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## Polarized mixtures with ionic tracers

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### Abstract

A model of a polarized mixture is developed and the effects of migration of ions are also accounted for. The rate of the polarization power in some way furnishes power to the mixture. The electrical external power is calculated and by means of a requirement of invariance of the power, the standard balance laws are deduced. The ions dissolved in the mixture and subject to the electric field are considered like tracers and their migration is discussed. We show that their migration is ruled by the Nernst–Planck equation. In the final section, we adapt the description of the model to the setting of complex bodies and the microstructural evolution equations are derived.

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### 1. Introduction

Roubicek [1] proposed in his paper a model of a mixture of ionic constituents; his model combines the Navier–Stokes equation with the Nernst–Planck equation (with a convective term in the flux) and finally the Poisson equation for the self-induced quasistatic electric field; Roubicek intended his continuum as a charged not a polarized mixture. In our point of view a continuum immersed in an electric field changes its behaviour in a polarized continuum. Moreover, the flux of ions should be studied not like a phase but, according to [2], like tracers carried by a mixture of different fluids; examples of tracers are the salts or the pollutants dissolved in water. In the following, we distinguish between phases and tracers; furthermore, we suppose that the phases of the mixture are non-reacting, to avoid carrying along cumbersome quantities which add very little to the understanding of the problem and to its mathematical approach. The problem of reacting mixtures has been widely discussed in [3, 4] and all those results can be easily integrated in the framework that we propose. For the sake of simplicity we suppose that the mixture is composed of  $N$  phases and that each phase carries only one tracer. This assumption will allow us to apply the *principle of phase separation* in the Coleman and Noll procedure [5]. However, the same arguments can be used

in a mixture with  $N$  phases and  $Z$  tracers using the *principle of equipresence*. Differently from the phases of the mixture, we consider the tracers (ions) as reactants and we suppose that their concentration is described by the equation

$$\frac{\partial c_a}{\partial t} + \operatorname{div} \mathbf{j}_a = \check{c}_a, \quad (1)$$

with  $a = 1, \dots, N$ . We make no assumption regarding the flux  $\mathbf{j}_a$ : its nature will be discussed in section 5. This paper is structured as follows: in section 2, we present a summary of the theory of mixtures and introduce the notation. In section 3, we derive a relationship which allows us to account for the power of polarization of a continuum; such a relationship corresponds to a similar one derived by Tiersten [6] for a magnetizable continuum. In section 4, we derive all the balance laws for each phase and for the mixture as a whole. The mathematical tool that we will use is the requirement of the invariance of the external power for observers, introduced by Mariano [7]. In section 5, we use the Coleman and Noll procedure for finding the constitutive restrictions. In such a way we derive that the flux of the ionic tracers is governed by the Nernst–Planck equation. In section 6, we describe the same mixture in the setting of complex bodies; the microstructural balances are derived to provide a better representation of the problem. We summarize here some standard notations used in the paper; we denote by small bold letters the vectors and by capital bold letters the tensors. Only the electrical vector  $\mathbf{E}$  and the electrical displacement  $\mathbf{D}$  (or respectively  $\mathbf{E}_a$  and  $\mathbf{D}_a$  when dealing with the  $a$ th phase) do not follow our convention, in respect of the classical notation in electrodynamics. We denote by the symbol ‘ $\cdot$ ’ the full contraction; when we deal with vectors the symbol ‘ $\cdot$ ’ indicates the standard scalar product; when we deal with tensors it contracts all the indices. Let  $\mathbf{A}$  and  $\mathbf{B}$  be two second-order tensors, then  $\mathbf{A} \cdot \mathbf{B} = A_{ij}B_{ij}$ . The product of two tensors contracts only one index; then  $\mathbf{A}\mathbf{B} = A_{ih}B_{hj}$ ; similarly for the product of a tensor and a vector (in such a case we write  $\mathbf{A}\mathbf{b} = A_{ij}b_j$ ).

## 2. Theory of mixtures

We present first a summary of results for the theory of mixtures [3] and we specialize such results for our framework. We consider a mixture of  $N$  bodies  $B_a = 1, \dots, N$ . Each constituent is assigned a fixed reference configuration with  $\mathbf{X}_a$  the position of a particle of that constituent in its reference configuration. Then the motion

$$\mathbf{x} = \chi_a(\mathbf{X}_a, t)$$

gives the spatial position  $\mathbf{x}$  occupied at time  $t$  by the particle labelled  $\mathbf{X}_a$ . We assume  $\chi_a$  to be sufficiently smooth and define

$$\dot{\mathbf{x}}_a = \partial_t \chi_a(\mathbf{X}_a, t)$$

$$\ddot{\mathbf{x}}_a = \partial_t^2 \chi_a(\mathbf{X}_a, t)$$

to be velocity and acceleration of the  $a$ th constituent. Moreover, with the usual definitions we write the deformation gradient

$$\mathbf{F}_a = \nabla \chi_a(\mathbf{X}_a, t)$$

supposed invertible, and we obtain the velocity gradient

$$\operatorname{grad} \dot{\mathbf{x}}_a = \dot{\mathbf{F}}_a \mathbf{F}_a^{-1}.$$

Mass density  $\rho_a$  is assigned to each phase; the total mass density of the mixture is defined as

$$\rho = \sum_a \rho_a, \quad (2)$$

the mean (or barycentric) velocity is given by

$$\dot{\mathbf{x}} = \dot{\mathbf{x}}(\mathbf{x}, t) = \frac{1}{\rho} \sum_a \rho_a \dot{\mathbf{x}}_a \quad (3)$$

and the diffusion velocity is defined as

$$\mathbf{u}_a = \mathbf{u}_a(\mathbf{x}, t) = \dot{\mathbf{x}}_a - \dot{\mathbf{x}}. \quad (4)$$

Consequently we have  $\dot{\mathbf{x}}_a = \dot{\mathbf{x}} + \mathbf{u}_a$  and  $\sum_a \rho_a \mathbf{u}_a = 0$ . We consider now a quantity  $\Gamma$ ; no importance is attached to its nature (scalar or vectorial or other); in considering the presence of more phases, it is important to know the material derivative of  $\Gamma$  following the  $a$ th constituent. It is given by

$$\dot{\Gamma}_a = \partial_t \Gamma(\mathbf{x}, t) + \text{grad } \Gamma \cdot \dot{\mathbf{x}}_a \quad (5)$$

and the material time derivative following the motion of  $\mathbf{x}$  is

$$\dot{\Gamma} = \partial_t \Gamma(\mathbf{x}, t) + \text{grad } \Gamma \cdot \dot{\mathbf{x}}. \quad (6)$$

By subtracting (6) from (5) we also obtain

$$\dot{\Gamma}_a - \dot{\Gamma} = \text{grad } \Gamma \cdot \mathbf{u}_a. \quad (7)$$

In general, the balance of the  $a$ th mass constituent is

$$\dot{\rho}_a + \rho_a \text{div } \dot{\mathbf{x}}_a = \check{r}_a,$$

for a chemical reacting mixture the rate of a generic quantity  $\Gamma_a$  is given by

$$\frac{d}{dt}(\rho_a \Gamma_a) = \rho_a \dot{\Gamma}_a + \check{r}_a \Gamma_a,$$

from now on, it is assumed that the mixture is chemically nonreacting and thus  $\check{r}_a \equiv 0$  is assumed. Other useful identities proposed by [3, 8] for  $\check{r}_a = 0$  are

$$\rho \dot{\Gamma} = \sum_a [\rho_a \dot{\Gamma}_a - \text{div}(\rho_a \Gamma_a \mathbf{u}_a)], \quad (8)$$

$$\rho_a \mathbf{u}_a \cdot \dot{\mathbf{u}}_a = \rho_a \mathbf{u}_a \cdot \dot{\mathbf{x}}_a - \rho_a \mathbf{u}_a \otimes \mathbf{u}_a \cdot \text{grad } \dot{\mathbf{x}}. \quad (9)$$

In the following, we will use such identities to find out the balances for a single phase and for the mixture as a whole. The following principles which describe the interactions among each phase and the behaviour of the mixture as a whole are of great help in finding the balances. We quote three metaphysical principles introduced by Truesdell [8] (for shortness MP):

- (i) All properties of the mixture must be a mathematical consequence of properties of the constituents.
- (ii) So as to describe the motion of a constituent, we may in imagination isolate it from the rest of the mixture, provided we allow properly for the actions of the other constituents upon it.
- (iii) The motion of a mixture is governed by the same equations as is a single body.

The first principle asserts that a whole is the sum of its parts, and the third one asserts that during its motion the body does not know if it is a mixture or not. The second can be interpreted as an action–reaction principle.

### 3. Electrodynamics of mixtures

We consider an electric dipole immersed in the electric field  $\mathbf{E}_a$  of the phase  $a$ th; in the following, we define with  $\mathbf{E}_a$  the self-induced phase electric field; we define with  $\mathbf{E} = \sum_a \mathbf{E}_a$  the total electric field and we call  $\mathbf{E}_0$  the external electric field. Moreover, we call  $\mathbf{d}$  the oriented distance of the positive charge from the negative one and  $q$  is the generic electric charge. The electric energy of the  $a$ th phase is given by the sum of the energy  $U_a^-$  of the negative charge with the energy  $U_a^+$  of the positive charge. Namely, if we call  $\phi_a$  the electric potential of the phase  $a$ th, we call  $\phi_0$  the external electric potential and  $\phi = \sum_a \phi_a$ , we write

$$U_a = U_a^- + U_a^+ = -q\phi_a(\mathbf{r}) + q\phi_a(\mathbf{r} + \mathbf{d}),$$

and, expanding in Taylor series the latest term in the previous equality, the following equation arises

$$\begin{aligned} U_a &= -q\phi_a(\mathbf{r}) + q\phi_a(\mathbf{r}) + q \operatorname{grad} \phi_a \mathbf{d} \\ &= q \mathbf{d} \operatorname{grad} \phi_a. \end{aligned} \quad (10)$$

We introduce the polarization vector  $\mathbf{p}_a$  of the phase  $a$ th as the product

$$\mathbf{p}_a = q \mathbf{d},$$

and recalling that  $\mathbf{E}_a = \operatorname{grad} \phi_a$  the electric energy (10) changes into

$$U_a = -\mathbf{E}_a \cdot \mathbf{p}_a. \quad (11)$$

In general, we can calculate the mechanical work that the electric field does on the dipole. We imagine that the charges constitute a rigid system and then the work has two contributions: one is due to a force  $\mathbf{f}_a$ , that is conjugated in the sense of the work with the displacement  $d\mathbf{l}$ , and the other is due to a couple  $\mathbf{m}_a$ , that is conjugated in the sense of the work with the rotation  $d\zeta$ . In general, we write

$$dL = \mathbf{f}_a \cdot d\mathbf{l} + \mathbf{m}_a \cdot d\zeta = -dU,$$

and we find from (11) that

$$\mathbf{f}_a = -\frac{\partial U_a}{\partial \mathbf{l}} = (\operatorname{grad} \mathbf{E}_a) \mathbf{p}_a, \quad (12)$$

similarly, we find the couple  $\mathbf{m}_a$  in the scalar form

$$m_a = -\frac{\partial U_a}{\partial \zeta} = -\frac{\partial}{\partial \zeta} (E_a p_a \cos \zeta) = E_a p_a \sin \zeta, \quad (13)$$

which in vectorial notation writes

$$\mathbf{m}_a = \mathbf{p}_a \times \mathbf{E}_a. \quad (14)$$

We calculate now the power developed by that couple; since we supposed that  $\mathbf{d}$  remains constant in modulus we can calculate the time derivative  $\dot{\mathbf{d}}$  by the Poisson formula

$$\dot{\mathbf{d}} = \boldsymbol{\omega} \times \mathbf{d}, \quad (15)$$

where  $\boldsymbol{\omega}$  is the angular velocity. The three vectors in (15) are orthogonal to each other and we can use such a property to find  $\boldsymbol{\omega}$ . We can write in modulus

$$\dot{d} = \omega d$$

and by the previous equation, considering that  $\boldsymbol{\omega}$ ,  $\mathbf{d}$  and  $\dot{\mathbf{d}}$  are mutually orthogonal, the modulus of the angular velocity is deduced in the vectorial form

$$\boldsymbol{\omega} = \frac{1}{d^2} \mathbf{d} \times \dot{\mathbf{d}}.$$

We can extend these results to a generic  $a$ th phase and calculate the power that the force (12) and the couple (13) develop. The contribution of force to the power is simply

$$\mathbf{f}_a \cdot \dot{\mathbf{x}}_a = (\text{grad } \mathbf{E}_a) \mathbf{p}_a \cdot \dot{\mathbf{x}}_a,$$

while the contribution of the couple to the power is

$$\begin{aligned} \mathbf{m}_a \cdot \boldsymbol{\omega} &= \frac{1}{d^2} (\mathbf{p}_a \times \mathbf{E}_a) \cdot (\mathbf{d}_a \times \dot{\mathbf{d}}_a) = \frac{1}{d^2} \epsilon_{ijk} p_{aj} E_{ak} \epsilon_{ilm} d_{ai} \dot{d}_{am} \\ &= \frac{1}{d^2} (\delta_{jl} \delta_{km} - \delta_{jm} \delta_{kl}) \frac{1}{d^2} (p_{aj} E_{ak} d_{ai} \dot{d}_{am}) = \frac{1}{d^2} p_{aj} \dot{d}_{aj} E_{ak} \dot{d}_{ak}, \end{aligned} \quad (16)$$

with  $\epsilon_{ijk}$  being Ricci's permutation tensor. Equation (16) in vectorial formalism writes

$$\mathbf{m}_a \cdot \boldsymbol{\omega} = \frac{1}{d^2} (q d_{aj} \dot{d}_{aj} E_{ak} \dot{d}_{ak}) = q E_{ak} \dot{d}_{ak} = \mathbf{E}_a \cdot \dot{\mathbf{p}}_a.$$

Moreover we want to introduce the electric displacement  $\mathbf{D}_a = \epsilon_0 \mathbf{E}_a + \mathbf{p}_a$ , with  $\epsilon_0$  being the vacuum permittivity. The electric displacement fulfils the requirement  $\text{div } \mathbf{D}_a = 0$ . We can make now some observation about the electrical force  $\mathbf{f}_a$ ; if we deal with one phase only, we can consider the electric field  $\mathbf{E}_a$  as the sum of the contribution of an external electric field  $\mathbf{E}_0$  and an electric part acting only inside the body that we call  $\bar{\mathbf{E}}_a$ , such that  $\mathbf{E}_a = \mathbf{E}_0 + \bar{\mathbf{E}}_a$ . In that way, the electric force writes

$$\mathbf{f}_a = (\text{grad } \bar{\mathbf{E}}_a) \mathbf{p}_a + (\text{grad } \mathbf{E}_0) \mathbf{p}_a \quad (17)$$

and introducing the Maxwell stress tensor  $\mathbf{T}_a^{\text{ms}}$  [9] as

$$\mathbf{T}_a^{\text{ms}} = \epsilon_0 \bar{\mathbf{E}}_a \otimes \mathbf{D}_a - \frac{1}{2} \epsilon_0 \bar{\mathbf{E}}_a \cdot \bar{\mathbf{E}}_a \mathbf{I},$$

we write (17) as

$$\mathbf{f}_a = \text{div } \mathbf{T}_a^{\text{ms}} + (\text{grad } \mathbf{E}_0) \mathbf{p}_a. \quad (18)$$

Hence, as a consequence of the hypothesis that we have only one phase, follows that we can write the external electrical power  $P_a^{\text{el}}$  for a generic part  $b_t$  of the body at time  $t$  in the form

$$P_a^{\text{el}} = \int_{b_t} \mathbf{T}_a^{\text{ms}} \mathbf{n} \cdot \dot{\mathbf{x}}_a + \int_{b_t} \rho_a (\text{grad } \mathbf{E}_0) \mathbf{p}_a \cdot \dot{\mathbf{x}}_a + \int_{b_t} \rho_a \mathbf{E}_a \cdot \dot{\mathbf{p}}_a \quad (19)$$

as proposed in [13]. In (19) we have considered the polarization vector as a polarization vector per unit of mass; in this way, the polarization vector will be considered from now on. Such form of the external power is appropriate when we describe a polarized material or a ferroelectric material (that has one phase only) but is not appropriate in the electrodynamic theory of the mixture because to deduce (19) we assumed that we can separate the external electric field from the unique phase we were considering, but we cannot count such contribution as times as the phases are. Hence we should write the external electrical power  $P_a^{\text{el}}$  as

$$P_a^{\text{el}} = \int_{b_t} \rho_a (\text{grad } \mathbf{E}_a) \mathbf{p}_a \cdot \dot{\mathbf{x}}_a + \int_{b_t} \rho_a \mathbf{E}_a \cdot \dot{\mathbf{p}}_a. \quad (20)$$

Balance equations are derived by following a procedure based on the requirement that the power of all external actions over a generic part of the body is invariant under changes in observers differing from one another by rigid-body motions. In general, we may define an observer like a representation of events. In the standard context, we only need the interval of time and a representation of the ambient space to describe the motion of the body. Let  $\mathcal{O}$  and  $\mathcal{O}^*$  be two synchronous observers in  $\mathbb{R}^3$ . If the transformation  $\mathcal{O} \rightarrow \mathcal{O}^*$  is isometric and time dependent, then a generic  $\mathbf{x}$  in  $\mathcal{O}$  changes in

$$(\mathbf{x}^* - \mathbf{x}_0) := \mathbf{w}(t) + \boldsymbol{\Omega}(t)(\mathbf{x} - \mathbf{x}_0)$$

where  $\mathbf{w}(t)$  and  $\mathbf{\Omega}(t)$  are, respectively, an arbitrary vector and an orthogonal tensor at time  $t$ . Then the velocities of the  $a$ th phase recorded by the two observers are related by

$$\dot{\mathbf{x}}_a^* = \mathbf{c}(t) + \mathbf{q}(t) \times (\mathbf{x} - \mathbf{x}_0) \quad (21)$$

where  $\mathbf{c}(t)$  is the translational velocity of  $\mathcal{O}^*$  with respect to  $\mathcal{O}$  and  $\mathbf{q}(t)$  is the angular velocity of  $\mathcal{O}^*$  with respect to  $\mathcal{O}$  and related to  $\mathbf{\Omega}(t)$  by

$$\mathbf{\Omega}^T(t) \dot{\mathbf{\Omega}}(t) = \mathbf{q}(t) \times .$$

Similarly, the rate of the polarization vector  $\mathbf{p}_a$  (per unit of mass) of the  $a$ th phase with respect to observer  $\mathcal{O}^*$  is given by

$$\dot{\mathbf{p}}_a^* = \mathbf{q}(t) \times \mathbf{p}_a. \quad (22)$$

Equations (21) and (22) will be applied to exploit the axiom of invariance of the power [7, 11]. As pointed out by Truesdell, it is possible to consider separately each constituent from the others, provided that we account for the action on the constituent itself provided by the other constituents. For this reason, we decompose the power of the  $a$ th component into a *proper* part  $P_a^{\text{prop}}(\dot{\mathbf{x}}_a)$ , the one that can be attributed to  $b_t$  as if it was isolated, and an exchange part  $P_a^{\text{exch}}(\dot{\mathbf{x}}_a)$  which accounts for the power of actions exerted on the first constituent. Note that although the two constituents occupy the same region in space, each constituent is a body *different* from the other, according to the classical theory of mixtures by Truesdell [8]. We write the external power for the  $a$ th phase as

$$P_a^{\text{ext}}(\dot{\mathbf{x}}_a, \dot{\mathbf{p}}_a, b_t) = P_a^{\text{prop}}(\dot{\mathbf{x}}_a, \dot{\mathbf{p}}_a, b_t) + P_a^{\text{exch}}(\dot{\mathbf{x}}_a, b_t), \quad (23)$$

where  $P_a^{\text{prop}}$  includes both mechanical and electrical force (as introduced in (20)); it can be exploited as

$$P_a^{\text{prop}}(\dot{\mathbf{x}}_a, \dot{\mathbf{p}}_a, b_t) = \int_{\partial b_t} \mathbf{T}_a \mathbf{n} \cdot \dot{\mathbf{x}}_a + \int_{b_t} \mathbf{b}_a \cdot \dot{\mathbf{x}}_a + \int_{b_t} \rho_a (\text{grad } \mathbf{E}_a) \mathbf{p}_a \cdot \dot{\mathbf{x}}_a + \int_{b_t} \rho_a \mathbf{E}_a \cdot \dot{\mathbf{p}}_a,$$

where  $\mathbf{b}_a$  is the bulk force for the  $a$ th phase and  $\mathbf{T}_a$  is the classical Cauchy stress tensor for classical continuum. In (23) we have also introduced the power exchanged between the phases; it writes

$$P_a^{\text{exch}} = \int_{b_t} \check{\mathbf{m}}_a \cdot \dot{\mathbf{x}}_a + \int_{b_t} \check{\boldsymbol{\omega}}_a \cdot \text{rot } \dot{\mathbf{x}}_a$$

which has been proposed by Mariano in [7]. Therefore, we can write (23) as

$$\begin{aligned} P_a^{\text{ext}}(\dot{\mathbf{x}}_a, \dot{\mathbf{p}}_a, b_t) &= \int_{\partial b_t} \mathbf{T}_a \mathbf{n} \cdot \dot{\mathbf{x}}_a + \int_{b_t} \mathbf{b}_a \cdot \dot{\mathbf{x}}_a + \int_{b_t} \check{\mathbf{m}}_a \cdot \dot{\mathbf{x}}_a \\ &+ \int_{b_t} \check{\boldsymbol{\omega}}_a \cdot \text{rot } \dot{\mathbf{x}}_a + \int_{b_t} \rho_a (\text{grad } \mathbf{E}_a) \mathbf{p}_a \cdot \dot{\mathbf{x}}_a + \int_{b_t} \rho_a \mathbf{E}_a \cdot \dot{\mathbf{p}}_a \end{aligned} \quad (24)$$

that coincides with the form of the external power proposed by Mariano [7] for simple bodies when  $\mathbf{p}_a$  is identically null. The external power  $P_a^{\text{ext}}$  for the phase is such that the *rule of total power* [7] applies. It writes

$$P^{\text{ext}}(\dot{\mathbf{x}}, \dot{\mathbf{p}}) = \sum_a P_a^{\text{ext}}(\dot{\mathbf{x}}, \dot{\mathbf{p}}_a). \quad (25)$$

We apply the axiom of invariance for the power to obtain the balance laws: we impose that

$$P_a^{\text{ext}}(\dot{\mathbf{x}}_a, \dot{\mathbf{p}}_a, b_t) = P_a^{\text{ext}}(\dot{\mathbf{x}}_a^*, \dot{\mathbf{p}}_a^*, b_t), \quad (26)$$

therefore, substituting (21), (22) and (24) into (26) we obtain

$$\begin{aligned} \mathbf{c}(t) \cdot \left[ \int_{\partial b_t} \mathbf{T}_a \mathbf{n} + \int_{b_t} \mathbf{b}_a + \int_{b_t} \check{\mathbf{m}}_a + \int_{b_t} \rho_a (\text{grad } \mathbf{E}_a) \mathbf{p}_a \right] \\ + \mathfrak{q}(t) \cdot \left[ \int_{\partial b_t} (\mathbf{x}_a - \mathbf{x}_0) \times \mathbf{T}_a \mathbf{n} + \int_{b_t} (\mathbf{x}_a - \mathbf{x}_0) \times \mathbf{b}_a + \int_{b_t} (\mathbf{x}_a - \mathbf{x}_0) \times \check{\mathbf{m}}_a \right. \\ \left. + \int_{b_t} (\mathbf{x}_a - \mathbf{x}_0) \times \rho_a (\text{grad } \mathbf{E}_a) \mathbf{p}_a + \int_{b_t} \mathbf{p}_a \times \rho_a \mathbf{E}_a + \int_{b_t} \check{\omega}_a \right] = 0. \end{aligned} \quad (27)$$

Equation (27) has to be verified for every choice of  $\mathbf{c}(t)$ ; then the local form of linear momentum balance arises

$$\text{div } \mathbf{T}_a + \mathbf{b}_a + \check{\mathbf{m}}_a + \rho_a (\text{grad } \mathbf{E}_a) \mathbf{p}_a = 0. \quad (28)$$

Equation (27) has to be also verified for every choice of  $\mathfrak{q}(t)$ . Hence, in indicial notation

$$\begin{aligned} \int_{\partial b_t} \epsilon_{ijk} (x_a - x_0)_j T_{aki} n_l + \int_{b_t} \epsilon_{ijk} (x_a - x_0)_j b_{ak} \\ + \int_{b_t} \epsilon_{ijk} (x_a - x_0)_j \check{m}_{ak} + \int_{b_t} \epsilon_{ijk} p_{aj} \rho_a E_{ak} + \int_{b_t} \check{\omega}_{aj} = 0. \end{aligned} \quad (29)$$

Applying the divergence theorem and equation (28) we have

$$\epsilon_{ijk} T_{akj} + \epsilon_{ijk} \rho_a p_{aj} E_{ak} = -\check{\omega}_{aj} \quad (30)$$

or, in symbolic notation

$$\epsilon(\mathbf{T}_a^T + \rho_a \mathbf{p}_a \otimes \mathbf{E}_a) = -\check{\omega}_a. \quad (31)$$

When  $\check{\omega}_a = 0$ , equation (31) coincides with the momentum balance found in [12]. We find now the balance equations for the whole mixture by applying the third metaphysical principle.

We explicitly write, now, the external power  $P^{\text{ext}}(\dot{\mathbf{x}}, \dot{\mathbf{p}}, b_t)$  of the mixture as a whole

$$P^{\text{ext}}(\dot{\mathbf{x}}, \dot{\mathbf{p}}) = \int_{\partial b_t} \mathbf{Tn} \cdot \dot{\mathbf{x}} + \int_{b_t} \mathbf{b} \cdot \dot{\mathbf{x}} + \int_{b_t} \rho (\text{grad } \mathbf{E}) \mathbf{p} \cdot \dot{\mathbf{x}} + \int_{b_t} \rho \mathbf{E} \cdot \dot{\mathbf{p}}, \quad (32)$$

with  $\mathbf{p}$  being the polarization vector (per unit of mass) for the mixture as a whole. We can estimate how every single quantity of each constituent acts on the quantities of the mixture applying the invariance of observers to (25). We obtain

$$\begin{aligned} \mathbf{c}(t) \cdot \left[ \int_{\partial b_t} \mathbf{Tn} + \int_{b_t} \mathbf{b} + \int_{b_t} \rho (\text{grad } \mathbf{E}) \mathbf{p} \right] + \mathfrak{q}(t) \cdot \left[ \int_{\partial b_t} (\mathbf{x} - \mathbf{x}_0) \times \mathbf{Tn} + \int_{b_t} (\mathbf{x} - \mathbf{x}_0) \times \mathbf{b} \right. \\ \left. + \int_{b_t} (\mathbf{x} - \mathbf{x}_0) \times \rho (\text{grad } \mathbf{E}) \mathbf{p} + \int_{b_t} \mathbf{p} \times \rho \mathbf{E} \right] \\ = \mathbf{c}(t) \cdot \sum_a \left[ \int_{\partial b_t} \mathbf{T}_a \mathbf{n} + \int_{b_t} \mathbf{b}_a + \int_{b_t} \check{\mathbf{m}}_a + \int_{b_t} \rho_a (\text{grad } \mathbf{E}_a) \mathbf{p}_a \right] \\ + \mathfrak{q}(t) \cdot \sum_a \left[ \int_{\partial b_t} (\mathbf{x} - \mathbf{x}_0) \times \mathbf{T}_a \mathbf{n} + \int_{b_t} (\mathbf{x} - \mathbf{x}_0) \times \mathbf{b}_a \right. \\ \left. + \int_{b_t} (\mathbf{x} - \mathbf{x}_0) \times \check{\mathbf{m}}_a + \int_{b_t} (\mathbf{x} - \mathbf{x}_0) \times \rho_a (\text{grad } \mathbf{E}_a) \mathbf{p}_a + \int_{b_t} \mathbf{p}_a \times \rho_a \mathbf{E}_a + \int_{b_t} \check{\omega}_a \right]. \end{aligned}$$

The above equality is verified if

$$\mathbf{b} = \sum_a \mathbf{b}_a, \quad \mathbf{T} = \sum_a \mathbf{T}_a, \quad (33)$$



$$\sum_a \check{\mathbf{m}}_a = \mathbf{0}, \quad \sum_a \check{\omega}_a = \mathbf{0}, \quad (34)$$

$$\rho \mathbf{p} = \sum_a \rho_a \mathbf{p}_a, \quad \rho (\text{grad } \mathbf{E}) \mathbf{p} = \sum_a \rho_a (\text{grad } \mathbf{E}_a) \mathbf{p}_a. \quad (35)$$

Equations (34)<sub>1</sub> and (34)<sub>2</sub> mean that the exchange of momentum and the exchange of moment for the whole mixture due to interactions between constituents are pointwise self-equilibrated, as prescribed by the second MP. We can write now the balance laws for the mixture as a whole recalling that

$$\text{div } \mathbf{T}_a + \mathbf{b}_a + \check{\mathbf{m}}_a + \rho_a (\text{grad } \mathbf{E}_a) \mathbf{p}_a = 0. \quad (36)$$

In general, we can decompose bulk force of *a*th phase in its inertial and non-inertial parts (see [11, 13, 14]) as

$$\mathbf{b}_a = \mathbf{b}_a^{\text{in}} + \mathbf{b}_a^{\text{ni}}. \quad (37)$$

We define the inertial part as the derivative of momentum (or, in a different way, we can say that the inertial part multiplied by velocity is the derivative of the kinetic energy changed in sign). Hence

$$\mathbf{b}_a^{\text{in}} = -\frac{d}{dt} (\rho_a \dot{\mathbf{x}}_a) = -\rho_a \ddot{\mathbf{x}}_a, \quad (38)$$

and now we can rewrite equation (36) as

$$\text{div } \mathbf{T}_a + \mathbf{b}_a^{\text{ni}} + \check{\mathbf{m}}_a + \rho_a (\text{grad } \mathbf{E}_a) \mathbf{p}_a = \rho_a \ddot{\mathbf{x}}_a.$$

We sum over *a* and recalling equation (8) with  $\Gamma_a \equiv \dot{\mathbf{x}}_a$ , and equation (35), it follows that

$$\text{div} \left( \mathbf{T} - \sum_a \rho_a \mathbf{u}_a \otimes \mathbf{u}_a \right) + \mathbf{b}^{\text{ni}} + \rho (\text{grad } \mathbf{E}) \mathbf{p} = \rho \ddot{\mathbf{x}}, \quad (39)$$

where  $\mathbf{T} = \sum_a \mathbf{T}_a$  is the inner part of the stress tensor and the term  $\sum_a (\rho_a \mathbf{u}_a \otimes \mathbf{u}_a)$  accounts for diffusion between phases. In the classical theory of mixtures  $\mathbf{T}$  is symmetric; in our case it is not. Indeed, by summing equation (31) over *a* and taking into account (34)<sub>2</sub>, we have

$$\epsilon (\mathbf{T}^T + \rho \mathbf{p} \otimes \mathbf{E}) = 0.$$

We define the *inner part* of the internal energy the weighted sum of all internal energies

$$\rho e_I = \sum_a \rho_a e_a. \quad (40)$$

This energy accounts only for the presence of the internal energies of every phase, but does not account for the exchanges of energy and diffusion between phases. By taking equation (8) with  $\Gamma_a \equiv e_a$  we can write

$$\sum_a \rho_a \dot{e}_a = \rho \dot{e}_I + \text{div} \left( \sum_a \rho_a e_a \mathbf{u}_a \right). \quad (41)$$

To account for the diffusion and exchanges between phases we define the internal energy as [15]

$$e = e_I + \sum_a \frac{1}{2} u_a^2.$$

We recall from equation (8), with  $\Gamma_a \equiv \frac{1}{2} \rho_a u_a^2$ , that

$$\rho \sum_a \frac{1}{2} \dot{c}_a u_a^2 = \sum_a \left[ \rho_a u_a \dot{u}_a - \text{div} \left( \frac{1}{2} \rho_a u_a^2 \mathbf{u}_a \right) \right]. \quad (42)$$

Such a relationship will be useful in the following. We write the energy balance in the form

$$\frac{d}{dt} \int_{b_t} \rho_a e_a = P_a^{\text{ext}} + \int_{\partial b_t} \mathbf{q}_a \cdot \mathbf{n} + \int_{b_t} (\rho_a r_a + \check{E}_a), \quad (43)$$

where the vector  $\mathbf{q}_a$  represents heat flux through the border  $\partial b_t$ ,  $\rho_a r_a$  is the source of internal heat and  $\check{E}_a$  is the exchange of energy between the phases as postulated in the third MP. Mechanical, electrical and exchange effects are included in  $P_a^{\text{ext}}$ , as defined in equation (24). In the definition of  $\check{E}_a$  we consider uniquely those terms accounting for the exchange of energy between the phases; we assume the form [3]

$$\check{E}_a = \check{e}_a - \check{\omega}_a \cdot \text{rot } \check{\mathbf{x}}_a. \quad (44)$$

If we substitute equation (44) into (43) taking the time derivative at the left-hand side, the resulting pointwise balance is

$$\rho_a \dot{e}_a = \mathbf{T}_a \cdot \text{grad } \check{\mathbf{x}}_a + \text{div } \mathbf{q}_a + \rho_a r_a + \rho_a \mathbf{E}_a \cdot \dot{\mathbf{p}}_a + \check{e}_a. \quad (45)$$

We try to manipulate equation (43) in order to find the energy balance law for the mixture as a whole. Since (4), (24) and (44) we can express (43) as

$$\begin{aligned} \int_{b_t} \rho_a \dot{e}_a &= \int_{\partial b_t} \mathbf{T}_a \mathbf{n} \cdot \dot{\mathbf{x}} + \int_{\partial b_t} \mathbf{T}_a^T \mathbf{u}_a \cdot \mathbf{n} + \int_{b_t} \rho_a (\text{grad } \mathbf{E}_a) \mathbf{p}_a \\ &+ \int_{b_t} \mathbf{b}_a \cdot \dot{\mathbf{x}} + \int_{b_t} \mathbf{b}_a \cdot \mathbf{u}_a + \int_{b_t} \check{\mathbf{m}}_a \cdot \dot{\mathbf{x}} + \int_{b_t} \check{\mathbf{m}}_a \cdot \mathbf{u}_a \\ &+ \int_{\partial b_t} \mathbf{q}_a + \int_{b_t} \rho_a r_a + \int_{b_t} \rho_a \mathbf{E}_a \cdot \dot{\mathbf{p}}_a + \int_{b_t} \check{e}_a \end{aligned} \quad (46)$$

and by equation (36) we get the pointwise balance

$$\begin{aligned} \rho_a \dot{e}_a &= \mathbf{T}_a \cdot \text{grad } \dot{\mathbf{x}} + \text{div} (\mathbf{q}_a + \mathbf{T}_a^T \mathbf{u}_a) + (\rho_a r_a + \mathbf{b}_a \cdot \mathbf{u}_a \\ &+ \rho_a (\text{grad } \mathbf{E}_a) \mathbf{p}_a \cdot \mathbf{u}_a) + \rho_a \mathbf{E}_a \cdot \dot{\mathbf{p}}_a + (\check{e}_a + \check{\mathbf{m}}_a \cdot \mathbf{u}_a). \end{aligned} \quad (47)$$

We sum up equation (47) over  $a$ , and by taking into account equation (41), we obtain the global balance of the inner part of the internal energy

$$\begin{aligned} \rho \dot{e}_I &= \mathbf{T} \cdot \text{grad } \dot{\mathbf{x}} + \text{div } \mathbf{q}_I + \rho r_I + \sum_a [\mathbf{b}_a \cdot \mathbf{u}_a + \rho_a (\text{grad } \mathbf{E}_a) \mathbf{p}_a \cdot \mathbf{u}_a] + \rho \mathbf{E} \cdot \dot{\mathbf{p}} \\ &+ \sum_a \text{div} (\rho_a \mathbf{p}_a \otimes \mathbf{u}_a) \cdot \sum_a \mathbf{E}_a + \sum_a (\check{e}_a + \check{\mathbf{m}}_a \cdot \mathbf{u}_a), \end{aligned} \quad (48)$$

where  $\mathbf{q}_I = \sum_a (\mathbf{q}_a + \mathbf{T}_a^T \mathbf{u}_a - \rho_a e_a \mathbf{u}_a)$  and  $\rho r_I = \sum_a \rho_a r_a$ . In (48), equation (8) with  $\Gamma_a \equiv \mathbf{p}_a$  has been used. The sum  $\sum_a \mathbf{b}_a \cdot \mathbf{u}_a$  contains both inertial and non-inertial terms. The addition between equations (42) and (48) provides the rate of total internal energy

$$\rho \dot{e} = \left( \mathbf{T} - \sum_a \rho_a \mathbf{u}_a \otimes \mathbf{u}_a \right) \cdot \text{grad } \dot{\mathbf{x}} + \text{div } \check{\mathbf{q}} + \rho \check{r} + \rho \mathbf{E} \cdot \dot{\mathbf{p}} + \sum_a (\check{e}_a + \check{\mathbf{m}}_a \cdot \mathbf{u}_a). \quad (49)$$

We impose that

$$\sum_a (\check{e}_a + \check{\mathbf{m}}_a \cdot \mathbf{u}_a) = 0 \quad (50)$$

and the balance (49) transforms into

$$\rho \dot{e} = \left( \mathbf{T} - \sum_a \rho_a \mathbf{u}_a \otimes \mathbf{u}_a \right) \cdot \text{grad } \dot{\mathbf{x}} + \rho \mathbf{E} \cdot \dot{\mathbf{p}} + \text{div } \check{\mathbf{q}} + \rho \check{r}, \quad (51)$$

where

$$\begin{aligned}\tilde{\mathbf{q}} &= \sum_a \left( \mathbf{q}_a + \mathbf{T}_a^T \mathbf{u}_a - \rho_a e_a \mathbf{u}_a - \frac{1}{2} \rho_a u_a^2 \mathbf{u}_a \right) \\ &= \mathbf{q}_I - \sum_a \frac{1}{2} \rho_a u_a^2 \mathbf{u}_a,\end{aligned}\tag{52}$$

$$\rho \tilde{r} = \rho r_I + \sum_a \left[ (\mathbf{b}_a^{\text{ni}} + \rho_a (\text{grad } \mathbf{E}_a) \mathbf{p}_a) \cdot \mathbf{u}_a \right] + \sum_a \text{div}(\rho_a \mathbf{p}_a \otimes \mathbf{u}_a) \cdot \sum_a \mathbf{E}_a.\tag{53}$$

We have written equation (50) for consistency. Such a result is equal to that found by Bowen [3] for the classical theory of mixtures when the sources of mass are neglected and equation (49) coincides with the energy balance proposed by Eringen [12] for a single phase when microstretch effects are absent; equations (50) and (51)–(53) are the form that the first principle of thermodynamics assumes for a polarized mixture as a whole.

#### 4. Constitutive restrictions

For exploiting the constitutive restrictions of the mixture we should introduce the entropy unbalance and the Helmholtz free energy  $\psi_a$  for the  $a$ th phase and apply the Coleman and Noll procedure [5]. The entropy inequality for the phase  $a$  is

$$\rho_a \dot{\eta}_a \geq \text{div } \mathbf{h}_a + \frac{\rho_a r_a}{\theta}.\tag{54}$$

We introduce now the Helmholtz free energy for the phase  $a$  as  $\psi_a^t = e_a - \theta \eta_a$ . We suppose that all the constituents have the same temperature  $\theta$ ; multiplying equation (54) by  $\theta$  and subtracting the result to equation (45) we obtain

$$\rho_a \dot{\psi}_a^t + \rho_a \eta_a \dot{\theta} \leq \mathbf{T}_a \cdot \text{grad } \dot{\mathbf{x}}_a + \rho_a \dot{\mathbf{p}}_a \cdot \mathbf{E}_a + \frac{\mathbf{q}_a}{\theta} \cdot \text{grad } \theta + \check{e}_a,\tag{55}$$

where we make the assumption that  $\mathbf{q}_a = \theta \mathbf{h}_a$  for consistency. The energy balance (45) and (55) contain no terms accounting for the migration of ions; then the energy  $\psi_a^t$  accounts only for the thermoelastic contribution of the free energy and accounts in no way for the migration of the ions. Then we should consider the global Helmholtz free energy as the sum of the terms  $\psi_a = \psi_a^t + \psi_a^m$ , where  $\psi_a^m$  is the migrative part of the ions that we propose in the form

$$\int_{b_i} \rho_a \dot{\psi}_a^m = - \int_{\partial b_i} \tilde{\mu}_a \mathbf{j}_a + \int_{b_i} \check{c}_a \tilde{\mu}_a,\tag{56}$$

the term  $\tilde{\mu}_a$  is a thermodynamic function power conjugated with the variation of mass; its nature will be explained in the following. Such a balance can be written in the pointwise form as

$$\rho_a \dot{\psi}_a^m = -\mathbf{j}_a \cdot \text{grad } \tilde{\mu}_a + \tilde{\mu}_a \check{c}_a,\tag{57}$$

where the balance (1) has been used. By summing equation (55) and (57) we get, from the definition of  $\psi_a$ , the inequality

$$\rho_a \dot{\psi}_a + \rho_a \eta_a \dot{\theta} \leq \mathbf{T}_a \cdot \text{grad } \dot{\mathbf{x}}_a + \rho_a \dot{\mathbf{p}}_a \cdot \mathbf{E}_a + \frac{\mathbf{q}_a}{\theta} \cdot \text{grad } \theta + \check{e}_a - \mathbf{j}_a \cdot \text{grad } \tilde{\mu}_a + \tilde{\mu}_a \check{c}_a\tag{58}$$

that coincides with the entropic inequality that Mariano proposed in [16, 17] to account for migrative effects using a different explanation. We apply the principle of phase separation to

exploit the constitutive restrictions; we propose for the Helmholtz free energy  $\psi_a$ , the stress tensor  $\mathbf{T}_a$ , the flux  $\mathbf{q}_a$  and the thermodynamic potential  $\tilde{\mu}_a$  the dependences

$$(\psi_a, \mathbf{T}_a, \mathbf{q}_a, \tilde{\mu}_a) = \mathfrak{F}(\theta, \text{grad } \theta, \mathbf{u}_a, \mathbf{F}_a, c_a, \mathbf{p}_a, \dot{\mathbf{p}}_a, \text{grad } \mathbf{p}_a), \quad (59a)$$

while for the term  $\check{\mathbf{m}}_a$  which accounts for interactions of  $a$ th constituent with the other constituents we propose

$$\check{\mathbf{m}}_a = \mathfrak{G}(\theta, \text{grad } \theta, \mathbf{u}_b, \mathbf{F}_b, c_b, \mathbf{p}_b, \dot{\mathbf{p}}_b, \text{grad } \mathbf{p}_b). \quad (59b)$$

We sum equation (58) for all the phases, and applying equation (50) we get

$$\sum_a \left[ \rho_a (\dot{\psi}_a + \dot{\theta} \eta_a) \leq \mathbf{T}_a \cdot \text{grad } \dot{\mathbf{x}}_a + \rho_a \dot{\mathbf{p}}_a \cdot \mathbf{E}_a + \frac{\mathbf{q}_a}{\theta} \cdot \text{grad } \theta - \check{\mathbf{m}}_a \cdot \mathbf{u}_a \right]. \quad (60)$$

We define now, for simplicity of notation, the quantities

$$\mathbf{w}_a := \text{grad } \mathbf{p}_a \quad \text{and} \quad \mathbf{g} := \text{grad } \theta.$$

Bearing in mind equation (59a) and applying the chain rule, the derivative of the free energy is

$$\begin{aligned} \dot{\psi}_a = & \frac{\partial \psi_a}{\partial \mathbf{F}_a} \cdot \dot{\mathbf{F}}_a + \frac{\partial \psi_a}{\partial \theta} \cdot \dot{\theta} + \frac{\partial \psi_a}{\partial \mathbf{g}} \cdot \dot{\mathbf{g}} + \frac{\partial \psi_a}{\partial \mathbf{p}_a} \cdot \dot{\mathbf{p}}_a \\ & + \frac{\partial \psi_a}{\partial \mathbf{w}_a} \cdot \dot{\mathbf{w}}_a + \frac{\partial \psi_a}{\partial \dot{\mathbf{p}}_a} \cdot \dot{\dot{\mathbf{p}}}_a + \frac{\partial \psi_a}{\partial \mathbf{u}_a} \cdot \dot{\mathbf{u}}_a + \frac{\partial \psi_a}{\partial c_a} \cdot \dot{c}_a. \end{aligned} \quad (61)$$

By recalling that  $\text{grad } \dot{\mathbf{x}}_a = \dot{\mathbf{F}}_a \mathbf{F}_a^{-1}$  and  $\overline{\text{grad}} (*)' = \text{grad} (*)' + \text{grad} (*) (\text{grad } \dot{\mathbf{x}}_a)$ , we substitute (61) into (60) and we have

$$\begin{aligned} \sum_a \left[ \left( \rho_a \frac{\partial \psi_a}{\partial \mathbf{F}_a} + \rho_a \mathbf{w}_a^\top \frac{\partial \psi_a}{\partial \mathbf{w}_a} - \mathbf{T}_a \cdot \mathbf{F}_a^{-\top} \right) \cdot \dot{\mathbf{F}}_a + \rho_a \left( \frac{\partial \psi_a}{\partial \theta} + \eta_a \right) \cdot \dot{\theta} \right. \\ \left. + \rho_a \frac{\partial \psi_a}{\partial \mathbf{g}} \cdot \dot{\mathbf{g}} + \rho_a \frac{\partial \psi_a}{\partial \mathbf{u}_a} \cdot \dot{\mathbf{u}}_a + \left( \rho_a \frac{\partial \psi_a}{\partial c_a} - \tilde{\mu}_a \right) \cdot \dot{c}_a - \frac{\mathbf{q}_a}{\theta} \cdot \nabla \theta + \check{\mathbf{m}}_a \cdot \mathbf{u}_a \right. \\ \left. + \mathbf{j}_a \cdot \text{grad } \tilde{\mu}_a + \rho_a \left( \frac{\partial \psi_a}{\partial \mathbf{p}_a} - \mathbf{E}_a \right) \cdot \dot{\mathbf{p}}_a + \rho_a \frac{\partial \psi_a}{\partial \mathbf{w}_a} \cdot \dot{\mathbf{w}}_a + \rho_a \frac{\partial \psi_a}{\partial \dot{\mathbf{p}}_a} \cdot \dot{\dot{\mathbf{p}}}_a \right] \leq 0. \end{aligned} \quad (62)$$

This inequality should be verified for every choice of the motion

$$(\dot{\mathbf{F}}_a, \dot{\theta}_a, \text{grad } \dot{\theta}_a, \dot{\mathbf{p}}_a, \text{grad } \dot{\mathbf{p}}_a, \dot{\dot{\mathbf{p}}}_a, \dot{\mathbf{u}}_a).$$

Necessary and sufficient conditions are

$$\rho_a \left( \frac{\partial \psi_a}{\partial \mathbf{F}_a} + \mathbf{w}_a^\top \frac{\partial \psi_a}{\partial \mathbf{w}_a} \right) \mathbf{F}_a^\top = \mathbf{T}_a, \quad \frac{\partial \psi_a}{\partial \theta} = -\eta_a, \quad \rho_a \frac{\partial \psi_a}{\partial \mathbf{u}_a} = 0, \quad (63a)$$

$$\rho_a \frac{\partial \psi_a}{\partial \dot{\mathbf{p}}_a} = 0, \quad \frac{\partial \psi_a}{\partial \nabla \theta} = 0, \quad \rho_a \frac{\partial \psi_a}{\partial c_a} = \tilde{\mu}_a,$$

$$\rho_a \frac{\partial \psi_a}{\partial \mathbf{w}_a} \cdot \dot{\mathbf{w}}_a = 0; \quad \frac{\partial \psi_a}{\partial \mathbf{p}_a} = \mathbf{E}_a; \quad (63b)$$

the first equality in equation (63b) does not mean, trivially, that  $\frac{\partial \psi_a}{\partial \mathbf{w}_a}$  is identically null, but that it is orthogonal to  $\dot{\mathbf{w}}_a$ . Equation (62) reduces to the residual inequality

$$\sum_a \left\{ -\frac{\mathbf{q}_a}{\theta} \cdot \text{grad } \theta + \check{\mathbf{m}}_a \cdot \mathbf{u}_a + \mathbf{j}_a \cdot \text{grad } \tilde{\mu}_a \right\} \leq 0. \quad (64)$$

Inequality (64) is verified if all terms occurring are less or equal to zero. The term  $-\frac{\mathbf{q}_a}{\theta} \cdot \text{grad } \theta \leq 0$  if  $\mathbf{q}_a = k_a \text{grad } \theta$  with  $k_a$  being a definite positive coefficient.

A possible solution for  $\check{\mathbf{m}}_a \cdot \mathbf{u}_a \leq 0$  could be

$$\check{\mathbf{m}}_a = \mathbf{M}_a(\theta, \text{grad } \theta, \mathbf{u}_b, \mathbf{F}_b, c_b) \mathbf{u}_a$$

with  $\mathbf{M}_a(\theta, \text{grad } \theta, \mathbf{u}_b, \mathbf{F}_b, c_b)$  being a definite-negative second-order tensor. The third term is negative if and only if we admit the constitutive restriction

$$\mathbf{j}_a = c_a \mathbf{B}_a \text{grad } \tilde{\mu}_a \quad (65)$$

with  $\mathbf{B}_a$  being a negative mobility tensor. We know from the irreversible thermodynamics that the flux  $\mathbf{j}_a$  has the form  $\mathbf{j}_a = c_a \mathbf{B}_a \tilde{\mathbf{F}}_a$  then by comparison we should admit that  $\tilde{\mathbf{F}}_a = \text{grad } \tilde{\mu}_a$  and this relation clarifies the nature of the thermodynamic function  $\tilde{\mu}_a$ : it is a thermodynamic potential and since  $\tilde{\mathbf{F}}_a$  has a dual nature, mechanical and electrical, the same should happen for the thermodynamic potential  $\tilde{\mu}_a$  that we decompose in the form

$$\tilde{\mu}_a = \mu_a + z_a F \phi_a, \quad (66)$$

where  $\mu_a$  is the standard state chemical potential for the  $a$ th component,  $z_a$  is the valence of the ion in the  $a$ th phase and  $F$  is the Faraday constant. Moreover, we suppose that the chemical potential  $\mu_a$  has the form

$$\mu_a = \mu_a^0 + R \theta \ln \gamma_a c_a,$$

where  $\mu_a^0$  is the chemical potential at the standard state,  $\gamma_a$  is the activity coefficient and  $R$  is the universal constant of gas. From all this consideration descend that (65) changes into

$$\begin{aligned} \mathbf{j}_a &= c_a \mathbf{B}_a \text{grad } \mu_a + c_a z_a F \mathbf{B}_a \text{grad } \phi_a \\ &= c_a \mathbf{B}_a R \theta \left( \text{grad } \ln \gamma_a + \frac{1}{c_a} \text{grad } c_a \right) + z_a F \mathbf{B}_a \text{grad } \phi_a. \end{aligned}$$

In a dilute mixture the activity coefficient becomes constant and thus the flux  $\mathbf{j}_a$  becomes

$$\mathbf{j}_a = \mathbf{D}_a \left( \text{grad } c_a + \frac{z_a F}{R \theta} \text{grad } \phi_a \right), \quad (67)$$

where we have grouped the terms  $\mathbf{D}_a = R \theta \mathbf{B}_a$ . We can recognize the flux occurring in (67) as the flux occurring in Nernst–Planck equation; then equation (1) is the Nernst–Planck equation. Roubicek [18] achieved the same results about the Nernst–Planck flux doing different considerations: he proposed first (67) as the simplest model for drift and diffusion in fluxes; moreover, by proposing an electrochemical potential equal to (66) he can generalize his flux arriving to a formulation of the forces causing the fluxes equal to (65); by these considerations Roubicek avoided all the technicism in the Coleman and Noll procedure. Moreover, Roubicek deduced the sign of the mobility tensor via an Onsager approach instead of using the entropy inequality (64) deduced via the Coleman and Noll procedure. Other particular cases of constitutive restrictions for the fluxes are discussed in [18].

The electric potential  $\phi_a$  can be determined solving the Maxwell's equation

$$\varepsilon_0 \text{div}(\varepsilon \text{grad } \phi_a) = Q_a,$$

where the term in the left-hand side is the total electric charge of the  $a$ th constituent.

## 5. Microstructured mixtures

We study now an enriched representation of the mixture by supposing it as a microstructured continuum. In the past decades (see [4] and related references), an effort has been made to develop a continuum theory in the theory of mixtures which accommodate the physical notion of microstructure. Since our mixture is polarized, its behaviour is not determined

solely by the deformation tensor and the volume fraction of the constituents but also by the polarization vector; this can be intended as an independent kinematic variable; it is necessary to determine an additional equation of balance of the forces in terms of the new variable. In fact, the polarization vector previously introduced can be viewed as a particular physical quantity called a *morphological descriptor* whose rate is power conjugated to a kind of forces called *microstructural forces*; in this contest, hence, such balance can be determined within the framework of the multifield theory (see [13]) and since the effect of the microstructural forces can be measured in terms of power, we can use again the tool of the principle of invariance of power. We admit that the microstructural force has a contact part and a body part, as in classical continuum. The microstructural external power  $P_a^{ms}$  writes

$$P_a^{ms} = \int_{\partial b_t} \mathbf{S}_a \mathbf{n} \cdot \dot{\mathbf{p}}_a + \int_{b_t} \beta_a \cdot \dot{\mathbf{p}}_a, \quad (68)$$

so the external power is now given by the sum of the electromechanical power (24) and the microstructural power (68). It yields

$$P_a^{ext} = \int_{\partial b_t} \mathbf{T}_a \mathbf{n} \cdot \dot{\mathbf{x}}_a + \int_{b_t} \mathbf{b}_a \cdot \dot{\mathbf{x}}_a + \int_{b_t} \rho_a (\text{grad } \mathbf{E}_a) \mathbf{p}_a \cdot \dot{\mathbf{x}}_a + \int_{b_t} \check{\mathbf{m}}_a \cdot \dot{\mathbf{x}}_a + \int_{b_t} \check{\omega}_a \cdot \text{rot } \dot{\mathbf{x}}_a + \int_{\partial b_t} \mathbf{S}_a \mathbf{n} \cdot \dot{\mathbf{p}}_a + \int_{b_t} \beta_a \cdot \dot{\mathbf{p}}_a.$$

We apply now the same mathematical machinery used previously and we find the new balance equations. By applying the same mathematical machinery that we used to find the equality (26) we obtain when the microstructural power (68) is considered in the invariance of the power

$$\begin{aligned} \mathbf{c}(t) \cdot & \left[ \int_{\partial b_t} \mathbf{T}_a \mathbf{n} + \int_{b_t} \mathbf{b}_a + \int_{b_t} \check{\mathbf{m}}_a + \int_{b_t} \rho_a (\text{grad } \mathbf{E}_a) \mathbf{p}_a \right] \\ & + \mathbf{q}(t) \cdot \left[ \int_{\partial b_t} (\mathbf{x}_a - \mathbf{x}_0) \times \mathbf{T}_a \mathbf{n} + \int_{b_t} (\mathbf{x}_a - \mathbf{x}_0) \times \mathbf{b}_a \right. \\ & + \int_{b_t} (\mathbf{x}_a - \mathbf{x}_0) \times \check{\mathbf{m}}_a + \int_{b_t} (\mathbf{x}_a - \mathbf{x}_0) \times \rho_a (\text{grad } \mathbf{E}_a) \mathbf{p}_a + \int_{b_t} \check{\omega}_a \\ & \left. + \int_{b_t} \mathbf{p}_a \times \mathbf{S}_a \mathbf{n} + \int_{b_t} \mathbf{p}_a \times \beta_a + \int_{b_t} \mathbf{p}_a \times \rho_a \mathbf{E}_a \right] = 0 \end{aligned} \quad (69)$$

that has to be verified for every choice of  $\mathbf{c}(t)$  and  $\mathbf{q}(t)$ . We are interested to manipulate the last line in equation (69) that is the one that does not appear in equation (27). In indicial notation we can write

$$\int_{\partial b_t} \epsilon_{ijk} p_{a_j} S_{a_{kl}} n_l + \int_{b_t} \epsilon_{ijk} p_{a_j} \beta_{a_k} + \int_{b_t} \epsilon_{ijk} p_{a_j} \rho_a E_{a_k} = 0.$$

For the theorem of divergence we get the pointwise form

$$\epsilon_{ijk} \left[ \frac{\partial p_{a_j}}{\partial x_l} S_{a_{kl}} + p_{a_j} \left( \frac{\partial}{\partial x_l} S_{a_{kl}} + \beta_{a_k} + \rho_a E_{a_k} \right) \right] = 0.$$

The terms between round brackets cannot disappear; we define a new term (that is called self-force) that is peculiar to complex bodies theory (see [13]). We obtain the microstructural balance equation (the one between round braces) already obtained in the same way in [13]

$$\text{div } \mathbf{S}_a + \beta_a + \rho_a \mathbf{E}_a = \mathbf{z}_a, \quad (70)$$

and by (69), (70) and (28) we get the angular momentum

$$\epsilon(\mathbf{T}_a^T + \text{grad } \mathbf{p}_a \mathbf{S}_a^T + \mathbf{p}_a \otimes \mathbf{z}_a) = -\check{\omega}_a$$

that coincides with [13] when  $\omega_a = 0$ . We find now the balance energy of the microstructured mixture for each phase and for the mixture as a whole. The balance of energy (43) writes now

$$\begin{aligned} \int_{b_i} \rho_a \dot{e}_a = & \int_{\partial b_i} \mathbf{T}_a \mathbf{n} \cdot \dot{\mathbf{x}}_a + \int_{b_i} \mathbf{b}_a \cdot \dot{\mathbf{x}}_a + \int_{b_i} \rho_a (\text{grad } \mathbf{E}_a) \mathbf{p}_a \cdot \dot{\mathbf{x}}_a + \int_{b_i} \dot{\mathbf{m}}_a \cdot \dot{\mathbf{x}}_a \\ & + \int_{\partial b_i} \mathbf{S}_a \mathbf{n} \cdot \dot{\mathbf{p}}_a + \int_{b_i} \beta_a \cdot \dot{\mathbf{p}}_a + \int_{\partial b_i} \mathbf{q}_a \cdot \mathbf{n} + \int_{b_i} \rho_a r_a + \int_{b_i} \check{e}_a, \end{aligned} \quad (71)$$

and by the divergence theorem and equations (28) and (70), we have the point-wise form

$$\rho_a \dot{e}_a = \mathbf{T}_a \cdot \text{grad } \dot{\mathbf{x}}_a + \mathbf{S}_a \cdot \text{grad } \dot{\mathbf{p}}_a + \mathbf{z}_a \cdot \dot{\mathbf{p}}_a + \text{div } \mathbf{q}_a + \rho_a r_a + \check{e}_a.$$

If we use the equality  $\dot{\mathbf{x}}_a = \dot{\mathbf{x}} + \mathbf{u}_a$  and  $\dot{\mathbf{p}}_a = \dot{\mathbf{p}} + (\text{grad } \mathbf{p}) \cdot \mathbf{u}_a$  we get from (71)

$$\begin{aligned} \rho_a \dot{e}_a = & \mathbf{T}_a \cdot \text{grad } \dot{\mathbf{x}} + \text{div} (\mathbf{q}_a + \mathbf{T}_a^T \mathbf{u}_a) + \mathbf{S}_a \cdot \text{grad } \dot{\mathbf{p}} + \mathbf{z}_a \cdot \dot{\mathbf{p}} \\ & + \text{div} (\mathbf{S}_a^T (\text{grad } \mathbf{p}) \mathbf{u}_a) + \mathbf{z}_a \cdot (\text{grad } \mathbf{p}) \mathbf{u}_a \\ & + [\rho_a r_a + \mathbf{b}_a \cdot \mathbf{u}_a + \rho_a (\text{grad } \mathbf{E}_a) \mathbf{p}_a \cdot \mathbf{u}_a] + (\check{e}_a + \dot{\mathbf{m}}_a \cdot \mathbf{u}_a), \end{aligned} \quad (72)$$

and if we take into account (41) and sum over  $a$ , we obtain the global balance of the inner part of internal energy

$$\begin{aligned} \rho \dot{e}_I = & \mathbf{T} \cdot \text{grad } \dot{\mathbf{x}} + \mathbf{S} \cdot \text{grad } \dot{\mathbf{p}} + \mathbf{z} \cdot \dot{\mathbf{p}} + \text{div } \mathbf{q}_I + \rho r_I + \sum_a [\mathbf{b}_a \cdot \mathbf{u}_a + \mathbf{z}_a \cdot (\text{grad } \mathbf{p}) \mathbf{u}_a \\ & + \rho_a (\text{grad } \mathbf{E}_a) \mathbf{p}_a \cdot \mathbf{u}_a] + \sum_a (\check{e}_a + \dot{\mathbf{m}}_a \cdot \mathbf{u}_a), \end{aligned} \quad (73)$$

where  $\mathbf{q}_I = \sum_a (\mathbf{q}_a + \mathbf{T}_a^T \mathbf{u}_a + \mathbf{S}_a^T (\text{grad } \mathbf{p}) \mathbf{u}_a - \rho_a e_a \mathbf{u}_a)$  and  $\rho r_I = \sum_a \rho_a r_a$  and  $\mathbf{S} = \sum_a \mathbf{S}_a$ . The sum  $\sum_a \mathbf{b}_a \cdot \mathbf{u}_a$  contains both inertial and non-inertial terms. The addition between equations (73) and (42) provides the rate of total internal energy

$$\begin{aligned} \rho \dot{e} = & \left( \mathbf{T} - \sum_a \rho_a \mathbf{u}_a \otimes \mathbf{u}_a \right) \cdot \text{grad } \dot{\mathbf{x}} + \mathbf{S} \cdot \text{grad } \dot{\mathbf{p}} + \mathbf{z} \cdot \dot{\mathbf{p}} \\ & + \text{div } \tilde{\mathbf{q}} + \rho \tilde{r} + \sum_a (\check{e}_a + \dot{\mathbf{m}}_a \cdot \mathbf{u}_a). \end{aligned} \quad (74)$$

We impose again equation (50) and the balance (74) transforms into

$$\rho \dot{e} = \left( \mathbf{T} - \sum_a \rho_a \mathbf{u}_a \otimes \mathbf{u}_a \right) \cdot \text{grad } \dot{\mathbf{x}} + \mathbf{S} \cdot \text{grad } \dot{\mathbf{p}} + \mathbf{z} \cdot \dot{\mathbf{p}} + \text{div } \tilde{\mathbf{q}} + \rho \tilde{r}, \quad (75)$$

where

$$\tilde{\mathbf{q}} = \mathbf{q}_I - \sum_a \frac{1}{2} \rho_a u_a^2 \mathbf{u}_a, \quad (76)$$

$$\rho \tilde{r} = \rho r_I + \sum_a [\mathbf{b}_a \cdot \mathbf{u}_a + \mathbf{z}_a \cdot (\text{grad } \mathbf{p}) \mathbf{u}_a + \rho_a (\text{grad } \mathbf{E}_a) \mathbf{p}_a \cdot \mathbf{u}_a]. \quad (77)$$

Equations (75)–(77) and (50) are the form that the first principle of thermodynamics assumes for a polarized mixture with microstructure. When microstructural terms are neglected the expressions provided by Bowen [3] are recovered. For finding the constitutive restrictions for our microstructured continuum we should account for microstructural power in equation (58) that changes into

$$\begin{aligned} \rho_a \dot{\psi}_a + \rho_a \eta_a \dot{\theta} \leq & \mathbf{T}_a \cdot \text{grad } \dot{\mathbf{x}}_a + \mathbf{S}_a \cdot \text{grad } \dot{\mathbf{p}}_a + \mathbf{z}_a \cdot \dot{\mathbf{p}}_a + \frac{\mathbf{q}_a}{\theta} \cdot \text{grad } \theta \\ & + \check{e}_a - \mathbf{j}_a \cdot \text{grad } \tilde{\mu}_a + \tilde{\mu}_a \dot{c}_a. \end{aligned} \quad (78)$$

We get the same results as in (63a) but (63b) changes into

$$\rho_a \frac{\partial \psi_a}{\partial \mathbf{w}_a} = \mathbf{S}_a, \quad \rho_a \frac{\partial \psi_a}{\partial \mathbf{p}_a} = \mathbf{z}_a$$

which is the new microstructural forces introduced in this section.

## 6. Conclusion

In this paper, we have derived a model of a polarized mixture. Differently from Samohyl [19], who proved Roubicek's model [1] after various simplifications and using a Hittorf approach, we have used the principle of invariance of the power to deduce the balance laws for each phase and for the mixture as a whole. Differently from them, we have considered the ionic constituents not as phases of the mixture, but as tracers and we have derived via the Coleman and Noll procedure that their diffusion is governed by the Nernst–Planck equation. Such a result is often postulated and deduced by phenomenological considerations and in some way enforced in the mathematical model. Instead, in our framework, it arises naturally. Roubicek's model can be retrieved imposing the polarization vector identically null and considering the mixture (as a whole) as a Newtonian fluid. The model has been improved in the final section where microstructural effects have been considered in the framework of the multifield theory.

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