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ON EVALUATION OF ELECTRIC CONDUCTIVITY BY MEAN OF A THERMODYNAMICAL MODEL FOR DIELECTRIC RELAXATION PHENOMENA. AN APPLICATION TO LIVER TISSUE

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ABSTRACT. In this paper we study the electric conductivity of continuous media in the contest of the non-equilibrium thermodynamics with internal variables. Namely, we shall use some recent results that allow to infer conductivity as function of the frequency of perturbation, only by means of dielectric measurements. Although the results obtained can be applied to several materials, we have applied them to the study of electric conductivity on porcine liver tissue obtaining the spectrum frequency of conductivity (real and imaginary part).

Dedicated to the 100–th anniversary of Professor Giuseppe Grioli.

1. Introduction.

At present one of the most important treatment of cancer is the resection of biological tissues affected by this pathology. But unfortunately many patients affected by cancer cannot be treated by mean of resection. So, in the last years have been developed alternative techniques which act locally without resects the part. One of this consists in the locally action of a alternating electric current at suitable frequency depending on the type of cancer and on his pathological level [39]-[41]. This causes locally inhibition growth of the tumor.

Moreover alternating current electrical stimulation enhanced chemotherapy. Obviously this last technique is no more invasive then resection one. Since this cause relevant electrical current flow through patients, (for low frequency, the conductivity in biological tissue is notable, dominated by the influence of electrolytic conduction caused by the presence of water as solvent), it results very important the knowledge of the electric conduction properties of the tissues for a detailed therapy [42].

On the other hand it results difficult conductivity measurements in vivo by mean of usual techniques, so we think that it can result useful to develop a model, in the contest of the not equilibrium thermodynamics with internal variables, which only by means of dielectric measurements (which result minimally invasive), is able to evaluate conduction properties as function of the frequency. Obviously we refer to ionic conduction for low frequencies.

In the present work we develop this model in the framework of not equilibrium thermodynamics with internal variables taking into account recent results [21] -[33] on the study of dielectric properties of material and in particular considering a model by us developed.

2. Remarks on thermodynamic theory with vectorial internal degrees of freedom for dielectric relaxation phenomena.

The non-equilibrium thermodynamic theory, proposed [1]-[5] and developed in [6]-[20], postulates that the usual variables are insufficient for study a medium that is subject to perturbations.

Generally, the specific entropy s will be (for an elastic dielectric) function of the specific internal energy u, the strain tensor ε_{ik} and the specific polarization $\boldsymbol{p}$. In [34]-[37] a new vector field $\boldsymbol{p}^{(1)}$, which play the role of vectorial thermodinamical internal variable, is introduced and the entropy is rewrited as

$$s = s\left(u, \varepsilon_{ik}, \boldsymbol{p}, \boldsymbol{p}^{(1)}\right) \tag{1}$$

The absolute temperature T and the vector fields $\boldsymbol{E}^{(eq)}$ and $\boldsymbol{E}^{(1)}$ are defined by

$$T^{-1} = \frac{\partial}{\partial u} s\left(u, \varepsilon_{ik}, \boldsymbol{p}, \boldsymbol{p}^{(1)}\right) , \tag{2}$$

$$\boldsymbol{E}^{(eq)} = -T \frac{\partial}{\partial \boldsymbol{p}}\, s\left(u, \varepsilon_{ik}, \boldsymbol{p}, \boldsymbol{p}^{(1)}\right) , \tag{3}$$

$$\boldsymbol{E}^{(1)} = T \frac{\partial}{\partial \boldsymbol{p}^{(1)}}\, s\left(u, \varepsilon_{ik}, \boldsymbol{p}, \boldsymbol{p}^{(1)}\right) , \tag{4}$$

In (3) and (4) $\boldsymbol{E}^{(eq)}$ and $\boldsymbol{E}^{(1)}$ are, respectively, the electric field in an equilibrium thermodynamical state and the vector thermodynamical affinity conjugate to the vector internal variable.

In particular it was shown that the vectorial internal variable which influences the polarization gives rise to dielectric relaxation phenomena and with the aid of such variable one can split up the polarization into two parts

$$\boldsymbol{p} = \boldsymbol{p}^{(0)} + \boldsymbol{p}^{(1)} . \tag{5}$$

The vectors $\boldsymbol{p}^{(0)}$ and $\boldsymbol{p}^{(1)}$ are called specific partial polarization vectors and both changes in these vectors are irreversible phenomena. Of course the polarization vectors are defined by

$$\boldsymbol{P} = \varrho \boldsymbol{p}, \quad \boldsymbol{P}^{(0)} = \varrho \boldsymbol{p}^{(0)}, \quad \boldsymbol{P}^{(1)} = \varrho \boldsymbol{p}^{(1)}, \tag{6}$$

where ϱ is the mass density and so from (5) we have:

$$\boldsymbol{P} = \boldsymbol{P}^{(0)} + \boldsymbol{P}^{(1)} . \tag{7}$$

In the theory it was introduced a new vector $\boldsymbol{E}^{ir)}$ defined as:

$$\boldsymbol{E}^{(ir)} \overset{def}{=} \boldsymbol{E} - \boldsymbol{E}^{(eq)} , \tag{8}$$

where $\boldsymbol{E}$ is the electric field which appear also in the Maxwell's equations.

In refs.[34]-[37], if the mass density is constant and neglecting possible cross-effects among dielectric relaxation and other irreversible phenomena, for isotropic media, the following results were obtained:

- the phenomenological equations for dielectric relaxation phenomena:

$$\begin{cases} \boldsymbol{E}^{(ir)} = L^{(0,0)} \dfrac{d}{dt} \boldsymbol{P} \\ \\ \dfrac{d}{dt} \boldsymbol{P}^{(1)} = L^{(1,1)} \boldsymbol{E}^{(1)} \,, \end{cases} \tag{9}$$

- the linear equations of state :

$$\begin{cases} \boldsymbol{E}^{(eq)} = a^{(0,0)} \boldsymbol{P}^{(0)} \,, \\ \\ \boldsymbol{E}^{(1)} = a^{(0,0)} \boldsymbol{P} - a^{(1,1)} \boldsymbol{P}^{(1)}, \end{cases} \tag{10}$$

In the equation (9) the vector $\boldsymbol{E}^{(ir)}$ is an internal electric field and ; the quantities $L^{(0,0)}$ and $L^{(1,1)}$ are called phenomenological coefficients and the first one has the dimension of a resistance and it is connected to the irreversible proceses related to change of the polarization vector $\boldsymbol{P}$, whereas the second one has the dimension of a conductivity and it is related to change of $\boldsymbol{P}^{(1)}$ and to the relative intensive variable conjugated to it. In the equation (10) the quantities $a^{(0,0)}$ and $a^{(1,1)}$ are state coefficients which have the dimension of a reciprocal dielectric constant [30], [31].

It is seen that three types of internal electric fields appear in the formalism of theory: $\boldsymbol{E}^{(eq)}, \boldsymbol{E}^{(1)}$ and $\boldsymbol{E}^{(ir)}$, while the polarization is additively composed of two parts: $\boldsymbol{P}^{(0)}$ and $\boldsymbol{P}^{(1)}$ (see (7)).
All the coefficients $L^{(0,0)}, L^{(1,1)}, a^{(0,0)}$ and $a^{(1,1)}$ are constants with respect to time but change with respect to frequency ω of the pertubation.
By eliminating from the eqs. (7), (9) and (10) the internal fields $\boldsymbol{E}^{(eq)}$ and $\boldsymbol{E}^{(1)}$ and the two fields $\boldsymbol{P}^{(0)}$ and $\boldsymbol{P}^{(1)}$ of which the polarization is composed, the following dynamical constitutive equation for dielectric relaxaxtion in isotropic media is obtained:

$$\chi^{(0)}_{(EP)} \boldsymbol{E} + \frac{d}{dt} \boldsymbol{E} = \chi^{(0)}_{(PE)} \boldsymbol{P} + \chi^{(1)}_{(PE)} \frac{d}{dt} \boldsymbol{P} + \chi^{(2)}_{(PE)} \frac{d^2}{dt^2} \boldsymbol{P} \tag{11}$$

where

$$\begin{cases} \chi^{(0)}_{(EP)} = a^{(1,1)} L^{(1,1)} \,, \\ \\ \chi^{(0)}_{(PE)} = a^{(0,0)} \left(a^{(1,1)} - a^{(0,0)}\right) L^{(1,1)} \,, \\ \\ \chi^{(1)}_{(PE)} = a^{(0,0)} + a^{(1,1)} L^{(0,0)} L^{(1,1)} \,, \\ \\ \chi^{(2)}_{(PE)} = L^{(0,0)} \,. \end{cases} \tag{12}$$

From (12) we see that

$$\sigma = \frac{1}{\chi^{(0)}_{(EP)}} \tag{13}$$

is the relaxation time.
In the following we consider the case in which almost one component of the polarization and electric fields is different from zero.

3. Theory of linear response.

Schematically a linear response experiment is represented in Fig.1

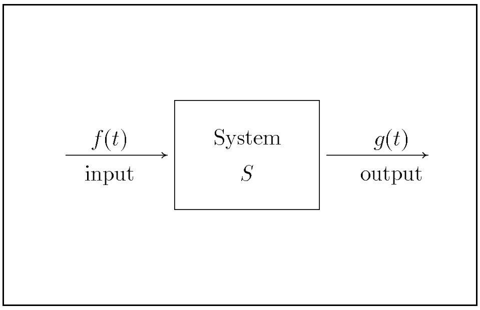

Figure 1. Schematic response experiment

It consists in the application of a pertubation $f(t)$ to a system S and in the analysis of the output $g(t)$ from the system.

In the linear response theory the relation between $g(t)$ and $f(t)$ is represented by the convolution

$$g(t) = f(t) \otimes h(t) \tag{14}$$

where $h(t)$ is the unknown quantity of the problem.

An important result of this theory is that harmonic input $f(t) = Ae^{i\omega t}$ always corresponds harmonic output of the same frequency but different phase and amplitude [29]

$$g(t) = B(\omega)e^{i[\omega t + \phi(\omega)]} \, . \tag{15}$$

Now, we consider a generic dielectric medium placed between the plain plates of a capacitor to which a sinusoidal voltage is applied. Consequently we have on the plates a sinusoidal surface charge, the density of which is characterized by the normal component of polarization vector $P = \boldsymbol{P} \cdot \boldsymbol{n}$ ($\boldsymbol{n}$ is the unit normal to the plates) generating a sinusoidal electric field inside capacitor.

The linear response theory predict that if P (cause) evolves sinusoidally, i.e.

$$P = P_0 e^{i\omega t} \, , \tag{16}$$

then the normal component ($E = \boldsymbol{E} \cdot \boldsymbol{n}$) of electric field inside the capacitor is characterized by

$$E = E_0(\omega)e^{i[\omega t + \phi(\omega)]} \, . \tag{17}$$

The polaritation P is defined as

$$P \; = \; \chi^*(\omega) \, E \; = \; (\chi_1(\omega) - i \, \chi_2(\omega)) \, E. \tag{18}$$

where χ^* is the complex dielectric susceptibility of the material and χ_1 and χ_2 are the corresponding real and immaginary parts.
From (18), by virtue of (16) and (17) one has:

$$\Gamma^*(\omega) \overset{def}{=} \frac{1}{\chi^*(\omega)} = \frac{E_0(\omega)}{P_0} e^{i\,\phi(\omega)}. \tag{19}$$

By putting

$$\Gamma^*(\omega) = \Gamma_1(\omega) + i\,\Gamma_2(\omega). \tag{20}$$

from (19) we obtained:

$$\begin{cases} \Gamma_1(\omega) = \dfrac{\chi_1(\omega)}{[\chi_1(\omega)]^2 + [\chi_2(\omega)]^2} = \dfrac{E_0(\omega)}{P_0}\, cos[\phi(\omega)], \\[2ex] \Gamma_2(\omega) = \dfrac{\chi_2(\omega)}{[\chi_1(\omega)]^2 + [\chi_2(\omega)]^2} = \dfrac{E_0(\omega)}{P_0}\, sin[\phi(\omega)]. \end{cases} \tag{21}$$

The quantities $\Gamma_1(\omega)$ and $\Gamma_2(\omega)$ are called *storage* and *loss* moduli, respectively, and are related to non dissipative phenomena and to dissipative ones [38].
From the equation (21) one has:

$$\begin{cases} \chi_1(\omega) = \dfrac{\Gamma_1(\omega)}{[\Gamma_1(\omega)]^2 + [\Gamma_2(\omega)]^2}, \\[2ex] \chi_2(\omega) = \dfrac{\Gamma_2(\omega)}{[\Gamma_1(\omega)]^2 + [\Gamma_2(\omega)]^2}. \end{cases} \tag{22}$$

In the following we consider all vectors in the complex form.
The immaginary part of P and E (see (16) and (17)) are

$$\begin{cases} \mathfrak{P} = P_0 \sin(\omega t), \\[1ex] \mathfrak{E} = E_0 \sin[(\omega t) + \phi]. \end{cases} \tag{23}$$

and by virtue of (21) we have:

$$\mathfrak{E} = P_0\,\Gamma_1(\omega)\,\sin(\omega t) + P_0\,\Gamma_2(\omega)\,\cos(\omega t). \tag{24}$$

By substituting the equation $(23)_1$ into the equation (11) a differential equation for $\mathfrak{E}$ can be obtained. By integration of this equation one has

$$\begin{aligned} \mathfrak{E} = {} & \frac{P_0\sigma}{1+\sigma^2\omega^2}\Big\{\omega\big[\chi^{(1)}_{(PE)} - \chi^{(0)}_{(PE)}\sigma + L^{(0,0)}\sigma\omega^2\big]\cos(\omega t) + \\ & \big[\chi^{(0)}_{(PE)} + (\chi^{(1)}_{(PE)}\sigma - L^{(0,0)})\omega^2\big]\sin(\omega t)\Big\} \end{aligned} \tag{25}$$

By comparing this result with (24) we have the following expressions:

$$\begin{cases} \Gamma_1(\omega) = \dfrac{\sigma}{1+\sigma^2\omega^2}\Big[\chi^{(0)}_{(PE)} + \big(\chi^{(1)}_{(PE)}\sigma - \chi^{(2)}_{(PE)}\big)\omega^2\Big], \\[2ex] \Gamma_2(\omega) = \dfrac{\sigma\,\omega}{1+\sigma^2\omega^2}\Big[\chi^{(1)}_{(PE)} - \chi^{(0)}_{(PE)}\sigma + \chi^{(2)}_{(PE)}\sigma\omega^2\Big], \end{cases} \tag{26}$$

From (12) and (26) one obtaines

$$\begin{cases} a^{(0,0)} \,=\, \Gamma_1(\omega) \,+\, \dfrac{\Gamma_2^{(1)}(\omega)}{\omega\sigma}\,, \\[2ex] a^{(1,1)} \,=\, \dfrac{\left[\Gamma_2^{(1)}(\omega) \,+\, \omega\,\sigma\,\Gamma_1(\omega)\right]^2}{\omega\,\sigma\,(1 \,+\, \omega^2\sigma^2)\,\Gamma_2^{(1)}(\omega)}\,, \\[2ex] L^{(1,1)} \,=\, \dfrac{\omega\,(1 \,+\, \omega^2\sigma^2)\,\Gamma_2^{(1)}(\omega)}{\left[\Gamma_2^{(1)}(\omega) \,+\, \omega\,\sigma\,\Gamma_1(\omega)\right]^2}\,, \end{cases} \tag{27}$$

where

$$\Gamma_2^{(1)}(\omega) \,=\, \Gamma_2(\omega) \,-\, \omega\, L^{(0,0)}\,, \tag{28}$$

We observe that from (24), by using $(9)_1$ one has:

$$\mathfrak{E} \,=\, \mathfrak{P}\,\Gamma_1(\omega) \,+\, \frac{\mathfrak{E}^{(ir)}\,\Gamma_2(\omega)}{\omega\, L^{(0,0)}}\,. \tag{29}$$

By comparing (29) and (8) we obtain

$$\mathfrak{E}^{(eq)} \,=\, \mathfrak{P}\,\Gamma_1(\omega)\,. \tag{30}$$

and

$$\Gamma_2 \,=\, \omega\, L^{(0,0)}\,. \tag{31}$$

It is known [38] that for low frequency $\Gamma_1(\omega)$ and $\Gamma_2(\omega)$ are constant and their values can be determined by experimental evalutations.

4. Complex conductivity for low frequency.

In the linear approximation, the electrodynamic properties of isotropic materials are studied by using the followig phenomenological relations:

$$\boldsymbol{D} \,=\, \varepsilon^*\,\boldsymbol{E}\,, \qquad \boldsymbol{j} \,=\, \sigma^*\,\boldsymbol{E}\,, \tag{32}$$

where $\boldsymbol{D}$ is the electric displacement field, $\boldsymbol{j}$ is the density of electric current, $\varepsilon^* = \varepsilon_1 - i\varepsilon_2$ is the complex dielectric permittivity and $\sigma^* \,=\, \sigma_1 + i\sigma_2$ is the complex conductivity [38]. By putting

$$\chi^* \,=\, \varepsilon^* \,-\, \varepsilon_0\,, \tag{33}$$

where ε_0 is constant dielectric permittivity in vacuum, from the relation (18) one has:

$$\begin{cases} \chi_1 \,=\, \varepsilon_1 - \varepsilon_0\,, \\[2ex] \chi_2 \,=\, \varepsilon_2\,. \end{cases} \tag{34}$$

In agreement with the linear response theory (see section 3) we consider that the input is

$$\boldsymbol{D} \,=\, D_0\, e^{i\omega t},, \tag{35}$$

and the output is given by

$$\boldsymbol{E} \,=\, E_0\, e^{i[\omega t - \phi(\omega)]},, \tag{36}$$

By using the following Maxwell's equation

$$\mathrm{rot}\boldsymbol{H} = \boldsymbol{j} + \frac{\partial}{\partial t}\boldsymbol{D}, \tag{37}$$

where $\boldsymbol{H}$ is the magnetic displacement field, by utilizing (32) and (35) we have:

$$\mathrm{rot}\boldsymbol{H} = \eta^* \frac{\partial}{\partial t}\boldsymbol{E}, \tag{38}$$

where

$$\eta^* \stackrel{def}{=} \eta_1 - i\,\eta_2 = \varepsilon^* - i\,\frac{\sigma^*}{\omega}. \tag{39}$$

is the total complex dielectric coefficient which can be measuremented from the experiments.
By separating the real and immaginary parts of the quantities which appear in (39) and in virtue of (22) and (34) one obtaines:

$$\begin{cases} \sigma_1 = \omega\left[\eta_2 - \dfrac{\Gamma_2(\omega)}{[\Gamma_1(\omega)]^2 + [\Gamma_2(\omega)]^2}\right], \\ \\ \sigma_2 = \omega\left[\eta_1 - \varepsilon_0 - \dfrac{\Gamma_1(\omega)}{[\Gamma_1(\omega)]^2 + [\Gamma_2(\omega)]^2}\right]. \end{cases} \tag{40}$$

The relations (40) show that the complex conductivity (σ^*) can be obtained from the values of the total complex dielectric coefficient (η^*) and from storage (Γ_1) and loss (Γ_2) moduli.

In ref.[33] it was shown that for low frequency one has:

$$\begin{cases} \Gamma_1(\omega) = \Gamma_{1R} + \dfrac{\Gamma_{2R}\,\omega\,\sigma}{1+\omega^2\,\sigma^2}, \left(\dfrac{\omega}{\omega_R} - 1\right), \\ \\ \Gamma_2(\omega) = \Gamma_{2R}\left[\dfrac{\dfrac{\omega}{\omega_R} + \omega^2\,\sigma^2}{1+\omega^2\,\sigma^2}\right]. \end{cases} \tag{41}$$

where $\Gamma_{1R} = \Gamma_1(\omega_R)$ and $\Gamma_{2R} = \Gamma_2(\omega_R)$ being ω_R the minimum value of ω in the range of low frequency.
In the case of a porcine liver tissue in Fig.2 the experimental values of real and immaginary parts of η^* are plotted and in Fig.3 we have the storage and loss moduli. Finally, in Fig.4, by utilizing the equations (40) and (41) the corrispondent complex dielectric coefficients are obtained.

5. Conclusion.

In this work we have developed a method, in the contest of the not equilibrium thermodynamics with internal variables which, only by means of dielectric measurements, is able to evaluate electric conduction properties as function of the frequency. Since dielectric measurements results minimally invasive this technique can be applied to the study of biological (in vivo) tissues. Moreover it furnish important information on some thermodynamic properties of the tissues.

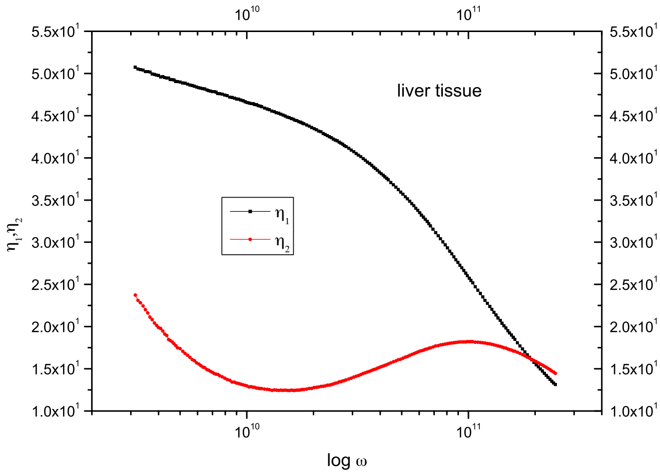

Figure 2. Real and immaginary part of η^* for porcine liver tissue.

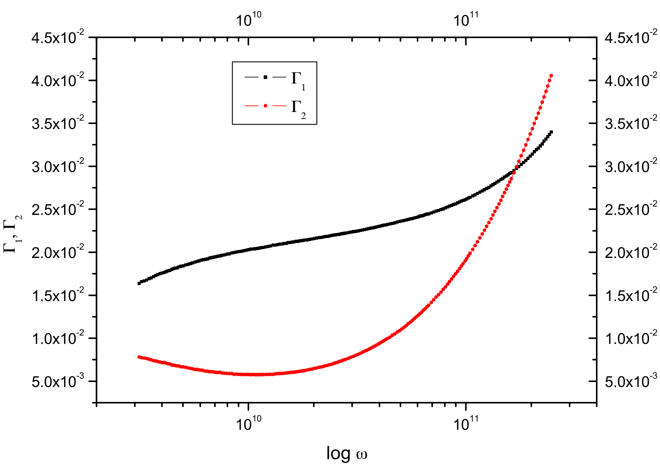

Figure 3. Storage and loss moduli for porcine liver tissue.

We have applied these results to physiological porcine tissue. In particular, the fit by mean of Havriliak-Negami (HN) phenomenological equation [38] of complex dielectric permittivity (imaginary part) data of a porcine liver tissue at 20C, has furnished a dc conductivity

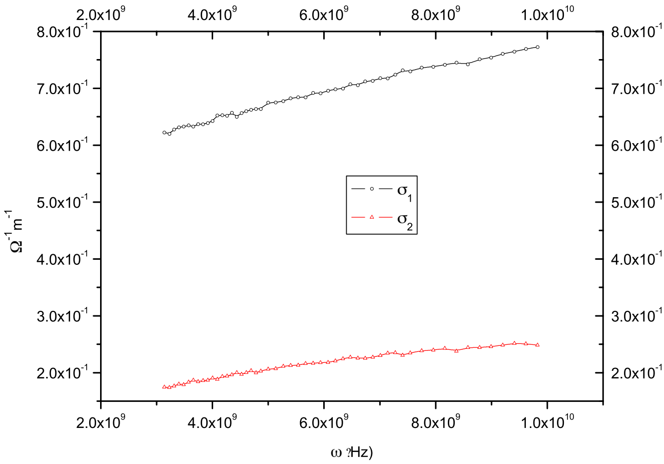

Figure 4. Real and immaginary part of σ^* for porcine liver tissue.

$\sigma = 6.5 \cdot 10^{-3} \Omega^{-1}\, cm^{-1}$. This value is in agreement with the values obtained by applying our theoretical results (see fig. 4). Indeed we have obtained a set of values as function of the frequency and the dc value is collocated inside the range of these values. It is important to observe that the knowledge only of dc conductivity can result insufficient for a detailed therapy based on locally action of a alternating electric current. So the result by us obtained (i.e. the knowledge of conductivity as function of the frequency) will be very useful for a mired therapy and future develop of this technique.

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