modern Aspects of Electrochemistry*, edited by B. E. Conway, J. Bockris, and R. E. White (Kluwer, New York, 1999), Vol. 32, pp. 143–248.

[40] W. H. Chen, *Linear Network Design and Synthesis* (McGraw-Hill, New York, 1964).

[41] B. Sapoval, R. Gutfraind, P. Meakin, M. Keddam, and H. Takenouti, Phys. Rev. E **48**, 3333 (1993).

[42] P. Agarwal, M. E. Orazem, and L. H. Garcia-Rubio, J. Electrochem. Soc. **139**, 1917 (1992).

[43] P. Agarwal, M. E. Orazem, and L. H. Garcia-Rubio, J. Electrochem. Soc. **142**, 4159 (1995).

[44] When the source is placed at infinity, the solution of the Dirichlet problem (6) with the constant boundary condition $u = 1$ is equal to 1, and its normal derivative on the boundary is 0, i.e., $\mathcal{M}\mathbf{1} = 0$. Consequently, whatever the domain Ω, the constant $\mathbf{1}$ is the eigenfunction of the Dirichlet-to-Neumann operator with the eigenvalue $\mu_0 = 0$.