

# Variational Theory of Mixtures in Continuum Mechanics

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## Abstract

In continuum mechanics, the equations of motion for mixtures were derived through the use of a variational principle by Bedford and Drumheller in [1978]. Only immiscible mixtures were investigated. We have chosen a different approach.

In this paper, we first write the equations of motion for each constituent of an inviscid miscible mixture of fluids without chemical reactions or diffusion. The theory is based on Hamilton's extended principle and regards the mixture as a collection of distinct continua.

The internal energy is assumed to be a function of densities, entropies and successive spatial gradients of each constituent. Our work leads to the equations of motion in an universal thermodynamic form in which interaction terms subject to constitutive laws, difficult to interpret physically, do not occur.

For an internal energy function of densities, entropies and spatial gradients, an equation describing the barycentric motion of the constituents is obtained.

The result is extended for dissipative mixtures and an equation of energy is obtained. A form of Clausius-Duhem's inequality which represents the second law of thermodynamics is deduced. In the particular case of compressible mixtures, the equations reproduce the classical results.

Far from critical conditions, the interfaces between different phases in a mixture of fluids are layers with strong gradients of density and entropy. The surface tension of such interfaces is interpreted.

*Key words:* Variational methods in continuum mechanics; Mixing; Multiphase flows; Phase equilibria of fluid mixtures.

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## 1 Introduction

The knowledge of equations describing processes occurring in fluid mixtures in one or several phases is scientifically and industrially very important ([Barrere & Prud'homme, 1973]; [Ishii, 1975]). Many papers concerning theoretical and experimental works for mixtures have been produced in continuum mechanics and physical chemistry. References in [Bedford & Drumheller, 1983] cover most of the works in continuum theory. The book by Rowlinson & Swinton [1982] gives the statistical methods.

Truesdell [1957,1965] first derived equations of balance and motion through the use of a continuum theory of mixtures. The mixture is then considered as a distribution of different continuous media in the same physical space, at time  $t$ . Each constituent of the mixture is identified with its reference space. The thermal and mechanical equations of balance are introduced for each constituent. They keep the usual form for a fluid description but they must include numerous terms of interaction between the different constituents. The study of the average motion, the motion of the barycentre of constituents with coefficients equal to their respective densities, are deduced from the sum of momenta, energy and entropy of each constituent. The terms including interaction between different constituents of the mixtures are difficult to interpret physically. They require constitutive postulates that are difficult to interpret experimentally.

Several assumptions are open to doubt. How must we choose an entropy? (Mixture entropy or entropy for each constituent?) What is the form of the second law of thermodynamics? Is it symbolized with one or several Clausius-Duhem's inequalities? Must we consider a temperature of the mixture or a temperature for each constituent?

Müller [1967]; Williams [1973]; Atkin & Craine [1976]; Sampio & Williams [1977]; Bowen [1979]; Nunziato & Walsh [1980]; Drew [1983] and many others argue about the various points of view.

In several papers Bedford and Drumheller [1978]; [B & D, 1979]; [B & D, 1980] presented a variational theory for immiscible mixtures (a continuum theory for mixtures whose constituents remain physically separated, such as a mixture of immiscible liquids or a fluid containing a distribution of particles, droplets, or bubbles). That the constituents remain physically separated has several implications for the theory. For instance, the authors use a variational principle in which a variation is added to the motion of only one constituent. However it is necessary to add to the variations of kinetic and potential energies a virtual work due to the forces not represented by a potential. Such forces are difficult to take into account in a variational principle deduced from the one by Hamilton. It is not possible to use such a method in a more general model.

In this paper a new mathematical systematic method that leads to the equations of motion and energy for miscible fluid mixtures without chemical reac-

tion and diffusion is propounded. The presented work is essentially different from the one by Bedford and Drumheller.

The mixture is represented by several distinct continuous media that occupy the same physical space at time  $t$ . The novelty consists in the fact that the used variational principle is applied to a lagrangian representation associated with a reference space for each component. The proposed method uses the knowledge of the internal energy of the mixture at every point of the physical space. This is not the case in [B & D].

For classical fluids, the method corresponds to Hamilton's principle in which one makes a variation of the reference position of the particle. It was proposed by Gouin [1987].

The inferred equations are written in a different form that facilitates the study of first integrals for conservative motions ( [Casal, 1966]; [Gouin, 1981]; [Casal & Gouin, 1985*b*, 1988*a*, 1989]).

For mixtures, the principle appears far more convenient than the method of only taking the variation of the average motion into consideration: it separately tests each component and leads to a thermodynamic form of the equation of motion for each of them.

The internal energy is assumed to be a function of different densities or concentrations of the mixture. Because of the form of the principle we use, one must consider an entropy for each component in the mixture. The total entropy of the system is the sum of the partial entropies.

To consider areas where strong gradients of density occur - for example shocks or capillary layers - the internal energy is chosen as a function of the successive derivatives of densities and entropies.

Two cases of conservative motions for mixtures are considered: isentropic motion and isothermal motion. These are only limiting mathematical cases for testing the method. The physical motion is intermediate, between these extremes.

An important medium is the one of *thermocapillary mixtures*. It corresponds to an energy taking into account the gradients of densities and entropies. Then, one obtains an equation of the barycentric motion of constituents. For a compressible mixture, the equations of motion involve a hydrostatic stress.

In the same way as for thermocapillary fluids, an additional term that has the physical dimension of a heat flux may be added to the energy equation ([Eglit, 1965]; [Berdichevskii, 1966]; [Casal & Gouin, 1985*a*]; [Dunn & Serrin, 1985]; [Gatignol & Seppecher, 1986]; [Seppecher, 1987]). A generalization of the Clausius-Duhem inequality is obtained for non-conservative mixtures. The inequality is deduced from the heat conduction inequality by introducing an irreversible stress tensor associated with a general dissipation function. The theory fits with the second law of thermodynamics.

From these results one generalizes equilibrium conditions obtained through interfaces in compressible fluid mixtures [Rocard, 1967]. An interpretation of capillarity stresses is deduced (rule of Antonov) [Emschwiller, 1964], and generalization of results by Vignes-Adler & Brenner [1985] may be investigated.

## 2 The motion of a continuous medium

### 2.1 Motion of a fluid with only one constituent

Recall that the motion of a continuous medium can be represented by a surjective differentiable mapping:

$$\mathbf{z} \rightarrow \mathbf{X} = \mathbf{M}(\mathbf{z}),$$

where  $\mathbf{z} = (t, \mathbf{x})$  belongs to  $\mathcal{W}$ , an open set in the time-space occupied by the fluid between time  $t_1$  and time  $t_2$ . The position of a particle in a reference space  $\mathcal{D}_o$  is denoted by  $\mathbf{X}$ ; its position at time  $t$  in  $\mathcal{D}_t$  is denoted by  $\mathbf{x}$  [Serrin, 1959]. Hamilton's principle - variational form of the principle of virtual powers - allows us to investigate the equation of motion.

The variations of motion of particles are deduced from:

$$\mathbf{X} = \Psi(\mathbf{x}, t; \beta)$$

for which  $\beta$  is a parameter defined in a neighborhood of zero; it is associated with a family of virtual motions of the fluid. The real motion corresponds to  $\beta = 0$ .

Virtual material displacements associated with any variation of real motion can be written [Gouin, 1987]:

$$\delta \mathbf{X} = \left. \frac{\partial \Psi}{\partial \beta} \right|_{\beta=0}. \quad (1)$$

Such a variation is dual with Serrin's [S, 1959]. This has been studied in the case of compressible perfect fluids [Gouin, 1978] and corresponds to the natural variation of the motion in a lagrangian representation.

The lagrangian of the fluid is:

$$L = \rho \left( \frac{1}{2} \mathbf{V}^* \mathbf{V} - \alpha - \Omega \right),$$

where  $\mathbf{V}$  denotes the velocity vector of the particles,  $\Omega$  the extraneous force potential defined in  $\mathcal{D}_t$ ,  $\alpha$  the specific internal energy,  $\rho$  the density and  $*$  the transposition in  $\mathcal{D}_t$ .

Between time  $t_1$  and time  $t_2$ , the hamiltonian action is written:

$$a = \int_{t_1}^{t_2} \int_{\mathcal{D}_t} L \, dv \, dt. \quad (2)$$

The use of virtual displacements (1) provides the equations of motion of compressible perfect fluids in a thermodynamic form. For fluids of grade  $n$ , the calculus is swift. It generalizes the equation (29,8) of fluids in [Serrin, 1959] that may be written in a form that is independent of their complexity [Gouin, 1987]:

$$\mathbf{\Gamma} = \theta \operatorname{grad} s - \operatorname{grad}(h + \Omega),$$

where  $\mathbf{\Gamma}$  denotes the acceleration,  $s$  the entropy,  $\theta$  a temperature and  $h$  a specific enthalpy.

## 2.2 Motion of a fluid mixture

For the sake of clarity, we study a mixture of two fluids. The method can be immediately extended to any number of constituents. No assumption has to be made about their composition or their miscibility.

The motion of a two-fluid continuum can be represented using two surjective differentiable mappings:

$$z \rightarrow \mathbf{X}_1 = \mathbf{M}_1(z) \quad \text{and} \quad z \rightarrow \mathbf{X}_2 = \mathbf{M}_2(z), \quad (3)$$

(Subscripts 1 and 2 are associated with each constituent).

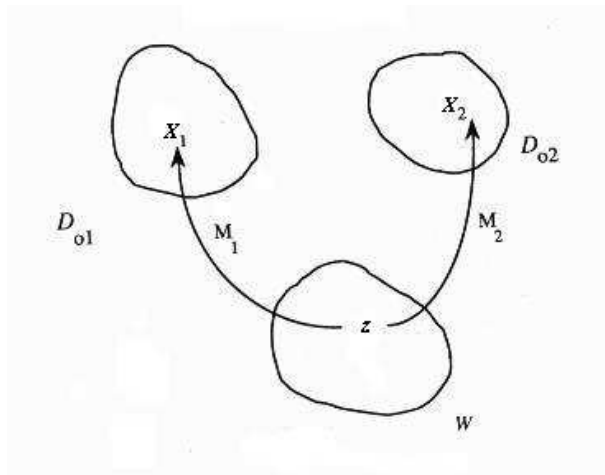


Fig. 1.

$\mathbf{X}_1$  and  $\mathbf{X}_2$  denote the positions of each constituent in reference spaces  $\mathcal{D}_{o1}$  and  $\mathcal{D}_{o2}$ . The variations of motion of particles are deduced from:

$$\mathbf{X}_1 = \Psi_1(\mathbf{x}, t; \beta_1) \quad \text{and} \quad \mathbf{X}_2 = \Psi_2(\mathbf{x}, t; \beta_2). \quad (4)$$

This is a generalization of the one in paragraph 2.1 where  $\beta_1$  and  $\beta_2$  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  $\beta_1 = 0$  and  $\beta_2 = 0$ ; the associated virtual displacements can be written:

$$\delta_1 \mathbf{X}_1 = \left. \frac{\partial \Psi_1}{\partial \beta_1} \right|_{\beta_1=0} \quad \text{and} \quad \delta_2 \mathbf{X}_2 = \left. \frac{\partial \Psi_2}{\partial \beta_2} \right|_{\beta_2=0}. \quad (5)$$

They generalize relation (1) given for a fluid with one constituent. The principle tests separately each constituent of the mixture and so is very efficient.

*Remark.* - It follows from the classical representation of a two-constituent mixture, that formula (4) can be written

$$\mathbf{x} = \varphi_1(\mathbf{X}_1, t; \beta_1) \quad \text{and} \quad \mathbf{x} = \varphi_2(\mathbf{X}_2, t; \beta_2). \quad (6)$$

A variation of the motion like Serrin's (p. 145, [S, 1959]) cannot be extended to any two-parameter family of virtual displacements: as a matter of fact, any field of virtual displacements associated with  $\varphi_1$  must be such that  $\delta \mathbf{x} = \frac{\partial \varphi_1}{\partial \beta_1}(\mathbf{X}_1, t; 0)$  and there is no reason for being identifiable with a vector field

written in the form  $\delta \mathbf{x} = \frac{\partial \varphi_2}{\partial \beta_2}(\mathbf{X}_2, t; 0)$ .

In the case of compressible fluids, writing (1) for the virtual displacement associated with a one-parameter family of virtual motion of the fluid is deduced from the variation defined by Serrin by the way of vector spaces isomorphism [Gouin, 1976]. *For mixtures, by using (5), a virtual displacement of miscible fluid mixtures can be considered.*

The lagrangian of the mixture is:

$$L = \frac{1}{2} \rho_1 \mathbf{V}_1^* \mathbf{V}_1 + \frac{1}{2} \rho_2 \mathbf{V}_2^* \mathbf{V}_2 - \varepsilon - \rho_1 \Omega_1 - \rho_2 \Omega_2.$$

Here,  $\mathbf{V}_1$  et  $\mathbf{V}_2$  denote the velocity vectors of each constituent,  $\rho_1$  and  $\rho_2$  are the densities,  $\Omega_1$  and  $\Omega_2$  are the extraneous force potentials depending only on  $\mathbf{z} = (t, \mathbf{x})$  and  $\varepsilon$  is the internal energy per unit volume.

The expansion of the lagrangian is general. In fact dissipative phenomena imply that  $\mathbf{V}_1$  is almost equal to  $\mathbf{V}_2$ . Because of the interaction of the constituents,  $\varepsilon$  does not always divide into energies related to each constituent of the mixture, as it does in the case of *simple mixtures of fluids* [Müller, 1968]. More generally, the lagrangian may be written

$$L = \frac{1}{2} \rho_1 \mathbf{V}_1^* \mathbf{V}_1 + \frac{1}{2} \rho_2 \mathbf{V}_2^* \mathbf{V}_2 - \eta$$

where  $\eta$  denotes the volumetric potential energy of the mixture. In our particular case,  $\eta$  is the sum of internal energy and extraneous force potentials. In fact, the following calculus would be similar (but even simpler). We use the

first form of the lagrangian in order to obtain classical expressions used for fluids.

Hamilton's action between time  $t_1$  and time  $t_2$  can be written as in (2). The mixture is assumed not to be chemically reacting. The conservation of masses requires that:

$$\rho_i \det F_i = \rho_{oi}(\mathbf{X}_i) \quad (7^1)$$

for the densities of each constituent, with subscript  $i$  belonging to  $\{1, 2\}$ . At fixed  $t$ , the jacobian mapping associated with each  $\mathbf{M}_i$  is denoted by  $F_i$ ;  $\rho_{oi}$  is the reference specific mass in  $\mathcal{D}_{oi}$ .

In differentiable cases, equation (7<sup>1</sup>) is equivalent to:

$$\frac{\partial \rho_i}{\partial t} + \operatorname{div} \rho_i \mathbf{V}_i = 0. \quad (7^2)$$

The volumetric internal energy  $\varepsilon$  is given by the thermodynamical behavior of the mixture and will appear in the equations of motion. Each constituent has a specific mass; similarly, two specific entropies  $s_1$  and  $s_2$  are supposed to be associated with constituents 1 and 2.

For a specific internal energy depending on derivatives of gradients of densities and entropies up to the  $n$ -th order:

$$\begin{aligned} \varepsilon = \varepsilon(s_1, \operatorname{grad} s_1, \dots, (\operatorname{grad})^{n-1} s_1; s_2, \operatorname{grad} s_2, \dots, (\operatorname{grad})^{n-1} s_2; \\ \rho_1, \operatorname{grad} \rho_1, \dots, (\operatorname{grad})^{n-1} \rho_1; \rho_2, \operatorname{grad} \rho_2, \dots, (\operatorname{grad})^{n-1} \rho_2), \end{aligned} \quad (8)$$

(we say, the mixture is of grade  $n$ ), the calculus is similar to than in ([Gouin, 1987]; [Casal & Gouin, 1988a]). The orders of gradients of  $\rho_1$ ,  $\rho_2$ ,  $s_1$ ,  $s_2$  can be chosen differently, but the exposition would be less clear. Let us note that the volumetric potential energy can be written:

$$\begin{aligned} \eta = \eta(s_1, \operatorname{grad} s_1, \dots, (\operatorname{grad})^{n-1} s_1; s_2, \operatorname{grad} s_2, \dots, (\operatorname{grad})^{n-1} s_2; \\ \rho_1, \operatorname{grad} \rho_1, \dots, (\operatorname{grad})^{n-1} \rho_1; \rho_2, \operatorname{grad} \rho_2, \dots, (\operatorname{grad})^{n-1} \rho_2, \mathbf{z}) \end{aligned}$$

with  $\mathbf{z} = (t, \mathbf{x})$ .

### 2.3 Examples of motions of a fluid mixture

Let us consider two examples of Hamilton's principle. Obviously, they are two limit cases deduced from a variational principle and incompatible with any dissipative process.

*First case:* Isentropic motions.

We assume that the specific entropy of each particle is constant:

$$\frac{ds_i}{dt} = 0, \quad \text{or} \quad \frac{\partial s_i}{\partial t} + \frac{\partial s_i}{\partial \mathbf{x}} \mathbf{V}_i = 0.$$

(Lie's derivative with respect to the velocity field of constituent  $i$  is equal to zero. The average motion of the mixture does not have Lie's derivative, so henceforth, we can expect each constituent of the mixture to possess entropy). The equation

$$s_i = s_{oi}(\mathbf{X}_i) \quad (9)$$

defines an isentropic motion.

Motion equations are deduced from Hamilton's principle. The two variations of hamiltonian action are:

$$\delta_i a = a'(\beta_i) \Big|_{\beta_i=0}.$$

For  $i \in \{1, 2\}$ , we deduce:

$$\begin{aligned} \delta_i a = \int_{t_1}^{t_2} \int_{\mathcal{D}_t} \left\{ \left( \frac{1}{2} \mathbf{V}_i^* \mathbf{V}_i - \varepsilon_{,\rho_i} - \Omega_i \right) \delta_i \rho_i + \rho_i \mathbf{V}_i^* \delta_i \mathbf{V}_i - \varepsilon_{,s_i} \delta_i s_i - \right. \\ \left. \left[ \varepsilon_{,s_i,\gamma} \delta_i s_{i,\gamma} + \dots + \varepsilon_{,s_i,\gamma_1,\dots,\gamma_{n-1}} \delta_i s_{i,\gamma_1,\dots,\gamma_{n-1}} \right] - \right. \\ \left. \left[ \varepsilon_{,\rho_i,\gamma} \delta_i \rho_{i,\gamma} + \dots + \varepsilon_{,\rho_i,\gamma_1,\dots,\gamma_{n-1}} \delta_i \rho_{i,\gamma_1,\dots,\gamma_{n-1}} \right] \right\} dv dt. \end{aligned}$$

Subscript  $\gamma$  corresponds to spatial derivatives associated with gradient terms; as usually, summation is made on repeated subscripts  $\gamma$ .

The quantity

$$h_i = \varepsilon_{,\rho_i} + \sum_{p=1}^{n-1} (-1)^p (\varepsilon_{,\rho_i,\gamma_1,\dots,\gamma_p})_{,\gamma_1,\dots,\gamma_p} \quad (10^1)$$

defines the specific enthalpy of the constituent  $i$  of the mixture, and

$$\theta_i = \frac{1}{\rho_i} \left[ \varepsilon_{,s_i} + \sum_{p=1}^{n-1} (-1)^p (\varepsilon_{,s_i,\gamma_1,\dots,\gamma_p})_{,\gamma_1,\dots,\gamma_p} \right] \quad (10^2)$$

defines the temperature of the constituent  $i$  of the mixture.

The motion of constituent  $i$  of the mixture is expressed by the equation

$$\mathbf{\Gamma}_i = \theta_i \text{grad } s_i - \text{grad}(h_i + \Omega_i). \quad (11)$$

*Appendix 1 gives details of the calculation.*

The fact that an entropy is introduced for each component implies the existence of a temperature for each fluid constituent. This is in accordance with



[Green and Naghdi, 1965]. In this first limit case, the variational principle does not lead to the equality of temperatures. The behavior of the two components corresponds to their thermodynamical independence (no exchange of heat between particles). The two components are only bounded by effects of compressibility. Such a model can be used in practice only if one includes the fact that some heat conduction exists and adjusts the values of the two temperatures. So, one verifies that equations obtained with the variational principle must be completed.

*Second case:* Only the whole entropy of the mixture is conserved.

We have:

$$\int_{\mathcal{D}_t} (\rho_1 s_1 + \rho_2 s_2) dv = K, \quad (12^1)$$

where  $K$  is constant (independent of the time).

Let us use the method applied in [Casal & Gouin, 1988b] for compressible fluids. The variation of the entropy of each component is assumed to be the sum of a variation associated with the virtual motion and another one,  $\delta_{oi}s_i$  related to the particle:

$$\delta_i s_i = \frac{\partial s_{oi}}{\partial \mathbf{X}_i} \delta_i \mathbf{X}_i + \delta_{oi} s_i,$$

where  $\delta_{oi}s_i$  and  $\delta_i \mathbf{X}_i$  are independent and  $\delta_{oi}$  must verify, with respect to component  $i$  of the mixture:

$$\delta_{oi} \int_{t_1}^{t_2} \int_{\mathcal{D}_t} (\rho_1 s_1 + \rho_2 s_2) dv = 0. \quad (12^2)$$

Classical methods of variational calculus provide the variation of the hamiltonian action: the variations  $\delta_i \mathbf{X}_i$  yield a motion equation of the form of (11). Relation (12<sup>2</sup>) implies: there exists a constant Lagrange multiplier  $\theta_o$ , *constant in space and in time*, such that:

$$\begin{aligned} \delta_{oi} a = \int_{t_1}^{t_2} \int_{\mathcal{D}_t} & \left( -\varepsilon_{,s_i} \delta_{oi} s_i - \varepsilon_{,s_i,\gamma} \delta_{oi} s_{i,\gamma} - \dots \right. \\ & \left. - \varepsilon_{,s_i,\gamma_1,\dots,\gamma_{n-1}} \delta_{oi} s_{i,\gamma_1,\dots,\gamma_{n-1}} + \rho_i \theta_o \delta_{oi} s_i \right) dv dt. \end{aligned}$$

Let us point out that adiabatic condition (12<sup>1</sup>) implies that even if the mixture is moving,  $\theta_o$  remains constant in space and time since  $\theta_o$  is a Lagrange multiplier associated with an integral constraint.

Considering variations  $\delta_{oi}s_i$  vanishing on the boundary of  $\mathcal{D}_t$ ; an integration by parts yields:

$$\delta_{oi} a = \int_{t_1}^{t_2} \int_{\mathcal{D}_t} \rho_i (\theta_o - \theta_i) \delta_{oi} s_i dv dt.$$

The principle: "for any  $\delta_{oi}s_i$  vanishing on the boundary of  $\mathcal{D}_t$ ,  $\delta_{oi}a = 0$ " leads to the equation for the temperature:

$$\theta_i = \theta_o, \quad (13)$$

*i.e.*, all the constituents have the same temperature  $\theta_o$ , constant in all the flow: the flow is *isothermal*.

This variational principle can be compared with the static one expressing that the equilibrium of a compressible fluid kept in a fixed adiabatic reservoir without exchange of mass and entropy with outside is obtained by writing the uniformity of temperature and pressure. It can be interpreted as a limit case of a mixture with an infinite heat conductivity.

Equation (11) is replaced by

$$\mathbf{\Gamma}_i + \text{grad}(g_i + \Omega_i) = 0, \quad (14)$$

where  $g_i = h_i - \theta_i s_i$  is the free specific enthalpy (or chemical potential) of constituent  $i$ .

When the fluid is compressible, Eqs (11) or (14) yield first integrals and theorems of circulation [Serrin, 1959]; [Casal, 1966]; [Gouin, 1981]; [Casal & Gouin, 1985*b*, 1989]. These properties can easily be extended to each constituent of an inviscid mixture.

Each constituent of the mixture in an isothermal equilibrium state satisfies

$$G_i = C_i \quad (15)$$

where  $G_i = g_i + \Omega_i$  and  $C_i$  is a constant.

An interface in a two-phase mixture is generally modelled by a surface without thickness. Far from critical conditions, this layer is of molecular size; density and entropy gradients are very large. A continuous model deals with such areas by using energy in the form (8) extending forms given in ([Rocard, 1967]; [Cahn & Hilliard, 1959]) for compressible fluids.

Equation (15) is satisfied for each constituent of a mixture in an isothermal equilibrium state. The fact that  $C_i$  values are the same in each bulk is also a consequence of Eq.(15). It follows that with extraneous forces being neglected in a two-phase mixture, if the two different phases are in isothermal equilibrium, then specific free enthalpies (or chemical potentials) of each bulk are equal. This result generalizes the classical law to mixtures of grade  $n$ : the different constituents keep their own chemical potential through a change of phases [Rocard, 1967].

### 3 Thermocapillary mixtures

The previous equations yield the equations of motion for each of the two fluids constituting the mixture. Usually, the chemical potentials  $h_i$  and  $g_i$  are rarely considered except for equilibrium; Eqs. (11) and (14) make use of them in the study of the motion.

In order to compare results given by the variational technics and the usual approach of mixture motions, we can try to study the mean motion and diffusive motions for two components. But how do we define these motions? In this paper, we consider the mean motion using an approach which is independent of the number of constituents.

For the mean motion,  $\rho = \sum_i \rho_i$  and  $\rho \mathbf{\Gamma} = \sum_i \rho_i \mathbf{\Gamma}_i$  (using  $\mathbf{\Gamma} = \sum_i \mathbf{\Gamma}_i$  has no physical meaning).

On the contrary,  $\rho \mathbf{\Gamma}$  has the physical dimension of a volumetric force and is an additive quantity in the same way as body forces or the stress tensor divergences. So, in this first article, we have not attempted to investigate the difficult question of the relative motion associated with "  $\mathbf{\Gamma}_1 - \mathbf{\Gamma}_2$  " and hence to see how diffusion behaves in miscible mixtures.

#### 3.1 Conservative motions for mixtures of thermocapillary fluids

In the case  $n = 2$ , we write the equations of motion by using the stress tensor. The mixture is said to be a *thermocapillary mixture* if the internal energy  $\varepsilon$  is written as:

$$\varepsilon = \varepsilon(s_1, \text{grad } s_1, s_2, \text{grad } s_2, \rho_1, \text{grad } \rho_1, \rho_2, \text{grad } \rho_2). \quad (16)$$

The expressions

$$\rho = \sum_{i=1}^2 \rho_i \quad \text{and} \quad \rho \mathbf{\Gamma} = \sum_{i=1}^2 \rho_i \mathbf{\Gamma}_i$$

introduce the total density and acceleration of the mixture. With denoting by  $\alpha$  the specific energy of the mixture, we have

$$\rho \alpha = \varepsilon,$$

and,

$$d\alpha = \sum_{i=1}^2 \frac{\mathcal{P}_i}{\rho \rho_i} d\rho_i + \frac{\rho_i}{\rho} \Theta_i ds_i + \frac{1}{\rho} \Phi_{i\gamma} d\rho_{i,\gamma} + \frac{1}{\rho} \Psi_{i\gamma} ds_{i,\gamma},$$

with

$$\mathcal{P}_i = \rho \rho_i \alpha_{,\rho_i}, \quad \Theta_i = \frac{1}{\rho_i} \varepsilon_{,s_i}, \quad \Phi_{i\gamma} = \varepsilon_{,\rho_{i,\gamma}}, \quad \Psi_{i\gamma} = \varepsilon_{,s_{i,\gamma}}.$$

Four new vectors  $\mathbf{\Phi}_i$  and  $\mathbf{\Psi}_i$  ( $i \in \{1, 2\}$ ) are introduced by the theory; it is an extension of the calculus written in [Casal & Gouin, 1988a].

For a compressible fluid (with only one constituent),  $\mathcal{P}$  and  $\Theta$  are respectively the pressure and the Kelvin temperature. The fluid is isotropic, so the internal energy is of the form

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

with  $\beta_{ij} = \text{grad } \rho_i \cdot \text{grad } \rho_j$ ,  $\chi_{ij} = \text{grad } \rho_i \cdot \text{grad } s_j$ ,  $\gamma_{ij} = \text{grad } s_i \cdot \text{grad } s_j$  ( $i \in \{1, 2\}$ ).

It follows that:

$$\begin{aligned}\Phi_i &= \sum_{j=1}^2 C_{ij} \text{grad } \rho_j + E_{ij} \text{grad } s_j, \\ \Psi_i &= \sum_{j=1}^2 D_{ij} \text{grad } s_j + E_{ij} \text{grad } \rho_j,\end{aligned}$$

with

$$C_{ij} = (1 + \delta_{ij})\varepsilon_{,\beta_{ij}}, \quad D_{ij} = (1 + \delta_{ij})\varepsilon_{,\gamma_{ij}}, \quad E_{ij} = \varepsilon_{,\chi_{ij}},$$

where  $\delta_{ij}$  is the Kronecker symbol. The simplest model is for  $C_{ij}$ ,  $D_{ij}$  and  $E_{ij}$  constant.

Assuming that  $\Omega_1 = \Omega_2 = \Omega$  (this is the case for gravity forces), we obtain a general formulation of the equation of motion for thermocapillary mixtures:

$$\rho \mathbf{\Gamma} = \text{div } \boldsymbol{\sigma} - \rho \text{grad } \Omega \quad (17)$$

or

$$\rho \Gamma_\gamma = \sigma_{\nu\gamma,\nu} - \rho \Omega_{,\gamma}.$$

The sum of  $\sigma_1$  and  $\sigma_2$  obtained by successive integrations by parts is conventionally called the generalization of the stress tensor. This is simply for the convenience of writing (in fact, the sum of stresses associated with different media is a non-sense).

Let

$$\boldsymbol{\sigma} = \sum_{i=1}^2 \boldsymbol{\sigma}_i,$$

where

$$\sigma_{i\nu\gamma} = -p_i \delta_{\nu\gamma} - \Phi_{i\nu} \rho_{i,\gamma} - \Psi_{i\nu} s_{i,\gamma}, \quad (18)$$

with

$$p_i = \mathcal{P}_i - \rho_i \text{div } \Phi_i.$$

The tensorial natures of entropy and density are different; that is the reason why only  $\text{div } \Phi$  appears in the pressure term. The calculus for this case appears in appendix 2. In appendix 4, we deduce Antonov's rule related to the surface tensions of an interface between two immiscible fluids from the expression of the stress tensor.

For mixtures with internal capillarity ([Gatignol & Seppecher, 1986]; [Seppecher, 1987]), only  $\Phi_i$ ,  $i \in \{1, 2\}$ , are not equal to zero. In the case of classical compressible mixtures, terms of gradients are null and  $\Phi_i$  and  $\Psi_i$  are zero;  $\sigma_{\nu\gamma}$  is

written:

$$-\mathcal{P}\delta_{v\gamma}$$

with  $\mathcal{P} = \sum_{i=1}^2 \mathcal{P}_i$  defining the pressure of the mixture.

Let us remark that  $\mathcal{P}_i$  with  $i \in \{1, 2\}$  does not correspond to the classic notion of partial pressures in ideal mixtures. This result fits with I. Müller's paper ([1968], p. 37): according to Müller terminology, if  $\varepsilon = \rho\alpha = \rho_1\alpha_1 + \rho_2\alpha_2$  with  $\alpha_i = \alpha_i(\rho_i, s_i)$ , such an internal energy corresponds to a simple mixture of fluids. If  $\Pi_i = \rho_i^2 \alpha_{i,\rho_i}(\rho_i, s_i)$ , then

$$\mathcal{P}_1 = \Pi_1 + \frac{\rho_1\rho_2}{\rho}(\alpha_1 - \alpha_2)$$

and

$$\mathcal{P}_2 = \Pi_2 + \frac{\rho_1\rho_2}{\rho}(\alpha_2 - \alpha_1);$$

with assuming that for every point in the mixture all the constituents have the same temperature  $\theta_i = \theta_0$ , then,  $\mathcal{P} = \Pi_1 + \Pi_2$  and  $\Pi_i$  represents the partial pressure of constituent  $i$  [Bruhat 1968].

*Example of binary system with complete miscibility: liquid-vapor equilibrium*

At a given temperature, the numerous constitutive equations represent  $\mathcal{P}$  as a function of densities of the constituents ([Soave, 1972]; [Simonet & Behar, 1976]; [Peng & Robinson, 1976]). These equations, very useful in petroleum industry, derive from subtle calculus on mixtures of Van der Waals fluids. Taking into account Eq. (15), they allow the study of a liquid bulk and a vapour bulk for two fluids that can be completely mixed.

A plane interface lies between two phases of a two-fluid mixture in isothermal equilibrium. This is an unidimensional problem with reference to the direction perpendicular to the interface. Body forces being neglected, Eq. (17) can be written:

$$\frac{d\sigma}{dz} = 0.$$

Vectors  $\Phi_i$  and  $\Psi_i$  are zero in the bulks in which  $\mathcal{P}_l = \mathcal{P}_v = \mathcal{P}_0$  ( $l$  and  $v$  refer to the bulks with the same pressure  $P_0$ ).

For equilibrium, eight variables  $\rho_{il}, \rho_{iv}, s_{il}, s_{iv}$  with  $i \in \{1, 2\}$  determine the properties of the two bulks. They are subject to six relations:

$$\begin{aligned} g_{1l} &= g_{1v}, \\ g_{2l} &= g_{2v}, \\ \theta_{1l} &= \theta_{1v} = \theta_{2l} = \theta_{2v}, \end{aligned}$$

and

$$\mathcal{P}_l = \mathcal{P}_v.$$

This fits with Gibbs law of phases that gives the system as "divariant" [Rocard, 1967]. Two additional conditions,  $\theta_{il} = \theta_{iv} = \theta_0$  ( $i \in \{1, 2\}$ ) and  $\mathcal{P}_l = \mathcal{P}_v = \mathcal{P}_0$ , set an equilibrium of the mixture.

### 3.2 Equation of motion and equation of energy for a thermocapillary mixture

#### Conservative motions

Some properties of mixtures are directly deduced from the equation (17) of motion.

Let us define

$$\begin{aligned} \mathbf{M}_i &= \mathbf{\Gamma}_i - \theta_i \text{grad } s_i + \text{grad}(h_i + \Omega_i), \\ B_i &= \frac{d\rho_i}{dt} + \rho_i \text{div } \mathbf{V}_i, \\ S_i &= \rho_i \theta_i \frac{ds_i}{dt}, \\ E_i &= \frac{\partial e_i}{\partial t} + \text{div} [(e_i - \sigma_i) \mathbf{V}_i] - \text{div } \mathbf{U}_i - \rho_i \frac{\partial \Omega_i}{\partial t}, \end{aligned}$$

with

$$e_i = \frac{1}{2} \rho_i \mathbf{V}_i^2 + \varepsilon_i + \rho_i \Omega_i, \quad \varepsilon_i = \frac{\rho_i \varepsilon}{\rho}$$

and

$$\begin{aligned} \mathbf{U}_i &= \frac{d\rho_i}{dt} \mathbf{\Phi}_i + \frac{ds_i}{dt} \mathbf{\Psi}_i \\ \left( \frac{d\rho_i}{dt} = \frac{\partial \rho_i}{\partial t} + \frac{d\rho_i}{d\mathbf{x}} \mathbf{V}_i \quad \text{and} \quad \frac{ds_i}{dt} = \frac{\partial s_i}{\partial t} + \frac{\partial s_i}{\partial \mathbf{x}} \mathbf{V}_i \right). \end{aligned}$$

**Theorem 1** *For a thermocapillary internal energy and for any motion of the mixture, the relation*

$$\sum_{i=1}^2 E_i - \rho_i \mathbf{M}_i^* \mathbf{V}_i - \left( \frac{1}{2} \mathbf{V}_i^2 + h_i + \Omega_i \right) B_i - S_i = 0 \quad (19)$$

*is identically satisfied.*

(Proof in appendix 3). Limit cases (the isentropic and isothermal motion of Sec. 2) yield the two corollaries:

**Corollary 2** - *Any isentropic motion of an thermocapillary mixture satisfies the equation of balance of energy:*

$$\sum_{i=1}^2 \frac{\partial e_i}{\partial t} + \text{div} [(e_i - \sigma_i) \mathbf{V}_i] - \text{div } \mathbf{U}_i - \rho_i \frac{\partial \Omega_i}{\partial t} = 0. \quad (20)$$

This results from the simultaneity of equations  $S_i = 0$ ,  $B_i = 0$  and  $\mathbf{M}_i = 0$ .

**Corollary 3** - *For any conservative motion of a thermocapillary perfectly heat conducting mixture, Eq. (13) is equivalent to:*

$$\sum_{i=1}^2 \frac{\partial f_i}{\partial t} + \operatorname{div}[(f_i - \sigma_i)\mathbf{V}_i] - \operatorname{div} \mathbf{U}_i - \rho_i \frac{\partial \Omega_i}{\partial t} = 0 \quad (21)$$

with  $f_i = \frac{1}{2} \rho_i \mathbf{V}_i^2 + \varphi_i + \rho_i \Omega_i$  and  $\varphi_i = \varepsilon_i - \rho_i \theta_i s_i$  corresponding to the specific free energy of constituent  $i$  at temperature  $\theta_0$ .

Equation (21) is called the *equation of balance of free energy*.

#### *Dissipative motions*

If we try to introduce dissipative phenomena, while keeping the form of the equations, we may only add an irreversible stress tensor  $\sigma_{Ii}$  for each constituent. So, for each fluid, ( $i \in \{1, 2\}$ ), supplementary energy flux vectors  $\operatorname{div}(\sigma_{Ii} \mathbf{V}_i)$  and dissipative forces  $\operatorname{tr}(\sigma_{Ii} \mathbf{\Delta}_i)$  have additive properties ( $\mathbf{\Delta}_i$  is the deformation tensor of constituent  $i$ ) and are introduced and summed. The only assumption for functions of dissipation,  $\sum_{i=1}^2 \operatorname{tr}(\sigma_{Ii} \mathbf{\Delta}_i) \geq 0$ , leads to a Clausius-Duhem inequality. So, the model fits with the second law of thermodynamics independently of any constitutive behavior for  $\sigma_{I1}$  and  $\sigma_{I2}$  (Chapman and Cowling [1970]).

Equation of motion (17) can be written:

$$\rho \mathbf{\Gamma} = \operatorname{div}(\sigma + \sigma_I) - \rho \operatorname{grad} \Omega$$

(as in Eq.(17), we are led to formally writing  $\sigma_I = \sigma_{I1} + \sigma_{I2}$ ).

Afterwards, the heat flux vector will be denoted by  $q$  and heat supply by  $r$ . It follows,

**Corollary 4** - *For any motion of a thermocapillary mixture, the equation of energy*

$$\sum_{i=1}^2 \frac{\partial e_i}{\partial t} + \operatorname{div}[(e_i - \sigma_i - \sigma_{Ii})\mathbf{V}_i] - \operatorname{div} \mathbf{U}_i - \rho_i \frac{\partial \Omega_i}{\partial t} + \operatorname{div} q - r = 0 \quad (22)$$

*is equivalent to the equation of entropy:*

$$\sum_{i=1}^2 \rho_i \theta_i \frac{ds_i}{dt} - \operatorname{tr}(\sigma_{Ii} \mathbf{\Delta}_i) + \operatorname{div} q - r = 0.$$

Assuming that the work of dissipative forces satisfies  $\sum_{i=1}^2 \operatorname{tr}(\sigma_{Ii} \mathbf{\Delta}_i) \geq 0$ , we

obtain a generalized form of *Planck's inequality*:

$$\sum_{i=1}^2 \rho_i \theta_i \frac{ds_i}{dt} + \operatorname{div} q - r \geq 0.$$

At any point of the fluid, each constituent is supposed to have the same temperature (not necessarily uniform). This requires that the time for relaxation of molecules is short in comparison with the time characterizing the flow. Then,

$$\theta = \theta_i.$$

By use of *Fourier's law* in the form:

$$q \cdot \operatorname{grad} \theta \leq 0,$$

we deduce a generalization of *Clausius-Duhem's inequality*:

$$\sum_{i=1}^2 \rho_i \frac{ds_i}{dt} + \operatorname{div} \left( \frac{q}{\theta} \right) - \frac{r}{\theta} \geq 0.$$

This Clausius-Duhem's inequality is a form of the second law of thermodynamics. Let us note that some authors separate  $q$  and  $r$  in  $q_i$  and  $r_i$ ; this does not seem necessary.

## Appendix 1

### Equations of motion for mixtures of perfect fluids

#### *Isentropic motion*

Let us denote by  $\boldsymbol{\xi}_i$  the variation  $\delta_i \mathbf{X}_i$ , we deduce from the two relations in lagrangian variables [Gouin, 1987]:

$$\delta_i \mathbf{V}_i = -\mathbf{F}_i \frac{\partial \boldsymbol{\xi}_i}{\partial t}, \quad \delta_i \rho_i = \rho_i \operatorname{div}_{oi} \boldsymbol{\xi}_i + \frac{\rho_i}{\rho_{oi}} \frac{\partial \rho_{oi}}{\partial \mathbf{X}_i} \boldsymbol{\xi}_i \quad (23)$$

and

$$\delta_i s_i = \frac{\partial s_i}{\partial \mathbf{X}_i} \delta_i \mathbf{X}_i,$$

where  $\frac{\partial}{\partial \mathbf{X}_i}$  is the linear form associated with the gradient and  $\operatorname{div}_{oi}$  is the divergence operator on  $\mathcal{D}_{oi}$ .

Variations of entropies satisfy relation (9). With assuming that terms on the edge of  $\mathcal{W}$  are zero, we obtain:



$$\begin{aligned} \delta_i a = & \int_{t_1}^{t_2} \int_{\mathcal{D}_t} \left\{ \left( \frac{1}{2} \mathbf{V}_i^* \mathbf{V}_i - \varepsilon_{,\rho_i} - \Omega_i \right) \delta_i \rho_i + \rho_i \mathbf{V}_i^* \delta_i \mathbf{V}_i - \varepsilon_{,s_i} \delta_i s_i \right. \\ & - \left[ \sum_{p=1}^{n-1} (-1)^p (\varepsilon_{,\rho_i, \gamma_1, \dots, \gamma_p})_{,\gamma_1, \dots, \gamma_p} \right] \delta_i \rho_i \\ & \left. - \left[ \sum_{p=1}^{n-1} (-1)^p (\varepsilon_{,s_i, \gamma_1, \dots, \gamma_p})_{,\gamma_1, \dots, \gamma_p} \right] \delta_i s_i \right\} dv dt, \quad \text{or} \end{aligned}$$

$$\delta_i a = \int_{t_1}^{t_2} \int_{\mathcal{D}_{oi}} \rho_{oi} \left[ \mathbf{R}_i \operatorname{div}_{oi} \boldsymbol{\xi}_i + \frac{\mathbf{R}_i}{\rho_{oi}} \frac{\partial \rho_{oi}}{\partial \mathbf{X}_i} \boldsymbol{\xi}_i - \mathbf{V}_i^* \mathbf{F}_i \frac{\partial \boldsymbol{\xi}_i}{\partial t} - \theta_i \frac{\partial s_i}{\partial \mathbf{X}_i} \boldsymbol{\xi}_i \right] dv_{oi} dt$$

with  $\mathbf{R}_i$  denotes  $\frac{1}{2} \mathbf{V}_i^* \mathbf{V}_i - h_i - \Omega_i$ .

But,

$$\operatorname{div}_{oi}(\rho_{oi} \mathbf{R}_i \boldsymbol{\xi}_i) = \rho_{oi} \mathbf{R}_i \operatorname{div}_{oi} \boldsymbol{\xi}_i + \mathbf{R}_i \frac{\partial \rho_{oi}}{\partial \mathbf{X}_i} \boldsymbol{\xi}_i + \rho_{oi} \frac{\partial \mathbf{R}_i}{\partial \mathbf{X}_i} \boldsymbol{\xi}_i.$$

So,

$$\delta_i a = \int_{t_1}^{t_2} \int_{\mathcal{D}_{oi}} \rho_{oi} \left[ -\frac{\partial \mathbf{R}_i}{\partial \mathbf{X}_i} + \frac{\partial}{\partial t} (\mathbf{V}_i^* \mathbf{F}_i) - \theta_i \frac{\partial s_i}{\partial \mathbf{X}_i} \right] \boldsymbol{\xi}_i dv_{oi} dt,$$

(terms given by integration on the edge of  $\mathcal{D}_{oi}$  are zero).

Finally, for each constituent,

$$\frac{\partial}{\partial t} (\mathbf{V}_i^* \mathbf{F}_i) = \frac{\partial \mathbf{R}_i}{\partial \mathbf{X}_i} + \theta_i \frac{\partial s_i}{\partial \mathbf{X}_i},$$

and by using of the relation

$$\frac{\partial}{\partial t} (\mathbf{V}_i^* \mathbf{F}_i) = \boldsymbol{\Gamma}_i^* \mathbf{F}_i + \mathbf{V}_i^* \frac{\partial \mathbf{V}_i}{\partial \mathbf{X}_i},$$

we obtain

$$\boldsymbol{\Gamma}_i^* \mathbf{F}_i + \frac{\partial}{\partial \mathbf{X}_i} \left( \frac{1}{2} \mathbf{V}_i^* \mathbf{V}_i \right) = \frac{\partial \mathbf{R}_i}{\partial \mathbf{X}_i} + \theta_i \frac{\partial s_i}{\partial \mathbf{X}_i} \quad \text{or} \quad \boldsymbol{\Gamma}_i^* = \theta_i \frac{\partial s_i}{\partial \mathbf{x}} - \frac{\partial}{\partial \mathbf{x}} (h_i + \Omega_i).$$

This leads to the vectorial form:

$$\boldsymbol{\Gamma}_i = \theta_i \operatorname{grad} s_i - \operatorname{grad} (h_i + \Omega_i) \quad (11)$$

## Appendix 2

### Equation of motion of thermocapillary mixtures

Equation (11) implies

$$\sum_{i=1}^2 \rho_i \boldsymbol{\Gamma}_{i\gamma} + \rho_i \Omega_{i,\gamma} = \sum_{i=1}^2 \varepsilon_{,s_i} s_{i,\gamma} - (\varepsilon_{,s_i,\nu})_{,\nu} s_{i,\gamma} - \rho_i (\varepsilon_{,\rho_i})_{,\gamma} + \rho_i [(\varepsilon_{,\rho_i,\nu})_{,\nu}]_{,\gamma}.$$

By noting that

$$\varepsilon_{,\gamma} = \sum_{i=1}^2 \varepsilon_{,s_i} s_{i,\gamma} + (\varepsilon_{,s_{i,\nu}})_{,\nu} s_{i,\nu\gamma} + \varepsilon_{,\rho_i} \rho_{i,\gamma} + \varepsilon_{,\rho_{i,\nu}} \rho_{i,\nu\gamma},$$

we obtain

$$\begin{aligned} & \sum_{i=1}^2 \rho_i \Gamma_{i\gamma} + \rho_i \Omega_{i,\gamma} = \\ & \varepsilon_{,\gamma} - \left\{ \sum_{i=1}^2 \varepsilon_{,s_{i,\nu}} s_{i,\nu\gamma} + \varepsilon_{,\rho_i} \rho_{i,\gamma} + \varepsilon_{,\rho_{i,\nu}} \rho_{i,\nu\gamma} + (\varepsilon_{,s_{i,\nu}})_{,\nu} s_{i,\gamma} + \right. \\ & \quad \left. \rho_i (\varepsilon_{,\rho_i})_{,\gamma} - \rho_i [(\varepsilon_{,\rho_{i,\nu}})_{,\nu}]_{,\gamma} \right\}, \end{aligned}$$

or

$$\sum_{i=1}^2 \rho_i \Gamma_{i\gamma} + \rho_i \Omega_{i,\gamma} = \sum_{i=1}^2 \left[ \varepsilon - \rho_i \varepsilon_{,\rho_i} + \rho_i (\varepsilon_{,\rho_{i,\nu}})_{,\nu} \right]_{,\gamma} - \left[ \Phi_{i\nu} \rho_{i,\gamma} + \Psi_{i\nu} s_{i,\gamma} \right]_{,\nu}.$$

In the case  $\Omega_1 = \Omega_2 = \Omega$ , this agrees with Eq. (17) when  $\rho\alpha = \varepsilon$ .

### Appendix 3

#### Proof of relation (19)

Relation (10<sup>1</sup>) yields

$$E_i = \frac{\partial e_i}{\partial t} + \operatorname{div} \left[ \rho_i \left( \frac{1}{2} \mathbf{V}_i^2 + h_i + \Omega_i \right) \mathbf{V}_i \right] - \operatorname{div} \left[ \frac{\partial \rho_i}{\partial t} \boldsymbol{\Phi}_i + \frac{\partial s_i}{\partial t} \boldsymbol{\Psi}_i \right] - \rho_i \frac{\partial \Omega_i}{\partial t}.$$

On the left hand side of Eq.(19), the extraneous force potential and inertia terms cancel out.

With  $e_i, h_i, \boldsymbol{\Phi}_i$  and  $\boldsymbol{\Psi}_i$  having been replaced by their respective values, it remains to be proved that the terms from the internal energy also cancel out. By using the convention that terms subscripted by  $i$  are *summed on*  $\{1, 2\}$ , the internal energy involves:

a) in  $E_i$ :  $\frac{\partial \varepsilon}{\partial t} + \operatorname{div}(\rho_i h_i \mathbf{V}_i) - \operatorname{div} \left( \frac{\partial \rho_i}{\partial t} \boldsymbol{\Phi}_i + \frac{\partial s_i}{\partial t} \boldsymbol{\Psi}_i \right),$

b) in  $\rho_i \mathbf{M}_i^* \mathbf{V}_i$ :  $-\rho_i \theta_i \operatorname{grad}^* s_i \mathbf{V}_i + \rho_i \operatorname{grad}^* h_i \mathbf{V}_i,$

c) in  $\left( \frac{1}{2} \mathbf{V}_i^2 + h_i + \Omega_i \right) B_i$ :  $h_i \left( \frac{d\rho_i}{dt} + \rho_i \operatorname{div} \mathbf{V}_i \right),$

d) in  $S : \rho_i \theta_i \left( \frac{ds_i}{dt} \right)$ .

This leaves the following in the first term of (19):

$$\begin{aligned} & \frac{\partial \varepsilon}{\partial t} + \operatorname{div}(\rho_i h_i \mathbf{V}_i) - \operatorname{div} \left( \frac{\partial \rho_i}{\partial t} \Phi_i + \frac{\partial s_i}{\partial t} \Psi_i \right) \\ & - \rho_i \theta_i \left( \frac{\partial s_i}{\partial t} \right) - \rho_i \operatorname{grad}^* h_i \mathbf{V}_i - h_i \left( \frac{d\rho_i}{dt} + \rho_i \operatorname{div} \mathbf{V}_i \right), \end{aligned}$$

or:

$$\frac{\partial \varepsilon}{\partial t} - (h_i + \operatorname{div} \Phi_i) \frac{\partial \rho_i}{\partial t} - (\rho_i \theta_i + \operatorname{div} \Psi_i) \frac{\partial s_i}{\partial t} - \Phi_i^* \frac{\partial \operatorname{grad} \rho_i}{\partial t} - \Psi_i^* \frac{\partial \operatorname{grad} s_i}{\partial t}.$$

Definitions (16) of  $\varepsilon$  and (10) of  $h_i$  and  $\theta_i$  show immediately that this expression is identically zero.

## Appendix 4

### Interpretation of capillary tensions associated with two immiscible fluids

We consider an interface between two immiscible fluids. The assumption that two fluids remain absolutely separated is not reflected in physical experiments. The two fluids interpenetrate each other in a thin layer (thickness about few molecular diameters). Energetic reasons justify the assumption [Brin, 1956]. The density of each constituent regularly changes between the value in bulk 1 and the one in bulk 2, with a profile in accordance with the one of a liquid-vapour interface; each density vanishes asymptotically in the complementary phase (see *Fig.2*).

In the interfacial layer, density gradients are important. In the isothermal case, the zone of mixture of two isotropic fluids can be represented with an internal energy of the form:

$$\varepsilon = \rho \alpha(\rho_1, \rho_2, \beta_1, \beta_2, \gamma)$$

with

$$\beta_i = (\operatorname{grad} \rho_i)^2 \quad \text{and} \quad \gamma = \operatorname{grad} \rho_1 \operatorname{grad} \rho_2.$$

The stress tensor reduced from Eq. (18) is:

$$\begin{aligned} \sigma = \sum_{i \neq j} & \left[ -\rho \rho_i \alpha_{,\rho_i} + \rho_i \operatorname{div}(C_i \operatorname{grad} \rho_i + D \operatorname{grad} \rho_i) \right] Id \\ & - C_i \operatorname{grad} \rho_i \operatorname{grad}^* \rho_i - D \operatorname{grad} \rho_i \operatorname{grad}^* \rho_j, \end{aligned}$$

with  $C_i = 2\rho\alpha_{,\beta_i}$  and  $D = \rho\alpha_{,\gamma}$ . Let us denote

$$\Pi = \sum_{i \neq j} \rho \rho_i \alpha_{,\rho_i} - \rho_i \operatorname{div}(C_i \operatorname{grad} \rho_i + D \operatorname{grad} \rho_i) + C_i (\operatorname{grad} \rho_i)^2 + D \operatorname{grad}^* \rho_i \operatorname{grad} \rho_j.$$

In each bulk, gradient terms are zero and  $\Pi$  takes the values:

$$\Pi_1 = \rho_1^2 \alpha_{,\rho_1}(\rho_1, 0, 0, 0, 0) \quad \text{and} \quad \Pi_2 = \rho_2^2 \alpha_{,\rho_2}(0, \rho_2, 0, 0, 0)$$

that correspond to the pressure in each phase of fluid.

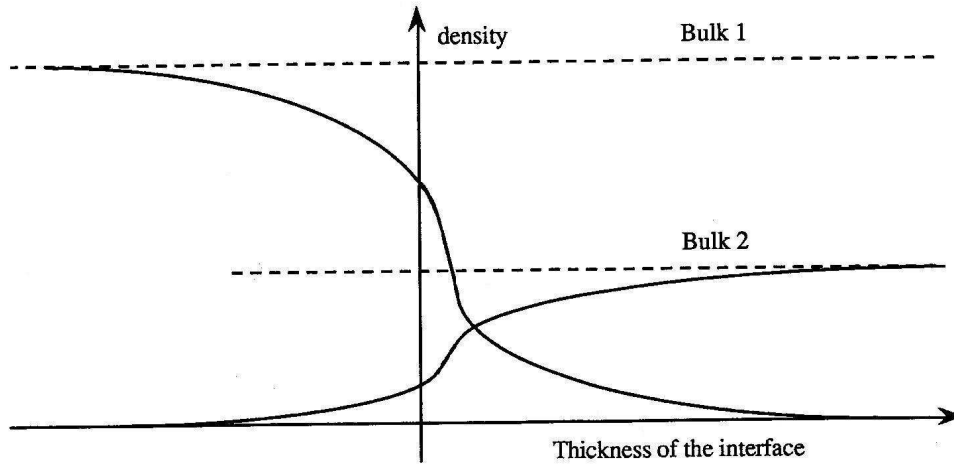


Fig. 2. Profiles of densities through the interface

When the extraneous force potential are neglected,

$$\operatorname{div} \sigma = 0,$$

which is the equation of the equilibrium state of the mixture.

For a flat interface normal to  $\operatorname{grad} \rho_1$  and  $\operatorname{grad} \rho_2$ , the eigenvalues of stress tensor  $\sigma$  are

$$\lambda_1 = -\Pi + C_1 (\operatorname{grad} \rho_1)^2 + C_2 (\operatorname{grad} \rho_2)^2 + 2D \operatorname{grad}^* \rho_1 \operatorname{grad} \rho_2,$$

(associated with the plane of interface), and

$$\lambda_2 = -\Pi$$

(associated with the direction normal to the plane of interface).

In a system of coordinates suitable for the interface (*i.e.* an orthonormal sys-

tem whose third direction is  $z$ , the stress tensor is written:

$$\sigma = \begin{bmatrix} \lambda_1 & 0 & 0 \\ 0 & \lambda_1 & 0 \\ 0 & 0 & \lambda_2 \end{bmatrix}.$$

The equation of balance momentum in the planar interface implies:

$$\lambda_2 = -\Pi_0,$$

where  $\Pi_0$  denotes the pressure that must be common to the two bulks.

The line force per unit of length on the edge of the interface is (*see Fig. 3*):

$$\mathcal{F} = \int_{z_1}^{z_2} \lambda_1 dz =$$

$$-\Pi_0(z_2 - z_1) + \int_{z_1}^{z_2} \{C_1(\text{grad } \rho_1)^2 + C_2(\text{grad } \rho_2)^2 + 2D\text{grad}^* \rho_1 \text{grad } \rho_2\} dz,$$

where  $z_2 - z_1$  corresponds to the physical size of the interface.

Let us note that, due to the thickness of the interface,  $-\Pi_0(z_2 - z_1)$  is negligible. Conditions on the edge are not the ones of first gradient fluid. Nevertheless, the problem concerns a plane interface and the mean radius of curvature  $R_m$  is such that  $R_m = \infty$ . Therefore, the constraint condition on the edge is in the form  $n^* \sigma$  where  $n^*$  is normal to the edge of the interface [Casal, 1972]. Let

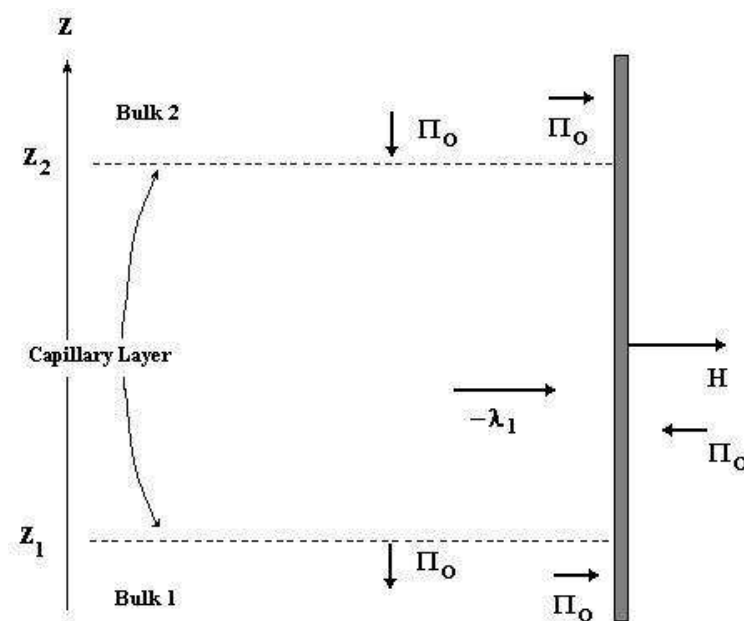


Fig. 3. Interpretation of the mixture surface tension

us note:

$$H_i = \int_{z_1}^{z_2} \{C_i(\text{grad } \rho_i)^2\} dz \quad \text{et} \quad H_{1,2} = \int_{z_1}^{z_2} 2D \text{grad}^* \rho_1 \text{grad } \rho_2 dz.$$

(The integrals converge in the two bulks). The line force per unit of length on the edge is:

$$H = H_1 + H_2 + H_{1,2}.$$

Here,  $H$  represents the surface tension of the flat interface in its equilibrium state expressed as a function of the surface tensions  $H_1$  and  $H_2$  of each bulk and a supplementary term  $H_{1,2}$  associated with the effect of the mixture. This is the expression of the surface tension of an interface between two immiscible fluids known as Antonov's rule [Emschwiller, 1964].

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