

# Anomalous diffusion governed by a fractional diffusion equation and the electrical response of an electrolytic cell

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The electrical response of an electrolytic cell in which the diffusion of mobile ions in the bulk is governed by a fractional diffusion equation of distributed order is analyzed. The boundary conditions at the electrodes limiting the sample are described by an integro-differential equation governing the kinetic at the interface. The analysis is carried out by supposing that the positive and negative ions have the same mobility and that the electric potential profile across the sample satisfies the Poisson's equation. The results cover a rich variety of scenarios, including the ones connected to anomalous diffusion. © 2011 American Institute of Physics. [doi:10.1063/1.3637944]

## I. INTRODUCTION

Anomalous diffusion problems constitute a fast growing field of research in several areas of physics, biology, ecology, geophysics, and many others.<sup>1-3</sup> The fact that the time dependence of the mean squared displacement is nonlinear, e.g.,  $\langle(z - \langle z \rangle)\rangle \sim t^\gamma$ , with  $\gamma \neq 1$ , is a noteworthy characteristic of an anomalous diffusion. This non-Brownian behavior can be found, for instance, in atom deposition into a porous substrate,<sup>4</sup> diffusion of high molecular weight polyisopropylacrylamide in nanopores,<sup>5</sup> highly confined hard disk fluid mixtures,<sup>6</sup> fluctuating particle fluxes,<sup>7</sup> diffusion on fractals,<sup>8</sup> ferrofluid<sup>9</sup> and colloids,<sup>10</sup> and many others. This anomalous behavior is usually related to the non-Markovian characteristics of the systems such as memory effects, fractality, and interactions. Likewise, different diffusive behaviors may also be exhibited by these systems such as the ones found in Refs. 11 and 12 for the case of long-range interaction, and in Refs. 13 and 14 for active intracellular transport. To face the high complexity of the behaviors of these systems, several formalisms have been considered,<sup>1-3,15-17</sup> among which are of particular importance the extensions of the diffusion equation such as the fractional diffusion equations.<sup>2,3</sup>

In electrolytic cells the anomalous response that generalizes the Warburg model for the electrical impedance was proposed by Macdonald in 1985.<sup>18</sup> In this pioneering work, the Warburg exponent of 1/2 was replaced by  $0 < \gamma \leq 1$  (primarily restricted to 1/2 or less), and some of its responses were explored therein. In the same direction, Bisquert and co-workers<sup>19-22</sup> have investigated several models of electrochemical impedance by treating the diffusion of mobile ions by means of fractional calculus in the time domain. As a step further in this direction, the complete mathematical problem of solving fractional diffusion equations for the mobile ions together with the Poisson's equation for the spatial profile of the electric potential has been analytically solved in Ref. 23, where the case of a pure fractional equation of order  $0 < \gamma \leq 1$  in the time derivative and the case of the fractional equation

of distributed order have been considered for perfect blocking electrodes. In Ref. 24, by means of a different strategy, fractional-type diffusional response appropriate for regions of finite length was also proposed, thus leading to an alternative model for the electrical impedance whose form is different from the ones treated in Ref. 23. Very recently, a comparison between these expressions and responses of alternate anomalous diffusion equations<sup>23,24</sup> has been carried out in details, showing that the anomalous diffusion may play an important role in describing the experimental behavior.<sup>25</sup> In addition, the comparison revealed that the expression connected to a pure fractional case is not rich enough to produce the best fits of the experimental data. Further modifications in the boundary conditions may be required to incorporate effects which were not conveniently described so far in association with fractional diffusion equations. Indeed, other possibilities to be explored could be the adoption of Chang-Jaffe boundary conditions to take into account specific adsorption at the electrodes<sup>26,27</sup> or the consideration of the adsorption-desorption process as being governed by a typical balance equation characterizing a chemical reaction of first kind (Langmuir's approximation), when the conservation of the number of particles is imposed.<sup>28-30</sup>

In this paper, we propose a new strategy. We face the mathematical problem of solving a fractional diffusion equation of distributed order<sup>31,33</sup> for the mobile ions coupled to the Poisson's equation for the electrical potential in the bulk, but now subjected to boundary conditions that are stated by means of an integro-differential expression. These boundary conditions embody, in particular, the usual kinetic equation for describing the adsorption-desorption process at the electrodes,<sup>34</sup> but is expressed in terms of a temporal kernel that can be judiciously chosen to cover scenarios which are not suitably described within the usual framework of blocking electrodes. These developments are performed in Sec. II, where the formulation and the solution of the mathematical problem are presented. In Sec. III, some results are discussed. Section IV is dedicated to some conclusions.

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## II. ELECTRICAL RESPONSE AND ANOMALOUS DIFFUSION

The procedure amounts to solve the fractional diffusion equation, for the bulk density of ions  $n_\alpha$  ( $\alpha = +$  for positive and  $\alpha = -$  for negative ones),

$$\int_0^1 d\bar{\gamma} \bar{\tau}(\bar{\gamma}) \frac{\partial \bar{\gamma}}{\partial t^{\bar{\gamma}}} n_\alpha(z, t) = -\frac{\partial}{\partial z} j_\alpha(z, t), \quad (1)$$

where  $\bar{\tau}(\bar{\gamma})$  is a distribution function of  $\bar{\gamma}$ . Note that the fractional time derivative of distributed order employed here is consistent with the definition presented by Chechkin *et al.*<sup>32</sup> The current density is given by

$$j_\alpha(z, t) = -D \frac{\partial}{\partial z} n_\alpha(z, t) \mp \frac{qD}{k_B T} n_\alpha(z, t) \frac{\partial V}{\partial z}. \quad (2)$$

In Eq. (2),  $D$  is the diffusion coefficient for the mobile ions (the same for positive and negative ones) of charge  $q$ ,  $V$  is the actual electric potential across a sample of thickness  $d$ , with the electrodes placed at the positions  $z = \pm d/2$ , of a Cartesian reference frame in which  $z$  is the axis normal to them,  $k_B$  is the Boltzmann constant, and  $T$  the absolute temperature. The fractional operator considered here is the Caputo's one, i.e.,

$$\frac{\partial^\gamma}{\partial t^\gamma} n_\alpha(z, t) = \frac{1}{\Gamma(k-\gamma)} \int_{t_0}^t dt' \frac{n_\alpha^{(k)}(z, t')}{(t-t')^{\gamma+1-k}}, \quad (3)$$

with  $k-1 < \gamma < k$  and  $n_\alpha^{(k)}(z, t) \equiv \partial_t^k n_\alpha(z, t)$ . In particular, we consider  $t_0 \rightarrow -\infty$  to analyze the response of the system to the periodic applied potential defined later on, as indicated by Ref. 35. The choice of  $\gamma \neq 1$  lead us to a more rich scenario in which different diffusive regimes may occur depending on the distribution  $\bar{\tau}(\bar{\gamma})$  for the fractional time derivative of distributed order. Simple cases can be recovered by means of suitable choices for  $\bar{\tau}(\bar{\gamma})$ , such as  $\bar{\tau}(\bar{\gamma}) = \tau \delta(\bar{\gamma} - 1)$ , which corresponds to the normal diffusive process, and  $\bar{\tau}(\bar{\gamma}) = \tau_\gamma^\gamma \delta(\bar{\gamma} - \gamma)$ ,  $0 < \gamma \leq 1$ , related to a pure fractional diffusion equation of order  $\gamma$ . Of special interest may be the choice  $\bar{\tau}(\bar{\gamma}) = \tau \delta(\bar{\gamma} - 1) + \tau_\gamma^\gamma \delta(\bar{\gamma} - \gamma)$ , that corresponds to a situation with two different regimes, one for long times and other one for short times.<sup>33</sup> Other forms of  $\bar{\tau}(\bar{\gamma})$  are also possible as, for instance, the situations worked out in Ref. 32, which may represent different scenarios characterized by different diffusive behaviors. An important remark on Eq. (1) refers to the use of the Caputo fractional derivative instead of the Riemann-Liouville considered in Ref. 23. It is worth mentioning that, in Ref. 23, the fractional derivative was incorporated after linearizing the system of partial differential equations in presence of usual time derivatives. Here, in order to face the complete problem of the electric response from the beginning and to avoid cumbersome calculations, which may appear due to the definition of the Riemann-Liouville fractional derivative, we use the Caputo fractional time derivative. In addition, the results obtained for Eq. (1) recovers the results found in Ref. 23 in the appropriate limits.

Equation (1) will be subjected to the boundary conditions,

$$j_\alpha(z, t)|_{z=\pm \frac{d}{2}} = \pm \int_{-\infty}^t d\bar{t} \bar{\kappa}(t-\bar{t}) \frac{d}{d\bar{t}} n_\alpha(z, \bar{t}) \Big|_{z=\pm \frac{d}{2}}, \quad (4)$$

where the right term can be related to an adsorption-desorption process. In fact, for the specific choice of  $\bar{\kappa}(t) = \kappa e^{-t/\tau}$ , we recover the adsorption-desorption processes at the surfaces governed by a kinetic equation that corresponds to the Lagumir approximation.<sup>34</sup> Others choices of  $\bar{\kappa}(t)$  can be performed to incorporate memory effects and, consequently, non-Debye relaxation processes.<sup>36</sup> The potential is determined by the Poisson's equation,

$$\frac{\partial^2}{\partial z^2} V(z, t) = -\frac{q}{\epsilon} [n_+(z, t) - n_-(z, t)], \quad (5)$$

which depends on the difference between the densities of charged particles. These equations give the dynamic of the system and satisfy the balance equation,

$$\frac{\partial}{\partial t} \int_{-d/2}^{d/2} dz \Psi_\pm(z, t) + \int_{-\infty}^t d\bar{t} \bar{\kappa}(t-\bar{t}) \times \frac{d}{d\bar{t}} \left[ \Psi_+ \left( \frac{d}{2}, \bar{t} \right) + \Psi_+ \left( -\frac{d}{2}, \bar{t} \right) \right] = 0, \quad (6)$$

with  $\Psi_\pm(z, t) = n_\pm(z, t) \pm n_-(z, t)$ . For the conditions employed here, we have  $\int_{-d/2}^{d/2} \Psi_\pm(z, t) dz = \text{constant}$ . A solution for the previous equations and, consequently, an expression for the electrical impedance may be found in the linear approximation by considering that  $n_\alpha(z, t) = N + \delta n_\alpha(z, t)$ , with  $N \gg \delta n_\alpha(z, t)$  and  $n_\alpha(z, t) = N$  for  $t = 0$ . In addition, we also consider  $\delta n_\alpha(z, t) = \eta_\alpha(z) e^{i\omega t}$  to analyze the impedance when the electrolytic cell is subjected to the time dependent potential  $V(z, t) = \phi(z) e^{i\omega t}$ , with  $V(\pm d/2, t) = \pm (V_0/2) e^{i\omega t}$ . After substituting these quantities in Eqs. (1), (4) and (5), we obtain a set of four coupled equations which may be decoupled by introducing the functions  $\psi_+(z) = \eta_+(z) + \eta_-(z)$  and  $\psi_-(z) = \eta_+(z) - \eta_-(z)$ . The first two equations are

$$\frac{d^2}{dz^2} \psi_\pm(z) = \alpha_\pm^2 \psi_\pm(z), \quad (7)$$

where  $\alpha_-^2 = F(i\omega)/D + 1/\lambda^2$  and  $\alpha_+^2 = F(i\omega)/D$ , in which  $F(i\omega) = \int_0^\infty d\bar{\gamma} \bar{\tau}(\bar{\gamma}) (i\omega)^{\bar{\gamma}}$  and  $\lambda = \sqrt{\epsilon k_B T / (2Nq^2)}$  is the Debye's screening length. The other two equations are

$$D \frac{d}{dz} \psi_-(z) + \frac{2qD}{k_B T} N \frac{d}{dz} \phi(z) = \mp i\omega \bar{\kappa}(i\omega) \psi_-(z), \quad (8)$$

$$D \frac{d}{dz} \psi_+(z) = \mp i\omega \bar{\kappa}(i\omega) \psi_+(z), \quad (9)$$

at  $z = \pm d/2$ , with  $\bar{\kappa}(i\omega) = e^{-i\omega t} \int_{-\infty}^t d\bar{t} \bar{\kappa}(t-\bar{t}) e^{i\omega \bar{t}}$ . The solutions of Eqs. (7) are

$$\psi_\pm(z) = C_{\pm,1} e^{\alpha_\pm z} + C_{\pm,2} e^{-\alpha_\pm z}, \quad (10)$$

where  $C_{\pm,1}$  and  $C_{\pm,2}$  are determined by the boundary conditions and the symmetry of the potential:  $V(z, t) = -V(-z, t)$ , which implies  $C_{-,1} = -C_{-,2}$  and, consequently,

$$\psi_-(z) = 2C_{-,1} \sinh(\alpha_- z), \quad (11)$$

$$\phi(z) = -\frac{2q}{\epsilon \alpha_-^2} C_{-,1} \sinh(\alpha_- z) + \bar{C} z. \quad (12)$$

The constants  $C_{-,1}$  and  $\bar{C}$  are determined by solving the system of equations,

$$\mathcal{E}C_{-,1} + \frac{qND\alpha_- \bar{C}}{k_B T \cosh(\alpha_- d/2)} = 0, \quad (13)$$

$$-\frac{2q}{\varepsilon\alpha_-^2} C_{-,1} \sinh\left(\alpha_- \frac{d}{2}\right) + \frac{d}{2} \bar{C} = \frac{V_0}{2}, \quad (14)$$

with  $\mathcal{E} = F(i\omega) + i\alpha_- \omega \bar{\kappa}(i\omega) \tanh(\alpha_- d/2)$ , which is obtained from the corresponding boundary condition for  $\psi_-(z)$ , i.e., from Eq. (8) and the condition imposed on the potential, for example, in  $z = d/2$ . Following the procedure employed in Ref. 34 and using the previous equations, we can obtain the current and the admittance,  $\mathcal{Y} = I/V$ , of the sample (cell). For the calculations performed here, the admittance is given by

$$\mathcal{Y} = 2iq \frac{\omega S}{\alpha_- V_0} \left\{ \frac{\varepsilon}{2q} \alpha_- C - \left[ \cosh\left(\alpha_- \frac{d}{2}\right) + \alpha_- \bar{\kappa}(i\omega) \sinh\left(\alpha_- \frac{d}{2}\right) \right] C_{-,1} \right\}, \quad (15)$$

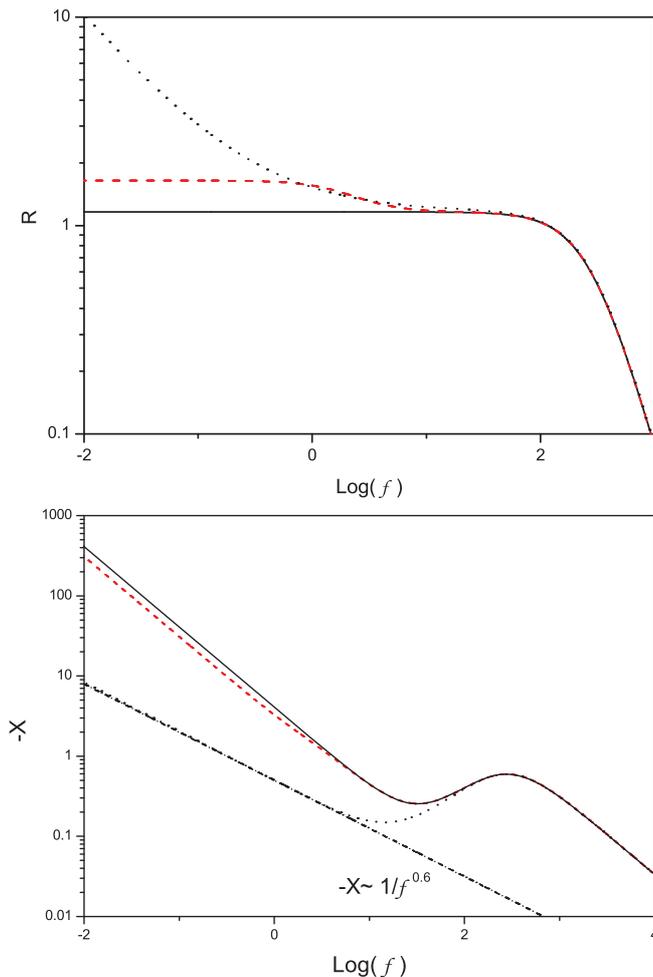


FIG. 1. Real (upper) and imaginary (lower) parts of the electrical impedance of the cell versus the frequency of the applied voltage,  $f = \omega/2\pi$ , for different  $\bar{\kappa}(i\omega)$ .

where  $S$  is the electrode area. The impedance of the cell, defined by  $\mathcal{Z} = 1/\mathcal{Y}$ , can be determined from the previous equation by means of simple calculations. It is given by

$$\mathcal{Z} = \frac{2}{i\omega\varepsilon S\alpha_-^2} \frac{\tanh(\alpha_- d/2)/(\lambda^2\alpha_-) + d\mathcal{E}/(2D)}{1 + \bar{\kappa}(i\omega)(1 + i\omega\lambda^2/D)\tanh(\alpha_- d/2)/(\lambda^2\alpha_-)}. \quad (16)$$

The presence of the kernel  $\bar{\kappa}(t)$  gives to the electrical impedance (16) a very general profile. As a matter of fact, for  $\bar{\tau}(\bar{\gamma}) = \delta(\bar{\gamma} - 1)$ , with  $\bar{\kappa}(t) = \kappa e^{-t/\tau}$ , the case worked out in Ref. 34 in which adsorption–desorption phenomena are incorporated to the analysis by means of a kinetic balance equation at the surfaces, is recovered. Moreover, for  $\tau(\bar{\gamma}) = \delta(\bar{\gamma} - 1)$ , with  $\bar{\kappa}(t) = 0$ , the usual form of the electrical impedance obtained in the situation of blocking electrodes is reobtained.

### III. RESULTS AND DISCUSSIONS

Figure 1 (upper part) illustrates the behavior of the real part of the impedance, i.e.,  $\text{Re } \mathcal{Z} = R = \text{Re}(1/\mathcal{Y})$ , by performing some choices for  $\bar{\kappa}(i\omega)$ , with  $\gamma = 1$ , in order to evidence the influence of the boundary conditions on the dynamics of the system. This figure considers

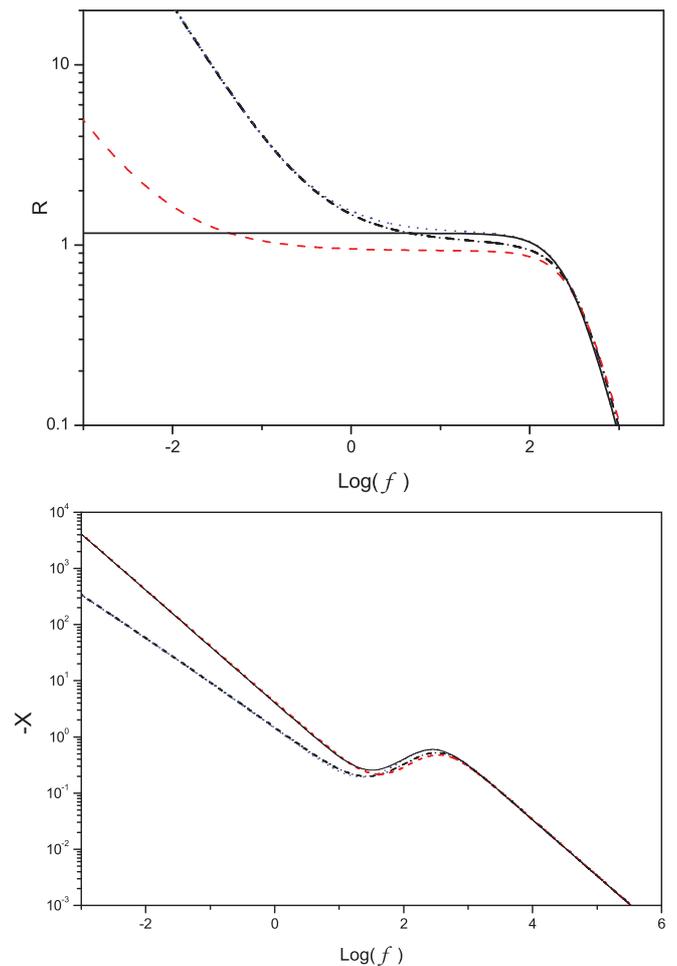


FIG. 2. Real and imaginary parts of the electrical impedance of the cell versus the frequency of the applied voltage,  $f = \omega/2\pi$ , for different values of  $\gamma$  and  $\theta$ .

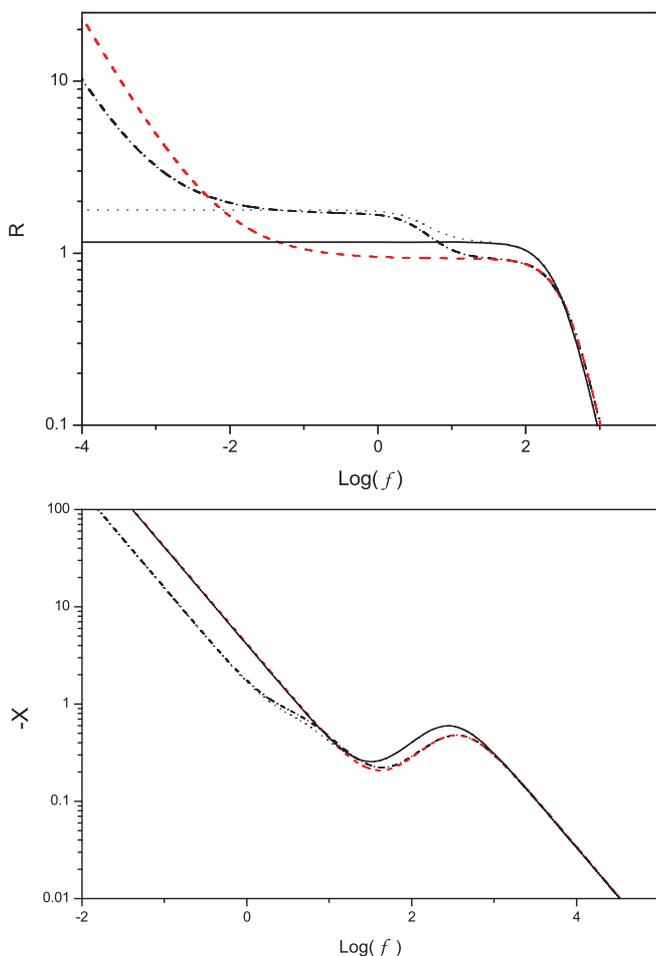


FIG. 3. Real and imaginary parts of the electrical impedance of the cell versus the frequency of the applied voltage,  $f = \omega/2\pi$ , for different values of  $\gamma$ .

$S = 2 \times 10^{-4} \text{ m}^2$ ,  $\varepsilon = 6.7\varepsilon_0$  (with  $\varepsilon_0 = 8.85 \times 10^{-12}$ ),  $D = 8.2 \times 10^{-11} \text{ m}^2\text{s}^{-1}$ ,  $\lambda \approx 3.04 \times 10^{-7} \text{ m}$ , and  $d = 25 \times 10^{-6} \text{ m}$ . The solid black line is the case  $\bar{\kappa}(i\omega) = 0$ , which corresponds to the usual situation characterized by perfect blocking electrodes, i.e.,  $\kappa = 0$  and  $\tau = 0$ .

The red dashed line is the case  $\bar{\kappa}(i\omega) = \kappa\tau/(1 + i\omega\tau)$ , which may be connected to an adsorption-desorption process with  $\kappa = 10^{-6} \text{ ms}^{-1}$  and  $\tau = 0.1 \text{ s}$ . The black dotted line considers  $\bar{\kappa}(i\omega) = \kappa\tau/(i\omega\tau)^\vartheta$ , with  $\kappa = 10^{-3} \text{ ms}^{-1}$ ,  $\tau = 10^{-4} \text{ s}$ , and  $\vartheta = 0.35$ . This case shows that the effect of boundary condition is to produce an anomalous diffusion. This anomalous behavior is also manifested in the lower case of Fig. 1, which shows the imaginary part of the impedance, i.e.,  $\text{Im } \mathcal{Z} = X = \text{Im}(1/\mathcal{Y})$ . Note that a straight line was incorporated in Fig. 1 to evidence the anomalous behavior of the imaginary part at low frequency. In Fig. 2, we consider the influence of the fractional diffusion equation on the impedance for  $\bar{\tau}(\bar{\gamma}) = \tau_1\delta(\bar{\gamma} - 1) + \tau_2\delta(\bar{\gamma} - \gamma)$ , which corresponds to a diffusive process characterized by two different regimes. One of them is the usual one and the other is dominated by the anomalous diffusion. We also consider in this analysis  $\bar{\kappa}(i\omega) = \kappa\tau/(i\omega\tau)^\vartheta$  in order to investigate the effect of the bulk and the surface on the dynamics of the ions. The black solid line is the usual situation, i.e.,  $\kappa = 0$

and  $\gamma = 1$ . The red dashed line corresponds to the fractional diffusion with  $\kappa = 0$ ,  $\tau_1 = 0.8$ ,  $\tau_2 = 0.2 \text{ s}^{\gamma-1}$ , and  $\gamma = 0.25$ . The black dashed-dotted line is the fractional diffusion case with  $\kappa = 5 \times 10^{-6} \text{ ms}^{-1}$ ,  $\tau = 0.1 \text{ s}^{-1}$ , and  $\vartheta = 0.25$ . The blue line corresponds to  $\gamma = 1$  with the values of  $\kappa$ ,  $\tau$ , and  $\vartheta$  equal to ones of the black dashed-dotted line. For this case, the role of the boundary conditions are dominant on the effect of the fractional time derivative of distributed order. In Fig. 3, the same scenario with  $\bar{\kappa}(i\omega) = \kappa\tau/(1 + i\omega\tau)$  is found. Note that the bulk effects, i.e., the fractional diffusion equation, govern the real part of the impedance in the low frequency limit, whereas the effects of the boundary condition are verified at intermediate frequency with the presence of a second plateau. The imaginary part of the impedance has the asymptotic behavior governed by the usual limits, only the intermediate frequency range manifests the effects of the fractional derivative and the boundary conditions.

#### IV. CONCLUSIONS

We have investigated the electrical response of an electrolytic cell by considering the diffusion of the ions governed by a fractional equation of distributed order subjected to a boundary condition expressed as an integro-differential equation. The fractional diffusion equation of distributed order is connected to anomalous diffusion and recovers the usual diffusion in the appropriated limit. It can also be used to investigate situations in which different diffusive regimes are present. The boundary conditions considered here extend the ones usually employed to investigate these systems and can lead us to situations connected to anomalous diffusion. The scenario investigated above embodies, as particular cases, several relevant problems such as the one investigated in Ref. 19 in the context of the fractional time derivative. Indeed, it takes simultaneously into account the presence of fractional derivative of distributed order, the equation of Poisson, and unusual, very general, boundary conditions to obtain Eq. (16). In this manner as well, a more general measure of the electrical response of the system to the action of an external field is established on analytical grounds. Along these lines, the very important situations presented in Refs. 23 and 24 can be also recovered from the formalism presented here in the appropriate limits without any further problem. Other generalizations, such as the ones discussed in Refs. 24 and 37, are still possible and can be considered in the framework of the general formalism we are presenting here.

The results show that in the low frequency limit the behavior of the real part of the impedance is more influenced by the bulk equation (diffusion equation) while the effect of the processes governed by boundary conditions, i.e., by the surfaces, depends on the choice of  $\bar{\kappa}(i\omega)$ . For the situations worked out here, the choice  $\bar{\kappa}(i\omega) \propto 1/(i\omega\tau)^\vartheta$  has a strong influence on the electrical response of the system at low frequency, in contrast to the choice  $\bar{\kappa}(i\omega) \propto 1/(1 + i\omega\tau)$ . These features may be related to the diffusive regimes of the ions in the sample which have a direct influence on the electrical response of the system. Actually, as discussed in Ref. 37, the dynamical aspects of the motion of ions may provide an important bridge between the experimental impedance

measurements and the theoretical description. Experimental evidences of the unusual behavior for the electrical response (which may be related to anomalous diffusion) are observed, for example, in the dielectric dispersion of water<sup>38</sup> and in disordered solids.<sup>37</sup> By analytically solving bulk fractional diffusion equations subjected to general boundary conditions, as we have done here, we hope that the results found can be useful to investigate the electrical response of the system, in particular when the anomalous diffusion is present.

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