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A method for experimental evaluation of phenomenological coefficients in media with dielectric relaxation

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Abstract

We show a method to measure experimentally the phenomenological coefficients and to verify some inequalities which occur in a thermodynamical model for dielectric relaxation proposed by one of us in some previous papers. Assuming a sinusoidal form for induction vector D (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. The comparison of these two forms, together with the introduction of an experimentally determinable relaxation time, allows us to determine univocally the above-mentioned phenomenological coefficients as functions of experimentally determinable coefficients only. This allows us to verify the aforementioned inequalities. Moreover, a condition for the applicability of Kluitenberg–Ciancio theory is determined. Finally 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.

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1. Remarks on Kluitenberg–Ciancio theory

In several previous paper [1–10] the connection between dielectric and magnetic relaxation phenomena and the occurrence of the macroscopic internal degrees of freedom were discussed.

Introducing a general assumption concerning the entropy it was shown that polarization $\boldsymbol{P}$ can be split in the form

$$\boldsymbol{P} = \boldsymbol{P}^{(0)} + \boldsymbol{P}^{(1)}, \tag{1.1}$$

where $\boldsymbol{P}^{(0)}$ is reversible part (*elastic*) and $\boldsymbol{P}^{(1)}$ irreversible part of $\boldsymbol{P}$, connected with dielectric after effects.

In the linear approximation and neglecting cross effects as, for instance, the influence of electric conduction, heat conduction and (mechanical) viscosity on electric relaxation, the following differential equation may be derived (see Ref. [3])

$$\chi_{(EP)}^{(0)}\boldsymbol{E} + \frac{\mathrm{d}\boldsymbol{E}}{\mathrm{d}t} = \chi_{(PE)}^{(0)}\boldsymbol{P} + \chi_{(PE)}^{(1)}\frac{\mathrm{d}\boldsymbol{P}}{\mathrm{d}t} + \chi_{(PE)}^{(2)}\frac{\mathrm{d}^2\boldsymbol{P}}{\mathrm{d}t^2}, \tag{1.2}$$

where $\boldsymbol{E}$ is the electric field and $\chi_{(EP)}^{(0)}$, $\chi_{(PE)}^{(i)}$ $(i = 0, 1, 2)$, are algebraic functions of the coefficients occurring in the phenomenological equations (describing the irreversible processes) and in the equations of state.

In Refs. [3,6] the following inequalities were derived:

$$\chi_{(EP)}^{(0)} \geqslant 0, \quad \chi_{(PE)}^{(i)} \geqslant 0 \quad (i = 0, 1, 2), \tag{1.3}$$

$$\chi_{(PE)}^{(1)} - \chi_{(EP)}^{(0)}\chi_{(PE)}^{(2)} \geqslant 0, \tag{1.4}$$

$$\chi_{(PE)}^{(1)}\chi_{(EP)}^{(0)} - \chi_{(PE)}^{(0)} \geqslant 0, \tag{1.5}$$

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which are connected with stability and with the non-negative character of the entropy production.

Using the Maxwell partial-derivative equations and the relaxation equation (1.2), in Ref. [6] it was shown that the inequalities (1.3)–(1.5) play an important role in the propagation of electromagnetic waves.

The goal of this work is to find a method to verify experimentally the inequalities (1.3)–(1.5) and to measure the phenomenological coefficients.

For this aim we have studied the behaviour of dielectric media, as PVC (PolyVinylChloride) and PMMA (PolyMethylMetaCrylateat), subject to a sinusoidal electric field at a constant temperature (100 °C for PVC and 90 °C for PMMA).

It has been possible to relate some experimentally measured quantities with the coefficients appearing in Eq. (1.2) and then to verify the validity of inequalities (1.3)–(1.5).

In Section 2, after a brief review of linear-response theory, we outline the experimental methods adopted to obtain the aforementioned results.

Section 3 is devoted to expressing the coefficients appearing in Eq. (1.2) in terms of the complex dielectric constant ε^* (the electric induction to which ε^* is connected, is the extensive-variable set as input by experimental conditions).

Finally, in Section 4, we plot the phenomenological coefficients appearing in Eq. (1.2) using the parameters measured on PVC and PMMA.

2. Complex dielectric constant

Schematically, a linear-response experiment is represented in Fig. 1.

It consists of 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

$$g(t) = f(t) \otimes h(t), \tag{2.1}$$

where $h(t)$ is the unknown quantity of the problem. An important result of this theory is that harmonic input

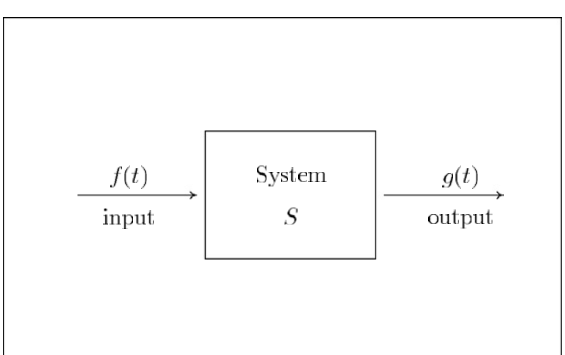

Fig. 1. Schematic response experiment.

$f(t) = Ae^{i\omega t}$ always corresponds to harmonic output of the same frequency but different phase and amplitude:

$$g(t) = B(\omega)e^{i[\omega t+\phi(\omega)]}. \tag{2.2}$$

Taking real and imaginary part, we have

$$A\cos(\omega t) \to B(\omega)\cos[\omega t + \phi(\omega)], \tag{2.3}$$

$$A\sin(\omega t) \to B(\omega)\sin[\omega t + \phi(\omega)]. \tag{2.4}$$

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.

$$D = D_0 \sin(\omega t), \tag{2.5}$$

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

$$E = E_0(\omega)\sin[\omega t + \phi(\omega)], \tag{2.6}$$

and so

$$E = D_0 s_1 \sin(\omega t) + D_0 s_2 \cos(\omega t), \tag{2.7}$$

where

$$s_1 = \frac{E_0(\omega)}{D_0}\cos\phi(\omega), \tag{2.8}$$

$$s_2 = \frac{E_0(\omega)}{D_0}\sin\phi(\omega). \tag{2.9}$$

The electric charge density on the plates is viewed as the cause determining the electric field inside capacitor (extensive variable). Consequently the effect can be identified with the normal component E (intensive variable). Such a viewpoint allows us to study dielectric relaxation phenomena.

Defining the *reciprocal complex dielectric constant*

$$s^* = \frac{E^*}{D^*} = s_1 + is_2, \tag{2.10}$$

with

$$E^* = E_0\, e^{i(\omega t+\phi(\omega))}, \tag{2.11}$$

$$D^* = D_0\, e^{i\omega t}, \tag{2.12}$$

the *complex dielectric constant* will be

$$\varepsilon^* = \frac{1}{s^*} = \varepsilon^* = \varepsilon' - i\varepsilon'', \tag{2.13}$$

where

$$\varepsilon' = \frac{s_1}{s_1^2 + s_2^2}, \quad \varepsilon'' = \frac{s_2}{s_1^2 + s_2^2}. \tag{2.14}$$