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# NON EQUILIBRIUM THERMODYNAMICS WITH INTERNAL VARIABLES IN KLUITENBERG'S THEORY

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ABSTRACT. We show a method to verify experimentally some inequalities which occur for phenomenological coefficients in the thermodynamical model for dielectric relaxation and viscoanelastic media developed in the ambit of non-equilibrium thermodynamic Kluitenberg's theory. In particular, for dielectric relaxation we assume a sinusoidal form for induction vector (extensive variable: cause), the electric field (intensive variable: effect) inside the system, which depends on unknown phenomenological coefficients, has been obtained by integration. Then we compare it with a similar form of the electric field obtained by experimental considerations, where well known experimentally determinable coefficients appear. We carry out dielectric measurements on **PMMA** and **PVC** at different frequencies and fixed temperature in order to obtain the phenomenological coefficients as functions of the frequency. For viscoanelastic media we consider the relative rheological equation and we compare the solution of this equation with a well known expression of the stress obtained, by experimentally considerations, in the linear response theory. This comparison will be able to determine the phenomenological an state coefficients as function of frequency dependent quantities experimentally measurable. This method will be applied to polymeric materials as **Polyisobutilene**.

## 1. Introduction.

The Gerrit Alfred Kluitenberg (1925-1994) scientific activity has been mainly devoted to the study of fundamental problems of irreversible thermodynamics processes. In the first period of his studies, under the leader-ship of S.R. De Groot, he carried out researchers on relativistic non-equilibrium thermodynamics obtaining very important results in a continuous mixture consisting of an arbitrary number of chemical components and in the macroscopic electromagnetic field in ponderable matter.
After that he conceived a new model studying, by a non-relativistic viewpoint, dielectric and magnetic relaxation phenomena in polarizable and magnetizable media. Recently the rheological and phenomenological equations, obtained by G.A. Kluitenberg and his partners in this model, have been experimentally tested confirming the goodness of the model. The author of this paper, being the first Gerrit Alfred Kluitenberg student, is very honoured for his invitation by Scientific Thermocon 2005 Committee to mention the scientific contribution of his instructor and he is very grateful to the destiny that has given to him the possibility to enjoy the affection and the leader-ship of a great scientist: Gerrit Alfred Kluitenberg.

## 2. Relativistic thermodynamics of irreversible processes.

In [1]-[6] a relativistic thermodynamic theory of irreversible processes in a continuous mixture consisting of an arbitrary number of chemical components was developed. The energy-momentum tensor of the macroscopic electromagnetic field in ponderable matter was investigate.
First, some useful notions such as densities, concentrations and flows of matter, the barycentric velocity and the barycentric Lorentz frame are introduced, from the relativistic microscopic fundamental laws the entropy balance is derived.
The phenomenological equations for isotropic media are given and it is shown that the Onsager relations are Lorentz invariant.
The Onsager relations are discussed also in media without and with polarization and magnetization effects and the phenomenological equations for isotropic and anisotropic media are given in four-dimensional and three-dimensional tensor form.

## 3. Thermodynamic theory for viscoanelastic media.

In [7]-[14] a thermodynamic theory for mechanical relaxation phenomena in continuous media was developed by using the general methods of non-equilibrium thermodynamics. It was assumed that several microscopic phenomena occur which give rise to inelastic strain and that the total inelastic deformation is additively composed of contributions of these phenomena.
If both elastic and inelastic deformations occur, it was shown that

$$\varepsilon_{\alpha\beta} = \varepsilon^{(el)}_{\alpha\beta} + \varepsilon^{(in)}_{\alpha\beta} \tag{1}$$

where $\varepsilon_{\alpha\beta}$ is the tensor of the total strain and $\varepsilon^{(el)}_{\alpha\beta}$ and $\varepsilon^{(in)}_{\alpha\beta}$ are tensors describing the elastic and inelastic strains, respectively.
In contradistinction to the elastic strains, the inelastic deformations are due to lattice defects and related phenomena (slip, dislocation, etc.).
If $n$ different types of microscopic phenomena give rise to inelastic strain we have

$$\varepsilon^{(in)}_{\alpha\beta} = \sum_{k=1}^{n} \varepsilon^{(k)}_{\alpha\beta} \tag{2}$$

where $\varepsilon^{(k)}_{\alpha\beta}$ is the contribution to the inelastic strain of the $k$-th microscopic phenomenon.
Since the $n$ microscopic phenomena are assumed to be different, the specific entropy $s$ is supposed depending on the specific internal energy $u$, on the total strain and on all the tensors $\varepsilon^{(k)}_{\alpha\beta}$ and so we have:

$$s = s(u, \varepsilon_{\alpha\beta}, \varepsilon^{(1)}_{\alpha\beta}, \ldots, \varepsilon^{(n)}_{\alpha\beta}) \tag{3}$$

Moreover, defining the temperature $T$ by

$$T^{-1} = \frac{\partial s}{\partial u}\,; \tag{4}$$

the equilibrium-stress tensor, $\tau_{\alpha\beta}^{(eq)}$, by

$$\tau_{\alpha\beta}^{(eq)} = -\rho T \frac{\partial s}{\partial \varepsilon_{\alpha\beta}} ; \tag{5}$$

(where $\varrho$ is the mass density) and the affinity-stress tensors conjugate to $\varepsilon_{\alpha\beta}^{(k)}$ by

$$\tau_{\alpha\beta}^{(k)} = \rho T \frac{\partial s}{\partial \varepsilon_{\alpha\beta}^{(k)}} \tag{6}$$

from the first law of thermodynamics it was obtained the following balance equation for the entropy

$$\varrho \frac{ds}{dt} = -\,\mathrm{div}\left(\frac{\mathbf{J}^{(q)}}{T}\right) + \sigma^{(s)} \tag{7}$$

where

$$\sigma^{(s)} = T^{-1}\left[ -T^{-1}\mathbf{J}^{(q)} \cdot \mathrm{grad}T + \tau_{ik}^{(vi)} \frac{d\varepsilon_{ik}}{dt} + \sum_{k=1}^{n} \tau_{ik}^{(k)} \frac{d\varepsilon_{ik}^{(k)}}{dt} \right] \tag{8}$$

is the entropy production.
In (7) and (8) $\mathbf{J}^{(q)}$ is the heat flow and

$$\tau_{ik}^{(vi)} = \tau_{ik} - \tau_{ik}^{(eq)} \tag{9}$$

the viscous stress tensor. Moreover, in (9), $\tau_{ik}$ is the mechanical stress tensor which occur in the first law of thermodynamics.
According to the usual procedure of non-equilibrium thermodynamics it can be obtained the linear rheological equations for isotropic visco-anelastic media, which for $n = 1$ have the following expressions:

$$\begin{aligned} R_{(d)0}^{(\tau)} \widetilde{\tau}_{ik} + \frac{d}{dt}\widetilde{\tau}_{ik} &= R_{(d)0}^{(\varepsilon)} \widetilde{\varepsilon}_{ik} + R_{(d)1}^{(\varepsilon)} \frac{d}{dt}\widetilde{\varepsilon}_{ik} + \\ &\quad + R_{(d)2}^{(\varepsilon)} \frac{d^2}{dt^2}\widetilde{\varepsilon}_{ik} , \end{aligned} \tag{10}$$

$$\begin{aligned} R_{(v)0}^{(\tau)} (\tau - \tau^0) + \frac{d}{dt}\tau &= R_{(v)0}^{(\varepsilon)} \varepsilon + R_{(v)1}^{(\varepsilon)} \frac{d}{dt}\varepsilon + \\ &\quad + R_{(v)2}^{(\varepsilon)} \frac{d^2}{dt^2}\varepsilon . \end{aligned} \tag{11}$$

In (10)-(11) $\widetilde{\tau}_{ik}$ and $\widetilde{\varepsilon}_{ik}$ are the deviators of the tensors $\tau_{\alpha\beta}$ and $\varepsilon_{\alpha\beta}$, respectively, while $\tau$ and $\varepsilon$ are their scalar parts ($\tau^0$ is the scalar part of the stress of the medium in a state of thermodynamic equilibrium ).
Moreover one has [10]:

$$R^{(\tau)}_{(d)0} = a^{(1,1)}\eta^{(1,1)}_s; \tag{12}$$

$$R^{(\varepsilon)}_{(d)0} = a^{(0,0)}(a^{(1,1)} - a^{(0,0)})\eta^{(1,1)}_s; \tag{13}$$

$$R^{(\varepsilon)}_{(d)1} = a^{(0,0)}(1 + 2\eta^{(0,1)}_s) + \tag{14}$$

$$+a^{(1,1)}[\eta^{(0,0)}_s\eta^{(1,1)}_s + (\eta^{(0,1)}_s)^2]; \tag{15}$$

$$R^{(\varepsilon)}_{(d)2} = \eta^{(0,0)}_s; \tag{16}$$

$$R^{(\tau)}_{(v)0} = b^{(1,1)}\eta^{(1,1)}_v; \tag{17}$$

$$R^{(\varepsilon)}_{(v)0} = b^{(0,0)}(b^{(1,1)} - b^{(0,0)})\eta^{(1,1)}_v; \tag{18}$$

$$R^{(\varepsilon)}_{(v)1} = b^{(0,0)}(1 + 2\eta^{(0,1)}_v) + \tag{19}$$

$$+b^{(1,1)}[\eta^{(0,0)}_v\eta^{(1,1)}_v + (\eta^{(0,1)}_v)^2]; \tag{20}$$

$$R^{(\varepsilon)}_{(v)2} = \eta^{(0,0)}_v. \tag{21}$$

In (12)-(16) the quantities $a^{(0,0)}$, $b^{(0,0)}$, $a^{(1,1)}$, $b^{(1,1)}$ are scalar constants (coefficients of state). The coefficients $\eta^{(0,0)}_s$ and $\eta^{(0,0)}_v$ may be called the shear and the volume viscosity, respectively, and $\eta^{(1,1)}_s$ and $\eta^{(1,1)}_v$ are fluidities and $\eta^{(0,1)}_s$ and $\eta^{(0,1)}_v$ are dimensionless coefficients connected with possible cross effect among viscous and anelastic flows.

## 4. Experimental approach of linear response theory for phenomenological coefficients of Kluitenberg's thermodynamic theory for visco-anelastic media

For shear phenomena, if cross-effect between viscous and inelastic flows can be neglected, the (12)-(16) reduce to:

$$R^{(\tau)}_{(d)0} = a^{(1,1)}\eta^{(1,1)}_s; \tag{22}$$

$$R^{(\varepsilon)}_{(d)0} = a^{(0,0)}(a^{(1,1)} - a^{(0,0)})\eta^{(1,1)}_s; \tag{23}$$

$$R^{(\varepsilon)}_{(d)1} = a^{(0,0)} + a^{(1,1)}\eta^{(1,1)}_s\eta^{(0,0)}_s; \tag{24}$$

$$R^{(\varepsilon)}_{(d)2} = \eta^{(0,0)}_s\,. \tag{25}$$

Dimensionally one has

$$\begin{aligned}
&\left[R^{(\tau)}_{(d)0}\right] = t^{-1} && \left[a^{(0,0)}\right] = ml^{-1}t^{-2}\\
&\left[R^{(\varepsilon)}_{(d)0}\right] = ml^{-1}t^{-3} && \left[a^{(1,1)}\right] = ml^{-1}t^{-2}\\
&\left[R^{(\varepsilon)}_{(d)1}\right] = ml^{-1}t^{-2} && \left[\eta^{(1,1)}_s\right] = \left(ml^{-1}t^{-1}\right)^{-1}\\
&\left[R^{(\varepsilon)}_{(d)2}\right] = ml^{-1}t^{-1} && \left[\eta^{(0,0)}_s\right] = ml^{-1}t^{-1}
\end{aligned} \tag{26}$$

It was shown [10] that from the principle of entropy production, the following inequalities hold :

$$\begin{array}{l} a^{(0,0)} > 0 \\ a^{(1,1)} > 0 \\ \eta_s^{(1,1)} > 0 \\ \eta_s^{(0,0)} > 0 \end{array} \tag{27}$$

Very recently, in [16], at the sake to verify experimentally the inequalities (27), using the approach of linear response theory [17], [19], it was shown as the phenomenological and state coefficients can be related to quantities that can be experimentally measurable.
Let a generic continuum medium be subject to three-dimensional harmonic shear deformation (extensive variable=cause) of the form [18]:

$$\tilde{\varepsilon}_{\alpha\beta} = \tilde{\varepsilon}_{\alpha\beta}^{(0)} \sin \omega t \tag{28}$$

where $\tilde{\varepsilon}_{\alpha\beta}^{(0)} = constant$ and $\omega = 2\pi\nu$ are, respectively, the amplitude and the angular frequency of the deformation.

Of course the medium will react by a stress [17] (intensive variable = effect) of the same frequency as the deformation but of different amplitude $\tilde{\tau}_{\alpha\beta}^{0}$ and with a phase lag $\varphi_{\alpha\beta}$. These will be functions of the frequency of deformation because they result from the time necessary for molecular rearrangement and from dissipative phenomena; so we have $\tilde{\tau}_{\alpha\beta}^{(0)} = \tilde{\tau}_{\alpha\beta}^{(0)}(\omega)$ and $\varphi_{\alpha\beta} = \varphi_{\alpha\beta}(\omega)$ [17].

The form of this stress will be (here we don't use Einstein's convention):

$$\tilde{\tau}_{\alpha\beta} = \tilde{\tau}_{\alpha\beta}^{(0)}(\omega) \sin\left[\omega t + \varphi_{\alpha\beta}(\omega)\right] \tag{29}$$

or

$$\tilde{\tau}_{\alpha\beta} = G_{\alpha\beta}^{(1)} \tilde{\varepsilon}_{\alpha\beta}^{(0)} \sin(\omega t) + G_{\alpha\beta}^{(2)} \tilde{\varepsilon}_{\alpha\beta}^{(0)} \cos(\omega t) \tag{30}$$

where

$$G_{\alpha\beta}^{(1)}(\omega) = \frac{\tilde{\tau}_{\alpha\beta}^{(0)}}{\tilde{\varepsilon}_{\alpha\beta}^{(0)}} \cos\varphi_{\alpha\beta}(\omega) \ , \tag{31}$$

$$G_{\alpha\beta}^{(2)}(\omega) = \frac{\tilde{\tau}_{\alpha\beta}^{(0)}}{\tilde{\varepsilon}_{\alpha\beta}^{(0)}} \sin\varphi_{\alpha\beta}(\omega) \tag{32}$$

The quantities $G_{\alpha\beta}^{(1)}(\omega)$ and $G_{\alpha\beta}^{(2)}(\omega)$, experimentally measured, are called *storage* and *loss moduli* and are related to non dissipative phenomena and to dissipative ones [19].
If we consider the case for which just one component of the strain and stress is different from zero, for example $\tilde{\varepsilon}_{12}^{(0)}$ and $\tilde{\tau}_{12}^{(0)}$, the equations (10), (29)-(32) become, respectively:

$$\frac{d\tau}{dt} + R_{(d)0}^{(\tau)} \tau = R_{(d)0}^{(\varepsilon)} \varepsilon + R_{(d)1}^{(\varepsilon)} \frac{d\varepsilon}{dt} + R_{(d)2}^{(\varepsilon)} \frac{d^2\varepsilon}{dt^2} \ , \tag{33}$$

$$\tau(\omega) = G_1(\omega)\varepsilon_0 \sin(\omega t) + G_2(\omega)\varepsilon_0 \cos(\omega t) \ , \tag{34}$$

$$G_1(\omega) = \frac{\tau_0(\omega)}{\varepsilon_0}\cos\varphi(\omega)\ , \tag{35}$$

$$G_2(\omega) = \frac{\tau_0(\omega)}{\varepsilon_0}\sin\varphi(\omega)\ . \tag{36}$$

where $\tilde{\tau}_{12}(\omega) = \tau(\omega)$, $\tilde{\tau}_{12}^{(0)}(\omega) = \tau_0(\omega)$, $\tilde{\varepsilon}_{12}(\omega) = \varepsilon(\omega)$, $\tilde{\varepsilon}_{12}^{(0)} = \varepsilon_0$, $\varphi_{12}(\omega) = \varphi(\omega)$, $G_{12}^{(1)}(\omega) = G_1(\omega)$, $G_{12}^{(2)}(\omega) = G_2(\omega)$.
Assuming that the medium is subjected to one-dimensional harmonic shear deformation of the form:

$$\varepsilon = \varepsilon_0 \sin\omega t \tag{37}$$

and substituting this expression into (33) it follows:

$$\frac{d\tau}{dt} + \frac{\tau}{\sigma} = \alpha\sin\omega t + \beta\cos\omega t \tag{38}$$

where

$$\begin{aligned}\alpha &= \left(R_0^{(\varepsilon)} - \omega^2 R_2^{(\varepsilon)}\right)\varepsilon_0\\ \beta &= R_1^{(\varepsilon)}\varepsilon_0\omega\\ \sigma &= \tfrac{1}{R_0^{(\varepsilon)}}\end{aligned}$$

the solution of (38) is :

$$\tau(t) = \tau_0(\omega)\sin[\omega t + \delta(\omega)] \tag{39}$$

where

$$\tau_0(\omega) = \sqrt{\frac{(\alpha^2+\beta^2)\sigma^2}{1+\omega^2\tau^2}} \qquad \cos\delta(\omega) = \frac{\alpha+\beta\omega\sigma}{\sqrt{(1+\omega^2\sigma^2)(\alpha^2+\beta^2)}}$$

$$\sin\delta(\omega) = \frac{\beta-\alpha\omega\sigma}{\sqrt{(1+\omega^2\sigma^2)(\alpha^2+\beta^2)}}$$

By equating of (39) with(34) one has:

$$\begin{cases} a^{(0,0)}(\omega) = \frac{G_1\left(1+\omega^2\sigma^2\right)-G_{1R/H}}{\omega^2\sigma^2} \\ a^{(1,1)}(\omega) = \frac{1}{\omega^2\sigma^2}\left\{\frac{\left[G_1\left(1+\omega^2\sigma^2\right)-G_{1R/H}\right]^2}{\left(G_1-G_{1R/H}\right)\left(1+\omega^2\sigma^2\right)}\right\} \\ \eta_s^{(1,1)}(\omega) = \omega^2\sigma\left\{\frac{\left(G_1-G_{1R/H}\right)\left(1+\omega^2\sigma^2\right)}{\left[G_1(1+\omega^2\sigma^2)-G_{1R/H}\right]^2}\right\} \\ \eta_s^{(0,0)}(\omega) = \frac{G_{1R/H}+G_2\omega\sigma-G_1}{\omega^2\sigma} \end{cases} \tag{40}$$

In (40)

$$G_{1R/H} = \frac{a^{(0,0)}\left(a^{(1,1)}-a^{(0,0)}\right)}{a^{(1,1)}}$$

where we select the values $G_{1R}$ or $G_{1H}$ for the symbol $G_{1R/H}$ depending on we refer to low or high frequency, respectively.

In this way we have obtained the variables $a^{(0,0)}, a^{(1,1)}, \eta_s^{(0,0)}, \eta_s^{(1,1)}$, for low and high frequency, as function of the frequency-dependent quantities $G_1$ e $G_2$ which are experimental determinable.
The coefficients (40) are plotted in Fig.1 for Poly-isobutylene material.

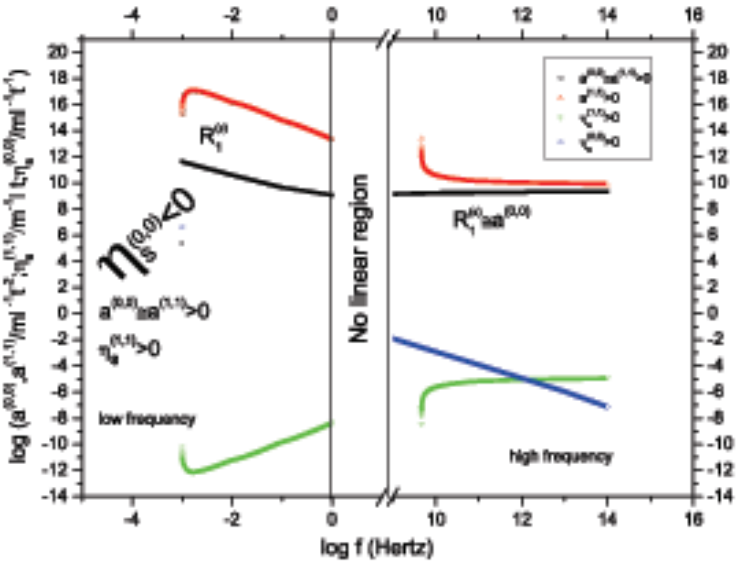


*Figure* 1. Poly-isoButylene; $M.w. = 10^6\, g/mol.\,, T_0 = 273\, K; G_{1R} \approx 10^{5.4} Pa; G_{1H} \approx 10^{9.38} Pa; \sigma \approx 10^{-5} s.$

## 5. Dielectric relaxation phenomena.

In [20] and [21] a thermodynamic theory for dielectric relaxation phenomena was proposed and it was shown that if there is a *hidden* vectorial internal variable, which influences the polarization $\mathbf{P}$, this leads to the possibility to write $\mathbf{P}$ in the form

$$\mathbf{P} = \mathbf{P}^{(0)} + \mathbf{P}^{(1)} \tag{41}$$

where $\mathbf{P}^{(1)}$ can be considered as internal variable, while in the linear approximation of the theory $\mathbf{P}^{(0)}$ is proportional to the electric field $\mathbf{E}$. This means that $\mathbf{P}$ is additively composed of a reversible (*elastic*) part $\mathbf{P}^{(0)}$ and an irreversible part $\mathbf{P}^{(1)}$ which is connected with dielectric after-effects.
Moreover, in the linear approximation [xxxx] one can eliminate the internal variable from the formalism and this leads to the Debye [26] equation

$$\chi^{(0)}_{(EP)}\mathbf{E} + \frac{d\mathbf{E}}{dt} = \chi^{(0)}_{(PE)}\mathbf{P} + \chi^{(1)}_{(PE)}\frac{d\mathbf{P}}{dt} \tag{42}$$

In (42) the quantities $\chi$ are phenomenological coefficients which are connected to the physical properties of the medium.
In the theory it was shown that if an instantaneous change in the electric field $\mathbf{E}$ occurs this is associated with a sudden change in the polarization. This is connected with the reversible character of $\mathbf{P}^{(0)}$.
In [27] it was noted that in principle an instantaneous increase or decrease in the polarization is connected with the motion of any kind of microscopic particles, that cannot be infinitely fast. For this reason in [28]-[32] it was proposed a generalization of the theory developed in [20] and [21] assuming that, in principle all changes in the polarization are irreversible phenomena.
Using the methods of irreversible thermodynamic the following phenomenological equation was obtained:

$$\chi^{(0)}_{(EP)}\mathbf{E} + \frac{d\mathbf{E}}{dt} = \chi^{(0)}_{(PE)}\mathbf{P} + \chi^{(1)}_{(PE)}\frac{d\mathbf{P}}{dt} + \chi^{(2)}_{(PE)}\frac{d^2\mathbf{P}}{dt^2} \tag{43}$$

where, from the positive character of the entropy production, the coefficients $\chi$ must satisfy to the following inequalities

$$\chi^{(0)}_{(EP)} \geq 0\,,\ \chi^{(0)}_{(PE)} \geq 0\,,\ \chi^{(2)}_{(PE)} \geq 0\,, \tag{44}$$

$$\chi^{(1)}_{(PE)} - \chi^{(0)}_{(EP)}\chi^{(2)}_{(PE)} \geq 0\,, \tag{45}$$

$$\chi^{(1)}_{(PE)} \geq 0\,, \tag{46}$$

$$\chi^{(1)}_{(PE)}\chi^{(0)}_{(EP)} - \chi^{(0)}_{(PE)} \geq 0\,, \tag{47}$$

It is seen form 43 that in this generalized model the relaxation dielectric phenomena are characterized of two relaxation times, as it was emphasized in [33] and [34] from experimental observations.

## 6. Experimental behavior of phenomenological coefficients in dielectric relaxation phenomena.

Very recently [35] it was shown that, using the linear response theory [17], a method to measure experimentally the phenomenological coefficients which occur in (43) and to verify the inequalities (44)-(47).

Schematically a linear response experiment is represented as in Fig.2.

It consists in the application of a perturbation $f(t)$ 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

$$g(t) = f(t) \bigotimes h(t) \tag{48}$$

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

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

$$g(t) = B(\omega)e^{i[\omega t + \phi(\omega)]} \tag{49}$$

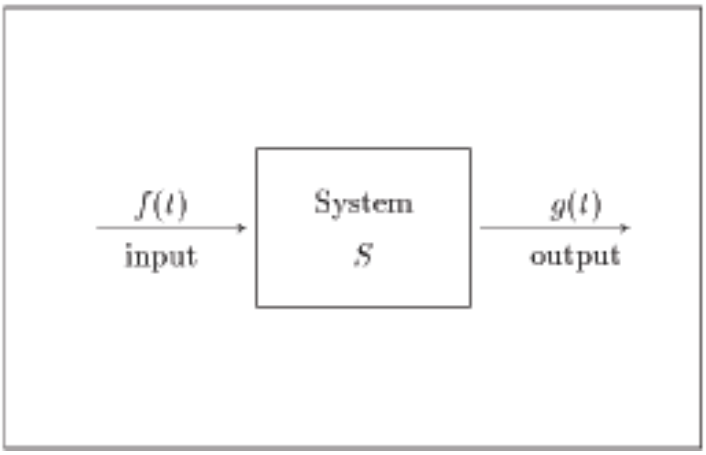


*Figure* 2. Schematic response experiment.

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 induction vector $D = \mathbf{d} \cdot \mathbf{n}$ ($\mathbf{n}$ is the unit normal to the plates) generating a sinusoidal electric field inside capacitor.

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

$$D = D_0 sin(\omega t) \tag{50}$$

then the normal component ($E = \mathbf{E} \cdot \mathbf{n}$) of electric field inside the capacitor is also sinusoidal and characterized by the same frequency but different phase and amplitude

$$E = E_0(\omega) sin[\omega t + \phi(\omega)] \tag{51}$$

and so

$$E = D_0 s_1 sin(\omega t) + D_0 s_2 cos(\omega t) \tag{52}$$

where

$$s_1 = \frac{E_0(\omega)}{D_0} cos\,\phi(\omega)\,, \tag{53}$$

$$s_2 = \frac{E_0(\omega)}{D_0} sin\,\phi(\omega)\,. \tag{54}$$

Defining the *reciprocal complex dielectric constant*:

$$s^* = \frac{E^*}{D^*} = s_1 + i\,s_2\,, \tag{55}$$

with

$$E^* = E_0\, e^{i(\omega t + \phi(\omega))}\,, \tag{56}$$

$$D^* = D_0\, e^{i\omega t}\,. \tag{57}$$

the *complex dielectric constant* will be:

$$\varepsilon^* = \frac{1}{s^*} = \varepsilon' - i\,\varepsilon'' \,, \tag{58}$$

where

$$\varepsilon' = \frac{s_1}{s_1^2 + s_2^2} \;,\; \varepsilon'' = \frac{s_2}{s_1^2 + s_2^2} \,, \tag{59}$$

Taking into account (53) and (54)

$$\varepsilon' = \frac{D_0}{E_0(\omega)} cos\phi(\omega) \quad \varepsilon'' = \frac{D_0}{E_0(\omega)} sin\phi(\omega) \,, \tag{60}$$

Dimensionally we have:

$$[\varepsilon'] = [\varepsilon''] = \frac{Q^2}{m\,l^3\,t^{-2}} \tag{61}$$

in the MKSA system ($Q$ = charge, $m$ = mass, $l$ = length, $t$ = time). The quantities (60) are experimentally measurable and can be proved to be proportional to stored and dissipated energy, respectively.

## 7. Phenomenological coefficients and frequency.

The polarization vector is defined by:

$$\mathbf{P} = \mathbf{D} - \varepsilon_0\,\mathbf{E} \tag{62}$$

By using the normal component $P = \mathbf{P} \cdot \mathbf{n}$ and setting:

$$h_i = \chi^{(i)}_{(PE)} \;\; (i = 0, 1, 2) \,, \qquad k_0 = \chi^{(0)}_{(EP)} \tag{63}$$

from (43) we have:

$$h_2\varepsilon_0\ddot{E} + (1 + h_1\varepsilon_0)\dot{E} + (h_0\varepsilon_0 + k_0)E = h_2\ddot{D} + h_1\dot{D} + h_0 D \,. \tag{64}$$

where the dot means derivative respect to time.

We observe that, dimensionally, one has:

$$[k_0] = t^{-1} \,, \qquad [h_0] = \frac{m\,l^3\,t^{-3}}{Q^2} \tag{65}$$

$$[h_1] = \frac{1}{\varepsilon_0} = \frac{m\,l^3\,t^{-2}}{Q^2} \,, \qquad [h_2] = \frac{m\,l^3\,t^{-1}}{Q^2} \tag{66}$$

Using (64) and (52) we obtain:

$$k_0 = \frac{\omega(\varepsilon_R-\varepsilon_0)(\varepsilon'^2+\varepsilon''^2-\varepsilon'\varepsilon_0)}{\varepsilon_R\omega\tau\Big[(\varepsilon'-\varepsilon_0)^2+\varepsilon''^2\Big]-(\varepsilon_R-\varepsilon_0)\varepsilon''\varepsilon_0}\,, \tag{67}$$

$$h_0 = \frac{\omega(\varepsilon'^2+\varepsilon''^2-\varepsilon'\varepsilon_0)}{\varepsilon_R\omega\tau\Big[(\varepsilon'-\varepsilon_0)^2+\varepsilon''^2\Big]-(\varepsilon_R-\varepsilon_0)\varepsilon''\varepsilon_0}\,, \tag{68}$$

$$h_1 = \frac{(\varepsilon_R-\varepsilon_0)\varepsilon''+\varepsilon_R\omega\tau(\varepsilon'-\varepsilon_0)}{\varepsilon_R\omega\tau\Big[(\varepsilon'-\varepsilon_0)^2+\varepsilon''^2\Big]-\varepsilon_0\varepsilon''(\varepsilon_R-\varepsilon_0)}\,, \tag{69}$$

$$h_2 = \frac{h_0}{\omega^2}\Big[\frac{(\varepsilon'-\varepsilon_R)(\varepsilon'-\varepsilon_0)+\varepsilon''^2}{(\varepsilon'-\varepsilon_0)^2+\varepsilon''^2}\Big]+\frac{\varepsilon''}{\omega\Big[(\varepsilon'-\varepsilon_0)^2+\varepsilon''^2\Big]}\,. \tag{70}$$

where

$$\varepsilon_R = \frac{h_0\varepsilon_0+k_0}{h_0} \tag{71}$$

It is well known that the following inequalities hold:

$$\varepsilon'-\varepsilon_0>0\,, \tag{72}$$

$$\varepsilon_R-\varepsilon_0>0\,, \tag{73}$$

$$\varepsilon_R-\varepsilon'>0\,, \tag{74}$$

and from (67)-(69) and (44)-(47)one obtains

$$k_0 > 0\,, \tag{75}$$

$$h_0 > 0\,, \tag{76}$$

$$h_1 > 0\,, \tag{77}$$

$$\text{if} \qquad \varepsilon_R\omega\tau\Big[(\varepsilon'-\varepsilon_0)^2+\varepsilon''\Big]-(\varepsilon_R-\varepsilon_0)\varepsilon''\varepsilon_0>0\,. \tag{78}$$

Using (75)-(78) from (70) it follows:

$$h_2>0\,, \tag{79}$$

if

$$\begin{aligned}(\varepsilon' &- \varepsilon_0)\Big[\varepsilon'(\varepsilon'-\varepsilon_0)(\varepsilon'-\varepsilon_R)+\varepsilon''^2(2\varepsilon'-\varepsilon_R)\Big]+\varepsilon''^4+\\ &+ \varepsilon''\varepsilon_R\omega\tau\Big[(\varepsilon'-\varepsilon_0)^2+\varepsilon''^2\Big]-\varepsilon''^2\varepsilon_0(\varepsilon_R-\varepsilon_0)>0\,.\end{aligned} \tag{80}$$

We can conclude that the inequalities (78) and (80) define the class of dielectric media which are described in the theory developed in [20] - [30].

Moreover from (70) it is easy to see that $h_2$ approaches zero for sufficiently large $\omega$, whereas $h_0, k_0$ and $h_1$ approach a positive finite value.

This means that for sufficiently high frequency, in the equation (43), the term connected with the second derivative vanishes and the phenomenological equation reduces to the Debye equation.

## 8. Experimental date.

We have applied this method to PMMA (PolyMethylMethaCrylate) and PVC (PolyVinylChloride) polymers in order to obtain phenomenological coefficients for such materials.
Then dielectric measurements were performed by Rheometric Scientific Analyzer (DETA)

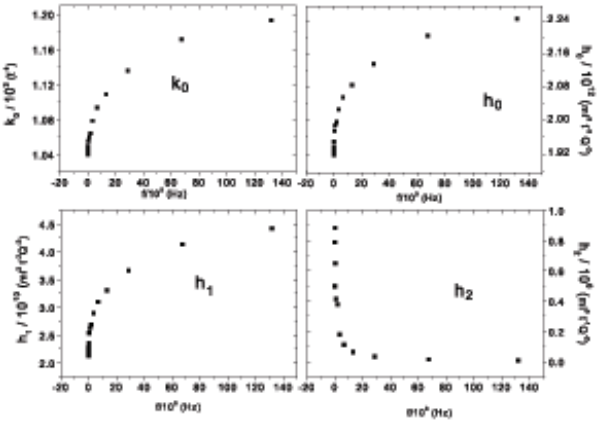


*Figure* 3. The trend of the phenomenological coefficients $h_0, h_1, k_0$ and $h_2$ for PolyMethylMethaCrylate (PMMA)in the range $10 - 10^5$ Hz.

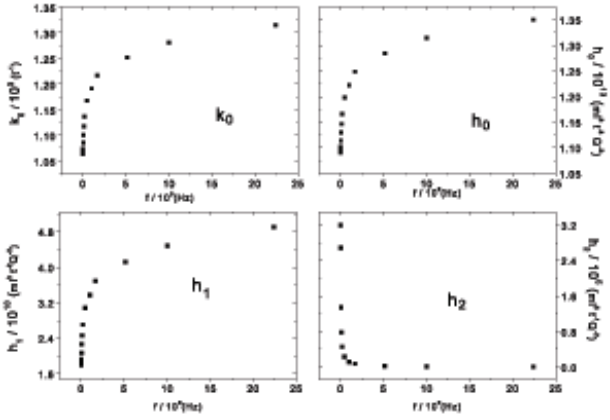


*Figure* 4. The trend of the phenomenological coefficients $h_0, h_1, k_0$ and $h_2$ for PolyVinylChloride (PVC) in the range $10^2 - 10^6$ Hz .

The analysis chamber is purged with nitrogen and spanned frequencies in the range 10 Hz - $10^5$ for PMMA and $10^2$ Hz - $10^6$ Hz for PVC.
The experimental results are shown in the figures (3) and (4) and are physically meaningful.

## References


[1] G.A. Kluitenberg, S. R. de Groot and P. Mazur, "Relativistic thermodynamics of irreversible processes I. Heat conduction, diffusion, viscous flow and chemical reactions; Formal part," *Physica* **19**, 689 (1953).

[2] G.A. Kluitenberg, S. R. de Groot and P. Mazur, "Relativistic thermodynamics of irreversible processes II. Heat conduction and diffusion. Physical part," *Physica* **19**, 1079 (1953).

[3] G.A. Kluitenberg, S. R. de Groot and P. Mazur, "Relativistic thermodynamics of irreversible processes III. Systems without polarization and magnetization in an electromagnetic field," *Physica* **20**, 199 (1954).

[4] G.A. Kluitenberg , *Relativistic thermodynamics of irreversible processes.* Proefschrift, Leiden (1954).

[5] G.A. Kluitenberg and S. R. de Groot, "Relativistic thermodynamics of irreversible processes IV. System with polarization and magnetization in an electromagnetic field," *Physica* **21**, 148 (1955).

[6] G.A. Kluitenberg and S. R. de Groot, "Relativistic thermodynamics of irreversible processes V. The energy-momentum tensor of the macroscopic electromagnetic field, the macroscopic forces acting on the matter and the first and second laws of thermodynamics," *Physica* **21**, 69 (1955).

[7] G.A. Kluitenberg, "On rheology and thermodynamics of irreversible processes," *Physica* **28**, 1173 (1962).

[8] G.A. Kluitenberg, "On the thermodynamics of viscosity and plasticity," *Physica* **29**, 633 (1963).

[9] G.A. Kluitenberg, "A unified thermodynamic theory for large deformations in elastic media and in Kelvin (Voigt) media, and for viscous fluid flow," *Physica* **30**, 1945 (1964).

[10] G.A. Kluitenberg, "A thermodynamic derivation of the stress-strain relations for Burgers media and related substances," *Physica* **38**, 513 (1968).

[11] G.A. Kluitenberg, "On plasticity, elastic relaxation phenomena, and a stress-strain relation, which characterizes Schofield-Scott Blair media," *Appl. Sci. Res.* **25**, 383 (1972).

[12] G.A. Kluitenberg, "A thermodynamic discussion of the possibility of singular yield conditions in plasticity theory," *Physica* **88A**, 122 (1977).

[13] V.Ciancio, G.A.Kluitenberg, "On linear dynamical equations of state for isotropic media - I - General formalism," *Physica* **93 A**, pp.273 (1978).

[14] V.Ciancio, "Propagation and attenuation of singular wave surfaces in linear inelastic media," *Physica* **97 A**, 127 (1979).

[15] V.Ciancio, G.A.Kluitenberg, "On linear dynamical equations of state for isotropic media - II - Some cases of special interest," *Physica* **99 A** , 592 (1979).

[16] V.Ciancio, A.Bartolotta, F.Farsaci, "Experimental confirmations on a thermodynamical theory for viscoanelastic media with memory," *Physica B* **394**, 8 (2007).

[17] N.G. McCrum, B.E. Read, G.Williams, *Anelastic and Dielectric Effects in Polymeric Solids,* (John Wiley&Sons, London-New York, Sydney, 1967).

[18] W. Graham,*Comprehensive polymer science,* vol.2,Chp.16, eds. Sir G.Allen, J.C. Bevington (Pergamon Press, 1989).

[19] I.M.Ward, D.M. Hadley, *An Introduction to the mechanical properties of solid polymers,* (Wiley, 1993).

[20] G.A.Kluitenberg, "On dielectric and magnetic relaxation phenomena and non-equilibrium thermodynamics," *Physica*, **68**, 75 (1973).

[21] G.A. Kluitenberg, "On dielectric and magnetic relaxation phenomena and vectorial internal degrees of freedom in thermodynamics," *Physica*, **87A**, 302 (1977).

[22] S.R. De Groot, *Thermodynamics of irreversible processes,* (North-Holland, Amsterdam, Interscience, New York, 1951).

[23] S.R. De Groot and P. Mazur, *Non-equilibrium Thermodynamics,* (North-Holland, Amsterdam, Interscience, New York, 1962).

[24] I. Prigogine, *Introduction to thermodynamics of irreversible processes,* (Interscience-John, Wiley, New York-London, 1961).

[25] I. Gyarmati, *Non-equilibrium thermodynamics,* (Springer, Berlin-Heidelberg-New York, 1970).

[26] P. Debye, *Polar molecules,* (Dover, New York, 1945).

[27] C.J.F. Böttcher and P. Bordewijk, *Theory of Electric Polarization, vol.II, Dielectric in Time-dependent Fields,* (Elsevier Publ., Amsterdam, Oxford, NewYork. 1978).
[28] G.A. Kluitenberg, "On vectorial internal variables and dielectric and magnetic relaxation phenomena", *Physica*, **109A**, 91 (1981).
[29] V. Ciancio, "On the generalized Debye equation for media with dielectric relaxation phenomena described by vectorial internal veriables," *J. Non-Equilib. Thermodynamics*, **14**, 239 (1989)
[30] V. Ciancio, G.A. Kluitenberg, "On electromagnetic waves in isotropic media with dielectric relaxation," *Acta Physica Hungarica*, **251** (1989)
[31] V.Ciancio, L. Restuccia, G.A. Kluitenberg, "A thermodynamic derivation of equations for dielectric relaxation phenomena in anisotropic polarizable media," *J. Non-Equilib. Thermodynamics*, **15**, 157 (1990)
[32] V. Ciancio, M. Dolfin, P. Vàn, "Thermodynamical theory of dia- and paramagnetic materials," *Int. Journal of Applied Electromagnetics and Mechanics*, **7**, 237 (1996)
[33] B. Gestblom, "Dielectric relaxation time of Bound water in biological materials", *J.Phys.Chem.*, 6064 (1991).
[34] Y.Z. Wei, A.C. Kumbharkhane, "Protein hydratation investigations with high frequency dielectric spectroscopy", *J. Phys. Chem.*,6644 (1994).
[35] V. Ciancio, F. Farsaci, G. Di Marco, "A method for experimental evaluation of phenomenological coeffcients in media with dielectric relaxation", *Physica B*, **387**, 130 (2007).

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