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Can one hear the shape of an electrode?
II. Theoretical study of the Laplacian transfer

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Abstract. The flux across resistive irregular interfaces driven by a force deriving from a Laplacian potential is computed on a rigorous basis. The theory permits one to relate the size of the active zone $A_{\text{act.}}$ to the derivative of the spectroscopic impedance $Z_{\text{spect.}}(r)$ with respect to the surface resistivity r through: $\mathrm{d}(Z_{\text{spect.}})/\mathrm{d}r = A_{\text{act.}}^{-1}$. It is shown that the macroscopic transfer properties through a system of arbitrary shape are determined by the characteristics of a *first-passage interface-interface random walk operator*. More precisely, it is the distribution of the harmonic measure (or normalized primary current) on the eigenmodes of this linear operator that controls the transfer. In addition, it is also shown that, whatever the dimension, the impedance of a weakly polarizable electrode for any irregular geometry scales under a homothety transformation as L^{d-1}, L being the size of the system and d its topological dimension. In this new formalism, the question addressed in the title is transformed in a open mathematical question: "Knowing the distribution of the harmonic measure on the eigenmodes of the self-transport operator, can one retrieve the shape of the interface?"

PACS. 05.40.+j Fluctuation phenomena, random processes, and Brownian motion – 61.43.Hv Fractals; macroscopic aggregates (including diffusion-limited aggregates) – 41.20.Cv Electrostatics; Poisson and Laplace equations, boundary-value problems

1 Introduction

The problem of transfer across irregular interfaces driven by Laplacian fields is a fundamental theoretical frame for systems in many different fields (electrochemistry, heterogeneous catalysis, NMR relaxation in porous media, transfer across biological membranes, ...). This problem can be stated in two ways: first, measuring the geometry and the transport parameters, can one compute the net flux across the system? Second, knowing the net flux across the system, can one retrieve the shape of the working interface?

In the work described in the preceding paper [1], a first answer to this question has been given. By transforming it in a purely mathematical problem named "problem I". In the present paper, a rigorous formulation of the Laplacian transfer is achieved, based on the exact correspondence between the electrode problem and a steady-state diffusion problem in the same geometry. This theory will lead us to formulate another mathematical problem, called "problem II".

The exact correspondence is illustrated in Figure 1 [2,3]. In the case of current through an electrochemical interface, the response is governed by the resistivity ρ of the electrolyte and by the interface resistivity r. The transport equation in the volume away from the surface is $\mathbf{J} = -\nabla V/\rho$, where $\mathbf{J}$ is the vector current in the electrolyte and the electric potential V obeys the Laplace equation $\Delta V = 0$ in the bulk of the electrolyte. Due to charge conservation, the boundary condition is obtained by stating that the normal current j_{n} coming from the bulk of the solution $(-\nabla_{\mathrm{n}} V/\rho)$, is equal to the current V/r crossing the electrode surface.

This problem is mathematically equivalent to the study of bulk and membrane diffusion in the same geometry. In this case, the flux of a neutral species across a membrane is limited both by the diffusion from the source and the finite rate of transfer across the membrane. The transport process can be described in terms of the vector flux $\boldsymbol{\Phi}$ at coordinate x. There are two flux processes in our system. First, there is bulk diffusion which obeys Fick's law, $\boldsymbol{\Phi} = -D\nabla C$, where C is the concentration of the particles of interest and D the diffusion coefficient. Secondly, there is a transfer equation across the membrane which obeys the equation $\boldsymbol{\Phi}_{\mathrm{n}} = -WC$, where W is the probability per unit time, surface, and concentration for a particle to cross the membrane. In the last equation, we have neglected back transfer, supposing that the concentration on the other side of the membrane is kept equal to zero. The conservation of the normal flux at the frontier can be written $C/\nabla_{\mathrm{n}} C = D/W = \Lambda$. In

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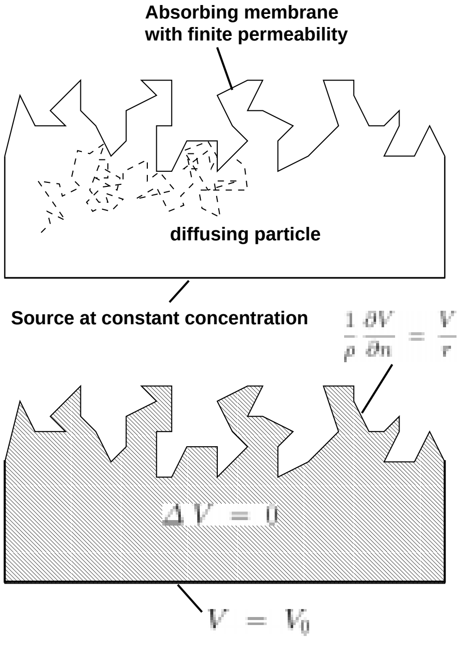

Fig. 1. Equivalence between electric and diffusion equations: the probability for a diffusing particle to be absorbed on a partially absorbing boundary (upper figure) is given by the solution of the Laplace equation on the same geometry with mixed boundary conditions on the absorbing boundary.

the steady state, the concentration satisfies the stationary diffusion equation $\Delta C = 0$. These equations are exactly equivalent to the current and potential equations provided that we exchange $\boldsymbol{\Phi}$ for $\mathbf{J}$, $-\nabla C$ for $-\nabla V$, D for ρ^{-1} and W for r^{-1}. Then it is possible to define a diffusion impedance Z_{D} of the cell by a relation between the total flux Ψ and the constant concentration C_{s} on the source: $\Psi = C_{\mathrm{s}}/Z_{\mathrm{D}}$.

2 General formulation

The diffusion equivalence is now used to calculate the impedance of the polarizable electrode. The following discussion is inspired by the papers of Halsey and Leibig, Ball, and Ruis-Estrada *et al.* [4–6]. The process is described schematically in Figure 2. We consider particles diffusing in a d-dimensional medium (over a simple hypercubic lattice) from a flat counter electrode called S (the Source) to an irregular working interface called M (the Membrane), so that we can approximate their trajectories with random walks. The interface here has a topological dimension equal to $d-1$ ($d = 2$ in Fig. 2).

In our picture, particles jump at random on the lattice with parameter a and at a hopping rate of one event per unit time τ. The concentration on the source C_{s} is related to the site occupation probability on the source p_{s} by

$$C_{\mathrm{s}} = \frac{p_{\mathrm{s}}}{a^d} \cdot \tag{1}$$

If a random walker attempts to step onto a site j belonging to the working electrode, the walk is terminated with a probability σ (the absorption or sticking probability) or is reflected with a probability $\varepsilon = 1 - \sigma$. If the source S is modelized as a set of s starting sites and the membrane M as a set of m arrival sites, two sets of probabilities can be defined:

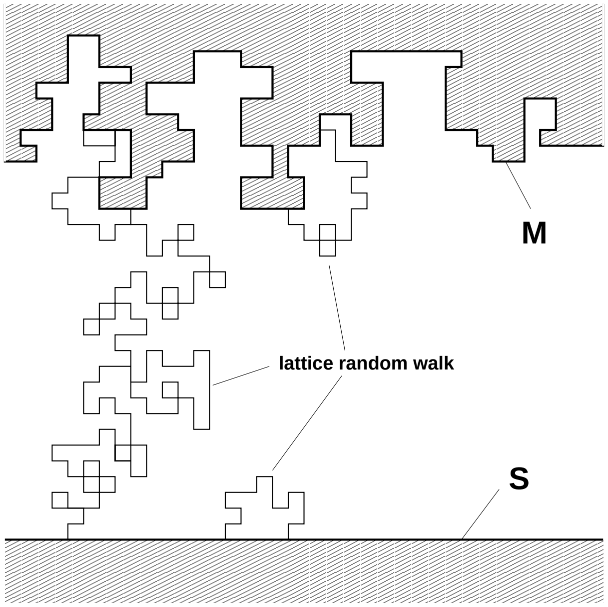

Fig. 2. Schematic representation of the lattice diffusion that we compute.

- p_{ij} = probability to land at first hit on site j of the *working* electrode M (membrane with m sites) when starting from site i of the *counter* electrode (source with s sites), $(1 \le i \le s, 1 \le j \le m)$.
- q_{jk} = probability to land at first hit on site k of the working electrode when starting from site j of the *working* electrode without touching to the *counter* electrode. $(1 \le j \le m, 1 \le k \le m)$.

Due to the reversibility property of the random walks, the probability to go from any site i to any site j is equal to the probability to go from site j to site i. Especially, $q_{jk} = q_{kj}$.

The general trajectory of a particle starting from S and being finally absorbed anywhere on M can then be described by the following successive events (Fig. 3):

- going from i on S to j on M with probability p_{ij},
- either being absorbed on j on M: probability $1-\varepsilon$ (end of the walk),
- or if not absorbed (probability ε), going from j to k on M without coming back to S: probability q_{jk}
- again either being absorbed on k on M: probability $1-\varepsilon$ (end of the walk),
- or if not absorbed, etc.

If the hopping rate equals to $1/\tau$ and if the sticking probability is equal to 1, the total flux can be written as:

$$\Phi(\sigma = 1) = \frac{c_{\mathrm{s}} a^d}{\tau} \sum_{i \in S,\ j \in M} p_{ij}. \tag{2}$$

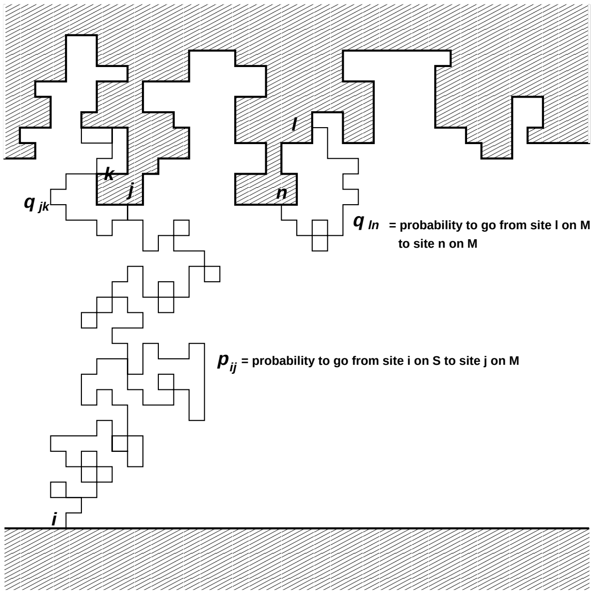

Fig. 3. Iterative process for a particle starting from the counter electrode S and being absorbed on the working electrode M after several reflections of probability ε.

The probability for a particle starting *anywhere* on the counter electrode to land at first hit on site j of the working electrode can be written:

$$P_{0,j} = \sum_{i \in S} p_{ij}. \tag{3}$$

A closing relation between the probabilities $(P_{0,j})$ and (q_{jk}) can also be written: for every site j on the electrode M, a random walker starting from j has to land either on M or on S. This can be translated into:

$$\forall j \in M, \quad P_{0,j} + \sum_{k \in M} q_{jk} = 1. \tag{4}$$

For $\varepsilon = 0$ (or $\sigma = 1$), the total flux is:

$$\Phi(\varepsilon = 0) = \frac{c_{\rm s}}{Z_{\rm cell}(\varepsilon = 0)} = \frac{c_{\rm s} a^d}{\tau} \left(\sum_j P_{0,j} \right). \tag{5}$$

This equation gives the value of the bulk admittance $R_0 = Z_{\rm cell}(0)$.

When the sticking probability smaller than 1, a particle starting from the counter electrode will contribute to the total flux if it is absorbed with probability $\sigma = (1-\varepsilon)$ at one of its collisions on the working electrode.

For a particle starting anywhere on the counter electrode, the probability of being absorbed on site j at *first* contact is $P_{0,j}\ (1-\varepsilon)$. The probability of being absorbed on site j after exactly *one* reflection anywhere on the working electrode can be written as:

$$\sum_{k \in M} P_{0,k} \varepsilon q_{kj}\, (1-\varepsilon).$$

More generally, the probability for a particle to be absorbed after exactly n reflections on the working electrode is:

$$\sum_{k_1,\dots,k_n} P_{0,k_1} \varepsilon q_{k_1 k_2}\ \varepsilon\ \dots\ q_{k_{n-1}k_n} \varepsilon q_{k_n j}\, (1-\varepsilon).$$

Thus, the total probability $P_{\varepsilon,j}$ of being finally absorbed at site j is the sum of the probabilities to be absorbed after 0, 1, ..., n, ... reflections on the electrode:

$$P_{\varepsilon,j} = \sum_{n=0}^{\infty} \sum_{k_1,\dots,k_n} P_{0,k_1} \varepsilon q_{k_1,k_2} \varepsilon \dots q_{k_{n-1}k_n} \varepsilon q_{k_n j} (1-\varepsilon). \tag{6}$$

Using these probabilities which represent the contribution of each site to the flux across the working electrode, the total flux of particles from S to M can be written as:

$$\Phi(\sigma = 1-\varepsilon) = \frac{c_{\rm s}}{Z_{\rm cell}(\varepsilon)} = \frac{c_{\rm s} a^d}{\tau} \sum_j P_{\varepsilon,j} \tag{7}$$

where these $P_{\varepsilon,j}$ represent the probabilities for a particle starting anywhere on the source to be finally absorbed on the working electrode, taking into account possible rebounds on the working electrode with probability ε.

A new vectorial formalism is now introduced: one defines a m-vector $\mathbf{P}_0$ as $(P_{0,j})_{(1 \le j \le m)}$, and a $m \times m$ matrix $\widetilde{Q}$ as $(q_{jk})_{(1 \le j \le m, 1 \le k \le m)}$. A remarkable property of this matrix (or operator) $\widetilde{Q}$ is that it is positive and symmetrical, due to properties of random walks: the probability to reach site k when starting from site j is the same as the probability to reach j when starting from k, and is never negative. Defining $\mathbf{1}$ as the m-vector $\underbrace{(11\dots1)}_{m \text{ times}}$ allows us to rewrite equation (4) as:

$$\mathbf{P}_0 = (I - \widetilde{Q})\mathbf{1}. \tag{8}$$

Equation (6) can now be expressed in a vectorial way:

$$\mathbf{P}_\varepsilon = (1-\varepsilon) \left(\sum_{n=0}^{\infty} \varepsilon^n\ \widetilde{Q}^n \right) \mathbf{P}_0. \tag{9}$$

One introduce another symmetrical operator, called $\widetilde{T}_\varepsilon$, which links $\mathbf{P}_\varepsilon$ to $\mathbf{P}_0$. This operator is:

$$\widetilde{T}_\varepsilon = (1-\varepsilon)(I - \varepsilon \widetilde{Q})^{-1}. \tag{10}$$

The total flux can finally be expressed as a scalar product [7]:

$$\Phi(\varepsilon) = \frac{c_{\rm s} a^d}{\tau}\ \mathbf{P}_\varepsilon \cdot \mathbf{1} = \frac{c_{\rm s} a^d}{\tau}\ (\widetilde{T}_\varepsilon \mathbf{P}_0) \cdot \mathbf{1}. \tag{11}$$

In the case of absorption at first hit ($\varepsilon = 0$), the operator $\widetilde{T}_0$ is simply the identity operator ($\widetilde{T}_0 = I$) and $\mathbf{P}_\varepsilon (= \mathbf{P}_0)$ represents the landing probabilities on the working electrode. It is proportional to the current densities flowing through the working electrode with Dirichlet boundary condition (also called the *primary current distribution* in electrochemistry).

In the general case ($\varepsilon > 0$), the vector $\mathbf{P}_\varepsilon = \widetilde{T_\varepsilon}\mathbf{P}_0$ can be interpreted as the current densities with reflection probability equal to ε. This is defined in electrochemistry as the *secondary current distribution*.

The behavior of the system is then characterized by the symmetrical positive $(m \times m)$ matrix $\widetilde{Q}$, which represents the transport probabilities from M to M through the bulk medium without any intermediate collision on M. It can then be called the *self-transport operator* of M. In this picture, $\widetilde{T}_\varepsilon$ would be a *screening* operator, transforming the "initial" landing probabilities $\mathbf{P}_0$ into $\mathbf{P}_\varepsilon$.

3 Spectroscopic impedance

From $\Phi_{\sigma=1-\varepsilon}$ and $\Phi_{\sigma=1}$, one can compute the *spectroscopic impedance* $Z_{\text{spect.}}(\varepsilon)$, defined in the previous paper as the difference between the total impedance of the cell with reflection probability ε and the impedance of the cell when the electrode is purely absorbing ($\varepsilon = 0$) [1]. It is expressed as

$$Z_{\text{spect.}}(\varepsilon) = Z_{\text{cell}}(\varepsilon) - R_0, \tag{12}$$

or, using the probability vectors $\mathbf{P}_0$ and $\mathbf{P}_\varepsilon$:

$$Z_{\text{spect.}}(\varepsilon) = \frac{\tau}{a^d}\left(\frac{1}{\mathbf{P}_\varepsilon \cdot \mathbf{1}} - \frac{1}{\mathbf{P}_0 \cdot \mathbf{1}}\right)\cdot \tag{13}$$

At this stage, it is convenient to notice the following identity, using equation (8) and the expression of $\widetilde{T_\varepsilon}$ given in equation (10):

$$\begin{aligned}(\mathbf{P}_0 - \mathbf{P}_\varepsilon)\cdot \mathbf{1} &= \varepsilon\left((I-\widetilde{Q})(I-\varepsilon\widetilde{Q})^{-1}\mathbf{P}_0\right)\cdot \mathbf{1}\\ &= \frac{\varepsilon}{1-\varepsilon}\,(\mathbf{P}_\varepsilon \cdot \mathbf{P}_0).\end{aligned} \tag{14}$$

Using this, we deduce the value of the electrode impedance:

$$Z_{\text{spect.}}(\varepsilon) = \frac{\tau}{a^d}\frac{\varepsilon}{1-\varepsilon}\frac{\mathbf{P}_\varepsilon \cdot \mathbf{P}_0}{(\mathbf{P}_\varepsilon \cdot \mathbf{1})(\mathbf{P}_0 \cdot \mathbf{1})}\cdot \tag{15}$$

"Normalized" probabilities $\mathbf{P}_{N,\varepsilon}$ are now introduced: they are proportional to the probabilities $\mathbf{P}_\varepsilon$ with the following normalization condition:

$$\sum_j P_{N,\varepsilon,j}\; a^{d-1} = a^{d-1}(\mathbf{P}_{N,\varepsilon}\cdot \mathbf{1}) = 1. \tag{16}$$

In other words, the probability vector

$$\mathbf{P}_{N,\varepsilon} = \frac{\mathbf{P}_\varepsilon}{a^{d-1}(\mathbf{P}_\varepsilon \cdot \mathbf{1})} \tag{17}$$

is now used instead of $\mathbf{P}_\varepsilon$. $\mathbf{P}_0$ is normalized in the same way. Using these normalized probabilities, the spectroscopic impedance takes the very simple form:

$$Z_{\text{spect.}}(\varepsilon) = \left(\frac{\tau}{a}\frac{\varepsilon}{1-\varepsilon}\right)(\mathbf{P}_{N,\varepsilon}\cdot \mathbf{P}_{N,0})a^{d-1}. \tag{18}$$

The first term, enclosed in parenthesis, can be interpreted as a surface resistivity, called r (see appendix A), leading to:

$$Z_{\text{spect.}}(\varepsilon) = r\;(\mathbf{P}_{N,\varepsilon}\cdot \mathbf{P}_{N,0})\;a^{d-1}. \tag{19}$$

Taking the continuum limit situation and calling ds the elementary surface on the working electrode M, one finally gets:

$$Z_{\text{spect.}}(\varepsilon) = r\int_M P_{N,0}(x)P_{N,\varepsilon}(x)\mathrm{d}s. \tag{20}$$

4 Heat impedance

The same theory permits one to calculate the *heat impedance* (Z_{heat}) as defined in the previous paper [1]. It represents the energy dissipation of the current flow through the electrode:

$$Z_{\text{heat}} = \int r\, j_{\text{n}}^2\,\mathrm{d}s = \sum_j \left(\frac{\tau}{a}\frac{\varepsilon}{1-\varepsilon}\right)P_{N,\varepsilon,j}^2 a^{d-1} \tag{21}$$

$$Z_{\text{heat}} = r(\mathbf{P}_{N,\varepsilon}\cdot \mathbf{P}_{N,\varepsilon})a^{d-1}. \tag{22}$$

By comparison with equation (19), one can notice that the difference between the spectroscopic impedance and the heat impedance is simply obtained by changing $\mathbf{P}_{N,0}$ in equation (19) into $\mathbf{P}_{N,\varepsilon}$ in equation (22). The square norm of $\mathbf{P}_{N,\varepsilon}$ can be computed by considering the derivative of $\mathbf{P}_\varepsilon$:

$$\frac{\partial \mathbf{P}_\varepsilon}{\partial \varepsilon} = (\widetilde{Q} - I)(I - \varepsilon\widetilde{Q})^{-2}\mathbf{P}_0 = -\left(\frac{\widetilde{T}_\varepsilon - I}{\varepsilon}\right)^2 \mathbf{1} \tag{23}$$

and then using that $(I - \widetilde{T}_\varepsilon)\;\mathbf{1} = \dfrac{\varepsilon}{1-\varepsilon}\mathbf{P}_\varepsilon$:

$$\frac{\partial(\mathbf{P}_\varepsilon\cdot \mathbf{1})}{\partial \varepsilon} = \frac{-1}{(1-\varepsilon)^2}\;\|\mathbf{P}_\varepsilon\|^2. \tag{24}$$

Putting this relation in equation (22) yields:

$$Z_{\text{heat}} = \varepsilon(1-\varepsilon)\frac{\partial}{\partial \varepsilon}\left(\frac{\tau}{a^d(\mathbf{P}_\varepsilon\cdot \mathbf{1})}\right)\cdot \tag{25}$$

Finally, this equation can be expressed in terms of the surface permeability r^{-1} by using the relation between microscopic and macroscopic parameters (see Eq. (60) in Appendix A), leading to a remarkably simple result:

$$Z_{\text{heat}} = r\;\frac{\mathrm{d}}{\mathrm{d}r}\,(Z_{\text{spect.}}). \tag{26}$$

Note that this result is valid whatever the topological dimension of the working electrode. In the special situation where the electrode impedance follows a linear law of the surface resistivity, the heat impedance and the spectroscopic impedance are equal.

Several conclusions can be drawn from this result. First the measurement of the spectroscopic impedance – the experimentally accessible quantity – gives the heat impedance. In terms of the active surface called $A_{\mathrm{act.,heat}}$, Z_{heat} can be written as $r/A_{\mathrm{act.,heat}}$, and then from equation (26):

$$\frac{\mathrm{d}}{\mathrm{d}r}\left(Z_{\mathrm{spect.}}\right)=\frac{1}{A_{\mathrm{act.,heat}}}\cdot \tag{27}$$

This shows that measurement of the spectroscopic impedance $Z_{\mathrm{spect.}}$ gives access to the heat active surface. This result is *general*, whatever the geometry, the topological dimension and the regime under consideration.

The derivative of the spectroscopic impedance $Z_{\mathrm{spect.}}$ is then equal to $(A_{\mathrm{act.,heat}})^{-1}$, which means that, as long as the spectroscopic impedance increases linearly with the surface resistivity, the effective active surface on the membrane remains constant, and both spectroscopic and heat impedances are equal.

When an increase of the surface resistivity induces an increase of the effective active surface, both impedances are different. This is due to an increase of the energy dissipation in the bulk, corresponding to the reorganization of the access current lines. The spectroscopic impedance is then greater than the heat impedance, until the surface resistivity reaches the point where the effective active surface is equal to the total surface of the membrane. From this point on, the heat impedance catches up with the spectroscopic impedance, and we find back the classical law of equation (44).

For all regimes, the energy dissipation in the bulk of the cell and in the working electrode can thus be deduced from the simple measurement of the total impedance of the cell:

$$Z_{\mathrm{heat}}=r\,d_rZ_{\mathrm{spect.}}=r\;d_r(Z_{\mathrm{cell}}) \tag{28}$$

$$Z_{\mathrm{heat}}^{\mathrm{bulk}}=Z_{\mathrm{cell}}-Z_{\mathrm{heat}}=-r^2d_r\left(\frac{Z_{\mathrm{cell}}}{r}\right)\cdot \tag{29}$$

In the particular case where the spectroscopic impedance follows a power law of the surface resistivity (such as $Z_{\mathrm{spect.}}=K\,r^{\gamma}$), equation (26) tells us that:

$$Z_{\mathrm{heat}}=\gamma K r^{\gamma}=\gamma Z_{\mathrm{spect.}}. \tag{30}$$

The effective active surface $A_{\mathrm{act.,heat}}$ then follows a power law of the surface resistivity with exponent $(1-\gamma)$. Moreover, we can deduce from this equation that the ratio of the energy dissipation between the interface and the bulk is γ.

5 Influence of the distance of the counter electrode

Up to now, all the calculations were carried for a fixed finite distance between the working electrode and the counter electrode. Thus, the operators $\widetilde{Q}$ and $\widetilde{T_\varepsilon}$, and the vectors $\mathbf{P}_\varepsilon$ and $\mathbf{P}_{N,\varepsilon}$ depend in principle on this distance, along with the impedances $Z_{\mathrm{spect.}}(\varepsilon)$ and $Z_{\mathrm{heat}}(\varepsilon)$. Numerical computations have shown that, in fact, these impedances are approximately independent of the distance δ between the electrodes, as soon as it is larger than the smallest feature of the working electrode [1]. This can be seen in the theoretical expressions of equations (19, 22) which depend only on the normalized distributions.

In this limit, $\widetilde{Q}$ tends to an "intrinsic self transport operator" $\widetilde{Q^{\mathrm{int}}}$, and distributions $\mathbf{P}_{N,0}$ and $\mathbf{P}_{N,\varepsilon}$ tend to finite values that can be called *intrinsic primary and secondary current distributions*, $\mathbf{P}_0^{\mathrm{int}}$ and $\mathbf{P}_\varepsilon^{\mathrm{int}}$:

$$\mathbf{P}_\varepsilon^{\mathrm{int}}=\lim_{\delta\to\infty}\frac{\mathbf{P}_\varepsilon}{a^{d-1}(\mathbf{P}_\varepsilon\cdot\mathbf{1})}\cdot \tag{31}$$

These quantities depend only on the working electrode topology. Note that $\mathbf{P}_0^{\mathrm{int}}$ is also often called the harmonic measure of the working electrode M.

An interesting property of the intrinsic situation (infinite distance) is that $\mathbf{P}_\varepsilon^{\mathrm{int}}$ can be derived from $\mathbf{P}_0^{\mathrm{int}}$ by a linear transformation (this is *not* true with normalized distributions for finite δ). It comes from the fact that the ratio $(\mathbf{P}_\varepsilon\cdot\mathbf{1})/(\mathbf{P}_0\cdot\mathbf{1})$ goes to 1 when δ goes to infinity.

Indeed, writing $\widetilde{T_\varepsilon}$ as:

$$\widetilde{T_\varepsilon}=I-\varepsilon(I-\varepsilon\widetilde{Q})^{-1}(I-\widetilde{Q}) \tag{32}$$

leads to:

$$\mathbf{P}_\varepsilon\cdot\mathbf{1}=\mathbf{P}_0\cdot\mathbf{1}-\mathbf{P}_0\cdot\Big(\varepsilon\;(I-\varepsilon\widetilde{Q})^{-1}\mathbf{P}_0\Big). \tag{33}$$

Thus, when the distance between both electrodes becomes infinite, $(\mathbf{P}_0\cdot\mathbf{1})$ and $(\mathbf{P}_\varepsilon\cdot\mathbf{1})$ are equivalent, since the second term in the right hand side varies as $\|\mathbf{P}_0\|^2$. The resulting identity

$$\lim_{\delta\to\infty}\frac{\mathbf{P}_\varepsilon\cdot\mathbf{1}}{\mathbf{P}_0\cdot\mathbf{1}}=1 \tag{34}$$

implies that a linear operator transforms $\mathbf{P}_0^{\mathrm{int}}$ into $\mathbf{P}_\varepsilon^{\mathrm{int}}$. This operator is given by:

$$\lim_{\delta\to\infty}(1-\varepsilon)(I-\varepsilon\widetilde{Q})^{-1}=(1-\varepsilon)(I-\varepsilon\widetilde{Q^{\mathrm{int}}})^{-1}=\widetilde{T_\varepsilon^{\mathrm{int}}}. \tag{35}$$

This can be summed up in the following picture

$$\begin{tikzcd}
\mathbf{P}_0 \arrow[r, "\text{normalize}"] \arrow[d, "\widetilde{T_\varepsilon}"'] & \mathbf{P}_{N,0} \arrow[r, "\delta\to\infty"] \arrow[d, "\text{non linear}"] & \mathbf{P}_0^{\mathrm{int}} \arrow[d, "\widetilde{T_\varepsilon^{\mathrm{int}}}"] \\
\mathbf{P}_\varepsilon \arrow[r] & \mathbf{P}_{N,\varepsilon} \arrow[r] & \mathbf{P}_\varepsilon^{\mathrm{int}}
\end{tikzcd}$$

In this frame, one can then define *intrinsic impedances* $Z_{\mathrm{spect.}}^{\mathrm{int}}$ and $Z_{\mathrm{heat}}^{\mathrm{int}}$ as:

$$Z_{\mathrm{spect.}}^{\mathrm{int}}=r(\mathbf{P}_\varepsilon^{\mathrm{int}}\cdot\mathbf{P}_0^{\mathrm{int}})a^{d-1}, \tag{36}$$

$$Z_{\mathrm{heat}}^{\mathrm{int}}=r(\mathbf{P}_\varepsilon^{\mathrm{int}}\cdot\mathbf{P}_\varepsilon^{\mathrm{int}})a^{d-1}. \tag{37}$$

Furthermore, the relation established in equation (26) still holds:

$$Z_{\text{heat}}^{\text{int}} = r\,\frac{\mathrm{d}}{\mathrm{d}r}\left(Z_{\text{spect.}}^{\text{int}}\right). \tag{38}$$

6 The low resistivity regime or weakly polarizable electrode

For a low surface resistivity, the reflection probability goes to zero ($\varepsilon \to 0$ and $\mathbf{P}_\varepsilon \to \mathbf{P}_0$). Equation (19) becomes:

$$Z_{\text{spect.}}(\varepsilon) \approx\ r\,\|\mathbf{P}_{N,0}\|^2\ a^{d-1} = r\left(\sum_j P_{N,j}^2\ a^{d-1}\right). \tag{39}$$

Taking the continuum limit situation we obtain:

$$Z_{\text{spect.}}(\varepsilon) = r\int_M P_N^2(x)\,\mathrm{d}s. \tag{40}$$

Extending the concept of active length developed in the previous paper to rough surfaces embedded in d dimension cells, one defines an active surface for the dissipation $A_{\text{act.,heat}}$ by:

$$A_{\text{act.,heat}} = \left[\int P_N^2\ \mathrm{d}A\right]^{-1}. \tag{41}$$

One then finds $A_{\text{act.,heat}} = r/Z_{\text{spect.}}$ in this regime, as verified in the previous paper for $2d$ electrodes.

If one applies a dilation transformation $x \to \Gamma x$ to all lengths, the landing probabilities $P_N(x)$ transform into $P_N(x)/\Gamma^{d-1}$ from the normalization condition. Then from equation (41), $A_{\text{act.,heat}}$ is transformed into $\Gamma^{d-1}A_{\text{act.,heat}}$, that is $A_{\text{act.,heat}}$ transforms like the power $(d-1)$ of the electrode diameter. This generalizes the Makarov result in the restricted sense used here. Namely, the active zone of a rough surface has a size which is proportional to the power $(d-1)$ of the electrode diameter under a dilation transformation [8,9].

Though this result could seem obvious, one should remind that in the case of an irregular electrode similar to a "nailboard" (with a finite number of singularities), it means that the active zone cannot be only reduced to the singularities (the tips of the nails), as it would remain constant under a dilation transformation and not scale with Γ^{d-1}.

7 The high resistivity regime or strongly polarizable electrode

In this limit ($\varepsilon \to 1$ or $\sigma \to 0$), the flux decreases and the spectroscopic impedance increases to infinity. The operator $\widetilde{T}_\varepsilon$ can be approximated by $\sigma(I-\widetilde{Q})^{-1}$, and the secondary current distribution $\mathbf{P}_\varepsilon$ deduced by using equation (8):

$$\mathbf{P}_\varepsilon = \widetilde{T}_\varepsilon\ \mathbf{P}_0 \approx \sigma\ (I-\widetilde{Q})^{-1}\ \mathbf{P}_0 = \sigma\ \mathbf{1}. \tag{42}$$

The spectroscopic impedance becomes in this case:

$$Z_{\text{spect.}}(\varepsilon) \approx \frac{\tau}{a^d\sigma}\,\frac{1}{(\mathbf{1}\cdot\mathbf{1})} = \frac{\tau}{a\sigma}\,\frac{1}{(ma^{d-1})}\,\cdot \tag{43}$$

The expression enclosed in parentheses in the upper equation is simply the number of sites of the working electrode multiplied by the elementary surface a^{d-1}: it is the total surface A_{ode} of the working electrode. We then find back the classical expression of the electrode impedance at high resistivity whatever its shape:

$$Z_{\text{spect.}} \simeq \frac{r}{A_{\text{ode}}}\,\cdot \tag{44}$$

8 Link with the Land Surveyor Method

In order to understand the previous calculations in terms of the *Land Surveyor Method* (LSM) presented in the previous paper [1], the system is now supposed to be constituted of a 2D medium embedded within two electrodes, one rough and one flat. Its thickness in the third dimension is called b. The value of the spectroscopic impedance comes directly from equation (19):

$$Z_{\text{spect.}} = \frac{r}{b}(\mathbf{P}_{N,\varepsilon}\cdot\mathbf{P}_{N,0})\ a. \tag{45}$$

According to our "brutal" interpretation of the Makarov's theorem, the length of the active zone, for the primary current distribution, is roughly equal to the diameter of the structure L. In this approximation, the normalized primary current distribution $\mathbf{P}_{N,0}$ can be written:

$$\mathbf{P}_{N,0} = \left(0,\cdots,\frac{1}{L},\cdots,0,\cdots,\frac{1}{L},\cdots,0\right) \tag{46}$$

where the number of non-zero components is equal to L/a.

The spectroscopic impedance of the electrode for any finite surface resistivity is then:

$$Z_{\text{spect.}} = \frac{r}{b}\frac{L}{a}\frac{1}{L}\langle P_{N,\varepsilon,j}\rangle a. \tag{47}$$

This expression can be compared to that obtained in equation (17) of the previous paper [1], based on the LSM approximation:

$$\frac{r}{b}\langle P_{N,\varepsilon,j}\rangle = \frac{\rho}{b}\frac{\langle L_{\text{c}}\rangle}{L}\,\cdot \tag{48}$$

This gives the mean value of the probability to be finally absorbed on a site of the active zone:

$$\langle P_{N,\varepsilon,j}\rangle = \frac{\rho}{r}\frac{\langle L_{\text{c}}\rangle}{L} = \frac{1}{L}\frac{\langle L_{\text{c}}\rangle}{\Lambda}\,\cdot \tag{49}$$

Or, using the harmonic mean of the "local" Dirichlet screening factor $\langle S\rangle_{\text{H}}$ (Eq. (22) in [1]) in the continuous limit:

$$\langle P_{N,\varepsilon,j}\rangle = \frac{1}{\langle S\rangle_{\text{H}}}\frac{1}{L} = \frac{1}{L^2}\int\frac{L_{\text{c}}}{\Lambda}\,\mathrm{d}s. \tag{50}$$

In the LSM, a particle hitting a site on the working electrode will explore a region of perimeter $\Lambda = r/\rho$ before being finally absorbed. Here, the transformation of the normalized primary current distribution $\mathbf{P}_{N,0}$ into the secondary current distribution $\mathbf{P}_{N,\varepsilon}$ can then be roughly interpreted as a "broadening" operation.

9 Spectral expansion

The expression for the electrode impedance (Eq. (19)) allows us to predict rigorously the behavior of the cell, not only in the limiting regimes of very low or very high surface resistivity, but also in the general regime where the parameter $\Lambda = r/\rho$ is of the same order of magnitude as the geometrical irregularities of the membrane. Nevertheless, it requires complete knowledge of the self-transport operator $\widetilde{Q}$.

We will now devise a new formulation for the spectroscopic impedance depending on the spectrum (distribution of eigenvalues) of the operator $\widetilde{Q}$, leading to a new understanding of the membrane behavior. Let us first examine the expression for the intrinsic spectroscopic impedance found in equation (36):

$$\begin{aligned} Z^{\rm int}_{\rm spect.}(\varepsilon) &= r(\mathbf{P}^{\rm int}_{\varepsilon} \cdot \mathbf{P}^{\rm int}_{0})\ a^{d-1} \\ &= r a^{d-1}\ \mathbf{P}^{\rm int}_{0} \cdot \left(\widetilde{T^{\rm int}_{\varepsilon}}\mathbf{P}^{\rm int}_{0}\right). \end{aligned} \tag{51}$$

As $\widetilde{Q^{\rm int}}$ is a positive symmetrical operator, it can be diagonalized: let us call $(q_\alpha)_{1\leq\alpha\leq m}$ its eigenvalues and $(C_\alpha)_{1\leq\alpha\leq m}$ the decomposition coefficients of $\mathbf{P}^{\rm int}_0$ on its eigenvectors $\boldsymbol{\alpha}$:

$$C_\alpha = \mathbf{P}^{\rm int}_0 \cdot \boldsymbol{\alpha}. \tag{52}$$

The scalar product $\mathbf{P}^{\rm int}_0 \cdot \left(\widetilde{T^{\rm int}_{\varepsilon}}\mathbf{P}^{\rm int}_{0}\right)$ can then be rewritten in the $\widetilde{Q^{\rm int}}$-eigenmodes representation:

$$\mathbf{P}^{\rm int}_0 \cdot \left(\widetilde{T^{\rm int}_{\varepsilon}}\mathbf{P}^{\rm int}_{0}\right) = \sum_{\alpha=1}^{m} \left(\frac{1-\varepsilon}{1-\varepsilon q_\alpha}\right) C_\alpha^2. \tag{53}$$

Taking the continuous limit is done by transforming the collection of coefficients $(C_\alpha^2\ a^{d-1})$ for each eigenvalue into a continuous distribution $C^2(q)\mathrm{d}q$:

$$Z^{\rm int}_{\rm spect.}(\varepsilon) = r\int_{-1}^{1}\left(\frac{1-\varepsilon}{1-\varepsilon q}\right) C^2(q)\,\mathrm{d}q, \tag{54}$$

$C^2(q)\ \mathrm{d}q$ plays here the role of a measure on the eigenvalues of operator $\widetilde{Q^{\rm int}}$ and could be called a *$\widetilde{Q}$-spectral decomposition of the harmonic measure.* Using equation (26) and the relation $r = \dfrac{\tau}{a}\dfrac{\varepsilon}{1-\varepsilon}$, a same formulation can be derived for the heat impedance:

$$Z^{\rm int}_{\rm heat}(\varepsilon) = r\int_{-1}^{1}\left(\frac{1-\varepsilon}{1-\varepsilon q}\right)^2 C(q)^2\ \mathrm{d}q. \tag{55}$$

These are general intrinsic expressions for the spectroscopic and heat impedance of the electrode in front of a semi-infinite bulk. It stands for any value of the reflection probability (or surface resistivity), any shape of the irregular electrode and any topological dimension d. It only requires the knowledge of the spectral behavior of the *self-transport* of the working electrode in front of a semi-infinite bulk and of the decomposition coefficients of the primary current distribution on the self-transport modes.

10 Conclusions

General theoretical expressions for both spectroscopic and heat impedances of the working electrode have been derived from a simple microscopic diffusive model. These expressions are valid *whatever the shape of the interface or its topological dimensional.* This work shows that all the properties of Laplacian transfer across a linear interface are ruled by the spectral properties of its self-transport operator $\widetilde{Q}$, and more precisely, on the decomposition of the primary current distribution (harmonic measure) on the eigenmodes of this operator.

A simple differential relation between the spectroscopic and the heat impedances has been proved (and verified on numerical simulations in the previous paper [1]).

It has also been shown that intrinsic expressions of impedances can be defined. They are independent of the height of the cell, and take only into account the working electrode topography. The physical question addressed in the title is then transformed into the following mathematical problem, which is called "problem II": "Can one determine the shape of an object from the *$\widetilde{Q}$-spectral decomposition* of its harmonic measure?"

To our knowledge, the answer to this question is open. Also remains the question of the possible links between "problem I" and "problem II".

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Appendix A: Lattice representation of transfer across a membrane

A real membrane must be represented by two types of site, called membrane surface site M, and absorbing site E (stands for empty), as schematized in Figure 4. The physical process at the surface is governed by several dynamics.

- A particle on a bulk site B can jump on a membrane site M, with jump probability per unit time $1/(4\tau)$.

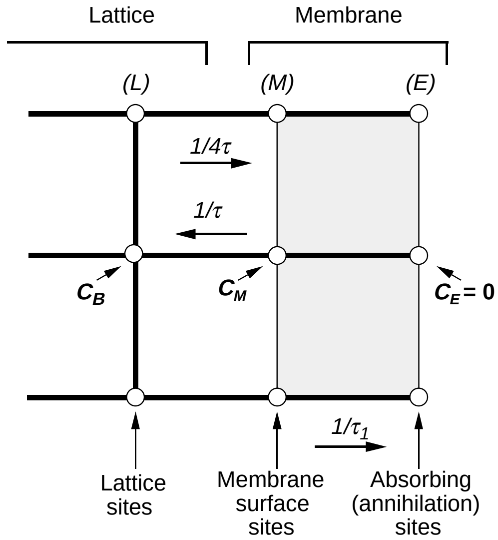

Fig. 4. Lattice gas representation of a membrane process: a two step modelization of the function of an absorption process on the membrane. One has to consider three different sites: first, sites in the interior of the system (L) with local concentration of particles C. Second, membrane sites (M) at the surface of the membrane (with steady state concentration $(1-\sigma)C$). Third, absorption sites (E) (with steady state zero concentration) corresponding to the passage through the membrane. We thus have an overall flux $\Phi = a\sigma/2\mathrm{d}t$ in the limits of our system, in order to keep the steady state in the system.

- A particle on a membrane site M may come back to a bulk site B, with a jump probability per unit time $1/\tau$, or be annihilated with rate $1/\tau_1$.

With these definitions, the permeability of the membrane W is given by the average flux per unit time across a flat membrane of length L by the equation:

$$\Phi = C_{\mathrm{M}} W L \tag{56}$$

where C_{M} is the concentration of the membrane sites. Given the fact that membrane sites are at a distance a, we can write the flux as $\Phi = a^2 C_{\mathrm{M}}(1/\tau_1)(L/a)$ from which we deduce

$$W = \frac{a}{\tau_1} \cdot \tag{57}$$

In the diffusion picture that we used in Section 2, the sticking probability is the relative probability that a particle having reached a site on M is effectively absorbed. This relative probability is

$$\sigma = \frac{\tau_1^{-1}}{(\tau_1^{-1} + (\tau)^{-1})} \cdot \tag{58}$$

From which using equation (57), we find

$$W = \frac{a}{\tau}\left(\frac{\sigma}{1-\sigma}\right) \tag{59}$$

or, using $\sigma = 1 - \varepsilon$:

$$W = \frac{a}{\tau}\left(\frac{1-\varepsilon}{\varepsilon}\right)\cdot \tag{60}$$

The absorption process takes place really in two steps as indicated in Figure 4. In steady state there exist three concentrations: first C_{B} in the bulk near the surface and C_{M} and $C_{\mathrm{E}} = 0$. Detailed balance between these populations can be written in steady state

$$\frac{\partial C_{\mathrm{M}}}{\partial t} = -\frac{C_{\mathrm{M}}}{\tau_1} - \frac{C_{\mathrm{M}}}{\tau} + \frac{C_{\mathrm{B}}}{4\tau} = 0 \tag{61}$$

and

$$C_{\mathrm{M}} = \frac{\dfrac{C_{\mathrm{B}}}{4\tau}}{(\tau_1^{-1} + \tau^{-1})} \cdot \tag{62}$$

Seen from the bulk the steady state flux is equal to

$$\Phi = \frac{C_{\mathrm{B}}}{4\tau} - \frac{C_{\mathrm{M}}}{\tau} \tag{63}$$

and using the value of C_{M} given by equation (62), one obtains

$$\Phi = \frac{C_{\mathrm{B}}\sigma}{4\tau} \cdot \tag{64}$$

This is the expression that was used in the simulations of reference [10], implying a pseudopermeability of the membrane given by $W' = \sigma a/4\tau$ instead of the real permeability $W = (a/\tau)\,\sigma/(1-\sigma)$. The real permeability takes care through the relation of equation (59) between σ and τ of the possibility for the permeability of the membrane to be infinite. Even if the permeability of the real membrane is infinite the transfer through the last line of bulk sites is finite.

Appendix B: Low and high resistivity limits in spectral formalism

For a better understanding of the behavior of the resistive electrode in terms of $\widetilde{Q}$-eigenmodes, it is interesting to see how one can find back the limits for low and high surface resistivity (already calculated in Sects. 6 and 7). First one can notice the following identity:

$$\sum_{\alpha} C_\alpha^2 = \|\mathbf{C}\|^2 = \|\mathbf{P}_0^{\mathrm{int}}\|^2 = \sum_k (P_{0,k}^{\mathrm{int}})^2. \tag{65}$$

The low surface resistivity limit of equation (53) is simply:

$$Z_{\mathrm{spect.}}(\varepsilon) \approx r a^{d-1}\left(\sum_{\alpha=1}^{m} C_\alpha^2\right) = r\left(\sum_{j=1}^{m} P_{N,j}^2\, a^{d-1}\right). \tag{66}$$

One can see that in this limit, the current distribution is distributed over all the eigenmodes. The sum of all contributions gives the square norm of the primary current distribution, as showed by equation (65).

For the high surface resistivity limit, it is useful to notice that one of the eigenvalues (q_α) of the operator $\widetilde{Q^{\text{int}}}$ is equal to 1. This eigenvalue corresponds to the eigenvector $\mathbf{u}_1 = \mathbf{1}/\|\mathbf{1}\|$, that represents an homogeneous distribution on the working electrode. The contributions of all other eigenvalues vanish then in equation (53) when ε goes to 1. It follows then that:

$$Z_{\text{spect.}}(\varepsilon) \approx r\, a^{d-1}\, C_1^2. \tag{67}$$

The contribution C_1 of the eigenvector $\mathbf{u}_1 = \mathbf{1}/\|\mathbf{1}\|$ to the normalized primary current distribution $\mathbf{P}_0^{\text{int}}$ is given by their scalar product $(\mathbf{P}_0^{\text{int}} \cdot \mathbf{u}_1)$. Since $(\mathbf{P}_0^{\text{int}} \cdot \mathbf{1})$ is equal to 1 by definition, the classical limit for high surface resistivity is obtained by noticing that $\|\mathbf{1}\|^2$ is simply the number of sites m of the working electrode:

$$Z_{\text{spect.}} \approx \frac{r}{m\, a^{d-1}} = \frac{r}{A_{\text{ode}}} \cdot \tag{68}$$

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