A thermodynamic theory on the interaction of thermal and diffusive effects in viscous fluids

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Abstract. In this paper thermodiffusion in a mixture of viscous fluids is described by using a procedure of classical irreversible thermodynamic (CIT) with internal variables. In particular, the deviation from local equilibrium is characterized by some vectorial internal variables [12]-[9] and a generalized entropy current density in terms of current multipliers ([40],[54]). The coupling between mass diffusion and heat conduction is taken into account and phenomenological generalizations of Fick's, Fourier's and Newton's laws are also obtained.

M.S.C. 2010: 35L65, 58J45, 76A05, 80A17.
Key words: Non-equilibrium thermodynamics; internal variables; viscous fluids; current multipliers; Fick law; Fourier law; Soret effect; Dufour effect.

1 Introduction

The thermodiffusion phenomena in binary fluids are studied in fluid dynamic, physics, biology and chemistry [32] and they are of fundamental interest both from a theoretical and experimental point of view.
Generally mass diffusion is described by Fick's law which, however, leads to parabolic differental equations describing pertubations which propagate with infinite velocity so that it is not applicable to transitory situations involving, for istance, high frequencies. In addition, Fick's law must be generalized in various fields of applications, such as the diffusion of polymers in solvents and transport through biological membranes [32]. Interesting coupling effects occur when mass diffusion is coupled with thermal effects. In this case it is necessary that also the Fourier's law must be generalized because, as is well known, it leads to parabolic equation for the heat propagation.
The thermodiffusion phenomena have been studied in the context of different thermodynamic schools such as *Classical Irreversible Thermodynamic* (CIT) [44]-[51], *Rational Thermodynamics* (RT) [51, 41] and in three recent approaches : *Extended Irreversible Thermodynamics* (EIT) [26, 32], *General Equation for the Non-Equilibrium Reversible-Irreversible Coupling* (GENERIC) [23]-[22] and *Internal Variables Theory* (IVT) [29]-[43].

BSG Proceedings, vol. 25, 2018, pp. 17-29.

In this paper, using the methodology of CIT we study with aid of internal variables thermodiffusion effects in viscous fluids.
In sect.2 we consider a two-component mixture of viscous fluids and formulate the conservation laws with the concept of total heat flux.
In sect.3 assuming a vector as internal variable which gives rise to thermodiffusion phenomena, the Gibbs relation is obtained. By using the concept of current density [40], introduced in sect.4, in sect.5 the phenomenological equations are obtained which generalize the Fourier's and Fick's law and the Newton's law for ordinary viscous flow. Finally, in sect.6, a particular case is considered and it is shown that the heat current and the diffusion flow can be split in two parts: one of these characterizes the Dufour's and Soret's effects, respectively, while the second parts satisfy hyperbolic equations.

2 The conservation laws for two-component mixture of viscous fluids

We consider a two-component mixture of viscous fluids in absence of chemical reactions.
Let $\varrho^{(1)}, \mathbf{v}^{(1)}, \varrho^{(2)}, \mathbf{v}^{(2)}$ be, respectively, the mass density and the velocity of the two components of the mixture and so the total density, ϱ , of the mixture is given by:

$$\varrho = \varrho^{(1)} + \varrho^{(2)} \,. \tag{2.1}$$

In the following the fluid "1" is considered [32] as the fluid which is flowing in the main fluid "2".
For the absence of chemical reactions the quantity $\varrho^{(i)}\,(i = 1, 2)$ satisfies to the following balance equation (see [15] p.12)

$$\frac{\partial \varrho^{(i)}}{\partial t} + \mathrm{div}(\varrho^{(i)}\mathbf{v}^{(i)}) = 0 \,. \tag{2.2}$$

By introducing the baricentric velocity $\mathbf{v}$:

$$\mathbf{v} = \varrho^{-1} \sum_{i=1}^{2} \varrho^{(i)}\mathbf{v}^{(i)} \,, \tag{2.3}$$

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

$$\boldsymbol{J}^{(i)} = \varrho^{(i)}(\mathbf{v}^{(i)} - \mathbf{v}) \,, \tag{2.4}$$

and, of course, we have

$$\boldsymbol{J}^{(1)} + \boldsymbol{J}^{(2)} = 0 \,. \tag{2.5}$$

This means that only one diffusion flow is independent and we will point out below

$$\boldsymbol{J} = \boldsymbol{J}^{(2)} \tag{2.6}$$

and from (2.5) one has

$$\boldsymbol{J} = -\boldsymbol{J}^{(1)} \,. \tag{2.7}$$

Since the barycentric substantial time derivative is

$$\frac{d}{dt} = \frac{\partial}{\partial t} + \mathbf{v} \cdot \mathrm{grad}\,, \tag{2.8}$$

by virtue of (2.1) and (2.2) we obtain the *mass conservation law*

$$\frac{d\varrho}{dt} + \varrho\,\mathrm{div}\,\mathbf{v} = 0\,. \tag{2.9}$$

By introducing the mass concentration $c^{(i)}$:

$$c^{(i)} = \frac{\varrho^{(i)}}{\varrho} \quad (i = 1, 2) \qquad \text{and so} \qquad c^{(1)} + c^{(2)} = 1\,, \tag{2.10}$$

we can put:

$$c = c^{(2)} \quad \text{and} \quad c = 1 - c^{(1)}\,. \tag{2.11}$$

From (2.2), (2.4), (2.6), (2.9), (2.10) and (2.11) one has

$$\varrho\,\frac{dc}{dt} = -\,\mathrm{div}\,\boldsymbol{J}\,. \tag{2.12}$$

The first law of thermodynamics reads

$$\varrho\,\frac{du}{dt} = -\,\mathrm{div}\,\mathbf{q}' - \tau_{\alpha\beta}\,\frac{d\varepsilon_{\alpha\beta}}{dt}\,, \qquad (\alpha, \beta = 1, 2, 3)\,, \tag{2.13}$$

where u is the specific internal energy, $\mathbf{q}'$ 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 (2.13) the total heat flux is

$$\mathbf{q}' = \mathbf{q} + \sum_{1}^{2} h^{(i)}\,\boldsymbol{J}^{(i)}\,, \tag{2.14}$$

where $\mathbf{q}$ is the conduction heat flux, $h^{(i)} (i = 1, 2)$ is the partial specific enthalpy of the i-th component.

Using (2.6) and (2.7) the equation (2.14) becomes

$$\mathbf{q}' = \mathbf{q} + h\,\boldsymbol{J}\,, \tag{2.15}$$

where

$$h = h^{(2)} - h^{(1)}\,, \tag{2.16}$$

and $h\,\boldsymbol{J}$ is the diffusion heat flux.

3 The Gibbs relation for two-component mixture of viscous fluids

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

$$S = S(u, \nu, c^{(1)}, c^{(2)}, \boldsymbol{\xi}) , \tag{3.1}$$

According to the maximum property of the entropy is an equilibrium state and the Morse Lemma [39], the entropy function can be casted into the form

$$S = S^{(eq)}(u, \nu, c^{(1)}, c^{(2)}) - \frac{1}{2} m_{\alpha\beta} \, \xi_\alpha \, \xi_\beta . \tag{3.2}$$

In (3.2) $S^{(eq)}$ 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 $\boldsymbol{\xi}$; $m_{\alpha\beta}(u, \nu, c^{(1)}, c^{(2)})$ is a constitutive tensor characterizing the material coefficients.
From (3.2) we have the following simmetries

$$m_{\alpha\beta} = m_{\beta\alpha} , \tag{3.3}$$

by introducing the following classical definitions

$$\left\{ \begin{array}{l} \dfrac{\partial S}{\partial u} = T^{-1} , \quad \dfrac{\partial S}{\partial \nu} = P \, T^{-1}, \\ \dfrac{\partial S}{\partial c^{(i)}} = -T^{-1} \, \mu^{(i)} , \quad (i = 1, 2) . \end{array} \right. . \tag{3.4}$$

where T is the absolute temperature, P is the pressure of the mixture and $\mu^{(i)}$ the chemical potential of the i^{th} component of mixture, with the aid of (3.4) and using (2.11) we obtain from (3.2) for the differential $d\,S$ of S

$$T \, dS = du + P \, d\nu + \mu \, dc - T \, m_{\alpha\beta} \, \xi_\beta \; d\xi_\alpha . \tag{3.5}$$

where $\mu = \mu^{(1)} - \mu^{(2)}$. Equation (3.5) is called Gibbs relation.

4 Entropy balance

It follows from (3.5) that one may also write for the Gibbs relation

$$T \frac{dS}{dt} = \frac{du}{dt} + P \frac{d\nu}{dt} + \mu \frac{dc}{dt} - T \, m_{\alpha\beta} \, \xi_\beta \, \frac{d\xi_\alpha}{dt} . \tag{4.1}$$

Now we observe that from equation (2.9) we have

$$\frac{d\nu}{dt} = \frac{1}{\varrho} \frac{d\epsilon}{dt} , \tag{4.2}$$

where

$$\epsilon \,=\, \varepsilon_{\alpha\beta}\,\delta_{\alpha\beta}\,, \tag{4.3}$$

so that by multiplying both sides of equation (4.1) by $\varrho\, T^{-1}$ and using the first law of thermodynamics (2.13) with (2.3) and equations (4.2) and (2.12), the Gibbs relation (4.1) becomes

$$\begin{aligned} \varrho\,\frac{dS}{dt} = &- \operatorname{div}\Big[T^{-1}\Big(\mathbf{q}+(h-\mu)\boldsymbol{J}\Big)\Big] \,-\, \boldsymbol{J}\cdot \operatorname{grad}\Big(\mu\, T^{-1}\Big) \,+ \\ &+ \Big(\mathbf{q}+h\,\boldsymbol{J}\Big)\cdot \operatorname{grad}\Big(T^{-1}\Big) \,-\, T^{-1}\,\Pi_{\alpha\beta}\,\frac{d\varepsilon_{\alpha\beta}}{dt} \,-\, \varrho\, m_{\alpha\beta}\,\xi_\beta\,\frac{d\xi_\alpha}{dt}\,. \end{aligned} \tag{4.4}$$

In (4.4) tensor $\Pi_{\alpha\beta} \,=\, \tau_{\alpha\beta} \,-\, P\,\delta_{\alpha\beta}$ is the viscous stress.
It is well known that in thermodynamics of non-equilibrium the entropy's balance equation assumes a fundamental role since the second law of thermodynamics must be satisfied by all the constitutive equations that characterize the material properties of the continuous media.
In its most general expression this equation has the following form

$$\varrho\frac{dS}{dt} \,=\, -\operatorname{div}\boldsymbol{J}^{(s)} \,+\, \sigma^{(s)}\,, \tag{4.5}$$

where $\boldsymbol{J}^{(s)}$ is the conductive current density of entropy and $\sigma^{(s)}$ is the entropy production.
In this paper, since the entropy transport is characterized by the presence of dissipative flows, we assume that the current density of the entropy assumes the following form

$$J^{(s)}_\alpha \,=\, B_{\alpha\beta}\,q_\beta \,+C_{\alpha\beta}\,J_\beta\,, \tag{4.6}$$

where $B_{\alpha\beta}$ and $C_{\alpha\beta}$ are second order tensorial constitutive functions to be constrained by the second law. They are the current multipliers introduced by Nyìri [40] and applied in the case of heat conduction [54], [55], [31] and recently in thermodiffusion flows [9].
From (4.4)-(4.6) we obtain for the entropy production the following expression

$$\begin{aligned} \sigma^{(s)} = &\Big(B_{\alpha\beta} \,-T^{-1}\,\delta_{\alpha\beta}\Big)\,\frac{\partial q_\beta}{\partial x^\alpha} + \Big(C_{\alpha\beta} \,-\, s\,T^{-1}\,\delta_{\alpha\beta}\Big)\,\frac{\partial J_\beta}{\partial x^\alpha} + \\ &\Big(\frac{\partial C_{\beta\alpha}}{\partial x_\beta} \,-\, T^{-1}\,\frac{\partial h}{\partial x_\alpha}\Big)\,J_\alpha \,+\, \frac{\partial B_{\alpha\beta}}{\partial x_\alpha}\,q_\alpha \,-T^{-1}\,\Pi_{\alpha\beta}\,\frac{d\varepsilon_{\alpha\beta}}{dt} \,-\, \varrho\, m_{\alpha\beta}\,\xi_\beta\,\frac{d\xi_\alpha}{dt}\,, \end{aligned} \tag{4.7}$$

where

$$s \,=\, h \,-\, \mu\,. \tag{4.8}$$

From (4.7) we see that the entropy production, $\sigma^{(s)}$, is determined as a sum of inner products among the thermodynamic fluxes and affinities Consequently the entropy production is due to different types of phenomena. The first four terms on the right hand side of (4.7) describe the contribution of thermodiffusion flows and the last two terms represent, respectively, the entropy production due to a viscous flow phenomenon and the irreversible process of the variation of internal vectorial variable.

fluxes	$B_{\alpha\beta} - T^{-1}\,\delta_{\alpha\beta}$	$C_{\alpha\beta} \,-\, s\,T^{-1}\,\delta_{\alpha\beta}$	J_α
affinities	$\dfrac{\partial q_\beta}{\partial x_\alpha}$	$\dfrac{\partial J_\beta}{\partial x_\alpha}$	$\dfrac{\partial C_{\beta\alpha}}{\partial x_\beta} - T^{-1}\,\dfrac{\partial h}{\partial x_\alpha}$

Table 1: Thermodynamic fluxes and affinities

fluxes	q_α	$\Pi_{\alpha\beta}$	$\varrho\, m_{\alpha\beta}\,\frac{d\xi_\alpha}{dt}$
affinities	$\dfrac{\partial B_{\beta\alpha}}{\partial x_\beta}$	$-\,T^{-1}\,\dfrac{\partial v_\beta}{\partial x_\alpha}$	$-\,\xi_\beta$

Table 2: Thermodynamic fluxes and affinities

5 Phenomenological equations

According to the usual procedure of non-equilibrium thermodynamics, in order to obtain the phenomenological equations that govern the behavior of the medium in presence of the considered irreversible phenomena, we assume that there exists a linear relationship between the fluxes and the thermodynamic affinities. The coefficients of the linear combinations between flows and affinities are the components of the phenomenological tensors that characterize the physical properties of the medium under examination. If the medium is isotropic, the phenomenological tensors of odd order are null and since in this case the flows and the affinities involved in the production of entropy (4.7) are vectors and double tensors it follows that the phenomenological tensors different from zero must be of order 2 or 4. So we have

$$m_{\alpha\beta} = m\,\delta_{\alpha\beta}\,, \tag{5.1}$$

and the following phenomenological equations hold:

$$q_\alpha \;=\; l_{11}\,\frac{\partial B_{\beta\alpha}}{\partial x^\beta} + l_{12}\left(\frac{\partial C_{\beta\alpha}}{\partial x_\beta} - T^{-1}\,\frac{\partial h}{\partial x_\alpha}\right) - n_1\,\xi_\alpha\,, \tag{5.2}$$

$$J_\alpha \;=\; l_{21}\,\frac{\partial B_{\beta\alpha}}{\partial x^\beta} + l_{22}\left(\frac{\partial C_{\beta\alpha}}{\partial x_\beta} - T^{-1}\,\frac{\partial h}{\partial x_\alpha}\right) - n_2\,\xi_\alpha\,, \tag{5.3}$$

$$\varrho\, m\,\frac{d\xi_\alpha}{dt} \;=\; l_{31}\,\frac{\partial B_{\beta\alpha}}{\partial x^\beta} + l_{32}\left(\frac{\partial C_{\beta\alpha}}{\partial x_\beta} - T^{-1}\,\frac{\partial h}{\partial x_\alpha}\right) - n_3\,\xi_\alpha\,, \tag{5.4}$$

$$\begin{aligned}\Pi_{\alpha\beta} \;=\; &-T^{-1}\left[m_{11}\,\frac{\partial v_\gamma}{\partial x_\gamma}\,\delta_{\alpha\beta} + m_{12}\,\frac{\partial v_\beta}{\partial x_\alpha} + m_{13}\,\frac{\partial v_\alpha}{\partial x_\beta}\right] + \\ &p_{11}\,\frac{\partial q_\gamma}{\partial x_\gamma}\,\delta_{\alpha\beta} + p_{12}\,\frac{\partial q_\alpha}{\partial x_\beta} + p_{13}\,\frac{\partial q_\beta}{\partial x_\alpha} + \\ &r_{11}\,\frac{\partial J_\gamma}{\partial x_\gamma}\,\delta_{\alpha\beta} + r_{12}\,\frac{\partial J_\alpha}{\partial x_\beta} + r_{13}\,\frac{\partial J_\beta}{\partial x_\alpha}\,,\end{aligned} \tag{5.5}$$

with $m_{12} = m_{13}\,, p_{12} = p_{13}\,, r_{12} = r_{13}$,

$$\begin{aligned} B_{\alpha\beta} =& T^{-1}\left[\delta_{\alpha\beta} + m_{21}\,\frac{\partial v_\gamma}{\partial x_\gamma}\,\delta_{\alpha\beta} + m_{22}\,\frac{\partial v_\beta}{\partial x_\alpha} + m_{23}\,\frac{\partial v_\alpha}{\partial x_\beta}\right] + \\ & p_{21}\,\frac{\partial q_\gamma}{\partial x_\gamma}\,\delta_{\alpha\beta} + p_{22}\,\frac{\partial q_\alpha}{\partial x_\beta} + p_{23}\,\frac{\partial q_\beta}{\partial x_\alpha} + \\ & r_{21}\,\frac{\partial J_\gamma}{\partial x_\gamma}\,\delta_{\alpha\beta} + r_{22}\,\frac{\partial J_\alpha}{\partial x_\beta} + r_{23}\,\frac{\partial J_\beta}{\partial x_\alpha}\,, \end{aligned} \tag{5.6}$$

$$\begin{aligned} C_{\alpha\beta} =& T^{-1}\left[s\,\delta_{\alpha\beta} + m_{31}\,\frac{\partial v_\gamma}{\partial x_\gamma}\,\delta_{\alpha\beta} + m_{32}\,\frac{\partial v_\beta}{\partial x_\alpha} + m_{33}\,\frac{\partial v_\alpha}{\partial x_\beta}\right] + \\ & p_{31}\,\frac{\partial q_\gamma}{\partial x_\gamma}\,\delta_{\alpha\beta} + p_{32}\,\frac{\partial q_\alpha}{\partial x_\beta} + p_{33}\,\frac{\partial q_\beta}{\partial x_\alpha} + \\ & r_{31}\,\frac{\partial J_\gamma}{\partial x_\gamma}\,\delta_{\alpha\beta} + r_{32}\,\frac{\partial J_\alpha}{\partial x_\beta} + r_{33}\,\frac{\partial J_\beta}{\partial x_\alpha}\,, \end{aligned} \tag{5.7}$$

In (5.2)-(5.5) $l_{ik}, n_i, m_{ij}, p_{ij}, \tau_{ij}$ $(i, j = 1, 2, 3; k = 1, 2)$ are the isotropic scalar conductivity coefficients.

The equation (5.2) may be regarded as a generalization of Fourier's law while the equation (5.3) may be regarded as a generalization of Fick's law. The equation (5.4) is the phenomenological equation for irreversible processes characterized by the internal variables. The equation (5.5) describes the viscous flow phenomenon and this relation may be considered as a generalization of Newton's law for ordinary viscous fluids. Finally, the equations (5.6) and (5.7) are the phenomelogical equations for the currents multipliers.

If $n_3 \neq 0$ and all parameters are constants, by using the equations (5.6) and (5.7) we can eliminate the current multipliers from (5.2)-(5.4) and the following evolution equations for the fluxes can be obtained:

$$\begin{aligned} \tau\,\frac{dq_\alpha}{dt} + q_\alpha =& \tau\,\frac{d}{dt}\left[A^{(1)}_{\alpha\beta}\,\frac{\partial}{\partial x_\beta}(T^{-1}) - l_{12}\,T^{-1}\,\frac{\partial \mu}{\partial x_\alpha} + D^{(1)}_1\,\frac{\partial^2 v_\alpha}{\partial x_\beta^2} + \right. \\ & D^{(1)}_2\,\frac{\partial^2 v_\beta}{\partial x_\alpha \partial x_\beta} + D^{(1)}_3\,\frac{\partial^2 q_\alpha}{\partial x_\beta^2} + D^{(1)}_4\,\frac{\partial^2 q_\beta}{\partial x_\alpha \partial x_\beta} + D^{(1)}_5\,\frac{\partial^2 J_\alpha}{\partial x_\beta^2} + \\ & \left. D^{(1)}_6\,\frac{\partial^2 J_\beta}{\partial x_\alpha \partial x_\beta}\right] + \left(A^{(1)}_{\alpha\beta} - \frac{n_1}{n_3}\,A^{(3)}_{\alpha\beta}\right)\frac{\partial}{\partial x_\beta}\left(T^{-1}\right) + \\ & \left(\frac{n_1}{n_3}\,l_{32} - l_{12}\right)T^{-1}\,\frac{\partial \mu}{\partial x_\alpha} + \left(D^{(1)}_1 - \frac{n_1}{n_3}\,D^{(3)}_1\right)\frac{\partial^2 v_\alpha}{\partial x_\beta^2} + \\ & \left(D^{(1)}_2 - \frac{n_1}{n_3}\,D^{(3)}_2\right)\frac{\partial^2 v_\beta}{\partial x_\alpha \partial x_\beta} + \left(D^{(1)}_3 - \frac{n_1}{n_3}\,D^{(3)}_3\right)\frac{\partial^2 q_\alpha}{\partial x_\beta^2} + \\ & \left(D^{(1)}_4 - \frac{n_1}{n_3}\,D^{(3)}_4\right)\frac{\partial^2 q_\beta}{\partial x_\alpha \partial x_\beta} + \left(D^{(1)}_5 - \frac{n_1}{n_3}\,D^{(3)}_5\right)\frac{\partial^2 J_\alpha}{\partial x_\beta^2} + \\ & \left(D^{(1)}_6 - \frac{n_1}{n_3}\,D^{(3)}_6\right)\frac{\partial^2 J_\beta}{\partial x_\alpha \partial x_\beta}\,, \end{aligned} \tag{5.8}$$

and

$$
\begin{aligned}
\tau \frac{dJ_\alpha}{dt} + J_\alpha = {} & \tau \frac{d}{dt} \Big[A^{(2)}_{\alpha\beta} \frac{\partial}{\partial x_\beta} (T^{-1}) - l_{22}\, T^{-1} \frac{\partial \mu}{\partial x_\alpha} + D^{(2)}_1 \frac{\partial^2 v_\alpha}{\partial x_\beta^2} + \\
& D^{(2)}_2 \frac{\partial^2 v_\beta}{\partial x_\alpha \partial x_\beta} + D^{(2)}_3 \frac{\partial^2 q_\alpha}{\partial x_\beta^2} + D^{(2)}_4 \frac{\partial^2 q_\beta}{\partial x_\alpha \partial x_\beta} + D^{(2)}_5 \frac{\partial^2 J_\alpha}{\partial x_\beta^2} + \\
& D^{(2)}_6 \frac{\partial^2 J_\beta}{\partial x_\alpha \partial x_\beta} \Big] + \Big(A^{(2)}_{\alpha\beta} - \frac{n_2}{n_3} A^{(3)}_{\alpha\beta} \Big) \frac{\partial}{\partial x_\beta} \Big(T^{-1} \Big) + \\
& \Big(\frac{n_2}{n_3} l_{32} - l_{22} \Big) T^{-1} \frac{\partial \mu}{\partial x_\alpha} + \Big(D^{(2)}_1 - \frac{n_2}{n_3} D^{(3)}_1 \Big) \frac{\partial^2 v_\alpha}{\partial x_\beta^2} + \\
& \Big(D^{(2)}_2 - \frac{n_2}{n_3} D^{(3)}_2 \Big) \frac{\partial^2 v_\beta}{\partial x_\alpha \partial x_\beta} + \Big(D^{(2)}_3 - \frac{n_2}{n_3} D^{(3)}_3 \Big) \frac{\partial^2 q_\alpha}{\partial x_\beta^2} + \\
& \Big(D^{(2)}_4 - \frac{n_2}{n_3} D^{(3)}_4 \Big) \frac{\partial^2 q_\beta}{\partial x_\alpha \partial x_\beta} + \Big(D^{(2)}_5 - \frac{n_2}{n_3} D^{(3)}_5 \Big) \frac{\partial^2 J_\alpha}{\partial x_\beta^2} + \\
& \Big(D^{(2)}_6 - \frac{n_2}{n_3} D^{(3)}_6 \Big) \frac{\partial^2 J_\beta}{\partial x_\alpha \partial x_\beta} \,,
\end{aligned}
\tag{5.9}
$$

where

$$\tau = \frac{\varrho\, m}{n_3} \tag{5.10}$$

$$
\begin{aligned}
A^{(i)}_{\alpha\beta} = {} & \Big[\big(l_{i1}\, m_{21} + l_{i2}\, m_{31} \big) \frac{\partial v_\gamma}{\partial x_\gamma} + l_{i1} + s\, l_{i2} \Big] \delta_{\alpha\beta} + \\
& \big(l_{i1}\, m_{22} + l_{i1}\, m_{32} \big) \frac{\partial v_\alpha}{\partial x_\beta} + \big(l_{i1}\, m_{23} + l_{i2}\, m_{33} \big) \frac{\partial v_\beta}{\partial x_\alpha} \,, \quad (i = 1,2,3) \,,
\end{aligned}
\tag{5.11}
$$

$$D^{(i)}_1 = T^{-1} \big(l_{i1}\, m_{22} + l_{i2}\, m_{32} \big) \,, \quad (i = 1,2,3) \,, \tag{5.12}$$

$$D^{(i)}_2 = T^{-1} \Big[l_{i1} \big(m_{21} + m_{23} \big) + l_{i2} \big(m_{31} + m_{33} \big) \Big] \,, \quad (i = 1,2,3) \,, \tag{5.13}$$

$$D^{(i)}_3 = l_{i1}\, p_{23} + l_{i2}\, p_{33} \,, \quad (i = 1,2,3) \,, \tag{5.14}$$

$$D^{(i)}_4 = l_{i1} \left(p_{21} + p_{22} \right) + l_{i2} \left(p_{31} + p_{32} \right) \,, \quad (i = 1,2,3) \,, \tag{5.15}$$

$$D^{(i)}_5 = l_{i1}\, r_{23} + l_{i2}\, r_{33} \,, \quad (i = 1,2,3) \,, \tag{5.16}$$

$$D^{(i)}_6 = l_{i1} \left(r_{21} + r_{22} \right) + l_{i2} \left(r_{31} + r_{32} \right) \,, \quad (i = 1,2,3) \,. \tag{5.17}$$

(5.18)

The equations (5.8) and (5.9) are, respectively, the evolution equation of the heat conduction and the diffusion flow as discussed in [9].

6 A particular case

In this section we consider the particular case in which:

$$
\begin{aligned}
& m_{21} = m_{22} = m_{23} = p_{21} = p_{22} = p_{23} = r_{21} = r_{22} = r_{23} = 0 \,, \\
& m_{31} = m_{32} = m_{33} = p_{31} = p_{32} = p_{33} = r_{31} = r_{32} = r_{33} = 0 \,.
\end{aligned}
\tag{6.1}
$$

In this case, from (5.6) and (5.7), one has:

$$B_{\alpha\beta} = T^{-1}\,\delta_{\alpha\beta} \quad ; \quad C_{\alpha\beta} = T^{-1}\,s\,\delta_{\alpha\beta}\,, \tag{6.2}$$

and the current density of the entropy [see (4.6) and (4.8)] becomes

$$J^{(s)}_\alpha = T^{-1}\left(q'_\alpha - \mu\,J_\alpha\right), \tag{6.3}$$

where

$$q'_\alpha = q_\alpha + h\,J_\alpha\,. \tag{6.4}$$

The expression (6.3) is the classical expression for the entropy flow for mixtures (see [15] pag. 49).
Using the (6.2) and (4.8) the equations (5.2)-(5.5) take the form:

$$q_\alpha = \left(l_{11} + s\,l_{12}\right)\frac{\partial}{\partial x_\alpha}(T^{-1}) - l_{12}\,T^{-1}\,\frac{\partial\mu}{\partial x_\alpha} - n_1\,\xi_\alpha\,, \tag{6.5}$$

$$J_\alpha = \left(l_{21} + s\,l_{22}\right)\frac{\partial}{\partial x_\alpha}(T^{-1}) - l_{22}\,T^{-1}\,\frac{\partial\mu}{\partial x_\alpha} - n_2\,\xi_\alpha\,, \tag{6.6}$$

$$\varrho\,m\,\frac{d\xi_\alpha}{dt} = \left(l_{31} + s\,l_{32}\right)\frac{\partial}{\partial x_\alpha}(T^{-1}) - l_{32}\,T^{-1}\,\frac{\partial\mu}{\partial x_\alpha} - n_3\,\xi_\alpha\,, \tag{6.7}$$

$$\Pi_{\alpha\beta} = T^{-1}\left[m_{11}\,\frac{\partial v_\gamma}{\partial x_\gamma}\,\delta_{\alpha\beta} + m_{12}\left(\frac{\partial v_\beta}{\partial x_\alpha} + \frac{\partial v_\alpha}{\partial x_\beta}\right)\right]. \tag{6.8}$$

The equation (6.8) is the Newton's law for ordinary viscous fluids.
Now we observe that the equation (6.5) can be written as

$$q_\alpha = q^{(0)}_\alpha + q^{(1)}_\alpha\,, \tag{6.9}$$

where

$$q^{(0)}_\alpha = \left(l_{11} + s\,l_{12}\right)\frac{\partial}{\partial x_\alpha}(T^{-1}) - l_{12}\,T^{-1}\,\frac{\partial\mu}{\partial x_\alpha}\,, \tag{6.10}$$

and

$$q^{(1)}_\alpha = -\,n_1\,\xi_\alpha\,. \tag{6.11}$$

Eliminating ξ_α between (6.7) and (6.11) we obtain

$$\tau\,\frac{dq^{(1)}_\alpha}{dt} + q^{(1)}_\alpha = \frac{n_1}{n_3}\left(l_{31} + s\,l_{32}\right)\frac{\partial}{\partial x_\alpha}(T^{-1}) + \frac{n_1 l_{32}}{n_3}\,T^{-1}\,\frac{\partial\mu}{\partial x_\alpha}\,, \tag{6.12}$$

where τ is expressed by (5.10).
From (6.9) we can see that the heat current is split into two parts [12, 13, 11] : the first one, $q^{(0)}_\alpha$, that characterizes Dufour effect (6.10) and the second part, $q^{(1)}_\alpha$ that is governed by Maxwell-Cattaneo-Vernotte type equation (MCV) [38, 1, 56] in which τ is the relaxation time.

Similarly, using (6.6), the diffusion flow can be written in the form

$$J_\alpha = J_\alpha^{(0)} + J_\alpha^{(1)} , \tag{6.13}$$

where

$$J_\alpha^{(0)} = \Big(l_{21} + s\, l_{22}\Big) \frac{\partial}{\partial x_\alpha}(T^{-1}) - l_{22}\, T^{-1} \frac{\partial \mu}{\partial x_\alpha} , \tag{6.14}$$

and

$$J_\alpha^{(1)} = - n_2\, \xi_\alpha . \tag{6.15}$$

Combining the equation (6.7) with (6.15) we have:

$$\tau \frac{dJ_\alpha^{(1)}}{dt} + J_\alpha^{(1)} = \frac{n_2}{n_3} \Big(l_{31} + s\, l_{32}\Big) \frac{\partial}{\partial x_\alpha}(T^{-1}) + \frac{n_2 l_{32}}{n_3} T^{-1} \frac{\partial \mu}{\partial x_\alpha} , \tag{6.16}$$

Therefore, also the diffusion flow can be split into two parts [12, 13, 11] : the first one, $J_\alpha^{(0)}$, that characterizes the Soret effect (6.14) and the second part, $J_\alpha^{(1)}$ that is governed by MCV type equation in which τ is the relaxation time.

7 Conclusions

In this paper, by using the general methods of classical irreversible thermodynamic (CIT), thermodiffusion phenomena have been studied in the contest of theory of internal variables (IV).

The choice of this methodology CIT-IV has been suggested by its flexibility characterized by the fact that it is not necessary *"a priori"* specify the physical meaning of the internal variables but only their influence on phenomena, occuring inside the material under consideration. For this reason the methodology of CIT-IV has been applied to a wide-scale phenomena in continuous media: *i.e* in thermodynamical theories of rheology [27]-[7] and in the study of dielectric and magnetic relaxation phenomena developed with theoretical results [30]-[10] conformed by experimental data [6]-[5].

The results obtained in this paper generalized the classical Fourier's and Fick's laws and the Newton's law for ordinary viscous fluids.

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