A THERMODYNAMIC THEORY WITH HIDDEN VECTORIAL VARIABLES ON POSSIBLE INTERACTIONS AMONG HEAT CONDUCTION, DIFFUSION PHENOMENA, VISCOUS FLOW AND CHEMICAL REACTIONS IN FLUID MIXTURES

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ABSTRACT. In this paper, by using a procedure of classical irreversible thermodynamics with internal variable (CIT-IT) some possible interactions among heat conduction, diffusion phenomena, viscous flows in fluid mixtures are studied. By introducing as internal variables n vectors which influence thermal and diffusion phenomena, phenomenological equations for these variables are derived. A general vector, J, consisting of heat and mass diffusion fluxes, is introduced and it is shown that, in isotropic media, J can be split in two parts: a first one which is governed by Fourier's law and the second one which satisfies to Maxwell-Cattaneo-Vernotte equation.

1. Introduction

During the last 15-20 years many theories of mixtures (Pavelka *et al.* 2014) have been proposed to study several models (Klika 2014) in porous media (Murad and Cushman 2000; Wiegand 2004; Malek and Rajagopal 2008; O'Dea *et al.* 2010) and biomechanics (Caplan and Essig 1983; Yang *et al.* 1994; Frijns *et al.* 1997; Wu *et al.* 1997; Please *et al.* 1998; Ateshian *et al.* 2006, 2010). From the point of view of classical thermodynamics pioneering works on the mixtures of fluids were conducted in *Classical Irreversible Thermodynamic* (CIT) by De Groot and Mazur (1962) and in *Rational Thermodynamics* (RT) by Truesdell (1969). Subsequently, various schools of non-equilibrium thermodynamics have developed some fundamental contribution and actually one can distinguish: *Extended Irreversible Thermodynamics* (EIT) (Jou *et al.* 2010), *Rational Extended Thermodynamics* (RET) (Müller and Ruggeri 1998a; Ruggeri and Sugiyama 2015), *General Equations for Non-Equilibrium Reversible-Irreversible Coupling* (GENERIC) (Öttinger and Grmela 1997a,b), *Internal Variables Theories* (IVT) (Kestin 1993; Maugin and Muschik 1994a,b). In these papers a comparative study of the coupling of flow with non-Fickean thermodiffusion in mixture of binary fluid has been developed within the framework of various theories of non-equilibrium thermodynamic as EIT (Lebon *et al.* 2003), GENERIC (Grmela *et al.* 2003) and IVT (Lhuiller *et al.* 2003). Let us note that the flexibility of the methodology, used in IVT, is due

to the fact that "*a priori*" the physical meaning of the internal variables is not specified but only their influence on phenomena, occurring inside the material under consideration, is pointed out. This feature has enabled scientists to be able to apply the IVT to a wide-scale phenomena in continuous media. Thermodynamical theories of rheology (Kluitenberg 1967b; Kluitenberg and Ciancio V. 1978; Ciancio V. and Kluitenberg 1979; Kluitenberg 1984; Ciancio V. and Verhás 1990, 1991) and dielectric and magnetic relaxation were developed (Kluitenberg 1981; Ciancio V. 1989; Ciancio V. and Kluitenberg 1989; Ciancio V. *et al.* 1990) with theoretical results confirmed by some experimental data (Ciancio A. *et al.* 2007; Ciancio V. *et al.* 2007a,b, 2008; Ciancio A. 2011).

It was recently shown by Ciancio V. and Restuccia (2016) that by using the usual procedures of *classical irreversible thermodynamics with internal variables* (CIT-IVT) it is possible to describe the relaxation of thermal phenomena thus obtaining some well known results which, generally, are justified by additional hypothesis suggest by kinetic theory as usually in the parallel approaches in the frame of *extended irreversible thermodynamics* (EIT) or of *rational extended thermodynamic* (RET).

In this paper we consider a *n*-components fluid mixture and by using the systematic methodology of CIT, we will show that thermal relaxation and diffusion phenomena may be studied with the aid of internal thermodynamic variables, obtaining some well known equations in EIT. We assume that *n* hidden vectorial variables influence the thermal transport and diffusion phenomena inside the medium and using the general procedure of non-equilibrium thermodynamics the phenomenological equations are derived both in the anisotropic and isotropic cases. In particular, after recalling the conservation laws in the fluid mixtures in the presence of chemical reactions (see Section **2**), in Section **3** the entropy balance is derived and it is shown that the entropy production can be characterized by the sum of flows of products and thermodynamic affinities. As the heat conduction and the flow phenomena are irreversible processes, the phenomenological equations for these phenomena are determined in Section **4**. The phenomenological equations are generalizations of the Fourier's law for the heat conduction, the Fick's law for the diffusion phenomena and the Newton's law for viscous fluid flow. In Section **5** the symmetry and Onsager-Casimir relations are discussed and, finally, in Section **6**, for isotropic media it is shown that the vector of conduction and diffusive flows can be split in two parts: a first contributions J_0, governed by Fourier law and a second contribution J_1 satisfies to Maxwell-Cattaneo-Vernotte equation (Maxwell 1871; Cattaneo 1948; Vernotte 1958; Gurtin and Pipkin 1968; Fichera 1992), in which relaxation times are present and it is shown that without further assumptions can be obtain the phenomenological equations of diffusive flows hypothesized in some previous papers (Francaviglia *et al.* 2006, 2008)

2. The laws of conservation in fluid mixture with chemical reactions

We consider a fluid mixture consisting of *n* chemical components amongst which *r* chemical reactions are possible. If $\rho^{(i)}$ is the density of the mass of the ith component, $(i = 1, 2, ..., n)$, the total density, ρ, of the mixture is given by:

$$\rho = \sum_{i=1}^{n} \rho^{(i)}. \tag{1}$$

The quantity $\rho^{(i)}$ (see De Groot and Mazur (1962), p.12) satisfies to the following balance equation

$$\frac{\partial \rho^{(i)}}{\partial t} + \mathrm{div}(\rho^{(i)} \mathbf{v}^{(i)}) = \sum_{\underline{k}=1}^{r} v_{i\underline{k}} \, j^{(\underline{k})}, \tag{2}$$

where $\mathbf{v}^{(i)}$ is the velocity of i-th components and $v_{i\underline{k}} \, j^{(\underline{k})}$ the production of substance i per unit volume in the $\underline{k}^{th}$ chemical reaction ($\underline{k} = 1, 2, ..., r$). The quantity $j^{(\underline{k})}$ is called the chemical reaction rate of reaction $\underline{k}$ and $\sum_{\underline{k}=1}^{r} v_{i\underline{k}} j^{(\underline{k})}$ a source term giving the production (or destruction) of substance i. Since mass is conserved in each separate chemical reaction we have

$$\sum_{i=1}^{n} v_{i\underline{k}} = 0, \qquad (\underline{k} = 1, 2, ..., r). \tag{3}$$

Introducing the barycentric velocity $\mathbf{v}$:

$$\mathbf{v} = \rho^{-1} \sum_{i=1}^{n} \rho^{(i)} \mathbf{v}^{(i)}, \tag{4}$$

the *diffusion flow* $J^{(i)}$ of substance i respect to the barycentric motion is defined as

$$J^{(i)} = \rho^{(i)}(\mathbf{v}^{(i)} - \mathbf{v}), \tag{5}$$

and, of course, we have

$$\sum_{i=1}^{n} J^{(i)} = 0. \tag{6}$$

This means that only $n-1$ diffusion flows are independent. Since the barycentric substantial time derivative is

$$\frac{d}{dt} = \frac{\partial}{\partial t} + \mathbf{v} \cdot \mathrm{grad}, \tag{7}$$

by virtue of (2) and (5) we have

$$\frac{d\rho^{(i)}}{dt} = -\mathrm{div} J^{(i)} - \rho^{(i)} \mathrm{div}\, \mathbf{v} + \sum_{\underline{k}=1}^{r} v_{i\underline{k}} \, j^{(\underline{k})}. \tag{8}$$

From (1), (3) and (6) one obtains the *law of conservation of mass*:

$$\frac{d\rho}{dt} + \rho \, \mathrm{div}\, \mathbf{v} = 0. \tag{9}$$

Introducing the mass fractions $c^{(i)}$:

$$c^{(i)} = \frac{\rho^i}{\rho}, \qquad \left(\sum_{i=1}^{n} c^{(i)} = 1 \right) \tag{10}$$

the equation (8) can be written

$$\rho \frac{dc^{(i)}}{dt} = -\mathrm{div} J^{(i)} + \sum_{\underline{k}=1}^{r} v_{i\underline{k}} \, j^{(\underline{k})}. \tag{11}$$

The first law of thermodynamics reads

$$\rho \frac{du}{dt} = -\mathrm{div} J^{'(q)} + \tau_{\alpha\beta} \frac{d\varepsilon_{\alpha\beta}}{dt}, \qquad (\alpha, \beta = 1, 2, 3), \tag{12}$$

where u is the specific internal energy, $J'^{(q)}$ is the total heat flux, $\tau_{\alpha\beta}$ is the mechanical stress tensor, $\varepsilon_{\alpha\beta}$ is the strain tensor and the usual summation convention for dummy indices is used. In (12) the total heat flux is

$$J'^{(q)} = J^{(q)} + \sum_{i^*=1}^{n-1} h_{i^*} J^{(i^*)}, \tag{13}$$

with

$$h_{i^*} = h^{(i^*)} - h^{(n)} \quad (i^* = 1, 2, ..., n-1) \tag{14}$$

where $J^{(q)}$ is the conduction heat flux, $h^{(i)}$, $(i = 1, 2, ..., n)$, is the partial specific enthalpy of the ith component, $J^{(i^*)}$ is the diffusion flux defined by (5) and $\sum_{i^*=1}^{n-1} h_{i^*} J^{(i^*)}$ is the diffusion heat flux.

3. Entropy balance

We assume that the local state of the mixture is given by the specific internal energy u, the specific volume $v = 1/\rho$, the mass fractions $c^{(i)}$, $i = 1, 2, ...n$, and by n independent vector variables $\xi^{(i)}$, $i = 1, 2, ...n$, so that the specific entropy can be given as a function of these variables, as well

$$s = s(u, v, c^{(i)}, \xi^{(i)}), \qquad i = 1, 2, ...n. \tag{15}$$

According to the maximum property of the entropy is an equilibrium state and the Morse lemma (Morse 1925), the entropy function can be casted into the form

$$s = s^{(eq)}(u, v, c^{(i)}) - \frac{1}{2} \sum_{i=1}^{n} m_{\alpha\beta}^{(i)} \xi_\alpha^{(i)} \xi_\beta^{(i)}. \tag{16}$$

In (16) $s^{(eq)}$ is the equilibrium entropy function depending on the internal energy, on the specific volume and on the mass fractions (the only equilibrium state variables); ξ_α is the α-th component of ξ; $m_{\alpha\beta}^{(i)}$ are constant constitutive tensor characterizing the material coefficients and the usual summation convention for dummy indices is used. From (16) we have the following symmetries

$$m_{\alpha\beta}^{(i)} = m_{\beta\alpha}^{(i)}, \qquad (i = 1, 2, ..., n), \tag{17}$$

and introducing the following classical definitions

$$\begin{cases} \dfrac{\partial s}{\partial u} = \dfrac{1}{T}, \quad P = T \dfrac{\partial s}{\partial v}, \\[2mm] \dfrac{\partial s}{\partial c^{(i)}} = -T \mu^{(i)}, \quad (i = 1, 2, ..., n), \end{cases} \tag{18}$$

where $\mu^{(i)}$ is the chemical potential of the ith component of mixture, from (15) we obtain the following Gibbs relation:

$$\rho T \frac{ds}{dt} = \rho \frac{du}{dt} + \rho P \frac{dv}{dt} - \rho \sum_{i^*=1}^{n-1} \mu_{i^*} \frac{dc^{(i^*)}}{dt} - \rho T \sum_{i=1}^{n} m_{\alpha\beta}^{(i)} \xi_\beta^{(i)} \frac{d\xi_\alpha^{(i)}}{dt}. \tag{19}$$

From (9) one has:

$$\frac{d\nu}{dt} = \frac{1}{\rho}\frac{d\varepsilon}{dt}, \tag{20}$$

where

$$\varepsilon = \varepsilon_{\alpha\beta}\,\delta_{\alpha\beta}, \tag{21}$$

so that substituting (11), (12) and (20) into (19) we have

$$\rho\,T\,\frac{ds}{dt} = -\operatorname{div}J^{'(q)} + \tau_{\alpha\beta}\frac{d\varepsilon_{\alpha\beta}}{dt} + P\frac{d\varepsilon}{dt} + \sum_{i=1}^{n}\operatorname{div}\left(\mu^{(i)}J^{(i)}\right) +$$
$$-\sum_{i=1}^{n}J^{(i)}\cdot\operatorname{grad}\mu^{(i)} + \sum_{k=1}^{r}A_{(\underline{k})}\,j^{(\underline{k})} - \rho\,T\sum_{i=1}^{n}m_{\alpha\beta}^{(i)}\,\xi_{\beta}^{(i)}\,\frac{d\xi_{\alpha}^{(i)}}{dt}, \tag{22}$$

where

$$A_{(\underline{k})} = -\sum_{i=1}^{n}\mu^{(i)}\,\nu_{i\underline{k}}. \tag{23}$$

From (22) and by virtue of (6) we obtain the following balance equation for the entropy :

$$\rho\frac{ds}{dt} = -\operatorname{div}\left[T^{-1}\left(J^{'(q)} - \sum_{i^*=1}^{n-1}\mu_{i^*}J^{(i^*)}\right)\right] + \sigma^{(s)}, \tag{24}$$

where

$$\mu_{i^*} = \mu^{(i^*)} - \mu^{(n)} \qquad (i^* = 1, 2, ..., n-1) \tag{25}$$

and the entropy production, $\sigma^{(s)}$ is given by

$$\sigma^{(s)} = J^{'(q)}\cdot\operatorname{grad}\left(\frac{1}{T}\right) - \sum_{i^*=1}^{n-1}J^{(i^*)}\cdot\operatorname{grad}\left(\frac{\mu_{i^*}}{T}\right) + T^{-1}\Pi_{\alpha\beta}\frac{d\varepsilon_{\alpha\beta}}{dt} +$$
$$+T^{-1}\sum_{k=1}^{r}A_{(\underline{k})}\,j^{(\underline{k})} - \rho\sum_{i=1}^{n}m_{\alpha\beta}^{(i)}\,\xi_{\beta}^{(i)}\,\frac{d\xi_{\alpha}^{(i)}}{dt}. \tag{26}$$

In (24) $\Pi_{\alpha\beta} = \tau_{\alpha\beta} + P\delta_{\alpha\beta}$ is the viscous stress. From (26) we see that the entropy production, $\sigma^{(s)}$, is determined as a sum of inner products among the thermodynamic fluxes:

$$J^{'(q)}, J^{(i^*)}, \Pi_{\alpha\beta}, j^{(\underline{k})}, \xi_{\beta}^{(i)}$$

and the affinities:

$$\operatorname{grad}T^{-1}, \operatorname{grad}\left(-\frac{\mu_{i^*}}{T}\right), T^{-1}\frac{d\varepsilon_{\alpha\beta}}{dt}, T^{-1}A_{(\underline{k})}, -\rho\,m_{\alpha\beta}^{(i)}\frac{d\xi_{\alpha}^{(i)}}{dt}.$$

Consequently the entropy production is due to five types of phenomena. The first term on the right hand side of (26) gives the contribution of total heat flux, the second and fourth terms describe the contribution of the diffusion flow and the chemical reaction rate, the third term represents the entropy production due to a viscous flow phenomenon and the last term represents the entropy production due to the irreversible process of the variation of internal vectorial variables.

4. Phenomenological equations

By using the form of the entropy production which has been determined in the previous section, we assume that the chemical reactions rate $j^{(\underline{k})}$ depends only on the chemical potentials $A_{(\underline{i})}$ and does not influence the other irreversible processes, (see De Groot and Mazur (1962), pag. 24), *i.e.*,

$$j^{(\underline{k})} = T^{-1} \sum_{\underline{k},\underline{i}=1}^{r} l_{\underline{k}\underline{i}} A_{(\underline{i})}. \tag{27}$$

and according the general ideas of non equilibrium thermodynamics (Ciancio V. and Kluitenberg 1979; Kluitenberg 1984), the phenomenological equations of the theory may be written in the form

$$J_{\alpha}'^{(q)} = L_{\alpha\beta}^{(q,q)} \frac{\partial}{\partial x^{\beta}} (T^{-1}) + \sum_{i^*=1}^{n-1} L_{\alpha\beta}^{(q,i^*)} \frac{\partial}{\partial x^{\beta}} (-\mu_{i^*} T^{-1}) +$$
$$T^{-1} L_{\alpha\beta\gamma}^{(q,0)} \frac{d\varepsilon_{\beta\gamma}}{dt} - \rho \sum_{i=1}^{n} \Upsilon_{\alpha\beta}^{(q,i)} m_{\beta\sigma}^{(i)} \frac{d\xi_{\sigma}^{(i)}}{dt}, \tag{28}$$

$$J_{\alpha}^{(i^*)} = L_{\alpha\beta}^{(i^*,q)} \frac{\partial}{\partial x^{\beta}} (T^{-1}) + \sum_{j^*=1}^{n-1} L_{\alpha\beta}^{(i^*,j^*)} \frac{\partial}{\partial x^{\beta}} (\mu_{j^*} T^{-1}) +$$
$$T^{-1} L_{\alpha\beta\gamma}^{(i^*,0)} \frac{d\varepsilon_{\beta\gamma}}{dt} - \rho \sum_{i=1}^{n} \Upsilon_{\alpha\beta}^{(i^*,i)} m_{\beta\sigma}^{(i)} \frac{d\xi_{\sigma}^{(i)}}{dt}, \tag{29}$$

$$\Pi_{\alpha\beta} = L_{\alpha\beta\gamma}^{(0,q)} \frac{\partial}{\partial x^{\gamma}} (T^{-1}) + \sum_{i^*=1}^{n-1} L_{\alpha\beta\gamma}^{(0,i^*)} \frac{\partial}{\partial x^{\gamma}} (\mu_{i^*} T^{-1}) +$$
$$T^{-1} L_{\alpha\beta\gamma\sigma}^{(0,0)} \frac{d\varepsilon_{\gamma\sigma}}{dt} - \rho \sum_{i=1}^{n} \Upsilon_{\alpha\beta\gamma}^{(0,i)} m_{\gamma\sigma}^{(i)} \frac{d\xi_{\sigma}^{(i)}}{dt}, \tag{30}$$

$$\xi_{\alpha}^{(i)} = \Xi_{\alpha\beta}^{(i,q)} \frac{\partial}{\partial x^{\beta}} (T^{-1}) + \sum_{i^*=1}^{n-1} \Xi_{\alpha\beta}^{(i,i^*)} \frac{\partial}{\partial x^{\beta}} (-\mu_{i^*} T^{-1}) +$$
$$T^{-1} \Xi_{\alpha\beta\gamma}^{(i,0)} \frac{d\varepsilon_{\beta\gamma}}{dt} - \rho \sum_{j=1}^{n} \bar{\Upsilon}_{\alpha\beta}^{(i,j)} m_{\beta\sigma}^{(j)} \frac{d\xi_{\sigma}^{(j)}}{dt}. \tag{31}$$

The tensors L, Υ and Ξ are called phenomenological tensors. The first sum on the right hand of the equation (28) represents the Dufour effect and this equation may be regarded as a generalization of Fourier's law. The first sum on the right hand of the equation (29) represents the Soret's effects and this equation may be regarded as a generalization of Fick's law. The equation (30) describes the viscous flow phenomenon and this relation may be considered as a generalization of Newton's law for ordinary viscous fluids. Finally, the equation (31) is the phenomenological equation for irreversible processes characterized by the internal variables.

5. Symmetry and Onsager-Casimir relations

Since the heat flow, J', the diffusion flows $J^{(i^*)}, i^* = 1, 2, ..., n-1$), the internal variables $\xi^{(i)}$, $i = 1, 2, ..., n$, and the velocity strain tensor $d\varepsilon_{\alpha\beta}/dt$ are odd functions of the microscopic particle velocities and the temperature gradient ∇T, the time derivatives of $\xi^{(i)}$ and of the gradientes of chemical potentials $\nabla(\mu_{i^*}/T)$, $i^* = 1, 2, ..., n-1$, are even functions of these velocities, the Onsager-Casimir relations read

$$L^{(q,q)}_{\alpha\beta} = L^{(q,q)}_{\beta\alpha}, L^{(0,0)}_{\alpha\beta\gamma\sigma} = L^{(0,0)}_{\gamma\sigma\alpha\beta}, L^{(q,0)}_{\alpha\beta\gamma} = -L^{(0,q)}_{\beta\gamma\alpha}, L^{(0,q)}_{\alpha\beta\gamma} = -L^{(q,0)}_{\gamma\alpha\beta},$$

$$\Upsilon^{(q,i)}_{\alpha\beta} = \Upsilon^{(q,i)}_{\beta\alpha}, \Upsilon^{(0,i)}_{\alpha\beta\gamma} = -\Upsilon^{(0,i)}_{\gamma\alpha\beta}, \Xi^{(i,0)}_{\alpha\beta\gamma} = -\Xi^{(0,i)}_{\gamma\alpha\beta}, (i = 1, 2, ..., n),$$

$$L^{(q,i^*)}_{\alpha\beta} = L^{(q,i^*)}_{\beta\alpha}, L^{(i^*,q)}_{\alpha\beta} = L^{(i^*,q)}_{\beta\alpha}, (i^* = 1, 2, ..., n-1),$$

$$L^{(0,i^*)}_{\alpha\beta\gamma} = -L^{(i^*,0)}_{\gamma\alpha\beta}, L^{(i^*,0)}_{\alpha\beta\gamma} = -L^{(0,i^*)}_{\beta\gamma\alpha}, (i^* = 1, 2, ..., n-1),$$

$$L^{(i^*,j^*)}_{\alpha\beta} = L^{(i^*,j^*)}_{\beta\alpha}, \qquad (i^*, j^* = 1, 2, ..., n-1),$$

$$L^{(i,j)}_{\alpha\beta} = L^{(i,j)}_{\beta\alpha}, \qquad (i, j = 1, 2, ..., n), \tag{32}$$

$$\Upsilon^{(i^*,i)}_{\alpha\beta} = \Upsilon^{(i^*,i)}_{\beta\alpha}, \qquad (i^* = 1, 2, ..., n-1), (i = 1, 2, ..., n),$$

$$L^{(i,i^*)}_{\alpha\beta} = L^{(i,i^*)}_{\beta\alpha}, \qquad (i = 1, 2, ..., n), (i^* = 1, 2, ..., n-1),$$

$$\Xi^{(i,q)}_{\alpha\beta} = \Xi^{(i,q)}_{\beta\alpha}, \qquad (i = 1, 2, ..., n),$$

$$\Xi^{(i,i^*)}_{\alpha\beta} = \Xi^{(i,i^*)}_{\beta\alpha}, \qquad (i^* = 1, 2, ..., n-1),$$

$$\bar{\Upsilon}^{(i,j)}_{\alpha\beta} = \bar{\Upsilon}^{(i,j)}_{\beta\alpha}, \qquad (i, j = 1, 2, ..., n).$$

The equations (32) reduce the number of independent components of the phenomenological tensors. The special case of isotropy will be discussed in the next section.

6. Phenomenological equations for isotropic media.

The phenomenological tensors are determined by the physical properties of the medium. If the medium is isotropic these tensors must be invariant with respect to all rotations and to inversion of the axis-frame. The existence of spatial symmetry properties in a material system may simplify the form of the phenomenological equations a such way that the Cartesian components of the fluxes do not depend on all Cartesian components of the thermodynamic forces (Jeffreys 1957; De Groot and Mazur 1962).

In this section, we consider perfect isotropic media for which the symmetry properties are invariant under orthogonal transformations with respect to all rotations and to inversion of the frame of axes. In this case it can be shown that the phenomenological tensors have the following forms

$$L^{(q,q)}_{\alpha\beta} = \lambda^{(q,q)}\delta_{\alpha\beta}, L^{(q,i^*)}_{\alpha\beta} = \lambda^{(q,i^*)}\delta_{\alpha\beta}, \Upsilon^{(q,i)}_{\alpha\beta} = \bar{\lambda}^{(q,i)}\delta_{\alpha\beta}, \tag{33}$$

$$m^{(i)}_{\beta\sigma} = a^{(i)}\delta_{\beta\sigma}, \tag{34}$$

$$L^{(i^*,q)}_{\alpha\beta} = \eta^{(i^*,q)}\delta_{\alpha\beta}, L^{(i^*,j^*)}_{\alpha\beta} = \eta^{(i^*,j^*)}\delta_{\alpha\beta}, \Upsilon^{(i^*,i)}_{\alpha\beta} = \bar{\eta}^{(i^*,i)}\delta_{\alpha\beta}, \tag{35}$$

$$L_{\alpha\beta\gamma+,\sigma}^{(0,0)} = T\left(\lambda_1^{(0,0)}\delta_{\alpha\beta}\,\delta_{\gamma\sigma} + \lambda_2^{(0,0)}\delta_{\alpha\gamma}\delta_{\beta\sigma} + \lambda_3^{(0,0)}\delta_{\alpha\sigma}\delta_{\beta\gamma}\right), \tag{36}$$

$$\Xi_{\alpha\beta}^{(i,q)} = v^{(i,q)}\delta_{\alpha\beta}\,,\ \Xi_{\alpha\beta}^{(i,i^*)} = v^{(i,i^*)}\delta_{\alpha\beta}\,,\ \bar{\Upsilon}_{\alpha\beta}^{(i,j)} = \bar{v}^{(i,j)}\delta_{\alpha\beta}\,, \tag{37}$$

while the phenomenological tensors of the third order vanish.

Introducing the equations (33)-(37) in (28)-(31) we have:

$$J'^{(q)} = \lambda^{(q,q)}\,\mathrm{grad}T^{-1} - \sum_{i^*=1}^{n-1}\lambda^{(q,i^*)}\mathrm{grad}(\mu_{i^*}T^{-1}) - \rho\sum_{i=1}^{n}\bar{\lambda}^{(q,i)}a^{(i)}\frac{d\xi^{(i)}}{dt}\,, \tag{38}$$

$$J^{(i^*)} = \eta^{(i^*,q)}\,\mathrm{grad}T^{-1} - \sum_{j^*=1}^{n-1}\eta^{(i^*,j^*)}\mathrm{grad}(\mu_{j^*}T^{-1}) - \rho\sum_{i=1}^{n}\bar{\eta}^{(i^*,i)}a^{(i)}\frac{d\xi^{(i)}}{dt}\,, \tag{39}$$

$$\Pi_{\alpha\beta} = \lambda_1^{(0,0)}\,\mathrm{div}\,\mathbf{v}\,\delta_{\alpha\beta} + \left(\lambda_2^{(0,0)} + \lambda_3^{(0,0)}\right)\frac{d\varepsilon_{\alpha\beta}}{dt}\,, \tag{40}$$

$$\xi^{(i)} = v^{(i,q)}\,\mathrm{grad}T^{-1} - \sum_{i^*=1}^{n-1}v^{(i,i^*)}\mathrm{grad}(\mu_{i^*}T^{-1}) - \rho\sum_{j=1}^{n}\bar{v}^{(i,j)}a^{(j)}\frac{d\xi^{(j)}}{dt}\,. \tag{41}$$

In the matricial form the equations (38) and (39) can be joined in the form

$$J = \Lambda^{(J)}\,\mathrm{grad}\,\chi + \mathbf{M}^{(J)}\frac{d\xi}{dt}\,. \tag{42}$$

In (42) we have put

$$J = \begin{pmatrix} J'^{(q)} \\ J^{(1)} \\ \vdots \\ J^{(n-1)} \end{pmatrix}, \qquad \chi = \begin{pmatrix} T^{-1} \\ -\mu_1 T^{-1} \\ \vdots \\ -\mu_{n-1}T^{-1} \end{pmatrix}, \qquad \xi = \begin{pmatrix} \xi^{(1)} \\ \xi^{(2)} \\ \vdots \\ \xi^{(n)} \end{pmatrix}, \tag{43}$$

$$\Lambda^{(J)} = \begin{pmatrix} \lambda^{(q,q)} & \lambda^{(q,1)} & \dots & \lambda^{(q,n-1)} \\ \eta^{(1,q)} & \eta^{(1,1)} & \dots & \eta^{(1,n-1)} \\ \vdots & \vdots & & \vdots \\ \eta^{(n-1,q)} & \eta^{(n-1,1)} & \dots & \eta^{(n-1,n-1)} \end{pmatrix}, \tag{44}$$

$$\mathbf{M}^{(J)} = -\rho\begin{pmatrix} \bar{\lambda}^{(q,1)}a^{(1)} & \bar{\lambda}^{(q,2)}a^{(2)} & \dots & \bar{\lambda}^{(q,n)}a^{(n)} \\ \bar{\eta}^{(1,1)}a^{(1)} & \bar{\eta}^{(1,2)}a^{(2)} & \dots & \bar{\lambda}^{(1,n)}a^{(n)} \\ \vdots & \vdots & & \vdots \\ \bar{\eta}^{(n-1,1)}a^{(1)} & \bar{\eta}^{(n-1,2)}a^{(2)} & \dots & \bar{\lambda}^{(n-1,n)}a^{(n)} \end{pmatrix}. \tag{45}$$

Let us now notice (Ciancio V. and Verhás 1990, 1991) that the form of the entropy function given in Section **3** does not make the choice of the dynamic variables uniquely, in fact, any orthogonal transformation of them leaves the entropy function unchanged. There follows that matrix of coefficients $\bar{v}^{i,j}$ in (41) might have a diagonal form (this means that the relaxation of a dynamic variable is independent on the others). In this case the equation (41) becomes

$$\xi = \Lambda^{(\xi)}\,\mathrm{grad}\,\chi + \mathbf{M}^{(\xi)}\frac{d\xi}{dt}\,. \tag{46}$$

where

$$\Lambda^{(\xi)} = \begin{pmatrix} \nu^{(1,q)} & \nu^{(1,1)} & \ldots & \nu^{(1,n-1)} \\ \nu^{(2,q)} & \nu^{(2,1)} & \ldots & \nu^{(2,n-1)} \\ \vdots & \vdots & & \vdots \\ \nu^{(n,q)} & \nu^{(n,1)} & \ldots & \nu^{(n,n-1)} \end{pmatrix}, \tag{47}$$

$$\mathbf{M}^{(\xi)} = -\rho \begin{pmatrix} \bar{\nu}^{(1,1)} a^{(1)} & 0 & \ldots & 0 \\ 0 & \bar{\nu}^{(2,2)} a^{(2)} & \ldots & 0 \\ \vdots & \vdots & & \vdots \\ 0 & 0 & \ldots & \bar{\nu}^{(n,n)} a^{(n)} \end{pmatrix}. \tag{48}$$

From (46) we have

$$\frac{d\xi}{dt} = \left(\mathbf{M}^{(\xi)}\right)^{-1} \xi - \left(\mathbf{M}^{(\xi)}\right)^{-1} \Lambda^{(\xi)} \operatorname{grad} \chi, \tag{49}$$

to be considered in (42) thus giving:

$$J = J_0 + J_1 \tag{50}$$

where

$$\begin{cases} J_0 = \mathscr{A} \operatorname{grad} \chi, \\ J_1 = \mathscr{B} \xi, \end{cases} \tag{51}$$

with

$$\begin{cases} \mathscr{A} = \Lambda^{(J)} - \mathbf{M}^{(J)} \left(\mathbf{M}^{(\xi)}\right)^{-1} \Lambda^{(\xi)}, \\ \mathscr{B} = \mathbf{M}^{(J)} \left(\mathbf{M}^{(\xi)}\right)^{-1}. \end{cases} \tag{52}$$

If $\det \mathscr{B} \neq 0$ from $(51)_2$ we have

$$\xi = \mathscr{B}^{-1} J_1, \tag{53}$$

from where together with (49) gives

$$\left(\mathscr{B} \mathbb{M}\right)^{-1} \frac{dJ_1}{dt} + J_1 = -\mathbb{M}^{-1} \mathbb{N} \operatorname{grad} \chi, \tag{54}$$

where

$$\begin{cases} \mathbb{M} = \frac{d\mathscr{B}^{-1}}{dt} - \left(\mathscr{B} \mathbf{M}^{(\xi)}\right)^{-1}, \\ \mathbb{N} = \left(\mathbf{M}^{(\xi)}\right)^{-1} \Lambda^{(\xi)}. \end{cases} \tag{55}$$

Now, we consider the particular case in which $\mathscr{A} = 0$. This means, in virtue of $(52)_1$, that

$$\Lambda^{(J)} = \mathbf{M}^{(J)} \left(\mathbf{M}^{(\xi)}\right)^{-1} \Lambda^{(\xi)}, \tag{56}$$

and from (50) and (51) one has

$$J_0 = 0, \quad \text{and} \quad J \equiv J_1 = \mathscr{B} \xi \tag{57}$$

i.e., in the present case each internal variable is a combination of all diffusive flows (see (53) and (43)) and satisfies to equation (54) which is of Maxwell-Cattaneo-Vernotte type. Thus,

we obtain, in the framework of thermodynamics of internal variables and without additional hypotheses *a priori* the phenomenological equations of diffusive flows hypothesized in two previous papers by Francaviglia *et al.* (2006, 2008).

In more general case, if $\mathscr{A} \neq 0$, from (50), (51) and (54) we obtain

$$\frac{dJ}{dt} = \mathscr{C} \operatorname{grad}\chi + \mathscr{A} \frac{d}{dt}(\operatorname{grad} \chi) - \mathscr{D}J \qquad (58)$$

where

$$\begin{cases} \mathscr{C} = \dfrac{d\mathscr{A}}{dt} - \mathscr{B}\mathbb{N} - \mathscr{B}\mathbb{M}\mathscr{A}\,, \\ \mathscr{D} = \mathscr{B}\mathbb{M}. \end{cases} \qquad (59)$$

In the stationary case the equation (58) reduces to:

$$J = \mathscr{D}^{-1} \mathscr{C} \operatorname{grad}\chi \qquad (60)$$

which is equivalent to the classical phenomenological equations describing the Soret e Dufor effects (see De Groot and Mazur (1962), pag. 273).

7. Conclusions

In this paper we have introduced *n* vectorial internal variables in order to characterize the deviation from local equilibrium of the entropy due to phenomena of mass and heat diffusion. Using the techniques of CIT with internal variables has been possible to describe the relaxation of these diffusive phenomena by deriving the phenomenological equations for all dissipative flows and for internal variables. The dissipative flows are decomposed into two contributions, the first to meet rules of Soret-Dufour type, the latter satisfies equations of MCV type. By neglecting the *n* internal variables we obtain the evolution equations for the flows of heat and mass diffusion of Jeffreys type that, as a special case, are reduced to those of MCV type.

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