The Kramers–Kronig relations for usual and anomalous Poisson–Nernst–Planck models

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Abstract
The consistency of the frequency response predicted by a class of electrochemical impedance expressions is analytically checked by invoking the Kramers–Kronig (KK) relations. These expressions are obtained in the context of Poisson–Nernst–Planck usual or anomalous diffusional models that satisfy Poisson’s equation in a finite length situation. The theoretical results, besides being successful in interpreting experimental data, are also shown to obey the KK relations when these relations are modified accordingly.

(Some figures may appear in colour only in the online journal)
to estimates of many more physically relevant electrical parameters than can any other available EIS model. The construction of any relevant theoretical model and, in particular, PNP or PNP modified models, has to be accompanied by checking their validity in the terms required by the KK relations.

In this paper, a set of recently proposed PNP models that are successful in interpreting the experimental EIS data [20–23] is considered. It is demonstrated that they also obey the KK relations if these relations are slightly modified. These PNP models satisfy Poisson’s equation in a finite length sample, e.g., a cell of thickness $d$ with flat electrodes of area $S$ placed at the positions $z = \pm d/2$ of a Cartesian reference system. For simplicity’s sake, the analysis is limited to the case of full dissociation, of mobile charges with equal mobilities, in the presence of an electric field, of electrical potential $V$, due to the action of an external power supply or to a charge separation. In this framework, the bulk densities, $n_p$ and $n_m$, where $p$ and $m$ stand for positive and negative ions, respectively, are obtained by solving the standard form of the continuity equations, written as

$$\frac{\partial n_p}{\partial t} = -\frac{\partial j_p}{\partial z} \quad \text{and} \quad \frac{\partial n_m}{\partial t} = -\frac{\partial j_m}{\partial z},$$

in which the densities of currents are defined as

$$j_{p,m} = -D_{p,m} \frac{\partial n_{p,m}}{\partial z} \pm \frac{qN}{k_B T} \frac{\partial V}{\partial z},$$

where $q$ is the electrical charge of the ions, $k_B$ is the Boltzmann constant, and $T$ the absolute temperature. In addition, in thermodynamical equilibrium, the material contains a density of $N$ positive and $N$ negative ions, per unit volume, uniformly distributed across the sample. The spatial profile of the electrical potential is governed by the Poisson equation in the form:

$$\frac{\partial^2 V(z,t)}{\partial z^2} = -\frac{\varepsilon}{\varepsilon} \left[ n_p(z,t) - n_m(z,t) \right],$$

where $\varepsilon$ is the dielectric coefficient of the medium.

This problem has been faced in the past [10, 24] and more recently [25–27] for some significant boundary conditions but the details of the calculations for all these cases will be omitted here to save space. In the case of blocking electrodes, for which

$$j_{p,m}(\pm d/2, t) = 0,$$

the impedance is given by

$$Z = -i \frac{2}{\omega \varepsilon \beta^2 S} \left\{ \frac{1}{\lambda^2 \beta^2} \tanh(\beta d/2) + i \frac{\omega d}{2D} \right\},$$

where $\omega$ is the frequency of the applied voltage,

$$\beta = \frac{1}{2} \sqrt{1 + i \frac{\omega}{D}},$$

with $\lambda = \sqrt{\varepsilon k_B T/(2Nq^2)}$ the Debye screening length, and $D_{n_0} = D_p = D$ is the diffusion coefficient assumed as the same for positive and negative ions.

The problem was also recently extended by assuming that the continuity equation contains a superposition of normal and fractional diffusion, the latter being characterized by a fractional coefficient $0 < \gamma \leq 1$, in the form

$$A \frac{\partial n_p}{\partial t} + B \frac{\partial^\gamma n_p}{\partial t^\gamma} = D \frac{\partial}{\partial z} \left[ \frac{\partial n_p}{\partial z} + \frac{qN}{k_B T} \frac{\partial V}{\partial z} \right],$$

where $A$ is dimensionless, while the dimension of $B$ is $t^{-\gamma}$. The insertion of coefficients $A$ and $B$ is done here only to promote the superposition of two diffusive regimes, for illustrative purposes. The expression for the electrical impedance obtained in this case is [28]

$$Z_e = -i \frac{2}{\omega \varepsilon \beta^2 S} \left\{ \frac{1}{\lambda^2 \beta} \tanh(\beta d/2) + i \frac{\omega d}{2D} \right\},$$

where

$$D_e = \frac{A + B(i\omega)^{-1}}{D}, \quad \beta_e = \frac{1}{\sqrt{1 + i \frac{\omega}{D_e} \lambda^2}}.$$

A further generalization of the problem was achieved by considering fractional time diffusion equations of distributed orders [29]. These equations may be formally written, for example, as

$$\int_0^1 d\gamma \, p(\gamma) \frac{\partial^\gamma}{\partial t^\gamma} n_{p,m}(z,t) = -\frac{\partial}{\partial z} j_{p,m}(z,t),$$

where $p(\gamma)$ is a distribution function of $\gamma$ and the fractional operator considered is the Caputo one [30], which can be defined as

$$\frac{\partial^\gamma}{\partial t^\gamma} n_{p,m}(z,t) \equiv \frac{1}{\Gamma(\gamma)} \int_0^t \frac{d\tau^\gamma}{(t-\tau)^{1-\gamma+k}} n_{p,m}(z,\tau),$$

with $0 < k \leq 1$ and $n_{p,m}(z,\tilde{t})$ representing the $k$th derivative with respect to $\tilde{t}$. As a particular case, it is useful to take the limit $t_1 \rightarrow -\infty$ when one aims at studying the response of the system to a periodic applied potential as is done here [30]. Note that equation (10) has the presence of fractional time operator of distributed order which, depending on the choice of $p(\gamma)$, can account for different diffusive regimes of the ions in the system, as will be discussed later. The order of these derivatives is consequently distributed according to the function $p(\gamma)$, that works as the weight factor for each regime (order). Thus, the general expression for the impedance is given by [31]

$$Z = -i \frac{2}{\omega \varepsilon \beta^2 S} \left\{ \frac{1}{\lambda^2 \beta} \tanh \left( \frac{\beta d}{2} \right) + \frac{d}{2D} F(i\omega) \right\},$$

where, now,

$$\beta = \frac{1}{\lambda^2 \beta} \sqrt{1 + F(i\omega) \frac{\lambda^2}{D}}.$$
with

$$F(\omega) = \int_0^1 d\gamma p(\gamma)(i\omega)\gamma.$$  \hspace{1cm} (14)

The presence of $F(\omega)$ in equations (12) and (13) is responsible for the incorporation of an arbitrary number of diffusive regimes into the description of the diffusion of ions through the sample. In addition, it is noteworthy that the general expression for the impedance, equation (12), has exactly the same functional form as equations (5) and (8), which, in turn, can be hereafter viewed as its particular cases.

Finally, to go one step further in the generalization process, one can consider again the fractional diffusion of distributed order governing the bulk behavior, but now subjected to the boundary conditions [32]

$$j_\alpha(z,t)|_{z=\pm \zeta} = \pm \int_{-\infty}^t \frac{d}{dt} \mathcal{N}_\alpha(z,T) \bigg|_{z=\pm \zeta}, \hspace{1cm} (15)$$

where $\alpha = p, m$ and the right-hand term can be related to an adsorption–desorption process. In fact, for the specific choice of $\mathcal{N}(t) = \kappa e^{-t/\tau}$, we recover the adsorption–desorption processes at the surfaces governed by a kinetic equation that corresponds to the Langmuir approximation [26]. Others choices of $\mathcal{N}(t)$ can be performed to incorporate memory effects and, consequently, non-Debye relaxation processes [33]. The impedance of the cell is

$$Z = \frac{2}{i\omega \pi \sigma_0 \zeta^2} \times \frac{\tanh(\alpha_+ d/2) / (\lambda^2 \alpha_+) + dC/(2D)}{1 + \mathcal{N}(i\omega) (1 + i\omega \lambda^2/D) \tanh(\alpha_+ d/2) / (\lambda^2 \alpha_+)}$$  \hspace{1cm} (16)

where $\alpha_+^2 = F(i\omega) / D + 1/\lambda^2$ and $\alpha_-^2 = F(i\omega) / D$.

The presence of the kernel $\mathcal{N}(t)$ in (16) gives to the electrical impedance a very general profile. This feature can be illustrated for two representative cases. When one considers that $p(\gamma) = \delta(\gamma - 1)$, with $\mathcal{N}(t) = \kappa e^{-t/\tau}$, the case worked out in [26], in which adsorption–desorption phenomena are incorporated into the analysis by means of a kinetic balance equation at the surfaces, is recovered. Moreover, when $p(\gamma) = \delta(\gamma - 1)$, with $\mathcal{N}(t) = 0$, the usual form of the electrical impedance obtained in the situation of blocking electrodes is reobtained. Thus, the possible choices of the kernel allow one to handle different expressions for the electrical impedance, suitable for a large variety of experimental situations.

In all the cases mentioned above, the system is governed by linear differential equations, of usual or fractional derivatives. Thus, we expect that the KK relations hold for the real (R) and imaginary (X) parts of Z. This is actually the case, as we show by means of the simple calculation below. Notice, however, that these relations differ from those reported in [6], equations (21) and (23), because the impedance diverges for $\omega \to 0$. To obtain the modified form of the KK relations, we have just to consider the analytic function, in the upper-half part of the complex plane

$$\int_\mathcal{C} \frac{Z(\omega')}{\omega' - \omega} d\omega' = \mathcal{P} \int_{-\infty}^\infty \frac{Z(\omega')}{\omega' - \omega} d\omega' + i\pi \lim_{\omega' \to \omega} \frac{Z(\omega')}{\omega' - \omega}, \hspace{1cm} (17)$$

where $\mathcal{C}$ is a path in the complex plane, and $\mathcal{P}$ denotes the principal value of the integral, on the real axis. The third contribution on the LHS, i.e.

$$-i\pi \lim_{\omega' \to \omega} \frac{Z(\omega')}{\omega' - \omega}, \hspace{1cm} (18)$$

is necessary because $Z(\omega)$ diverges for $\omega = 0$. Since $Z$ is analytic in $\mathcal{C}$, from equation (17) we get

$$Z(\omega) = i\pi \lim_{\omega' \to \omega} \omega' Z(\omega') + \mathcal{P} \int_{-\infty}^\infty \frac{Z(\omega')}{\omega' - \omega} d\omega'. \hspace{1cm} (19)$$

Considering that $Z = R + iX$, from equation (19) we obtain the KK relations as

$$R(\omega) = \frac{1}{\omega} \mathcal{L}_R + \frac{1}{\pi} \mathcal{P} \int_{-\infty}^\infty \frac{X(\omega')}{\omega' - \omega} d\omega' \hspace{1cm} \text{and} \hspace{1cm} (20)$$

$$X(\omega) = \frac{1}{\omega} \mathcal{L}_X - \frac{1}{\pi} \mathcal{P} \int_{-\infty}^\infty \frac{R(\omega')}{\omega' - \omega} d\omega', \hspace{1cm} (21)$$

where

$$\mathcal{L}_R = \lim_{\omega' \to 0} \omega' R(\omega') \hspace{1cm} \text{and} \hspace{1cm} (22)$$

$$\mathcal{L}_X = \lim_{\omega' \to 0} \omega' X(\omega').$$

For $\gamma < 1$, we have

$$\mathcal{L}_R = \lim_{\omega' \to 0} \omega' R(\omega') = 0 \hspace{1cm} \text{and} \hspace{1cm} (23)$$

$$\mathcal{L}_X = \lim_{\omega' \to 0} \omega' X(\omega') = \mathcal{L},$$

where $\mathcal{L}$ is a finite quantity. Thus, the KK relations for the class of problems we are considering are

$$R(\omega) = \frac{1}{\omega} \mathcal{P} \int_{-\infty}^\infty \frac{X(\omega')}{\omega' - \omega} d\omega' \hspace{1cm} (24)$$

$$X(\omega) = \frac{1}{\omega} \mathcal{L} - \frac{1}{\pi} \mathcal{P} \int_{-\infty}^\infty \frac{R(\omega')}{\omega' - \omega} d\omega', \hspace{1cm} (25)$$

which can be conveniently rewritten, respectively, as

$$R(\omega) = \frac{2}{\pi} \mathcal{P} \int_0^\infty \frac{\omega' X(\omega') - \omega X(\omega)}{\omega'^2 - \omega^2} d\omega' \hspace{1cm} (26)$$

$$X(\omega) = \frac{1}{\omega} \mathcal{L} - \frac{2}{\pi} \mathcal{P} \int_0^\infty \frac{R(\omega') - R(\omega)}{\omega'^2 - \omega^2} d\omega'. \hspace{1cm} (27)$$

A similar approach for establishing KK relations comes into place in optics, when the material under investigation is a conductor at zero frequency, so that

$$\chi(\omega) = i\sigma(\omega)/\omega,$$

where $\chi$ is the susceptibility and $\sigma$ is the conductance. In this case as well, $\chi$ diverges for low frequencies (in particular, its
imaginary part does so), while $\sigma(0)$ is a finite quantity. An extensive discussion of this problem is given in the work of Lucarini et al [34]. We are now ready to apply this formalism to the electrical impedance expressions presented before.

Consider first equation (12), whose low frequency limit is given by the expression

$$Z \approx \frac{2\lambda}{i\omega S} \left[ 1 + \frac{d}{2D} F(i\omega) \right]$$

and, consequently,

$$\mathcal{L} = \frac{2\lambda}{i\omega S}$$

because, from equation (14), it follows that $\lim_{\omega \to 0} F(i\omega) = 0$, for $0 < \gamma < 1$. This quantity coincides with the inverse of the total capacitance of the sample, in the dc limit. Indeed, it coincides with the inverse of the resulting series capacitance of two equal capacitances $C_D = \varepsilon S/\lambda$, that can be identified with the capacitance of the surface layer, i.e., the Gouy–Chapman double-layer capacitance. It is then clear that the entire class of expressions of the kind considered in equation (12), for which $\lim_{\omega \to 0} F(i\omega) \to 0$, obeys the modified KK relations and, as expected, are good candidates as theoretical tools for interpreting EIS experimental data.

Consider now equation (16), for the case characterized by $\varkappa(t) = \kappa e^{-t/\tau}$, i.e., $\varkappa(i\omega) = \kappa \frac{1}{1 + i\omega \tau}$, which, as mentioned before, represents, in the frequency domain, the usual kinetic equation connected with the adsorption–desorption phenomenon (Langmuir’s approximation) in the time domain. It is possible to show that the low frequency limit of equation (16) is given by

$$Z \approx \frac{2\lambda}{i\omega S} \frac{\lambda}{\lambda + F(i\omega)} \left[ 1 + \frac{\lambda}{2D} \left[ F(i\omega) + io\varkappa(i\omega) \right] \right]$$

which, by means of equation (23), allows one to obtain

$$\mathcal{L} = \frac{2\lambda}{\varepsilon S} \frac{1}{1 + \kappa \tau / \lambda}.$$  (31)

In figure 1, the exact results, equations (12) and (16), and the approximated ones, i.e., equations (28) and (30), are illustrated for the cases discussed above in order to compare their low frequency behavior.

Similarly to the previous result obtained, i.e., for equation (29), equation (31) is also connected with the inverse of the total capacitance of the sample, but now taking into account the influence of the adsorption process occurring at the surfaces of the electrodes. Thus, in the case in which the adsorption process is present, the effective thickness intervening in the capacitance of the double-layer is the sum of the Debye screening length and the quantity $\kappa \tau$, which has dimensions of length. In a phenomenological perspective, it represents an effective thickness of the layer over which the accumulation of charge occurs near to the interface. Again, the KK relations are obeyed by the general expression, equation (16), for a large class of choices for $\varkappa(i\omega)$ that remains finite in the low frequency domain. These choices have their counterparts in the time domain which, in general, is more helpful to interpret the phenomena occurring near the interface in terms of boundary conditions. This feature is remarkably illustrated in the particular case analyzed above (Langmuir’s approximation). In this example, the emergence of an adsorbing layer was automatically incorporated into the resulting double-layer capacitance, renormalizing it and allowing for a simple interpretation of the phenomenological parameters entering the kinetic equation. Notwithstanding, even if obtained for a particular case, this noticeable result permits one to expect that the resulting effects of other
significant phenomena occurring near to the electrodes could be incorporated into the description of the global properties of the electrolytic cell in the PNP or Poisson–Nernst–Planck anomalous (PNPA) models.

To summarize, the consistency of the frequency response of a class of electrochemical impedance expressions, obtained in the ambit of usual or anomalous (PNP or PNPA) models, as well as some of their generalizations that take into account different types of boundary conditions, have been theoretically analyzed. The slightly modified expressions of the KK relations presented here, and obeyed by these expressions, can be also used to verify the correctness of the impedance data obtained by means of the EIS technique in the field of electrochemistry and condensed matter physics.

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