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The Hamilton Principle for Fluid Binary Mixtures with two Temperatures

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Abstract. – *For binary mixtures of fluids without chemical reactions, but with components having different temperatures, the Hamilton principle of least action is able to produce the equation of motion for each component and a balance equation of the total heat exchange between components. In this nonconservative case, a Gibbs dynamical identity connecting the equations of momenta, masses, energy and heat exchange allows to deduce the balance equation of energy of the mixture. Due to the unknown exchange of heat between components, the number of obtained equations is less than the number of field variables. The second law of thermodynamics constrains the possible expression of a supplementary constitutive equation closing the system of equations. The exchange of energy between components produces an increasing rate of entropy and creates a dynamical pressure term associated with the difference of temperature between components. This new dynamical pressure term fits with the results obtained by classical thermodynamical arguments in* [1] *and confirms that the Hamilton principle can afford to obtain the equations of motions for multi-temperature mixtures of fluids.*

1. – Introduction.

The theory of mixtures considers generally two different kinds of continua: homogeneous mixtures (each component occupies the whole mixture volume) and heterogeneous ones (each component occupies only a part of the mixture volume). At least four approaches to the construction of two-fluids models are known.

The first one for studying the heterogeneous two-flows is an averaging method (Ishii [2]; Nigmatulin [3]). The averaged equations of motion are obtained by applying an appropriate averaging operator to the balance laws of mass, energy, etc..., valid inside each phase [4, 5]. A second approach known as Landau method [6, 7] was used for the construction of a quantum liquid model and was purposed for the homogeneous mixtures of fluids [8]. For the total mixture, the method requires the balances of mass, momentum, energy, complemented with the Galilean invariance principle and the second law of thermodynamics [9]. A third approach is presented in extended thermodynamics; the mixtures are considered as a collection of different media co-existing in the physical space. This approach is done in the context of rational thermodynamics

[10] founded on the postulate that each constituent obeys the same balance laws as a single fluid [11, 12, 13]. The thermodynamical processes must verify the second law of thermodynamics and it is possible to purpose phenomenological constitutive equations which allow to obtain the structure of constitutive or production terms (as Fick's law, Fourier's Law etc.) and to close the system of equations.

There exists a different approach based on the Hamilton principle which is used for the construction of conservative (non-dissipative) mathematical models of continua. The principle was initiated by Lin [14], Serrin [15] and many others to obtain the governing equations of one component continua [15, 16, 17] and involves an Hamilton action. The variations of the Hamilton action are constructed in terms of virtual motions of continua which may be defined both in Lagrangian and Eulerian coordinates [15, 16].

Here, we use variations in the case of fluid mixtures. The variational approach to the construction of two-fluid models has been used by many authors (Bedford & Drumheller [18]; Berdichevsky [19]; Geurst [20]; Gouin [21]; Gavrilyuk & Gouin [22]; Gouin & Ruggeri [23]).

To study thermodynamical processes by the Hamilton principle, the entropy of the total mixture or the entropies of components are added to the field parameters instead of temperatures. The Lagrangian is the difference between the kinetic energy and an internal potential per unit volume depending on the densities, the entropies and the relative velocities of the mixture components (and a potential due to external forces). The internal potential per unit volume can be interpreted as a Legendre transformation of the internal energy. In this case, it is not necessary to distinguish molecular mixtures from heterogeneous fluids when each component occupies only a part of the mixture volume [24, 25]. Consequently, the terms including interaction between different components of the mixture do not require constitutive postulates difficult to interpret experimentally. They come from the direct knowledge of the internal potential per unit volume.

The assumption of a common temperature for all the components is open to doubt for the suspensions of particles [26] as well as in the mixtures of gases in the early universe [27]. By using the Hamilton principle, the existence of several temperatures (one temperature for each component) must be associated with the existence of several entropies (one specific entropy for each component). That will be the aim of this paper: the internal potential per unit volume is a function of the densities, the entropies and the difference of velocity between components.

The plan of the article is as follows:

In section 2, we formulate an extended form of the Hamilton principle of stationary action allowing to produce the governing equations of motion for each component of a binary mixture. From the invariance of time, we deduce an equation of the exchange of heat between components. With two temperatures (one temperature for each component), the system of governing equations together with the balance of masses is not closed: Hamilton's principle is not able to get a complete set of equations when exchange of energies occurs between components. In this case, we need an additive constitutive equation to close the system.

In section 3, we obtain a Gibbs dynamical identity. This identity allows to obtain the equation of energy for the total mixture. The equation of motion for the total mixture and the equation of energy are in divergence form; as in [28], it is not the same for the component equations of motion.

In section 4, we consider the case of weakly dissipative mixtures and introduce an average temperature of the total mixture. The average temperature corresponds to a local equilibrium different from the real state, with nonequal component temperatures but with the same total internal energy. The total pressure of the mixture in the real state is different from the pressure associated with the mixture at the local equilibrium [29, 30]. The entropy variation rate of the mixture must be in accordance with the second law of thermodynamics which implies an additive constitutive equation for the pressure. The constitutive equation depends on the physical properties of the two constituents and we focus on the fact that the new pressure term does not obey the same rule than the other terms due to dissipation.

In section 5, as an example, we reconsider the special case of a mixture of perfect gases.

Finally, we compare our results with the conclusions obtained in [1] by using classical arguments of rational thermodynamics.

2. – Governing equations in conservative cases.

In a Galilean system of coordinates, the motion of a two-fluid continuum can be represented by two diffeomorphisms

$$\boldsymbol{Z}_a = \Phi_a(\boldsymbol{z}), \qquad (a = 1,2)$$

or

$$\lambda = t \qquad \text{and} \qquad \boldsymbol{X}_a = \phi_a(t,\boldsymbol{x}),$$

where $\boldsymbol{z} = (t,\boldsymbol{x})$ denotes Eulerian coordinates in a four-dimensional domain ω in the time-space and $\boldsymbol{Z}_a = (\lambda,\boldsymbol{X}_a)$ denotes Lagrangian coordinates of the component a in a four-dimensional reference space ω_a. The conservation of matter for each component requires that

$$\rho_a \det F_a = \rho_{a0}(\boldsymbol{X}_a) \;\text{ with }\; F_a = \frac{\partial \boldsymbol{x}}{\partial \boldsymbol{X}_a}, \tag{1}$$

where ρ_{a0} is the reference density in ω_a and $\det(\partial\boldsymbol{x}/\partial\boldsymbol{X}_a)$ is the Jacobian determinant of the motion of the component a of density ρ_a. In differentiable cases equations (1) are equivalent to the equations of density balances

$$\frac{\partial\rho_a}{\partial t}+\operatorname{div}(\rho_a\boldsymbol{v}_a)=0, \tag{2}$$

where $\boldsymbol{v}_a$ denotes the velocity of each component a.

The Lagrangian of the binary system is

$$L=\sum_{a=1}^{2}\left(\frac{1}{2}\,\rho_a\boldsymbol{v}_a^2-\rho_a\Omega_a\right)-\eta(\rho_1,\rho_2,s_1,s_2,\boldsymbol{u}),$$

where the summation is taken over the fluid components ($a=1,\,2$) and s_a are the specific entropies, $\boldsymbol{u}=\boldsymbol{v}_2-\boldsymbol{v}_1$ is the relative velocity of components, Ω_a are the external force potentials, η is a potential per unit volume of the mixture. The Lagrangian L is a function of $\rho_a,\boldsymbol{v}_a,s_a$ and we introduce the quantities

$$R_a\equiv\frac{\partial L}{\partial\rho_a}=\frac{1}{2}\boldsymbol{v}_a^2-\frac{\partial\eta}{\partial\rho_a}-\Omega_a, \tag{3}$$

$$\boldsymbol{k}_a^T\equiv\frac{1}{\rho_a}\frac{\partial L}{\partial\boldsymbol{v}_a}=\boldsymbol{v}_a^T-\frac{(-1)^a}{\rho_a}\frac{\partial\eta}{\partial\boldsymbol{u}}, \tag{4}$$

$$\rho_a\,T_a\equiv-\frac{\partial L}{\partial s_a}=\frac{\partial\eta}{\partial s_a}, \tag{5}$$

where ^{T} denotes the transposition and $\dfrac{\partial L}{\partial\boldsymbol{v}_a}$, $\dfrac{\partial\eta}{\partial\boldsymbol{u}}$ are linear forms. Equation (5) defines the temperatures T_a $(a=1,2)$ which are dynamical quantities depending on ρ_1,ρ_2,s_1,s_2 and $\boldsymbol{u}$.

To obtain the equations of component motions by means of the Hamilton principle, we consider variations of particle motions in the form of surjective mappings,

$$\boldsymbol{X}_a=\boldsymbol{\Xi}_a(t,\boldsymbol{x};\kappa_a),$$

where scalars κ_a are defined in a neighborhood of zero; they are associated with a two-parameter family of virtual motions. The real motions correspond to $\kappa_a=0$ such that $\boldsymbol{\Xi}_a(t,\boldsymbol{x};0)=\boldsymbol{\phi}_a(t,\boldsymbol{x})$; the associated virtual displacements generalize what is obtained for a single fluid [16, 24],

$$\delta_a\boldsymbol{X}_a=\frac{\partial\boldsymbol{\Xi}_a(t,\boldsymbol{x};\kappa_a)}{\partial\kappa_a}\Big|_{\kappa_a=0}. \tag{6}$$

The Hamilton action is

$$a=\int_{\omega}L\;dv\,dt.$$

We first consider the Hamilton principle in the form

$$\delta_a a \equiv \left(\frac{da}{d\kappa_a}\right)_{|_{\kappa_a=0}} = \delta_a \int_\omega L \, dv \, dt = 0,$$

under constraints (1), with $\delta_a a$ being the variations of a associated with equation (6).

From the definition of virtual motions, we obtain in Appendix A the values of $\delta_a \boldsymbol{v}_a(\boldsymbol{x},t)$, $\delta_a \rho_a(\boldsymbol{x},t)$ and $\delta_a s_a(\boldsymbol{x},t)$ where $\delta_a \upsilon(t,\boldsymbol{x})$ is the variation of υ at $(t, \boldsymbol{x})$ fixed. By taking into account the formulae in Appendix A and the definitions (3-5), we get

$$\delta_a a = \int_\omega \left(R_a \delta_a \rho_a + \rho_a \boldsymbol{k}_a^T \, \delta_a \boldsymbol{v}_a - \rho_a T_a \delta_a s_a\right) dv \, dt$$

$$= \int_{\omega_a} \left(R_a \operatorname{div}_a(\rho_{a0} \, \delta_a \boldsymbol{X}_a) - \rho_{a0} \, \boldsymbol{k}_a^T \, F_a \, \frac{\partial}{\partial \lambda}(\delta_a \boldsymbol{X}_a) - \rho_{a0} \, T_a \, \frac{\partial s_{a0}}{\partial \boldsymbol{X}_a} \delta_a \boldsymbol{X}_a\right) dv_a \, dt,$$

where div_a is the divergence operator with respect to the coordinates $\boldsymbol{X}_a$. In the last expression all quantities are considered as functions of $(t, \boldsymbol{X}_a)$; the functions are assumed to be smooth enough in the domain ω_a and $\delta_a \boldsymbol{X}_a = 0$ on its boundary. Hence, we get

$$\delta_a a = \int_{\omega_a} \rho_{a0} \left(-\frac{\partial R_a}{\partial \boldsymbol{X}_a} + \frac{\partial}{\partial \lambda}(\boldsymbol{k}_a^T \, F_a) - T_a \frac{\partial s_{a0}}{\partial \boldsymbol{X}_a}\right) \delta_a \boldsymbol{X}_a \, dv_a \, dt,$$

and we obtain the equations of component motions in Lagrangian coordinates,

$$\frac{\partial}{\partial \lambda}(\boldsymbol{k}_a^T \, F_a) - \frac{\partial R_a}{\partial \boldsymbol{X}_a} - T_a \frac{\partial s_{a0}}{\partial \boldsymbol{X}_a} = 0,$$

where $\boldsymbol{k}_a^T$ is defined by equation (4).

By taking into account the identity $\dfrac{d_a F_a}{dt} - \dfrac{\partial \boldsymbol{v}_a}{\partial \boldsymbol{x}} F_a = 0$ and for $\lambda = t$, we rewrite the equations in Eulerian coordinates,

$$\frac{d_a \boldsymbol{k}_a^T}{dt} + \boldsymbol{k}_a^T \frac{\partial \boldsymbol{v}_a}{\partial \boldsymbol{x}} = \frac{\partial R_a}{\partial \boldsymbol{x}} + T_a \frac{\partial s_a}{\partial \boldsymbol{x}} \, . \tag{7}$$

The covector $\boldsymbol{k}_a^T$ is an essential quantity; indeed, $\rho_a \boldsymbol{k}_a$ (and not $\rho_a \boldsymbol{v}_a$) is the momentum for the component a of the mixture.

To obtain the equation of energy, *we need a second variation of motions associated with the time parameter*. The variation corresponds to a virtual motion in the form

$$\lambda = \varphi(t; \kappa),$$

where scalar κ is defined in a neighborhood of zero. The real motion of the mixture corresponds to $\kappa = 0$ such that $\varphi(t;0) = t$; the associated virtual displacement is

$$\delta\lambda = \frac{\partial\varphi(t;\kappa)}{\partial\kappa}\Big|_{\kappa=0}.$$

For a single fluid, the entropy is defined on a reference space ω_o associated with Lagrangian variables; in conservative motion the specific entropy is conserved along the trajectories and in the reference space the entropy depends only on Lagrangian variables $\boldsymbol{X}$ and not on λ.

In multi-component fluids, due to exchanges of energy between the components, the entropies cannot be conserved along component paths; in the reference spaces ω_a, the specific entropies s_a depend also on λ

$$s_a = s_{a0}(\lambda, \boldsymbol{X}_a).$$

The variation of Hamilton's action associated with the second family of virtual motions yields

$$\delta a \equiv \delta\int_\omega L \; d\boldsymbol{x}\, dt = \int_\omega \frac{\partial L}{\partial\lambda}\; \delta\lambda \; dv\, dt \; = 0.$$

From $\displaystyle\frac{\partial L}{\partial\lambda} = \sum_{a=1}^{2}\frac{\partial L}{\partial s_a}\frac{\partial s_{a0}}{\partial\lambda}$, we deduce when $\lambda = t$, $\displaystyle\frac{\partial L}{\partial\lambda} = -\sum_{a=1}^{2}\rho_a T_a\frac{d_a s_a}{dt}$, where $\displaystyle\frac{d_a s_a}{dt} = \frac{\partial s_a}{\partial t} + \frac{\partial s_a}{\partial\boldsymbol{x}}\,\boldsymbol{v}_a$ is the material derivative with respect to velocity $\boldsymbol{v}_a$. We obtain for the total mixture

$$\sum_{a=1}^{2}\rho_a T_a\frac{d_a s_a}{dt} = 0. \tag{8}$$

Due to equations (2) we obtain the equivalent form

$$\sum_{a=1}^{2} Q_a = 0 \qquad \text{with} \qquad Q_a = \left(\frac{\partial\rho_a s_a}{\partial t} + \operatorname{div}(\rho_a \mathrm{s}_a\boldsymbol{v}_a)\right)T_a. \tag{9}$$

Equation (9) expresses that the exchange of energy between components has a null total amount.

3. – Gibbs dynamical identity and equation of energy.

Let us prove that equation (9) leads to the equation of energy of the mixture. We introduce the quantities $\boldsymbol{M}_a$, B_a, S and E such that

$$\boldsymbol{M}_a^T = \rho_a \frac{d_a \boldsymbol{k}_a^T}{dt} + \rho_a \boldsymbol{k}_a^T \frac{\partial \boldsymbol{v}_a}{\partial \boldsymbol{x}} - \rho_a \frac{\partial R_a}{\partial \boldsymbol{x}} - \rho_a \, T_a \frac{\partial s_a}{\partial \boldsymbol{x}},$$

$$B_a = \frac{\partial \rho_a}{\partial t} + \operatorname{div}(\rho_a \boldsymbol{v}_a),$$

$$S = \sum_{a=1}^{2} Q_a,$$

$$E = \sum_{a=1}^{2} \frac{\partial}{\partial t}\left(\rho_a\left(\frac{1}{2}\boldsymbol{v}_a^2 + \Omega_a\right) + \eta - \frac{\partial \eta}{\partial \boldsymbol{u}}\,\boldsymbol{u}\right) + \operatorname{div}\big(\rho_a \boldsymbol{v}_a(\boldsymbol{k}_a^{\mathrm{T}} \boldsymbol{v}_a - \mathrm{R}_a)\big) - \rho_a \frac{\partial \Omega_a}{\partial \mathrm{t}},$$

where $\eta - \dfrac{\partial \eta}{\partial \boldsymbol{u}}\,\boldsymbol{u} = f$ is the Legendre transformation of η with respect to $\boldsymbol{u}$ and corresponds to the volume internal energy of the mixture. We prove in Appendix B the following property:

THEOREM. – *For any motion of the mixture, we have the algebraic identity*

$$E - \left(\sum_{a=1}^{2} M_a^T \boldsymbol{v}_a + (\boldsymbol{k}_a^T \boldsymbol{v}_a - R_a + T_a s_a)\, B_a\right) - S \equiv 0. \tag{10}$$

Relation (10) is the general expression of the *Gibbs identity* in dynamics. Analogous identities were obtained earlier for thermocapillary mixtures [24] and bubbly liquids [31] . Due to the equations of balance of masses (2), momenta (7) and energy (9), deduced from Hamilton's principle, which are respectively

$$B_a = 0, \quad \boldsymbol{M}_a = 0 \ \ (a = 1,2) \quad \text{and} \quad S = 0,$$

we obtain from identity (10):

COROLLARY. – *The motions of a mixture satisfy the equation of energy balance in the form*

$$\sum_{a=1}^{2} \frac{\partial}{\partial t}\left(\rho_a\left(\frac{1}{2}\boldsymbol{v}_a^2 + \Omega_a\right) + f\right) + \operatorname{div}\left(\rho_a \boldsymbol{v}_a\left(\boldsymbol{k}_a^T \boldsymbol{v}_a - \mathrm{R}_a\right)\right) - \rho_a \frac{\partial \Omega_a}{\partial \mathrm{t}} = 0\,. \tag{11}$$

Equation (11) appears as the equation of energy when f is the *total internal energy.*

The equations of component motions are not written in divergence form. Nevertheless by summing equations (7) in the form $\boldsymbol{M}_a^T = 0$ and taking into account equations (1) in the form $B_a = 0$, we obtain by a calculation similar as in [23, 24, 25] the *balance equation for the total momentum* in a divergence form:

$$\sum_{a=1}^{2}\frac{\partial\rho_a\,\boldsymbol{v}_a^T}{\partial t}+\operatorname{div}\Big(\rho_a\,\boldsymbol{v}_a\,\boldsymbol{k}_a^{\mathrm{T}}+\Big(\rho_a\,\frac{\partial\eta}{\partial\rho_a}-\eta\Big)\boldsymbol{I}\Big)\;+\rho_a\,\frac{\partial\Omega_a}{\partial\boldsymbol{x}}=0, \tag{12}$$

where $\boldsymbol{I}$ is the identity tensor. In the following, $\rho\,\boldsymbol{v}=\sum_{a=1}^{2}\rho_a\,\boldsymbol{k}_a=\sum_{a=1}^{2}\rho_a\boldsymbol{v}_a$ is the total momentum and $\rho=\sum_{a=1}^{2}\rho_a$ is the mixture density.

System ((2), (7), (11)), consequence of the Hamilton principle, is a non closed system of equations. In a single conservative fluid, the system of motion equations is closed by the entropy conservation. In case of mixtures with two entropies, the Hamilton principle is not able to close the system of motion equations; we need additional arguments to obtain the evolution equations for each entropy s_a by considering the behaviors of Q_a.

A possibility to close the system of equations is to consider the case when the momenta and heat exchanges between the components are rapid enough to have a common temperature. This case is connected with a conservative equation for the total specific entropy [24].

Another possibility, used by Landau for quantum fluids [7], is to assume that the total specific entropy s is convected along the first component trajectory

$$\frac{\partial\rho_1 s}{\partial t}\;+\;div\;(\rho_1 s\,\boldsymbol{v}_1)=0.$$

In this case, the constitutive functions are $\rho_1, s, \boldsymbol{v}_1, \rho_2, \boldsymbol{v}_2$, where ρ_a $(a=1,2)$ are submitted to the constraints (2) and the case of Helium superfluid is a special case of our study corresponding to $s_1=s$ and $s_2=0$. Such an hypothesis is not acceptable for classical fluids. These assumptions are not valid for heterogeneous mixtures where each phase has different pressures and temperatures [26, 27].

In the following we consider the case when the mixture is *weakly out of equilibrium* such that the difference of velocities $\boldsymbol{u}$ and the difference of temperatures T_2-T_1 are small enough with respect to the main field variables.

4. – Mixtures weakly out of equilibrium.

For the sake of simplicity, we neglect the external forces. Generally, the volume potential η is developed in the form [22, 31] (1)

$$\eta(\rho_1,\rho_2,s_1,s_2,\boldsymbol{u})=e(\rho_1,\rho_2,s_1,s_2)-b(\rho_1,\rho_2,s_1,s_2)\,\boldsymbol{u}^2,$$

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(1) In [1], the internal energy is the sum of the internal energies of the components $\Big(\rho\,\varepsilon=\sum_{a=1}^{2}\rho_a\varepsilon_a(\rho_a,s_a)\Big)$.

where b is a positive function of ρ_1, ρ_2, s_1, s_2. Properties of convexity of the function η are studied in [25]. When $|\boldsymbol{u}|$ is small enough, the equations of motions are hyperbolic [25]. We consider the linear approximation when $|\boldsymbol{u}|$ is small with respect to $|\boldsymbol{v}_1|$ and $|\boldsymbol{v}_2|$. In linear approximation the volume potential is equal to the volume internal energy e,

$$\eta(\rho_1, \rho_2, s_1, s_2, \boldsymbol{u}) \approx e(\rho_1, \rho_2, s_1, s_2) = \rho\, \varepsilon(\rho_1, \rho_2, s_1, s_2),$$

where ε denotes the internal energy per unit mass. Let us note that the diffusion vector $\boldsymbol{j} = \rho_1(\boldsymbol{v}_1 - \boldsymbol{v}) \equiv \rho_2(\boldsymbol{v} - \boldsymbol{v}_2)$ is a small momentum vector deduced respectively from velocities and densities of the components. The equations of density balances can be written in the form

$$\frac{d\rho}{dt} + \rho \operatorname{div} \boldsymbol{v} = 0 \qquad \text{and} \qquad \rho \frac{dc}{dt} + \operatorname{div} \boldsymbol{j} = 0, \tag{13}$$

where $c = \dfrac{\rho_1}{\rho}$ denotes the concentration of component 1 and $\dfrac{d}{dt} = \dfrac{\partial}{\partial t} + \dfrac{\partial}{\partial \boldsymbol{x}}\,.\,\boldsymbol{v}$ is the material derivative with respect to the average velocity of the mixture.

The divergence of a linear operator $\boldsymbol{A}$ is the covector $\operatorname{div}\boldsymbol{A}$ such that, for any constant vector $\boldsymbol{a}$, $(\operatorname{div}\boldsymbol{A})\,\boldsymbol{a} = \operatorname{div}(\boldsymbol{A}\,\boldsymbol{a})$ and we write $\boldsymbol{v}_a\boldsymbol{v}_a^T \equiv \boldsymbol{v}_a \otimes \boldsymbol{v}_a$.

Let us denote by $h_a \equiv \dfrac{\partial e}{\partial \rho_a}$ the specific enthalpy of the component a.

For processes with weak diffusion, the equations of component motions get the form,

$$\rho_a\, \boldsymbol{\Gamma}_a \equiv \frac{\partial \rho_a \boldsymbol{v}_a}{\partial t} + \operatorname{div}(\rho_a \boldsymbol{v}_a \otimes \boldsymbol{v}_a)^T = \rho_a T_a \operatorname{grad} s_a - \rho_a \operatorname{grad} h_a.$$

The equation of total momentum (12) is reduced to

$$\frac{\partial \rho \boldsymbol{v}}{\partial t} + \operatorname{div}\left(\sum_{a=1}^{2}(\rho_a \boldsymbol{v}_a \otimes \boldsymbol{v}_a) - \boldsymbol{t}\right)^T = 0,$$

where $\boldsymbol{t} = \sum\limits_{a=1}^{2} \boldsymbol{t}_a$ is the total stress tensor such that

$$\boldsymbol{t}_{a\nu\gamma} = -p_a\, \delta_{\nu\gamma}, \quad \text{with} \quad p_a = \rho \rho_a \varepsilon_{,\rho_a} = \rho_a e_{,\rho_a} - \frac{\rho_a e}{\rho}\,, \quad p = \sum_{a=1}^{2} p_a\,.$$

The equation of energy (11) writes in the simpler form

$$\frac{\partial}{\partial t}\left(e + \sum_{a=1}^{2} \frac{1}{2}\, \rho_a \boldsymbol{v}_a^2\right) + \operatorname{div}\left(e\, \boldsymbol{v} + \sum_{a=1}^{2}\left(\frac{1}{2}\, \rho_a \boldsymbol{v}_a^2 - \boldsymbol{t}_a\right)\boldsymbol{v}_a\right) = 0.$$

The internal energy is a natural function of densities and entropies. Due to equation (5),

$$\rho_1\, T_1 = \rho\, \frac{\partial \varepsilon}{\partial s_1}(\rho_1, \rho_2, s_1, s_2) \quad \text{and} \quad \rho_2\, T_2 = \rho\, \frac{\partial \varepsilon}{\partial s_2}(\rho_1, \rho_2, s_1, s_2). \tag{14}$$

Let us denote by $\bar{\varepsilon}$ the expression of the specific internal energy as a function of ρ, c, s_1, s_2 such that $\bar{\varepsilon}(\rho, c, s_1, s_2) = \varepsilon(\rho_1, \rho_2, s_1, s_2)$; we get

$$\rho\,\frac{d\varepsilon}{dt} = \rho\,\frac{\partial\bar{\varepsilon}}{\partial\rho}\,\frac{d\rho}{dt} + \rho\,\frac{\partial\bar{\varepsilon}}{\partial c}\,\frac{dc}{dt} + \rho\,\frac{\partial\bar{\varepsilon}}{\partial s_1}\,\frac{ds_1}{dt} + \rho\,\frac{\partial\bar{\varepsilon}}{\partial s_2}\,\frac{ds_2}{dt}\,.$$

Due to the fact that $\rho^2\,\dfrac{\partial\bar{\varepsilon}}{\partial\rho} = p$ and $\dfrac{\partial\bar{\varepsilon}}{\partial c} = h_1 - h_2$, we obtain

$$\rho\,\frac{d\varepsilon}{dt} = \frac{p}{\rho}\,\frac{d\rho}{dt} + \rho\,(h_1 - h_2)\,\frac{dc}{dt} + \rho_1\,T_1\,\frac{ds_1}{dt} + \rho_2\,T_2\,\frac{ds_2}{dt}\,. \tag{15}$$

By taking into account that

$$\frac{d_a s_a}{dt} = \frac{ds_a}{dt} + \frac{\partial s_a}{\partial \boldsymbol{x}}(\boldsymbol{v}_a - \boldsymbol{v})$$

and by using equations (8), (13), equation (15) yields

$$\rho\,\frac{d\varepsilon}{dt} + p\,\mathrm{div}\,\boldsymbol{v} + (h_1 - h_2)\,\mathrm{div}\boldsymbol{j} + (T_1\,\mathrm{grad}\,s_1 - \mathrm{T}_2\,\mathrm{grad}\,s_2)^T\boldsymbol{j} = 0. \tag{16}$$

Due to equations (14), the internal energy can be expressed as a function of densities and temperatures of components

$$\tilde{\varepsilon}(\rho_1, \rho_2, T_1, T_2) = \varepsilon(\rho_1, \rho_2, s_1, s_2).$$

As we did in [1], we define the average temperature T associated with T_1 and T_2 through the implicit solution of the equation

$$\tilde{\varepsilon}(\rho_1, \rho_2, T, T) = \tilde{\varepsilon}(\rho_1, \rho_2, T_1, T_2). \tag{17}$$

We denote by $\Theta_a = T_a - T$ the difference between component and average temperatures which are non-equilibrium thermodynamical variables. Near equilibrium, equation (17) can be expanded to the first order; then

$$\sum_{a=1}^{2} c_v^a\,\Theta_a = 0 \qquad \text{with} \qquad c_v^a = \frac{\partial\tilde{\varepsilon}}{\partial T_a}(\rho_1, \rho_2, T, T). \tag{18}$$

Due to the fact that

$$\rho\,d\varepsilon = \sum_{a=1}^{2}\ \rho_a\,T_a\,ds_a + \frac{p_a}{\rho_a}\,d\rho_a,$$

then

$$\rho\,c_v^1 = T\sum_{a=1}^{2}\rho_a\,\frac{\partial s_a}{\partial T_1}(\rho_1, \rho_2, T, T) \text{ and } \rho\,c_v^2 = T\sum_{a=1}^{2}\rho_a\,\frac{\partial s_a}{\partial T_2}(\rho_1, \rho_2, T, T). \tag{19}$$

The definition of the total entropy s of the mixture is

$$\rho\, s=\sum_{a=1}^{2}\rho_a s_a(\rho_1,\rho_2,T_1,T_2). \tag{20}$$

The first order expansion of equation (20) yields

$$\rho\, s=\sum_{a=1}^{2}\rho_a s_a(\rho_1,\rho_2,T,T)+\rho_a s_a\,\frac{\partial s_a}{\partial T_1}(\rho_1,\rho_2,T,T)\,\Theta_1+\rho_a s_a\,\frac{\partial s_a}{\partial T_2}(\rho_1,\rho_2,T,T)\,\Theta_2 .$$

Due to Relations (18), (19)

$$\rho\, s=\sum_{a=1}^{2}\rho_a s_a(\rho_1,\rho_2,T,T)$$

and the specific entropy s does not depend on Θ_1 and Θ_2 but only on ρ_1,ρ_2 and T. We denote by $\hat\varepsilon$ the internal specific energy as a function of ρ, c, T:

$$\hat\varepsilon(\rho,c,T)=\tilde\varepsilon(\rho_1,\rho_2,T,T),$$

which satisfies the Gibbs equation

$$Tds=d\hat\varepsilon-\frac{p_o}{\rho^2}\,d\rho+(\mu_2-\mu_1)dc,$$

where $p_o(\rho,c,T)$ is the equilibrium pressure at temperature T and $\mu_2-\mu_1$, difference of component chemical potentials, is the chemical potential of the whole mixture.

By taking into account of equation (13), we get

$$\rho\,\frac{d\hat\varepsilon}{dt}+p_o\,\mathrm{div}\,\boldsymbol{v}+(\mu_1-\mu_2)\,\mathrm{div}\boldsymbol{j}-\rho\,T\,\frac{ds}{dt}=0.$$

Moreover,

$$\rho\,\frac{ds}{dt}=\sum_{a=1}^{2}\rho_a\,\frac{d_a s_a}{dt}+\mathrm{div}\,[(s_2-s_1)\boldsymbol{j}\,]. \tag{21}$$

Equation (21) yields the relation between the material derivatives of entropy s and entropies s_1 and s_2. By taking into account of these results in equation (16) and $\hat\varepsilon(\rho,c,T)=\varepsilon(\rho_1,\rho_2,s_1,s_2)$, we obtain

$$T\sum_{a=1}^{2}\rho_a\,\frac{d_a s_a}{dt}+(p-p_o)\,\mathrm{div}\,\boldsymbol{v}\;+((h_1-h_2)-(\mu_1-\mu_2)+T\,(s_2-s_1))\,\mathrm{div}\boldsymbol{j}$$
$$+\big(\Theta_1\,\mathrm{grad}\,s_1-\Theta_2\,\mathrm{grad}\,s_2\big)^{\mathrm{T}}\boldsymbol{j}\;=\;0. \tag{22}$$

The differences of temperatures $\Theta_1\equiv T_1-T$ and $\Theta_2\equiv T_2-T$ are small with respect to T and $\boldsymbol{j}$ is a small diffusion term with respect to the mixture momentum $\rho\boldsymbol{v}$; consequently, in an approximation to the first order, the term

$$\left(\Theta_1 \operatorname{grad} s_1 - \Theta_2 \operatorname{grad} s_2\right)^T \boldsymbol{j}$$

is negligible. Let us consider

$$K \equiv \big((h_1 - h_2) - (\mu_1 - \mu_2) + T\,(s_2 - s_1)\big)\,\operatorname{div}\boldsymbol{j}\ ;$$

we get

$$K = \big((h_1 - T_1 s_1) - (h_2 - T_2 s_2) - (\mu_1 - \mu_2) + \Theta_1 s_1 + \Theta_2 s_2\big)\,\operatorname{div}\boldsymbol{j}\ .$$

In an approximation to the first order, the term $\big(\Theta_1 s_1 + \Theta_2 s_2\big)\operatorname{div}\boldsymbol{j}$ is negligible. Due to the fact that $\mu_a(\rho_1,\rho_2,T_1,T_2) = h_a - T_a s_a$ is the chemical potential of the component a, when $\boldsymbol{j}$ is a small diffusion velocity with respect to average velocity $\boldsymbol{v}$, the term

$$\big(\mu_1(\rho_1,\rho_2,T_1,T_2) - \mu_2(\rho_1,\rho_2,T_1,T_2) - \mu_1(\rho_1,\rho_2,T,T) - \mu_2(\rho_1,\rho_2,T,T)\big)\,\operatorname{div}\boldsymbol{j}$$

is vanishing in an approximation to the first order.

Consequently, in an approximation to the first order, equation (22) reduces to

$$\sum_{a=1}^{2} \rho_a \,\frac{d_a s_a}{dt} = -\frac{1}{T}(p - p_o)\,\operatorname{div}\boldsymbol{v}. \tag{23}$$

The exchange of energy between components must obey the second law of thermodynamics: the total entropy rate is an increasing function of time and we consider the second law of thermodynamics in the form

$$\sum_{a=1}^{2}\left(\frac{\partial \rho_a s_a}{\partial t} + \operatorname{div}(\rho_a \mathrm{s}_a \boldsymbol{v}_a)\right) \geq 0 \tag{24}$$

Due to relations (2) the Clausius-Duhem inequality (24) is equivalent to

$$\sum_{a=1}^{2} \rho_a \,\frac{d_a s_a}{dt} \geq 0\,.$$

Relation (23) implies that the second member must be positive. Therefore, as usual in thermodynamics of irreversible processes, the entropy inequality requires

$$\pi \equiv p - p_o = -\Lambda\,\operatorname{div}\boldsymbol{v}\,. \tag{25}$$

This expression defines the Lagrange multiplier Λ of proportionality such that $\Lambda \geq 0$. The dynamical pressure π is the difference between the pressure in the process out of equilibrium with different temperatures for the components and the pressure of the mixture assumed in local thermodynamical equilibrium with the common average temperature T. Let us notice that equations (9, 25) allow to obtain Q_a values. In fact,

$$\rho_1 T\,(T_2 - T_1)\frac{d_1 s_1}{dt} = \Lambda\, T_2\ (\mathrm{div}\,\boldsymbol{v})^2 \quad \text{and} \quad \rho_2 T\,(T_1 - T_2)\frac{\mathrm{d}_2 s_2}{\mathrm{dt}} = \Lambda\, T_1\ (\mathrm{div}\,\boldsymbol{v})^2$$

and the system of field equations is closed.

5. – Special case of mixture of perfect gases [13].

The internal energy of the mixture is the sum of the internal energies of the different gas components. We represent these energies as function of density and temperature of components

$$\tilde{\varepsilon}(\rho_1, \rho_2, T_1, T_2) = \rho_1\, \tilde{\varepsilon}_1(\rho_1, T_1) + \rho_2\, \tilde{\varepsilon}_2(\rho_2, T_2).$$

Then,

$$p = p_1(\rho_1, T_1) + p_2(\rho_2, T_2),$$

where p_1 and p_2 are the pressures associated with $\tilde{\varepsilon}_1$ and $\tilde{\varepsilon}_2$. An expansion to the first order in $T_1 - T = \Theta_1$ and $T_2 - T = \Theta_2$ yields

$$p = p_1(\rho_1, T) + p_2(\rho_2, T) + \frac{\partial p_1}{\partial T_1}(\rho_1, T)\,\Theta_1 + \frac{\partial p_2}{\partial T_2}(\rho_2, T)\,\Theta_2.$$

From the definition of the average temperature T we obtain as in [29],

$$\rho_1\, \tilde{\varepsilon}_1(\rho_1, T) + \rho_2\, \tilde{\varepsilon}_2(\rho_2, T) = \rho_1\, \tilde{\varepsilon}_1(\rho_1, T_1) + \rho_2\, \tilde{\varepsilon}_2(\rho_2, T_2).$$

Consequently, from equation (25), we get

$$\pi = \frac{\partial p_1}{\partial T_1}(\rho_1, T)\,\Theta_1 + \frac{\partial p_2}{\partial T_2}(\rho_2, T)\,\Theta_2.$$

Let $T_1 = T + \beta\,\Theta,\ T_2 = T + (1+\beta)\,\Theta,$ where $\Theta = T_2 - T_1,$ an expansion of equation (17) to the first order yields the value of β

$$C_v^{(1)}(\rho_1, T)\,\beta\,\Theta + C_v^{(2)}(\rho_2, T)\,(1+\beta)\,\Theta = 0, \ \text{with} \ C_v^{(a)} = \frac{\partial \tilde{\varepsilon}_a}{\partial T_a}(\rho_a, T).$$

Consequently, when $p_a = k_a \rho_a T_a$, we obtain

$$\pi = \frac{\rho_1 \rho_2}{\rho_1 C_v^{(1)} + \rho_2\, C_v^{(2)}}\,(k_2\, C_v^{(1)} - k_1 C_v^{(2)})\,\Theta$$

In accordance with results obtained by Ruggeri & Simić [30] and Gouin & Ruggeri [23], to verify the Clausius-Duhem inequality (24), Θ must be in the form

$$\Theta = L_T(\gamma_1 - \gamma_2)\, div\, \boldsymbol{v} \quad \text{with} \quad L_T = M\, \frac{\rho_1 C_v^{(1)}}{\rho_2 C_v^{(2)}}\, (\rho_1 C_v^{(1)} + \rho_2 C_v^{(2)}) \text{ and } \; M \geq 0$$

where γ_a is the ratio of specific heats of component a.

6. – Conclusion.

The method by Hamilton can be easily extended to multi-component mixtures with multi-temperatures. We obtain the equations of component motions and the equation of the total mixture energy. The entropy is not conserved and the second law of thermodynamics reveals the existence of a new dynamical pressure term. As diffusion is a property of fluid mixtures with different component velocities, the dynamical pressure term is a property of fluid mixtures with different component temperatures. The dynamical pressure can be measured with the change of volume. In the special case of mixture of gases, the dynamical pressure term comes from the fact the gases are molecularly different.
The Hamilton principle points out that the dynamical pressure can be obtained by neglecting viscosity, friction or external heat fluxes. This is a main property of mixtures with multi-temperatures and this fact may have some applications in plasma of gases and in the evolution of the early universe [32].
In Appendix C, we highlight that constitutive equations for diffusion, viscosity and heat flux for mixtures without chemical reaction are consequence of dissipative terms whereas the dynamical pressure term can exist with different component temperatures even if the bulk viscosity is null.
The results are in complete accordance with the ones by Ruggeri & Simic [30] and Gouin & Ruggeri [1]. This is an important verification of the fact that the Hamilton principle can be extended to nonconservative mixture motions when components have different temperature. A difference with classical thermodynamics methods is that the volume internal energy is not necessary the sum of the volume internal energies of the components. In this paper, the volume internal energy is a nonseparate function of densities and entropies (or temperatures) and is consequently more general than in [1] and [30].

Appendix A.

The definition of Lagrangian coordinates $\boldsymbol{X}_a$ implies $\dfrac{\partial \boldsymbol{X}_a}{\partial t} + \dfrac{\partial \boldsymbol{X}_a}{\partial \boldsymbol{x}} \boldsymbol{v}_a = 0.$
By taking the derivative with respect to κ_a, we obtain the following equation for virtual displacements (equation (6)) associated with the first virtual motion

family

$$\frac{\partial \delta_a \boldsymbol{X}_a}{\partial t} + \frac{\partial \delta_a \boldsymbol{X}_a}{\partial \boldsymbol{x}} \boldsymbol{v}_a + \frac{\partial \boldsymbol{X}_a}{\partial \boldsymbol{x}} \delta_a \boldsymbol{v}_a = 0.$$

Then, we get

$$\delta_a \boldsymbol{v}_a (\boldsymbol{x}, t) = - F_a \frac{d_a}{dt} (\delta_a \boldsymbol{X}_a).$$

Equation (1) yields

$$\delta_a \rho_a (\boldsymbol{x}, t) \det F_a (\boldsymbol{x}, t) + \rho_a \delta_a (\det F_a) = \frac{\partial \rho_{a0}}{\partial \boldsymbol{X}_a} \delta_a \boldsymbol{X}_a. \tag{26}$$

By using the Euler-Jacobi identity

$$\delta_a (\det F_a) = \det F_a (\boldsymbol{x}, t) \ tr \left(F_a^{-1} \delta_a F_a \right)$$

with

$$\delta_a F_a (\boldsymbol{x}, t) = - F_a (\boldsymbol{x}, t) \delta_a F_a^{-1} (\boldsymbol{x}, t) F_a (\boldsymbol{x}, t)$$

and

$$\delta_a F_a^{-1} (\boldsymbol{x}, t) = \frac{\partial \delta_a \boldsymbol{X}_a}{\partial \boldsymbol{x}},$$

we deduce

$$\delta_a (\det F_a) = - \det F_a \ tr \left(\delta_a F_a^{-1} F_a \right) = - \det F_a \ tr \left(\frac{\partial \delta_a \boldsymbol{X}_a}{\partial \boldsymbol{X}_a} \right),$$

or,

$$\delta_a (\det F_a) = - \det F_a \ div_a (\delta_a \boldsymbol{X}_a). \tag{27}$$

By substituting equation (27) into equation (26), we obtain

$$\delta_a \rho_a (\boldsymbol{x}, t) = \rho_a \ div_a (\delta_a \boldsymbol{X}_a) + \frac{\rho_a}{\rho_{a0}} \frac{\partial \rho_{a0}}{\partial \boldsymbol{X}_a} \delta_a \boldsymbol{X}_a = \frac{div_a (\rho_{a0} \delta_a \boldsymbol{X}_a)}{det F_a},$$

$$\delta_a s_a (\boldsymbol{x}, t) = \frac{\partial s_{a0}}{\partial \boldsymbol{X}_a} \delta_a \boldsymbol{X}_a.$$

Appendix B.

The proof of the Gibbs identity is obtained by summing the following algebraic identities $a - e$.

For the external potentials Ω_a,

a.

$$\frac{\partial\, \rho_a \Omega_a}{\partial t} + div\,(\rho_a \Omega_a \boldsymbol{v}_a) - \rho_a \frac{\partial \Omega_a}{\partial \boldsymbol{x}} \boldsymbol{v}_a - B_a \Omega_a - \rho_a \frac{\partial \Omega_a}{\partial t} \equiv 0$$

For the velocity fields $\boldsymbol{v}_a$,

b.

$$\frac{\partial}{\partial t}\left(\frac{1}{2}\, \rho_a \boldsymbol{v}_a^2\right) + div\left(\rho_a \boldsymbol{v}_a\left(\boldsymbol{v}_a^2 - \frac{1}{2}\boldsymbol{v}_a^2\right)\right)$$

$$- B_a\left(\boldsymbol{v}_a^2 - \frac{1}{2}\boldsymbol{v}_a^2\right) - \left(\rho_a \frac{d_a \boldsymbol{v}_a^T}{dt} + \rho_a \boldsymbol{v}_a^T \frac{\partial \boldsymbol{v}_a}{\partial \boldsymbol{x}} - \rho_a \frac{\partial}{\partial \boldsymbol{x}}\left(\frac{1}{2}\boldsymbol{v}_a^2\right)\right)\boldsymbol{v}_a \equiv 0$$

Let us introduce $\boldsymbol{i}^T = -\dfrac{\partial \eta}{\partial \boldsymbol{u}}$. Then

$$\frac{\partial}{\partial t}\left(\eta - \frac{\partial \eta}{\partial \boldsymbol{u}}\boldsymbol{u}\right) = \frac{\partial \boldsymbol{i}^T}{\partial t}\boldsymbol{u} + \sum_{a=1}^{2}\left(\frac{\partial \eta}{\partial \rho_a}\frac{\partial \rho_a}{\partial t} + \rho_a\, T_a \frac{\partial s_a}{\partial t}\right)$$

and the three following identities $c - e$ prove the formula

c.

$$\frac{\partial \eta}{\partial \rho_a}\frac{\partial \rho_a}{\partial t} + div\left(\frac{\partial \eta}{\partial \rho_a}\, \rho_a \boldsymbol{v}_a\right) - \rho_a \frac{\partial}{\partial \boldsymbol{x}}\left(\frac{\partial \eta}{\partial \rho_a}\right)\boldsymbol{v}_a - \frac{\partial \eta}{\partial \rho_a}\left(\frac{\partial \rho_a}{\partial t} + div\,(\rho_a \boldsymbol{v}_a)\right) \equiv 0,$$

d.

$$\rho_a\, T_a \frac{\partial s_a}{\partial t} + \rho_a\, T_a \frac{\partial s_a}{\partial \boldsymbol{x}}\boldsymbol{v}_a - \rho_a\, T_a \frac{d_a s_a}{dt} \equiv 0,$$

e.

$$\frac{\partial \boldsymbol{i}^T}{\partial t}\eta + \sum_{a=1}^{2} div\left((-1)^a\left(\frac{\boldsymbol{i}^T}{\rho_a}\boldsymbol{v}_a\right)\rho_a \boldsymbol{v}_a\right) - \left(\rho_a \frac{d_a}{dt}\left((-1)^a \frac{\boldsymbol{i}^T}{\rho_a}\right) + \rho_a (-1)^a \frac{\boldsymbol{i}^T}{\rho_a}\frac{\partial \boldsymbol{v}_a}{\partial \boldsymbol{x}}\right)\boldsymbol{v}_a$$

$$- (-1)^a\left(\frac{\boldsymbol{i}^T}{\rho_a}\boldsymbol{v}_a\right)\left(\frac{\partial \rho_a}{\partial t} + div\,(\rho_a \boldsymbol{v}_a)\right) \equiv 0.$$

Appendix C.

We consider a more general case of a mixture when the Hamilton principle cannot be applied. This case consists of a weak dissipative process with diffusion, viscosity and heat transfers. The balance of masses, momenta and energy are simply expressed by adding dissipative terms to the expressions obtained in section 4

$$B_a = 0, \quad \boldsymbol{M}_a^d = 0 \ \ (a = 1, 2) \quad \text{and} \quad E^d = 0, \tag{28}$$

such that

$$\begin{aligned} B_a &= \frac{\partial \rho_a}{\partial t} + \operatorname{div}(\rho_a \boldsymbol{v}_a), \\ \boldsymbol{M}_a^d &= \boldsymbol{M}_a - (\operatorname{div} \sigma_a^d)^T - \boldsymbol{m}_a, \\ E^d &= E + \sum_{a=1}^{2} \operatorname{div} \boldsymbol{q}_a - \sigma_a^d \boldsymbol{v}_a. \end{aligned}$$

On the right hand side, $\boldsymbol{q}_a$ is the heat flux vector, $\boldsymbol{m}_a$ is the momentum production and σ_a^d is the viscous part of the stress tensor of constituent a. Due to the total conservation of momentum of the mixture, $\sum_{a=1}^{2} \boldsymbol{m}_a = 0$ [12].

The *dynamics Gibbs identity* (10) can be transformed as

$$S^d + \sum_{a=1}^{2} \boldsymbol{M}_a^{d\,T} \boldsymbol{v}_a - \left(\frac{1}{2}\boldsymbol{v}_a^2 - h_a + T_a s_a\right) B_a \equiv E^d,$$

with

$$S^d = S + \operatorname{div} \boldsymbol{q} + \sum_{a=1}^{2} \boldsymbol{m}_a^T \boldsymbol{v}_a - \operatorname{tr}(\sigma_a^d \boldsymbol{D}_a),$$

where $\boldsymbol{D}_a = \dfrac{1}{2}\left(\dfrac{\partial \boldsymbol{v}_a}{\partial \boldsymbol{x}} + \left(\dfrac{\partial \boldsymbol{v}_a}{\partial \boldsymbol{x}}\right)^T\right)$ and $\boldsymbol{q} = \sum_{a=1}^{2} \boldsymbol{q}_a$.

The second law of thermodynamics is expressed in the form

$$\sum_{a=1}^{2} \rho_a \frac{d_a s_a}{dt} + \operatorname{div} \frac{\boldsymbol{q}_a}{T_a} \geq 0. \tag{29}$$

In the second order approximation, with small external heat fluxes $\boldsymbol{q}_a$ and small difference of temperature $T_1 - T_2$, equation (29) is equivalent to

$$\sum_{a=1}^{2} \rho_a \frac{d_a s_a}{dt} + \operatorname{div} \frac{\boldsymbol{q}}{T} \geq 0.$$

If we write $\boldsymbol{m} = \boldsymbol{m}_1 = -\boldsymbol{m}_2$, we obtain by calculations similar to section 4

$$T\left[\sum_{a=1}^{2} \rho_a \frac{d_a s_a}{dt} + \operatorname{div} \frac{\boldsymbol{q}}{T}\right] + \Sigma = 0,$$

where

$$\Sigma = (p - p_o)\,\mathrm{div}\,\boldsymbol{v} + \frac{\boldsymbol{q}}{T}\,\mathrm{grad}\,T - \boldsymbol{m}^T\boldsymbol{u} - \sum_{a=1}^{2} \mathrm{tr}\,(\sigma_a^d \boldsymbol{D}_a) \leq 0$$

is the entropy production.

Classical methods of thermodynamics of irreversible process (*TIP*) yield equation (25) for the dynamical pressure term together with Fourier and Navier-Stokes laws [11].

Term $\boldsymbol{m}^T\boldsymbol{u}$ yields the coefficient χ of proportionality such that $\chi \geq 0$ and

$$\boldsymbol{m} = -\chi\,\boldsymbol{u} \equiv \chi\,(\boldsymbol{v}_1 - \boldsymbol{v}_2).$$

For slow isothermal motions, the difference between the components of equations $(28)_2$ yields in an approximation to the first order

$$\frac{\boldsymbol{M}_1}{\rho_1} - \frac{\boldsymbol{M}_2}{\rho_2} = \mathrm{grad}\,(\mu_1 - \mu_2).$$

Here $\mu_a = \dfrac{\partial \eta}{\partial \rho_a} - T_a s_a$ denotes the chemical potential of component a at temperature T.

By neglecting the viscous terms, we obtain

$$\mathrm{grad}\,\mu = \frac{\rho}{\rho_1\rho_2}\,\boldsymbol{m} \quad (\mu = \mu_1 - \mu_2) \quad \text{or} \quad \mathrm{grad}\,\mu = -\kappa\,\boldsymbol{u} \quad \text{with} \quad \kappa = \frac{\rho}{\rho_1\rho_2}\,\chi,$$

which is an expression of the Fick law.

Therefore, in this formulation, our results coincide with the ones obtained by arguments of classical thermodynamics [1].

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