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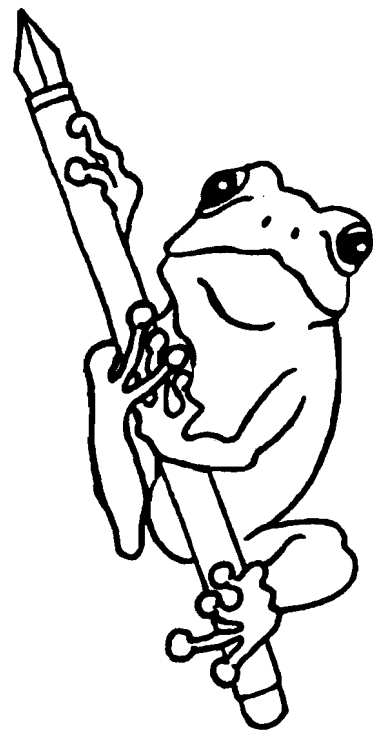Department of Mathematics and Computing Science

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ON SOME GENERALIZATION OF THE DEBYE EQUATION FOR DIELECTRIC RELAXATION

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ON SOME GENERALIZATIONS OF THE DEBYE EQUATION
FOR DIELECTRIC RELAXATION*⁾

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In some previous papers one of us (G.A.K.) discussed dielectric relaxation phenomena with the aid of non-equilibrium thermodynamics. In particular the Debye equation for dielectric relaxation in polar liquids was derived. It was also noted that generalizations of the Debye equation may be derived if one assumes that several microscopic phenomena occur which give rise to dielectric relaxation and that the contributions of these microscopic phenomena to the macroscopic polarization may be introduced as vectorial internal degrees of freedom in the entropy. If it is assumed that there are n vectorial internal degrees of freedom an explicit form for the relaxation equation may be derived, provided the developed formalism may be linearized. This relaxation equation has the form of a linear relation among the electric field E, the first n derivatives with respect to time of this field, the polarization vector P and the first $n + 1$ derivatives with respect to time of P. It is the purpose of the present paper to give full details of the derivations of the above mentioned results. It is also shown in this paper that if a part of the total polarization P is reversible (*i.e.* if this part does not contribute to the entropy production) the coefficient of the time derivative of order $n + 1$ of P in the relaxation equation is zero.

1. Introduction

Macroscopic discussions on the thermodynamics of polarizable and magnetizable media in an electromagnetic field are given by De Groot and Mazur[1], Mazur and Prigogine[2], Kluitenberg[3] and by Kluitenberg and De Groot[4,5]. The relativistic thermodynamics has been developed in the references 3-5. A review has been given by Meixner and Reik[6].

Furthermore, using the general methods of non-equilibrium thermodynamics, one of us (G.A.K.) has developed a thermodynamic theory for some types of dielectric and magnetic relaxation phenomena, by assuming that a polar and an axial vector field occur as internal thermodynamic degrees of freedom and that these fields influence the polarization and magnetization, respectively (see reference 7). Snoek's equation for magnetic after-effects and Debye's theory for dielectric relaxation phenomena in polar fluids are obtained as a special case of this theory.

In reference 8 it is shown that if there is a "hidden" vectorial internal variable Z, which influences the polarization P, this leads to the possibility to write the total polarization P in the form

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

where $P^{(0)}$ has the property that it vanishes for all values of $P^{(1)}$ if the medium is in a state where the electric field E and the mechanical elastic stress vanish and the temperature of the medium equals some reference temperature. $P^{(1)}$ is a function of Z only and may replace Z as internal variable. $P^{(1)}$ is a measurable quantity in contradistinction to an arbitrary "hidden" vectorial internal degree of freedom which is not measurable in general.

In reference 8 a relaxation equation is derived for $P^{(1)}$ and it is shown that $P^{(0)}$ is proportional to E. Furthermore, it has been shown that the theory (with $P^{(1)}$ as internal variable) becomes formally completely analogous to the Debye theory if the equations of state are linearized. Sudden changes in $P^{(1)}$ are impossible while sudden changes in $P^{(0)}$ are possible if sudden changes occur in the electric field E. For this reason $P^{(0)}$ may be called the elastic part of the polarization and $P^{(1)}$ the inelastic part. Finally, in reference 9 the theory developed in the references 7 and 8 is generalized and a different formulation is given by assuming that in principle all changes in the polarization are irreversible phenomena so that both changes in $P^{(0)}$ and $P^{(1)}$ are irreversible processes (see also reference 10 in which Böttcher and Bordewijk note that a change of the polarization cannot be infinitely fast because it is connected with the motion of any kind of microscopic particles). In reference 9 relaxation equations for $P^{(0)}$ and $P^{(1)}$ are obtained. In the linear approximation one obtains for isotropic media the relaxation equation

$$\chi_{(EP)}^{(0)} E + \frac{dE}{dt} = \chi_{(PE)}^{(0)} P + \chi_{(PE)}^{(1)} \frac{dP}{dt} + \chi_{(PE)}^{(2)} \frac{d^2 P}{dt^2}, \tag{1.2}$$

if the internal degree of freedom is eliminated from the formalism. If changes in $P^{(0)}$ are reversible processes (1.2) reduces to the Debye equation. Furthermore, the quantities $\chi_{(EP)}^{(0)}$, $\chi_{(PE)}^{(0)}$, $\chi_{(PE)}^{(1)}$ and $\chi_{(PE)}^{(2)}$ in (1.2) are constants.

In section 14 of reference 9 it is noted that generalizations of the Debye equation may be derived if one assumes that an arbitrary number of phenomena occur which give rise to dielectric relaxation and that it is possible to describe these microscopic phenomena with the aid of n macroscopic vectorial internal variables which are introduced as internal degrees of freedom in the Gibbs relation. Furthermore, an explicit form for the relaxation equation may be derived, provided that the developed formalism may be linearized. It is the purpose of the present paper to give full details of the derivation of these results with the aid of the methods of non-equilibrium thermodynamics[1) 6) 11) 12) 13)].

In section 2 we give the first law of thermodynamics for a polarizable continuous medium in an electromagnetic field.

In section 3 we introduce the assumption that the entropy depends not only on the internal energy, the strain tensor and the vector of the total polarization, but also on n vector fields $p^{(1)}, p^{(2)}, \cdots, p^{(n)}$, which play the role of internal degrees of freedom.

In section 4 the Gibbs relation and the entropy balance are derived and it is shown that the entropy production is a sum of contributions due to viscous mechanical flow phenomena, heat conduction, electric conduction and dielectric relaxation. Every contribution is an inner product of two vectors or of two second order tensors of which one is a flux and the other is the thermodynamic force conjugate to the flux.

In section 5 the phenomenological equations connected with irreversible changes in the polarization and with the generalized laws of Ohm, Fourier and Newton are formulated and the symmetry relations and the Onsager-Casimir relations for the phenomenological coefficients are derived.

The phenomenological equations and the entropy production are also formulated for the case that the medium is isotropic. Furthermore, from the nonnegative character of the entropy production, some inequalities are derived for the phenomenological tensors.

In section 6 a reference state (with temperature T_0) is introduced in which the equilibrium stress tensor is a multiple of the unit tensor and the equilibrium electric field and the vectorial thermodynamic affinities conjugate to the partial specific polarizations vanish. The strain tensor $\varepsilon_{\alpha\beta}$, the vector of the specific total polarization p and the specific partial polarizations $p^{(k)}$ ($k = 1, 2, \cdots, n$) are measured with respect to this state, i.e. $\varepsilon_{\alpha\beta}$, p and $p^{(k)}$ ($k = 1, 2, \cdots, n$) vanish in the reference state. This state is a state of thermodynamic equilibrium. If we introduce a suitable form for the specific free energy f, we obtain the linearized equations of state.

In section 7 a set of equations is derived which has a mathematical structure which is completely analogous to the structure of the equations obtained in section 15 of reference 14 for mechanical phenomena in continuous isotropic media.

By applying the same procedure as used in reference 14 the following dielectric relaxation equation for isotropic media is obtained

$$\chi_{(EP)}^{(0)}\mathbf{E} + \chi_{(EP)}^{(1)}\frac{d\mathbf{E}}{dt} + \cdots + \chi_{(EP)}^{(n-1)}\frac{d^{(n-1)}\mathbf{E}}{dt^{(n-1)}} + \frac{d^n\mathbf{E}}{dt^n} = \tag{1.3}$$

$$= \chi_{(PE)}^{(0)}\mathbf{P} + \chi_{(PE)}^{(1)}\frac{d\mathbf{P}}{dt} + \cdots + \chi_{(PE)}^{(n)}\frac{d^n\mathbf{P}}{dt^n} + \chi_{(PE)}^{(n+1)}\frac{d^{(n+1)}\mathbf{P}}{dt^{(n+1)}},$$

where $\chi_{(EP)}^{(k)}$ ($k = 0, 1, \cdots, n-1$) and $\chi_{(PE)}^{(k)}$ ($k = 0, 1, \cdots, n+1$) are constants. It is seen that (1.3) has the form of a linear relation among the electric field $\mathbf{E}$, the first n derivatives with respect to time of this vector, the polarization vector $\mathbf{P}$ and the first $n + 1$ derivatives with respect to time of $\mathbf{P}$.

In section 8 it is seen that:

i) If the equilibrium electric field is equal to the electric field of Maxwell ($\mathbf{E}^{(eq)} = \mathbf{E}$), $\chi_{(PE)}^{(n+1)}$ vanishes and the theory developed in this paper reduces to the case that the polarization is additively composed of a reversible and of n irreversible parts. In particular, if $n = 1$ the Debye equation for dielectric relaxation in polar fluids is obtained.

ii) If no internal vectorial degrees of freedom occur the theory reduces to the De Groot-Mazur theory.

2. The first law of thermodynamics

Let us consider a polarizable medium in an electromagnetic field. Maxwell's equations for the electromagnetic field read

$$\text{rot}\,\mathbf{H} - \frac{1}{c}\,\frac{\partial \mathbf{D}}{\partial t} = \frac{1}{c}\,\mathbf{j}^{(el)}\,,\tag{2.1}$$

$$\text{div}\,\mathbf{D} = \rho^{(el)}\,,\tag{2.2}$$

$$\text{rot}\,\mathbf{E} + \frac{1}{c}\,\frac{\partial \mathbf{B}}{\partial t} = 0\,,\tag{2.3}$$

$$\text{div}\,\mathbf{B} = 0\,,\tag{2.4}$$

where $\mathbf{E}$ and $\mathbf{B}$ are the electric and magnetic field strengths, respectively, $\mathbf{D}$ is the electric displacement field, $\mathbf{H}$ is the magnetic displacement field, $\rho^{(el)}$ is the electric charge density, $\mathbf{j}^{(el)}$ is the density of the electric current and c is the velocity of light.

The time derivative $\frac{d}{dt}$ is the substantial derivative with respect to time defined by

$$\frac{d}{dt} = \frac{\partial}{\partial t} + \sum_{\gamma=1}^{3} v_\gamma\,\frac{\partial}{\partial x_\gamma}\,,\tag{2.5}$$

where $\frac{\partial}{\partial t}$ is the local derivative with respect to time. Furthermore, x_1, x_2 and x_3 are the coordinates of a point in space with respect to an orthogonal Cartesian frame of axes fixed in space and v_1, v_2 and v_3 are the components of the velocity field with respect to this frame.

The first law of thermodynamics for a dielectric medium reads (see for example formula (39) on p. 384 of reference 1)

$$\rho\,\frac{du}{dt} = -\text{div}\,\mathbf{J}^{(q)} + \sum_{\alpha,\beta=1}^{3} \tau_{\alpha\beta}\,\frac{d\varepsilon_{\alpha\beta}}{dt} + \mathbf{j}^{(el)}\cdot\mathbf{E} + \rho\mathbf{E}\cdot\frac{d\mathbf{p}}{dt}\,.\tag{2.6}$$

In (2.6) u is the specific internal energy (energy per unit of mass), $\mathbf{J}^{(q)}$ is the heat flow, $\tau_{\alpha\beta}$ is the mechanical stress tensor and $\varepsilon_{\alpha\beta}$ is the strain tensor defined by

$$\varepsilon_{\alpha\beta} = \frac{1}{2}\left[\frac{\partial u_\alpha}{\partial x_\beta} + \frac{\partial u_\beta}{\partial x_\alpha}\right]\quad(\alpha,\beta = 1,2,3)\,,\tag{2.7}$$

where $\mathbf{u}$ is the displacement field of the medium. From the definition (2.7), it is obvious that $\varepsilon_{\alpha\beta}$ is a symmetric tensor field.

If the strains and rotations of the medium are small from a kinematical point of view, we have in a first approximation

$$\frac{d}{dt}\,\varepsilon_{\alpha\beta} = \frac{1}{2}\left[\frac{\partial v_\alpha}{\partial x_\beta} + \frac{\partial v_\beta}{\partial x_\alpha}\right]\quad(\alpha,\beta = 1,2,3)\,.\tag{2.8}$$

Now, if we define for an arbitrary second order tensor field $A_{\alpha\beta}$ its scalar part by

$$A = \frac{1}{3} \sum_{\gamma=1}^{3} A_{\gamma\gamma} \qquad (2.9)$$

and its deviator by

$$\bar{A}_{\alpha\beta} = A_{\alpha\beta} - \frac{1}{3} \delta_{\alpha\beta} \sum_{\gamma=1}^{3} A_{\gamma\gamma} \qquad (2.10)$$

($\delta_{\alpha\beta}$ is the unit tensor), it follows from (2.9) and (2.10) that

$$\sum_{\gamma=1}^{3} \bar{A}_{\gamma\gamma} = 0 \qquad (2.11)$$

and that

$$A_{\alpha\beta} = \bar{A}_{\alpha\beta} + A \, \delta_{\alpha\beta} \; . \qquad (2.12)$$

It should be noted that $\bar{A}_{\alpha\beta}$ is a symmetric tensor field if and only if $A_{\alpha\beta}$ is a symmetric tensor field. Moreover, it is seen that the scalar part and the deviator of $\varepsilon_{\alpha\beta}$ are given by

$$\varepsilon = \frac{1}{3} \, \text{div} \, \mathbf{u} \qquad (2.13)$$

and by

$$\bar{\varepsilon}_{\alpha\beta} = \frac{1}{2} \left[\frac{\partial u_{\alpha}}{\partial x_{\beta}} + \frac{\partial u_{\beta}}{\partial x_{\alpha}} - \frac{2}{3} \delta_{\alpha\beta} \, \text{div} \, \mathbf{u} \right] \; , \qquad (2.14)$$

respectively.

In (2.6) ρ is the total mass density satisfying the conservation law

$$\frac{\partial \rho}{\partial t} = -\text{div} \, \rho \, \mathbf{v} \; . \qquad (2.15)$$

If we introduce the specific volume v, by

$$v = \rho^{-1} \; , \qquad (2.16)$$

(2.15) may also be written as

$$\rho \, \frac{dv}{dt} = \text{div} \, \mathbf{v} \; . \qquad (2.17)$$

From (2.13) and (2.17) we obtain

$$\rho \, \frac{dv}{dt} = 3 \, \frac{d\varepsilon}{dt} \; . \qquad (2.18)$$

In (2.18), in a first approximation, ρ may be replaced by $1/v_0$, where v_0 is the specific volume in the reference state (*i.e.* the state of the medium with respect to which the displacements of the medium are measured) and this leads to

$$v = v_0(1+3\varepsilon).\tag{2.19}$$

Furthermore, in (2.6) $\mathbf{p}$ is the specific polarization defined by

$$\mathbf{p} = v\,\mathbf{P},\tag{2.20}$$

where the polarization $\mathbf{P}$ is given by

$$\mathbf{P} = \mathbf{D} - \mathbf{E}.\tag{2.21}$$

3. The Gibbs relation

Let us introduce the physical assumption that the total specific polarization is additively composed of $n + 1$ partial specific polarizations, (see equation (14.1) of reference 9)

$$\mathbf{p} = \mathbf{p}^{(0)} + \mathbf{p}^{(1)} + \cdots + \mathbf{p}^{(n)} \tag{3.1}$$

and let us assume that the specific entropy (i.e. the entropy per unit of mass) depends not only on the specific internal energy u, the strain tensor $\varepsilon_{\alpha\beta}$ and the specific polarization $\mathbf{p}$, but also on the n vector fields $\mathbf{p}^{(1)}, \mathbf{p}^{(2)}, \cdots, \mathbf{p}^{(n)}$, which represent n thermodynamic internal degrees of freedom. Hence, it is assumed that (see section 14 of reference 9)

$$s = s(u, \varepsilon_{\alpha\beta}, \mathbf{p}, \mathbf{p}^{(1)}, \mathbf{p}^{(2)}, \cdots, \mathbf{p}^{(n)}) . \tag{3.2}$$

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

$$T^{-1} = \frac{\partial}{\partial u} s(u, \varepsilon_{\alpha\beta}, \mathbf{p}, \mathbf{p}^{(1)}, \mathbf{p}^{(2)}, \cdots, \mathbf{p}^{(n)}) , \tag{3.3}$$

$$\tau_{\alpha\beta}^{(eq)} = -\rho T \frac{\partial}{\partial \varepsilon_{\alpha\beta}} s(u, \varepsilon_{\alpha\beta}, \mathbf{p}, \mathbf{p}^{(1)}, \mathbf{p}^{(2)}, \cdots, \mathbf{p}^{(n)}) , \tag{3.4}$$

$$\mathbf{E}^{(eq)} = -T \frac{\partial}{\partial \mathbf{p}} s(u, \varepsilon_{\alpha\beta}, \mathbf{p}, \mathbf{p}^{(1)}, \mathbf{p}^{(2)}, \cdots, \mathbf{p}^{(n)}) , \tag{3.5}$$

$$\mathbf{E}^{(k)} = T \frac{\partial}{\partial \mathbf{p}^{(k)}} s(u, \varepsilon_{\alpha\beta}, \mathbf{p}, \mathbf{p}^{(1)}, \mathbf{p}^{(2)}, \cdots, \mathbf{p}^{(n)}) \quad (k = 1, 2, \cdots, n) . \tag{3.6}$$

From (3.2)-(3.6) it follows that

$$T ds = du - v \sum_{\alpha,\beta=1}^{3} \tau_{\alpha\beta}^{(eq)} d\varepsilon_{\alpha\beta} - \mathbf{E}^{(eq)} \cdot d\mathbf{p} + \sum_{k=1}^{n} \mathbf{E}^{(k)} \cdot d\mathbf{p}^{(k)} . \tag{3.7}$$

An expression of the type (3.7) for ds is called Gibbs relation.

The equation (3.3) is the usual relation between temperature and entropy. In (3.4)-(3.7) $\tau_{\alpha\beta}^{(eq)}$ is the equilibrium stress tensor, $\mathbf{E}^{(eq)}$ is the equilibrium electric field and the vectors $\mathbf{E}^{(k)}$ are the vectorial thermodynamic affinities conjugate to the internal variables $\mathbf{p}^{(k)}$ ($k = 1, 2, \cdots, n$).

For a fluid

$$\tau_{\alpha\beta}^{(eq)} = -P^{(eq)} \delta_{\alpha\beta} \quad \text{(fluid)} \tag{3.8}$$

and (3.7) becomes with the aid of (2.8), (2.13) and (2.18)

$$T ds = du + P^{(eq)} dv - \mathbf{E}^{(eq)} \cdot d\mathbf{p} + \sum_{k=1}^{n} \mathbf{E}^{(k)} \cdot d\mathbf{p}^{(k)} , \tag{3.9}$$

where $P^{(eq)}$ is the scalar hydrostatic equilibrium pressure.

From (3.2) and (3.1) it is seen that the entropy may also be considered as a function of $u, \varepsilon_{\alpha\beta}, \mathbf{p}^{(0)}, \mathbf{p}^{(1)}, \mathbf{p}^{(2)}, \cdots, \mathbf{p}^{(n)}$. Hence, one has

$$s = s(u, \varepsilon_{\alpha\beta}, \mathbf{p}^{(0)}, \mathbf{p}^{(1)}, \cdots, \mathbf{p}^{(n)}) \tag{3.10}$$

and using (3.1), one may write for (3.7)

$$Tds = du - v \sum_{\alpha,\beta=1}^{3} \tau_{\alpha\beta}^{(eq)} \, d\varepsilon_{\alpha\beta} - \mathbf{E}^{(eq)} \cdot d\mathbf{p}^{(0)} + \sum_{k=1}^{n} (\mathbf{E}^{(k)} - \mathbf{E}^{(eq)}) \cdot d\mathbf{p}^{(k)} . \tag{3.11}$$

Now, if we define

$$\mathbf{E}_{(ir)}^{(k)} = \mathbf{E}^{(k)} - \mathbf{E}^{(eq)} \qquad (k = 1, 2, \cdots, n), \tag{3.12}$$

(3.11) becomes

$$Tds = du - v \sum_{\alpha,\beta=1}^{3} \tau_{\alpha\beta}^{(eq)} \, d\varepsilon_{\alpha\beta} - \mathbf{E}^{(eq)} \cdot d\mathbf{p}^{(0)} + \sum_{k=1}^{n} \mathbf{E}_{(ir)}^{(k)} \cdot d\mathbf{p}^{(k)} . \tag{3.13}$$

From (3.11) it follows that

$$T^{-1} = \frac{\partial}{\partial u} \, s(u, \varepsilon_{\alpha\beta}, \mathbf{p}^{(0)}, \mathbf{p}^{(1)}, \cdots, \mathbf{p}^{(n)}), \tag{3.14}$$

$$\tau_{\alpha\beta}^{(eq)} = -\rho \, T \, \frac{\partial}{\partial \varepsilon_{\alpha\beta}} \, s(u, \varepsilon_{\alpha\beta}, \mathbf{p}^{(0)}, \mathbf{p}^{(1)}, \cdots, \mathbf{p}^{(n)}), \tag{3.15}$$

$$\mathbf{E}^{(eq)} = -T \, \frac{\partial}{\partial \mathbf{p}^{(0)}} \, s(u, \varepsilon_{\alpha\beta}, \mathbf{p}^{(0)}, \mathbf{p}^{(1)}, \cdots, \mathbf{p}^{(n)}), \tag{3.16}$$

$$\mathbf{E}_{(ir)}^{(k)} = T \, \frac{\partial}{\partial \mathbf{p}^{(k)}} \, s(u, \varepsilon_{\alpha\beta}, \mathbf{p}^{(0)}, \mathbf{p}^{(1)}, \cdots, \mathbf{p}^{(n)}) \qquad (k = 1, 2, \cdots, n). \tag{3.17}$$

The partial specific polarization $\mathbf{p}^{(0)}$ which occurs in the equations (3.1), (3.10), (3.11) and (3.13)-(3.17) may be introduced such that, in a reference state, where the temperature T has an arbitrarily chosen but fixed value T_0,

$$\mathbf{p}^{(0)} = 0 \quad \text{for all values of } \mathbf{p}^{(1)}, \mathbf{p}^{(2)}, \cdots, \mathbf{p}^{(n)} \text{if } T = T_0, \quad \tau_{\alpha\beta}^{(eq)} = -P_0 \, \delta_{\alpha\beta} \text{ and } \mathbf{E}^{(eq)} = 0, \tag{3.18}$$

where P_0 is a scalar.

The proof of (3.18) is given in section 3 of reference 9 for the case in which there is only one partial specific polarization introduced as internal degree of freedom. But the detailed mathematical proof to the general case of n partial specific polarizations is analogous to the proof given for the case of mechanical relaxation phenomena in continuous media in reference 15.

4. Entropy balance

In the section 3 we have discussed the expressions (3.7), (3.9) and (3.13) for the differential ds of the specific entropy s. From (3.7) it follows that

$$T \frac{ds}{dt} = \frac{du}{dt} - v \sum_{\alpha,\beta=1}^{3} \tau_{\alpha\beta}^{(eq)} \frac{d\varepsilon_{\alpha\beta}}{dt} - \mathbf{E}^{(eq)} \cdot \frac{d\mathbf{p}}{dt} + \sum_{k=1}^{n} \mathbf{E}^{(k)} \cdot \frac{d\mathbf{p}^{(k)}}{dt} . \tag{4.1}$$

By eliminating the internal energy u from (2.6) and (4.1), one obtains the entropy balance

$$\rho \frac{ds}{dt} = -\text{div} \frac{\mathbf{J}^{(q)}}{T} + \sigma^{(s)} , \tag{4.2}$$

where $\frac{\mathbf{J}^{(q)}}{T}$ is the conductive flow of entropy and $\sigma^{(s)}$ is the entropy production per unit volume and per unit time given by

$$\sigma^{(s)} = T^{-1} \left\{ \sum_{\alpha,\beta=1}^{3} \tau_{\alpha\beta}^{(vi)} \frac{d\varepsilon_{\alpha\beta}}{dt} + \mathbf{J}^{(q)} \cdot \mathbf{X}^{(q)} + \mathbf{j}^{(el)} \cdot \mathbf{E} + \right.$$

$$\left. + \rho \mathbf{E}^{(ir)} \cdot \frac{d\mathbf{p}}{dt} + \rho \sum_{k=1}^{n} \mathbf{E}^{(k)} \cdot \frac{d\mathbf{p}^{(k)}}{dt} \right\} \geq 0 . \tag{4.3}$$

In (4.3) the tensor $\tau_{\alpha\beta}^{(vi)}$ is the viscous stress tensor defined by

$$\tau_{\alpha\beta}^{(vi)} = \tau_{\alpha\beta} - \tau_{\alpha\beta}^{(eq)} , \tag{4.4}$$

the vectors $\mathbf{X}^{(q)}$ and $\mathbf{E}^{(ir)}$ are given by

$$\mathbf{X}^{(q)} = -T^{-1} \text{ grad } T \tag{4.5}$$

and by

$$\mathbf{E}^{(ir)} = \mathbf{E} - \mathbf{E}^{(eq)} . \tag{4.6}$$

The terms in (4.3) with the viscous stress tensor $\tau_{\alpha\beta}^{(vi)}$, the heat flow $\mathbf{J}^{(q)}$ and the electric current $\mathbf{j}^{(el)}$ give the contributions to the entropy production of viscous mechanical flow phenomena, heat conduction and electric conduction, respectively. The terms with $\frac{d\mathbf{p}}{dt}$ and $\frac{d\mathbf{p}^{(k)}}{dt}$ $(k = 1,2,\cdots,n)$ are connected with entropy production due to dielectric relaxation. Moreover, in (4.3) the entropy source strength $\sigma^{(s)}$ must be zero if the thermodynamic equilibrium conditions are satisfied within the system.

Finally, using (3.1) one may also write for (4.3)

$$\sigma^{(s)} = T^{-1} \left\{ \sum_{\alpha\beta=1}^{3} \tau_{\alpha\beta}^{(vi)} \frac{d\varepsilon_{\alpha\beta}}{dt} + \mathbf{J}^{(q)} \cdot \mathbf{X}^{(q)} + \mathbf{j}^{(el)} \cdot \mathbf{E} + \rho \mathbf{E}^{(ir)} \cdot \frac{d\mathbf{p}^{(0)}}{dt} + \right.$$

$$+ \rho \sum_{k=1}^{n} (\mathbf{E}^{(k)} + \mathbf{E}^{(ir)}) \cdot \frac{d\mathbf{p}^{(k)}}{dt} \bigg\} . \qquad (4.7)$$

It is seen from (4.7) that changes in $\mathbf{p}^{(0)}$ and $\mathbf{p}^{(k)}$ ($k = 1,2, \cdots , n$) contribute to the entropy production. Then, if the electric field $\mathbf{E}$ of Maxwell's equations equals the equilibrium electric field $\mathbf{E}^{(eq)}$, defined by (3.5) and (3.16), $\dfrac{d\mathbf{p}^{(0)}}{dt}$ does not contribute to the entropy production and changes in $\mathbf{p}^{(0)}$ are reversible processes.

Furthermore, if the vectorial internal degrees of freedom $\mathbf{p}^{(k)}$ ($k = 1,2, \cdots , n$) vanish, $\mathbf{p} = \mathbf{p}^{(0)}$ and in (4.7) the last term on the right-hand vanishes (as in the theory of De Groot-Mazur, see reference 1). These two cases will be discussed in section 8 of this paper.

5. Phenomenological equations and symmetry relations

It is seen from (4.3) that the entropy production is a sum of terms, where each term is the inner product of two vectors or of two second order tensors of which one is a flux and the other is the thermodynamic force or "affinity" conjugate to the flux.

According to the usual procedure of nonequilibrium thermodynamics (see references 1, 6 and 15), we have for a polarizable continuous medium by virtue of the expression (4.3) for the entropy production the following phenomenological equations, in which the irreversible flows are linear functions of the thermodynamic forces:

$$E_\alpha^{(ir)} = \rho \sum_{\beta=1}^{3} L_{(P)\alpha\beta}^{(0,0)} \frac{dp_\beta}{dt} + \sum_{k=1}^{n} \sum_{\beta=1}^{3} L_{(P)\alpha\beta}^{(0,k)} E_\beta^{(k)} +$$

$$+ \sum_{\beta=1}^{3} L_{(P)\alpha\beta}^{(0,el)} E_\beta + \sum_{\beta=1}^{3} L_{(P)\alpha\beta}^{(0,q)} X_\beta^{(q)} + \sum_{\beta,\gamma=1}^{3} L_{(P)\alpha\beta\gamma}^{(0,vi)} \frac{d\varepsilon_{\beta\gamma}}{dt} , \tag{5.1}$$

$$\rho \frac{dp_\alpha^{(j)}}{dt} = \rho \sum_{\beta=1}^{3} L_{(P)\alpha\beta}^{(j,0)} \frac{dp_\beta}{dt} + \sum_{k=1}^{n} \sum_{\beta=1}^{3} L_{(P)\alpha\beta}^{(j,k)} E_\beta^{(k)} +$$

$$+ \sum_{\beta=1}^{3} L_{(P)\alpha\beta}^{(j,el)} E_\beta + \sum_{\beta=1}^{3} L_{(P)\alpha\beta}^{(j,q)} X_\beta^{(q)} +$$

$$+ \sum_{\beta,\gamma=1}^{3} L_{(P)\alpha\beta\gamma}^{(j,vi)} \frac{d\varepsilon_{\beta\gamma}}{dt} \qquad (j = 1,2,\cdots,n) , \tag{5.2}$$

$$j_\alpha^{(el)} = \rho \sum_{\beta=1}^{3} L_{(P)\alpha\beta}^{(el,0)} \frac{dp_\beta}{dt} + \sum_{k=1}^{n} \sum_{\beta=1}^{3} L_{(P)\alpha\beta}^{(el,k)} E_\beta^{(k)} +$$

$$+ \sum_{\beta=1}^{3} L_{\alpha\beta}^{(el,el)} E_\beta + \sum_{\beta=1}^{3} L_{\alpha\beta}^{(el,q)} X_\beta^{(q)} + \sum_{\beta,\gamma=1}^{3} L_{\alpha\beta\gamma}^{(el,vi)} \frac{d\varepsilon_{\beta\gamma}}{dt} , \tag{5.3}$$

$$J_\alpha^{(q)} = \rho \sum_{\beta=1}^{3} L_{(P)\alpha\beta}^{(q,0)} \frac{dp_\beta}{dt} + \sum_{k=1}^{n} \sum_{\beta=1}^{3} L_{(P)\alpha\beta}^{(q,k)} E_\beta^{(k)} +$$

$$+ \sum_{\beta=1}^{3} L_{\alpha\beta}^{(q,el)} E_\beta + \sum_{\beta=1}^{3} L_{\alpha\beta}^{(q,q)} X_\beta^{(q)} + \sum_{\beta,\gamma=1}^{3} L_{\alpha\beta\gamma}^{(q,vi)} \frac{d\varepsilon_{\beta\gamma}}{dt} , \tag{5.4}$$

$$\tau_{\alpha\beta}^{(vi)} = \rho \sum_{\gamma=1}^{3} L_{(P)\alpha\beta\gamma}^{(vi,0)} \frac{dp_\gamma}{dt} + \sum_{k=1}^{n} \sum_{\gamma=1}^{3} L_{(P)\alpha\beta\gamma}^{(vi,k)} E_\gamma^{(k)} +$$

$$+ \sum_{\gamma=1}^{3} L_{\alpha\beta\gamma}^{(vi,el)} E_\gamma + \sum_{\gamma=1}^{3} L_{\alpha\beta\gamma}^{(vi,q)} X_\gamma^{(q)} + \sum_{\gamma,\zeta=1}^{3} L_{\alpha\beta\gamma\zeta}^{(vi,vi)} \frac{d\varepsilon_{\gamma\zeta}}{dt} . \tag{5.5}$$

The equations (5.1) and (5.2) are connected with irreversible changes in the polarization. The equations (5.3) and (5.4) are generalizations of Ohm's law and of Fourier's law and (5.5) is a

generalization of Newton's law for viscous fluid flow.

The quantities $L_{(P)\alpha\beta}^{(0,0)}$, $L_{(P)\alpha\beta}^{(0,k)}$ ($k = 1, \cdots, n$), $L_{(P)\alpha\beta}^{(0,el)}$ etc., which occur in (5.1)-(5.5), are phenomenological tensors. In principle, all irreversible phenomena can influence each other. This is expressed by (5.1)-(5.5). For instance, the third, the fourth and the fifth terms on the right-hand sides of (5.1) and (5.2) describe the influences of electric conduction, heat conduction and mechanical viscosity on dielectric relaxation. Phenomena of this type are called cross effects.

By virtue of (2.7) $\varepsilon_{\alpha\beta}$ is symmetric and hence it follows from (3.4) that also $\tau_{\alpha\beta}^{(eq)}$ is a symmetric tensor. Furthermore, we suppose that the mechanical stress tensor is symmetric. This tensor occurs in the first law of thermodynamics (2.6) and in the equations of motion. Hence, it follows from the definition (4.4) that the viscous stress tensor $\tau_{\alpha\beta}^{(vi)}$ is a symmetric tensor.

Because of the symmetry of $\varepsilon_{\alpha\beta}$ and $\tau_{\alpha\beta}^{(vi)}$, one can choose the tensors $L_{(P)\alpha\beta\gamma}^{(0,vi)}$, $L_{(P)\alpha\beta\gamma}^{(j,vi)}$ ($j = 1,2, \cdots, n$), $L_{\alpha\beta\gamma}^{(el,vi)}$, $L_{\alpha\beta\gamma}^{(q,vi)}$, $L_{(P)\alpha\beta\gamma}^{(vi,0)}$, $L_{(P)\alpha\beta\gamma}^{(vi,j)}$ ($j = 1,2, \cdots, n$), $L_{\alpha\beta\gamma}^{(vi,el)}$, $L_{\alpha\beta\gamma}^{(vi,q)}$, $L_{\alpha\beta\gamma\zeta}^{(vi,vi)}$ so that they satisfy the symmetry relations

$$L_{(P)\alpha\beta\gamma}^{(0,vi)} = L_{(P)\alpha\gamma\beta}^{(0,vi)} , \qquad\qquad L_{(P)\alpha\beta\gamma}^{(vi,0)} = L_{(P)\beta\alpha\gamma}^{(vi,0)} , \qquad\qquad (5.6)$$

$$L_{(P)\alpha\beta\gamma}^{(j,vi)} = L_{(P)\alpha\gamma\beta}^{(j,vi)} \qquad (j = 1,2, \cdots, n) , \quad L_{(P)\alpha\beta\gamma}^{(vi,j)} = L_{(P)\beta\alpha\gamma}^{(vi,j)} \qquad (j = 1,2, \cdots, n) , \quad (5.7)$$

$$L_{\alpha\beta\gamma}^{(el,vi)} = L_{\alpha\gamma\beta}^{(el,vi)} , \qquad\qquad L_{\alpha\beta\gamma}^{(vi,el)} = L_{\beta\alpha\gamma}^{(vi,el)} , \qquad\qquad (5.8)$$

$$L_{\alpha\beta\gamma}^{(q,vi)} = L_{\alpha\gamma\beta}^{(q,vi)} , \qquad\qquad L_{\alpha\beta\gamma}^{(vi,q)} = L_{\beta\alpha\gamma}^{(vi,q)} , \qquad\qquad (5.9)$$

$$L_{\alpha\beta\gamma\zeta}^{(vi,vi)} = L_{\beta\alpha\gamma\zeta}^{(vi,vi)} = L_{\alpha\beta\zeta\gamma}^{(vi,vi)} = L_{\beta\alpha\zeta\gamma}^{(vi,vi)} . \qquad\qquad (5.10)$$

$\mathbf{E}^{(ir)}$, $\mathbf{E}^{(k)}$ ($k = 1,2, \cdots, n$), $\mathbf{E}$, $\mathbf{X}^{(q)}$ and $\tau_{\alpha\beta}^{(vi)}$ are even functions of the microscopic particle velocities, while $\frac{d\mathbf{p}}{dt}$, $\frac{d\mathbf{p}^{(k)}}{dt}$ ($k = 1,2, \cdots, n$), $\mathbf{j}^{(el)}$, $\mathbf{J}^{(q)}$ and $\frac{d\varepsilon_{\alpha\beta}}{dt}$ are odd functions of these velocities. Hence, for the cross effects which occur in (5.1)-(5.5) the Onsager-Casimir reciprocal relations read

$$L_{(P)\alpha\beta}^{(0,0)} = L_{(P)\beta\alpha}^{(0,0)} , \qquad\qquad L_{(P)\alpha\beta}^{(j,k)} = L_{(P)\beta\alpha}^{(k,j)} \qquad (j,k=1,2,\cdots,n) , \qquad (5.11)$$

$$L_{\alpha\beta}^{(el,el)} = L_{\beta\alpha}^{(el,el)} , \qquad\qquad L_{\alpha\beta}^{(q,q)} = L_{\beta\alpha}^{(q,q)} , \qquad\qquad\qquad\qquad\qquad (5.12)$$

$$L_{\alpha\beta\gamma\zeta}^{(vi,vi)} = L_{\gamma\zeta\alpha\beta}^{(vi,vi)} , \qquad\qquad L_{(P)\alpha\beta}^{(0,j)} = -L_{(P)\beta\alpha}^{(j,0)} \qquad (j=1,2,\cdots,n) , \qquad (5.13)$$

$$L_{(P)\alpha\beta}^{(0,el)} = -L_{(P)\beta\alpha}^{(el,0)} , \qquad\qquad L_{(P)\alpha\beta}^{(0,q)} = -L_{(P)\beta\alpha}^{(q,0)} , \qquad\qquad\qquad\qquad (5.14)$$

$$L_{(P)\alpha\beta}^{(j,el)} = L_{(P)\beta\alpha}^{(el,j)} \quad (j=1,2,\cdots,n) , \qquad L_{(P)\alpha\beta}^{(j,q)} = L_{(P)\beta\alpha}^{(q,j)} \quad (j=1,2,\cdots,n) , \qquad (5.15)$$

$$L_{\alpha\beta}^{(el,q)} = L_{\beta\alpha}^{(q,el)} , \qquad\qquad L_{(P)\alpha\beta\gamma}^{(0,vi)} = L_{(P)\beta\gamma\alpha}^{(vi,0)} , \qquad\qquad\qquad\qquad\qquad (5.16)$$

$$L_{(P)\alpha\beta\gamma}^{(j,vi)} = -L_{(P)\beta\gamma\alpha}^{(vi,j)} , \quad (j=1,2,\cdots,n) , \qquad L_{\alpha\beta\gamma}^{(el,vi)} = -L_{\beta\gamma\alpha}^{(vi,el)} , \quad L_{\alpha\beta\gamma}^{(q,vi)} = -L_{\beta\gamma\alpha}^{(vi,q)} . \qquad (5.17)$$

The relations (5.11)-(5.17) reduce the number of independent components of the phenomenological tensors. Further reduction may occur as a consequence of symmetry properties of the medium. If the medium under consideration is isotropic these tensors must be invariant with respect to all rotations and to inversion of the frame of axes. In this case the tensor $L_{\alpha\beta\gamma\zeta}^{(vi,vi)}$ of order four which also satisfies the Onsager relations (see (5.13)) has the form

$$L_{\alpha\beta\gamma\zeta}^{(vi,vi)} = \frac{1}{2}\,\eta_s(\delta_{\alpha\gamma}\,\delta_{\beta\zeta}+\delta_{\beta\gamma}\,\delta_{\alpha\zeta}) + \frac{1}{3}\,(\eta_v-\eta_s)\,\delta_{\alpha\beta}\,\delta_{\gamma\zeta} , \qquad (5.18)$$

where the scalars η_s and η_v are the shear viscosity and the volume viscosity, respectively.

Let $L_{\alpha\beta\gamma}$ and $L_{\alpha\beta}$ be two arbitrary tensors of order three and order two, respectively. If the medium is isotropic these tensors have the form

$$L_{\alpha\beta\gamma} = 0 , \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad (5.19)$$

and

$$L_{\alpha\beta} = L\,\delta_{\alpha\beta} . \qquad\qquad\qquad\qquad\qquad\qquad\qquad (5.20)$$

We introduce (5.18)-(5.20) in (5.1)-(5.5) and we neglect for simplicity all cross effects, except for possible cross effects among the different types of dielectric relaxation phenomena described by (5.1) and (5.2). One then obtains

$$\mathbf{E}^{(ir)} = \rho L_{(P)}^{(0,0)}\,\frac{d\mathbf{p}}{dt} + \sum_{k=1}^{n} L_{(P)}^{(0,k)}\,\mathbf{E}^{(k)} , \qquad\qquad\qquad\qquad (5.21)$$

$$\rho\,\frac{d\mathbf{p}^{(j)}}{dt} = \rho L_{(P)}^{(j,0)}\,\frac{d\mathbf{p}}{dt} + \sum_{k=1}^{n} L_{(P)}^{(j,k)}\,\mathbf{E}^{(k)} \qquad (j=1,2,\cdots,n) , \qquad (5.22)$$

$$\mathbf{j}^{(el)} = L^{(el,el)}\,\mathbf{E} , \qquad\qquad\qquad\qquad\qquad\qquad\qquad (5.23)$$

$$\mathbf{J}^{(q)} = -T^{-1} L^{(q,\,q)} \operatorname{grad} T \; , \tag{5.24}$$

$$\tau_{\alpha\beta}^{(vi)} = \eta_s \frac{d\tilde{\varepsilon}_{\alpha\beta}}{dt} + \eta_v \frac{d\varepsilon}{dt} \, \delta_{\alpha\beta} \; . \tag{5.25}$$

These equations are analogous to the equations (5.18)-(5.21) and (5.23) of reference 9. In (5.24) we used the definition (4.5) of $\mathbf{X}^{(q)}$. In (5.25) we used (5.18), the relations (2.9)-(2.12) for the deviator and the trace and, finally, the symmetry of $\varepsilon_{\alpha\beta}$.

The equations (5.23)-(5.25) are the well-known Ohm's law for electric conduction, Fourier's law for heat conduction and Newton's law for viscous fluid flow, respectively.

The Onsager-Casimir relations for the scalar phenomenological coefficients which occur in the phenomenological equations (5.21) and (5.22) read

$$L_{(P)}^{(j,\,0)} = -L_{(P)}^{(0,\,j)} \qquad (j = 1,2,\cdots,n) \; , \tag{5.26}$$

and

$$L_{(P)}^{(j,\,k)} = L_{(P)}^{(k,\,j)} \qquad (j, k = 1,2,\cdots,n) \; . \tag{5.27}$$

See also the second of the equations (5.13) and the second of the equations (5.11), respectively.

Substituting (5.21)-(5.25) in the expression (4.3) for the entropy production and using (2.9), (2.12), (4.5), (5.26) and (5.27), one obtains

$$\sigma^{(s)} = T^{-1} \left\{ \rho^2 L_{(P)}^{(0,0)} \left[\frac{d\mathbf{p}}{dt} \right]^2 + \sum_{j,\,k=1}^{n} L_{(P)}^{(j,\,k)} \, \mathbf{E}^{(k)} \cdot \mathbf{E}^{(j)} + \right.$$

$$\left. + L^{(el,\,el)} \mathbf{E}^2 + T^{-2} L^{(q,\,q)} (\operatorname{grad} T)^2 + \eta_s \sum_{\alpha,\beta=1}^{3} \left[\frac{d\tilde{\varepsilon}_{\alpha\beta}}{dt} \right]^2 + 3\eta_v \left[\frac{d\varepsilon}{dt} \right]^2 \right\} \; . \tag{5.28}$$

From the nonnegative character of the entropy production it follows that the phenomenological coefficients satisfy inequalities as

$$L_{(P)}^{(0,0)} \geq 0 \; , \quad L_{(P)}^{(j,\,j)} \geq 0 \quad (j = 1,2,\cdots,n) \; , \tag{5.29}$$

$$L^{(el,\,el)} \geq 0 \; , \quad L^{(q,\,q)} \geq 0 \; , \quad \eta_s \geq 0, \; \eta_v \geq 0 \; . \tag{5.30}$$

In (5.28) the terms with $\left[\dfrac{d\mathbf{p}}{dt} \right]^2$ and $\mathbf{E}^{(k)} \cdot \mathbf{E}^{(j)}$ ($j = 1,2,\cdots,n$) are connected with entropy production due to dielectric relaxation, the terms with $\mathbf{E}^2$, $(\operatorname{grad} T)^2$ and $\left[\dfrac{d\tilde{\varepsilon}_{\alpha\beta}}{dt} \right]^2$ and $\left[\dfrac{d\varepsilon}{dt} \right]^2$ are due to the thermodynamic forces conjugate to the electric conduction, heat conduction and viscous flow, respectively.

6. The reference state and linear equations of state for isotropic media

The specific free energy f (free energy per unit of mass) is defined by

$$f = u - Ts . \tag{6.1}$$

Using the Gibbs relation (3.7) we obtain for the differential of f

$$df = -sdT + v \sum_{\alpha,\beta=1}^{3} \tau_{\alpha\beta}^{(eq)} d\varepsilon_{\alpha\beta} + \mathbf{E}^{(eq)} \cdot d\mathbf{p} - \sum_{k=1}^{n} \mathbf{E}^{(k)} \cdot d\mathbf{p}^{(k)} . \tag{6.2}$$

Because of (6.2) we have

$$s = -\frac{\partial}{\partial T} f(T, \varepsilon_{\alpha\beta}, \mathbf{p}, \mathbf{p}^{(1)}, \mathbf{p}^{(2)}, \cdots, \mathbf{p}^{(n)}) , \tag{6.3}$$

$$\tau_{\alpha\beta}^{(eq)} = \rho \frac{\partial}{\partial \varepsilon_{\alpha\beta}} f(T, \varepsilon_{\alpha\beta}, \mathbf{p}, \mathbf{p}^{(1)}, \mathbf{p}^{(2)}, \cdots, \mathbf{p}^{(n)}) , \tag{6.4}$$

$$\mathbf{E}^{(eq)} = \frac{\partial}{\partial \mathbf{p}} f(T, \varepsilon_{\alpha\beta}, \mathbf{p}, \mathbf{p}^{(1)}, \mathbf{p}^{(2)}, \cdots, \mathbf{p}^{(n)}) \tag{6.5}$$

and

$$\mathbf{E}^{(k)} = -\frac{\partial}{\partial \mathbf{p}^{(k)}} f(T, \varepsilon_{\alpha\beta}, \mathbf{p}, \mathbf{p}^{(1)}, \mathbf{p}^{(2)}, \cdots, \mathbf{p}^{(n)}) \quad (k = 1, \cdots, n) . \tag{6.6}$$

In (6.4) we also used the relation $v = \rho^{-1}$ (see (2.16)).

Next, we introduce the concept of reference state. Let T_0 and P_0 be arbitrary but fixed values of the temperature and the hydrostatic pressure, respectively. We now consider a state of the medium in which the temperature is uniform and has the constant value T_0 and the mechanical stress is given by $\tau_{\alpha\beta} = -P_0 \delta_{\alpha\beta}$, where also P_0 does not depend on position or time. Furthermore, we shall assume that the electric field $\mathbf{E}$ which occurs in Maxwell's equations vanishes in the medium. Such a state with specified temperature, mechanical stress and electric field may be obtained by suitable experimental arrangements.

We also require that the reference state is a state of thermodynamic equilibrium. In order to discuss this question we first note that $\tau_{\alpha\beta}^{(eq)}$, $\mathbf{E}^{(eq)}$ and $\mathbf{E}^{(1)}, \mathbf{E}^{(2)}, \cdots, \mathbf{E}^{(n)}$ are functions of the temperature T, the strain tensor $\varepsilon_{\alpha\beta}$ and the polarizations $\mathbf{p}, \mathbf{p}^{(1)}, \mathbf{p}^{(2)}, \cdots, \mathbf{p}^{(n)}$ (see (6.4)-(6.6)). It should be noted that $\rho = v^{-1}$ where v depends on the strain tensor (see, for instance, (2.16) and (2.19)). We now require that in the reference state the values $\mathbf{p}_0, \mathbf{p}_0^{(1)}, \mathbf{p}_0^{(2)}, \cdots, \mathbf{p}_0^{(n)}$ for the polarizations and the value $\varepsilon_{(0)\alpha\beta}$ for the strain tensor are such that

$$\tau_{\alpha\beta}^{(eq)}(T_0, \varepsilon_{(0)\alpha\beta}, \mathbf{p}_0, \mathbf{p}_0^{(1)}, \mathbf{p}_0^{(2)}, \cdots, \mathbf{p}_0^{(n)}) = -P_0 \delta_{\alpha\beta} , \tag{6.7}$$

$$\mathbf{E}^{(eq)}(T_0, \varepsilon_{(0)\alpha\beta}, \mathbf{p}_0, \mathbf{p}_0^{(1)}, \mathbf{p}_0^{(2)}, \cdots, \mathbf{p}_0^{(n)}) = 0 \tag{6.8}$$

and

$$\mathbf{E}^{(k)}(T_0, \varepsilon_{(0)\alpha\beta}, \mathbf{p}_0, \mathbf{p}_0^{(1)}, \mathbf{p}_0^{(2)}, \cdots, \mathbf{p}_0^{(n)}) = 0 \quad (k = 1, 2, \cdots, n) . \tag{6.9}$$

Since the tensor $\tau_{\alpha\beta}^{(eq)}$ is symmetric (6.7), (6.8) and (6.9) is a set of $3n + 9$ equations for the 6

independent components of the strain tensor $\varepsilon_{(0)\alpha\beta}$ and the $3(n+1)$ components of the polarization vectors $p_0, p_0^{(1)}, p_0^{(2)}, \cdots, p_0^{(n)}$.

We assumed that $E, E^{(eq)}, E^{(1)}, E^{(2)}, \cdots, E^{(n)}$ vanish in the reference state. Hence, $E^{(ir)} = E - E^{(eq)}$ (see (4.6)) also vanishes and the three last terms on the right-hand side of the expression (4.7) for the entropy production are zero. Since it is assumed that T is uniform $X^{(q)} = -T^{-1} \operatorname{grad} T$ vanishes and the second term on the right-hand side of (4.7) is also zero. Finally, the first term on the right-hand side of (4.7) is zero since $\tau_{\alpha\beta}^{(vi)} = \tau_{\alpha\beta} - \tau_{\alpha\beta}^{(eq)}$ (see (4.4)) and since we supposed that $\tau_{\alpha\beta}$ and $\tau_{\alpha\beta}^{(eq)}$ both equal $-P_0 \delta_{\alpha\beta}$. It is now seen from (4.7) that in the reference state there is no entropy production. Such a state is called a state of thermodynamic equilibrium.

We will measure the strain in an arbitrary state with respect to the reference state. Hence, in the reference state the strain is zero, i.e. $\varepsilon_{(0)\alpha\beta} = 0$. Furthermore, we shall make the physical assumption that the polarizations $p_0, p_0^{(1)}, p_0^{(2)}, \cdots, p_0^{(n)}$ vanish, i.e. in the reference state all polarizations vanish.

In order to obtain the dielectric relaxation equation illustrating the type of results to which the theory leads, we shall assume that in a first approximation the electric fields $E^{(eq)}$ and $E^{(j)}$ ($j = 1, 2, \cdots, n$) are linear functions of the polarizations $p, p^{(1)}, p^{(2)}, \cdots, p^{(n)}$. Except for the case of very strong fields such a linearization is usually permissible (see reference 10).

We postulate the following form for the specific free energy f of a dielectric medium

$$f = f^{(1)} + f^{(2)}, \tag{6.10}$$

where

$$f^{(1)} = f^{(1)}(T, \varepsilon_{\alpha\beta}) \tag{6.11}$$

and

$$f^{(2)} = \frac{1}{2} \rho \left[a_{(P)}^{(0,0)} \left\{ p \cdot \left[p - 2 \sum_{k=1}^{n} p^{(k)} \right] \right\} + \sum_{j,k=1}^{n} a_{(P)}^{(j,k)} p^{(j)} \cdot p^{(k)} \right]. \tag{6.12}$$

We will assume that in (6.12) the scalars $a_{(P)}^{(0,0)}$ and $a_{(P)}^{(j,k)}$ ($j, k = 1, 2, \cdots, n$) are constants and that

$$a_{(P)}^{(j,k)} = a_{(P)}^{(k,j)} \quad (j, k = 1, 2, \cdots, n). \tag{6.13}$$

Furthermore, we define the fields $P^{(0)}$ and $P^{(k)}$ ($k = 1, 2, \cdots, n$) by

$$P^{(0)} = \rho p^{(0)}, \quad P^{(k)} = \rho p^{(k)} \quad (k = 1, 2, \cdots, n). \tag{6.14}$$

From (3.1), (2.20) and (6.14) we now obtain

$$P = P^{(0)} + P^{(1)} + \cdots + P^{(n)}. \tag{6.15}$$

Using (2.20) and (6.10)-(6.15) we have from (6.5) and (6.6)

$$\mathbf{E}^{(eq)} = a_{(P)}^{(0,0)} \left[\mathbf{P} - \sum_{k=1}^{n} \mathbf{P}^{(k)} \right] = a_{(P)}^{(0,0)} \, \mathbf{P}^{(0)} \, , \tag{6.16}$$

$$\mathbf{E}^{(j)} = a_{(P)}^{(0,0)} \, \mathbf{P} - \sum_{k=1}^{n} a_{(P)}^{(j,k)} \, \mathbf{P}^{(k)} \qquad (j = 1,2, \cdots, n) \, . \tag{6.17}$$

The relations (6.16) and (6.17) are called equations of state. If the mass density ρ is constant the phenomenological equations (5.21) and (5.22) for the irreversible dielectric relaxation phenomena may be written in the form

$$\mathbf{E}^{(ir)} = L_{(P)}^{(0,0)} \, \frac{d\mathbf{P}}{dt} + \sum_{j=1}^{n} L_{(P)}^{(0,j)} \, \mathbf{E}^{(j)} \, , \tag{6.18}$$

$$\frac{d\mathbf{P}^{(j)}}{dt} = L_{(P)}^{(j,0)} \, \frac{d\mathbf{P}}{dt} + \sum_{i=1}^{n} L_{(P)}^{(j,i)} \, \mathbf{E}^{(i)} \qquad (j = 1,2, \cdots, n) \, , \tag{6.19}$$

where we have used (6.14) and (2.20).

7. Dielectric relaxation equation for isotropic linear media

In this section we shall discuss the dynamical constitutive equations for dielectric relaxation in isotropic media which follow from the theory if one assumes linear equations of state and constant phenomenological coefficients.

Using (4.6) the phenomenological equation (6.18) becomes

$$\mathbf{E} = \mathbf{E}^{(eq)} + L_{(P)}^{(0,0)} \frac{d\mathbf{P}}{dt} + \sum_{j=1}^{n} L_{(P)}^{(0,j)} \mathbf{E}^{(j)} . \tag{7.1}$$

With the aid of the linear equations of state (6.16) and (6.17) the equations (7.1) and (6.19) can be written in the following form

$$\sum_{k=1}^{n} c_k^{(1)} P_\alpha^{(k)} = Q_{(0,0)\alpha}^{(1)} , \tag{7.2}$$

$$\frac{dP_\alpha^{(j)}}{dt} + \sum_{k=1}^{n} h_{jk} P_\alpha^{(k)} = Q_{(j,0)\alpha} \quad (j = 1,2, \cdots, n) , \tag{7.3}$$

where

$$c_k^{(1)} = a_{(P)}^{(0,0)} + \sum_{j=1}^{n} L_{(P)}^{(0,j)} a_{(P)}^{(j,k)} \quad (k = 1,2, \cdots, n) , \tag{7.4}$$

$$h_{jk} = \sum_{i=1}^{n} L_{(P)}^{(j,i)} a_{(P)}^{(i,k)} \quad (j,k = 1,2, \cdots, n) , \tag{7.5}$$

$$Q_{(0,0)\alpha}^{(1)} = a_{(P)}^{(0,0)} \left[1 + \sum_{k=1}^{n} L_{(P)}^{(0,k)} \right] P_\alpha + L_{(P)}^{(0,0)} \frac{dP_\alpha}{dt} - E_\alpha , \tag{7.6}$$

$$Q_{(j,0)\alpha} = a_{(P)}^{(0,0)} \left[\sum_{k=1}^{n} L_{(P)}^{(j,k)} \right] P_\alpha + L_{(P)}^{(j,0)} \frac{dP_\alpha}{dt} \quad (j = 1,2, \cdots, n) . \tag{7.7}$$

It is seen that the mathematical structure of (7.2) and (7.3) is completely analogous to the structure of the equations (15.2) and (15.3) of reference 14, obtained in the thermodynamic theory for mechanical phenomena in continuous isotropic media. It is also seen that the definitions (7.4)-(7.7) are analogous to (15.4)-(15.7) of reference 14.

Using the same methods as in section 15 of reference 14, we shall show that it is possible to eliminate the partial polarization vectors (the internal degrees of freedom) from the differential equations (7.2) and (7.3), provided that the phenomenological coefficients are constants and the polarization vectors and the electric field vector have time derivatives of a sufficiently high order.

For this purpose, it is useful to introduce the following notations

$$\begin{cases} \dfrac{d^0 E_\alpha}{dt^0} = E_\alpha \,, \quad \dfrac{d^0 P_\alpha}{dt^0} = P_\alpha \,, \quad \dfrac{d^0 P_\alpha^{(j)}}{dt^0} = P_\alpha^{(j)} \quad (j = 1, 2, \cdots, n) \,, \\[3mm] \dfrac{d^0 Q_{(0,0)\alpha}^{(1)}}{dt^0} = Q_{(0,0)\alpha}^{(1)} \,, \quad \dfrac{d^0 Q_{(j,0)\alpha}}{dt^0} = Q_{(j,0)\alpha} \quad (j = 1, 2, \cdots, n) \,. \end{cases}$$

(7.8)

Furthermore, we define the following quantities

$$c_k^{(i+1)} = \sum_{j=1}^{n} c_j^{(i)} h_{jk} \qquad (i, k = 1, 2, \cdots, n) \,,$$

(7.9)

$$Q_{(0,m)\alpha}^{(1)} = \frac{d^m Q_{(0,0)\alpha}^{(1)}}{dt^m} =$$

$$= a_{(P)}^{(0,0)} \left[1 + \sum_{k=1}^{n} L_{(P)}^{(0,k)} \right] \frac{d^m P_\alpha}{dt^m} + L_{(P)}^{(0,0)} \frac{d^{m+1} P_\alpha}{dt^{m+1}} - \frac{d^m E_\alpha}{dt^m}$$

$$(m = 0, 1, \cdots, n) \,,$$

(7.10)

$$Q_{(j,m)\alpha} = \frac{d^m Q_{(j,0)\alpha}}{dt^m} =$$

$$= a_{(P)}^{(0,0)} \left[\sum_{k=1}^{n} L_{(P)}^{(j,k)} \right] \frac{d^m P_\alpha}{dt^m} + L_{(P)}^{(j,0)} \frac{d^{m+1} P_\alpha}{dt^{m+1}}$$

$$(j = 1, 2, \cdots, n \,; \; m = 0, 1, \cdots, n-1) \,,$$

(7.11)

and

$$Q_{(0,m)\alpha}^{(i+1)} = \sum_{j=1}^{n} c_j^{(i)} Q_{(j,m)\alpha} - Q_{(0,m+1)\alpha}^{(i)}$$

$$(i = 1, 2, \cdots, n \,; \; m = 0, 1, \cdots, n-i) \,.$$

(7.12)

In (7.10) and (7.11) we have used the definitions (7.6) and (7.7).

Using the same procedure as in section 15 of reference 14 we can obtain the set of equations

$$\sum_{k=1}^{n} c_k^{(j)} P_\alpha^{(k)} = Q_{(0,0)\alpha}^{(j)} \qquad (j = 1, 2, \cdots, n) \,,$$

(7.13)

$$\sum_{k=1}^{n} c_k^{(n)} \frac{dP_\alpha^{(k)}}{dt} = Q_{(0,1)\alpha}^{(n)} \,,$$

(7.14)

$$\frac{dP_\alpha^{(j)}}{dt} + \sum_{k=1}^{n} h_{jk} P_\alpha^{(k)} = Q_{(j,0)\alpha} \qquad (j = 1, 2, \cdots, n) \,.$$

(7.15)

These equations are analogous to the equations (15.16), (15.17) and (15.18), respectively, of section 15 of reference 14.

By multiplying both sides of (7.15) by $c_j^{(n)}$ and summing over j we obtain with the aid of (7.9), (7.14) and (7.12)

$$\sum_{k=1}^{n} c_k^{(n+1)} P_\alpha^{(k)} = Q_{(0,0)\alpha}^{(n+1)} \, . \tag{7.16}$$

Finally, (7.13) and (7.16) can be combined in the set

$$\sum_{k=1}^{n} c_k^{(j)} P_\alpha^{(k)} = Q_{(0,0)\alpha}^{(j)} \qquad (j = 1, 2, \cdots, n+1) \, . \tag{7.17}$$

This is a set of $3(n+1)$ equations for the $3n$ independent components of the partial polarizations $P_\alpha^{(1)}, P_\alpha^{(2)}, \cdots, P_\alpha^{(n)}$.

Next, we introduce the matrix C defined by

$$C = \begin{bmatrix} c_1^{(1)} & c_2^{(1)} & \cdots & c_n^{(1)} \\ c_1^{(2)} & c_2^{(2)} & \cdots & c_n^{(2)} \\ \cdots & \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots \\ c_1^{(n)} & c_2^{(n)} & \cdots & c_n^{(n)} \\ c_1^{(n+1)} & c_2^{(n+1)} & \cdots & c_n^{(n+1)} \end{bmatrix} \, . \tag{7.18}$$

If the rank of the matrix C is n, a necessary and sufficient condition for the solvability of the equations (7.17) is

$$\begin{vmatrix} c_1^{(1)} & c_2^{(1)} & \cdots & c_n^{(1)} & Q_{(0,0)\alpha}^{(1)} \\ c_1^{(2)} & c_2^{(2)} & \cdots & c_n^{(2)} & Q_{(0,0)\alpha}^{(2)} \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ c_1^{(n)} & c_2^{(n)} & \cdots & c_n^{(n)} & Q_{(0,0)\alpha}^{(n)} \\ c_1^{(n+1)} & c_2^{(n+1)} & \cdots & c_n^{(n+1)} & Q_{(0,0)\alpha}^{(n+1)} \end{vmatrix} = 0 \, . \tag{7.19}$$

In reference 14 it is demonstrated that the rank of the matrix C is n if and only if

$$\begin{vmatrix} c_1^{(1)} & c_2^{(1)} & \cdots & c_n^{(1)} \\ c_1^{(2)} & c_2^{(2)} & \cdots & c_n^{(2)} \\ \cdots & \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots \\ c_1^{(n)} & c_2^{(n)} & \cdots & c_n^{(n)} \end{vmatrix} \neq 0 \, . \tag{7.20}$$

Next, we apply the Cayley-Hamilton theorem to the matrix H (which is the $n \times n$ matrix with elements h_{ij} defined by (7.5)). This theorem states that a square matrix satisfies its characteristic equation. Thus, we have

$$H^n + h_1 H^{n-1} + \cdots + h_{n-1} H + h_n E = 0. \tag{7.21}$$

In (7.21) E is the $n \times n$ unit matrix and the coefficients h_i $(i = 0,1, \cdots, n)$ are homogeneous polynomials of degree i in the elements h_{ij}, $(i, j = 1,2, \cdots, n)$.

In particular,

$$h_0 = 1, \qquad h_1 = -\sum_{i=1}^{n} h_{ii}, \tag{7.22}$$

and

$$h_n = (-1)^n \det h_{ij} = (-1)^n \begin{vmatrix} h_{11} & h_{12} & \cdots & h_{1n} \\ h_{21} & h_{22} & \cdots & h_{2n} \\ \cdots & \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots \\ h_{n1} & h_{n2} & \cdots & h_{nn} \end{vmatrix}. \tag{7.23}$$

The relations (7.22) and (7.23) become with the aid of (7.5)

$$h_1 = -\sum_{i,j=1}^{n} L_{(P)}^{(j,i)} a_{(P)}^{(i,j)}, \tag{7.24}$$

$$h_n = (-1)^n (\det L_{(P)}^{(i,j)})(\det a_{(P)}^{(i,j)}). \tag{7.25}$$

We assume that

$$\det a_{(P)}^{(i,j)} = \begin{vmatrix} a_{(P)}^{(1,1)} & a_{(P)}^{(1,2)} & \cdots & a_{(P)}^{(1,n)} \\ a_{(P)}^{(2,1)} & a_{(P)}^{(2,2)} & \cdots & a_{(P)}^{(2,n)} \\ \cdots & \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots \\ a_{(P)}^{(n,1)} & a_{(P)}^{(n,2)} & \cdots & a_{(P)}^{(n,n)} \end{vmatrix} \neq 0 \tag{7.26}$$

and that

$$\det L_{(P)}^{(i,j)} = \begin{vmatrix} L_{(P)}^{(1,1)} & L_{(P)}^{(1,2)} & \cdots & L_{(P)}^{(1,n)} \\ L_{(P)}^{(2,1)} & L_{(P)}^{(2,2)} & \cdots & L_{(P)}^{(2,n)} \\ \cdots & \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots \\ L_{(P)}^{(n,1)} & L_{(P)}^{(n,2)} & \cdots & L_{(P)}^{(n,n)} \end{vmatrix} > 0. \tag{7.27}$$

The latter inequality holds because of the positive definite character of the entropy production. One has $\det L_{(P)}^{(i,j)} = 0$ if one or more of the n irreversible phenomena which give rise to dielectric relaxation do not occur. For example, if $L_{(P)}^{(1,j)} = 0$ $(j = 1,2, \cdots, n)$, i.e. if the first of these phenomena does not occur.

By applying the same procedure as used in reference 14, we obtain the following equation which is analogous to equation (15.30) of reference 14.

$$\sum_{m=0}^{n} (-1)^m h_{n-m} Q^{(1)}_{(0,m)\alpha} +$$

$$+ \sum_{m=0}^{n-1} (-1)^m \left[\sum_{i=m+1}^{n} h_{n-i} \left\{ \sum_{j=1}^{n} c_j^{(i-m)} Q_{(j,m)\alpha} \right\} \right] = 0 . \tag{7.28}$$

Let us multiply both sides of this relation by $(-1)^{n+1}$. Using the definitions (7.10) and (7.11) for $Q^{(1)}_{(0,m)\alpha}$ and $Q_{(j,m)\alpha}$ we then obtain after a rearrangement of terms

$$\sum_{m=0}^{n} (-1)^{m+n} h_{n-m} \frac{d^m E_\alpha}{dt^m} =$$

$$= a_{(P)}^{(0,0)} \sum_{m=0}^{n-1} (-1)^{m+n} \left\{ h_{n-m} \left[1 + \sum_{k=1}^{n} L_{(P)}^{(0,k)} \right] + \right.$$

$$\left. + \sum_{i=m+1}^{n} h_{n-i} \left[\sum_{j,k=1}^{n} c_j^{(i-m)} L_{(P)}^{(j,k)} \right] \right\} \frac{d^m P_\alpha}{dt^m} -$$

$$- \sum_{m=1}^{n} (-1)^{m+n} \left\{ h_{n-m+1} L_{(P)}^{(0,0)} + \sum_{i=m}^{n} h_{n-i} \left[\sum_{j=1}^{n} c_j^{(i-m+1)} L_{(P)}^{(j,0)} \right] \right\} \frac{d^m P_\alpha}{dt^m} +$$

$$+ a_{(P)}^{(0,0)} \left[1 + \sum_{k=1}^{n} L_{(P)}^{(0,k)} \right] \frac{d^n P_\alpha}{dt^n} + L_{(P)}^{(0,0)} \frac{d^{n+1} P_\alpha}{dt^{n+1}} . \tag{7.29}$$

The equation (7.29) represents the dielectric relaxation equation in the case of isotropic media. It is analogous to the relation (15.32) of reference 14 and it can be written in the following form

$$\chi_{(EP)}^{(0)} \mathbf{E} + \chi_{(EP)}^{(1)} \frac{d\mathbf{E}}{dt} + \cdots + \chi_{(EP)}^{(n-1)} \frac{d^{n-1}\mathbf{E}}{dt^{n-1}} + \frac{d^n \mathbf{E}}{dt^n} =$$

$$\chi_{(PE)}^{(0)} \mathbf{P} + \chi_{(PE)}^{(1)} \frac{d\mathbf{P}}{dt} + \cdots + \chi_{(PE)}^{(n)} \frac{d^n \mathbf{P}}{dt^n} + \chi_{(PE)}^{(n+1)} \frac{d^{n+1}\mathbf{P}}{dt^{n+1}} , \tag{7.30}$$

where $\chi_{(EP)}^{(k)}$ $(k = 0, 1, \cdots, n-1)$ and $\chi_{(PE)}^{(k)}$ $(k = 0, 1, \cdots, n+1)$ are constants. In particular,

$$\chi_{(EP)}^{(m)} = (-1)^{m+n} h_{n-m} \qquad (m = 0, 1, \cdots, n-1) , \tag{7.31}$$

$$\chi_{(PE)}^{(0)} = (-1)^n a_{(P)}^{(0,0)} \left\{ h_n \left[1 + \sum_{k=1}^{n} L_{(P)}^{(0,k)} \right] + \sum_{i=1}^{n} h_{n-i} \left[\sum_{j,k=1}^{n} c_j^{(i)} L_{(P)}^{(j,k)} \right] \right\} , \tag{7.32}$$

$$\chi_{(PE)}^{(n)} = a_{(P)}^{(0,0)} \left[1 + \sum_{k=1}^{n} L_{(P)}^{(0,k)} \right] - h_1 L_{(P)}^{(0,0)} - \sum_{j=1}^{n} c_j^{(1)} L_{(P)}^{(j,0)} , \tag{7.33}$$

$$\chi_{(PE)}^{(n+1)} = L_{(P)}^{(0,0)} \tag{7.34}$$

and, if $n \geq 2$,

$$\chi_{(PE)}^{(m)} = (-1)^{m+n} \left\{ a_{(P)}^{(0,0)} h_{n-m} \left[1 + \sum_{k=1}^{n} L_{(P)}^{(0,k)} \right] - h_{n-m+1} L_{(P)}^{(0,0)} + \right.$$

$$\left. + a_{(P)}^{(0,0)} \sum_{i=m+1}^{n} h_{n-i} \left[\sum_{j,k=1}^{n} c_j^{(i-m)} L_{(P)}^{(j,k)} \right] - \sum_{i=m}^{n} h_{n-i} \left[\sum_{j=1}^{n} c_j^{(i-m+1)} L_{(P)}^{(j,0)} \right] \right\} \tag{7.35}$$

$$(n \geq 2; m = 1, 2, \cdots, n-1) .$$

The equation (7.30) is the relation (14.4) of reference 9 which we wished to derive in this paper.

From (7.30) it follows that, if the linearization discussed in the preceding section is permissible (see reference 10) and if the rank of the matrix C is n (the case in which the rank of C is less than n is left out of consideration in this paper), there is a linear relation among E, the first n derivatives with respect to time of this vector, the polarization vector P and the first $n + 1$ derivatives with respect to time of P.

The relation (7.30) may be called relaxation equation or dynamical constitutive equation. If an electric field is suddenly applied to a dielectric for which the theory holds, there is no instantaneous response of the polarization.

It should also be noted that (7.28)-(7.35) are analogous to (15.30) and (15.32)-(15.38) of reference 14.

Finally, we may give a simplified expression for $\chi_{(PE)}^{(0)}$ and $\chi_{(EP)}^{(0)}$. Let us consider $\det a_{(P)}^{(i,j)}$ defined by (7.26) and let us denote by $A_{(P)}^{(j,k)}$ the $(n-1) \times (n-1)$ subdeterminant of $\det a_{(P)}^{(i,j)}$ which is conjugate to the element $a_{(P)}^{(j,k)}$.

Using the same procedure as in reference 14 the expression (7.32) for $\chi_{(PE)}^{(0)}$ and the expression for $\chi_{(EP)}^{(0)}$ obtained from (7.31) (in the case $m = 0$) can be written in the form

$$\chi_{(PE)}^{(0)} = a_{(P)}^{(0,0)} \left\{ \sum_{j,k=1}^{n} (a_{(P)}^{(i,k)} - a_{(P)}^{(0,0)})(-1)^{j+k} A_{(P)}^{(j,k)} \right\} \det L_{(P)}^{(j,k)} , \tag{7.36}$$

and

$$\chi_{(EP)}^{(0)} = (-1)^n h_n = (\det a_{(P)}^{(i,j)})(\det L_{(P)}^{(i,j)}) , \tag{7.37}$$

cf. (16.15) and (16.16) of reference 14.

If the medium is in a state of equilibrium, where the time derivatives of the electric field E and polarization vector P vanish, we have because of (7.30)

$$\chi_{(EP)}^{(0)} E = \chi_{(PE)}^{(0)} P , \tag{7.38}$$

or, with the aid of (7.36), (7.37) and (7.26), we have

$$E = a_{(P)}^{(0,0)} \left\{ 1 - \frac{a_{(P)}^{(0,0)}}{\det a_{(P)}^{(i,j)}} \sum_{j,\,k=1}^{n} (-1)^{j+k} A_{(P)}^{(j,k)} \right\} P .$$

(7.39)

We note that if the polarization P is defined by

$$P = P^{(0)} + P^{(1)} ,$$

(7.40)

(i.e. if we consider the case in which $n = 1$) the theory developed in this paper reduces to the theory given in reference 9.

8. The case in which the polarization is additively composed of a reversible and n irreversible parts

If we suppose that $E^{(ir)}$ vanishes, one obtains from (4.6)

$$E^{(eq)} = E .$$
(8.1)

Furthermore, the Gibbs relation (3.7) can then be written in the form

$$Tds = du - v \sum_{\alpha,\beta=1}^{3} \tau_{\alpha\beta}^{(eq)} d\varepsilon_{\alpha\beta} - E \cdot dp + \sum_{k=1}^{n} E^{(k)} \cdot dp^{(k)} ,$$
(8.2)

the expression (4.3) for the entropy production reduces to

$$\sigma^{(s)} = T^{-1} \left\{ \sum_{\alpha,\beta=1}^{3} \tau_{\alpha\beta}^{(vi)} \frac{d\varepsilon_{\alpha\beta}}{dt} + J^{(q)} \cdot X^{(q)} + j^{(el)} \cdot E + \rho \sum_{k=1}^{n} E^{(k)} \cdot \frac{dp^{(k)}}{dt} \right\}$$
(8.3)

and the linear equation of state (6.16) for isotropic media reads

$$E = a_{(P)}^{(0,0)} P^{(0)} .$$
(8.4)

From (8.3) it follows that changes in $P^{(0)} = \rho p^{(0)}$ are reversible processes because such changes do not contribute to the entropy production. From (8.4) it is seen that there corresponds an instantaneous change in $P^{(0)}$ to a sudden change of the electric field E. For this reason $P^{(0)}$ becomes the reversible (elastic) part of the polarization and $P^{(1)} + P^{(2)} + \cdots + P^{(n)}$ the irreversible part of the polarization.

Furthermore, from (5.21) and also from (6.18) it follows that $E^{(ir)}$ vanishes if and only if $L_{(P)}^{(0,0)}$ and $L_{(P)}^{(0,k)}$ vanish ($k = 1,2, \cdots, n$). Because of the Onsager-Casimir relations (5.26) we also have $L_{(P)}^{(k,0)} = 0$ for $k = 1,2, \cdots, n$. Thus, it is seen that the phenomenological equation (6.19) may be written in the form

$$\frac{dP^{(j)}}{dt} = \sum_{i=1}^{n} L_{(P)}^{(j,i)} E^{(i)} \qquad (j = 1,2, \cdots, n) .$$
(8.5)

The dynamical constitutive equation (7.30) becomes (see in particular (7.34))

$$\chi_{(EP)}^{(0)} E + \chi_{(EP)}^{(1)} \frac{dE}{dt} + \cdots + \chi_{(EP)}^{(n-1)} \frac{d^{n-1}E}{dt^{n-1}} + \frac{d^{n}E}{dt^{n}} =$$

$$= \chi_{(PE)}^{(0)} P + \chi_{(PE)}^{(1)} \frac{dP}{dt} + \cdots + \chi_{(PE)}^{(n)} \frac{d^{n}P}{dt^{n}} ,$$
(8.6)

where the expressions (7.34), (7.31), (7.36), (7.33) and (7.35) for the coefficients reduce to

$$\chi_{(PE)}^{(n+1)} = 0 ,$$
(8.7)

$$\chi_{(EP)}^{(m)} = (-1)^{m+n} h_{n-m} \qquad (m = 0,1, \cdots, n-1) ,$$
(8.8)

$$\chi_{(PE)}^{(0)} = a_{(P)}^{(0,0)} \left\{ \sum_{j,k=1}^{n} (a_{(P)}^{(i,k)} - a_{(P)}^{(0,0)})(-1)^{j+k} A_{(P)}^{(j,k)} \right\} \det L_{(P)}^{(j,k)} , \qquad (8.9)$$

$$\chi_{(PE)}^{(n)} = a_{(P)}^{(0,0)} , \qquad (8.10)$$

and, if $n \geq 2$,

$$\chi_{(PE)}^{(m)} = (-1)^{m+n} \left\{ a_{(P)}^{(0,0)} h_{n-m} + a_{(P)}^{(0,0)} \sum_{i=m+1}^{n} h_{n-i} \left[\sum_{j,k=1}^{n} c_j^{(i-m)} L_{(P)}^{(j,k)} \right] \right\}$$

$$(n \geq 2; m = 1, 2, \cdots, n-1) . \qquad (8.11)$$

This result is analogous to the results obtained in section 17 of reference 1 and in section 9 of reference 9.

9. The De Groot-Mazur theory

The theory developed in this paper reduces to the De Groot-Mazur theory in the limiting case in which the phenomenological coefficients $L_{(P)}^{(j,k)}$ and $L_{(P)}^{(j,0)} = -L_{(P)}^{(0,j)}$ (see 5.26)) vanish $(j, k = 1, 2, \cdots, n)$.

In this case we obtain from (5.22) and (6.19) that $\mathbf{p}^{(j)}$ and $\mathbf{P}^{(j)}$ $(j = 1, 2, \cdots, n)$ are constant vectors and we can assume that

$$\mathbf{p}^{(j)} = \mathbf{P}^{(j)} = 0 \qquad (j = 1, 2, \cdots, n) \tag{9.1}$$

(i.e. there are no internal vectorial degrees of freedom).

This case is completely analogous (with the same results) to the case discussed in section 8 of reference 9.

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