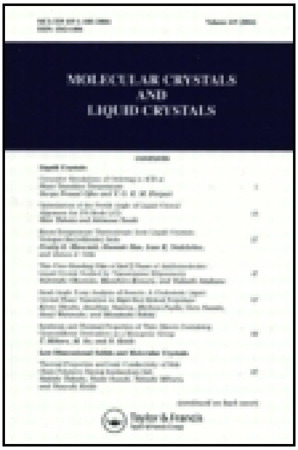

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

On the Concept of Electrical Impedance for an Electrolytic Cell

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Version of record first published: 22 Sep 2010

To cite this article: F. C. M. Freire, G. Barbero & M. Scalerandi (2008): On the Concept of Electrical Impedance for an Electrolytic Cell, Molecular Crystals and Liquid Crystals, 480:1, 151-159

To link to this article: http://dx.doi.org/10.1080/15421400701826092

Mol. Cryst. Liq. Cryst., Vol. 480, pp. 151–159, 2008
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400701826092

On the Concept of Electrical Impedance for an Electrolytic Cell

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The analysis of the electrical impedance of an electrolytic cell in the shape of a slab is performed. We have solved, numerically, the differential equations governing the phenomenon of the redistribution of the ions in the presence of an external electric field, and compared the results with the ones obtained by solving the linear approximation of these equations. The control parameters in our study are the amplitude and the frequency of the applied voltage, assumed a simple harmonic function of the time. We show that for the large amplitudes of the applied voltage, the actual current is no longer harmonic at low frequencies. From this result it follows that the concept of electrical impedance of a cell is a useful quantity only in the case where the linear approximation of the fundamental equations of problem work well.

Keywords: electrical impedance; electrolytic cell

I. INTRODUCTION

According to the impedance spectroscopy technique, a sample of the material to be characterized from the dielectrical point of view is submitted to an external voltage of amplitude V_0 and frequency $f = \omega/(2\pi)$, and the electrical current in the external circuit, I, is measured [1]. By assuming that the system is linear, the current I is harmonic as the applied voltage, and the amplitude of the current is proportional to V_0 [2,3]. In this framework, the electrical impedance $\mathcal{Z}$ defined as the ratio between the applied voltage and the the current, is independent of the amplitude of the applied voltage. Hence the

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impedance spectroscopy technique is based on the fundamental assumption that the system behaves as a linear system [4]. Only in this case the electrical impedance is a useful quantity.

When the system behaves nonlinearly, even if the applied voltage is harmonic, the electrical current in the circuit contains all the harmonics of higher order. The presence of second and third order harmonics is responsible for a deviation from the ellipsoidal shape of the parametric curve representing the current vs. the applied voltage. Consequently, the electrical impedance depends on the amplitude of the applied voltage and on the time. In this case, it is no longer possible to derive the dielectric properties of the medium from the analysis of the electrical impedance only, althought non-linear dielectric studies can give information on the critical behaviours near to the critical points of order-disorder phase transitions [5,6].

Our aim is to investigate under which conditions the concept of electrical impedance can be useful from an experimental point of view. In our analysis we consider the case of an electrolytic cell [7]. In this case the fundamental equations describing the redistribution of the ions in the presence of an external electric field are the continuity and drift-diffusion equations for the ions and the Poisson equation for the actual electrical potential [8].

II. GENERAL EQUATIONS

Let us consider a cell in the shape of a slab of thickness d filled with an electrolyte. We suppose that in thermodynamical equilibrium the density of dissociated ions is N and that dissociation and recombination are negligible. The ions are assumed to be identical in all aspects, except for the sign of the electrical charge q. We assume that the adsorption phenomenon of the ions can be neglected [9,10], and that the electrodes are perfectly blocking. In this framework, in the absence of an external electric field, the liquid is locally neutral. When an external electric field is applied, the ions move under the action of the electric field. The liquid remains globally neutral, but locally charged. For the description of our system we use a Cartesian reference frame having the z-axis perpendicular to the limiting surfaces, located at $z = \pm d/2$.

We write the density of ions n_r in the form $n_r = N + \delta n_r$, with $r = p, m$, where p and m mean plus and minus. Since N is the bulk density of ions in the absence of external potential, δn_r represents the perturbation of the bulk density due to the external electric field [11]. A weak external electric field produces only a weak perturbation of the bulk densities of ions. From now on, the sentence *small electric field* will mean that $\delta n_r << N$. In this case it is possible to linearize the bulk differential equations, as in Ref. [12]

$$\frac{\partial(\delta n_r)}{\partial t}=D\,\frac{\partial}{\partial z}\left\{\frac{\partial(\delta n_r)}{\partial z}\pm\frac{qN}{K_BT}\,\frac{\partial V}{\partial z}\right\},\tag{1}$$

and the Poisson equation [3,13,14]

$$\frac{\partial^2 V}{\partial z^2}=-\frac{q}{\varepsilon}\,(\delta n_p-\delta n_m),\tag{2}$$

where $\delta n_r=\delta n_r(z,t)$ and $V=V(z,t)$. The boundary conditions become

$$\begin{aligned}\frac{\partial(\delta n_r)}{\partial z}\pm\frac{qN}{K_BT}\,\frac{\partial V}{\partial z}&=0,\quad \text{for}\quad z=\pm d/2,\\ V(\pm d/2,t)&=(V_0/2)\,\exp(i\omega t),\end{aligned}\tag{3}$$

respectively. We look for solution of the system in the form

$$\begin{aligned}\delta n_r(z,t)&=\eta_r(z)\,\exp(i\omega t),\\ V(z,t)&=\phi(z)\,\exp(i\omega t).\end{aligned}\tag{4}$$

The electric field is given by $E=-\partial V/\partial z$. It follows $E(z,t)=-\phi'(z)\,\exp(i\omega t)$, where the prime means derivation with respect to z. In particular, the surface electric field is $E(d/2,t)=-\phi'(d/2)\,\exp(i\omega t)$. By means of the Gauss theorem, the surface density of charge sent by the power supply on the electrode can be calculated as $\Sigma(t)=-\varepsilon E(d/2,t)$. The total surface electric charge is $Q=\Sigma S$, where S is the surface area of the electrodes. The complex electrical current in the external circuit is $\mathcal{I}=dQ/dt$. As reported elsewhere [12], we get

$$\mathcal{I}(t)=i\omega\varepsilon S\left\{-2\,\frac{q}{\varepsilon\beta}\,p_0\,\cosh(\beta d/2)+c\right\}\,\exp(i\omega t).\tag{5}$$

where

$$\begin{aligned}p_0&=-\frac{Nq\beta}{2K_BT}\\ &\quad\frac{1}{(1/\lambda^2\beta)\sinh(\beta d/2)+i(\omega d/2D)\cosh(\beta d/2)}V_0,\\ c&=i\frac{\omega}{D}\\ &\quad\frac{\cosh(\beta d/2)}{(1/\lambda^2\beta)\sinh(\beta d/2)+i(\omega d/2D)\cosh(\beta d/2)}V_0,\end{aligned}\tag{6}$$

$\lambda = \sqrt{\varepsilon K_B T/(2Nq^2)}$ is the Debye length [13], and

$$\beta = \frac{1}{\lambda}\sqrt{1 + i\frac{\omega}{D}\lambda^2}. \tag{7}$$

The electrical impedance of the cell, defined as $\mathcal{Z} = \Delta V(t)/\mathcal{I}(t)$, is

$$\mathcal{Z} = -i\frac{2}{\omega\varepsilon\beta^2 S}\left\{\frac{1}{\lambda^2\beta}\tanh(\beta d/2) + I\frac{\omega d}{2D}\right\}. \tag{8}$$

The linear analysis is valid as far as $|\delta n_r(z,t)| \ll N$, it follow that the linear analysis is valid only when

$$V_0 \ll U = V_T\left|\frac{1}{\lambda^2\beta^2} + i\frac{\omega d}{2D\beta}\coth\left(\frac{\beta d}{2}\right)\right|, \tag{9}$$

where $V_T = K_B T/q$ is the thermal voltage, of the order of 25 mV for monovalent ions at room temperature [12].

In the limit $\omega \to 0$ from Eq. (9) we obtain $U \to V_T$, as expected [1]. In the opposite limit where $\omega \to \infty$, U diverges as $\sqrt{\omega}$. This divergence is not surprising. In fact, for large ω the ions cannot follow the rapid variations of the applied voltage, and the medium behaves as a true dielectric material.

In stead of solving the linearized equations of the problem, as discussed above, the complete set of nonlinear equations can be solved numerically. Here, we use, as reported elsewhere [8], a Finite Difference (FD) approach [15–17]. We adopt the usual discretisation of both time and space and applied an explicit forward scheme to define both space and time derivatives.

III. DEVIATIONS FROM THE LINEAR REGIME

The concept of electrical impedance, as defined in last section, is meaningful only for a linear system. It is then important to define under which conditions the linear approximation of the evolution equations is a reasonable assumption. In this Section we present a comparison of the numerical results with that obtained from the analytical solution for the linearized case.

For the analysis, we have considered parameters typical of a commercial liquid crystal: monovalent ions ($q = 1.6 \cdot 10^{-19}\mathrm{A \cdot s}$), $N = 4.2 \cdot 10^{20}\mathrm{m}^{-3}$, $T = 300\,\mathrm{K}$, $\varepsilon = 6.7\varepsilon_0$, $D = 8.2 \cdot 10^{-12}\mathrm{m}^2/\mathrm{s}$, $d = 25\,\mu$ m and $S = 2 \cdot 10^{-4}\,\mathrm{m}^2$ [18]. With these parameters, the Debye length is $\lambda \sim 0.1\,\mu$ m. Furthermore, we have chosen $V_0 = 0.1$ V and

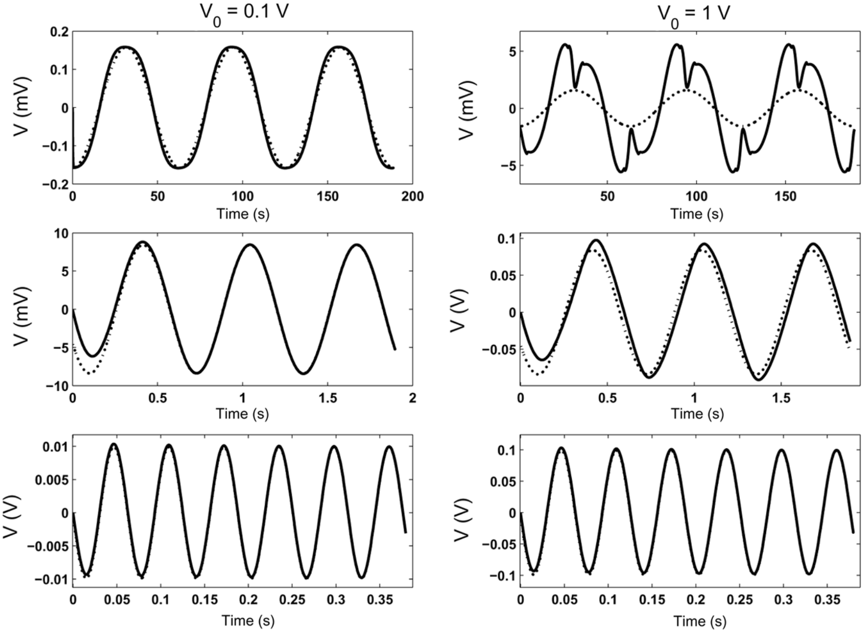

FIGURE 1 Temporal evolution of the actual potential in a point close to the center of the specimen ($z = -d/2$), for two different values of the applied potential (column) and for three different values of the frequency (line), $\omega = 1{,}10{,}100\,\text{rad/s}$ respectively. The numerical solution (solid line) is compared with the linear approximation (dotted line).

$V_0 = 1$ V, to cover the wide excursion usually reported in experiments both for low and high voltages [19–21]. Angular frequency is fixed to $\omega = 1, 10, 100\,\text{rad/s}$.

Results reported in Figures 1 and 2 indicate that the linear approximation (dotted line) is a reasonable approximation at low values of the applied potentials, where no evidence of higher order harmonics is present. On the contrary, for larger values of V_0, the linear approximation fails to describe correctly the behavior of the system at low frequencies, while the agreement improves when the frequency is increased.

IV. GENERALIZED IMPEDANCE

The impedance is in general defined from the relation between the applied potential and the response of the system in terms of electric

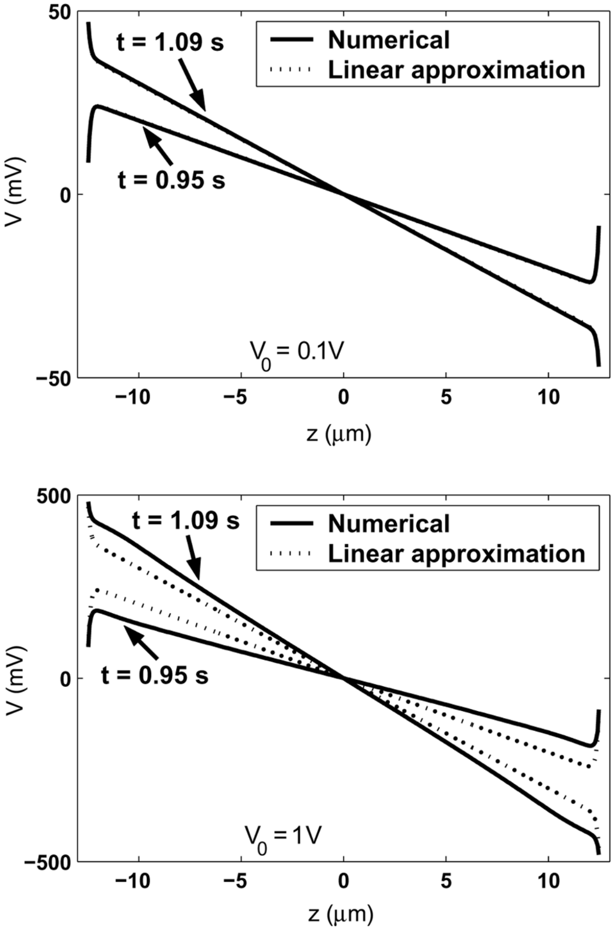

FIGURE 2 Profile along the specimen of the actual potential at different times for different values of the applied potential. The numerical solution (solid line) is compared with the linear approximation (dotted line), with a frequency $\omega = 10\,\text{rad/s}$.

current: $\mathcal{Z} = \Delta V/\mathcal{I}$. As such the impedance is a complex quantity and, in the linear approximation, its modulus is $Z = |\mathcal{Z}| = V_0/I_0$.

Unfortunately, when the system is nonlinear, the definition given for the impedance is no longer meaningful. In fact, whenever distortions from the linear case appears, Z becomes time and amplitude dependent. For this reason, we propose the introduction of a generalized electrical impedance Z_G which, in the limit of vanishing applied

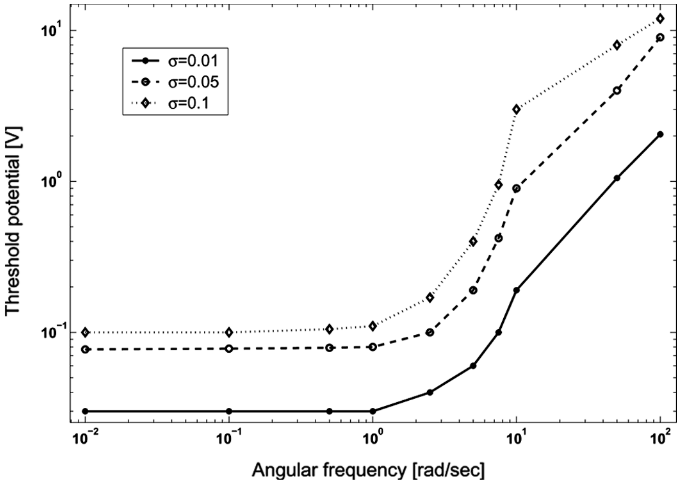

FIGURE 3 Threshold potential for the validity of the linear approximation as a function of frequency. The linear approximation is valid only for potentials lower than the threshold, i.e., in the region below the curve. The three curves refer to different choices of the error tolerance σ for the electrical impedance.

potential, converges to the value defined in the linear analysis. To this purpose, we introduce the function

$$\xi(t;V_0) = 2\frac{I^2(t;V_0)}{V_0^2}. \tag{10}$$

In the linear case (in which $V_0 \to 0$), the average value of ξ gives the square of the modulus of the electric admittance: $Y = 1/|Z|$. It follow that the quantity

$$\Delta_Z = \frac{Z_G(V_0) - Z(0)}{Z(0)}, \tag{11}$$

provides information about the deviation of the electrical impedance at a given amplitude from the one expected from the linear analysis. We can define a threshold voltage V_C, defined as the amplitude of the applied potential at which $|\Delta_Z|$ is larger than an assigned precision σ, which may be determined, e.g. by the experimental accuracy. V_C is reported as function of the frequency in Figure 3 for different values of the precision σ.

The general behavior is in agreement with previously reported predictions, based only on the validity of the linear approximation $\delta \ll N$ [22], i.e., the threshold voltage is in the thermal range and independent from frequency for low frequencies, while increases almost exponentially at large frequencies.

V. CONCLUSIONS

We have solved numerically the fundamental equations of the problem under investigation, by considering as electrolyte a commercial nematic liquid crystal. We have analyzed the phenomenon in the low frequency region ($\omega \leq 100\,\mathrm{rad/s}$). According to our analysis, in the range in which the amplitude of the applied voltage is of the order of the thermal voltage, the presence of the external voltage perturbs the ions distributions only close to the electrodes, on a surface layer whose thickness is comparable with Debye's length. Consequently, the linear approximation works well in the bulk of the sample. In this framework, the concept of electrical impedance is useful, and the impedance spectroscopy technique can give useful information on the dielectric properties of the medium. On the contrary, when the amplitude of the applied voltage is of the order of 1 V, the distribution of ions is strongly perturbed in all the sample. In this case, in the low frequency range, the concept of electrical impedance is meaningless, and the measurement by means of impedance spectroscopy methods of the dielectric parameters is questionable.

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