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Role of the displacement current on Warburg-type behavior

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We investigate the role of the displacement current in the analysis of the electric response of an electrolytic cell to an external stimulus. We show that several models proposed to interpret the spectra deduced by means of the impedance spectroscopy technique are questionable. In particular, we demonstrate that even in the frequency range below the Debye frequency the role of the displacement current is fundamental, and its omission leads to incorrect results for the impedance of the cell. In our analysis, the boundary conditions on the bulk current density are of Nernstian and of Ohmic type. The analysis is limited to a fully dissociated electrolyte, and for only one type of mobile ions, as discussed in several papers devoted to the subject. Particular attention is given to the spatial dependence of the current density. We show that Warburg-like behavior is never predicted in the framework of the Poisson-Nernst-Planck model, if the electric impedance of the cell is correctly evaluated. From this conclusion, valid for media with only one type of mobile ions, it follows that if Warburg-like behavior is experimentally observed the theoretical interpretation is still an open problem, and its origin is probably related to the boundary conditions.

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I. INTRODUCTION

The electric response of a dielectric medium to an external electric field depends on its effective dielectric constant, related to the molecular properties of the medium itself, and on the electrodes used to apply the external stimulus. In the case where the applied voltage is a simple harmonic function of the time $\Delta V(t) = V_0 \exp(i\omega t)$, of amplitude V_0, and of circular frequency ω, the response of the cell is related to its electric impedance defined as the ratio between $\Delta V(t)$ and the current $I(t)$ across the sample, that is, by $Z = \Delta V(t)/I(t)$. In the limit of small V_0, the system behaves in a linear manner, and $I(t) = I_0(\omega)\exp(i\omega t)$, where $I_0(\omega) \propto V_0$. In this limit the impedance is independent of V_0. Usually $Z(\omega)$ is decomposed as $Z(\omega) = R(\omega) + i X(\omega)$, where $R(\omega)$ and $X(\omega)$ are the resistance and reactance of the cell, respectively, in the series representation. These quantities are related to the dissipative and reactive phenomena taking place in the conduction phenomenon. In the low frequency region, i.e., for frequency smaller than a few MHz, the ions present in the medium contribute to the electric response. An analysis of the frequency dependence of the electric impedance of the cell can give information on the ionic densities and ionic diffusion coefficients [1–3]. The theoretical description of the electrical impedance of a material to an external electric field is usually made by means of a model based on the equations of continuity for the positive and negative ions, and on the equation of Poisson for the actual electrical field in the sample [4,5]. Several versions of this model have been proposed along the years to interpret experimental data obtained in different contexts by Macdonald and coworkers [6]. In the cases where the ions dissolved in the insulating liquid limited by blocking electrodes have the same diffusion coefficient, the parametric plot of $R(\omega)$ versus $X(\omega)$ (Nyquist plot) is a semicircle, the center of which is on the real axis, passing through the origin of the reference frame. If the electrodes are not blocking, the parametric plot can show a deformed curve that in some cases can be decomposed in simple semicircles. Similar parametric plots are predicted in the case where only one group of ions is mobile. This latter case has been considered by several authors for its simplicity [7] and technological importance [8–13]. In some cases the parametric plot consists of a high frequency semicircle related to the dielectric relaxation of the bulk followed by a frequency region where $R(\omega)$ and $X(\omega)$ are proportional to $1/\sqrt{\omega}$. In this region the parametric curve of $X(\omega)$ versus $R(\omega)$ is a straight line of slope 1, known as Warburg behavior [14]. Several papers have been devoted to the theoretical justification of the Warburg-like impedance [8–12,15–17]. In a recent review by Lai and Haile these models are discussed and their limits underlined [18], in particular the absence of mathematical rigor in the derivation of the impedance of the cell. In a recent paper, we have analyzed the electric response of an insulating material in the Nernstian approximation when the charge carriers are injected in the system by the electrodes [19], and shown that a Warburg-like impedance is not predicted. In the present paper, we consider the case of a medium that contains, in thermodynamical equilibrium, a bulk density of ions n_0 small enough that the generation and recombination phenomenon can be neglected. Our aim is to show that the models discussed in Refs. [8–13], called in the following pure diffusion models, are questionable because the displacement and drift currents have been omitted in the determination of the electric impedance of the cell. If only drift current is omitted, the model will be called hereinafter the diffusion model. We show that when the displacement current is included in these models the Warburg-type behavior disappears. From this result follows that the

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theoretical interpretation of Warburg-type impedance is still absent, for the case where only one group of ions is mobile.

The remainder of the paper is organized as follows. In Sec. II an elementary discussion on the displacement current is reported. The case where the generation and recombination phenomenon takes place is also investigated, and its consequence on the position independence of the electric current across a sample in the shape of a slab is analyzed. In Sec. III the simple case where only the ions of one sign are mobile is discussed. The general solution of the problem is reported in Sec. IV, and the expression of the electric impedance in terms of the integration constants is deduced for the Nernstian case. In Sec. V, the case where the electrodes are described by Ohmic boundary conditions is considered. To compare our results with similar calculations performed by other authors, we considered also the very particular case where the conduction current is due only to diffusion. In this framework, drift current is assumed to be negligible. This approximation is very often used [20–23]. A comparison with the impedance expressions derived in the framework of pure diffusion models [8–12] is presented in Secs. V and VI, and the anomalies contained in the pure diffusion models are critically analyzed. The conclusions are reported in Sec. VI, where it is stressed that the theoretical interpretation of Warburg's impedance is still an open problem in electrochemistry.

II. THE DISPLACEMENT CURRENT

More than 100 years ago Maxwell proposed to modify Ampere's law $\nabla \times \mathbf{B} = \mu_0 \mathbf{j}$, where $\mathbf{B}$ and $\mathbf{j}$ are the magnetic field and the electric current density, and μ_0 is the magnetic permittivity of the vacuum. The reason was related to the simple observation that from it one derives $\nabla \cdot \mathbf{j} = 0$, that is valid only in the stationary case. To overcome this difficulty Maxwell proposed to modify Ampere's law by introducing the displacement current according to

$$\nabla \times \mathbf{B} = \mu_0 \left(\mathbf{j} + \varepsilon \frac{\partial \mathbf{E}}{\partial t} \right), \tag{1}$$

where ε is the dielectric constant of the medium. With this modification from Eq. (1) the equation of continuity, stating the conservation of the electric charge,

$$\frac{\partial \rho}{\partial t} + \nabla \cdot \mathbf{j} = 0, \tag{2}$$

where ρ is the bulk density of electric charge, is identically satisfied if Poisson's equation $\nabla \cdot \mathbf{E} = (1/\varepsilon)\rho$ is taken into account. In particular it follows that the total current

$$\mathbf{J} = \mathbf{j} + \varepsilon \frac{\partial \mathbf{E}}{\partial t} \tag{3}$$

is a solenoidal vector. In the simple case where the sample is a slab of thickness d, all physical quantities depend only on the coordinate along the normal to the limiting surfaces, z, and from Eq. (3) we derive that the z component of the total current density $J_z = J$ is position independent across the sample.

To analyze the importance of the displacement current, let us consider the case where the external electric field is a harmonic function of the time t of the type $\mathbf{E} = \mathbf{E_0} \exp(i\omega t)$, where, as before, ω is the circular frequency of the external field of amplitude E_0, and the isotropic medium is characterized by an electrical conductivity σ. In this framework the conduction current is $\mathbf{j} = \sigma \mathbf{E}$ and the displacement current $\varepsilon \partial \mathbf{E}/\partial t = i\omega\varepsilon \mathbf{E}$. The two contributions are comparable when $\sigma \sim \omega\varepsilon$. In the case of a metal, where $\sigma \sim 10^7\ (\Omega\,\mathrm{m})^{-1}$ and $\varepsilon \sim 10 \times \varepsilon_0$, the two contributions are comparable for $\omega \sim 10^{17}$ rad/s. From this observation it follows that for usual conductors the displacement current can be neglected in the low frequency region, and the quasistationary description works well. If the medium under consideration is an electrolytic solution, the electric conductivity is given by $\sigma = n_0 q \mu$, where n_0 is the bulk density of ions, q is its electric charge, and μ is the electric mobility. Assuming $n_0 \sim 10^{22}\ \mathrm{m}^{-3}$, $q = 1.6 \times 10^{-19}\,\mathrm{A\,s}$, $\mu = 40 \times 10^{-9}\ \mathrm{m}^2/(\mathrm{V\,s})$, and $\varepsilon \sim 10 \times \varepsilon_0$, we get that the conduction current is comparable with the displacement current for $\omega \sim 4 \times 10^3$ rad/s, i.e., for frequency of the order of a few kHz. From this simple observation it follows that the displacement current can play an important role in the determination of the electric impedance of an electrolytic cell for frequencies in the range from mHz up to a few Mhz, which is usually explored with the impedance spectroscopy technique [24]. However, for some unclear reasons, it is simply neglected in several papers devoted to the characterization of nonmetallic conductors by means of the impedance spectroscopy technique without any justification [8–13].

We observe that only when taking into account the displacement current the total current across the cell is position independent, and the concept of electric impedance, defined as the ratio of the applied voltage over the current across the cell, is meaningful. When it is neglected, the conduction current is position dependent, and therefore it is simply impossible to define the impedance of the cell since the current is variable across the cell.

It is of some importance to note that the total electric current across a cell in the shape of a slab is position independent even in the case where the phenomenon of generation (G) and recombination (R) is considered. To show this in some detail, let us consider an insulating medium containing neutral particles that can be dissociated by means of some mechanism, in positive and negative ions. We indicate by n, p, and m their bulk particle density, respectively, and by $\mathbf{j_n}$, $\mathbf{j_p}$, and $\mathbf{j_m}$ we indicate their bulk current density, respectively. The continuity equations for n, p, and m are

$$\frac{\partial n}{\partial t} = -\nabla \cdot \mathbf{j_n} - G + R, \tag{4}$$

$$\frac{\partial p}{\partial t} = -\nabla \cdot \mathbf{j_p} + G - R, \tag{5}$$

$$\frac{\partial m}{\partial t} = -\nabla \cdot \mathbf{j_m} + G - R, \tag{6}$$

independently of the functional form relating the bulk density of currents to the bulk density of particles and to the actual electric field in the medium. The actual electric field in the sample is related to the net charge density by the equation of Poisson:

$$\nabla \cdot \mathbf{E} = \frac{q}{\varepsilon}(p - m), \tag{7}$$

where q is the ionic charge and ε is the dielectric constant of the medium in which the ions are dissolved. The total electric current is

$$\mathbf{J} = q(\mathbf{j_p} - \mathbf{j_m}) + \varepsilon\,\frac{\partial \mathbf{E}}{\partial t}. \tag{8}$$

From Eq. (8), taking into account Eq. (7) we get

$$\nabla \cdot \mathbf{J} = q\left\{\left(\nabla \cdot \mathbf{j_p} + \frac{\partial p}{\partial t}\right) - \left(\nabla \cdot \mathbf{j_m} + \frac{\partial m}{\partial t}\right)\right\} = 0, \tag{9}$$

for all G and R terms. As discussed before, even in this case, for a one-dimensional problem, J is constant across the cell, and the impedance of the cell is simply given by $Z = \Delta V/(JS)$, where ΔV is the difference of potential applied to the cell, and S is the surface area of the electrodes.

III. SIMPLE PROBLEM

We limit now our analysis to the simple problem where only the positive ions are moving. This case corresponds to a hydrogel containing ions, such that the negative ions are stuck on the network of the gel, as discussed in Ref. [25]. The sample is assumed in the shape of a slab of thickness d, and the Cartesian reference frame has the z axis perpendicular to the electrodes, placed at $z = \pm d/2$. The external difference of potential applied to the sample is supposed to be a harmonic function of the type $\Delta V(t) = V_0 \exp(i\omega t)$, of amplitude V_0 and circular frequency ω. We indicate by n_0 the bulk density of ions in thermodynamical equilibrium, by p the actual bulk density of cations in the presence of the external field, and by D_p their diffusion coefficient in the considered insulating liquid. The electric potential across the sample is indicated by V. In this case the fundamental equations of the problem, neglecting the G-R phenomenon, are

$$\frac{\partial p}{\partial t} = \frac{\partial}{\partial z}\left\{D_p\,\frac{\partial p}{\partial z} + \mu_p\,p\,\frac{\partial V}{\partial z}\right\}, \tag{10}$$

representing the equation of continuity, and

$$\frac{\partial^2 V}{\partial z^2} = -\frac{q}{\varepsilon}(p - n_0), \tag{11}$$

which is Poisson's equation. We assume that the electric mobility, μ_p, and the diffusion coefficient, D_p, are related by a generalization of the Einstein relation $\mu_p/D_p = a/V_{\rm th}$, where $V_{\rm th} = k_B T/q$. The parameter a could be frequency dependent, as discussed in a simple example in the Appendix. For $a = 1$ we recover Einstein's relation. We assume that V_0 is such that $p - n_0 \ll n_0$ and introduce the reduced quantities $u_p = (p - n_0)/n_0$, $u_v = V/V_{\rm th}$, and $\zeta = z/d$, in such a manner that $-1/2 \leqslant \zeta \leqslant 1/2$. The bulk density of current of the positive ions is

$$j_p = -\frac{D_p n_0}{d}\left(\frac{\partial u_p}{\partial \zeta} + a\,\frac{\partial u_v}{\partial \zeta}\right). \tag{12}$$

From Eq. (12) it is evident that for $a = 0$ we recover the case of diffusion, and for large a the case of drift (where drift dominates the conduction current). In terms of the reduced quantities Eqs. (10) and (11) can be rewritten as

$$\frac{\partial u_p}{\partial t} = \omega_d\left(\frac{\partial^2 u_p}{\partial \zeta^2} + a\,\frac{\partial^2 u_v}{\partial \zeta^2}\right), \tag{13}$$

$$\frac{\partial^2 u_v}{\partial \zeta^2} = -(d/\Lambda)^2\,u_p, \tag{14}$$

where $\Lambda = \sqrt{\varepsilon k_B T/(n_0 q^2)}$ is the Debye length for the present problem, and $\omega_d = D_p/d^2$ is the diffusion circular frequency. For further consideration it is useful to introduce Debye's relaxation circular frequency $\omega_D = D_p/\Lambda^2$, and express the frequency in units of ω_D as $\Omega = \omega/\omega_D$.

When the excitation is harmonic we have $u_p(\zeta,t) = \phi_p(\zeta)\,\exp(i\omega t)$ and $u_v(\zeta,t) = \phi_v(\zeta)\,\exp(i\omega t)$, where $\phi_p(\zeta)$ and $\phi_v(\zeta)$ are solutions of the ordinary differential equations

$$\phi_p''(\zeta) = 4\,M^2(a + i\,\Omega)\,\phi_p(\zeta), \tag{15}$$

$$\phi_v''(\zeta) = -4\,M^2\,\phi_p(\zeta), \tag{16}$$

where the prime means a derivation with respect to ζ, and $M = d/(2\Lambda)$. The total electric current density across the cell is given by

$$J = J_0\{(\phi_p' + a\phi_v') + i\Omega\,\phi_v'\}\,\exp(i\omega t), \tag{17}$$

where $J_0 = \varepsilon\omega_D\,V_{\rm th}/d$ is an intrinsic electric current density. The contribution to J of the conduction current is

$$J_{\rm cond} = J_0\,(\phi_p' + a\phi_v')\,\exp(i\omega t), \tag{18}$$

whereas the contribution due to the displacement current is

$$J_{\rm disp} = i\,J_0\,\Omega\,\phi_v'\,\exp(i\omega t). \tag{19}$$

Solutions of Eqs. (15) and (16) are

$$\phi_p(\zeta) = A_1\,\sinh(2\,M\sqrt{a + i\,\Omega}\;\zeta) + A_2\,\cosh(2\,M\sqrt{a + i\,\Omega}\;\zeta) \tag{20}$$

and

$$\phi_v(\zeta) = -\frac{1}{a + i\,\Omega}\,\phi_p(\zeta) + B_1\zeta + B_2, \tag{21}$$

where A_1, A_2, B_1, and B_2 are integration constants to be determined by means of the boundary conditions discussed below. Substituting ϕ_p and ϕ_v given by Eqs. (20) and (21) into the expression (17) we get

$$J = J_0\,B_1\,(a + i\Omega)\,\exp(i\omega t). \tag{22}$$

From Eq. (22) it follows that J is position independent in the cell. It depends only on the integration constant related to the linear term in ζ of the potential expression. The impedance of the cell, defined by $Z = \Delta V(t)/[J(t)S]$, in our case is

$$Z = R_0\,\frac{u_0}{B_1(a + i\Omega)}, \tag{23}$$

where $u_0 = qV_0/K_B T$, and $R_0 = d/(\varepsilon\omega_D S)$ is a characteristic resistance of the sample.

Equation (23) is general. It can be applied as soon as the boundary conditions of the problem are defined. The boundary conditions on the electric potential, due to the presence of the external power supply, are

$$\phi_v(\pm 1/2) = \pm u_0/2. \tag{24}$$

The boundary conditions on the bulk density of ions or on the ionic currents depend on the model.

IV. NERNSTIAN MODEL

A. General considerations

In the framework of the Nernstian model [8–12] the potential of the electrode fixes the bulk density of ions just in front of the electrodes itself, according to the relations

$$\phi_p(1/2) = k_1 \frac{u_0}{2} \quad \text{and} \quad \phi_p(-1/2) = -k_2 \frac{u_0}{2}, \tag{25}$$

in the limit of small u_0. The perturbation of the bulk density of ions due to the presence of the applied potential is responsible for a diffusion current of charged particles across the sample. In this case, a simple calculation yields

$$B_1 = u_0 \frac{a + i\Omega + (k_1 + k_2)/2}{(a + i\Omega)} \tag{26}$$

and the impedance of the cell, according to Eq. (23), is

$$Z_N(k_1,k_2,a;\Omega) = \frac{R_0}{a + i\Omega + (k_1 + k_2)/2}, \tag{27}$$

where the subscript N indicates that we are working in the Nernstian approximation. In the symmetric case where $k_1 = k_2 = k$ from Eq. (27) we get

$$Z_N(k,k,a;\Omega) = \frac{R_0}{a + i\Omega + k}, \tag{28}$$

whereas in the case where $k_1 = k$ and $k_2 = 0$ we have

$$Z_N(k,0,a;\Omega) = \frac{R_0}{a + i\Omega + k/2}. \tag{29}$$

Figure 1 shows the frequency dependence of $R_N(k,k,a;\Omega) = \text{Re}[Z_N(k,k,a;\Omega)]$ [Fig. 1(a)], $X_N(k,k,a;\Omega) = \text{Im}[Z_N(k,k,a;\Omega)]$ [Fig. 1(b)], and their parametric plot $-X_N(k,k,a;\Omega)$ versus $R_N(k,k,a;\Omega)$ [Fig. 1(c)], for $a = 0$ corresponding to a diffusive current (solid line), for $a = 1$ corresponding to the Einstein approximation (dashed line), and for $a = 10$ corresponding to a case where the diffusion current is small with respect to the drift current (dotted line). We observe that for this symmetric case, in the dc limit the behavior of the cell is of pure Ohmic type, and

$$\lim_{\Omega \to 0} Z_N(k,k,a;\Omega) = \frac{R_0}{a + k}. \tag{30}$$

The relaxation frequency, well visible in the spectrum of $X_N(k,k,a;\Omega)$, is $\Omega_r = a + k$.

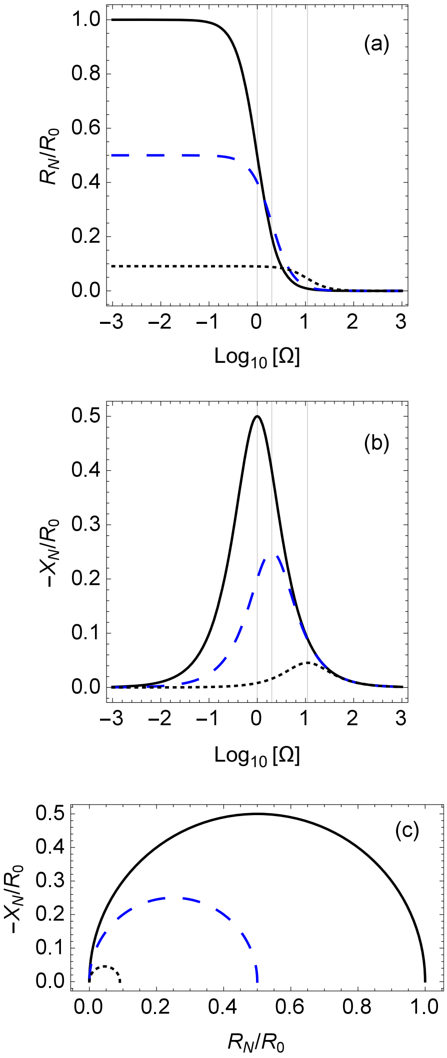

FIG. 1. Frequency dependence of R_N/R_0 (a) and $-X_N/R_0$ (b) and parametric plot of $-X_N/R_0$ vs R_N/R_0 (c) for a symmetric cell in the Nernstian approximation, when $a = 0$, diffusive current (solid line); $a = 1$, Einstein approximation (dashed line); and $a = 10$, important drift (dotted line). The curves are drawn for $k = 1$. The vertical lines are the circular relaxation frequencies $\Omega_r = a + k$.

As discussed in the Introduction, to compare our results with those derived by means of pure diffusion models [8–12], we have to limit our analysis to the case in which the conduction current is only due to the diffusion. In this framework, the drift component of the conduction current is assumed to be negligible with respect to the diffusion component. This approximation is widely used, despite the fact that its physical origin is unclear [20–23]. It is based on the hypothesis that in the bulk the net electric field is zero. The electric current is generated by the modification of the bulk density of ions close to the electrodes, and it has only a diffusive origin. In the following, to perform this limit we will assume $a = 0$. This is a delicate point for the following reason. The drift current is negligible when the electric field responsible for the drift is very small, as in supported liquid. However, the electric field is surely not negligible close to the electrodes, where the overpotential is responsible for the response of the cell to the external stimulus. In the surface layer the actual electric field is usually rather large, since the overpotential vanishes over a few Debye lengths. Consequently, in the surface layer, the drift current is not expected to be negligible with respect to the diffusion current. This type of problem has not been mentioned in [8–12] because Poisson's equation was not considered. In the following to compare our results with those obtained by [8–12] we suppose that the current is still due to the diffusion, but we will take into account Poisson's equation.

In the diffusion approximation, where $a = 0$, and for the symmetric electrodes case, the electric current density across the cell is

$$J = J_0\, u_0 (k + i\Omega)\, e^{i\omega t}, \tag{31}$$

as it follows from Eq. (22), and the impedance of the cell, given by Eq. (27), can be written as

$$Z_N(k,k,0;\Omega) = \frac{R_0}{k + i\Omega}. \tag{32}$$

From Eq. (32) it follows that the resistance, $R_N(k,k,0;\Omega)$, and reactance, $X_N(k,k,0;\Omega)$, of the cell are given by

$$R_N(k,k,0;\Omega) = R_0\, \frac{k}{k^2 + \Omega^2},$$

$$X_N(k,k,0;\Omega) = -R_0\, \frac{\Omega}{k^2 + \Omega^2}. \tag{33}$$

The parametric plot of $-X_N(k,k,0;\Omega)$ versus $R_N(k,k,0;\Omega)$ is a semicircle crossing the real axis at the origin of the reference frame and at R_0/k, with center on the real axis in $R_0/(2k)$. This parametric plot is similar to that predicted by a Debye model for a medium having a complex dielectric constant characterized by a single relaxation time [24].

The same problem ($a = 0$) in the framework of the Nernstian approximation has been considered by means of pure diffusion models [8–12] where, moreover, the displacement current has been neglected. With a calculation similar to that presented above, the expression for the reduced ionic density is found to be

$$\phi_p(\zeta) = k\, \frac{u_0}{2}\, \frac{\sinh(2\, M\, \sqrt{i\Omega}\, \zeta)}{\sinh(M \sqrt{i\Omega})}, \tag{34}$$

coinciding with Eq. (20) written for the present case. In the subsequent analysis, and in the framework of pure diffusion models, the total electric current density in the cell is identified with the diffusion current $j = J_0 \phi_p' \exp(i\omega t)$, that taking into account Eq. (34) can be rewritten as

$$j = k u_0\, J_0\, M\, \sqrt{i\Omega}\, \frac{\cosh(2\, M\, \sqrt{i\Omega}\, \zeta)}{\sinh(M \sqrt{i\Omega})}\, e^{i\omega t}. \tag{35}$$

We underline that, if the displacement current is neglected, the electric current across the cell is independent of the electric potential distribution. In this case the equation of Poisson does not play any role in the determination of the impedance of the cell. As it is evident from Eq. (35) the current density is not constant across the cell. It is an even function of ζ. In Ref. [11] the current was, arbitrarily, evaluated on the electrodes obtaining

$$j = k u_0\, J_0\, M\, \sqrt{i\Omega}\, \tanh(M \sqrt{i\Omega})\, e^{i\omega t}. \tag{36}$$

The impedance of the cell is then

$$Z_D = \frac{R_0}{k}\, \frac{\tanh(M \sqrt{i\Omega})}{M \sqrt{i\Omega}}, \tag{37}$$

where the subscript D stands for Z obtained in the framework of pure diffusion models. Note that $M\sqrt{i\Omega} = (1/2)\sqrt{i\omega/\omega_d}$, where $\omega_d = D_p/d^2$ is the diffusion circular frequency introduced above. It follows that in the model proposed in Refs. [8–12] the circular relaxation frequency is independent of the bulk density of ions. In Fig. 2, we compare the parametric plot of $-X$ versus R obtained (i) from Z_N, given by Eq. (32), that includes displacement current, and (ii) from the expression reported in Ref. [11], deduced by neglecting the displacement current, that is, Z_D. The relaxation frequency from $Z_N(k,k,0;\Omega)$ is $\Omega_r(N) = k$, whereas from the expression Z_D it is $\Omega_r(D) = \pi^2/(2M)^2$, as is evident from the spectrum of R [Fig. 2(a)] and of X [Fig. 2(b)]. In the parametric plot of $-X_D$ versus R_D is present, in the high frequency range, a linear dependence of X_D on R_D, that in several papers has been claimed as a demonstration of the Warburg impedance [14], and hence explained as a consequence of the pure diffusion motion of the charge carriers in the medium. This is questionable because the model used to derive this conclusion seems not to be correct. Once the displacement current is taken into account, the linear part of the parametric plot disappears and the semicircular behavior is recovered. In Fig. 3 left, we show

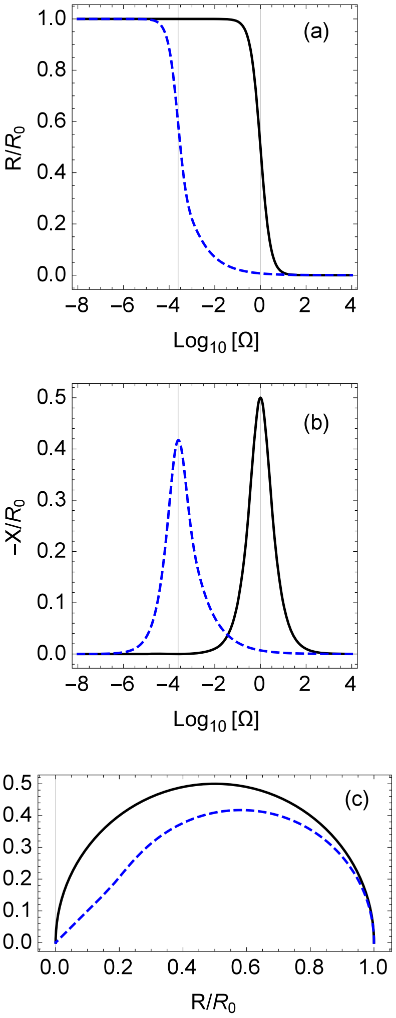

FIG. 2. Comparison of the frequency dependence of the real (a) and imaginary (b) part of the electric impedance of the cell derived by means of the complete model (solid lines) and of the pure diffusion model (dashed lines), where the total electric current is identified only with the conduction current due to diffusion. The parametric plots are reported in panel (c). The vertical lines are the circular relaxation frequencies determined by means of the two models. The linear part present in the curves derived by means of pure diffusion models has been identified in the past with a Warburg-like impedance.

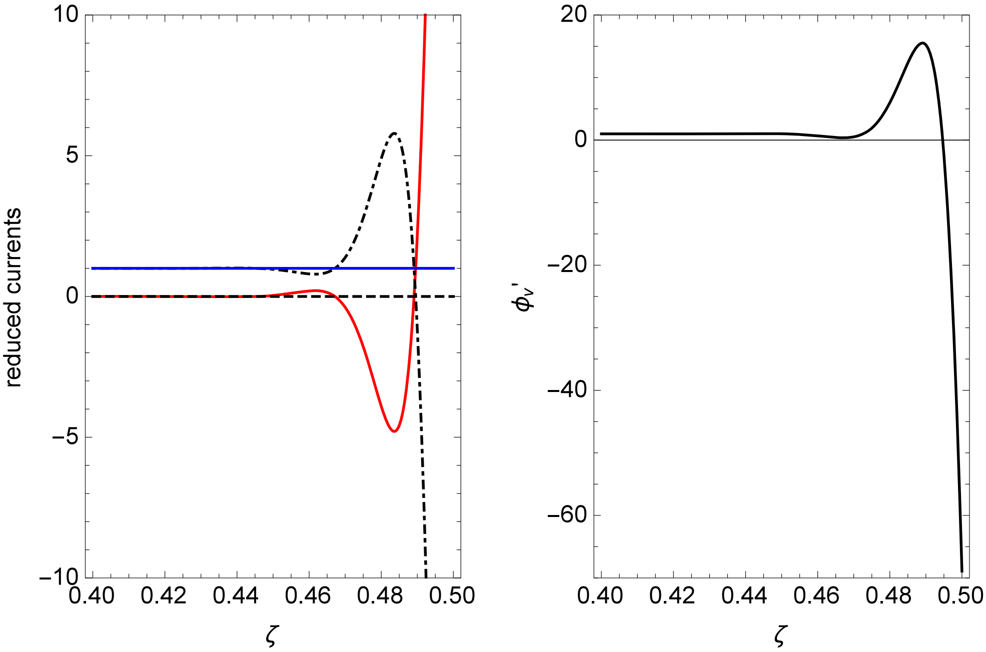

FIG. 3. Left: Total reduced current (blue horizontal line) for zero drift (dashed line) at the frequency $\Omega = 0.01$ and its nonzero components, diffusion (red solid line) and displacement current (black dot-dashed line), for the symmetric case of the Nernstian approximation. Right: Electric field in the cell. Note that the electric field is not zero far from the electrodes, thus neglecting drift seems questionable.

the current components over the total current, versus ζ, in the proximity of the electrode as a function of the position, ζ, for $a = 0$. The calculation of the currents has been performed at a low frequency $\Omega = 0.01$ in order to test if the displacement current could be neglected as usually assumed in the literature. The horizontal solid line represents the total current in the cell, that is constant at all positions before normalization. The solid red line represents the diffusion current $J_{\rm dif}$ and the dot-dashed black line represents the displacement current $J_{\rm disp}$. Note that $J_{\rm disp}$ is constant far from the electrodes and much larger than $J_{\rm dif}$, and its amplitude close to the electrode is similar to the amplitude of the diffusion current. Figure 3 right shows the electric field in the cell. ϕ_v' is constant but not zero far from the electrode, therefore one has to be cautious with the hypothesis of the supported system. Figure 4 left shows the current components for the case $a = 1$, that is, when drift is allowed. From this figure, one concludes that, in general, the drift current (dashed line) cannot be omitted either in the interfacial region or in the bulk where it may be dominant in respect to the diffusion current. This latter observation is also of some importance in respect to the supported electrolyte approximation. Note also that the displacement current in the bulk compares with the drift component, while close to the electrode it is certainly not negligible. Figure 4 right shows the electric field in the cell. As is shown, in the surface layer the electric field is found to be rather large.

B. Adsorbing electrodes

In the framework of the Nernstian model an electrode is called *adsorbing* if it is able to fix the surface bulk density of ions to its thermodynamical equilibrium value. This means that, in the analysis presented above, the corresponding k_1 or k_2 phenomenological parameters entering into the boundary conditions (25) vanish. As is clear from Eq. (27), if $k_1 = k_2 = 0$ the electric impedance of the cell limited by two adsorbing electrodes is

$$Z_N(0,0,a;\Omega) = \frac{R_0}{a + i\,\Omega}, \tag{38}$$

i.e., it coincides with the impedance of a Debye model characterized by a single relaxation time. In the particular case where $a = 0$, the impedance corresponds to a pure capacitive reactance. If only one of the electrodes is adsorbing, the corresponding impedance is given by Eq. (29). It is equivalent to the impedance of a symmetric cell limited by nonadsorbing electrodes with $k_1 = k_2 = k/2$. In the diffusive case Eq. (29) yields

$$Z_N(k,0,0;\Omega) = \frac{R_0}{k/2 + i\Omega}. \tag{39}$$

We analyze in some detail the cell limited by one adsorbing electrode to underline the strange results that are obtained when the displacement current is neglected in the determination of the impedance in the pure diffusive case, as done, among others by Bisquert [11]. In the case where $k_1 = k$ and $k_2 = 0$ the profile of the bulk density of the charge carriers is

$$\phi_p(\zeta) = \frac{k}{4}u_0\left\{\frac{\sinh(2M\sqrt{i\Omega}\;\zeta)}{\sinh(M\;\sqrt{i\;\Omega})} + \frac{\cosh(2M\sqrt{i\Omega}\;\zeta)}{\cosh(M\;\sqrt{i\;\Omega})}\right\}. \tag{40}$$

If the displacement current is neglected, the electric current density in the cell is given by Eq. (18), that in the present case

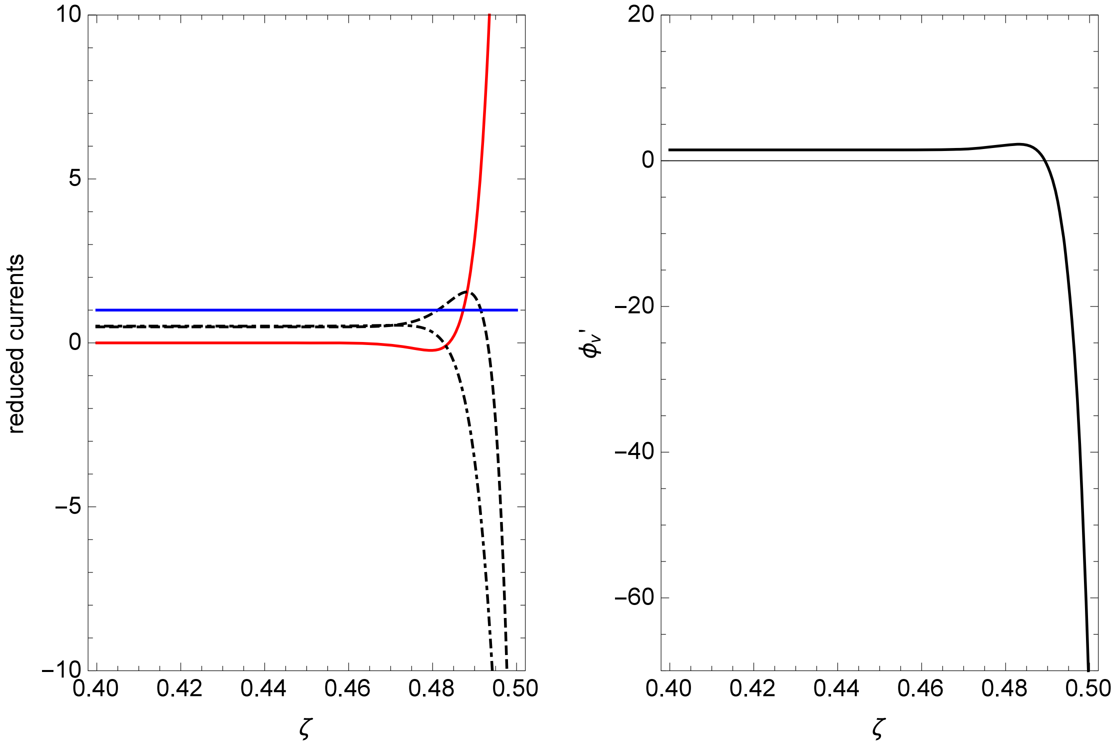

FIG. 4. Left: Total reduced current (blue horizontal line) at the frequency $\Omega = 0.01$ and its components, diffusion (red solid line), drift (dashed line), and displacement current (black dot-dashed line), for the symmetric case of the Nernstian approximation. Right: Electric field in the cell.

takes the form

$$j = \frac{k}{2}\, u_0\, J_0\, M\sqrt{i\,\Omega}\left\{\frac{\cosh(2M\sqrt{i\Omega}\;\zeta)}{\sinh(M\sqrt{i\Omega})} + \frac{\sin(2M\sqrt{i\Omega}\;\zeta)}{\cosh(M\sqrt{i\Omega})}\right\}. \tag{41}$$

The electric current density is not constant across the cell, and it does not have a defined symmetry in ζ.

If j is evaluated, in an arbitrary manner, at $\zeta = 1/2$ (nonadsorbing electrode), we get

$$j(1/2) = k u_0 J_0 M\sqrt{i\Omega}\coth(2M\sqrt{i\Omega}), \tag{42}$$

and the corresponding impedance of the cell, in the scheme proposed in Ref. [11], is given by

$$Z_D(1/2) = 2\frac{R_0}{k}\,\frac{\tanh(2M\sqrt{i\Omega})}{2M\sqrt{i\Omega}}. \tag{43}$$

The comparison of $Z_N(k,0,0;\Omega)$ given by Eq. (39) with Z_D given by Eq. (43) has the characteristics shown in Fig. 2.

If j is evaluated on the adsorbing electrode, at $\zeta = -1/2$, we have

$$j(-1/2) = k u_0 J_0 M\sqrt{i\Omega}\;\frac{1}{\sinh(2M\sqrt{i\Omega})}, \tag{44}$$

and the impedance of the cell becomes

$$Z_D(-1/2) = 2\frac{R_0}{k}\,\frac{\sinh(2M\sqrt{i\Omega})}{2M\sqrt{i\Omega}}. \tag{45}$$

Expression (45) is nonsense. It predicts negative resistance for some values of the frequency. This nonsense, as underlined above, is related to the assumption that the displacement current is negligible. This assumption works well only in the limit of $\Omega \to 0$. In this limit expressions (39), (43), and (45) tend to the correct value $2R_0/k$, as expected.

C. Reflecting electrodes

An electrode is called *reflecting* if the current density of particles vanishes on it. In the domain of electrochemical impedance spectroscopy an electrode having this property is also called blocking. We consider now the case where the boundary conditions on the potential are of the type of Eq. (24) and those on the ionic density are

$$\phi_p(1/2) = k\frac{u_0}{2} \quad \text{and} \quad \phi_p'(-1/2) = 0, \tag{46}$$

corresponding to a reflecting electrode at $\zeta = -1/2$. In the diffusion case, the solution of the problem can be obtained by means of the procedure discussed above. A simple calculation gives for the impedance of the cell the expression

$$Z_c = 2R_0\,\frac{\cosh(2M\sqrt{i\Omega})}{(k + 2i\Omega)\cosh(2M\sqrt{i\Omega}) - k}. \tag{47}$$

In the limit $\Omega \to 0$, Z_c diverges, indicating that no dc current can flow across the cell, in agreement with the hypothesis that one of the electrodes is blocking. In the dc limit, from Eq. (47), we get

$$\lim_{\Omega\to 0} Z_c = \frac{5kM^4}{3(1+kM^2)^2}R_0 - i\frac{R_0}{(1+kM^2)\Omega}. \tag{48}$$

In the case of large Ω from Eq. (47) we obtain

$$\lim_{\Omega\to\infty} Z_c = 2\frac{R_0}{k+2i\Omega}, \tag{49}$$

from which it is evident that in the limit of large Ω the impedance coincides with that of a cell having an adsorbing electrode [see Eq. (39)], characterized by a dc resistance $2R_0/k$. An expansion in the power series of Z, expression (47), to the second order in Ω shows that there exists a critical value of k, defined by

$$k_c = \frac{-23+\sqrt{2191}}{2M^2}, \tag{50}$$

such that, for $k \geqslant k_c$, R tends first to $2R_0/k$, and then decreases to the value given by Eq. (48). In this case, before diverging, the reactance changes sign in a small frequency range. This effect is well visible in Fig. 5 where are shown the real [Fig. 5(a)] and imaginary [Fig. 5(b)] parts of Z_c versus Ω, and the parametric plot of $-X_c$ versus R_c [Fig. 5(c)]. In contrast, for $k \leqslant k_c$, R tends monotonically to the value given by Eq. (48). This situation is shown in Fig. 6. We observe that the case $k \geqslant k_c$ looks a little bit strange, for the decreasing of the resistance of the cell in the dc limit. Probably it simply indicates that Nernstian boundary conditions are valid only for weak enough current at the interface, related to small values of k. Hence k_c gives, probably, an indication on the maximum value of the phenomenological parameter k.

In the present case, the profile of charge carriers is given by

$$\phi_p(\zeta) = \frac{k}{2}u_0\frac{\sinh(M\sqrt{i\Omega})\,\sinh(2M\sqrt{i\Omega}\,\zeta) + \cosh(M\sqrt{i\Omega})\,\cosh(2M\sqrt{i\Omega}\,\zeta)}{\cosh(2M\sqrt{i\Omega})}. \tag{51}$$

If the displacement current is neglected the electric current density is found to be

$$j = ku_0J_0M\sqrt{i\Omega}\frac{\sinh(M\sqrt{i\Omega})\,\cosh(2M\sqrt{i\Omega}\,\zeta) + \cosh(M\sqrt{i\Omega})\,\sinh(2M\sqrt{i\Omega}\,\zeta)}{\cosh(2M\sqrt{i\Omega})}. \tag{52}$$

This current density is ζ dependent. It vanishes at $\zeta = -1/2$. If it is arbitrarily evaluated at $\zeta = 1/2$, a simple calculation gives

$$j(1/2) = ku_0J_0M\sqrt{i\omega}\,\tanh(2M\sqrt{i\Omega}). \tag{53}$$

The corresponding impedance

$$Z_D = 2\,\frac{R_0}{k}\,\frac{\coth(2M\sqrt{i\Omega})}{2M\sqrt{i\Omega}} \tag{54}$$

is coinciding with the expression reported in Ref. [11]. From Eq. (54) we deduce that in the limit of $\Omega \to 0$, the impedance tends to

$$\lim_{\Omega\to 0} Z_D = \frac{2R_0}{3k} - i\frac{R_0}{2kM^2\Omega}, \tag{55}$$

showing that in the parametric plot of $-X_D$ versus R_D, the vertical asymptote is located at $R_D(0) = 2R_0/(3k)$. In the high frequency region it tends to

$$\lim_{\Omega\to\infty} Z_D = \frac{R_0}{k}\,\frac{1}{M\sqrt{i\Omega}}, \tag{56}$$

presenting, in the parametric plot, the linear part, attributed to Warburg. As before, we note that although the expression (54) is very elegant, its physical meaning is unclear.

V. OHMIC MODEL

A. General considerations

In previous sections we have investigated in some detail the impedance of an electrolytic cell assuming that the boundary conditions on the ionic bulk density just in front of the electrode are fixed by the difference of potential between the electrode itself and the bulk, mathematically expressed by Eqs. (25). These boundary conditions are expected to work well in the state of thermodynamical equilibrium, where the current across the cell is absent. In this case, it can be considered as the expression of Boltzmann statistics for charged particles in the presence of an external field. In the presence of an electric current these boundary conditions are not so obvious. According to the analysis of the previous section, Nerstian boundary conditions could be valid only for low enough current. A discussion on them has been reported by Bisquert [11]. Other boundary conditions very often used in electrochemistry are those proposed by Chang and Jaffe [26], where the current density at the surface is proportional to the variation of the bulk density of ions just in front of the electrode with respect to the value of equilibrium. Boundary conditions of this type are used to describe the evaporation phenomenon [27], or the external heat conduction. In the latter case, it is known as Newton's law. The effect of the Chang-Jaffe boundary conditions on the electric impedance of an electrolytic cell has been investigated by Macdonald and Franceschetti long ago [28]. Another type of boundary conditions proposed some years ago assumes that the current density at the surface is proportional to the surface electric field [29], known as the Ohmic model. In the simple case where only one group of ions is mobile, as in the case considered in the present paper, it is possible to show that the Chang-Jaffe model and Ohmic model are equivalent [30]. This means that fixing a phenomenological parameter for one model it is possible to determine, in a unique manner, the phenomenological parameter of the other model in such a manner that the two expressions of the impedance coincide [30]. In a recent paper we have analyzed the analogies and differences between the two models [31].

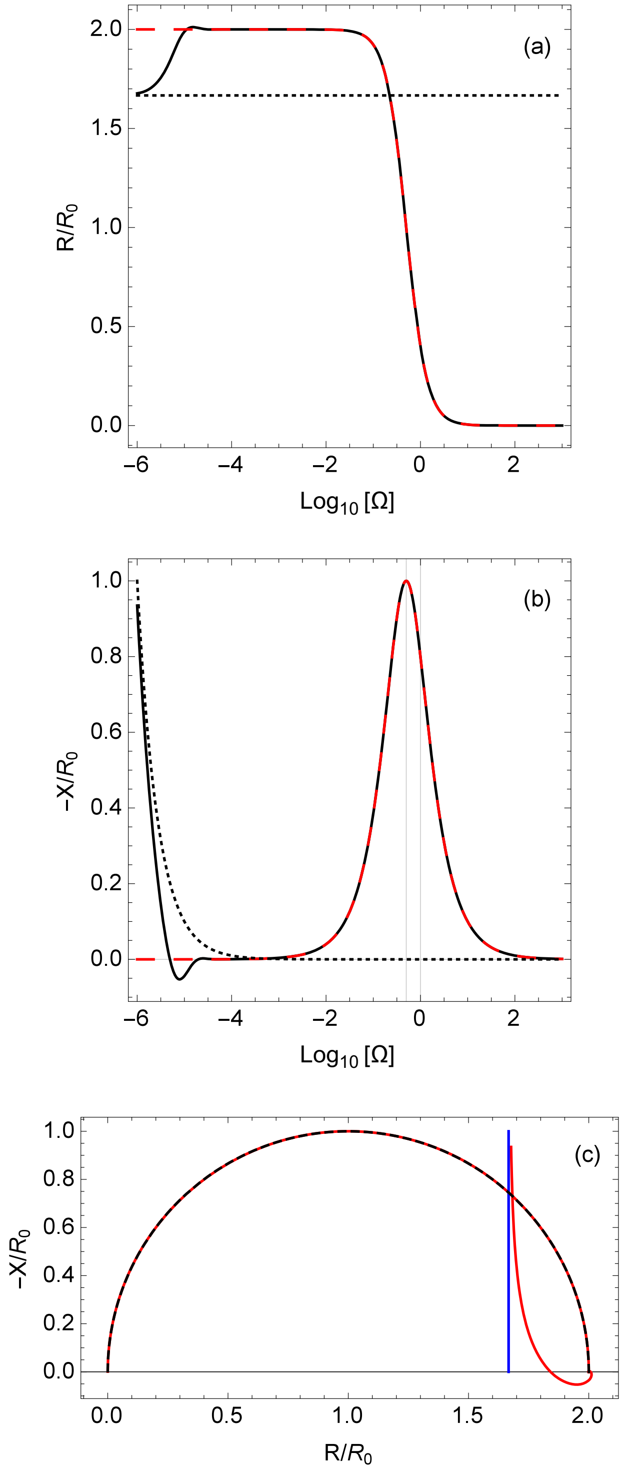

FIG. 5. Frequency dependence of the real (a) and imaginary (b) part of the impedance, and parametric plot of the imaginary vs the real part (c). The cell in the pure diffusive regime is limited by a reflecting electrode, at $\zeta = -1/2$. On the electrode at $\zeta = 1/2$ the boundary condition is of Nernstian type characterized by $k = 1$. Full expression of the real and imaginary parts of the impedance is shown by the solid line, while approximated expressions valid in the high and low frequency regions are shown by the red dashed and black dotted lines, respectively. In panel (a), the horizontal lines are the plateaus corresponding to $5R_0/(3k)$ and to $2R_0$. In panel (c) the vertical asymptote corresponds to $5R_0/(3k)$.

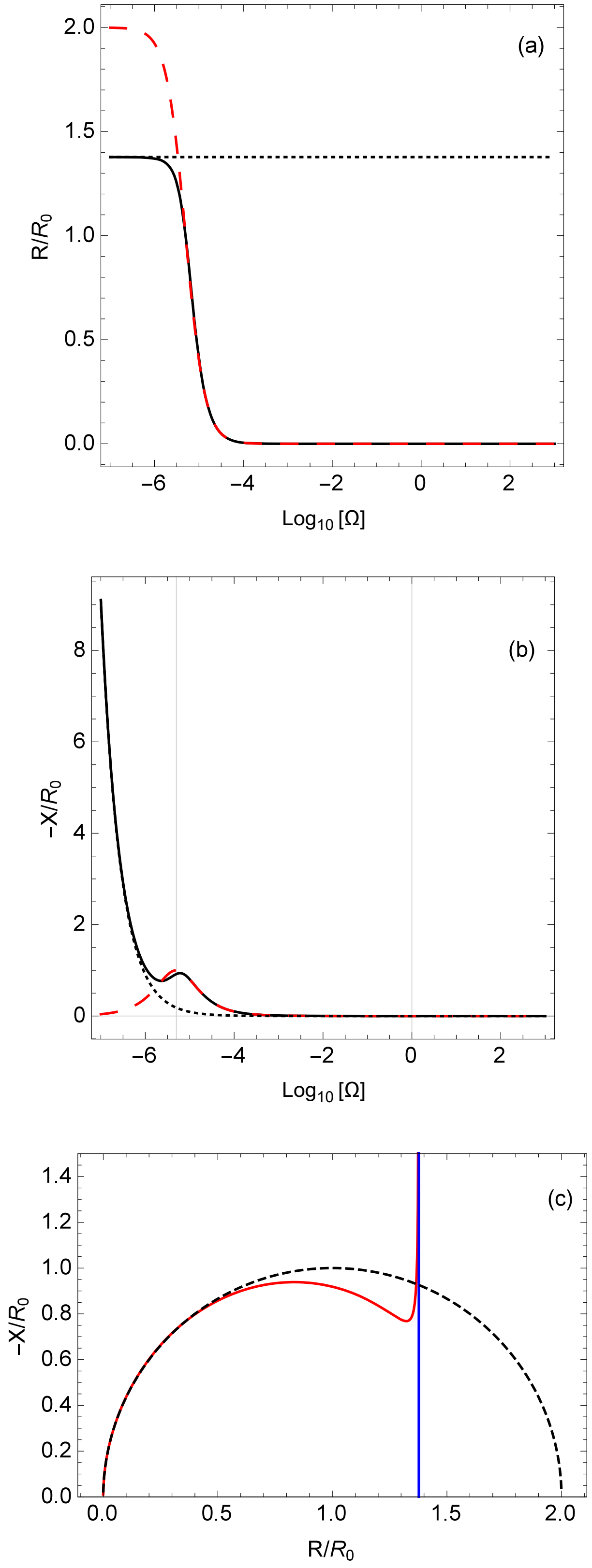

FIG. 6. Same as Fig. 5, with $k = 10^{-5} \leqslant k_c$.

Our aim is now to evaluate the impedance of the cell, in the same framework used above, assuming Ohmic boundary conditions, in order to verify if a Warburg-type behavior is present.

In particular, we are interested in the pure diffusive case, where $a = 0$. The case of $a = 1$, corresponding to the Einstein-Smolucowski relation, has been considered in Refs. [32,33]. In the framework of the Ohmic model the boundary conditions on the current density of particles are

$$j_p(1/2) = s_1\, E(1/2) \quad \text{and} \quad j_p(-1/2) = s_2\, E(-1/2), \tag{57}$$

where $s_{1,2}$ are the phenomenological parameters of the Ohmic model and $E(\pm 1/2)$ are the surface electric fields. In terms of the reduced quantities introduced above, in the linear approximation, Eqs. (57) can be rewritten as

$$\phi_p' + (a - h_1)\,\phi_v' = 0, \tag{58}$$

$$\phi_p' + (a - h_2)\,\phi_v' = 0, \tag{59}$$

at $\zeta = \pm 1/2$, respectively, where $h_1 = s_1/s_c$ and $h_2 = s_2/s_c$, with $s_c = \varepsilon\omega_D/q$, are dimensionless parameters of the Ohmic model. In this case the integration constants A_1, A_2, B_1, and B_2 are easily determined from the boundary conditions (24), (58), and (59), and the electric impedance of the cell is evaluated by means of Eq. (23). A simple calculation gives for the impedance $Z(h_1,h_2,a;\Omega)$ the expression

$$Z = R_0\,\frac{2M(a+i\Omega)(h_1+i\Omega)(h_2+i\Omega) + \sqrt{a+i\Omega}[-2h_1h_2 + a(h_1+h_2+2i\Omega) - i(h_1+h_2)\Omega]\,\tanh[M\sqrt{a+i\Omega}]}{2M(a+i\Omega)^2(h_1+i\Omega)(h_2+i\Omega)}. \tag{60}$$

From Eq. (60) it follows that in the dc limit we get

$$\lim_{\Omega\to 0} Z(h_1,h_2,a;\Omega) = R_0\,\frac{2ah_1h_2M + \sqrt{a}[-2h_1h_2 + a(h_1+h_2)]\,\tanh[\sqrt{a}\,M]}{2a^2h_1h_2M}, \tag{61}$$

from which it follows that, as soon as $a \neq 0$, $h_1 \neq 0$, and $h_2 \neq 0$, in the considered limit the cell behaves as a pure resistance.

B. Symmetric and blocking electrodes

In the following, we limit our analysis to the case $h_1 = h_2 = h$, that we term symmetric, and to the case $h_1 = h$ and $h_2 = 0$, corresponding to a cell limited by one blocking electrode. Using Eq. (60) we get for the two cases

$$Z(h,h,a;\Omega) = R_0\,\frac{M(h+i\Omega)(-ia+\Omega) - i(a-h)\sqrt{a+i\Omega}\,\tanh[M\sqrt{a+i\Omega}]}{M(a+i\Omega)^2(-ih+\Omega)}, \tag{62}$$

$$Z(h,0,a;\Omega) = R_0\,\frac{2M(h+i\Omega)\Omega(-ia+\Omega) + \sqrt{a+i\Omega}[-a(h+2i\Omega) + ih\Omega]\,\tanh[M\sqrt{a+i\Omega}]}{2M(a+i\Omega)^2\Omega(-ih+\Omega)}. \tag{63}$$

In the diffusive case, expressions (62) and (63) can be rewritten as

$$Z(h,h,0;\Omega) = -i\,R_0\,\frac{M(h+i\Omega)\Omega + ih\sqrt{i\Omega}\,\tanh[M\sqrt{i\Omega}]}{M\Omega^2(h+i\Omega)}, \tag{64}$$

$$Z(h,0,0;\Omega) = -i\,R_0\,\frac{2M(h+i\Omega)\Omega^2 + ih\sqrt{i\Omega}\,\Omega\,\tanh[M\sqrt{i\Omega}]}{2M\Omega^3(h+i\Omega)}. \tag{65}$$

In the limit of $\Omega \to 0$, from Eqs. (64) and (65) we get

$$Z(h,h,0;\Omega) = \left(\frac{1}{h} + \frac{M^2}{3}\right)R_0 - i\,\frac{15 + (5 + 2hM^2)hM^2}{15h^2}\,R_0\,\Omega + \mathcal{O}(\Omega^2), \tag{66}$$

$$Z(h,0,0;\Omega) = \frac{R_0}{2i\Omega} + \frac{3 + hM^2}{6h}\,R_0 + \mathcal{O}(\Omega). \tag{67}$$

From the expansion of $Z(h,h,0;\Omega)$, we infer that in the dc limit Z tends to a pure resistance given by

$$\lim_{\Omega\to 0} Z(h,h,0;\Omega) = \left(\frac{1}{h} + \frac{M^2}{3}\right)R_0 \sim \frac{M^2}{3}\,R_0, \tag{68}$$

for $h \sim 1$ and $M \gg 1$. In contrast, from the expansion of $Z(h,0,0;\Omega)$ it follows that in the dc limit it diverges, as expected. The impedance of the cell is equivalent to a series of a capacitance C_s and a resistance R_s defined by

$$C_s = 2\varepsilon\,\frac{S}{d} \quad \text{and} \quad R_s = \frac{3 + hM^2}{6h}R_0 \sim \frac{1}{6}M^2R_0 = \frac{1}{24}\,\frac{d^3}{\varepsilon D_p S}. \tag{69}$$

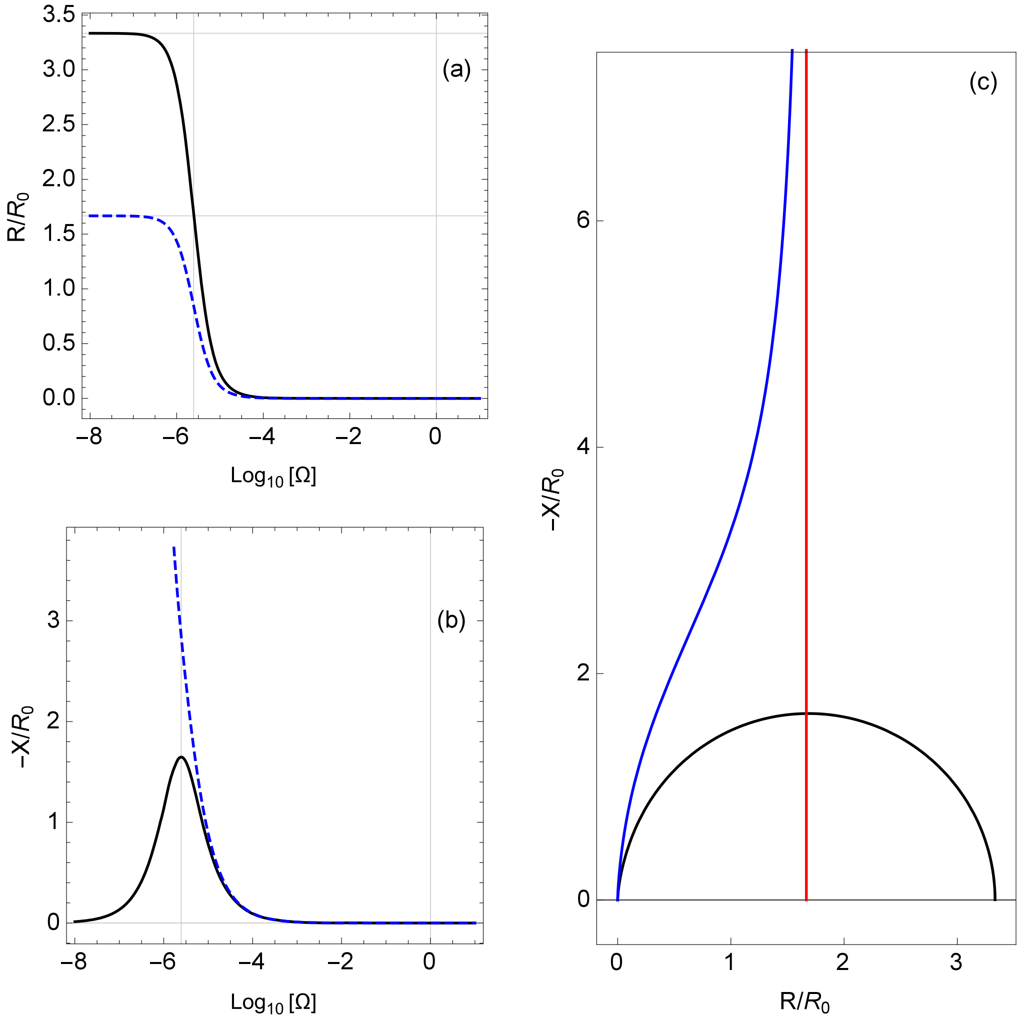

FIG. 7. Spectra of the real (a), imaginary (b), and parametric (c) plot of the real part with respect to the imaginary part, of $Z(h,h,0)$ (black solid line) and $Z(h,0,0)$ (dashed blue line). In the same figure are also reported the dc values for the resistances deduced by Eqs. (68) and (69). The relaxation frequency, visible in panel (b), is $\Omega_r = \pi^2/(2M)^2$. In the parametric plot (c), the vertical asymptote (red line) is defined by Eq. (69), and the corresponding frequency is Ω_r. The curves are drawn for $M = 10^3$, $h = 2$.

In the limit of $\Omega \to \infty$ from Eqs. (64) and (65) we obtain

$$Z(h,h,0;\Omega) = \frac{R_0}{i\Omega} + \frac{hR_0}{\sqrt{2}\,M}\;\Omega^{-5/2}, \tag{70}$$

$$Z(h,0,0;\Omega) = \frac{R_0}{i\Omega} + \frac{hR_0}{2\sqrt{2}\,M}\;\Omega^{-5/2}, \tag{71}$$

from which one derives that in the high frequency region the series capacitances for $Z(h,h,0)$ and $Z(h,0,0)$ coincide with the capacitance of the cell free of ions, $C_s(\Omega \to \infty) = \varepsilon S/d$. The resistance of $Z(h,h,0)$ is the double of the resistance of $Z(h,0,0)$ and tends to zero as $\Omega^{-5/2}$. For all frequencies, the real part of $Z(h,h,0;\Omega)$ is, practically, the double of the real part of $Z(h,0,0;\Omega)$.

In Fig. 7, we compare the spectra of the real [Fig. 7(a)], imaginary [Fig. 7(b)], and parametric [Fig. 7(c)] plot of the real part with respect to the imaginary part, of $Z(h,h,0)$ and $Z(h,0,0)$. In the same figure are also reported the dc values for the resistances deduced by Eqs. (68) and (69). From the spectrum of the imaginary part of $Z(h,h,0)$ it is evident that the relaxation frequency is, for $h = 2$ of the order of $\Omega_r = \pi^2/(2M)^2$, as predicted in Ref. [34]. Since for $h = 0$ the symmetric cell behaves as a condenser, as follows from Eq. (64), Ω_r is expected to depend on h. A numerical calculation shows that, for $h > h^* = \pi^2/(8M^2)$, Ω_r is practically independent of h, whereas for $h < h^*$ the relaxation frequency tends rapidly to zero. In the parametric plot the vertical asymptote is defined by Eq. (69), and the corresponding frequency is Ω_r. In Fig. 8, we show the logarithm of the real part of $Z(h,0,0)$ and the approximated expression given by the real part of Eq. (71) versus log[Ω]. From this figure it is evident that the logarithm of the real part of $Z(h,0,0)$ is practically frequency independent in the low frequency region, depends on Ω^{-2} in the intermediate frequency region, and varies as $\Omega^{-5/2}$ in the high frequency region.

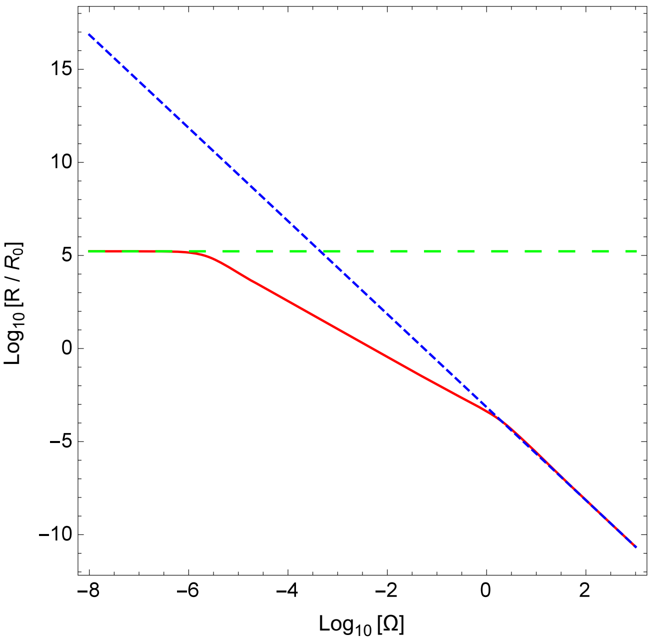

FIG. 8. Frequency dependence of the logarithm of the real part of $Z(h,0,0)$, and the approximated expression given by the real part of Eq. (71). Note that it is practically frequency independent in the low frequency region, dependent on Ω^{-2} in the intermediate frequency region, and dependent on $\Omega^{-5/2}$ in the high frequency region. The curves are drawn for $M = 10^3$, $h = 2$.

VI. CONCLUSIONS

We have investigated the response of an electrolytic cell to an external harmonic electric field, in the linear approximation by means of the Poisson-Nernst-Planck model. Our analysis has been mainly focused on the diffusive case, where the conduction current is due only to diffusion. We have shown that if the displacement current is omitted, the electric current is not constant across the cell. Therefore, it is not possible to define the impedance of the cell in the usual manner, that is, as the ratio between the applied voltage and the current across the cell, at least without an evaluation of the current density at an arbitrary point. Our analysis has been performed first assuming Nernstian boundary conditions, where the bulk density at the surface is fixed by the potential of the electrode with respect to the bulk. In this case, we have compared our results with those reported some years ago, on a similar problem in Ref. [11], obtained in the framework of a pure diffusion model, that is, the total electric current is identified with the ionic diffusion current [8–12]. In the case of a symmetric sample limited by Nernstian electrodes, our expression for the impedance does not contain, in the high frequency region, the linear dependence, in the parametric representation, of the reactance versus the resistance, known as Warburg's impedance. Furthermore the relaxation frequency, defined by the maximum of the reactance, according to our model depends on the ionic concentration and on the phenomenological parameter entering into the Nernstian boundary conditions. In contrast, according to pure diffusive models the relaxation frequency coincides with the diffusion circular frequency. Similar differences are observed when one of the electrodes is completely adsorbing. In this case the pure diffusion model discussed in Ref. [11] predicts an electrical impedance for the cell strongly dependent on the position where the current is evaluated. If it is evaluated on the reflecting electrode the results are nonphysical, because the resistance of the cell could be negative. If the current is evaluated on the other electrode, the reactance diverges at the relaxation frequency and presents again in the high frequency region the Warburg-like impedance. We have investigated also the response of the cell for Ohmic boundary conditions. For a cell with one blocking electrode, we have found that in the low frequency region the reactance diverges at the relaxation frequency. Our model predicts three power law dependencies for the real part of the impedance: (i) in the low frequency range, it is independent of the frequency; (ii) for moderate frequency it depends upon the frequency with a power of −2; and (iii) in the high frequency region it depends upon the frequency with a power of −2.5.

Our conclusion is that the models proposed to interpret Warburg-type impedance based only on the diffusion equation, generalized to take into account the traps, although able to reproduce the main characteristic of the experimental spectra, are not physically based. Therefore misleading conclusions could be drawn concerning the properties of the electrodes and of the electrolytic cell in general. There are several other models based on the transmission lines able to predict a frequency dependence of the impedance similar to Warburg's impedance. However, it is not very simple to relate the lumped electrical elements with physical mechanisms responsible for the electric response of the cell to the external electric field. Our personal point of view is that these kinds of models are only fitting models unable to help in the understanding of the physical mechanisms contributing to the electric behavior of the cell or, worse, misleading models. We are convinced that, for the one mobile ion approximation, if the Warburg impedance is observed, its explanation has to be searched for in the boundary conditions. Hence, the theoretical interpretation of Warburg's impedance is still lacking.

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APPENDIX

In a simple model for the motion of the ions in an insulating liquid, it is assumed that Newton's equation of the ions in the presence of an electric field is

$$m\,\frac{d\mathbf{v}}{dt} = q\,\mathbf{E} - \kappa\,\mathbf{v}, \tag{A1}$$

where m is the mass of the ion, including the hydration effect, and $\mathbf{v}$ is its velocity in the presence of the electric field $\mathbf{E}$. In this simple approach the dissipative effects are taken into account by means of a friction force of viscous origin, described by a coefficient κ depending on the shape of the ion and on the viscosity of the liquid, η. In the simple case where the shape of the mobile ion can be assumed to be spherical of radius r, $\kappa = 6\pi r\eta$ [35]. This model is very rough, however a few indications of the frequency dependence of the ionic mobility on the frequency can be derived operating as follows.

If the electric field is time independent, in the steady state, the velocity of the ion is related to the electric field by $\mathbf{v} = (q/\kappa)\,\mathbf{E}$. It follows that the ionic mobility is $\mu_0 = q/\kappa$, where the subscript zero means that the electric field is continuous.

If the external electric field is a harmonic function of the time of the type $\mathbf{E} = \mathbf{E_0}\,\exp(i\omega t)$, in the steady state, $\mathbf{v} = \mathbf{v_0}\,\exp(i\omega t)$, as follows from Eq. (A1). The amplitude of the velocity of drift along the electric field is

$$\mathbf{v_0} = \frac{\mu_0}{1 + i\,(\omega/\omega_r)}\,\mathbf{E_0}, \tag{A2}$$

where $\mu_0 = q/\kappa$ as before, and $\omega_r = \kappa/m$ is a characteristic circular frequency related to the inertial (m), and dissipative (κ), properties of the ion in the given liquid. In the present case we get

$$\mathbf{v} = \frac{\mu_0}{1 + i\,(\omega/\omega_r)}\,\mathbf{E}, \tag{A3}$$

from which the effective ionic mobility defined by $\mathbf{v} = \mu(\omega)\,\mathbf{E}$ is found to be

$$\mu(\omega) = \frac{\mu_0}{1 + i\,(\omega/\omega_r)}. \tag{A4}$$

Although Eq. (A4) has been obtained in the framework of a very simple model, it contains reasonable frequency dependence of $\mu = \mu(\omega)$. As expected, for $\omega \to \infty$, $\mu \to 0$.

[1] Y. Wang, C.-N. Sun, F. Fan, J. R. Sangoro, M. B. Berman, S. G. Greenbaum, T. A. Zawodzinski, and A. P. Sokolov, Phys. Rev. E **87**, 042308 (2013).

[2] A. Serghei, M. Tress, J. R. Sangoro, and F. Kremer, Phys. Rev. B **80**, 184301 (2009).

[3] R. J. Kortschot, A. P. Philipse, and B. H. Erné, J. Phys. Chem. C **118**, 11584 (2014).

[4] J. Ross Macdonald, Phys. Rev. **92**, 4 (1953).

[5] G. Barbero and A. L. Alexe-Ionescu, Liq. Cryst. **32**, 943 (2005).

[6] All the works of Macdonald are accessible, in PDF format, at http://jrossmacdonald.com.

[7] G. Barbero, J. Chem. Phys. **135**, 234505 (2011).

[8] H. Gerisher, Z. Phys. Chem. Neue Folge **198**, 286 (1951).

[9] C. Ho, I. D. Rainstrick, and R. A. Huggins, J. Electrochem. Soc. **127**, 343 (1980).

[10] B. A. Boukamp and H. J. Bouwmeester, Solid State Ionics **157**, 29 (2003).

[11] J. Bisquert, J. Phys. Chem. **106**, 325 (2002).

[12] A. A. Moya, Phys. Chem. Chem. Phys. **18**, 3812 (2016).

[13] H. Sanabria and J. H. Miller, Jr., Phys. Rev. E **74**, 051505 (2006).

[14] E. Warburg, Ann. Phys. Chem. **303**, 493 (1899).

[15] D. R. Franceschetti, J. Chem. Phys. **86**, 6495 (1987).

[16] D. R. Franceschetti, J. R. Macdonald, and R. P. Buck, J. Electrochem. Soc. **138**, 1368 (1991).

[17] J. Jamnik and J. Meier, J. Electrochem. Soc. **146**, 4183 (1999).

[18] W. Lai and S. Haile, J. Am. Ceram. Soc. **88**, 2979 (2005).

[19] G. Barbero, Phys. Chem. Chem. Phys. **18**, 29537 (2016).

[20] S. Sodergren, A. Hagfeldt, J. Olsson, and S.-E. Lindquist, J. Phys. Chem. **98**, 5552 (1994).

[21] F. Cao, G. Oskam, G. J. Meyer, and P. C. Searson, J. Phys. Chem. **100**, 17021 (1996).

[22] L. Dloczik, O. Ileperuma, I. Laurermann, L. M. Peter, E. A. Pomarev, G. Redmond, N. J. Shaw, and I. Uhlendorf, J. Phys. Chem. **101**, 10281 (1997).

[23] A. Solbrandt, A. Henningsson, S. Sodergren, H. Lindstrum, A. Hagfeldt, and S.-E. Lindquist, J. Phys. Chem. **103**, 1078 (1999).

[24] *Impedance Spectroscopy*, edited by J. Ross Macdonald (Wiley, New York, 1987).

[25] K. Iván, N. Kischner, P. L. Simon, V. Jakab, Z. Noszticzius, J. H. Merkin, and S. K. Scott, Phys. Chem. Chem. Phys. **4**, 1339 (2002).

[26] H. Chang and G. Jaffe, J. Chem. Phys. **20**, 1071 (1952).

[27] J. Crank, *The Mathematics of Diffusion* (Clarendon, Oxford, 1975), p. 193.

[28] J. R. Macdonald and D. R. Franceschetti, J. Chem. Phys. **68**, 1614 (1978).

[29] G. Barbero, F. Batalioto, and A. M. Figueiredo Neto, J. Appl. Phys. **101**, 054102 (2007).

[30] G. Barbero and M. Scalerandi, J. Chem. Phys. **136**, 084705 (2012).

[31] I. Lelidis, J. R. Macdonald, and G. Barbero, J. Phys. D **49**, 025503 (2016).

[32] A. L. Alexe-Ionescu, G. Barbero, S. Bianco, G. Cicero, and C. F. Pirri, J. Electroanal. Chem. **669**, 21 (2012).

[33] I. Lelidis and G. Barbero, J. Phys. Chem. C **118**, 8245 (2014).

[34] J. R. Macdonald, J. Chem. Phys. **54**, 2026 (1971).

[35] L. D. Landau and E. I. Lifchitz, *Mecanique des Fluids* (MIR, Moscow, 1970).