

# Hidden vectorial variables in the theory of dielectric relaxation

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**HIDDEN VECTORIAL VARIABLES  
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RELAXATION**

by

L. Restuccia

G.A. Kluitenberg



Reports on Applied and Numerical Analysis  
Department of Mathematics and Computing Science  
Eindhoven University of Technology  
P.O. Box 513  
5600 MB Eindhoven  
The Netherlands

For the compositor  
 $\underline{\psi} \underline{\phi}$  means  $\psi \phi$  in bold face

# HIDDEN VECTORIAL VARIABLES AS SPLITTING OPERATORS FOR THE POLARIZATION VECTOR IN THE THERMODYNAMIC THEORY OF DIELECTRIC RELAXATION<sup>(\*)</sup>

by

LILIANA RESTUCCIA

Dipartimento di Matematica

Università di Messina

Messina

Italia

and

GERRIT ALFRED KLUITENBERG

Department of Mathematics and Computing Science

Eindhoven University of Technology

Eindhoven

The Netherlands

## Synopsis

In some previous papers it has been shown that dielectric after-effects may be studied with the aid of thermodynamic vectorial internal variables. In this paper it is assumed that  $n$  "hidden" vectorial degrees of freedom  $\mathbf{Z}^{(k)}$ , which influence the polarization of the medium, give rise to dielectric relaxation phenomena and it is shown that with the aid of such vector fields the specific polarization vector  $\mathbf{p}$  may be split in  $n + 2$  parts:  $\mathbf{p}^{(0)}, \mathbf{p}^{(1)}, \dots, \mathbf{p}^{(n)}, \mathbf{p}^{(n+1)}$ .  $\mathbf{p}^{(0)}$  has the property that it vanishes for all values of  $\mathbf{p}^{(1)}, \mathbf{p}^{(2)}, \dots, \mathbf{p}^{(n)}$ , if the medium is in a state where the electric field and the mechanical stress tensor vanish and the temperature of the medium equals some reference temperature. The  $n$  specific polarization vectors  $\mathbf{p}^{(k)}$  may replace the  $n$  vectorial variables  $\mathbf{Z}^{(k)}$  ( $k=1, 2, \dots, n$ ) as internal degrees of freedom.  $\mathbf{p}^{(n+1)}$  is a constant vector. Furthermore, it is shown that the two expressions for the entropy production derived by using either the  $n$  variables  $\mathbf{Z}^{(k)}$  or the  $n$  variables  $\mathbf{p}^{(k)}$  are equivalent.

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## 1. Introduction

In some previous papers <sup>1-4</sup>), using non-equilibrium thermodynamics <sup>5-9</sup>), it is shown that dielectric after-effects may be investigated with the aid of thermodynamic vectorial internal variables. Some well-known equations for these relaxation phenomena may be obtained.

The internal variable may be either a "hidden" macroscopic vectorial parameter  $\mathbf{Z}$  (which influences the polarization) or a part of the specific polarization  $\mathbf{p}$ . In reference 2 it is shown that with the aid of a "hidden" vectorial internal variable  $\mathbf{Z}$ , the specific polarization vector  $\mathbf{p}$  may be split in two parts  $\mathbf{p}^{(0)}$  and  $\mathbf{p}^{(1)}$ , i.e.

$$\mathbf{p} = \mathbf{p}^{(0)} + \mathbf{p}^{(1)}. \quad (1.1)$$

$\mathbf{p}^{(0)}$  vanishes for all values of  $\mathbf{Z}$  if the medium is in thermodynamic states where the temperature  $T$  equals some reference temperature  $T_0$  and the mechanical stress tensor  $\tau_{\alpha\beta}$  and the electric field  $\mathbf{E}$  of Maxwell's equations vanish.  $\mathbf{p}^{(1)}$  only depends on  $\mathbf{Z}$  and may replace  $\mathbf{Z}$  as vectorial internal degree of freedom. Moreover,  $\mathbf{p}^{(0)}$  is proportional to  $\mathbf{E}$  and for this reason it is called reversible (or elastic) part of  $\mathbf{p}$ ,  $\mathbf{p}^{(1)}$  is the irreversible (or anelastic) part of  $\mathbf{p}$  because it is connected with dielectric after-effects and, in contradistinction to an arbitrary "hidden" vectorial degree of freedom, it is a measurable quantity.

The theory developed in <sup>2</sup>) becomes formally completely analogous to the Debye theory for dielectric relaxation phenomena in polar fluids (discussed also in reference 1) if one linearizes the equations of state and assumes that

$$\mathbf{p} = \mathbf{p}^{(def)} + \mathbf{p}^{(dip)}, \quad (1.2)$$

where  $\mathbf{p}^{(def)}$  is the polarization due to the deformation of the molecules proportional to the electric field  $\mathbf{E}$  and  $\mathbf{p}^{(dip)}$  is the polarization due to the orientation of the permanent dipoles of the molecules which may be considered as internal degree of freedom.

In reference 3 a generalization of the theory formulated in reference 2 is given noting that in principle all changes in the polarization are irreversible phenomena (see also reference 10) and it is shown that if there is a hidden vector field  $\mathbf{Z}$  which is a thermodynamic variable and which influences the polarization, one can split the polarization vector  $\mathbf{p}$  in two parts  $\mathbf{p}^{(0)}$  and  $\mathbf{p}^{(1)}$  which are both irreversible.

In the present paper we assume that several microscopic phenomena give rise to dielectric relaxation (see also reference 4) and that it is possible to give a complete description of the thermodynamic state of the medium by introducing in the expression for the entropy  $n$  "hidden" polar vectorial internal variables  $\mathbf{Z}^{(k)}$  ( $k = 1, 2, \dots, n$ ).

In Section I (by applying a procedure discussed in reference 11 in the case that  $n$  "hidden" tensorial internal variables are connected with mechanical relaxation phenomena) it is seen that with

the aid of such hidden vectorial variables  $\mathbf{Z}^{(k)}$  it is possible to split the specific polarization vector  $\mathbf{p}$  in  $n + 2$  parts  $\mathbf{p}^{(k)}$  ( $k=0,1,2, \dots, n, n+1$ ).  $\mathbf{p}^{(0)}$  vanishes for all values of  $\mathbf{p}^{(1)}, \mathbf{p}^{(2)}, \dots, \mathbf{p}^{(n)}$  if the medium is in thermodynamic states where the temperature  $T$  equals some reference temperature  $T_0$  and the mechanical stress tensor  $\tau_{\alpha\beta}$  and the electric field  $\mathbf{E}$  vanish. While the  $n$  specific polarization vectors  $\mathbf{p}^{(k)}$  are certain functions of  $\mathbf{Z}^{(k)}, \mathbf{Z}^{(k+1)}, \dots, \mathbf{Z}^{(n)}$  ( $k=1,2, \dots, n$ ) and may replace the  $n$  variables  $\mathbf{Z}^{(k)}$  as internal degrees of freedom in the expression for the entropy and one obtains two equivalent descriptions which are related by vector-valued transformations with their inverse.  $\mathbf{p}^{(n+1)}$  is a constant vector describing a possible residual polarization.

In Section 2 the balance equation for the entropy is obtained and it is shown that the two forms for the entropy production, derived by using either the  $n$  variables  $\mathbf{Z}^{(k)}$  or the  $n$  variables  $\mathbf{p}^{(k)}$  are equivalent.

Finally, it is seen that if the electric field  $\mathbf{E}$  of Maxwell's equations equals the equilibrium-electric field  $\mathbf{E}^{(eq)}$ ,  $\mathbf{p}^{(0)}$  becomes the reversible part of the polarization  $\mathbf{p}$ . On the other hand, if  $\mathbf{p} = \mathbf{p}^{(0)}$  (i.e. there are no internal degrees of freedom) one obtains the De Groot-Mazur theory.

## 2. Transformation of internal vectorial variables

We consider a polarizable medium in which several microscopic phenomena occur which give rise to dielectric after-effects. We assume that the thermodynamic state of the medium may be described by the density of the internal energy  $u$ , the strain tensor  $\varepsilon_{\alpha\beta}$ , the specific total polarization vector  $\mathbf{p}$  and  $n$  "hidden" polar macroscopic vectorial variables  $\mathbf{Z}^{(k)}$  ( $k=1,2,\dots,n$ ) of which we do not specify the physical nature and which influence the dielectric properties of the medium. Hence, the entropy  $s$  is given by

$$s = s(u, \varepsilon_{\alpha\beta}, \mathbf{p}, \mathbf{Z}^{(1)}, \mathbf{Z}^{(2)}, \dots, \mathbf{Z}^{(n)}). \quad (2.1)$$

We shall define the temperature  $T$ , the tensor field  $\tau_{\alpha\beta}^{(eq)}$ , the vector fields  $\mathbf{E}^{(eq)}$  and  $\mathbf{G}^{(k)}$  ( $k=1,2,\dots,n$ ) by

$$T^{-1} = \frac{\partial}{\partial u} s(u, \varepsilon_{\alpha\beta}, \mathbf{p}, \mathbf{Z}^{(1)}, \mathbf{Z}^{(2)}, \dots, \mathbf{Z}^{(n)}), \quad (2.2)$$

$$\tau_{\alpha\beta}^{(eq)} = -\rho T \frac{\partial}{\partial \varepsilon_{\alpha\beta}} s(u, \varepsilon_{\alpha\beta}, \mathbf{p}, \mathbf{Z}^{(1)}, \mathbf{Z}^{(2)}, \dots, \mathbf{Z}^{(n)}), \quad (2.3)$$

$$\mathbf{E}^{(eq)} = -T \frac{\partial}{\partial \mathbf{p}} s(u, \varepsilon_{\alpha\beta}, \mathbf{p}, \mathbf{Z}^{(1)}, \mathbf{Z}^{(2)}, \dots, \mathbf{Z}^{(n)}) \quad (2.4)$$

and

$$\mathbf{G}^{(k)} = T \frac{\partial}{\partial \mathbf{Z}^{(k)}} s(u, \varepsilon_{\alpha\beta}, \mathbf{p}, \mathbf{Z}^{(1)}, \mathbf{Z}^{(2)}, \dots, \mathbf{Z}^{(n)}) \quad (k=1,2,\dots,n). \quad (2.5)$$

From (2.1) one obtains for the differential of  $s$

$$Tds = du - v \sum_{\alpha,\beta=1}^3 \tau_{\alpha\beta}^{(eq)} d\varepsilon_{\alpha\beta} - \mathbf{E}^{(eq)} \cdot d\mathbf{p} + \sum_{k=1}^n \mathbf{G}^{(k)} \cdot d\mathbf{Z}^{(k)}. \quad (2.6)$$

In (2.6) we have used (2.2) - (2.5) and the following definition

$$\rho = v^{-1}, \quad (2.7)$$

where  $\rho$  is the mass density and  $v$  is the specific volume (volume per unit of mass).

An expression of the type (2.6) for  $ds$  is called Gibbs relation.

Equation (2.2) is the usual relation between temperature and entropy. It is seen from (2.3), (2.4) and (2.6) that  $\tau_{\alpha\beta}^{(eq)}$  and  $\mathbf{E}^{(eq)}$  have the dimensions of the mechanical stress tensor and the electric field, respectively. We shall call  $\tau_{\alpha\beta}^{(eq)}$  the equilibrium-stress tensor and  $\mathbf{E}^{(eq)}$  the equilibrium-electric field. In (2.5) the vectors  $\mathbf{G}^{(k)}$  are the vectorial thermodynamic affinities conjugate to the internal degrees of freedom  $\mathbf{Z}^{(k)}$  ( $k=1,2,\dots,n$ ). If we neglect the term  $\sum_{k=1}^n \mathbf{G}^{(k)} \cdot d\mathbf{Z}^{(k)}$  in (2.6) we obtain De Groot-Mazur theory.

We shall define the specific thermodynamic potential  $g$  by

$$g = u - Ts - v \sum_{\alpha, \beta=1}^3 \tau_{\alpha\beta}^{(eq)} \epsilon_{\alpha\beta} - \mathbf{E}^{(eq)} \cdot \mathbf{p}. \quad (2.8)$$

By virtue of (2.6), we obtain from (2.8)

$$dg = -sdT - \sum_{\alpha, \beta=1}^3 \epsilon_{\alpha\beta} d(v \tau_{\alpha\beta}^{(eq)}) - \mathbf{p} \cdot d\mathbf{E}^{(eq)} - \sum_{k=1}^n \mathbf{G}^{(k)} \cdot d\mathbf{Z}^{(k)}. \quad (2.9)$$

Hence,

$$g = g(T, v \tau_{\alpha\beta}^{(eq)}, \mathbf{E}^{(eq)}, \mathbf{Z}^{(1)}, \mathbf{Z}^{(2)}, \dots, \mathbf{Z}^{(n)}) \quad (2.10)$$

and

$$\mathbf{p} = - \frac{\partial}{\partial \mathbf{E}^{(eq)}} g(T, v \tau_{\alpha\beta}^{(eq)}, \mathbf{E}^{(eq)}, \mathbf{Z}^{(1)}, \mathbf{Z}^{(2)}, \dots, \mathbf{Z}^{(n)}). \quad (2.11)$$

It follows that there is a vector-valued function  $\underline{\phi}$  of the variables  $T, v \tau_{\alpha\beta}^{(eq)}, \mathbf{E}^{(eq)}$  and  $\mathbf{Z}^{(k)}$  ( $n=1, 2, \dots, n$ ) such that

$$\mathbf{p} = \underline{\phi}(T, v \tau_{\alpha\beta}^{(eq)}, \mathbf{E}^{(eq)}, \mathbf{Z}^{(1)}, \mathbf{Z}^{(2)}, \dots, \mathbf{Z}^{(n)}). \quad (2.12)$$

We introduce arbitrary (but fixed) values for the temperature and for the specific volume  $v$  (for instance the temperature  $T_0$  and the specific volume  $v_0$  in the reference state) and we suppose that in this reference state

$$\tau_{0\alpha\beta}^{(eq)} = 0, \quad \mathbf{E}_0^{(eq)} = 0 \quad (2.13)$$

and we indicate by  $\mathbf{Z}_0^{(k)}$  arbitrary (but fixed) values for the vectors  $\mathbf{Z}^{(k)}$  ( $k=1, 2, \dots, n$ ).

Next, we define the polar vectors  $\mathbf{p}^{(0)}, \mathbf{p}^{(1)}, \dots, \mathbf{p}^{(n)}, \mathbf{p}^{(n+1)}$  by

$$\begin{aligned} \mathbf{p}^{(0)} &= \underline{\phi}(T, v \tau_{\alpha\beta}^{(eq)}, \mathbf{E}^{(eq)}, \mathbf{Z}^{(1)}, \mathbf{Z}^{(2)}, \dots, \mathbf{Z}^{(n)}) - \\ &\quad - \underline{\phi}(T_0, v_0 \tau_{0\alpha\beta}^{(eq)}, \mathbf{E}_0^{(eq)}, \mathbf{Z}_0^{(1)}, \mathbf{Z}_0^{(2)}, \dots, \mathbf{Z}_0^{(n)}), \end{aligned} \quad (2.14)$$

$$\begin{aligned} \mathbf{p}^{(1)} &= \underline{\phi}(T_0, v_0 \tau_{0\alpha\beta}^{(eq)}, \mathbf{E}_0^{(eq)}, \mathbf{Z}_0^{(1)}, \mathbf{Z}_0^{(2)}, \dots, \mathbf{Z}_0^{(n)}) - \\ &\quad - \underline{\phi}(T_0, v_0 \tau_{0\alpha\beta}^{(eq)}, \mathbf{E}_0^{(eq)}, \mathbf{Z}_0^{(1)}, \mathbf{Z}_0^{(2)}, \dots, \mathbf{Z}_0^{(n)}), \end{aligned} \quad (2.15)$$

$$\begin{aligned} \mathbf{p}^{(k)} &= \underline{\phi}(T_0, v_0 \tau_{0\alpha\beta}^{(eq)}, \mathbf{E}_0^{(eq)}, \mathbf{Z}_0^{(1)}, \dots, \mathbf{Z}_0^{(k-1)}, \mathbf{Z}_0^{(k)}, \mathbf{Z}_0^{(k+1)}, \dots, \mathbf{Z}_0^{(n)}) - \\ &\quad - \underline{\phi}(T_0, v_0 \tau_{0\alpha\beta}^{(eq)}, \mathbf{E}_0^{(eq)}, \mathbf{Z}_0^{(1)}, \dots, \mathbf{Z}_0^{(k-1)}, \mathbf{Z}_0^{(k)}, \mathbf{Z}_0^{(k+1)}, \dots, \mathbf{Z}_0^{(n)}) \\ &\quad, \quad (k=2, \dots, n-1) \end{aligned} \quad (2.16)$$

$$\begin{aligned} \mathbf{p}^{(n)} &= \underline{\phi}(T_0, v_0 \tau_{0\alpha\beta}^{(eq)}, \mathbf{E}_0^{(eq)}, \mathbf{Z}_0^{(1)}, \dots, \mathbf{Z}_0^{(n-1)}, \mathbf{Z}_0^{(n)}) - \\ &\quad - \underline{\phi}(T_0, v_0 \tau_{0\alpha\beta}^{(eq)}, \mathbf{E}_0^{(eq)}, \mathbf{Z}_0^{(1)}, \dots, \mathbf{Z}_0^{(n-1)}, \mathbf{Z}_0^{(n)}), \end{aligned} \quad (2.17)$$

$$\mathbf{p}^{(n+1)} = \underline{\phi}(T_0, \nu_0, \tau_{\alpha\beta}^{(eq)}, \mathbf{E}_0^{(eq)}, \mathbf{Z}_0^{(1)}, \dots, \mathbf{Z}_0^{(n-1)}, \mathbf{Z}_0^{(n)}). \quad (2.18)$$

In (2.18)  $\mathbf{p}^{(n+1)}$  is a constant vector describing a possible residual polarization. In general  $\mathbf{p}^{(n+1)} = 0$ .

From definitions (2.12) and (2.14) - (2.18) we obtain

$$\mathbf{p} = \mathbf{p}^{(0)} + \mathbf{p}^{(1)} + \dots + \mathbf{p}^{(n)} + \mathbf{p}^{(n+1)}. \quad (2.19)$$

Because of (2.19) the polar vectorial variables  $\mathbf{p}^{(k)}$  ( $k=0,1,\dots,n,n+1$ ) are called partial specific polarizations. They have the following properties

$$\mathbf{p}^{(0)} = 0 \text{ for all values of } \mathbf{Z}^{(1)}, \mathbf{Z}^{(2)}, \dots, \mathbf{Z}^{(n)} \text{ if } T = T_0, \tau_{\alpha\beta}^{(eq)} = 0, \mathbf{E}^{(eq)} = 0, \quad (2.20)$$

$$\mathbf{p}^{(k)} = 0 \text{ for all values of } \mathbf{Z}^{(k+1)}, \dots, \mathbf{Z}^{(n)} \text{ if } \mathbf{Z}^{(k)} = \mathbf{Z}_0^{(k)} \text{ (} k=1,2,\dots,n-1 \text{)} \quad (2.21)$$

$$\mathbf{p}^{(n)} \text{ is a function only of } \mathbf{Z}^{(n)}, \mathbf{p}^{(n)} = 0 \text{ if } \mathbf{Z}^{(n)} = \mathbf{Z}_0^{(n)}. \quad (2.22)$$

However, in the following we suppose that

$$\mathbf{p}^{(n+1)} = 0. \quad (2.23)$$

Thus, it is seen that with the aid of  $n$  polar hidden vectorial variables the specific polarization  $\mathbf{p}$  may be split in  $n+2$  parts  $\mathbf{p}^{(0)}, \mathbf{p}^{(1)}, \dots, \mathbf{p}^{(n)}, \mathbf{p}^{(n+1)}$  which satisfy equations (2.20) - (2.23).

It is also important to note that from (2.14) - (2.17) it follows that there exist functions  $\underline{\phi}^{(0)}$  and  $\underline{\phi}^{(k)}$  such that

$$\begin{aligned} \mathbf{p}^{(0)} &= \underline{\phi}^{(0)}(T, \nu, \tau_{\alpha\beta}, \mathbf{E}^{(eq)}, \mathbf{Z}^{(1)}, \mathbf{Z}^{(2)}, \dots, \mathbf{Z}^{(n)}), \\ \mathbf{p}^{(k)} &= \underline{\phi}^{(k)}(\mathbf{Z}^{(k)}, \mathbf{Z}^{(k+1)}, \dots, \mathbf{Z}^{(n)}) \text{ (} k=1,2,\dots,n \text{)}. \end{aligned} \quad (2.24)$$

We shall suppose that the functions  $\underline{\phi}^{(k)}$  and the range of the values of  $\mathbf{Z}^{(k)}, \mathbf{Z}^{(k+1)}, \dots, \mathbf{Z}^{(n)}$  ( $k=1,2,\dots,n$ ), which are of physical interest are such that the inverse function theorem may be applied to  $\underline{\phi}^{(k)}$ . A detailed mathematical discussion of the inverse function theorem is given, for instance, in reference 12 (p. 144-146).

Hence, we assume that the functions  $\underline{\phi}^{(k)}$  have inverse functions  $\underline{\psi}^{(k)}$  such that

$$\mathbf{Z}^{(k)} = \underline{\psi}^{(k)}(\mathbf{p}^{(k)}, \mathbf{p}^{(k+1)}, \dots, \mathbf{p}^{(n)}) \text{ (} k=1,2,\dots,n \text{)}. \quad (2.25)$$

We shall use the notations

$$A_{\alpha\beta}^{(k,j)} = \frac{\partial \phi_{\alpha}^{(k)}}{\partial Z_{\beta}^{(j)}} \text{ (} k,j=1,2,\dots,n; \alpha,\beta=1,2,3 \text{)} \quad (2.26)$$

and



$$[A_{\alpha\beta}^{(k,j)}]^{-1} = \frac{\partial \psi_{\alpha}^{(k)}}{\partial p_{\beta}^{(j)}} \quad (k, j = 1, 2, \dots, n; \alpha, \beta = 1, 2, 3). \quad (2.27)$$

From (2.25) - (2.27) we obtain

$$\sum_{j=1}^n \sum_{\gamma=1}^3 A_{\alpha\gamma}^{(k,j)} [A_{\gamma\beta}^{(j,l)}]^{-1} = \sum_{j=1}^n \sum_{\gamma=1}^3 [A_{\alpha\gamma}^{(k,j)}]^{-1} A_{\gamma\beta}^{(j,l)} = \delta_{\alpha\beta}^{(k,l)},$$

$$(k, l = 1, 2, \dots, n; \alpha, \beta = 1, 2, 3) \quad (2.28)$$

where the operator  $\delta_{\alpha\beta}^{(k,l)} = \delta_{\alpha\beta} \delta_{kl}$ .

Moreover, from (2.25) - (2.27) it follows that

$$A_{\alpha\beta}^{(k,j)} = A_{\alpha\beta}^{(k,j)} (\mathbf{Z}^{(1)}, \mathbf{Z}^{(2)}, \dots, \mathbf{Z}^{(n)}) = A_{\alpha\beta}^{(k,j)} (\mathbf{p}^{(1)}, \mathbf{p}^{(2)}, \dots, \mathbf{p}^{(n)}), \quad (2.29)$$

$$[A_{\alpha\beta}^{(k,j)}]^{-1} = [A_{\alpha\beta}^{(k,j)}]^{-1} (\mathbf{p}^{(1)}, \mathbf{p}^{(2)}, \dots, \mathbf{p}^{(n)}) = [A_{\alpha\beta}^{(k,j)}]^{-1} (\mathbf{Z}^{(1)}, \mathbf{Z}^{(2)}, \dots, \mathbf{Z}^{(n)}), \quad (2.30)$$

and that

$$A_{\alpha\beta}^{(k,j)} = 0, \quad [A_{\alpha\beta}^{(k,j)}]^{-1} = 0 \quad \text{if } j < k. \quad (2.31)$$

By virtue of (2.25) one has from (2.1)

$$s = s(u, \varepsilon_{\alpha\beta}, \mathbf{p}, \mathbf{p}^{(1)}, \mathbf{p}^{(2)}, \dots, \mathbf{p}^{(n)}) \quad (2.32)$$

and equation (2.20) may be written in the form

$$\mathbf{p}^{(0)} = 0 \quad \text{for all values of } \mathbf{p}^{(1)}, \mathbf{p}^{(2)}, \dots, \mathbf{p}^{(n)} \quad \text{if } T = T_0, \tau_{\alpha\beta}^{(eq)} = 0, \mathbf{E}^{(eq)} = 0. \quad (2.33)$$

From (2.2) and (2.25) one has for the temperature

$$T^{-1} = \frac{\partial}{\partial u} s(u, \varepsilon_{\alpha\beta}, \mathbf{p}, \mathbf{p}^{(1)}, \dots, \mathbf{p}^{(n)}). \quad (2.34)$$

In an analogous way, using (2.3) - (2.5) and (2.25),  $\tau_{\alpha\beta}^{(eq)}$  and the polar vector fields  $\mathbf{E}^{(eq)}$  and  $\mathbf{E}^{(k)}$  are defined by

$$\tau_{\alpha\beta}^{(eq)} = -\rho T \frac{\partial}{\partial \varepsilon_{\alpha\beta}} s(u, \varepsilon_{\alpha\beta}, \mathbf{p}, \mathbf{p}^{(1)}, \mathbf{p}^{(2)}, \dots, \mathbf{p}^{(n)}), \quad (2.35)$$

$$\mathbf{E}^{(eq)} = -T \frac{\partial}{\partial \mathbf{p}} s(u, \varepsilon_{\alpha\beta}, \mathbf{p}, \mathbf{p}^{(1)}, \mathbf{p}^{(2)}, \dots, \mathbf{p}^{(n)}), \quad (2.36)$$

$$\mathbf{E}^{(k)} = T \frac{\partial}{\partial \mathbf{p}^{(k)}} s(u, \varepsilon_{\alpha\beta}, \mathbf{p}, \mathbf{p}^{(1)}, \mathbf{p}^{(2)}, \dots, \mathbf{p}^{(n)}), \quad (k = 1, 2, \dots, n). \quad (2.37)$$

From (2.32) and the preceding relations one gets

$$Tds = du - v \sum_{\alpha, \beta=1}^3 \tau_{\alpha\beta}^{(eq)} d\varepsilon_{\alpha\beta} - \mathbf{E}^{(eq)} \cdot d\mathbf{p} + \sum_{k=1}^n \mathbf{E}^{(k)} \cdot d\mathbf{p}^{(k)}. \quad (2.38)$$

By virtue of (2.19) and (2.23), expression (2.32) for the entropy can be written as follows

$$s = s(u, \varepsilon_{\alpha\beta}, \mathbf{p}^{(0)}, \mathbf{p}^{(1)}, \dots, \mathbf{p}^{(n)}). \quad (2.39)$$

Hence, one may also write equation (2.38) in the form

$$Tds = du - \nu \sum_{\alpha,\beta=1}^3 \tau_{\alpha\beta}^{(eq)} d\varepsilon_{\alpha\beta} - \mathbf{E}^{(eq)} \cdot d\mathbf{p}^{(0)} + \sum_{k=1}^n \mathbf{E}_{(ir)}^{(k)} \cdot d\mathbf{p}^{(k)}, \quad (2.40)$$

where the polar vector fields  $\mathbf{E}_{(ir)}^{(k)}$  are defined by

$$\mathbf{E}_{(ir)}^{(k)} = \mathbf{E}^{(k)} - \mathbf{E}^{(eq)} \quad (k=1,2,\dots,n). \quad (2.41)$$

Now, by virtue of (2.39) and (2.40), we have

$$T^{-1} = \frac{\partial}{\partial u} s(u, \varepsilon_{\alpha\beta}, \mathbf{p}^{(0)}, \mathbf{p}^{(1)}, \dots, \mathbf{p}^{(n)}), \quad (2.42)$$

$$\tau_{\alpha\beta}^{(eq)} = -\rho T \frac{\partial}{\partial \varepsilon_{\alpha\beta}} s(u, \varepsilon_{\alpha\beta}, \mathbf{p}^{(0)}, \mathbf{p}^{(1)}, \dots, \mathbf{p}^{(n)}), \quad (2.43)$$

$$\mathbf{E}^{(eq)} = -T \frac{\partial}{\partial \mathbf{p}^{(0)}} s(u, \varepsilon_{\alpha\beta}, \mathbf{p}^{(0)}, \mathbf{p}^{(1)}, \dots, \mathbf{p}^{(n)}), \quad (2.44)$$

$$\mathbf{E}_{(ir)}^{(k)} = T \frac{\partial}{\partial \mathbf{p}^{(k)}} s(u, \varepsilon_{\alpha\beta}, \mathbf{p}^{(0)}, \mathbf{p}^{(1)}, \dots, \mathbf{p}^{(n)}) \quad (k=1,2,\dots,n). \quad (2.45)$$

From (2.37) and (2.5) one obtains with the aid of (2.25) and (2.27)

$$E_{\alpha}^{(k)} = \sum_{j=1}^n \sum_{\beta=1}^3 G_{\beta}^{(j)} [A_{\beta\alpha}^{(j,k)}]^{-1} \quad (k=1,2,\dots,n; \alpha,\beta=1,2,3). \quad (2.46)$$

Equations (2.46) by virtue of (2.31) become

$$E_{\alpha}^{(k)} = \sum_{j=1}^k \sum_{\beta=1}^3 G_{\beta}^{(j)} [A_{\beta\alpha}^{(j,k)}]^{-1}. \quad (2.47)$$

Using (2.28) one obtains from (2.46)

$$G_{\alpha}^{(k)} = \sum_{j=1}^n \sum_{\beta=1}^3 E_{\beta}^{(j)} A_{\beta\alpha}^{(j,k)} \quad (k=1,2,\dots,n; \alpha,\beta=1,2,3), \quad (2.48)$$

which with the aid of (2.31) become

$$G_{\alpha}^{(k)} = \sum_{j=1}^k \sum_{\beta=1}^3 E_{\beta}^{(j)} A_{\beta\alpha}^{(j,k)}. \quad (2.49)$$

It is obvious that the procedure which leads to equations (2.19) and (2.32) is not unique. For instance, it is seen from (2.14) - (2.17) that  $\mathbf{p}^{(0)}, \mathbf{p}^{(1)}, \dots, \mathbf{p}^{(n)}, \mathbf{p}^{(n+1)}$  depend on the choice of the reference temperature and on the choice of the values for the mechanical stress  $\tau_{\alpha\beta}^{(eq)}$  and the field  $\mathbf{E}_{\beta}^{(eq)}$ . Therefore, instead of the values zero (see (2.13)) one may choose different (but fixed) values. Moreover, it is possible to consider  $\mathbf{p}$  as a function of  $T, \varepsilon_{\alpha\beta}, \mathbf{E}^{(eq)}, \mathbf{Z}^{(1)}, \mathbf{Z}^{(2)}, \dots, \mathbf{Z}^{(n)}$  and to find a function, say  $\phi^*$ , so that  $\mathbf{p} = \phi^*(T, \varepsilon_{\alpha\beta}, \mathbf{E}^{(eq)}, \mathbf{Z}^{(1)}, \mathbf{Z}^{(2)}, \dots, \mathbf{Z}^{(n)})$  and, by the same procedure previously used, to obtain analogous equations to (2.14) - (2.17). However, in order to

find (2.14) - (2.17) (or analogous equations), it is essential that the  $n$  "hidden" vectorial variables  $\mathbf{Z}^{(k)}$  influence the dielectric properties of the medium. This means that in (2.10) the function  $g$  must depend not only on  $T$ ,  $\nu \tau_{\alpha\beta}^{(eq)}$  and  $\mathbf{E}^{(eq)}$  but also  $\mathbf{Z}^{(k)}$  ( $k=1,2,\dots,n$ ), i.e. it is not possible that  $g$  is the sum of two functions  $g^{(1)}$  and  $g^{(2)}$ , where  $g^{(1)}$  depends only on  $T$ ,  $\nu \tau_{\alpha\beta}^{(eq)}$ ,  $\mathbf{E}^{(eq)}$  and  $g^{(2)}$  depends only on  $T$ ,  $\nu \tau_{\alpha\beta}^{(eq)}$  and  $\mathbf{Z}^{(k)}$ .

### 3. Entropy balance

The first law of thermodynamics for a polarizable medium in an electromagnetic field reads

$$\rho \frac{du}{dt} = -\text{div } \mathbf{J}^{(q)} + \sum_{\alpha, \beta=1}^3 \tau_{\alpha\beta} \frac{d\varepsilon_{\alpha\beta}}{dt} + \mathbf{j}^{(el)} \cdot \mathbf{E} + \rho \mathbf{E} \cdot \frac{d\mathbf{p}}{dt}. \quad (3.1)$$

In this equation  $\mathbf{J}^{(q)}$  and  $\mathbf{j}^{(el)}$  are the vectors of the density of the heat flow and of the electric current respectively,  $\rho^{(el)}$  is the electric charge density,  $\tau_{\alpha\beta}$  is the mechanical stress tensor which occurs in the equations of motion,  $\mathbf{E}$  is the electric field of Maxwell's equations and  $\frac{d\varepsilon_{\alpha\beta}}{dt}$ , in the case of deformations and rotations of the medium which are small from a kinematical point of view, is defined, in a first approximation, by

$$\frac{d\varepsilon_{\alpha\beta}}{dt} = \frac{1}{2} \left[ \frac{\partial v_\alpha}{\partial x_\beta} + \frac{\partial v_\beta}{\partial x_\alpha} \right] \quad (\alpha, \beta = 1, 2, 3). \quad (3.2)$$

In (3.2)  $\frac{d}{dt}$  is the substantial derivative with respect to time defined by

$$\frac{d}{dt} = \frac{\partial}{\partial t} + \sum_{\gamma=1}^3 v_\gamma \frac{\partial}{\partial x_\gamma}, \quad (3.3)$$

where  $v_\gamma$  is the  $\gamma$ -component of the velocity field  $\mathbf{v}$  of the medium and  $x_\gamma$  is the  $\gamma$ -component of the position vector  $\mathbf{x}$  ( $\gamma = 1, 2, 3$ ). We use an orthogonal Cartesian frame which is fixed in space.

It follows from (2.6), (2.38) and (2.40) that the Gibbs relation may be written in the forms

$$T \frac{ds}{dt} = \frac{du}{dt} - v \sum_{\alpha, \beta=1}^3 \tau_{\alpha\beta}^{(eq)} \frac{d\varepsilon_{\alpha\beta}}{dt} - \mathbf{E}^{(eq)} \cdot \frac{d\mathbf{p}}{dt} + \sum_{k=1}^n \mathbf{G}^{(k)} \cdot \frac{d\mathbf{Z}^{(k)}}{dt}, \quad (3.4)$$

$$T \frac{ds}{dt} = \frac{du}{dt} - v \sum_{\alpha, \beta=1}^3 \tau_{\alpha\beta}^{(eq)} \frac{d\varepsilon_{\alpha\beta}}{dt} - \mathbf{E}^{(eq)} \cdot \frac{d\mathbf{p}}{dt} + \sum_{k=1}^n \mathbf{E}^{(k)} \cdot \frac{d\mathbf{p}^{(k)}}{dt}, \quad (3.5)$$

$$T \frac{ds}{dt} = \frac{du}{dt} - v \sum_{\alpha, \beta=1}^3 \tau_{\alpha\beta}^{(eq)} \frac{d\varepsilon_{\alpha\beta}}{dt} - \mathbf{E}^{(eq)} \cdot \frac{d\mathbf{p}^{(0)}}{dt} + \sum_{k=1}^n \mathbf{E}_{(ir)}^{(k)} \cdot \frac{d\mathbf{p}^{(k)}}{dt}. \quad (3.6)$$

By eliminating  $\frac{du}{dt}$  from (3.1) and (3.4) one gets the balance equation for the entropy

$$\rho \frac{ds}{dt} = -\text{div } \frac{\mathbf{J}^{(q)}}{T} + \sigma^{(s)}, \quad (3.7)$$

where  $\sigma^{(s)}$  is the entropy production per unit of mass and per unit of time, given by

$$\sigma^{(s)} = T^{-1} (-T^{-1} \mathbf{J}^{(q)} \cdot \text{grad } T + \sum_{\alpha, \beta=1}^3 \tau_{\alpha\beta}^{(vi)} \frac{d\varepsilon_{\alpha\beta}}{dt} +$$

$$+ \mathbf{j}^{(el)} \cdot \mathbf{E} + \rho \mathbf{E}^{(ir)} \cdot \frac{d\mathbf{p}}{dt} + \rho \sum_{k=1}^n \mathbf{G}^{(k)} \cdot \frac{d\mathbf{Z}^{(k)}}{dt}. \quad (3.8)$$

In (3.8) we have utilized equation (2.7) and we have used the notations

$$\tau_{\alpha\beta}^{(vi)} = \tau_{\alpha\beta} - \tau_{\alpha\beta}^{(eq)}, \quad (3.9)$$

$$\mathbf{E}^{(ir)} = \mathbf{E} - \mathbf{E}^{(eq)}. \quad (3.10)$$

In (3.8)  $T^{-1} \mathbf{J}^{(q)}$  is the entropy flow and the entropy source strength  $\sigma^{(s)}$  is postulated a non negative quantity,  $\sigma^{(s)}$  must be zero if the thermodynamic equilibrium conditions are satisfied for the system. From (3.8) it is seen that the entropy production is additively composed of five different contributions. The term containing the viscous stress tensor  $\tau_{\alpha\beta}^{(vi)}$  represents the entropy production due to mechanical flow-phenomena, the terms with  $\mathbf{J}^{(q)}$  and  $\mathbf{j}^{(el)}$  give the contributions to the entropy production due to the heat flow and the electric current, respectively and finally the terms with  $\frac{d\mathbf{p}}{dt}$  and  $\frac{d\mathbf{Z}^{(k)}}{dt}$  ( $k=1,2,\dots,n$ ) are connected with irreversible dielectric relaxation phenomena. From (2.25) and (2.27) one finds

$$\frac{dZ_{\alpha}^{(k)}}{dt} = \sum_{j=1}^n \sum_{\beta=1}^3 [A_{\alpha\beta}^{(k,j)}]^{-1} \frac{dp_{\beta}^{(j)}}{dt} \quad (k=1,2,\dots,n). \quad (3.11)$$

By virtue of (2.31) equation (3.11) can be written in the form

$$\frac{dZ_{\alpha}^{(k)}}{dt} = \sum_{j=k}^n \sum_{\beta=1}^3 [A_{\alpha\beta}^{(k,j)}]^{-1} \frac{dp_{\beta}^{(j)}}{dt}. \quad (3.12)$$

Using (2.28), one obtains from (3.11)

$$\frac{dp_{\alpha}^{(k)}}{dt} = \sum_{j=1}^n \sum_{\beta=1}^3 A_{\alpha\beta}^{(k,j)} \frac{dZ_{\beta}^{(j)}}{dt}, \quad (k=1,2,\dots,n). \quad (3.13)$$

Because of (2.31) the preceding relation may be written in the form

$$\frac{dp_{\alpha}^{(k)}}{dt} = \sum_{j=k}^n \sum_{\beta=1}^3 A_{\alpha\beta}^{(k,j)} \frac{dZ_{\beta}^{(j)}}{dt}. \quad (3.14)$$

Equations (3.13) may also be derived from (2.24) and (2.26).

From (2.48), (3.11) and (2.28) one obtains

$$\sum_{k=1}^n \sum_{\alpha=1}^3 G_{\alpha}^{(k)} \frac{dZ_{\alpha}^{(k)}}{dt} = \sum_{k=1}^n \sum_{\alpha=1}^3 E_{\alpha}^{(k)} \frac{dp_{\alpha}^{(k)}}{dt}. \quad (3.15)$$

With the aid of this relation one may write expression (3.8) for the entropy production in the form

$$\begin{aligned} \sigma^{(s)} = T^{-1} (-T^{-1} \mathbf{J}^{(q)} \cdot \text{grad } T + \sum_{\alpha, \beta=1}^3 \tau_{\alpha\beta}^{(vi)} \frac{d\varepsilon_{\alpha\beta}}{dt} + \mathbf{j}^{(el)} \cdot \mathbf{E} + \\ + \rho \mathbf{E}^{(ir)} \cdot \frac{d\mathbf{p}}{dt} + \rho \sum_{k=1}^n \mathbf{E}^{(k)} \cdot \frac{d\mathbf{p}^{(k)}}{dt}). \end{aligned} \quad (3.16)$$

Finally, if equation (2.19) and (2.23) is used, equation (3.16) becomes

$$\begin{aligned} \sigma^{(s)} = T^{-1} \{-T^{-1} \mathbf{J}^{(q)} \cdot \text{grad } T + \sum_{\alpha, \beta=1}^3 \tau_{\alpha\beta}^{(vi)} \frac{d\varepsilon_{\alpha\beta}}{dt} + \mathbf{j}^{(el)} \cdot \mathbf{E} + \\ + \rho \mathbf{E}^{(ir)} \cdot \frac{d\mathbf{p}^{(0)}}{dt} + \rho \sum_{k=1}^n (\mathbf{E}^{(k)} + \mathbf{E}^{(ir)}) \cdot \frac{d\mathbf{p}^{(k)}}{dt}\}. \end{aligned} \quad (3.17)$$

From (3.17) it follows that if the electric field  $\mathbf{E}$  of Maxwell's equations equals the equilibrium-electric field  $\mathbf{E}^{(eq)}$ ,  $\mathbf{E}^{(ir)}$  vanishes (see equation (3.10)),  $\mathbf{p}^{(0)}$  becomes the reversible part of the polarization vector  $\mathbf{p}$  and  $\mathbf{p}^{(1)}, \mathbf{p}^{(2)}, \dots, \mathbf{p}^{(n)}$  the irreversible parts. If  $\mathbf{E}$  and  $\mathbf{E}^{(eq)}$  are different, no part of the polarization vector  $\mathbf{p}$  is reversible. On the other hand, if there are no internal degrees of freedom  $\mathbf{Z}^{(k)}$  ( $k=1, 2, \dots, n$ ), the variables  $\mathbf{p}^{(k)}$  vanish,  $\mathbf{p} = \mathbf{p}^{(0)}$  and one obtains for  $\sigma^{(s)}$  the expression derived by De Groot-Mazur in reference 5.

The same expressions (3.16) and (3.17) for the production of the entropy may be obtained with the help of the first law of thermodynamics (3.1) and equations (3.5) and (3.6). The latter equations are derived using the assumption that we have as internal variables  $\mathbf{p}^{(1)}, \mathbf{p}^{(2)}, \dots, \mathbf{p}^{(n)}$ .

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