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ON DIELECTRIC RELAXATION EQUATION FOR ANISOTROPIC POLARIZABLE REACTING FLUID MIXTURES

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ABSTRACT. In this paper a linear theory for dielectric relaxation phenomena in polarizable reacting fluid mixtures is developed, in the frame of thermodynamics of irreversible processes with internal variables. The microscopic irreversible phenomena giving rise to dielectric relaxation are described splitting the total specific polarization in two irreversible parts and introducing one of these partial specific polarizations as internal variable in the thermodynamic state vector. The phenomenological equations for these fluid mixtures are derived and, in the linear case, a generalized Debye equation for dielectric relaxation phenomena is derived. Special cases are also treated. Linear theories for polarizable continuous media with dielectric relaxation phenomena were derived in the same frame of non-equilibrium thermodynamics with internal variables in previous papers by one of the authors (LR). A phenomenological theory for these phenomena was developed by Maugin for complex materials, using microscopic considerations and introducing particular partial polarizations per unit mass. The obtained results in this paper have applications in several fields of applied sciences, as, for instance, in medicine and biology, where complex fluids presenting dielectric relaxation, are constitued by different types of molecules, with own dielectric susceptibility and relaxation time.

1. Introduction

In Kluitenberg (1973, 1977, 1981), Restuccia and Kluitenberg (1987, 1988, 1990), Restuccia and Turrisi (1990), Ciancio and Restuccia (1990), Ciancio *et al.* (1990), Restuccia and Kluitenberg (1992, 1995), dielectric relaxation phenomena in polarizable media were studied using the standard methods of irreversible thermodynamics with internal variables (Prigogine 1947; MacDougall 1951; Meixner and Reik 1959; Prigogine 1961; De Groot and Mazur 1962; Kluitenberg 1984; Muschik and Restuccia 2006; Jou *et al.* 2010; Jou and Restuccia 2011). In particular, in Kluitenberg (1973), assuming that polarization P is given by the sum of one reversible part $P^{(0)}$ and one irreversible part $P^{(1)}$, Kluitenberg derived in the linear approximation, for polarizable isotropic media, the following *classical Debye equation* (Debye 1945)

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

where $\chi_{(\text{EP})}^{(0)}$, $\chi_{(\text{PE})}^{(0)}$ and $\chi_{(\text{PE})}^{(1)}$ are constant quantities, algebraic functions of the coefficients occurring in the phenomenological equations and in the equations of state. Subsequently, Kluitenberg (1977), assuming that the total polarization **P** is composed of two irreversible parts, i. e. $\mathbf{P} = \mathbf{P}^{(0)} + \mathbf{P}^{(1)}$, obtained the following dielectric relaxation equation

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

where $\chi^{(0)}_{(\text{EP})}$ and $\chi^{(k)}_{(\text{PE})}$ (k = 0, 1, 2) are constant quantities, algebraic functions of the coefficients occurring in the phenomenological equations and in the equations of state. In Restuccia and Kluitenberg (1988) it was assumed assumed that an arbitrary number *n* of microscopic phenomena give rise to the polarization vector **P** and that this vector can be split in n + 1 parts, i.e.

$$\boldsymbol{P} = \boldsymbol{P}^{(0)} + \sum_{k=1}^{n} \boldsymbol{P}^{(k)},$$
(3)

where $\mathbf{P}^{(0)}$ and $\mathbf{P}^{(0)}(k = 1,...,n)$ have irreversible character. In the isotropic case the following generalized Debye equation (Debye 1945) for dielectric relaxation phenomena was obtained, having the form of a linear relation among the electric field \mathbf{E} , the first *n* time derivatives of this field, the total polarization \mathbf{P} and the first n + 1 time derivatives of \mathbf{P}

$$\chi^{(0)}_{(\text{EP})}\boldsymbol{E} + \chi^{(1)}_{(\text{EP})}\frac{d\boldsymbol{E}}{dt} + \dots + \chi^{(n-1)}_{(\text{EP})}\frac{d^{n-1}\boldsymbol{E}}{dt^{n-1}} + \frac{d^{n}\boldsymbol{E}}{dt^{n}} = \chi^{(0)}_{(\text{PE})}\boldsymbol{M} + \chi^{(1)}_{(\text{PE})}\frac{d\boldsymbol{P}}{dt} + \dots + \chi^{(n)}_{(\text{PE})}\frac{d^{n}\boldsymbol{P}}{dt^{n}} + \chi^{(n+1)}_{(\text{PE})}\frac{d^{n+1}\boldsymbol{P}}{dt^{n+1}},$$
(4)

 $\chi_{(\text{PE})} \mathcal{H} + \chi_{(\text{PE})} \frac{1}{dt} + \dots + \chi_{(\text{PE})} \frac{1}{dt^n} + \chi_{(\text{PE})} \frac{1}{dt^{n+1}}, \quad (4)$ where *n* is the number of phenomena that give rise to the polarization **P** and $\chi_{(\text{EP})}^{(k)}, k =$ 0, 1, ..., n-1, and $\chi^{(k)}_{(\text{PE})}, k = 0, 1, ..., n+1$, are constant quantities, algebraic functions of the coefficients occurring in the phenomenological equations and in the equations of state. Here, we consider anisotropic polarizable reacting fluid mixtures, where irreversible microscopic phenomena give rise to dielectric relaxation, and these phenomena are described splitting the total polarization in two irreversible parts and introducing one of these partial polarizations as internal variable in the thermodynamic state vector, see Restuccia and Kluitenberg (1987), where magnetizable and polarizable reacting fluid mixtures were studied. In Sections 2 and 3, the model of the considered media and the governing equations all the processes inside them are presented, and the entropy balance equation is derived. In Sections 4, 5 and 6 the phenomenological equations, the Onsager-Casimir relations and the linear laws of state, with respect to a considered reference state, are obtained. In Section 7, in the linear case, a generalized Debye equation for dielectric relaxation phenomena in polarizable reacting fluid mixtures is derived. Finally, in Section 8 particular cases are treated. The obtained results have applications in several fields of applied sciences, as, for instance, in medicine and biology, where complex fluids are taken into consideration, in which different types of molecules, having different dielectric susceptibilities and relaxation tims, present dielectric relaxation phenomena and contribute to the total polarization. In Maugin (1976, 1977a,b, 1980, 1988) a phenomenological description of relaxation phenomena was given for polarizable continuous media with n different ionic species, by means of microscopic

considerations and introducing partial polarizations per unit mass. The continuum theory for polarizable bodies developed by Maugin gives an explanation to internal mechanisms in polarizable bodies with internal variables. In Restuccia *et al.* (2016) an analogous magnetic relaxation equation for anisotropic magnetizable reacting fluid mixtures was derived.

2. Fundamental equations

The Galilean approximation all the processes occurring inside polarizable fluid mixtures, consisting of *n* chemical components, among which *r* chemical reactions are possible, are governed by the balance equations and by Maxwell equations. The deformations and rotations of the considered media are supposed small from a kinematical point of view. The standard Cartesian tensor notation in a rectangular coordinate system is used and the equations governing the behaviour of these polarizable media are considered in a current configuration \mathcal{K}_t (De Groot and Mazur 1962; Restuccia and Kluitenberg 1987).

First, we consider the mass conservation balance law

$$\frac{\partial \rho}{\partial t} = -\operatorname{div}(\rho \boldsymbol{\nu}),\tag{5}$$

where ρ is the total mass density given by

$$\boldsymbol{\rho} = \sum_{k=1}^{n} \boldsymbol{\rho}^{(k)},\tag{6}$$

with $\rho^{(k)}$ the mass density of chemical component *k* and *v* the barycentric velocity defined by

$$\boldsymbol{\nu} = \frac{1}{\rho} \sum_{k=1}^{n} \rho^{(k)} \boldsymbol{\nu}^{(k)}, \tag{7}$$

being $\mathbf{v}^{(k)}$ the velocity of component k. By virtue of (7), Eq. (5) takes the following form

$$\frac{\partial \boldsymbol{\rho}}{\partial t} = -\operatorname{div}\left(\sum_{k=1}^{n} \boldsymbol{\rho}^{(k)} \boldsymbol{v}^{(k)}\right). \tag{8}$$

We define the mass fractions $c^{(k)}$ (or concentrations of *n* components) by

$$c^{(k)} = \frac{\rho^{(k)}}{\rho}, \quad k = 1, \dots, n,$$
 (9)

from which, using Eq. (6), one has

$$\sum_{k=1}^{n} c^{(k)} = 1.$$
 (10)

We introduce the diffusion flow $J_{(diff)}^{(k)}$ of substance k with respect to the barycentric motion by

$$\mathbf{J}_{(diff)}^{(k)} = \boldsymbol{\rho}^{(k)} (\mathbf{v}^k - \mathbf{v}), \quad k = 1, \dots, n,$$
(11)

from which, by virtue of (6) and (7), we derive

$$\sum_{k=1}^{n} \boldsymbol{J}_{(diff)}^{(k)} = 0, \tag{12}$$

i. e. only n-1 of the *n* diffusion flows are independent.

We have the following balance equations for $c^{(k)}$

$$\rho \frac{dc^{(k)}}{dt} = -\operatorname{div} \boldsymbol{J}_{(diff)}^{(k)} + \sum_{h=1}^{r} \boldsymbol{v}^{(kh)} \boldsymbol{J}_{(chem)}^{(h)}, \quad k = 1, \dots, n,$$
(13)

where the quantity $v^{(kh)}$, divided by the molecular mass $M^{(k)}$ of component *k*, is proportional to the stoichiometric coefficient with which the component *k* appears in the chemical reaction *h*, $J^{(h)}_{(chem)}$ is the chemical reaction rate of reaction *h*, and $v^{(kh)}J^{(h)}_{(chem)}$ is the production of component *k* per unit volume and unit time arising from the *h*-th chemical reaction.

Maxwell's equations (in the rationalized Gauss system) for polarizable media read

$$\operatorname{rot} \boldsymbol{H} - \frac{1}{c} \frac{\partial \boldsymbol{D}}{\partial t} = \frac{1}{c} \boldsymbol{I},$$

$$\operatorname{div} \boldsymbol{D} = \boldsymbol{\rho}^{(\mathrm{el})},$$

$$\operatorname{rot} \boldsymbol{E} + \frac{1}{c} \frac{\partial \boldsymbol{H}}{\partial t} = 0,$$

$$\operatorname{div} \boldsymbol{H} = 0,$$

(14)

where *c* is the speed of light, *E* is the electric field, *D* and *H* are the electric and magnetic displacement vectors, $\rho^{(el)}$ is the electric charge per unit volume (electric charge density), *I* is the density of the total electric current.

Introducing the total charge e per unit of mass of the system, given by

$$e = \frac{1}{\rho} \sum_{k=1}^{n} \rho^{(k)} e^{(k)} = \sum_{k=1}^{n} c^{(k)} e^{(k)}, \qquad (15)$$

with $e^{(k)}$ the charge per unit of mass of component k, where Eq. (9) was used, in (14)₂ we define $\rho^{(el)}$ by the expression

$$\rho^{(\text{el})} = \rho e = \sum_{k=1}^{n} \rho^{(k)} e^{(k)}, \qquad (16)$$

which satisfies the law of conservation of charge

$$\frac{\partial \rho^{(\text{el})}}{\partial t} = -\operatorname{div} \boldsymbol{I}.$$
(17)

In Eqs. $(14)_1$ and (17) *I* is defined by

$$I = \sum_{k=1}^{n} \rho^{(k)} e^{(k)} \mathbf{v}^{(k)}.$$
(18)

Using the definition (11) and Eq. (16), Eq. (18) can take the form

$$\boldsymbol{I} = \boldsymbol{\rho}^{(\text{el})} \boldsymbol{v} + \sum_{k=1}^{n} e^{(k)} \boldsymbol{J}^{(k)}_{(diff)}, \tag{19}$$

where $\rho^{(el)} \mathbf{v}$ is the electric current due to convection and $\sum_{k=1}^{n} e^{(k)} \mathbf{J}_{(diff)}^{(k)}$ represents the electric current due to relative motion of the various components, called conduction current

$$\mathbf{j}^{(el)} = \sum_{k=1}^{n} e^{(k)} \mathbf{J}^{(k)}_{(diff)}.$$
(20)

Let us define the polarization vector **P** by

$$\boldsymbol{P} = \boldsymbol{D} - \boldsymbol{E},\tag{21}$$

and the specific polarization vector \boldsymbol{p} by

$$\boldsymbol{p} = \frac{1}{\rho} \boldsymbol{P}.$$
 (22)

The first law of thermodynamics for polarizable fluid mixtures in an electromagnetic field, in Galilean approximation, reads

$$\rho \frac{du}{dt} = -\operatorname{div} \boldsymbol{J}^{(q)} + \tau_{\alpha\beta} \frac{d\boldsymbol{\varepsilon}_{\alpha\beta}}{dt} + \boldsymbol{j}^{(el)} \cdot \boldsymbol{E} + \rho \boldsymbol{E} \cdot \frac{d\boldsymbol{p}}{dt},$$
(23)

where *u* is the specific internal energy of the system, $J^{(q)}$ is the heat flow density, $\tau_{\alpha\beta}$ is the mechanical stress tensor and $\varepsilon_{\alpha\beta}$ is the small strain tensor.

If we suppose that the deformations and the rotations of the medium are small from a kinematical point of view, in a first approximation $\frac{d\varepsilon_{\alpha\beta}}{dt}$ is given by

$$\frac{d\varepsilon_{\alpha\beta}}{dt} = \frac{1}{2} \left(v_{\alpha,\beta} + v_{\beta,\alpha} \right), \quad \alpha,\beta = 1,2,3.$$
(24)

In Eq. (23) all the quantities are per unit of volume and per unit of time. On the right hand side of Eq. (23) the first term is the heat supply, the second term is the work done by mechanical stress, the third term is the Joule heat, $\rho E \cdot \frac{dp}{dt}$ is the work done by the electric field to change the polarization.

Let us introduce $A^{*(h)}$, the chemical affinity of the reaction *h*, and $\mu^{(k)}$, the thermodynamic or chemical potential of component *k*, by the relation

$$A^{*(h)} = \sum_{k=1}^{n} \mu^{(k)} \mathbf{v}^{(kh)}, \quad h = 1, \dots, r.$$
(25)

From Eq. (13) we obtain

$$\frac{\rho}{T} \sum_{k=1}^{n} \mu^{(k)} \frac{dc^{(k)}}{dt} = -\operatorname{div}\left(\sum_{k=1}^{n} \mu^{(k)} J^{(k)}_{(diff)}\right)$$
$$-\sum_{k=1}^{n} J^{(k)}_{(diff)} \cdot \operatorname{grad}\left(\frac{\mu^{(k)}}{T}\right) - \frac{1}{T} \sum_{h=1}^{r} A^{(h)} J^{(h)}_{(chem)},$$
(26)

where

$$\mathbf{A}^{(h)} = -\mathbf{A}^{*(h)}, \quad h = 1, \dots, r.$$
 (27)

By virtue of (20) the internal energy balance (23) reads

$$\rho \frac{du}{dt} = -div \boldsymbol{J}^{(q)} + \tau_{\alpha\beta} \frac{d\boldsymbol{\varepsilon}_{\alpha\beta}}{dt} + \sum_{k=1}^{n} e^{(k)} \boldsymbol{J}^{(k)}_{(diff)} \cdot \boldsymbol{E} + \rho \boldsymbol{E} \cdot \frac{d\boldsymbol{p}}{dt}.$$
 (28)

3. Entropy balance equation

Let us introduce the physical assumption that the total specific polarization is additevely composed of two irreversible parts, i.e.

$$\boldsymbol{p} = \boldsymbol{p}^{(0)} + \boldsymbol{p}^{(1)},$$

with $p^{(0)}$ and $p^{(1)}$ two partial specific polarizations describing irreversible microscopic phenomena, giving rise to dielectric relaxation. Furthermore, let us assume that the specific entropy *s* (i.e. the entropy per unit of mass) depends not only on the specific internal energy *u*, the small strain tensor $\varepsilon_{\alpha\beta}$, the concentrations $c^{(k)}$ of the *n* fluid components, k = 1, ..., n, and the specific polarization **p**, but also on $p^{(1)}$, which represents an internal variable, describing the dielectric relaxation phenomena. Hence, it is assumed

$$s = s\left(u, \varepsilon_{\alpha\beta}, \boldsymbol{p}, \boldsymbol{p}^{(1)}, c^{(1)}, \dots, c^{(n)}\right).$$
⁽²⁹⁾

Following the general philosophy of classical irreversible thermodynamics, dissipative fluxes, gradients and time derivatives of the physical fields are not included in the state space and for the system the local equilibrium hypotesis is assumed: out equilibrium each point of the system is considered as a thermodynamic cell of elementary volume, where the reversible thermodynamics is applicable. According to the reversible thermodynamics, we shall define the equilibrium temperature *T* (absolute temperature), the equilibrium stress tensor $\tau_{\alpha\beta}^{(eq)}$, the equilibrium electric field $E^{(eq)}$, the vectorial thermodynamic affinity $E^{(1)}$, conjugate to the internal variable $p^{(1)}$, and the thermodynamic or chemical potential $\mu^{(k)}$ of the component *k*, respectively, by

Considering very small deviations with respect to a thermodynamic equilibrium state, we expand the entropy (29) into Taylor's series with respect to this state, and confining our considerations to the liner terms, we obtain the differential of the entropy s in the following form

$$Tds = du - \frac{1}{\rho} \tau_{\alpha\beta}^{(\text{eq})} d\varepsilon_{\alpha\beta} - \boldsymbol{E}^{(\text{eq})} \cdot d\boldsymbol{p} + \boldsymbol{E}^{(1)} \cdot d\boldsymbol{p}^{(1)} - \sum_{k=1}^{n} \mu^{(k)} dc^{(k)}, \qquad (31)$$

where we have used Eqs. (30). Eq. (31) is called Gibbs relation.

Let us introduce the definitions of viscous stress tensor, $\tau_{\alpha\beta}^{(\mathrm{vi})}$, by

$$\tau_{\alpha\beta}^{(\mathrm{vi})} = \tau_{\alpha\beta} - \tau_{\alpha\beta}^{(\mathrm{eq})},\tag{32}$$

irreversible electric field, $\boldsymbol{E}^{(ir)}$, by

$$\boldsymbol{E}^{(\mathrm{ir})} = \boldsymbol{E} - \boldsymbol{E}^{(\mathrm{ir})},\tag{33}$$

and entropy flux, $J^{(s)}$, by

$$\mathbf{J}^{(s)} = \frac{1}{T} \left(\mathbf{J}^{(q)} = -\sum_{k=1}^{n} \mu^{(k)} \mathbf{J}^{(k)}_{(diff)} \right).$$
(34)

In (34) $J^{(s)}$ is the entropy flux which is additively composed of two parts: the "reduced" heat flux $\frac{J^{(q)}}{T}$ and the part connected with the diffusion flows $J^{(k)}_{(diff)}$, k = 1, ..., n. By eliminating the internal energy *u* from (23) and (31), using (26), (32)-(34), we obtain the following entropy balance equation

$$\rho \frac{ds}{dt} = -\operatorname{div} \boldsymbol{J}^{(s)} + \frac{1}{T} \left(-\frac{1}{T} \boldsymbol{J}^{(q)} \cdot \operatorname{grad} T + \tau_{\alpha\beta}^{(\operatorname{vi})} \frac{d\boldsymbol{\varepsilon}_{\alpha\beta}}{dt} + \rho \boldsymbol{E}^{(ir)} \cdot \frac{d\boldsymbol{p}}{dt} + \rho \boldsymbol{E}^{(1)} \cdot \frac{d\boldsymbol{p}^{(1)}}{dt} + \sum_{h=1}^{r} A^{(h)} J^{(h)}_{(chem)} \right) - \sum_{k=1}^{n} \boldsymbol{J}^{(k)}_{(diff)} \cdot \operatorname{grad} \left(\frac{\mu^{(k)}}{T} \right) + \frac{1}{T} \boldsymbol{j}^{(el)} \cdot \boldsymbol{E}.$$
(35)

Let us introduce the thermodynamic force $\boldsymbol{\chi}^{(k)}$, conjugate to $\boldsymbol{J}_{(diff)}^{(k)}$, by

$$\boldsymbol{\chi}^{(k)} = -\left[T \operatorname{grad}\left(\frac{\mu^{(k)}}{T}\right) - e^{(k)}\boldsymbol{E}\right], \quad k = 1, 2, ..., n,$$
(36)

and we write the following expression, obtained with the aid of Eqs. (12) and (20)

$$-\sum_{k=1}^{n} \boldsymbol{J}_{(diff)}^{(k)} \cdot \operatorname{grad}\left(\frac{\mu^{(k)}}{T}\right) + \frac{1}{T} \boldsymbol{j}^{(el)} \cdot \boldsymbol{E} = \frac{1}{T} \sum_{k=1}^{n} \boldsymbol{J}_{(diff)}^{(k)} \cdot \boldsymbol{\chi}^{(k)}$$
$$= \frac{1}{T} \sum_{k=1}^{n-1} \boldsymbol{J}_{(diff)}^{(k)} \cdot \left(\boldsymbol{\chi}^{(k)} - \boldsymbol{\chi}^{(n)}\right) = \frac{1}{T} \sum_{k=1}^{n-1} \boldsymbol{J}_{(diff)}^{(k)} \cdot \boldsymbol{\chi}^{(k)},$$
(37)

where we have called

$$\mathbf{X}^{(k)} = \mathbf{\chi}^{(k)} - \mathbf{\chi}^{(n)}, \quad k = 1, \dots, n-1.$$
 (38)

By virtue of (37), Eq. (35) takes the form

$$\rho \frac{ds}{dt} = -\operatorname{div} \boldsymbol{J}^{(s)} + \boldsymbol{\sigma}^{(s)}, \tag{39}$$

where $\sigma^{(s)}$ is given by

$$\boldsymbol{\sigma}^{(s)} = \frac{1}{T} \left(-\frac{1}{T} \boldsymbol{J}^{(q)} \cdot \operatorname{grad} T + \tau_{\alpha\beta}^{(\mathrm{vi})} \frac{d\boldsymbol{\varepsilon}_{\alpha\beta}}{dt} + \rho \boldsymbol{E}^{(ir)} \cdot \frac{d\boldsymbol{p}}{dt} \right)$$

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$$+\rho \boldsymbol{E}^{(1)} \cdot \frac{d\boldsymbol{p}^{(1)}}{dt} + \sum_{h=1}^{r} A^{(h)} J^{(h)}_{(chem)} + \sum_{k=1}^{n-1} \boldsymbol{J}^{(k)}_{(diff)} \cdot \boldsymbol{X}^{(k)} \bigg).$$
(40)

In (40) the entropy production $\sigma^{(s)}$ (a non-negative quantity) is zero if the system is in thermodynamic equilibrium. From (40) it is seen that the quantity contained in the brackets in $\sigma^{(s)}$ is additively composed of six contributions: the first term arises from heat conduction, the second is connected with the gradient of the velocity field giving rise to viscous effects, the terms with $\frac{d\mathbf{p}}{dt}$ and $\frac{d\mathbf{p}^{(1)}}{dt}$ are connected with entropy production due to dielectric relaxation, the last two terms are due to chemical reactions and diffusion of matter, respectively.

4. Phenomenological equations

From (40) it is seen that the expression contained in the brackets in $\sigma^{(s)}$ is a bilinear form composed of a sum of terms, where each term is the inner product of two factors of which one is a flux and the other is the thermodynamic force or "affinity" conjugate to the flux. Following the usual procedures of non-equilibrium thermodynamics (Prigogine 1947; MacDougall 1951; Meixner and Reik 1959; Prigogine 1961; De Groot and Mazur 1962; Kluitenberg 1984; Muschik and Restuccia 2006; Jou *et al.* 2010) we have for polarizable reacting fluid mixtures the following phenomenological equations in which the irreversible fluxes are linear functions of thermodynamic forces

$$E_{\alpha}^{(\mathrm{ir})} = \rho L_{(P)\alpha\beta}^{(0,0)} \frac{dp_{\beta}}{dt} + \rho L_{(P)\alpha\beta}^{(0,1)} E_{\beta}^{(1)} - \frac{1}{T} L_{(P)\alpha\beta}^{(0,q)} T_{,\beta} + \sum_{k=1}^{n-1} L_{(PD)\alpha\beta}^{(0,k)} X_{\beta}^{(k)} + \sum_{h=1}^{r} L_{(PC)\alpha}^{(0,h)} A^{(h)} + L_{(P)\alpha\beta\gamma}^{(0,vi)} \frac{d\varepsilon_{\beta\gamma}}{dt},$$
(41)

$$\rho \frac{dp_{\alpha}^{(1)}}{dt} = \rho L_{(P)\alpha\beta}^{(1,0)} \frac{dp_{\beta}}{dt} + L_{(P)\alpha\beta}^{(1,1)} E_{\beta}^{(1)} - \frac{1}{T} L_{(P)\alpha\beta}^{(1,q)} T_{,\beta} + \sum_{k=1}^{n-1} L_{(PD)\alpha\beta}^{(1,k)} X_{\beta}^{(k)} + \sum_{h=1}^{r} L_{(PC)\alpha}^{(1,h)} A^{(h)} + L_{(P)\alpha\beta\gamma}^{(1,v)} \frac{d\varepsilon_{\beta\gamma}}{dt},$$
(42)

$$J_{\alpha}^{(q)} = \rho L_{(P)\alpha\beta}^{(q,0)} \frac{dp_{\beta}}{dt} + L_{(P)\alpha\beta}^{(q,1)} E_{\beta}^{(1)} - \frac{1}{T} L_{\alpha\beta}^{(q,q)} T_{,\beta} + \sum_{k=1}^{n-1} L_{(D)\alpha\beta}^{(q,k)} X_{\beta}^{(k)} + \sum_{h=1}^{r} L_{(PC)\alpha}^{(0,h)} + L_{(P)\alpha\beta\gamma}^{(1,vi)} \frac{d\varepsilon_{\beta\gamma}}{dt},$$
(43)

$$J_{(diff)\alpha}^{(j)} = \rho L_{(DP)\alpha\beta}^{(j,0)} \frac{dp_{\beta}}{dt} + L_{(DP)\alpha\beta}^{(j,1)} \epsilon_{\beta}^{(1)} - \frac{1}{T} L_{(D)\alpha\beta}^{(j,q)} T_{,\beta} + \sum_{k=1}^{n-1} L_{(DD)\alpha\beta}^{(j,k)} X_{\beta}^{(k)} + \sum_{h=1}^{r} L_{(DC)\alpha}^{(j,h)} A^{(h)} + L_{(D)\alpha\beta\gamma}^{(j,v)} \frac{d\varepsilon_{\beta\gamma}}{dt}, \qquad j = 1, \dots, n-1,$$
(44)

$$J_{(chem)}^{(l)} = \rho L_{(CP)\beta}^{(l,0)} \frac{dp_{\beta}}{dt} + L_{(CP)\beta}^{(l,1)} E_{\beta}^{(1)} - \frac{1}{T} L_{(C)\beta}^{(l,q)} T_{,\beta} + \sum_{k=1}^{n-1} L_{(CD)\beta}^{(l,k)} X_{\beta}^{(k)} + \sum_{h=1}^{r} L_{(CC)}^{(l,h)} A^{(h)} + L_{(C)\beta\gamma}^{(l,v)} \frac{d\varepsilon_{\beta\gamma}}{dt}, \qquad l = 1, \dots, r,$$
(45)

$$\tau_{\alpha\beta}^{(\mathrm{vi})} = \rho L_{(P)\alpha\beta\gamma}^{(vi,0)} \frac{dp_{\gamma}}{dt} + L_{(P)\alpha\beta\gamma}^{(vi,1)} E_{\gamma}^{(1)} - \frac{1}{T} L_{\alpha\beta\gamma}^{(vi,q)} T_{\gamma} + \sum_{k=1}^{n-1} L_{(D)\alpha\beta\gamma}^{(vi,k)} X_{\gamma}^{(k)} + \sum_{h=1}^{r} L_{(C)\alpha\beta}^{(vi,h)} A^{(h)} + L_{\alpha\beta\gamma\delta}^{(vi,vi)} \frac{d\varepsilon_{\gamma\delta}}{dt}.$$
(46)

In Eqs. (41) and (42) $T_{,\beta} = \frac{\partial T}{\partial x^{\beta}}$ and $\alpha, \beta, \gamma = 1, 2, 3$.

Eqs. (41) and (42) are connected with irreversible changes in the polarization. Eqs. (43)-(45) describe the irreversible processes of heat flow, diffusion flow and chemical reactions. Eq. (46) is a generalization of Newton's law for viscous fluid flow.

The quantities $L_{(P)\alpha\beta}^{(0,0)}$, $L_{(P)\alpha\beta}^{(0,1)}$, $L_{(P)\alpha\beta}^{(0,q)}$,... which occur in (41)-(46) are called phenomenological tensors. For instance, $L_{\alpha\beta}^{(q,q)}$ is the thermal tensor, $L_{(P)\alpha\beta\gamma\delta}^{(v,vi)}$ is the viscosity tensor, $L_{(DD)\alpha\beta}^{(j,k)}$ (j,k = 1,2,...,n-1) is a polar tensor of order two connected with the diffusion flow of substance k, $L_{(CC)}^{(l,h)}$ is a scalar connected with the chemical affinity of the reaction h (l,h = 1,2,...,r), $L_{(P)\alpha\beta\gamma}^{(vi,0)}$ is a polar tensor of order three connected with the influence of the viscous flow on the dielectric relaxation. In principle, all irreversible phenomena described by (41)-(46) can influence each other. For instance, the third, fourth, fifth and sixth term on the right-hand sides of (41) and (42) describe the influences of heat flow, diffusion flow, chemical reactions and viscous flow on dielectric relaxation. Phenomena of this type are called cross effects. The strain tensor $\varepsilon_{\alpha\beta}$ is symmetric, then the equilibrium stress tensor $\tau_{\alpha\beta}^{(eq)}$ is also symmetric (see (30)₂). Hence, it follows that the viscous stress $\tau_{\alpha\beta}^{(vi)}$ is also a symmetric tensor (see (32)).

Because of the symmetry of $\varepsilon_{\alpha\beta}$ and $\tau_{\alpha\beta}^{(vi)}$ one has

$$\begin{split} L^{(0,vi)}_{(P)\alpha\beta\gamma} &= L^{(0,vi)}_{(P)\alpha\gamma\beta}, \qquad L^{(1,vi)}_{(P)\alpha\beta\gamma} = L^{(1,vi)}_{(P)\alpha\gamma\beta}, \qquad L^{(q,vi)}_{(P)\alpha\beta\gamma} = L^{(q,vi)}_{(P)\alpha\gamma\beta}, \\ L^{(vi,1)}_{(P)\alpha\beta\gamma} &= L^{(vi,1)}_{(P)\beta\alpha\gamma}, \qquad L^{(vi,q)}_{\alpha\beta\gamma} = L^{(vi,q)}_{\beta\alpha\gamma}, \qquad L^{(vi,0)}_{(P)\alpha\beta\gamma} = L^{(vi,0)}_{(P)\beta\alpha\gamma}, \\ L^{(l,vi)}_{(C)\alpha\beta} &= L^{(l,vi)}_{(C)\beta\alpha}, \qquad L^{(vi,h)}_{(C)\alpha\beta} = L^{(vi,h)}_{(C)\beta\alpha} \quad (l,h=1,2,\ldots,r), \\ L^{(j,vi)}_{(D)\alpha\beta\gamma} &= L^{(j,vi)}_{(D)\alpha\gamma\beta}, \qquad L^{(vi,k)}_{(D)\alpha\beta\gamma} = L^{(vi,k)}_{(D)\beta\alpha\gamma} \quad (j,k=1,2\ldots,n-1), \\ L^{(vi,vi)}_{\alpha\beta\gamma\delta} &= L^{(vi,vi)}_{\beta\alpha\gamma\delta} = L^{(vi,vi)}_{\beta\alpha\gamma\delta}. \end{split}$$

Furthermore, $\boldsymbol{E}^{(ir)}$, $\boldsymbol{E}^{(i)}$, $A^{(h)}$ (h = 1, 2, ..., r), $T^{-1} \operatorname{grad} T$, $\boldsymbol{X}^{(k)}$ (k = 1, 2, ..., n - 1), $\tau_{\alpha\beta}^{(\mathrm{vi})}$ are even functions of the microscopic particle velocities, while $\rho \frac{d\boldsymbol{p}}{dt}$, $\rho \frac{d\boldsymbol{p}^{(1)}}{dt}$, $\boldsymbol{J}^{(q)}$,

 $J_{(diff)}^{(k)}$ $(k = 1, 2, ..., n-1), J^{(l)}$ $(l = 1, 2, ..., r), \frac{d\varepsilon_{\alpha\beta}}{dt}$ are odd functions of these velocities. Hence, according to the usual procedure of non-equilibrium thermodynamics, we have for the phenomenological tensors, which occur in (41)-(46), the following Onsager-Casimir reciprocity relations

$$\begin{split} L_{(P)\alpha\beta}^{(0,0)} &= L_{(P)\beta\alpha}^{(0,0)}, \quad L_{(P)\alpha\beta}^{(1,1)} = L_{(P)\beta\alpha}^{(1,1)}, \quad L_{(P)\alpha\beta}^{(q,q)} = L_{(P)\beta\alpha}^{(q,q)}, \\ L_{(P)\alpha\beta}^{(0,1)} &= -L_{(P)\beta\alpha}^{(1,0)}, \quad L_{(P)\alpha\beta}^{(0,q)} = -L_{(P)\beta\alpha}^{(0,q)}, \\ L_{(PD)\alpha\beta}^{(0,k)} &= -L_{(DP)\beta\alpha}^{(k,0)}, \quad L_{(DD)\alpha\beta}^{(j,k)} = L_{(DD)\alpha}^{(k,j)}, \quad (j = 1, 2, \dots, n - 1), \\ L_{(PC)\alpha}^{(0,k)} &= -L_{(CP)\alpha}^{(k,0)}, \quad L_{(DC)\alpha}^{(j,k)} = -L_{(CD)\alpha}^{(v,k)}, \quad (k = 1, 2, \dots, n - 1), \\ L_{(PD)\alpha\beta}^{(1,q)} &= L_{(DP)\alpha\beta}^{(k,1)}, \quad L_{(D)\alpha\beta\gamma}^{(k,v)} = -L_{(D)\beta\alpha}^{(v,k)}, \quad (k = 1, 2, \dots, n - 1), \\ L_{(PC)\alpha}^{(1,q)} &= L_{(DP)\alpha\beta}^{(k,1)}, \quad L_{(D)\alpha\beta\gamma}^{(q,k)} = L_{(D)\beta\alpha}^{(q,k)}, \quad (k = 1, 2, \dots, n - 1), \\ L_{(PC)\alpha}^{(1,q)} &= L_{(CP)\alpha}^{(k,1)}, \quad L_{(CC)}^{(k,1)} = L_{(CC)}^{(v,k)}, \quad (l, h = 1, 2, \dots, r), \\ L_{(C)\alpha}^{(q,h)} &= L_{(C)\alpha}^{(h,q)}, \quad L_{(C)\alpha\beta}^{(h,v)} = -L_{(C)\beta\alpha}^{(v,h)}, \quad (l, h = 1, 2, \dots, r), \\ L_{(P)\alpha\beta\gamma}^{(q,h)} &= L_{(P)\beta\gamma\alpha}^{(v,0)}, \quad L_{(P)\alpha\beta\gamma}^{(1,v)} = -L_{(P)\beta\gamma\alpha}^{(v,1)}, \\ L_{(P)\alpha\beta\gamma}^{(0,v)} &= L_{(P)\beta\gamma\alpha}^{(v,0)}, \quad L_{(P)\alpha\beta\gamma}^{(1,v)} = -L_{(P)\beta\gamma\alpha}^{(v,1)}, \\ L_{(P)\alpha\beta\gamma}^{(1,v)} &= L_{(P)\beta\gamma\alpha}^{(1,v)}$$

$$L^{(\mathbf{q},\mathbf{v}\mathbf{i})}_{\alpha\beta\gamma} = -L^{(\mathbf{v}\mathbf{i},\mathbf{q})}_{\beta\gamma\alpha}, \quad L^{(\mathbf{v}\mathbf{i},\mathbf{v}\mathbf{i})}_{\alpha\beta\gamma\delta} = L^{(\mathbf{v}\mathbf{i},\mathbf{v}\mathbf{i})}_{\gamma\delta\alpha\beta}.$$
(48)

The relations (47) and (48) reduce the number of independent components of the phenomenological coefficients.

If one substitutes the phenomenological laws (41) - (46) in the expression (40) for the entropy production, taking into account (47) and (48), one derives for the entropy production a form, that is a positive definite quadratic form, and from its positive definite character several inequalities may be derived for the components of the phenomenological coefficients. For instance we obtain

$$L_{(P)\alpha\alpha}^{(0,0)} \ge 0, \quad L_{(P)\alpha\alpha}^{(1,1)} \ge 0, \qquad L_{(DD)}^{(jj)} (j = 1, 2, \dots, n-1) \ge 0,$$
(49)
$$L_{\alpha\alpha}^{(q,q)} \ge 0, \quad L_{(CC)}^{(hh)} (h = 1, 2, \dots, r) \ge 0, \quad L_{\alpha\beta\alpha\beta}^{(vi,vi)} \ge 0.$$

Also, by virtue of symmetry and Onsager-Casimir relations we have

(1)

$$L_{\alpha\beta\beta\alpha}^{(vi,vi)} \ge 0, \quad L_{\beta\alpha\alpha\beta}^{(vi,vi)} \ge 0, \quad L_{\beta\alpha\beta\alpha}^{(vi,vi)} \ge 0.$$
(50)

In the following, we will assume that in the phenomenological equations (41)-(46), all cross effects are neglected, except for possible cross effects among the different types of dieletric relaxation phenomena, and, then, we have

$$E_{\alpha}^{(ir)} = L_{(P)\alpha\beta}^{(0,0)} \frac{dP_{\beta}}{dt} + L_{(P)\alpha\beta}^{(0,1)} E_{\beta}^{(1)},$$
(51)

$$\frac{dP_{\alpha}^{(1)}}{dt} = L_{(P)\alpha\beta}^{(1,0)} \frac{dP_{\beta}}{dt} + L_{(P)\alpha\beta}^{(1,1)} E_{\beta}^{(1)},$$
(52)

$$\tau_{\alpha\beta}^{(\nu i)} = L_{\alpha\beta\gamma\zeta}^{(\nu i,\nu i)} \frac{d\varepsilon_{\gamma\zeta}}{dt},\tag{53}$$

$$J_{\alpha}^{(q)} = -\frac{1}{T} L_{\alpha\beta}^{(q,q)} T_{,\beta},$$
 (54)

$$J_{(\text{diff})\alpha}^{(j)} = \sum_{k=1}^{n-1} L_{(\text{DD})\alpha\beta}^{(j,k)} X_{\beta}^{(k)}$$
(55)
(j = 1,...,n-1),

$$J_{(\text{chem})}^{(l)} = \sum_{h=1}^{r} L_{(\text{CC})}^{(l,h)} A^{(h)}$$
(56)
$$(l = 1, r)$$

Eq. (54) is Fourier's law for the heat flux.

5. Reference state and thermodynamic equilibrium state

Now, let us consider a reference state of the medium (indicated by the symbol "₍₀₎"), and we require that it is also a state of thermodynamic equilibrium. Let us suppose that in this reference state we have an arbitrary (but fixed) uniform temperature $T_{(0)}$, the concentrations $c^{(k)}$, k = 1, ..., n, of the components of the fluid mixtures assume the fixed values $c_{(0)}^{(k)}$ and the mechanical stress tensor $\tau_{\alpha\beta}$ and the electric field \boldsymbol{E} vanish in the medium. We notice that $\tau_{\alpha\beta}^{(eq)}$, $\boldsymbol{E}^{(eq)}$ and $\boldsymbol{E}^{(1)}$ are functions of the temperature $T_{(0)}$, of the strain tensor $\varepsilon_{\alpha\beta}$, the polarizations \boldsymbol{p} and $\boldsymbol{p}^{(1)}$ and the concentrations $c_{(0)}^{(k)}$. We require that in this state the value $\varepsilon_{(0)\alpha\beta}$ for the strain tensor and the values $\boldsymbol{p}_{(0)}$ and $\boldsymbol{p}_{(0)}^{(1)}$ for the polarization vectors are such that

$$\tau_{\alpha\beta}^{(eq)}\left(T_{(0)}, \varepsilon_{(0)\,\alpha\beta}, \boldsymbol{p}_{(0)}, \boldsymbol{p}_{(0)}^{(1)}, c_{(0)}^{(1)}, \dots, c_{(0)}^{(n)}\right) = 0,\tag{57}$$

$$\boldsymbol{E}^{(eq)}\left(T_{(0)}, \boldsymbol{\varepsilon}_{(0)\,\alpha\beta}, \boldsymbol{p}_{(0)}, \boldsymbol{p}_{(0)}^{(1)}, c_{(0)}^{(1)}, \dots, c_{(0)}^{(n)}\right) = 0,\tag{58}$$

$$\boldsymbol{E}^{(1)}\left(T_{(0)}, \boldsymbol{\varepsilon}_{(0)\,\alpha\beta}, \boldsymbol{p}_{(0)}, \boldsymbol{p}_{(0)}^{(1)}, c_{(0)}^{(1)}, \dots, c_{(0)}^{(n)}\right) = 0,\tag{59}$$

$$\mu^{(k)}\left(T_{(0)}, \boldsymbol{\varepsilon}_{(0)\,\alpha\beta}, \boldsymbol{p}_{(0)}, \boldsymbol{p}_{(0)}^{(1)}, \boldsymbol{c}_{(0)}^{(1)}, \dots, \boldsymbol{c}_{(0)}^{(n)}\right) = 0,$$

$$k = 1, \dots, n. \tag{60}$$

Being the tensor $\tau_{\alpha\beta}^{(eq)}$ symmetric, Eqs. (57)-(60) form a set of 12 + n equations for the values of the 6 independent components of the symmetric strain tensor $\varepsilon_{(0)\alpha\beta}$, the values of the 6 components of the vectors $\boldsymbol{p}_{(0)}$ and $\boldsymbol{p}_{(0)}^{(1)}$ and the *n* concentrations $c_0^{(k)}$ (k = 1, 2, ..., n). We choose the tensor $\varepsilon_{\alpha\beta}$ and the vectors \boldsymbol{p} , $\boldsymbol{p}^{(1)}$, so that they vanish in the reference state. Thus, $\varepsilon_{(0)\alpha\beta} = 0$, $p_{(0)\alpha} = p_{(0)\alpha}^{(1)} = 0$. Furthermore, we choose

for
$$T = T_{(0)}$$
, $\varepsilon_{(0)\alpha\beta} = 0$, $p_{(0)\alpha} = p_{(0)\alpha}^{(1)} = 0$, $c^{(k)} = c_{(0)}^{(k)}$ $(k = 1, ..., n)$. (61)

A medium is in a state of thermodynamic equilibrium if the entropy production (40) vanishes. It follows that the reference state is a state of thermodynamic equilibrium, provided that $\varepsilon_{\alpha\beta}$ and the vectors $\boldsymbol{p}_{(0)}$ and $\boldsymbol{p}^{(1)}$ (determined by (57)-(59)) are kept constant. In our case they are chosen equal to zero. Moreover, the electric field must be kept vanishing in this state of thermodynamic equilibrium (see 36) where we assume that there are not chemical reactions. By virtue of phenomenological equation (46), the viscous stress tensor $\tau_{\alpha\beta}^{(vi)}$ vanishes in the thermodynamic equilibrium and hence $\tau_{\alpha\beta} = \tau_{\alpha\beta}^{(eq)}$. Finally, because in the reference state the medium has uniform temperature $T_{(0)}$, the term grad T vanishes in this state.

6. Linear equations of state for anisotropic polarizable reacting fluid mixtures

Let us introduce the specific free energy f, defined by f = u - Ts. Using Gibbs relation (31), we obtain the following expression for the differential of f,

$$df = -sdT + v\tau_{\alpha\beta}^{(eq)}d\boldsymbol{\varepsilon}_{\alpha\beta} + \boldsymbol{E}^{(eq)} \cdot d\boldsymbol{p} - \boldsymbol{E}^{(1)} \cdot d\boldsymbol{p}^{(1)} + \sum_{k=1}^{n} \boldsymbol{\mu}^{(k)}d\boldsymbol{c}^{(k)}.$$
 (62)

The following definitions are valid

$$s = -\frac{\partial}{\partial T} f\left(T, \boldsymbol{\varepsilon}_{\alpha\beta}, \boldsymbol{p}, \boldsymbol{p}^{(1)}, c^{(1)}, \dots, c^{(n)}\right), \tag{63}$$

$$\tau_{\alpha\beta}^{(\text{eq})} = \rho \frac{\partial}{\partial \varepsilon_{\alpha\beta}} f\left(T, \varepsilon_{\alpha\beta}, \boldsymbol{p}, \boldsymbol{p}^{(1)}, c^{(1)}, \dots, c^{(n)}\right), \tag{64}$$

$$\boldsymbol{E}^{(eq)} = \frac{\partial}{\partial \boldsymbol{p}} f\left(T, \boldsymbol{\varepsilon}_{\alpha\beta}, \boldsymbol{p}, \boldsymbol{p}^{(1)}, c^{(1)}, \dots, c^{(n)}\right), \tag{65}$$

$$\boldsymbol{E}^{(1)} = -\frac{\partial}{\partial \boldsymbol{p}^{(1)}} f\left(T, \boldsymbol{\varepsilon}_{\alpha\beta}, \boldsymbol{p}, \boldsymbol{p}^{(1)}, c^{(1)}, \dots, c^{(n)}\right),$$
(66)

$$\mu^{(k)} = \frac{\partial}{\partial c^{(k)}} f\left(T, \boldsymbol{\varepsilon}_{\alpha\beta}, \boldsymbol{p}, \boldsymbol{p}^{(1)}, c^{(1)}, \dots, c^{(n)}\right)$$

$$(k = 1, 2, \dots, n).$$
(67)

Now, we postulate the following form for the specific free energy f for polarizable anisotropic reacting fluid mixtures

$$f = f^{(1)} + f^{(2)}, (68)$$

where

$$f^{(1)} = v_{(0)} \left\{ \frac{1}{2} a_{\alpha\beta\gamma\zeta} \varepsilon_{\alpha\beta} \varepsilon_{\gamma\zeta} + a_{\alpha\beta} \varepsilon_{\alpha\beta} (T - T_{(0)}) \right\}$$

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$$+\sum_{k=1}^{n} b^{(k)} \left(c^{(k)} - c^{(k)}_{(0)}\right) (T - T_{(0)}) + \sum_{k=1}^{n} b^{(k)}_{\alpha\beta} \left(c^{(k)} - c^{(k)}_{(0)}\right) \varepsilon_{\alpha\beta} + \frac{1}{2} \sum_{i,k=1}^{n} b^{(i,k)} \left(c^{(i)} - c^{(i)}_{(0)}\right) \left(c^{(k)} - c^{(k)}_{(0)}\right) \right\} - \varphi(T),$$
(69)
$$f^{(2)} = \frac{1}{2} \rho_{(0)} \left\{a^{(0,0)}_{(P)\alpha\beta} p_{\alpha} \left(p_{\beta} - 2p^{(1)}_{\beta}\right) + a^{(1,1)}_{(P)\alpha\beta} p^{(1)}_{\alpha} p^{(1)}_{\beta}\right\} + (T - T_{(0)}) \left(a^{(0)}_{(P)\alpha} p_{\alpha} - a^{(1)}_{(P)\alpha} p^{(1)}_{\alpha}\right) + \sum_{k=1}^{n} \left(c^{(k)} - c^{(k)}_{(0)}\right) \left(b^{(0,k)}_{(P)\alpha} p_{\alpha} - b^{(1,k)}_{(P)\alpha} p^{(1)}_{\alpha}\right).$$
(70)

In (69)
$$v_{(0)}$$
 is the specific volume in the reference state, given by $v_{(0)} = \frac{1}{\rho_{(0)}}$, supposed constant, and in the following indicated by $v = \frac{1}{\rho}$, $\varphi(T)$ is some function of the temperature, $b^{(k)}$ are supposed to be constants and also $a_{\alpha\beta\gamma\zeta}$, $a_{\alpha\beta}$, $b^{(k)}_{\alpha\beta}$, $b^{(i,k)}$ are supposed to be constants and they satisfy the following symmetry relations

$$a_{\alpha\beta\gamma\zeta} = a_{\beta\alpha\gamma\zeta} = a_{\alpha\beta\zeta\gamma} = a_{\beta\alpha\zeta\gamma} = a_{\gamma\zeta\alpha\beta} = a_{\gamma\zeta\beta\alpha} = a_{\zeta\gamma\alpha\beta} = a_{\zeta\gamma\beta\alpha},$$

$$a_{\alpha\beta} = a_{\beta\alpha}, \quad b_{\alpha\beta}^{(k)} = b_{\beta\alpha}^{(k)} \quad b^{(i,k)} = b^{(k,i)} \quad (i,k=1,2,\dots,n).$$
(71)

In (70) the vectors $a_{(P)\alpha}^{(0)}$, $a_{(P)\alpha}^{(1)}$, $b_{(P)\alpha}^{(0,k)}$ and $b_{(P)\alpha}^{(1,k)}$ (k = 1, 2, ..., n) are supposed to be constants and also the tensors $a_{(P)\alpha\beta}^{(0,0)}$, $a_{(P)\alpha\beta}^{(1,1)}$ are supposed to be constants and they may be chosen so that they satisfy the following symmetry relations

$$a_{(P)\alpha\beta}^{(0,0)} = a_{(P)\beta\alpha}^{(0,0)}, \quad a_{(P)\alpha\beta}^{(1,1)} = a_{(P)\beta\alpha}^{(1,1)}.$$
(72)

The tensors present in (71) and (72) are determined by the physical properties of the medium in the reference state. From (63) and (68) - (72) the specific entropy takes the form

$$s = -\left\{a_{(\mathbf{P})}^{(0)} \alpha p_{\alpha} - a_{(\mathbf{P})}^{(1)} \alpha p_{\alpha}^{(1)} + \sum_{k=1}^{n} b^{(k)} \left(c^{(k)} - c_{(0)}^{(k)}\right)\right\} - v a_{\alpha\beta} \varepsilon_{\alpha\beta} + \frac{d\varphi}{dT}.$$
 (73)

From (64) and (68)-(71) we obtain for the equilibrium stress tensor the expression

$$\tau_{\alpha\beta}^{(eq)} = a_{\alpha\beta\gamma\zeta}\varepsilon_{\alpha\beta} + a_{\alpha\beta}(T - T_{(0)}) + \sum_{k=1}^{n} b_{\alpha\beta}^{(k)}\left(c^{(k)} - c_{(0)}^{(k)}\right).$$
(74)

Now, we define the fields $\boldsymbol{P}^{(0)}$ and $\boldsymbol{P}^{(1)}$ by

$$\boldsymbol{P}^{(0)} = \boldsymbol{\rho} \boldsymbol{p}^{(0)}$$
 and $\boldsymbol{P}^{(1)} = \boldsymbol{\rho} \boldsymbol{p}^{(1)}$. (75)

Finally, from (65), (66) and (68)-(72) we have the following equations of state

$$E_{\alpha}^{(eq)} = a_{(P)\alpha\beta}^{(0,0)} \left(P_{\beta} - P_{\beta}^{(1)} \right) + a_{(P)\alpha}^{(0)} (T - T_0) + \sum_{k=1}^{n} b_{(P)\alpha}^{(0,k)} \left(c^{(k)} - c_{(0)}^{(k)} \right), \tag{76}$$

$$E_{\alpha}^{(1)} = a_{(P)\alpha\beta}^{(0,0)} P_{\beta} - a_{(P)\alpha\beta}^{(1,1)} P_{\beta}^{(1)} + a_{(P)\alpha}^{(1)} (T - T_{(0)}) + \sum_{k=1}^{n} b_{(P)\alpha}^{(1,k)} \left(c^{(k)} - c_{(0)}^{(k)} \right),$$
(77)

$$\mu^{(k)} = v \left\{ b^{(k)} (T - T_{(0)}) + b^{(k)}_{\alpha\beta} \varepsilon_{\alpha\beta} + \sum_{i=1}^{n} b^{(i,k)} \left(c^{(i)} - c^{(i)}_{(0)} \right) + b^{(0,k)}_{(P)\alpha\beta} P_{\alpha} - b^{(1,k)}_{(P)\alpha} P^{(1)}_{\alpha} \right\}, \qquad k = 1, \dots, n.$$
(78)

7. Generalized Debye equation for anisotropic reacting fluid mixtures

(1)

(1)

Taking into account Eqs. (33), (76) and (77), Eqs. (51) and (52) may be written, respectively, in the form

$$c_{\alpha\beta}^{(1)} P_{\beta}^{(1)} = Q_{(0,0)\alpha}^{(1)}, \tag{79}$$

and

$$\frac{dP_{\beta}^{(1)}}{dt} + h_{\beta\gamma}P_{\gamma}^{(1)} = Q_{(1,0)\beta}.$$
(80)

In Eq. (79) we have

$$c_{\alpha\beta}^{(1)} = a_{(P)\alpha\beta}^{(0,0)} + L_{(P)\alpha\gamma}^{(0,1)} a_{(P)\gamma\beta}^{(1,1)},$$

$$Q_{(0,0)\alpha}^{(1)} = \left(a_{(P)\alpha\beta}^{(0,0)} + L_{(P)\alpha\gamma}^{(0,1)} a_{(P)\gamma\beta}^{(0,0)}\right) P_{\beta} + L_{(P)\alpha\beta}^{(0,0)} \frac{dP_{\beta}}{dt} - E_{\alpha} + \left(a_{(P)\alpha}^{(0)} + L_{(P)\alpha\beta}^{(0,0)} a_{(P)\alpha\beta}^{(0,0)}\right) \left(T - T_{(0)}\right) + \sum_{i=1}^{n} \left(b_{(P)\alpha}^{(0,k)} + L_{(P)\alpha\beta}^{(0,1)} b_{(P)\alpha}^{(1,k)}\right) \left(c_{i}^{(k)} - c_{i}^{(k)}\right).$$
(81)
$$(81)$$

$$+ L_{(P)\alpha\beta}^{(0,1)} a_{(P)\beta}^{(1)} \left(T - T_{(0)} \right) + \sum_{k=1}^{n} \left(b_{(P)\alpha}^{(0,k)} + L_{(P)\alpha\beta}^{(0,1)} b_{(P)\beta}^{(1,k)} \right) \left(c^{(k)} - c_{(0)}^{(k)} \right).$$
(82)

In Eq. (80) we have

$$h_{\beta\gamma} = L_{(P)\beta\eta}^{(1,1)} a_{(P)\eta\gamma}^{(1,1)} + L_{(P)\beta\gamma}^{(1,0)}$$
(83)

and

$$Q_{(1,0)\beta} = L_{(P)\beta\eta}^{(1,1)} a_{(P)\eta\gamma}^{(0,0)} P_{\gamma} + L_{(P)\beta\gamma}^{(1,0)} \frac{dP_{\gamma}}{dt} + L_{(P)\beta\gamma}^{(1,1)} a_{(P)\gamma}^{(1)} (T - T_{(0)}) + \sum_{k=1}^{n} L_{(P)\beta\gamma}^{(1,1)} b_{(P)\beta\eta}^{(1,k)} \left(c^{(k)} - c^{(k)}_{(0)} \right).$$
(84)

Assuming that the coefficients in (79) and (80) are constant, it follows from (79) that

$$c_{\alpha\beta}^{(1)} \frac{dP_{\beta}^{(1)}}{dt} = \frac{dQ_{(0,0)\alpha}^{(1)}}{dt}$$
(85)

provided that all derivatives exist in (85). Multiplying both sides of Eq. (80) by $c_{\alpha\beta}^{(1)}$ and summing over β , with the aid of (79), we obtain

$$c_{\alpha\beta}^{(1)}h_{\beta\gamma}P_{\gamma}^{(1)} = c_{\alpha\beta}^{(1)}Q_{(1,0)\beta} - \frac{dQ_{(0,0)\alpha}^{(1)}}{dt}$$
(86)

Assuming that it is possible to define the inverse matrix $(c_{\alpha\beta}^{(1)})^{-1}$, such that $(c_{\alpha\beta}^{(1)})^{-1}c_{\beta\gamma}^{(1)} = c_{\alpha\beta}^{(1)}(c_{\beta\gamma}^{(1)})^{-1} = \delta_{\alpha\gamma}$, using the expression for $\boldsymbol{P}^{(1)}$, given by (79), in (86), i.e.

$$P_{\alpha}^{(1)} = \left(c_{\alpha\beta}^{(1)}\right)^{-1} Q_{(0,0)\beta}^{(1)}, \tag{87}$$

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we get the following dielectric relaxation equation

$$\begin{aligned} \chi^{(0)}_{(\mathrm{EP})\,\alpha\beta} E_{\beta} + \frac{dE_{\alpha}}{dt} &= \chi^{(0)}_{(\mathrm{PE})\,\alpha\beta} P_{\beta} \chi^{(1)}_{(\mathrm{PE})\,\alpha\beta} \frac{dP_{\beta}}{dt} \\ &+ \chi^{(2)}_{(\mathrm{PE})\,\alpha\beta} \frac{d^2 P_{\beta}}{dt^2} + \chi^{(0)}_{(\mathrm{T})\,\alpha} (T - T_{(0)}) + \chi^{(1)}_{(\mathrm{T})\,\alpha} \frac{dT}{dt} \\ &+ \sum_{k=1}^{n} \chi^{(0,k)}_{(C)\,\alpha} \left(c^{(k)} - c^{(k)}_{(0)} \right) + \frac{d}{dt} \sum_{k=1}^{n} \chi^{(1,k)}_{(C)\,\alpha} \left(c^{(k)} - c^{(k)}_{(0)} \right), \end{aligned}$$
(88)

where

$$\boldsymbol{\chi}_{(EP)\alpha\beta}^{(0)} = c_{\alpha\gamma}^{(1)} h_{\gamma\zeta} \left(c_{\zeta\beta}^{(1)} \right)^{-1},$$

$$\chi^{(0)}_{(\rm PE)\,\alpha\beta} = c^{(1)}_{\alpha\gamma} \left\{ h_{\gamma\zeta} \left(c^{(1)}_{\zeta\eta} \right)^{-1} \left(a^{(0,0)}_{(P)\eta\beta} + L^{(0,1)}_{(P)\eta\mu} a^{(0,0)}_{(P)\mu\beta} \right) - L^{(1,1)}_{(P)\gamma\mu} a^{(0,0)}_{(P)\mu\beta} \right\},$$
(89)

$$\chi^{(1)}_{(\rm PE)} \alpha_{\beta} = c^{(1)}_{\alpha\gamma} \left\{ h_{\gamma\zeta} \left(c^{(1)}_{\zeta\eta} \right)^{-1} L^{(0,0)}_{(P)\eta\beta} - L^{(1,0)}_{(P)\gamma\beta} \right\} + a^{(0,0)}_{(P)\alpha\beta} + L^{(0,1)}_{(P)\alpha\eta} a^{(0,0)}_{(P)\eta\beta}$$
(90)

$$\chi^{(2)}_{(PE)\alpha\beta} = L^{0,0}_{(P)\alpha\beta}$$

$$\chi^{(0)}_{(T)\alpha} = c^{(1)}_{\alpha\gamma} \left\{ h_{\gamma\zeta} \left(c^{(1)}_{\zeta\eta} \right)^{-1} \left(a^{(0)}_{(P)\eta} + L^{(0,1)}_{(P)\eta\beta} a^{(1)}_{(P)\beta} \right) - L^{(1,1)}_{(P)\gamma\beta} a^{(1)}_{(P)\beta} \right\},\tag{91}$$

$$\chi^{(1)}_{(T)\alpha} = a^{(0)}_{(P)\alpha} + L^{(0,1)}_{(P)\alpha\beta} a^{(1)}_{(P)\beta},$$

$$\chi_{(C)\alpha}^{(0,k)} = c_{\alpha\gamma}^{(1)} \left\{ h_{\gamma\zeta} \left(c_{\zeta\eta}^{(1)} \right)^{-1} \left(b_{(P)\eta}^{(0,k)} + L_{(P)\eta\beta}^{(0,1)} b_{(P)\beta}^{(1,k)} \right) - L_{(P)\gamma\beta}^{(1,1)} b_{(P)\beta}^{(1,k)} \right\},$$
(92)
$$\chi_{(C)\alpha}^{(1,k)} = b_{(P)\alpha}^{(0,k)} + L_{(P)\alpha\beta}^{(0,1)} b_{(P)\beta}^{(1,k)}$$

Hence, it is seen that the linearization of the theory leads to a relaxation equation for anisotropic polarizable reacting fluid mixtures which has the form of a linear relation among the temperature, the concentrations of the n chemical components, the electric field, the total polarization, the first time derivatives of the temperature, the n concentrations, the electric field and of the total polarization, and the second derivative with respect to time of this last vector.

8. Particular cases

In this Section we derive two special cases, that for isotropic polarizable one component fluid reduce to *Debye relaxation equation* and *De Groot-Mazur relaxation equation*, respectively.

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8.1. Special case: $E = E^{(eq)}$. In the *special case* where $E = E^{(eq)}$, then $E^{(ir)}$ vanishes, and from (51) one gets

$$L^{(0,0)}_{(P)\alpha\beta} = 0, \text{ and } L^{(0,1)}_{(P)\alpha\beta} = -L^{(1,0)}_{(P)\beta\alpha} = 0.$$
 (93)

Hence, the dielectric relaxation equation (88) becomes

$$\chi^{(0)}_{(\mathrm{EP})\alpha\beta}E_{\beta} + \frac{dE_{\alpha}}{dt} = \chi^{(0)}_{(\mathrm{PE})\alpha\beta}P_{\beta} + \chi^{(1)}_{(\mathrm{PE})\alpha\beta}\frac{dP_{\beta}}{dt} + \chi^{(0)}_{(\mathrm{T})\alpha}(T - T_{(0)})$$

$$+\chi^{(1)}_{(\mathrm{T})\alpha}\frac{dT}{dt} + \sum_{k=1}^{n}\chi^{(0,k)}_{(C)\alpha}\left(c^{(k)} - c^{(k)}_{(0)}\right) + \frac{d}{dt}\sum_{k=1}^{n}\chi^{(1,k)}_{(C)\alpha}\left(c^{(k)} - c^{(k)}_{(0)}\right),\tag{94}$$

where

$$\chi^{(0)}_{(EP)\alpha\beta} = a^{(0,0)}_{(P)\alpha\gamma} L^{(1,1)}_{(P)\gamma\eta} a^{(1,1)}_{(P)\eta\zeta} \left(a^{(0,0)}_{(P)\zeta\beta}\right)^{-1},\tag{95}$$

$$\chi^{(0)}_{(PE)\alpha\beta} = a^{(0,0)}_{(P)\alpha\eta} L^{(1,1)}_{(P)\eta\gamma} \left(a^{(1,1)}_{(P)\gamma\beta} - a^{(0,0)}_{(P)\gamma\beta} \right), \quad \chi^{(1)}_{(PE)\alpha\beta} = a^{(0,0)}_{(P)\alpha\beta}, \tag{96}$$

$$\chi^{(0)}_{(T)\alpha} = a^{(0,0)}_{(P)\alpha\beta} L^{(1,1)}_{(P)\beta\gamma} \left\{ a^{(1,1)}_{(P)\gamma\eta} \left(a^{(0,0)}_{(P)\eta\zeta} \right)^{-1} a^{(0)}_{(P)\zeta} - a^{(1)}_{(P)\gamma} \right\},\tag{97}$$

$$\chi^{(1)}_{(\mathrm{T})\alpha} = a^{(0)}_{(\mathrm{P})\alpha},$$
 (98)

$$\chi^{(0,k)}_{(C)\alpha} = a^{(0,0)}_{(P)\alpha\beta} L^{(1,1)}_{(P)\beta\gamma} \left\{ a^{(1,1)}_{(P)\gamma\eta} \left(a^{(0,0)}_{(P)\eta\zeta} \right)^{-1} b^{(0,k)}_{(P)\zeta} - b^{(1,k)}_{(P)\gamma} \right\},\tag{99}$$

$$\chi^{(1,k)}_{(C)\alpha} = b^{(0,k)}_{(P)\alpha}$$

In the case where we have only a polarizable one component fluid (i. e. the *n* concentrations $c^k (k = 1, 2, ...n)$ are not present as independent variables in the thermodynamic state vector), Eq. (94) reduces to *Debye relaxation equation* for an anisotropic medium

$$\chi^{(0)}_{(\text{EP})\,\alpha\beta}E_{\beta} + \frac{dE_{\alpha}}{dt} = \chi^{(0)}_{(\text{PE})\,\alpha\beta}P_{\beta} + \chi^{(1)}_{(\text{PE})\,\alpha\beta}\frac{dP_{\beta}}{dt} + \chi^{(0)}_{(\text{T})\alpha}(T - T_{(0)}) + \chi^{(1)}_{(\text{T})\alpha}\frac{dT}{dt}, \quad (100)$$

where $\chi^{(0)}_{(\text{EP})\alpha\beta}$, $\chi^{(0)}_{(\text{PE})\alpha\beta}$, $\chi^{(1)}_{(\text{PE})\alpha\beta}$, $\chi^{(0)}_{(\text{T})\alpha}$, $\chi^{(1)}_{(\text{T})\alpha}$ are given by (95)-(98). Eq. (100) in the isotropic case, when the tensors $\boldsymbol{\chi}$, describing the properties of the system, have the form $\chi_{\alpha\beta} = \chi \delta_{\alpha\beta}$ and $\chi_{\alpha} = 0$, takes the form (1) (see Kluitenberg 1973).

In this case the polarization vector \boldsymbol{P} is composed of two parts $\boldsymbol{P} = \boldsymbol{P}^{(0)} + \boldsymbol{P}^{(1)}$, where the contribution $\boldsymbol{P}^{(0)}$ has reversible character and the contribution $\boldsymbol{P}^{(1)}$ has irreversible character.

8.2. Special case: $P^{(1)} = 0$. In the *special case* where

$$L_{(P)\alpha\beta}^{(1,1)} = 0, \text{ and } L_{(P)\alpha\beta}^{(1,0)} = -L_{(P)\beta\alpha}^{(0,1)} = 0,$$
 (101)

Eqs. (51) and (52) become

$$E_{\alpha}^{(ir)} = L_{(P)\alpha\beta}^{(0,0)} \frac{dP_{\beta}}{dt}, \quad \text{and} \quad \frac{dP_{\alpha}^{(1)}}{dt} = 0.$$
(102)

It is seen that $\mathbf{P}^{(1)}$ is constant and it can be supposed that $\mathbf{P}^{(1)} = \mathbf{0}$ (i.e. there is no internal variable). Equation (88) reduces to a generalized dielectric relaxation equation for *De Groot-Mazur media* (see Kluitenberg 1973, 1977, 1981);

$$E_{\alpha} = \chi^{(1)}_{(\rm PE)\,\alpha\beta} P_{\beta} + \chi^{(2)}_{(\rm PE)\,\alpha\beta} \frac{dP_{\beta}}{dt} + \chi^{(1)}_{(\rm T)\,\alpha} T + \sum_{k=1}^{n} \chi^{(1,k)}_{(C)\,\alpha} \left(c^{(k)} - c^{(k)}_{(0)} \right), \tag{103}$$

where

$$\chi^{(1)}_{(PE)\alpha\beta} = a^{(0,0)}_{(P)\alpha\beta}, \qquad \chi^{(2)}_{(PE)\alpha\beta} = L^{(0,0)}_{(P)\alpha\beta},$$
$$\chi^{(1)}_{(T)\alpha} = a^{(0)}_{(P)\alpha}, \qquad \chi^{(1,k)}_{(C)\alpha} = b^{(0,k)}_{(P)\alpha}. \tag{104}$$

In the case where we have only a polarizable one component fluid, Eq. (94) reduces to *De Groot-Mazur relaxation equation* for an anisotropic medium

$$E_{\alpha} = \chi^{(1)}_{(\text{PE})\alpha\beta} P_{\beta} + \chi^{(2)}_{(\text{PE})\alpha\beta} \frac{dP_{\beta}}{dt} + \chi^{(1)}_{(\text{T})\alpha} T, \qquad (105)$$

where $\chi^{(1)}_{(\rm PE)\alpha\beta}$, $\chi^{(2)}_{(\rm PE)\alpha\beta}$, $\chi^{(1)}_{(\rm T)\alpha}$ are given by (104). In the isotropic case, when the tensors χ , describing the properties of the system, have the form $\chi_{\alpha\beta} = \chi \delta_{\alpha\beta}$ and $\chi_{\alpha} = 0$, Eq. (105) takes the form of the classical De Groot-Mazur dielectric equation

$$E_{\alpha} = \chi^{(1)}_{(\text{PE})} P_{\alpha} + \chi^{(2)}_{(\text{PE})} \frac{dP_{\alpha}}{dt}.$$
(106)

9. Conclusions

The paper deals with anisotropic polarizable reacting fluid mixtures, where different types of irreversible microscopic phenomena give rise to dielectric relaxation. The obtained results can be applied in several physical situations, in medicine and biology and other different fields of applied sciences, where complex media are used. A phenomenological approach to describe relaxation phenomena in polarizable continuous media with *n* different ionic species was given by Maugin, by means of microscopic considerations and introducing partial polarizations per unit mass. In this paper the standard procedures of irreversible thermodynamics with internal variables are used. The total specific polarization is assumed composed of two irreversible parts, the phenomenological equations are derived, and, linearizing the theory, the dielectric relaxation equation for these polarizable anisotropic media is derived. The obtained results are applied to two special cases, that, in the isotropic case, and for a polarizable one-component fluid, reduce to Debye and De Groot-Mazur dielectric relaxation equations.

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References

- Ciancio, V. and Restuccia, L. (1990). "On the invariance of Onsager reciprocal relations in the thermodynamic theory of dielectric relaxation phenomena". *Physica A* **162**, 489–498. DOI: 10. 1016/0378-4371(90)90430-Z.
- Ciancio, V., Restuccia, L., and Kluitenberg, G. A. (1990). "A thermodynamic derivation of equations for dielectric relaxation phenomena in anisotropic polarizable media"". *Journal of Non-Equilibrium Thermodynamics* **15**(2), 157–171. DOI: 10.1515/jnet.1990.15.2.157.
- De Groot, S. and Mazur, P. (1962). Non-equilibrium Thermodynamics. North-Holland Pub. Co.
- Debye, P. (1945). Polar molecules. Dover. DOI: 10.1002/jctb.5000484320.
- Jou, D., Casas-Vasquez, J., and Lebon, G. (2010). Extended irreversible thermodynamics. Springer. DOI: 10.1007/978-90-481-3074-0.
- Jou, D. and Restuccia, L. (2011). "Mesoscopic transport equations and contemporary thermodynamics: an introduction". *Contemporary Physics* **52**(5), 465–474. DOI: 10.1080/00107514.2011.595596.
- Kittel, C. (2005). Introduction to Solid State Physics. Wiley & Sons, Inc.
- Kluitenberg, G. A. (1973). "On dielectric and magnetic relaxation phenomena and non-equilibrium thermodynamics". *Physica* **68**(1), 75–92. DOI: **10.1016/0031-8914(73)90131-6**.
- Kluitenberg, G. A. (1977). "On dielectric and magnetic relaxation phenomena and vectorial internal degrees of freedom in thermodynamics". *Physica A* **87**(2), 302–330. DOI: 10.1016/0378-4371(77) 90019-X.
- Kluitenberg, G. A. (1981). "On vectorial internal variables and dielectric and magnetic relaxation phenomena". *Physica A* **109**(1–2), 91–122. DOI: 10.1016/0378-4371(81)90039-X.
- Kluitenberg, G. A. (1984). "Plasticity and Nonequilibrium Thermodynamics". In: *The Constitutive Law in Thermoplasticity*. Ed. by T. Lehmann. Vol. 281. CISM International Centre for Mechanical Sciences (Courses and Lectures). Vienna: Springer, pp. 135–160. DOI: 10.1007/978-3-7091-2636-3_4.
- MacDougall, F. H. (1951). "Thermodynamics of Irreversible Processes. By S. R. de Groot." *The Journal of Physical Chemistry* 55(9), 1577–1578. DOI: 10.1021/j150492a019.
- Maugin, G. A. (1976). "Deformable Dielectrics I Field equations for a dielectric made of several molecular species". Archives of Mechanics 28, 676–682.
- Maugin, G. (1977a). "Deformable Dielectrics II Voigt's intramolecular force balance in elastic dielectrics". Archives of Mechanics 29, 143–159.
- Maugin, G. (1977b). "Deformable Dielectrics III A model of interactions". *Archives of Mechanics* **29**, 251–258.
- Maugin, G. (1980). "The method of virtual power in Continuum Mechanics: application to coupled fields". *Acta Mechanica* **35**(1), 1–70. DOI: 10.1007/BF01190057.
- Maugin, G. (1988). Continuum mechanics of electromagnetic solids. North-Holland Pub. Co.
- Meixner, J. and Reik, H. G. (1959). "Thermodynamik der Irreversiblen Prozesse". In: *Handbuch der Physik*. Ed. by F. S. Berlin: Springer-Verlag, p. 110.
- Muschik, W. and Restuccia, L. (2006). "Terminology and classification of special versions of continuum thermodynamics". *Communications to SIMAI Congress* 1, 1–6. DOI: 10.1685/CSC06120.
- Prigogine, I. (1947). *Étude Thermodinamique des Phénomènes Irréversibles*. Dunod, Paris et Editions Desoer.
- Prigogine, I. (1961). Introduction to Thermodynamics of Irreversible Processes. Interscience Publishers John Wiley & Sons.
- Restuccia, L. and Kluitenberg, G. A. (1987). "On possible interactions among dielectric relaxation, magnetic relaxation, heat conduction, electric conduction, diffusion phenomena, viscous flow and chemical reactions in fluid mixtures". *Atti Accademia Peloritana dei Pericolanti, Classe I di Scienze Matematiche, Fisiche e Naturali* LXV, 309–336.

- Restuccia, L. and Kluitenberg, G. A. (1988). "On generalizations of the Debye equation for dielectric relaxation". *Physica A* **154**(1), 157–182. DOI: 10.1016/0378-4371(88)90186-0.
- Restuccia, L. and Kluitenberg, G. A. (1990). "Hidden vectorial variables as splitting operators for the polarization vector in the thermodynamic theory of dielectric relaxation". *Journal of Non-Equilibrium Thermodynamics* 15(4), 335–346. DOI: 10.1515/jnet.1990.15.4.335.
- Restuccia, L. and Kluitenberg, G. A. (1992). "On the heat dissipation function for dielectric relaxation phenomena in anisotropic media". *International Journal of Engineering Science* **30**, 305–315. DOI: 10.1016/0020-7225(92)90075-R.
- Restuccia, L. and Kluitenberg, G. A. (1995). "On the heat dissipation function for dielectric relaxation phenomena in isotropic media". Atti dell'Accademia di Scienze, Lettere e Arti di Palermo, 1–21.
- Restuccia, L., Palese, L., and Labianca, A. (2016). "On magnetic relaxation equation for anisotropic reacting fluid mixtures". *ROMAI Journal* 12(2), 141–160.
- Restuccia, L. and Turrisi, E. (1990). "On the total energy flux in reacting fluid mixtures in which dielectric and magnetic relaxation phenomena occur". *Atti Accademia Peloritana dei Pericolanti, Classe I di Scienze Matematiche, Fisiche e Naturali* LXVIII, 93–109.
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