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# Mixture of Fluids involving Entropy Gradients and Acceleration Waves in Interfacial Layers

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## Abstract

Through an Hamiltonian action we write down the system of equations of motions for a mixture of thermocapillary fluids under the assumption that the internal energy is a function not only of the gradient of the densities but also of the gradient of the entropies of each component. A Lagrangian associated with the kinetic energy and the internal energy allows to obtain the equations of momentum for each component and for the barycentric motion of the mixture. We obtain also the balance of energy and we prove that the equations are compatible with the second law of thermodynamics. Though the system is of parabolic type, we prove that there exist two tangential acceleration waves that characterize the interfacial motion. The dependence of the internal energy of the entropy gradients is mandatory for the existence of this kind of waves. The differential system is non-linear but the waves propagate without distortion due to the fact that they are linearly degenerate (exceptional waves).

*Key words:* Fluid mixtures, acceleration waves, interfacial layers

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## 1 Introduction

Liquid-vapor and two-phase interfaces are generally represented by a material surface endowed with an energy related to Laplace's surface tension. In fluid mechanics and thermodynamics, the interface appears as a surface separating two media. This surface has its own characteristic behavior and energy properties [1]. Theoretical and experimental detailed studies show that, when working far from critical conditions, the capillary layer has a thickness equivalent to a few molecular beams [2].

Molecular models such as those used in kinetic theory of gas lead in interfacial layers to laws of state associated with non-convex internal energies, e.g., the van der Waals models [3,4,5]. These models appear advantageous as they provide as even more precise verification of Maxwell's rule applied to isothermal phase transition [6]. Nonetheless, they present two disadvantages:

First, for densities that lie between phase densities, the pressure may become negative. Simple physical experiments can be used, however, to cause traction that leads to these negative pressure values [7,8].

Second, in the field between bulks, internal energy cannot be represented by a convex surface associated with the variation of densities and entropy. This fact seems to contradict the existence of steady equilibrium state of the matter in this type of region.

To overcome these disadvantages, the thermodynamic investigative replaces the non-convex portion corresponding to internal energy with a plane domain. The fluid can no longer be considered as a continuous medium. The interface is represented as a material surface with a null thickness. In this case, the only possible representation of the dynamic behavior of the interface is one of a discontinuous surface, and its essential structure remains unknown.

In the equilibrium state it is possible to eliminate the above disadvantages by appropriately modifying the stress tensor of the capillary layer, which is expressed in an anisotropic form. As a consequence, the energy of the continuous medium must change [3,4,9]. A representation of the energy near the critical point therefore allows the study of interfaces of non-molecular size. This approach is not new and, in fact, dates back to van der Waals [10] and Korteweg [11]; it corresponds to what is known as the Landau-Ginzburg theory [5]. The representation proposed in the present study is based on the notion of internal energy which is more convenient to use when the temperature is not uniform. One of the problems that complicates this study of phase transformation dynamics is the apparent contradiction between Korteweg's classical stress theory and the Clausius-Duhem inequality [12]. Proposal made by Eglit [13], Dunn and Serrin [14], Casal and Gouin [15] and others rectify this apparent anomaly for liquid-vapor interfaces of a pure fluid.

To study capillary layers and bulk phases, the simplest model in continuum

mechanics considers an internal energy  $\varepsilon$  as the sum of two terms: a first one corresponding to a medium with a uniform composition equal to the local one and a second one associated with the non-uniformity of the fluid [3,10]. The second term is approximated by a gradient expansion, typically truncated to the second order. In the simplest version of the theory we have  $\varepsilon = \rho \alpha(\rho, s) + \frac{1}{2} m (\nabla \rho)^2$ , where  $\rho$  is the matter density,  $s$  the specific entropy,  $\alpha$  the specific internal energy of the fluid assumed to be homogeneous and  $m$  is a coefficient independent of  $s$ ,  $\nabla \rho$  and of any higher derivatives. Obviously, the model is simpler than models associated with the renormalization-group theory [16]. Nevertheless, it has the advantage of easily extending well-known results for equilibrium cases to the dynamics of interfaces [17,18]. In such a model,  $s$  varied with  $\rho$  through the interface in the same way as in the bulk, then  $s$  would always be that function of  $\rho$  which, at given temperature  $T$  satisfied

$$\frac{\partial \alpha}{\partial s}(\rho, s) = T. \quad (1)$$

With this assumption,  $s = s(\rho)$  and  $\varepsilon = \varepsilon(\rho)$ , so that the points representing single-phase states in the  $\rho, s, \varepsilon$  space lie on a curve instead of on a surface  $\varepsilon = \varepsilon(\rho, s)$ . This was the original assumption of van der Waals which was later justified by Ornstein in 1909 for a system composed of molecules with long-ranged but weak attractive force; *this assumption is not exact for more realistic potentials*<sup>1</sup>.

As coexistence curves these are no way peculiar; the only peculiarity is that the single-phase states -in this version of this approximation- have collapsed onto the coexistence curve instead being represented by the points of an extended two-dimensional region of which the coexistence curve is merely a boundary. There is then no proper two-density description of the one-phase states of a one-component system in the lowest order of the mean-field approximation. There is such a description of the two-states, where not even in mean-field approximation is there any discernible peculiarity; but in practice the potential for the two-density form of the van der Waals theory is then not constructed by the prescription in (1) but by other means. For example Rowlinson and Widom introduce in [4], chapter 9, an energy arising from the mean-field theory and depending on the deviations of the densities  $s$  and  $\rho$ , say, from their values at the critical point and the gradients of these densities. It is also seen that in  $c$ -components systems,  $c + 1$  densities -the densities  $\rho_1, \dots, \rho_c$  of the  $c$  components and the entropy density  $s$ - may vary independently through the interface.

Aside from the question of accuracy, there are also qualitative features of some interfaces in physical-chemistry, especially in systems of more than one component, that require two or more independently varying densities for their description. An example is strong positive or negative adsorption of a component

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<sup>1</sup> Main sentences in this paragraph and more precisely the comments on static interfaces are issued from the book of Rowlinson and Widom [4] and its bibliography.

$i$  associated with a non-monotonic profile  $\rho_i(z)$  where  $z$  is the spatial variable. In the one-density theory based on the approximation  $\frac{\partial\alpha}{\partial s} - T = 0$  and  $\frac{\partial\alpha}{\partial\rho_i} = 0$  for all  $j \neq i$ , the resulting one-density model leads inevitably to a monotonic  $\rho_i(z)$ . In a theory based on two or more densities, by contrast, we may have a realistic trajectory with which is associated non-monotonic behavior of one or more of the components if we suppose  $\rho_j(z)$  to be monotonic.

We must also allow the independent variation of at least two densities, entropy included, if we are to account contact angles in three-phase equilibrium : J. Cahn made the remark that we might use a two- (or more-) density van der Waals theory to describe the case of non-spreading in the three phase equilibrium, ([4], chapter 8). Then, at equilibrium, Rowlinson and Widom pointed out that for single fluids the model must be extended by taking into account not only the strong variations of matter density through the interfacial layer but also the strong variations of entropy.

Also in dynamics, for an *extended Cahn and Hilliard fluid*, the volume internal energy  $\varepsilon$  is proposed with a gradient expansion depending not only on  $\text{grad } \rho$  but also on  $\text{grad } s$  corresponding to a strong heat supply in the change of phases:  $\varepsilon = f(\rho, s, \nabla\rho, \nabla s)$ . The medium is then called a *thermocapillary fluid* [19,20].

To extend the model to fluid mixtures corresponding to  $c$ -component systems and realistic potentials in molecular theory of fluid interfaces, the internal energy is assumed to be a functional of the different densities of the mixture. In all the cases where strong gradient of densities occurs - for example shocks or capillary layers - the internal energy is chosen as a function of successive derivatives of densities of matter and entropies. To be in accordance with the physical phenomena presented in [4], one will consider the internal energy of a two-component fluid mixture with an internal energy depending also on the gradients of entropy of each component. The internal energy is a Galilean invariant, it does not depend on the reference frame; hence the internal energy depends also on the relative velocity between the two components of the mixture.

The conservative motions of *thermocapillary fluid mixture* are relevant to the so-called second gradient theory [21] and we obtain a complete set of balance equations for conservative motions; we extend this result to the dissipative case. Our goal is simply to verify the consistency of our model with the second law of thermodynamics. We consider a special case of dissipative thermocapillary mixtures where the introduction of dissipative forces is only done in the framework of the first gradient theory; we deduce the Fick law as a consequence of a friction behavior between the components and from the equations of motion of the components. In such a case, extended thermodynamic principle (as Gibbs identity) provides a set of equations that satisfy the entropy principle, thereby making these irreversible motions compatible with the second law of thermodynamics.

The idea of studying interface motions as localized traveling waves in a multi-gradient theory is not new and can be traced throughout many problems of condensed matter and phase-transition physics [22]. In Cahn and Hilliard's model [3], the direction of solitary waves was along the gradient of density [17,22]. The introduction of the model of thermocapillary fluid mixture provides a better understanding of the behavior of motions in fluid mixture interfaces: it is possible to obtain the previous solitary waves but also a new kind of adiabatic waves may be forecasted. These waves are associated with the spatial second derivatives of entropy and matter densities. For this new kind of adiabatic waves, the direction of propagation is normal to the gradient of densities. In the case of a thick interface, the waves are tangential to the interface and the wave velocities depend on the constitutive equations. Finally we observe that, also if the differential system associated with the wave motions is non-linear, the waves propagate without distortion due to the fact that they are linearly degenerate (exceptional waves)[23].

## 2 Equations of thermocapillary mixtures

### 2.1 Conservative motions of thermocapillary mixtures

To derive the governing equations and boundary conditions in the dissipative-free case, we use the Hamilton principle of least action [24]. In continuum mechanics, the principle with a system endowed with an infinite number of degrees of freedom was initiated by Lin [25], Herivel [26], Serrin [27], Berdichevsky [28] and many others; it was proposed by Gouin for fluid mixtures [29]. The main idea is to propose a Lagrangian which yields the behavior of the medium as the difference between a kinetic and a potential energy per unit volume. Then, the variations of the Hamilton action obtained as a linear functional of virtual displacements allow to find the governing equations and boundary conditions. For real media, the irreversibility is introduced both in equations of motion and equation of energy by using a classical approach through the dissipative function, diffusion and heat fluxes.

We study a mixture of two fluids: the motion of a two-fluid continuum can be represented using two surjective mappings (i=1,2)

$$(t, \mathbf{x}) \rightarrow \mathbf{X}_i = \mathbf{\Lambda}_i(t, \mathbf{x})$$

where  $(t, \mathbf{x})$  belongs to  $[t_1, t_2] \times D_t$ , a set in the time-space occupied by the fluid between times  $t_1$  and  $t_2$ . Variables  $\mathbf{X}_i$  denote the positions of each component of the mixture in reference spaces  $D_{0i}$ . Variations of particle motions

are deduced from virtual motions

$$\mathbf{X}_i = \Xi_i(t, \mathbf{x}, \varkappa_i),$$

where scalars  $\varkappa_i$  are defined in a neighborhood of zero; they are associated with a two parameter family of virtual motions of the mixture. The real motion corresponds to  $\varkappa_i = 0$ , the associated virtual displacements are [29]

$$\delta_i \mathbf{X}_i = \left. \frac{\partial \Xi_i}{\partial \varkappa_i} \right|_{\varkappa_i=0}.$$

They generalize what is obtained for a single fluid [30]. To the virtual displacements  $\delta_i \mathbf{X}_i$ , we associated its image  $\zeta_i$  in the physical space  $D_t$  occupied by the fluid mixture at time  $t$  [24,31],

$$\zeta_i = -\frac{\partial \mathbf{x}}{\partial \mathbf{X}_i} \delta_i \mathbf{X}_i.$$

Conservation of matter for each component requires that

$$\rho_i \det \left( \frac{\partial \mathbf{x}}{\partial \mathbf{X}_i} \right) = \rho_{i0}(\mathbf{X}_i), \quad (2)$$

where  $\rho_{i0}$  is the reference volume mass in  $D_{0i}$  and  $\det \left( \frac{\partial \mathbf{x}}{\partial \mathbf{X}_i} \right)$  the Jacobian determinant of the motion of component  $i$ . In differentiable cases eqs (2) are equivalent to the equations of balance of matter densities  $\rho_i$

$$\frac{\partial \rho_i}{\partial t} + \operatorname{div}(\rho_i \mathbf{u}_i) = 0, \quad (3)$$

where  $\mathbf{u}_i$  denotes the velocity vectors of each component  $i$ . Now, we assume that the mixture has an entropy for each component [32]; for conservative motions, the equations of conservation of specific entropies  $s_i$  are

$$\frac{\partial \rho_i s_i}{\partial t} + \operatorname{div}(\rho_i s_i \mathbf{u}_i) = 0. \quad (4)$$

Then, relations

$$s_i = s_{i0}(\mathbf{X}_i)$$

define an isentropic motion of the fluid mixture. We deduce the following relations of tensorial quantities [24,29]

$$\delta_i \mathbf{u}_i = \frac{d_i \zeta_i}{dt} - \frac{\partial \mathbf{u}_i}{\partial \mathbf{x}} \zeta_i, \quad \delta_i \rho_i = -\operatorname{div}(\rho_i \zeta_i), \quad \delta_i s_i = -\frac{\partial s_i}{\partial \mathbf{x}} \zeta_i. \quad (5)$$

where  $\frac{d_i}{dt} = \frac{\partial}{\partial t} + \mathbf{u}_i \cdot \nabla$  denotes the material derivative relatively to the component  $i$ . We assume that the volume potential energy of the mixture is in the form

$$\varepsilon = \varepsilon(\rho_i, s_i, \nabla \rho_i, \nabla s_i, \mathbf{w}),$$

with  $\mathbf{w} = \mathbf{u}_1 - \mathbf{u}_2$  the relative velocity of the two components of the mixture. This means that the fluid mixture is a function not only of the densities of matter  $\rho_i$  and specific entropies  $s_i$  but also of the gradients of  $\rho_i$  and  $s_i$ . The fact that  $\varepsilon$  depends on two entropies is classically adopted in the literature [29,33,34]. Moreover, for a two-velocity medium, there is no coordinate system within the framework of which any motion could be disregarded. So, the standard definition of potential energy leads to its dependence on the relative motion of the components. The dependence of  $\varepsilon$  with respect to the relative velocity is analog to take into account the added mass effect in heterogeneous two-fluid theory as done by berdichevsky [28] and Geurst [35,36]. Let us note we can assume also that  $\varepsilon$  is depending on  $(t, \mathbf{x})$ ; by this way, we introduce directly the extraneous potential of the body forces.

The potential  $\varepsilon$  is related with the volume internal energy  $\varpi$  of the mixture through the transformation

$$\varpi = \varepsilon - \frac{\partial \varepsilon}{\partial \mathbf{w}} \mathbf{w},$$

so that,

$$e = \sum_{i=1}^2 \frac{1}{2} \rho_i \mathbf{u}_i^2 + \varpi$$

is the total energy of the system [24,37].

The equation of motion of component  $i$  is given by a variational method associated with a Hamilton action; the vector field  $\mathbf{x} \in D_t \rightarrow \zeta_i$  is two time continuously differentiable. The Lagrangian of the mixture is

$$L = \sum_{i=1}^2 \frac{1}{2} \rho_i \mathbf{u}_i^2 - \varepsilon,$$

and consequently, the Hamilton action between the times  $t_1$  and  $t_2$  is

$$I = \int_{t_1}^{t_2} \int_{D_t} L \, d\mathbf{x} dt.$$

From the definition of virtual motions, we obtain immediately two variations of the action of Hamilton associated with  $i = 1, 2$ ,

$$\begin{aligned} \delta_i I = \int_{t_1}^{t_2} \int_{D_t} & \left( \left( \frac{1}{2} u_i^2 - \epsilon_{,\rho_i} \right) \delta_i \rho_i - \epsilon_{,\rho_i,\gamma} \delta_i \rho_{i,\gamma} + \rho_i K_{i\gamma} \delta_i u_{i\gamma} \right. \\ & \left. - \epsilon_{,s_i} \delta_i s_i - \epsilon_{,s_i,\gamma} \delta_i s_{i,\gamma} \right) d\mathbf{x} dt, \end{aligned}$$

where subscript  $\gamma$  corresponds to spatial derivatives associated with gradient terms; as usually summation is made on repeated subscript  $\gamma$  from 1 to 3;

$\mathbf{K}_i = \mathbf{u}_i + (-1)^i \frac{1}{\rho_i} \left( \frac{\partial \epsilon}{\partial \mathbf{w}} \right)^T$  where index  $T$  denotes the transposition. Then, by integration by part we obtain,

$$\begin{aligned} \delta_i I = & \int_{t_1}^{t_2} \int_{D_t} \left( \left( \frac{1}{2} u_i^2 - \epsilon_{,\rho_i} + (\epsilon_{,\rho_i,\gamma})_{,\gamma} \right) \delta_i \rho_i + \rho_i \mathbf{K}_{i\gamma} \delta_i u_{i\gamma} \right. \\ & \left. - (\epsilon_{,s_i} - (\epsilon_{,s_i,\gamma})_{,\gamma}) \delta_i s_i - (\epsilon_{,\rho_i,\gamma} \delta_i \rho_i)_{,\gamma} - (\epsilon_{,s_i,\gamma} \delta_i s_i)_{,\gamma} \right) dx dt. \end{aligned}$$

Let us denote by

$$\rho_i \theta_i \equiv \frac{\widehat{\partial} \epsilon}{\widehat{\partial} s_i} \quad \text{and} \quad h_i \equiv \frac{\widehat{\partial} \epsilon}{\widehat{\partial} \rho_i}, \quad (6)$$

where  $\widehat{\partial}$  is the *variational derivative operator*. That is to say,

$$\rho_i \theta_i = \epsilon_{,s_i} - (\epsilon_{,s_i,\gamma})_{,\gamma} \equiv \epsilon_{,s_i} - \text{div } \boldsymbol{\Psi}_i \quad \text{and} \quad h_i = \epsilon_{,\rho_i} - (\epsilon_{,\rho_i,\gamma})_{,\gamma} \equiv \epsilon_{,\rho_i} - \text{div } \boldsymbol{\Phi}_i,$$

with,

$$\boldsymbol{\Psi}_i \equiv \frac{\partial \epsilon}{\partial \nabla s_i} \quad \text{and} \quad \boldsymbol{\Phi}_i \equiv \frac{\partial \epsilon}{\partial \nabla \rho_i}.$$

Introducing  $R_i = \frac{1}{2} u_i^2 - h_i$ , and taking into account of the expressions for  $\theta_i$  and  $h_i$  given by eqs (6), we get

$$\delta_i I = \int_{t_1}^{t_2} \int_{D_t} \{ R_i \delta_i \rho_i + \rho_i \mathbf{K}_i \cdot \delta_i \mathbf{u}_i - \rho_i \theta_i \delta_i s_i - \text{div} (\boldsymbol{\Phi}_i \delta_i \rho_i + \boldsymbol{\Psi}_i \delta_i s_i) \} dx dt,$$

and from relations (5), we obtain

$$\begin{aligned} \delta_i I = & \int_{t_1}^{t_2} \int_{D_t} \left\{ -R_i \text{div} (\rho_i \boldsymbol{\zeta}_i) + \rho_i \mathbf{K}_i \cdot \left( \frac{d_i \boldsymbol{\zeta}_i}{dt} - \frac{\partial \mathbf{u}_i}{\partial \mathbf{x}} \boldsymbol{\zeta}_i \right) \right. \\ & \left. + \rho_i \theta_i \frac{\partial s_i}{\partial \mathbf{x}} \boldsymbol{\zeta}_i - \text{div} (\boldsymbol{\Phi}_i \delta_i \rho_i + \boldsymbol{\Psi}_i \delta_i s_i) \right\} dx dt. \end{aligned}$$

Consequently,

$$\begin{aligned} \delta_i I = & \int_{t_1}^{t_2} \int_{D_t} \left\{ \rho_i \left( \frac{\partial R_i}{\partial \mathbf{x}} + \theta_i \frac{\partial s_i}{\partial \mathbf{x}} - \frac{d_i \mathbf{K}_i^T}{dt} - \mathbf{K}_i^T \frac{\partial \mathbf{u}_i}{\partial \mathbf{x}} \right) \boldsymbol{\zeta}_i \right. \\ & \left. + \frac{\partial}{\partial t} (\rho_i \mathbf{K}_i^T \boldsymbol{\zeta}_i) - \text{div} (\rho_i R_i \boldsymbol{\zeta}_i - \rho_i \mathbf{u}_i \mathbf{K}_i^T \boldsymbol{\zeta}_i + \boldsymbol{\Phi}_i \delta_i \rho_i + \boldsymbol{\Psi}_i \delta_i s_i) \right\} dx dt. \end{aligned}$$

The Stokes formula and relation (5) yield

$$\begin{aligned} \delta_i I = & \int_{t_1}^{t_2} \int_{D_t} \rho_i \left( \frac{\partial R_i}{\partial \mathbf{x}} + \theta_i \frac{\partial s_i}{\partial \mathbf{x}} - \frac{d_i \mathbf{K}_i^T}{dt} - \mathbf{K}_i^T \frac{\partial \mathbf{u}_i}{\partial \mathbf{x}} \right) \boldsymbol{\zeta}_i dx dt \quad (7) \\ & + \int_{t_1}^{t_2} \int_{\partial D_t} g \rho_i \mathbf{K}_i^T \boldsymbol{\zeta}_i \\ & - \mathbf{n} \cdot \left( \rho_i R_i \boldsymbol{\zeta}_i - \rho_i \mathbf{u}_i \mathbf{K}_i^T \boldsymbol{\zeta}_i - \boldsymbol{\Phi}_i \frac{\partial \rho_i}{\partial \mathbf{x}} \boldsymbol{\zeta}_i - \boldsymbol{\Psi}_i \frac{\partial s_i}{\partial \mathbf{x}} \boldsymbol{\zeta}_i - \rho_i \boldsymbol{\Phi}_i \text{div } \boldsymbol{\zeta}_i \right) d\sigma_x dt, \end{aligned}$$

where  $\partial D_t$  (of mesure  $d\sigma_{\mathbf{x}}$ ) is the boundary of  $D_t$ ,  $\mathbf{n}$  is the unit external normal vector to  $\partial D_t$  and  $g$  is the velocity of  $\partial D_t$ . If we consider a vector field  $\mathbf{x} \in D_t \rightarrow \boldsymbol{\zeta}_i$  and its first derivatives vanishing simultaneously on the boundary  $\partial D_t$ , the Hamilton principle expressed in the form:  $\forall \boldsymbol{\zeta}_i, \delta_i a = 0$  leads to

$$\forall \boldsymbol{\zeta}_i, \int_{t_1}^{t_2} \int_{D_t} \rho_i \left( \frac{\partial R_i}{\partial \mathbf{x}} + \theta_i \frac{\partial s_i}{\partial \mathbf{x}} - \frac{d_i \mathbf{K}_i^T}{dt} - \mathbf{K}_i^T \frac{\partial \mathbf{u}_i}{\partial \mathbf{x}} \right) \boldsymbol{\zeta}_i d\mathbf{x} dt = 0$$

and consequently,

$$\frac{d_i \mathbf{K}_i}{dt} + \left( \frac{\partial \mathbf{u}_i}{\partial \mathbf{x}} \right)^T \mathbf{K}_i = \nabla R_i + \theta_i \nabla s_i. \quad (8)$$

Let us note that the value of the first member of eq. (8) is equal to

$$\frac{d_i \mathbf{u}_i}{dt} + (-1)^i \frac{d_i}{dt} \left( \frac{1}{\rho_i} \frac{\partial \epsilon}{\partial \mathbf{w}} \right)^T + \left( \frac{\partial \mathbf{u}_i}{\partial \mathbf{x}} \right)^T \mathbf{u}_i + \frac{(-1)^i}{\rho_i} \left( \frac{\partial \mathbf{u}_i}{\partial \mathbf{x}} \right)^T \left( \frac{\partial \epsilon}{\partial \mathbf{w}} \right)^T$$

and eq. (8) yields

$$\begin{aligned} \rho_i \frac{d_i \mathbf{u}_i}{dt} + (-1)^i \left( \operatorname{div} \mathbf{u}_i \left( \frac{\partial \epsilon}{\partial \mathbf{w}} \right)^T + \frac{d_i}{dt} \left( \frac{\partial \epsilon}{\partial \mathbf{w}} \right)^T + \left( \frac{\partial \mathbf{u}_i}{\partial \mathbf{x}} \right)^T \left( \frac{\partial \epsilon}{\partial \mathbf{w}} \right)^T \right) \\ = \rho_i \theta_i \nabla s_i - \rho_i \nabla h_i. \end{aligned}$$

Taking into account of eq. (3) of conservation of mass of component  $i$ , we deduce

$$\begin{aligned} \frac{\partial \rho_i \mathbf{u}_i}{\partial t} + \operatorname{div}(\rho_i \mathbf{u}_i \otimes \mathbf{u}_i) + (-1)^i \left( \operatorname{div} \mathbf{u}_i \left( \frac{\partial \epsilon}{\partial \mathbf{w}} \right)^T + \frac{\partial}{\partial t} \left( \frac{\partial \epsilon}{\partial \mathbf{w}} \right)^T \right. \\ \left. + \frac{\partial}{\partial \mathbf{x}} \left( \frac{\partial \epsilon}{\partial \mathbf{w}} \right)^T \mathbf{u}_i + \left( \frac{\partial \mathbf{u}_i}{\partial \mathbf{x}} \right)^T \left( \frac{\partial \epsilon}{\partial \mathbf{w}} \right)^T \right) = \rho_i \theta_i \nabla s_i - \rho_i \nabla h_i, \end{aligned}$$

and due to the fact that

$$\operatorname{div} \mathbf{u}_i \left( \frac{\partial \epsilon}{\partial \mathbf{w}} \right)^T + \frac{\partial}{\partial \mathbf{x}} \left( \frac{\partial \epsilon}{\partial \mathbf{w}} \right)^T \mathbf{u}_i = \operatorname{div} \left( \left( \frac{\partial \epsilon}{\partial \mathbf{w}} \right)^T \otimes \mathbf{u}_i \right),$$

we get the equations of motion of the two components in the form

$$\begin{aligned} & \frac{\partial \rho_i \mathbf{u}_i}{\partial t} + \operatorname{div}(\rho_i \mathbf{u}_i \otimes \mathbf{u}_i) + (-1)^i \left( \frac{\partial}{\partial t} \left( \frac{\partial \epsilon}{\partial \mathbf{w}} \right)^T + \left( \frac{\partial \mathbf{u}_i}{\partial \mathbf{x}} \right)^T \left( \frac{\partial \epsilon}{\partial \mathbf{w}} \right)^T \right. \\ & \left. + \operatorname{div} \left( \left( \frac{\partial \epsilon}{\partial \mathbf{w}} \right)^T \otimes \mathbf{u}_i \right) \right) = \rho_i \theta_i \nabla s_i - \rho_i \nabla h_i. \end{aligned} \quad (9)$$

We consider only the isotropic case where the potential energy  $\epsilon$  of the mixture can be written in terms of the isotropic invariants

$$\beta_{ij} = \nabla \rho_i \cdot \nabla \rho_j, \quad \chi_{ij} = \nabla \rho_i \cdot \nabla s_j, \quad \gamma_{ij} = \nabla s_i \cdot \nabla s_j, \quad (i, j = 1, 2) \quad \text{and} \quad \omega = \frac{1}{2} \mathbf{w}^2.$$

$$\epsilon = \epsilon(\rho_i, s_i, \beta_{ij}, \chi_{ij}, \gamma_{ij}, \omega),$$

Then, the equation of motion of each component of the mixture is

$$\begin{aligned} & \frac{\partial \rho_i \mathbf{u}_i}{\partial t} + \operatorname{div}(\rho_i \mathbf{u}_i \otimes \mathbf{u}_i) + \\ & (-1)^i \left( \frac{\partial}{\partial t} (a \mathbf{w}) + a \left( \frac{\partial \mathbf{u}_i}{\partial \mathbf{x}} \right)^T \mathbf{w} + \operatorname{div}(a \mathbf{w} \otimes \mathbf{u}_i) \right) = \rho_i \theta_i \nabla s_i - \rho_i \nabla h_i, \end{aligned} \quad (10)$$

$$\text{where } a = \frac{\partial \epsilon}{\partial \omega}.$$

In this case,  $\Psi_i$  and  $\Phi_i$  can be written

$$\Psi_i = \sum_{j=1}^2 D_{ij} \nabla \rho_j + E_{ij} \nabla s_j, \quad \Phi_i = \sum_{j=1}^2 C_{ij} \nabla \rho_j + D_{ij} \nabla s_j,$$

with  $C_{ij} = (1 + \delta_{ij}) \epsilon_{,\beta_{ij}}$ ,  $D_{ij} = \epsilon_{,\chi_{ij}}$ ,  $E_{ij} = (1 + \delta_{ij}) \epsilon_{,\gamma_{ij}}$ , where  $\delta_{ij}$  is the Kronecker symbol.

The simplest model is when  $C_{ij} = C_{ji}$ ,  $D_{ij}$ ,  $E_{ij} = E_{ji}$  are constant. Then,

$$\epsilon = e(\rho_i, s_i, \mathbf{w}) + \sum_{i,j=1}^2 \frac{1}{2} C_{ij} \nabla \rho_i \cdot \nabla \rho_j + D_{ij} \nabla \rho_i \cdot \nabla s_j + \frac{1}{2} E_{ij} \nabla s_i \cdot \nabla s_j \quad (11)$$

where the associated quadratic form with respect to the vectors  $\nabla \rho_i$  and  $\nabla s_i$  is in the form  $\sum_{i,j=1}^2 \frac{1}{2} C_{ij} \nabla \rho_i \cdot \nabla \rho_j + D_{ij} \nabla \rho_i \cdot \nabla s_j + \frac{1}{2} E_{ij} \nabla s_i \cdot \nabla s_j$ . This quadratic form is assumed positive such as the effect of gradient terms increases the value of the internal energy with respect to a mixture in a homogeneous configuration.

2.2 *Equation of total momentum and equation of energy for conservative motions of thermocapillary mixtures*

We limit first to the conservative case. We notice that the equation of motion of each component is not in divergence form. Nevertheless, by summing eqs (10) with respect to  $i$ , we obtain the balance equation for the total momentum in a divergence form. In fact, eqs (10) imply

$$\left( \sum_{i=1}^2 \frac{\partial \rho_i \mathbf{u}_i}{\partial t} + \operatorname{div}(\rho_i \mathbf{u}_i \otimes \mathbf{u}_i) \right) - \operatorname{div}(a \mathbf{w} \otimes \mathbf{w}) = a \left( \frac{\partial \mathbf{w}}{\partial \mathbf{x}} \right)^T \mathbf{w} + \left( \sum_{i=1}^2 \rho_i \theta_i \nabla s_i - \rho_i \nabla h_i \right) \quad (12)$$

In coordinates, the second member of eq. (12) is

$$a w_\nu w_{\gamma,\nu} + \sum_{i=1}^2 \epsilon_{,s_i} s_{i,\gamma} - (\epsilon_{,s_i,\nu})_{,\nu} s_{i,\gamma} - \rho_i (\epsilon_{,\rho_i})_{,\gamma} + \rho_i (\epsilon_{,\rho_i,\nu\nu})_{,\gamma} ,$$

where  $\nu$  is summed from 1 to 3. Noting that

$$\epsilon_{,\gamma} = \sum_{i=1}^2 \epsilon_{,s_i} s_{i,\gamma} + \epsilon_{,s_i,\nu} s_{i,\nu\gamma} + \epsilon_{,\rho_i} \rho_{i,\gamma} + \epsilon_{,\rho_i,\nu} \rho_{i,\nu\gamma} + a w_\nu w_{\gamma,\nu} , \quad (13)$$

we obtain

$$\begin{aligned} & a w_\nu w_{\gamma,\nu} + \sum_{i=1}^2 \epsilon_{,s_i} s_{i,\gamma} - (\epsilon_{,s_i,\nu})_{,\nu} s_{i,\gamma} - \rho_i (\epsilon_{,\rho_i})_{,\gamma} + \rho_i (\epsilon_{,\rho_i,\nu\nu})_{,\gamma} = \epsilon_{,\gamma} - \\ & \sum_{i=1}^2 \epsilon_{,s_i,\nu} s_{i,\nu\gamma} + \epsilon_{,\rho_i} \rho_{i,\gamma} + \epsilon_{,\rho_i,\nu} \rho_{i,\nu\gamma} + (\epsilon_{,s_i,\nu})_{,\nu} s_{i,\gamma} + \rho_i (\epsilon_{,\rho_i})_{,\gamma} - \rho_i (\epsilon_{,\rho_i,\nu\nu})_{,\gamma} \\ & = \epsilon_{,\gamma} + \sum_{i=1}^2 \left( -\rho_i \epsilon_{,\rho_i} + \rho_i (\epsilon_{,\rho_i,\nu})_{,\nu} \right)_{,\gamma} - (\Phi_{i\nu} \rho_{i,\gamma} + \Psi_{i\nu} s_{i,\gamma})_{,\nu} , \end{aligned}$$

and consequently the equation of motion for the total momentum is

$$\frac{\partial \rho \mathbf{u}}{\partial t} + \operatorname{div} \left( \sum_{i=1}^2 (\rho \mathbf{u}_i \otimes \mathbf{u}_i) - \rho a \mathbf{w} \otimes \mathbf{w} - \boldsymbol{\sigma} \right) = 0 \quad (14)$$

where  $\rho = \rho_1 + \rho_2$  is the total volume mass,  $\rho \mathbf{u} = \rho_1 \mathbf{u}_1 + \rho_2 \mathbf{u}_2$  is the total momentum and  $\boldsymbol{\sigma} = \boldsymbol{\sigma}_1 + \boldsymbol{\sigma}_2$  is the total stress tensor such that

$$\sigma_{i\nu\gamma} = (-P_i + \rho_i \operatorname{div} \Phi_i) \delta_{\nu\gamma} - \Phi_{i\nu} \rho_{i,\gamma} - \Psi_{i\nu} s_{i,\gamma} , \text{ with } P_i = \rho_i \epsilon_{,\rho_i} - \frac{\rho_i \epsilon}{\rho} .$$

Let us notice that if  $\epsilon$  depends also on  $(t, \mathbf{x})$  corresponding to an external force potential, an additive term appears as body force in relation (13) and in eq. (14) the body force appears in the second member. This is not the case in eqs (9) which include the body forces coming from  $\epsilon$  (depending on  $(t, \mathbf{x})$ ) in terms  $h_i$ . For the sake of simplicity, we do not introduce the body force in equation of the total momentum and equation of total energy.

The equation of energy of the total mixture is obtained in the divergence form. Let us define

$$\begin{aligned} \mathbf{M}_i &= \frac{\partial \rho_i \mathbf{u}_i}{\partial t} + \operatorname{div}(\rho_i \mathbf{u}_i \otimes \mathbf{u}_i) + \\ &(-1)^i \left( \frac{\partial}{\partial t}(a \mathbf{w}) + a \left( \frac{\partial \mathbf{u}_i}{\partial \mathbf{x}} \right)^T \mathbf{w} + \operatorname{div}(a \mathbf{w} \otimes \mathbf{u}_i) \right) - \rho_i \theta_i \nabla s_i + \rho_i \nabla h_i, \\ G_i &= \frac{\partial \rho_i}{\partial t} + \operatorname{div}(\rho_i \mathbf{u}_i), \\ S &= \sum_{i=1}^2 \left( \frac{\partial \rho_i s_i}{\partial t} + \operatorname{div}(\rho_i s_i \mathbf{u}_i) \right) \theta_i, \\ E &= \frac{\partial}{\partial t} \left( \left( \sum_{i=1}^2 \frac{1}{2} \rho_i \mathbf{u}_i^2 \right) + \varepsilon - a \mathbf{w}^2 \right) + \\ &\operatorname{div} \left( \left( \sum_{i=1}^2 \rho_i \left( \mathbf{K}_i \cdot \mathbf{u}_i - \frac{1}{2} \mathbf{u}_i^2 - \boldsymbol{\sigma}_i \right) \mathbf{u}_i \right) + \varepsilon \mathbf{u} - \mathbf{U} \right), \end{aligned}$$

where  $\mathbf{U} = \sum_{i=1}^2 \left( \frac{d_i \rho_i}{dt} \boldsymbol{\Phi}_i + \frac{d_i s_i}{dt} \boldsymbol{\Psi}_i \right)$  corresponds to the *interstitial working*: in the same way as for *Cahn and Hilliard fluids*, an additional term that has the physical dimension of a heat flux must be added to the equation of energy [13,14,15,28].

**THEOREM:** *For all motions of a thermocapillary fluid mixture, the relation*

$$E - S + \sum_{i=1}^2 \left( \frac{1}{2} \mathbf{u}_i^2 - h_i + \theta_i s_i \right) G_i - \mathbf{M}_i \cdot \mathbf{u}_i \equiv 0 \quad (15)$$

*is identically satisfied.*

The proof comes from the following algebraic calculation:

$$\begin{aligned} \mathbf{M}_i^T \mathbf{u}_i - \left( \frac{1}{2} \mathbf{u}_i^2 - h_i \right) G_i + \rho_i \theta_i \frac{d_i s_i}{dt} &\equiv \frac{\partial}{\partial t} \left( \frac{1}{2} \rho_i \mathbf{u}_i^2 \right) + \operatorname{div} \left( \left( \frac{1}{2} \rho_i \mathbf{u}_i^2 \right) \mathbf{u}_i \right) + h_i G_i \\ + \rho_i \theta_i \frac{\partial s_i}{\partial t} + \rho_i \frac{\partial h_i}{\partial \mathbf{x}} \mathbf{u}_i + (-1)^i &\left( \left( \frac{\partial a \mathbf{w}}{\partial t} \right)^T + a \mathbf{w}^T \frac{\partial \mathbf{u}_i}{\partial \mathbf{x}} + \operatorname{div} \left( a \mathbf{u}_i \mathbf{w}^T \right) \right) \mathbf{u}_i \end{aligned}$$

Let us note that

$$\begin{aligned} \frac{\partial \varepsilon}{\partial t} + \operatorname{div} \left( \sum_{i=1}^2 \rho_i h_i \mathbf{u}_i \right) &\equiv a \mathbf{w}^T \frac{\partial \mathbf{w}}{\partial t} + \sum_{i=1}^2 \varepsilon_{,\rho_i} \frac{\partial \rho_i}{\partial t} + \operatorname{div} \left( \frac{\partial \rho_i}{\partial t} \frac{\partial \varepsilon}{\partial \nabla \rho_i} \right) \\ - \frac{\partial \rho_i}{\partial t} \operatorname{div} \left( \frac{\partial \varepsilon}{\partial \nabla \rho_i} \right) + \varepsilon_{,s_i} \frac{\partial s_i}{\partial t} + \frac{\partial \varepsilon}{\partial \nabla s_i} \nabla \frac{\partial s_i}{\partial t} + h_i \operatorname{div} (\rho_i \mathbf{u}_i) + \rho_i \frac{\partial h_i}{\partial \mathbf{x}} \mathbf{u}_i, \end{aligned}$$

yields

$$\begin{aligned} \sum_{i=1}^2 h_i G_i &\equiv \frac{\partial \varepsilon}{\partial t} - a \mathbf{w}^T \frac{\partial \mathbf{w}}{\partial t} + \\ \sum_{i=1}^2 \operatorname{div} (\rho_i h_i \mathbf{u}_i) - \operatorname{div} \left( \frac{\partial \rho_i}{\partial t} \frac{\partial \varepsilon}{\partial \nabla \rho_i} \right) - \varepsilon_{,s_i} \frac{\partial s_i}{\partial t} - \frac{\partial \varepsilon}{\partial \nabla s_i} \nabla \frac{\partial s_i}{\partial t} - \rho_i \frac{\partial h_i}{\partial \mathbf{x}} \mathbf{u}_i. \end{aligned}$$

Consequently,

$$\begin{aligned} \sum_{i=1}^2 \left( \mathbf{M}_i^T \mathbf{u}_i - \left( \frac{1}{2} \mathbf{u}_i^2 - h_i + \theta_i s_i \right) G_i \right) + S &\equiv \\ \frac{\partial}{\partial t} \left( \left( \sum_{i=1}^2 \frac{1}{2} \rho_i \mathbf{u}_i^2 \right) + \varepsilon \right) - a \mathbf{w}^T \frac{\partial \mathbf{w}}{\partial t} + \sum_{i=1}^2 \operatorname{div} \left( \rho_i \left( \frac{1}{2} \mathbf{u}_i^2 + h_i \right) \mathbf{u}_i \right) \\ - \operatorname{div} \left( \frac{\partial \rho_i}{\partial t} \Phi_i + \frac{\partial s_i}{\partial t} \Psi_i \right) + (-1)^i \left( \left( \frac{\partial a \mathbf{w}}{\partial t} \right)^T \mathbf{u}_i + a \mathbf{w}^T \frac{\partial \mathbf{u}_i}{\partial \mathbf{x}} \mathbf{u}_i + \operatorname{div} (a \mathbf{u}_i \mathbf{w}^T) \mathbf{u}_i \right) &\equiv \\ \frac{\partial}{\partial t} \left( \left( \sum_{i=1}^2 \frac{1}{2} \rho_i \mathbf{u}_i^2 \right) + \varepsilon - a \mathbf{w}^2 \right) + \sum_{i=1}^2 \operatorname{div} \left( \rho_i \left( \mathbf{K}_i^T \mathbf{u}_i - \frac{1}{2} \mathbf{u}_i^2 + h_i \right) \mathbf{u}_i \right) \\ - \operatorname{div} \left( \frac{\partial \rho_i}{\partial t} \Phi_i + \frac{\partial s_i}{\partial t} \Psi_i \right) \end{aligned}$$

Taking into account of the relations

$$\frac{\partial \rho_i}{\partial t} \Phi_i \equiv \frac{d_i \rho_i}{dt} \Phi_i - \Phi_i \frac{\partial \rho_i}{\partial \mathbf{x}} \mathbf{u}_i \quad \text{and} \quad \frac{\partial s_i}{\partial t} \Psi_i \equiv \frac{d_i s_i}{dt} \Psi_i - \Psi_i \frac{\partial s_i}{\partial \mathbf{x}} \mathbf{u}_i$$

and the definition of the total stress tensor,

$$\boldsymbol{\sigma} \equiv \varepsilon - \sum_{i=1}^2 \left( \rho_i \varepsilon_{,\rho_i} - \rho_i \operatorname{div} \Phi_i \right) \mathbf{Id} - \Phi_i \frac{\partial \rho_i}{\partial \mathbf{x}} - \Psi_i \frac{\partial s_i}{\partial \mathbf{x}},$$

where  $\mathbf{Id}$  is the identity tensor, we deduce immediately the algebraic identity (15).  $\square$

COROLLARY: *All conservative motions of a thermocapillary mixture satisfy the equation of energy balance*

$$\begin{aligned} & \frac{\partial}{\partial t} \left( \left( \sum_{i=1}^2 \frac{1}{2} \rho_i \mathbf{u}_i^2 \right) + \varepsilon - a \mathbf{w}^2 \right) + \\ & \operatorname{div} \left( \left( \sum_{i=1}^2 \rho_i \left( \mathbf{K}_i \cdot \mathbf{u}_i - \frac{1}{2} \mathbf{u}_i^2 - \boldsymbol{\sigma}_i \right) \mathbf{u}_i \right) + \varepsilon \mathbf{u} - \mathbf{U} \right) = 0. \end{aligned} \quad (16)$$

This result comes from the simultaneity of relations  $G_i = 0$ ,  $S_i = 0$  and  $\mathbf{M}_i = 0$ .

Let us note that  $\varepsilon - a \mathbf{w}^2$  corresponds to the volume internal energy  $\varpi$  of the mixture.

### 2.3 Dissipative motions of thermocapillary mixtures

The conservative fluid mixture model presented in section 2.1 is relevant to the so-called *second gradient theory* [21], [38]. In our form of equations of mass conservation for each component (2), equation of the total momentum of the mixture (14), equation of energy (16), the diffusion term  $J = \rho_1(\mathbf{u}_1 - \mathbf{u})$  does not directly appear but is deduced respectively from the velocities and densities of the components.

Our aim is to verify the consistency of our model with the second law of thermodynamics. The introduction of dissipative forces is simply done in the framework of the *first gradient theory* [21]: the dissipative forces applied to the continuous medium are divided into volume forces  $\mathbf{f}_i^d$  and surface forces associated with the Cauchy stress tensor  $\boldsymbol{\sigma}_i^d$ . Then, the virtual work of dissipative forces  $\delta T_i$  applied to the component  $i$  is in the form

$$\delta T_i = \mathbf{f}_i^d \cdot \boldsymbol{\zeta}_i - \operatorname{tr} \left( \boldsymbol{\sigma}_i^d \frac{\partial \boldsymbol{\zeta}_i}{\partial \mathbf{x}} \right),$$

where  $\delta T_i$  is a differential form. For such dissipative motions, no production of masses due to chemical reactions appears.

For the same virtual displacement of two components,  $\boldsymbol{\zeta} = \boldsymbol{\zeta}_i$ , ( $i = 1, 2$ ), the total virtual work of dissipative forces is

$$\delta T = \sum_{i=1}^2 \mathbf{f}_i^d \cdot \boldsymbol{\zeta} - \operatorname{tr} \left( \boldsymbol{\sigma}_i^d \frac{\partial \boldsymbol{\zeta}}{\partial \mathbf{x}} \right).$$

When  $\boldsymbol{\zeta}$  is a translation, the work  $\delta T$  is equal to zero and consequently,

$$\sum_{i=1}^2 \mathbf{f}_i^d = 0 \quad \text{or} \quad \mathbf{f}_2^d = -\mathbf{f}_1^d \equiv \mathbf{f}^d \quad (17)$$

We specify later the behavior of forces  $\mathbf{f}_i^d$  (they will be associated with the diffusion term) and stress tensors  $\boldsymbol{\sigma}_i^d$ . Taking into account of the dissipative effects, the equations of motion for each component become

$$\begin{aligned} \frac{\partial \rho_i \mathbf{u}_i}{\partial t} + \operatorname{div}(\rho_i \mathbf{u}_i \otimes \mathbf{u}_i) + (-1)^i \left( \frac{\partial}{\partial t}(a \mathbf{w}) + a \left( \frac{\partial \mathbf{u}_i}{\partial \mathbf{x}} \right)^T \mathbf{w} + \operatorname{div}(a \mathbf{w} \otimes \mathbf{u}_i) \right) \\ = \rho_i \theta_i \nabla s_i - \rho_i \nabla h_i + \operatorname{div} \boldsymbol{\sigma}_i^d + \mathbf{f}_i^d \end{aligned} \quad (18)$$

Taking into account of relation (17), the equation of the total momentum writes

$$\frac{\partial \rho \mathbf{u}}{\partial t} + \operatorname{div} \left( \sum_{i=1}^2 (\rho \mathbf{u}_i \otimes \mathbf{u}_i) - \rho a \mathbf{w} \otimes \mathbf{w} - \boldsymbol{\sigma} - \boldsymbol{\sigma}^d \right) = 0 \quad (19)$$

with  $\boldsymbol{\sigma}^d = \boldsymbol{\sigma}_1^d + \boldsymbol{\sigma}_2^d$ .

The introduction of the heat flux vector  $\mathbf{q}$  and the heat supply  $r$  comes from classical methods in thermodynamics [32,34,39]. If we write,

$$\begin{aligned} \mathbf{M}_i^d &= \mathbf{M}_i - \operatorname{div} \boldsymbol{\sigma}_i^d - \mathbf{f}_i^d, \\ S^d &= S - r + \operatorname{div} \mathbf{q} + \sum_{\alpha=1}^2 \mathbf{f}_i^d \cdot \mathbf{u}_i - \operatorname{tr}(\boldsymbol{\sigma}_i^d \boldsymbol{\Delta}_i), \\ E^d &= E - r + \operatorname{div} \mathbf{q} - \sum_{\alpha=1}^2 \operatorname{div} \boldsymbol{\sigma}_i^d \mathbf{u}_i, \end{aligned}$$

with  $\boldsymbol{\Delta}_i = \frac{1}{2} \left( \frac{\partial \mathbf{u}_i}{\partial \mathbf{x}} + \left( \frac{\partial \mathbf{u}_i}{\partial \mathbf{x}} \right)^T \right)$  represents the velocity deformation tensor of each component, relation (15) writes as

$$E^d - S^d - \sum_{i=1}^2 \mathbf{M}_i^d \cdot \mathbf{u}_i - (\mathbf{K}_i \cdot \mathbf{u}_i - R_i - \theta_i s_i) G_i \equiv 0 \quad (20)$$

which can be considered as the dynamic form of the *Gibbs identity*.

For the components of the mixture, equations of momenta and equations of masses are in the form

$$\mathbf{M}_i^d = 0, \quad G_i = 0. \quad (21)$$

The *Gibbs identity* (20) and eqs (21) imply  $S^d = E^d$ . If we assume that  $S^d = 0$ , i.e.,

$$\sum_{i=1}^2 \left( \frac{\partial \rho_i s_i}{\partial t} + \operatorname{div}(\rho_i s_i \mathbf{u}_i) \right) \theta_i + \mathbf{f}_i^d \cdot \mathbf{u}_i - \operatorname{tr}(\boldsymbol{\sigma}_i^d \boldsymbol{\Delta}_i) - r + \operatorname{div} \mathbf{q} = 0, \quad (22)$$

it is equivalent to write  $E^d = 0$ , i.e.,

$$\begin{aligned} & \frac{\partial}{\partial t} \left( \left( \sum_{i=1}^2 \frac{1}{2} \rho_i \mathbf{u}_i^2 \right) + \varepsilon - a \mathbf{w}^2 \right) + \\ & \operatorname{div} \left( \left( \sum_{i=1}^2 \rho_i \left( \mathbf{K}_i \cdot \mathbf{u}_i - \frac{1}{2} \mathbf{u}_i^2 - \boldsymbol{\sigma}_i - \boldsymbol{\sigma}_i^d \right) \mathbf{u}_i \right) + \varepsilon \mathbf{u} - \mathbf{U} + \mathbf{q} \right) - r = 0. \end{aligned} \quad (23)$$

Eq. (22) is the *equation of entropy* and Eq. (23) is the *equation of energy*.

In the conservative case, the system is closed with two different temperatures  $\theta_i$  ( $i = 1, 2$ ). In the dissipative case we need additional arguments to obtain equations for each entropy  $s_i$  which could remplace equations (4). A possibility is to consider the case when the exchanges of momentum and energy between the two components are rapid enough to have a common temperature (this is not the case of heterogeneous mixtures where each phase may have different pressures and temperatures [40]). Then, in dissipative case, if we know all the dissipative functions, the governing system is closed. Note also that it could be possible to consider a common temperature and entropy both for conservative and dissipative case. This case is connected with a conservative equation for the common entropy  $s$  (see Appendix). Another possibility is to assume that the entropy is transported along the  $i$ th component (say, for example  $i = 1$ ) which was used for quantum fluids by Landau [41]

$$\frac{\partial \rho_1 s}{\partial t} + \operatorname{div} (\rho_1 s \mathbf{u}_1) = 0.$$

In this case, the independent functions are  $\rho_1, s, \mathbf{u}_1, \rho_2, \mathbf{u}_2$ , where  $\rho_i$  are submitted to the constraints (3) and the case of Helium superfluid is a special case of our study corresponding to  $s_2 = 0$  and  $s = s_1$ . Using of this hypothesis is nevertheless doubtful for classical fluids.

Hence, we may suppose a common temperature only for dissipative case. This means that

$$\theta = \theta_1 = \theta_2 \quad (24)$$

This hypothesis closes the system (21-22).

*Now we focus on the governing equations for each components of the mixture:*

$$\mathbf{M}_i^d = 0 \quad (i = 1, 2).$$

For slow motions, we rewrite these equations in the following form :

$$\mathbf{M}_i^d \simeq \rho_i \nabla h_i - \rho_i \theta \nabla s_i - \operatorname{div} \boldsymbol{\sigma}_i^d - \mathbf{f}_i^d = 0.$$

If we consider the case when the motion of each component is regular enough, an approximative case is the case of *solid displacements* for the motion of each component; then,  $\operatorname{div} \boldsymbol{\sigma}_i^d \simeq 0$  and consequently,

$$\mathbf{M}_i^d \simeq \rho_i \nabla \mu_i - \mathbf{f}_i^d = 0,$$

where  $\mu_i = h_i - \theta s_i$  is the chemical potential of the component  $i$  of the mixture at the temperature  $\theta$ .

Considering the difference  $\mathbf{M}_2^d - \mathbf{M}_1^d$  and using relation (17), we obtain,

$$\frac{\mathbf{f}_2^d}{\rho_2} - \frac{\mathbf{f}_1^d}{\rho_1} \equiv \frac{\rho \mathbf{f}^d}{\rho_1 \rho_2} = \nabla \mu, \quad (25)$$

where  $\mu = \mu_2 - \mu_1$  is the chemical potential of the mixture [42,43]. Let us introduce the diffusion flux  $\mathbf{J}$ ,

$$\mathbf{J} \equiv \rho_1(\mathbf{u}_1 - \mathbf{u}) = \frac{\rho_1 \rho_2}{\rho} \mathbf{w}. \quad (26)$$

Equation (25) implies,

$$\mathbf{f}^d \cdot \mathbf{w} = \nabla \mu \cdot \mathbf{J}. \quad (27)$$

The term  $\nabla \mu \cdot \mathbf{J}$  corresponds to the entropy production due to the diffusion process. Expression (27) is the connection between the mechanical drag force between components of the mixture and the thermodynamical process of diffusion; consequently, Eq. (22) yields

$$\sum_{i=1}^2 \left( \frac{\partial \rho_i s_i}{\partial t} + \text{div}(\rho_i s_i \mathbf{u}_i) \right) \theta_i - \text{tr}(\boldsymbol{\sigma}_i^d \boldsymbol{\Delta}_i) - r + \text{div} \mathbf{q} - \nabla \mu \cdot \mathbf{J} = 0.$$

We have obtained the equations of balance of masses, equation of total momentum, Eq. (25) between the components and equation of total energy by using an energetic method. They are the extension of classical mixture equations to equations of mixtures of fluids involving density gradients.

#### 2.4 Second law of thermodynamics

Relation (22) may be rewritten in the form

$$\left( \sum_{i=1}^2 \frac{\partial \rho_i s_i}{\partial t} + \text{div}(\rho_i s_i \mathbf{u}_i) \right) + \text{div} \frac{\mathbf{q}}{\theta} - \frac{r}{\theta} = \frac{1}{\theta} \left( \sum_{i=1}^2 \text{tr}(\boldsymbol{\sigma}_i^d \boldsymbol{\Delta}_i) \right) + \mathbf{f}^d \cdot \mathbf{w} - \nabla \theta \cdot \frac{\mathbf{q}}{\theta^2}$$

This last equation yields the entropy production due to the diffusion, viscosity and heat flux processes. Due to  $\theta > 0$ , if we assume

$$\left( \sum_{i=1}^2 \text{tr}(\boldsymbol{\sigma}_i^d \boldsymbol{\Delta}_i) \right) + \mathbf{f}^d \cdot \mathbf{w} - \nabla \theta \cdot \frac{\mathbf{q}}{\theta} \geq 0, \quad (28)$$

we get the Clausius-Duhem inequality in the form

$$\left( \sum_{i=1}^2 \frac{\partial \rho_i s_i}{\partial t} + \text{div}(\rho_i s_i \mathbf{u}_i) \right) + \text{div} \frac{\mathbf{q}}{\theta} - \frac{r}{\theta} \geq 0.$$

Let us notice that (28) is satisfied if  $tr(\boldsymbol{\sigma}_i^d \boldsymbol{\Delta}_i) \geq 0$ ,  $\mathbf{f}^d \cdot \mathbf{w} \geq 0$  and  $\nabla\theta \cdot \mathbf{q} \leq 0$ . The following constitutive laws are classically adopted for  $\boldsymbol{\sigma}_i^d$ ,  $\mathbf{f}^d$  and  $\mathbf{q}$ :

The stress tensor  $\boldsymbol{\sigma}_i^d$  is a symmetric isotropic tensor function of  $\boldsymbol{\Delta}_i$  such that  $\sum_{i=1}^2 tr(\boldsymbol{\sigma}_i^d \boldsymbol{\Delta}_i) \geq 0$  (a special case of such a function is  $\boldsymbol{\sigma}_i^d = \lambda_i(tr \boldsymbol{\Delta}_i)\mathbf{Id} + 2\mu_i\boldsymbol{\Delta}_i$  with  $\mu_i \geq 0$  and  $3\lambda_i + 2\mu_i \geq 0$ ).

The heat flux vector satisfies the Fourier law

$$\mathbf{q} = -\chi \nabla\theta \quad \text{with } \chi \geq 0.$$

The linear approximation known in the literature as the *Stokes drag formula* is adopted [41,42]

$$\mathbf{f}^d = k \mathbf{w}, \quad k \geq 0, \quad \text{with } \mathbf{f}_2^d = -\mathbf{f}_1^d \equiv \mathbf{f}^d \quad \text{and } \mathbf{w} = \mathbf{u}_1 - \mathbf{u}_2.$$

Let us note that relations (25) and (26) together with the drag formula yield the property of the diffusion flux

$$\mathbf{J} = \frac{1}{k} \nabla \mu, \quad (29)$$

which is the general form of the Fick law [39,41]. So, the Fick law is not directly a linear phenomenological law as the Fourier law but a direct consequence of equations of motion and the Stokes drag force hypothesis which was previously noticed by Bowen for a different model [42].

### 3 Acceleration Waves

Now, we will consider conservative motions of thermocapillary mixtures only. As it is well known, wave phenomena - in particular discontinuity waves (waves across the front of which some derivatives of the field variables have jumps) - are typical of models that are described through hyperbolic differential systems. A classical example of discontinuity waves in continuum mechanics are the so-called *acceleration waves* in which, among the other variables, the acceleration jumps across the front while the velocity is continuous [44].

Dissipative systems and in particular models for diffusive processes have usual differential system with a parabolic structure and discontinuity waves are not admissible. A typical example of non admissibility is the one of Navier-Stokes-Fourier fluids. In this case a possible approach to obtain hyperbolic system is the method of the Extended Thermodynamic theory [32], valid also for rarefied gases.

Nevertheless in parabolic systems some discontinuity waves may propagate for particular initial data. The aim of this paper is to prove that for the present model of thermocapillarity fluid binary mixtures there exists the possibility of propagation of two tangential acceleration waves, provided that the internal energy is at least a function of the entropy gradient of one component. For this aim, we first briefly recall some very well known questions about discontinuity waves.

A wave is a discontinuity wave if the wave front with Cartesian equation  $\phi(t, \mathbf{x}) = 0$  separates the space in two subspaces in which there exists regular solutions of the differential system but across the normal direction of the front some derivatives of the field suffers a jump [23].

As usual, we indicate the jump with a square bracket,

$$[ \ ] = ( \ )_{\phi=0^-} - ( \ )_{\phi=0^+}$$

and we introduce the map between  $(t, \mathbf{x})$  and  $(\phi, \boldsymbol{\xi})$ , where  $\boldsymbol{\xi} \equiv \boldsymbol{\xi}(t, \mathbf{x})$  represents the tangential manifold of the wave surface in time-space. Therefore the assumptions for the discontinuity waves are expressed for a generic function  $f$  in the form,

$$\left\{ \begin{array}{l} [f] = 0; \quad \left[ \frac{\partial^k f}{\partial \xi_{\gamma_1} \cdots \partial \xi_{\gamma_k}} \right] = 0 \quad \forall k; \\ \text{where there exists } p \geq 1 \text{ such that} \\ \left[ \frac{\partial^j f}{\partial \phi^j} \right] = 0 \quad \text{for } 1 \leq j \leq p-1; \\ \delta^k f \equiv \left[ \frac{\partial^k f}{\partial \phi^k} \right] \neq 0 \quad \text{for } k \geq p. \end{array} \right. \quad (30)$$

Taking into account (30) and the Hadamard lemma [45], we have

$$\left[ \frac{\partial^p f}{\partial x_{\gamma_1} \cdots \partial x_{\gamma_p}} \right] = \delta^p f \, n_{i_1} \cdots n_{i_p}; \quad \left[ \frac{\partial^p f}{\partial t^p} \right] = (-\lambda)^p \delta^p f$$

where  $\lambda$  and here  $\mathbf{n} \equiv (n_i)$  are respectively the normal velocity and the unit normal vector to the wave front.

The advantages of the previous symbols are that there exists a chain rule between the field derivative in the differential systems and the corresponding jump relation,

$$\partial_t \rightarrow -\lambda \delta; \quad \partial_{\gamma} \rightarrow n_{\gamma} \delta. \quad (31)$$

We apply now this procedure to our differential systems assuming that across the wave front  $\rho_i$ ,  $s_i$  and its first derivatives are continuous and there are

jumps for the second derivative ( $p = 2$ ) while the velocity is continuous and suffer a jump in the first derivative ( $p = 1$ )

$$\begin{aligned} [\rho_i] = [s_i] = [\delta\rho_i] = [\delta s_i] = 0; \quad [\delta^2\rho_i] \neq 0; \quad [\delta^2 s_i] \neq 0; \\ [\mathbf{u}_i] = 0; \quad [\delta\mathbf{u}_i] \neq 0; \quad i = 1, 2. \end{aligned} \quad (32)$$

### 3.1 Jump conditions:

From the balance of mass of the two components (3), taking into account of eqs (32) and the chain rule (31), we obtain that the normal components of the first derivative of the velocities are continuous,

$$[\delta u_{in}] = 0, \quad (33)$$

where  $u_{in} = \mathbf{n} \cdot \mathbf{u}_i$ .

If we differentiate the entropy balance law of each component (4), with respect  $\mathbf{x}$ , we obtain for the discontinuities

$$-v_i \delta^2 s_i + \nabla s_i \cdot \delta\mathbf{u}_i = 0, \quad (34)$$

where

$$v_i = \lambda - u_{in}$$

are the relative velocities of the wave front with respect to the fluid components. From the balance of momentum we obtain

$$\begin{aligned} -\rho_i v_i \delta\mathbf{u}_i + (-1)^i a \{v_i \delta(\mathbf{u}_2 - \mathbf{u}_1) + (\delta\mathbf{u}_i \cdot (\mathbf{u}_1 - \mathbf{u}_2)) \mathbf{n}\} \\ -\rho_i \{ \nabla s_i [\theta_i] - [\nabla h_i] \} = 0. \end{aligned} \quad (35)$$

From eq. (6) we obtain

$$\begin{aligned} B_i \equiv -\rho_i [\theta_i] &= \sum_{j=1}^2 (D_{ji} \delta^2 \rho_j + E_{ji} \delta^2 s_j) \\ \mathbf{A}_i \equiv -[\nabla h_i] &= \mathbf{n} \sum_{j=1}^2 (C_{ij} \delta^3 \rho_j + D_{ij} \delta^3 s_j). \end{aligned} \quad (36)$$

Then relation (35) becomes

$$-\rho_i v_i \delta\mathbf{u}_i + (-1)^i a \{v_i \delta(\mathbf{u}_2 - \mathbf{u}_1) + (\delta\mathbf{u}_i \cdot (\mathbf{u}_1 - \mathbf{u}_2)) \mathbf{n}\} + B_i \nabla s_i - \rho_i \mathbf{A}_i = 0.$$

If we multiply by  $\mathbf{n}$  and we take into account of relation (33), we obtain

$$\rho_i \mathbf{A}_i \cdot \mathbf{n} = (-1)^i a \delta\mathbf{u}_i \cdot (\mathbf{u}_1 - \mathbf{u}_2) + B_i \nabla s_i \cdot \mathbf{n}, \quad (37)$$

then, we get the final jump conditions from the momentum equations

$$\rho_i v_i \delta \mathbf{u}_i + (-1)^i a v_i \delta (\mathbf{u}_1 - \mathbf{u}_2) - B_i \nabla_t s_i = 0, \quad (38)$$

where

$$\nabla_t s_i = \nabla s_i - (\nabla s_i \cdot \mathbf{n}) \mathbf{n} \quad (39)$$

denotes the tangential component of the gradient of entropy of each component.

Therefore we obtain the algebraic system of 8 equations (33), (34) and (38) for the 10 scalar unknowns  $\delta^2 \rho_i$ ,  $\delta^2 s_i$  and  $\delta \mathbf{u}_i$  ( $i = 1, 2$ ). Consequently, we need two more conditions that are obtained by compatibility conditions coming from boundary conditions associated with the equation of motion for each component. In fact, we notice in Appendix that if  $\rho_i, s_i, \nabla \rho_i, \nabla s_i$  are continuous through a surface of weak discontinuities, then  $\text{div } \Phi_i$  must be also continuous through the surface

$$[\text{div } \Phi_i] = 0.$$

We notice additively that these two conditions are compatible with the Rankine-Hugoniot conditions associated to the total momentum (14) and the total energy balance law (16): In fact, eq. (14) yields

$$[\boldsymbol{\sigma}_1 + \boldsymbol{\sigma}_2] = 0,$$

while from eq. (16), we get

$$[\boldsymbol{\sigma}_1 u_{1n} + \boldsymbol{\sigma}_2 u_{2n}] = 0.$$

Then, we obtain the two supplementary equations

$$[\text{div } \Phi_i] = \sum_{j=1}^2 (C_{ij} \delta^2 \rho_j + D_{ij} \delta^2 s_j) = 0 \quad (40)$$

and the system for the discontinuities becomes an homogeneous closed system of 10 equations for 10 scalar unknowns  $\delta^2 \rho_i$ ,  $\delta^2 s_i$  and  $\delta \mathbf{u}_i$  ( $i = 1, 2$ ) in the

form,

$$\left\{ \begin{array}{l} [\delta u_{in}] = 0 \\ \rho_i v_i \delta \mathbf{u}_i + (-1)^i a v_i \delta(\mathbf{u}_1 - \mathbf{u}_2) - \sum_{j=1}^2 (D_{ji} \delta^2 \rho_j + E_{ji} \delta^2 s_j) \nabla_t s_i = 0 \\ -v_i \delta^2 s_i + \nabla s_i \cdot \delta \mathbf{u}_i = 0 \\ \sum_{j=1}^2 (C_{ij} \delta^2 \rho_j + D_{ij} \delta^2 s_j) = 0 \end{array} \right. \quad (41)$$

We observe that the conditions (36), (37) are constraints for the jump of the third derivatives of densities and entropies  $\delta^3 \rho_j$ ,  $\delta^3 s_j$ .

Now we consider the weak discontinuities near the equilibrium of the fluid mixture; then

$$\mathbf{u}_i = 0.$$

Consequently  $v = \lambda$  is the velocity of the acceleration wave. Due to the fact that thermocapillary mixtures can be considered as a mathematical model for interfacial layers between two mixture bulks [29], the gradients of tensorial quantities  $\rho_i$  and  $s_i$  are orthogonal to the interfacial layers and consequently are collinear,

$$\nabla s_1 = b \nabla s_2.$$

Then the second and the third equations of system (41) allow to eliminate  $\mathbf{u}_i$  and to get

$$c_s^2 ((a - \rho_1) \delta^2 s_1 - a b \delta^2 s_2) + \sum_{j=1}^2 (D_{j1} \delta^2 \rho_j + E_{j1} \delta^2 s_j) (\nabla_t s_1)^2 = 0$$

and

$$c_s^2 (-a b \delta^2 s_1 + b^2 (a - \rho_2) \delta^2 s_2) + \sum_{j=1}^2 (D_{j2} \delta^2 \rho_j + E_{j2} \delta^2 s_j) (\nabla_t s_1)^2 = 0$$

where

$$c_s^2 = \frac{v^2}{(\nabla_t s_1)^2}.$$

Therefore we obtain a system of compatibility between the variables  $\delta^2 \rho_j$  and

$\delta^2 s_j$  in the form

$$\left\{ \begin{array}{l} C_{11} \delta^2 \rho_1 + C_{12} \delta^2 \rho_2 + D_{11} \delta^2 s_1 + D_{12} \delta^2 s_2 = 0 \\ C_{12} \delta^2 \rho_1 + C_{22} \delta^2 \rho_2 + D_{21} \delta^2 s_1 + D_{22} \delta^2 s_2 = 0 \\ D_{11} \delta^2 \rho_1 + D_{21} \delta^2 \rho_2 + (E_{11} + (a - \rho_1) c_s^2) \delta^2 s_1 \\ \quad + (E_{12} - a b c_s^2) \delta^2 s_2 = 0 \\ D_{12} \delta^2 \rho_1 + D_{22} \delta^2 \rho_2 + (E_{12} - a b c_s^2) \delta^2 s_1 \\ \quad + (E_{22} + (a - \rho_2) b^2 c_s^2) \delta^2 s_2 = 0 \end{array} \right. \quad (42)$$

Let us denote

$$\mathbf{C} = \mathbf{C}^T = \begin{vmatrix} C_{11} & C_{12} \\ C_{12} & C_{22} \end{vmatrix}, \quad \mathbf{D} = \begin{vmatrix} D_{11} & D_{12} \\ D_{21} & D_{22} \end{vmatrix},$$

$$\mathbf{E} = \mathbf{E}^T = \begin{vmatrix} E_{11} & E_{12} \\ E_{12} & E_{22} \end{vmatrix}, \quad \mathbf{B} = \mathbf{B}^T = \begin{vmatrix} \rho_1 - a & ab \\ ab & (\rho_2 - a)b^2 \end{vmatrix}$$

$$\delta^2 \boldsymbol{\rho} = \begin{vmatrix} \delta^2 \rho_1 \\ \delta^2 \rho_2 \end{vmatrix}, \quad \delta^2 \mathbf{s} = \begin{vmatrix} \delta^2 s_1 \\ \delta^2 s_2 \end{vmatrix}$$

and system (42) is writing

$$\left\{ \begin{array}{l} \mathbf{C} \delta^2 \boldsymbol{\rho} + \mathbf{D} \delta^2 \mathbf{s} = 0 \\ \mathbf{D}^T \delta^2 \boldsymbol{\rho} + (\mathbf{E} - c_s^2 \mathbf{B}) \delta^2 \mathbf{s} = 0 \end{array} \right. ,$$

which implies

$$(\mathbf{A} - c_s^2 \mathbf{B}) \delta^2 \mathbf{s} = 0. \quad (43)$$

where

$$\mathbf{A} = \mathbf{E} - \mathbf{D}^T \mathbf{C}^{-1} \mathbf{D} .$$

From eq.(43) it is simple to verify the property,

**THEOREM:** *If  $\mathbf{E} \mathbf{C} - \mathbf{D}^2$  is positive definite and if we consider small diffusion, i.e.  $a < \rho^*$  with*

$$\rho^* = \frac{\rho_1 \rho_2}{\rho_1 + \rho_2}$$

then,  $\mathbf{A}$  and  $\mathbf{B}$  are both symmetric and definite positive, all the eigenvalues  $c_s^2$  of eq. (43) are positive and two discontinuity waves exist.

### 3.2 Exceptional waves:

As in the hyperbolic case, a wave is *exceptional or linearly degenerate* (see e.g. [23]) if

$$\delta\lambda \equiv 0. \quad (44)$$

In this case the wave behavior is similar to the behavior in linear case and we do not get any distortion of the wave or shock formation.

It is simple matter to prove that both the waves fulfill the exceptionality condition. In fact, taking into account of relations (31),(39), we have

$$\delta\nabla_t s \equiv 0$$

and from (43) we obtain that  $\lambda$  is function of the modulo of the tangential gradient of entropy

$$\lambda \equiv \lambda(|\nabla_t s|)$$

and then (44) holds.

## 4 Results and discussion:

In this paper we prove that the model of thermocapillary fluid mixtures with dissipation yields a system of equations of motions compatible with the second law of thermodynamics at least in simple dissipative cases. The equation of motion and the equation of energy of the barycentric motion of the mixture are in a divergence form in conservative cases.

Consequently, Hamilton's principle applied to fluid dynamics is a direct and systematic method to obtain the equations of conservative motions. This principle extended to each component of a mixture of conservative fluids is able to deduce the same number of balance equations than unknown functions. The method yields a non ambiguous framework for the case of non-conservative mixtures (with viscosity, diffusion and heat transfer). Non additional assumption but constitutive behavior compatible with the second law of thermodynamics is necessary. One obtains the dynamic Gibbs relation and Fick's law as a consequence of governing equations.

We have seen that the dependance of an entropy gradient is necessary for the existence of isentropic waves of acceleration along the interfaces: the fact that

the internal energy depends not only on the gradient of matter densities but also on the gradient of entropy, yields a new kind of waves which does not appear in simpler models. They are exceptional waves in the sense of Boillat and Lax [23] and they appear only in, at least, systems with two dimensions. These second order waves are of weak energy and consequently they are not easy to show up. Recent experiments in space laboratories in micro-gravity conditions, for carbonic dioxide near its critical point, have showed the possibility of such waves [46]. The experimental evidence of such adiabatic waves with other physical reasons we have presented in the introduction should strengthen the necessity to take into account of the dependence of entropy gradients together with density gradients in the expression of the internal energy for continuum models of capillarity and phase transitions.

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## 5 Appendix:

### 5.1 Compatibility conditions for weak discontinuities

We obtain also the compatibility due to the boundary conditions. For this aim we rewrite the variations of the Hamilton action when the equations of the motion (8) are verified. Then, from relation (7), we obtain,

$$\delta_i I = \int_{t_1}^{t_2} \int_{\partial D_i} g \rho_i \mathbf{K}_i^T \boldsymbol{\zeta}_i - \mathbf{n} \cdot \left( \rho_i R_i \boldsymbol{\zeta}_i - \rho_i \mathbf{u}_i \mathbf{K}_i^T \boldsymbol{\zeta}_i - \boldsymbol{\Phi}_i \frac{\partial \rho_i}{\partial \mathbf{x}} \boldsymbol{\zeta}_i - \boldsymbol{\Psi}_i \frac{\partial s_i}{\partial \mathbf{x}} \boldsymbol{\zeta}_i - \rho_i \boldsymbol{\Phi}_i \operatorname{div} \boldsymbol{\zeta}_i \right) d\sigma_x dt.$$

For a vector field  $\mathbf{x} \in D_t \rightarrow \boldsymbol{\zeta}_i$  vanishing with its first derivatives on the boundary  $\partial D_t$ , we deduce immediately on a surface of discontinuity  $\Sigma_t$  (where  $\rho_i, s_i$  and its first derivatives are continuous and there are jumps for the second derivative) the value of the variation of the Hamilton action,

$$\begin{aligned} \delta_i I &= \int_{t_1}^{t_2} \int_{\Sigma_t} g \left[ \rho_i \mathbf{K}_i^T \boldsymbol{\zeta}_i \right] \\ &- \mathbf{n} \cdot \left[ \rho_i R_i \boldsymbol{\zeta}_i - \rho_i \mathbf{u}_i \mathbf{K}_i^T \boldsymbol{\zeta}_i - \boldsymbol{\Phi}_i \frac{\partial \rho_i}{\partial \mathbf{x}} \boldsymbol{\zeta}_i - \boldsymbol{\Psi}_i \frac{\partial s_i}{\partial \mathbf{x}} \boldsymbol{\zeta}_i - \rho_i \boldsymbol{\Phi}_i \operatorname{div} \boldsymbol{\zeta}_i \right] d\sigma_x dt \\ &\equiv - \int_{t_1}^{t_2} \int_{\Sigma_t} \mathbf{n} \cdot [\rho_i R_i] \boldsymbol{\zeta}_i d\sigma_x dt. \end{aligned}$$

Due to the fact that  $\delta_i I = 0$  for a vector field  $\mathbf{x} \in D_t \rightarrow \boldsymbol{\zeta}_i$ , we obtain  $[\rho_i R_i] = 0$ , and deduce the compatibility conditions (40) across the wave front,

$$[\operatorname{div} \boldsymbol{\Phi}_i] \equiv \sum_{j=1}^2 (C_{ij} \delta^2 \rho_j + D_{ij} \delta^2 s_j) = 0.$$

## 5.2 Mixture with an entropy for the total fluid

The equations of balance of matter densities  $\rho, \rho_1$  are in the form

$$\begin{aligned} \frac{\partial \rho}{\partial t} + \operatorname{div}(\rho \mathbf{u}) &= 0, \\ \frac{\partial \rho_1}{\partial t} + \operatorname{div}(\rho_1 \mathbf{u}_1) &= 0, \end{aligned} \tag{45}$$

where  $\rho$  and  $\mathbf{u}$  denote the density and the velocity of the total mixture,  $\rho_1$  and  $\mathbf{u}_1$  denote the density and the velocity of one of the two components (it is equivalent to consider the total density  $\rho$  and the concentration  $c = \rho_1/\rho$  between the two components of the mixture such that eq. (45) is equivalent to  $\partial(\rho c)/\partial t + \operatorname{div}(\rho c \mathbf{u}) = 0$ ). For conservative motions, the equation of conservation of the total specific entropy  $s$  is

$$\frac{\partial \rho s}{\partial t} + \operatorname{div}(\rho s \mathbf{u}) = 0.$$

We consider a volume potential energy of the mixture in the form

$$\varepsilon = \varepsilon(\rho, \rho_1, s, s_1, \nabla \rho, \nabla \rho_1, \nabla s, \omega).$$

with  $\omega = \frac{1}{2} \mathbf{w}^2$ , where  $\mathbf{w} = \mathbf{u} - \mathbf{u}_1$ . As in the section 2, it is possible to deduce the equations of motions through the Hamilton action. We denote

$$\rho \theta = \frac{\widehat{\partial \varepsilon}}{\widehat{\partial s}}, \quad h = \frac{\widehat{\partial \varepsilon}}{\widehat{\partial \rho}}, \quad h_1 = \frac{\widehat{\partial \varepsilon}}{\widehat{\partial \rho_1}} \quad \text{and} \quad a = \frac{\partial \varepsilon}{\partial \omega}.$$

(In fact, the potential energy of the mixture depends only on the insentropic invariants  $(\nabla \rho)^2, (\nabla \rho_1)^2, \nabla \rho \cdot \nabla \rho_1, (\nabla s)^2$ ). By analogous calculations associated with a Lagrangian of the mixture in the form

$$L = \frac{1}{2} \rho \mathbf{u}^2 - \varepsilon,$$

and virtual motions such as  $\mathbf{X} = \Xi(t, \mathbf{x}, \boldsymbol{\varkappa})$  and  $\mathbf{X}_1 = \Xi_1(t, \mathbf{x}, \boldsymbol{\varkappa}_1)$ , we obtain as in section 2, the equations of motion

$$\begin{aligned} & \frac{\partial \rho \mathbf{u}}{\partial t} + \operatorname{div}(\rho \mathbf{u} \otimes \mathbf{u}) + \\ & - \left( \frac{\partial}{\partial t}(a \mathbf{w}) + a \frac{\partial \mathbf{u}^T}{\partial \mathbf{x}} \mathbf{w} + \operatorname{div}(a \mathbf{w} \otimes \mathbf{u}) \right) = \rho \theta \nabla s - \rho \nabla h \end{aligned} \quad (46)$$

and

$$\left( \frac{\partial}{\partial t}(a \mathbf{w}) + a \frac{\partial \mathbf{u}_1^T}{\partial \mathbf{x}} \mathbf{w} + \operatorname{div}(a \mathbf{w} \otimes \mathbf{u}_1) \right) + \rho_1 \nabla h_1 = 0 \quad (47)$$

with

$$\rho \theta = \rho \epsilon_{,s} - \operatorname{div} \boldsymbol{\Psi}, \quad h = \rho \epsilon_{,\rho} - \operatorname{div} \boldsymbol{\Phi}, \quad \text{and} \quad h_1 = \rho_1 \epsilon_{,\rho_1} - \operatorname{div} \boldsymbol{\Phi}_1,$$

where

$$\boldsymbol{\Psi} = \frac{\partial \varepsilon}{\partial \nabla s}, \quad \boldsymbol{\Phi} = \frac{\partial \varepsilon}{\partial \nabla \rho}, \quad \boldsymbol{\Phi}_1 = \frac{\partial \varepsilon}{\partial \nabla \rho_1}.$$

By summing eqs (46,47), we obtain the balance equation for the total momentum in a divergence form

$$\frac{\partial \rho \mathbf{u}}{\partial t} + \operatorname{div}(\rho \mathbf{u} \otimes \mathbf{u} - \rho a \mathbf{w} \otimes \mathbf{w} - \boldsymbol{\sigma}) = 0$$

where  $\boldsymbol{\sigma}$  is the stress tensor such that

$$\sigma_{\nu\gamma} = (-P + \rho \operatorname{div} \boldsymbol{\Phi} + \rho_1 \operatorname{div} \boldsymbol{\Phi}_1) \delta_{\nu\gamma} - \Phi_{\nu\rho,\gamma} - \Phi_{1\nu\rho_1,\gamma} - \Psi_{\nu s,\gamma},$$

where  $P = \epsilon - \rho \epsilon_{,\rho} - \rho_1 \epsilon_{,\rho_1}$ . The equation of energy of the total mixture is also obtained in the divergence form

$$\frac{\partial}{\partial t} \left( \frac{1}{2} \rho \mathbf{u}^2 + \varepsilon - a \mathbf{w}^2 \right) + \operatorname{div} \left( \left( \frac{1}{2} \rho \mathbf{u}^2 - a \mathbf{w} \cdot \mathbf{u} - \sigma \right) \mathbf{u} - \mathbf{U} + \varepsilon \mathbf{u} \right) = 0.$$

with  $\mathbf{U} = \frac{d\rho}{dt} \Phi + \frac{d_1\rho_1}{dt} \Phi_1 + \frac{ds}{dt} \Psi$  and it is possible by a similar calculation than in section 3 to deduce an acceleration wave associated with the entropy gradient.

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