General Formulation of Laplacian Transfer Across Irregular Surfaces

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We describe a simple way to study the response of an irregular resistive interface to a Laplacian field. Using this method, one can find the response of an arbitrary electrochemical electrode from its geometry alone. The same method applies to the study of the steady-state transfer across irregular membranes with finite permeability.

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In this Letter I present a new way to consider and to compute the impedance of irregular interfaces using a simple and general argument. It applies to any irregular electrode and, in particular, to self-similar electrodes. In addition, it permits us to compute the response from the geometry of the interface only.

The idea is to substitute the problem of Laplacian transfer across a real electrode (which presents a finite transfer rate), by a problem of Laplacian field obeying the Dirichlet boundary condition ($V = 0$) but with a different geometry obtained by coarse graining. The coarse-graining scale is directly related to the transport coefficients of both the electrolyte and the electrode. Using the general properties of Dirichlet-Laplace fields, one finds an effective screening factor which gives the size of the zone which is really active on the initial geometry and, hence, its admittance.

To calculate the response of an electrochemical cell with an irregular electrode, as in Fig. 1, one has to solve the Laplace equation ($\Delta V = 0$) which governs the potential

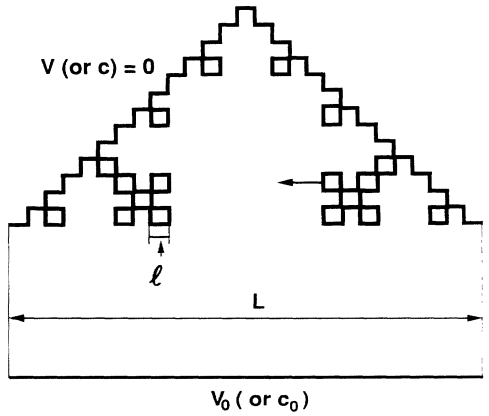

FIG. 1. Electrochemical cell with a self-similar electrode. The irregular electrode of interest (the working electrode in electrochemistry) has an inner cutoff ℓ and a size or diameter L. The arrow indicates the orientation of the normal. This Letter deals with the electrochemical problem in which the applied voltage is V_0 on the planar counter electrode and 0 on the working electrode. There exists an exactly equivalent diffusion problem in which a planar source of diffusion is maintained at a constant concentration c_0 and particles diffuse towards an irregular membrane with finite permeability W.

distribution in the bulk of the electrolyte with a boundary condition that reflects the electrochemical process at the working surface. This surface possesses a finite admittance, and what is known about the properties of Laplacian fields on surfaces without impedance (with $V = 0$) cannot be applied directly. This is unfortunate since the Dirichlet-Laplace problem on an irregular electrode has been thoroughly studied, at least in $d = 2$. More specifically, an important theorem, Makarov's theorem, describing the properties of the charge distribution on an irregular (possibly fractal) electrode capacitor can be used [1]. This theorem states that the information dimension of the harmonic measure (for instance the electrostatic charge for the capacitor case) on a singly connected object in $d = 2$ is exactly equal to 1. This very special property of the Laplacian field can be illustrated in the following manner: Whatever the shape of an electrode capacitor, the size of the region where the charge accumulates is proportional to the overall size (or diameter) L of the electrode under a dilation transformation.

This result generalizes to arbitrary geometry, a fact which has been known for a long time for simple geometries. It has a simple but profound meaning in terms of the screening efficiency of the geometrical irregularity, and this is what we wish to illustrate and use. For this, we consider the simplest description of an irregular surface: the ratio of the length of the perimeter L_p divided by its size or diameter L [2],

$$S = L_p/L . \tag{1}$$

This number S has a direct physical significance: it really measures the screening efficiency of the irregularity of the structure for Dirichlet Laplacian fields. If, whatever the geometry, the active zone has a size L, then as

$$L = L_p/S . \tag{2}$$

the factor $1/S$ can be considered to be the "screening efficiency" due to the geometrical irregularity. This is the physical significance of Makarov's theorem. Note that when we discuss fractal lines we consider only physical objects with a finite inner cutoff ℓ so that S is always finite.

The above result cannot be applied directly to the screening of the current in an electrochemical cell, because the boundary condition on the electrode is not

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$V = 0$. In the simplest linear regime, a "flat" element of an electrode surface with unit area behaves as a resistor r across a capacitance γ. The Faraday resistor r describes the finite rate of the electrochemical reaction, and γ describes the charge accumulation at the interface. (For a review of the early works on fractal electrodes see Refs. [3] and [4] and the references therein.) Because of charge conservation, the current $j_\perp = -V(r^{-1} + j\gamma\omega)$ crossing the electrode surface must be equal to the Ohmic current $j_\perp = -\nabla_\perp V/\rho$ reaching it from the bulk (ρ being the electrolyte resistivity). As a consequence, the dc boundary condition can be written as

$$V/\nabla_\perp V = \Lambda \quad \text{with} \quad \Lambda = r/\rho\,. \tag{3}$$

The real boundary condition then introduces a physical length scale Λ in the problem. The procedure that we describe now is to switch from the real geometry obeying the real boundary condition to a coarse-grained geometry obeying the Dirichlet boundary condition, with the coarse-graining depending on Λ. In that new geometry we will apply Eq. (2) to obtain the effective screening, hence, the size of the working zone of the real electrode.

To be more specific, we describe this analysis for the situation of an electrode in a planar $d = 2$ cell, as represented in Fig. 1. Consider a part i of the surface with a perimeter length $L_{p,i}$. If the thickness of the cell is b, this surface possesses an admittance $Y_i = bL_{p,i}/r$. The admittance to access the surface is of order $Y_{\rm acc} = b/\rho$, because in $d = 2$ the admittance of a square of electrolyte with thickness b is equal to b/ρ, whatever its size. Depending on the size of the region i, there exists two situations: $Y_i < Y_{\rm acc}$ or $Y_i > Y_{\rm acc}$. If $L_{p,i}$ is small, $Y_i < Y_{\rm acc}$ and the current is limited by the surface admittance. On the contrary, if $L_{p,i}$ is large enough, we have $Y_i > Y_{\rm acc}$, and the current is limited by the resistance to access the surface. But in the latter situation we are, in a first approximation, back to the case of a pure Laplacian field with the boundary condition $V = 0$. The idea then is to coarse grain the real geometry to a scale $L_i = L_{\rm cg}$ such that the perimeter $L_{p,{\rm cg}}$ in a region of size (diameter) $L_{\rm cg}$ is given by the critical condition $Y_i = Y_{\rm acc}$ or

$$L_{p,{\rm cg}} = \Lambda\,. \tag{4}$$

A coarse-grained site is then a region of perimeter equal to $\Lambda = r/\rho$. Because of its definition, such a region can be considered as acting uniformly. At the same time, in the new coarse-grained geometry we are dealing with a pure Dirichlet Laplacian field, and we can then use the screening factor $1/S_{\rm cg}$ of this object to find its effective active surface. Note that if we performed the coarse graining to a scale larger than $L_{\rm cg}$, it would no longer be correct to consider a uniform distribution of the current within a macrosite and that consequently we would not be able to find the size of the active zone. Calling N_p the number of yardsticks of length $L_{\rm cg}$ needed to measure the perimeter of the electrode, the number S of the coarse-grained object is simply

$$S_{\rm cg} = N_p/N\,, \tag{5}$$

where $N = L/L_{\rm cg}$ is the number of yardsticks needed to measure the size (or diameter) of the electrode. The quantity $1/S_{\rm cg}$ is the effective fraction of the surface which is active, and the admittance of the electrode will simply be given by

$$Y(r) = Y_p(r)/S_{\rm cg}\,, \tag{6}$$

where $Y_p(r)$ would be the surface admittance of a "stretched" electrode with a length L_p. In this frame the number $S_{\rm cg}$ of the coarse-grained object determines directly how the admittance of the total surface is reduced by the screening effects. If we consider a self-similar electrode with an inner cutoff ℓ and a fractal dimension D_f, there exists a simple relation between the size $L_{\rm cg}$ of the coarse graining and the length of the perimeter:

$$\Lambda = \ell(L_{\rm cg}/\ell)^{D_f}. \tag{7}$$

Using Eqs. (5)–(7), one obtains for the admittance of a self-similar electrode of macroscopic size L and thickness b the value $Y = Lb(\ell\rho)^{(1-D_f)/D_f} r^{-1/D_f}$. To obtain the general ac response we substitute r by $(r^{-1} + j\gamma\omega)^{-1}$. For blocking electrodes with $r^{-1} = 0$ we have

$$Y(\omega) = Lb(\ell\rho)^{(1-D_f)/D_f}(j\gamma\omega)^{1/D_f}. \tag{8}$$

The dc form of this result has been verified by numerical simulation and the ac form (the so-called constant phase angle response) has been verified by experiments on model electrodes as described in detail in Ref. [5].

However, this simple argument is more general and permits us, as we show below, to compute the response of irregular electrodes even for nonscaling geometries. First, we show how this method can be used from the image of the electrode. All we need is to have a "flexible" measuring rod of length $\Lambda = r/\rho$ [or $|\Lambda(\omega)| = 1/\rho\gamma\omega$ for blocking electrodes] that we use to measure the length of the perimeter from one end to the other. To perform this task we need a number N_p of flexible rods. Note that here we do not measure the irregular object with a rigid yardstick as is usually considered in measuring fractals. On the contrary, starting at one end of the irregular object, we map the object with the flexible rod of length Λ, and the distance in real space between the ends of this rod determines a distance L_1. This length is a "local yardstick" associated with Λ and the local geometry. Then we place a second flexible rod of length Λ from the end of the first rod and find a new yardstick length L_2, and so on. The total number of rods (of length Λ) needed to map the object is N_p, and the number S of the coarse-grained electrode is N_p/N, where N is the number of yardsticks which measures the size. The real electrode has a perimeter $N_p\Lambda$ and a total admittance $Y_p(r) = N_p\Lambda b/r = N_p b/\rho$. Dividing by S, as in Eq. (6), we find

$$Y = Nb/\rho\,. \tag{9}$$

We then obtain that the modulus of the admittance of an irregular electrode in $d = 2$ is simply the square

admittance b/ρ multiplied by the number of yardsticks to measure the size (or diameter) L of the electrode. This shows that deterministic and random fractals with same inner and outer cutoffs and the same fractal dimension have the same response. The reason is now trivial, because what really matters is the total number of macrosites, whatever their individual size, which may be distributed over some range of sizes.

We now apply this method to nonscaling geometries as shown in Fig. 2. The dc admittance of the perimeter surface is now $Y_p = (N'_p + N''_p)b\Lambda/r$ with $N'_p = L'/L'_{cg}$ and $N''_p = (L''/L''_{cg})^{D_f}$. To obtain the admittance of this electrode we have to divide this value by S of the entire electrode. The macrosites do not have the same size if they correspond to the planar part, for which the yardstick is simply $L'_{cg} = \Lambda$, or if they correspond to the fractal part for which the yardstick is given by $L''_{cg} = \ell(\Lambda/\ell)^{1/D_f}$ from Eq. (7). The total number of yardsticks on the object is now $N_p = N'_p + N''_p$, whereas the number of yardsticks to measure the size is $N = N' + N''$ with $N' = L'/L'_{cg}$ and $N'' = L''/L''_{cg}$. Applying Eq. (6) to $S = (N'_p + N''_p)/(N' + N'')$, one finds for the admittance $Y = (N' + N'')b/\rho$ or $Y = L'b/r + L''b(\ell\rho)^{(1-D_f)/D_f} r^{-1/D_f}$. This is the sum of the admittances of the two electrodes in parallel. Our general argument then makes restitution of the essential property of Laplacian transfer: The admittance of two electrode in parallel is the sum of the individual admittances. This indicates that this method is general. The ac response of blocking electrodes is obtained by replacing r by $(j\gamma\omega)^{-1}$. Note that we have used the number N of yardsticks to measure the total size as equal to the sum $N' + N''$ of the number of yardsticks and to measure the sizes of the two different parts. If we wish to use Eq. (5), we have to use an average yardstick $\langle L_{cg}\rangle$ defined by $L/\langle L_{cg}\rangle = L'/L'_{cg} + L''/L''_{cg}$. The average yardstick $\langle L_{cg}\rangle$ must be obtained by this harmonic mean.

In the known cases of self-affine electrodes like the Cantor bar electrode of [6] or the Sierpinski electrode of [7], the pores have different aspect ratios. For this case a coarse-grained pore can still be defined by $Y_l = Y_{acc}$ but not by $L_{p,cg} = \Lambda$. As explained in a somewhat different language in [4,7], the impedance can be found from the total surface of these coarse-grained pores which are all accessible at the same time due to the particular geometry.

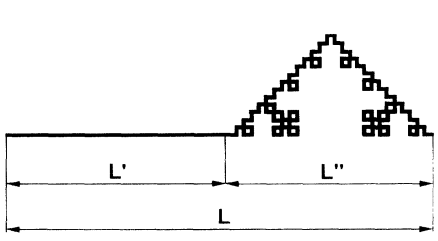

FIG. 2. Example of an electrode with a nonscaling geometry. This electrode is built by the association of a planar electrode of length L', with a self-similar electrode of length L''.

In conclusion, we have given a simple and general method to find the response of irregular electrodes in the linear response regime from their geometry alone. In particular, we have shown for one example how to find, from first principles, the response of a nonscaling irregular object. Apart from the image, all that is needed are the values of the microscopic transport coefficients (here for instance the electrolyte resistivity and the Faraday resistance). The same method applies to the equivalent problem of the steady-state diffusion rate towards an irregular membrane with finite permeability W as indicated in Fig. 1. Here the variable is the concentration c instead of the electric potential V. The concentration obeys the steady-state diffusion equation $\Delta c = 0$. The flux in the bulk is given by Fick's law $\Phi = -D\nabla c$, where D is the diffusion coefficient, in exact analogy with Ohm's law, and the flux crossing the membrane is $\Phi = -Wc$ also in exact analogy with the effect of the Faraday resistance on the current at the surface. As a consequence, there is a steady-state diffusion admittance whose value for a membrane with the geometry of Fig. 2 is given by Eq. (8), provided that we replace ρ by D^{-1} and $j\gamma\omega$ by W [8]. In the diffusion case, the value of Λ is $\Lambda = D/W$, and a coarse-grained site has the size of the region where a random walker is really absorbed due to the finite permeability.

The simplicity of this method probably makes it a good candidate for the study of the response of irregular electrodes in the nonlinear regime, where the local current across the electrode is related to the local voltage by a nonlinear relation $j = f(V)$. In the same spirit, it could probably be applied to the study of active transfer across irregular membranes or to multiparticle heterogeneous catalysis.

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