Modélisation of fluid-fluid interfaces with material properties

by

R. GATIGNOL and P. SEPPECHER

Laboratoire de Mécanique Théorique, Associé au C.N.R.S.-U.A. n° 229,
Université P.-et-M.-Curie, 4, place Jussieu, 75252 Paris Cedex 05

ABSTRACT

The interfaces are seen as thin three-dimensional layers. The fluid inside these layers is a mixture the internal energy of which depends on the density gradient of each constituent. The internal strengths are described by a second gradient theory. The corresponding equation set is then integrated through the layer. So we obtain the evolution equations of the interfacial physical quantities in which there enter the parameters of the fluids on both sides of the interface. Then by an asymptotic proccess the interfacial layer may be considered as a carrier surface of material quantities. As a special case the balance laws are derived for an interface without mass but carrying a surfactant. At last using the linear thermodynamic of the irreversible proccesses we give the interfacial transport coefficients.

RESUME

Les interfaces sont assimilées à des couches tridimensionnelles de faible épaisseur. Le fluide contenu dans ces couches est un mélange dont l'énergie interne dépend des gradients des densités de chaque constituant. Les efforts intérieurs y sont décrits par une théorie du second gradient. Le système d'équations décrivant l'évolution du milieu est intégré sur l'épaisseur de la couche. On obtient ainsi des équations liant l'évolution des paramètres interfaciaux aux paramètres décrivant les deux fluides de part et d'autre de l'interface. Par un processus asymptotique l'interface peut alors être considérée comme une surface porteuse de propriétés matérielles. Les lois de conservation sont en particulier, explicitées dans le cas d'une interface sans masse transportant un surfactant. En utilisant la thermodynamique linéaire des processus irréversibles on donne les coefficients de transport interfaciaux.

1. INTRODUCTION

The interfacial region between two fluids is often regarded as a discontinuity surface with an internal energy connected to the phenomenon of surface tension. But in some problems it is important to give to the interface a more complex structure and to take more material properties into account. Such is the case with the introduction of surface viscosities which increase the dissipation.

In this paper, in order to give an understanding to the derivation of the relevant equations of interfacial balances, we regard the interface as a thin transition layer in which the space variations of some parameters are much larger than outside. Inside the interfacial region we use the laws of continuum mechanics ; by the virtual power method for a class of virtual motions, the definition of the internal strengths is given by the so-called "second gradient theory" (1). Limiting oneself to a layer with a thickness that is small compared to the radius of the

mean curvature of the interface, it is possible by asymptotic approximation, to replace the interfacial layer by a discontinuity surface carrying material properties. The surface quantities are defined by integration over the thickness of the layer. Then we can write down the laws of interfacial balances as well as an expression for the interfacial entropy production.

First we note that from a physical point of view the properties of the medium in the interfacial region are appreciably different from these of the two adjacent fluids. It is difficult to precise the thickness of the layer. But the experimental work of Palmer, as mentionned in the book of Hirschfelder, Curtiss and Bird (2), allows to say that the thickness for a liquid-vapor interface is larger and larger, when the critical point is approached. It may be several hundreds of molecular diameters. More, the volumic mass is observed to be a continuous function of position in the direction normal to the interface.

Under conditions well away from the critical point, however, the layer thickness is only a few molecular diameters (3), (4). Nevertheless the three-dimensional character of the phase interface is explicitly recognized in statistical mechanical calculations in order to obtain an expression for the surface tension (4).
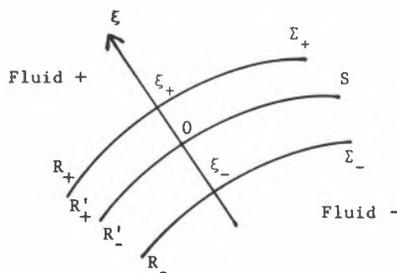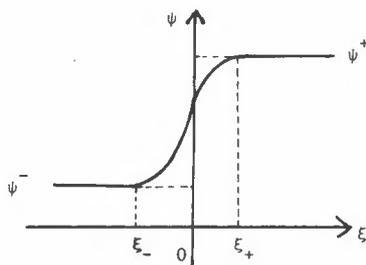

Figure 1

Figure 2

(1)

Let us consider a thin transition region with a finite thickness, located inside a layer limited by two surfaces Σ_- and Σ_+, and dividing two continuous media denoted by the indices $-$ and $+$ (Fig. 1). A mass transfer may occur through the interfacial layer. We suppose that the media $-$ and $+$ are two Newtonian fluids, or more generally two mixtures of such fluids ; at the equilibrium their stress tensors are spherical. On the contrary in the transition layer we have for the medium a preferential direction, so that the stress tensor is not spherical at the equilibrium.

The parameters in the two media $-$ and $+$ (volumic mass, pressure, viscosity coefficients, ...) are different but they smoothly connect one another through the layer. To be specific, we introduce an imaginary surface S inside the interfacial region and we denote by ξ the normal unit vector to S pointing from fluid $-$ to fluid $+$ (Fig. 1). The space is divided into four regions : R_-, R'_-, R'_+ and R_+. On Fig. 2, we give a possible profile for a quantity ψ when we go across the layer in the normal direction.

We can emphasize the two following points of view : the first one is related to the definition of the "true" interfacial quantities and the second to those of the "excess" interfacial quantities.

A "true" interfacial quantity is introduced by integration along the thickness of the layer of the real physical quantity describing the medium

$$\psi^s_{tr} = \int_{\xi_-}^{\xi_+} \psi \, d\xi$$

An "excess" interfacial quantity is defined by the following integral

$$(2) \qquad \psi_{ex}^s = \int_{\xi_-}^0 (\psi - \psi_-) d\xi + \int_0^{\xi_+} (\psi - \psi_+) d\xi \;,$$

where ψ_- (or ψ_+) represents the value of the quantity ψ in the medium $-$ (or $+$) under the assumption that this medium occupies all the region $R_- \cup R'_-$ (or $(R_+ \cup R'_+)$ limited by the boundary S and that ψ_- (or ψ_+) coincides with the true value of ψ in R_- (or R_+).

With the introduction of the excess values, the media $-$ and $+$ are seen as if they were filling the whole regions $R_- \cup R'_-$ and $R_+ \cup R'_+$ respectively, while the quantity ψ in excess, ψ_{ex}^s, is concentrated on the geometric surface S. That is corroborated by the equality

$$\int_{X_-}^{X_+} \psi \, d\xi = \int_{X_-}^0 \psi_- \, d\xi + \psi_{ex}^s + \int_0^{X_+} \psi_+ \, d\xi$$

where X_- and X_+ are two values taken by the variable ξ in the media $-$ or $+$.

The thickness of the interfacial layer is not well defined, but we can expect that the given expression for ψ_{ex}^s does not depend on it. On the other hand, this expression strongly depends on the precise localisation of the surface S. This description with the quantities in excess has been first given by Gibbs (1928) (5). A suitable choice for the surface S is the one for which the interfacial mass in excess, ρ_{ex}^s, is zero (then S is called equimolecular localisation surface). Lastly we can say that with the excess values, the equations on S between the two media $-$ and $+$ are exactly jump relations.
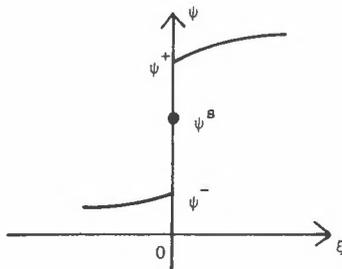
With the introduction of the "true" interfacial quantities we consider a different approach. The order of magnitude of the ratio of the gradients of the densities of each component inside and outside the interface region is characterized by a small adimensional parameter ε.

In the microscopic description (the order ε) the variation of a quantity ψ along the normal direction is described by a graph similar to that given on the figure 2 (it is possible to have for ψ a more complicated function).

In the macroscopic description, (the order 1), the interfacial layer is seen as a surface S without thickness. The value of the quantity ψ on the surface S is undefined a priori, but keeping the memory of the variation of ψ through the layer, we may affect the material surfacic quantity ψ_{tr}^s as the value of ψ on the surface S (Fig. 3).

Figure 3

Thereby we can consider that we have two three-dimensional media separated by a two-dimensional medium. Such a shematisation is easy to understand if we have no mass transfer between the interfacial medium and the adjacent media.

In the case where the material particles of the interfacial medium are not always the same, we must distinguish between two velocities : the material velocity $\mathbf{v}^s$ of the particles belonging to the layer and the velocity $\mathbf{w}^s$ of the geometric surface S. A discussion about

this difference has been recently given, (6), (7).

The order of magnitude of the thickness of the interfacial layer alone is well defined. The value of a true interfacial quantity depends on the choice of the region limited by Σ_- and Σ_+. The thickness of the layer is only asymptotically given, and, for the true values, the exact position of the surface S on which the layer is strinked is of slight consequence.

The derivation of the interfacial balance equations using the existence of an interfacial layer, is the concern of many works. We only mention those of Deemer and Slattery (8), Albano, Bedeaux and Vlieger (9), Dumais (10) and Goodrich (11) for the "excess" quantities, and those of Ishii (12) and Gogosov, Naletova, Chung Za Bin and Shaposhnikova (13) for the "true" quantities. However the detailed description of the interfacial layer is rarely taken into account (Deemer and Slattery (8), Goodrich (11), Gogosov et al.(13)), except in the many works on the definition and the calculus of the surface tension alone (for instance Brenner   (14), Gouin (15)).

In many works relative to the interfaces with a material structure, these interfaces are presented as a two-dimensional continuum on which the material quantities are introduced by analogy with the three-dimensional continuum. The interfacial balance laws are then postulated in an integral form (Barrère and Prud'homme (16), Delhaye (17), (18), Deemer and Slattery (8)).

Lastly let us mention the approach of Daher and Maugin (19) who apply the theorem of the virtual power, and those of Bedeaux, Albano and Mazur (20) where the interface is seen as a singular surface with the material quantities connected to Dirac distributions. In this last work the local balance laws are written in the distribution language for a three-dimensional continuum enclosing a singular surface and they lead very nicely to the interfacial balance laws. The transversality property and the symmetry of the interfacial stress tensor are then very easy to obtain.

In this paper, in the section II, we give detailed description of the interfacial region using the second gradient theory ; we present this theory in the case of a mixture with n components. The section III concerns the schematisation of the interfacial layer by a surface S without thickness. The point of view of the true quantities is adopted. The general form of an interfacial balance law is given when we only keep the terms of order ε^0.

The balance laws for the interfacial mass, momentum, energy and entropy are detailed in section IV and we explain how to take the appearance of a surfactant on the surface into account. Again in section IV, the transversality condition and the symmetry property of the interfacial stress tensor are discussed. In the last section we derive the expression for the irreversible entropy production and, by using the linear thermodynamic of the irreversible processes, we give the transport coefficients.

2. THREE-DIMENSIONAL DESCRIPTION OF THE INTERFACIAL ZONE

The interfacial zone is considered as a three-dimensional fluid continuum with one or more components. In this section we present and discuss the set of equations which describe its evolution. It is well known that the equations of Newtonian fluids or even these of Newtonian fluid mixtures cannot describe phenomena as capillarity. Indeed no specific energy due to the interface presence can appear in the scope of Newtonian fluids. Moreover the stress tensor is spheric at equilibrium and the characteristic anisotropy of interfaces does not appear.

So these equations are not suitable for the description of the evolution inside the interfacial zones.

Then we are going to construct the set of equations describing a more general fluid : a fluid "endowed with internal capillarity" (Casal and Gouin (21)). To this end we apply the thermodynamic principles in a less limitative way than the classic theory. The interfacial regions are characterized by the presence of density gradients that are large. It is natural to think that the excess of energy on the interfaces is a consequence of these large gradients. Therefore we assume that the internal energy of the fluid is a function of its entropy, of the volumic mass of each component and of the gradients of these volumic mass.

Already in 1901, Korteweg (22) suggested such a function for the internal energy. However the study of such materials encountered an important difficulty : this expression for the energy seems to be incompatible with the thermodynamic second principle (Gurtin (23)). In order to overcome this difficulty Dunn and Serrin 1984 (24), have added an energy flux term called "flux of intersticial working" in the energy balance law ; then they have precised what possible form this flux could take.

A more appropriated description for the internal strengths than the classic description with a unique stress tensor allows to remove these difficulties. It naturally introduces an extra flux for the mechanic flux in the energy balance law with a well specified value. This appropriated description is obtained by using the principle of virtual powers in the class of virtual motions given by the second gradient theory (Germain (1)). This method has been used by Casal and Gouin (21) in the case where the medium has one component only. Here these results are extended to the case of a mixture (25).

2.1 Application of the virtual power principle

Let us consider an isotropic medium which is a mixture with n components of volumic mass ρ^i and velocity $\mathbf{V}^i$, $i \in \{1,\dots,n\}$. We denote by ρ the mass volumic of the mixture and by $\mathbf{V}$ its barycentric velocity. We assume that we have no chemical reaction. The mass balance laws for each component leads to the n following equations :

$$(3) \qquad \frac{d}{dt}\,\rho^{\,i} + \rho^{\,i}\,\boldsymbol{\nabla}.\mathbf{V} + \boldsymbol{\nabla}.\mathbf{J}^i = 0$$

with $\qquad\qquad \mathbf{J}^i = \rho^{\,i}(\mathbf{V}^i - \mathbf{V}) \qquad$ and $\qquad \dfrac{d}{dt} = \dfrac{\partial}{\partial t} + \boldsymbol{\nabla}.\mathbf{V}$

First let us recall the virtual power principle : in a Galilean frame and for an absolute chronology the virtual power of the acceleration quantities of a system $\mathcal{D}$ is equal to the sum of the virtual power of internal and external forces for each considered virtual motion. The class $\tilde{V}$ of considered virtual motions is the space of fields of n vectors $\tilde{\mathbf{v}}^i$ with continuous second partial derivatives (second gradient theory). The virtual power of the internal strengths is an objective form on $\tilde{V}$ (an objective quantity is a quantity which does not depend on the frame where it is expressed).

$$(4) \qquad \tilde{P}^{int} = -\int_{\mathcal{D}} \sum_{i=1}^{n} (\mathbf{a}^i.\tilde{\mathbf{v}}^i + \mathbb{B}^i : \boldsymbol{\nabla}\,\tilde{\mathbf{v}}^i + \mathbb{C}^i \vdots \boldsymbol{\nabla}\,\boldsymbol{\nabla}\,\mathbf{v}^i)dv$$

where $\mathbf{a}^i$, $\mathbb{B}^i$ and $\mathbb{C}^i$ are tensors of order 1, 2 and 3. The tensors $\boldsymbol{\nabla}\,\boldsymbol{\nabla}\,\tilde{\mathbf{v}}^i$ are symmetrical with respect to the first two indices, so the way to write the expression (4) is not unique.

It becomes unique if we lay down conditions to the tensors $\mathbb{C}^i$ that is to say the symmetry with respect to the first two indices (25). The objectivity property of $\tilde{p}^{int}$ has the following consequences :

$$(5) \qquad \sum_{i=1}^{n} \mathbf{a}^i = 0 \quad , \quad \sum_{i=1}^{n} \mathbb{B}^i \quad \text{is a symmetric tensor.}$$

For simplicity, the virtual power of the external forces is supposed of the form

$$(6) \qquad \tilde{p}^{ext} = \int_{\mathcal{D}} \mathbf{f}^{ext}.\tilde{\mathbf{v}} \, dv + \int_{\partial\mathcal{D}} \mathbf{F}^{ext}.\tilde{\mathbf{v}} \, ds$$

where
$$\tilde{\mathbf{v}} = (1/\rho) \sum_{i=1}^{n} \rho^i \, \tilde{\mathbf{v}}^i \quad \text{with} \quad \rho = \sum_{i=1}^{n} \rho^i \, .$$

The external forces are of simple form and they act in a similar way on each constituent of the mixture.

The virtual power of the acceleration quantities is a priori

$$\tilde{p}^{acc} = \int_{\mathcal{D}} \sum_{i=1}^{n} (\rho^i \, \Gamma^i.\tilde{\mathbf{v}}^i) dv \quad \text{with} \quad \Gamma^i = \frac{\partial}{\partial t} \mathbf{v}^i + \mathbf{v}^i.\nabla \, \mathbf{v}^i \, ,$$

where Γ^i is the acceleration vector of the i component. We assume

$$(7) \qquad \tilde{p}^{acc} = \int_{\mathcal{D}} \rho \, \Gamma.\tilde{\mathbf{v}} \, dv \quad \text{with} \quad \Gamma = \frac{\partial}{\partial t} \mathbf{v} + \mathbf{v}.\nabla \, \mathbf{v} \, .$$

It amounts to the same to suppose $\Gamma^i \simeq \Gamma, \forall \, i \in \{1,\ldots,n\}$. The velocities of the different components are very near each other in order that we could assume that the inertial forces play a weak part in the diffusion phenomena (25).

From the virtual power principle, for each system $\mathcal{D}$ and for each virtual motion of $\tilde{\mathcal{U}}$, we have

$$(8) \qquad \int_{\mathcal{D}} \left((\rho \, \Gamma - \mathbf{f}^{ext}).\tilde{\mathbf{v}} + \sum_{i=1}^{n} (\mathbf{a}^i.\tilde{\mathbf{v}}^i + \mathbb{B}^i : \nabla \, \tilde{\mathbf{v}}^i + \mathbb{C}^i \vdots \nabla \, \nabla \, \tilde{\mathbf{v}}^i)\right) dv = \int_{\partial\mathcal{D}} \mathbf{F}^{ext}.\tilde{\mathbf{v}} \, ds$$

By integrating by part the terms $\mathbb{B}^i : \nabla \, \tilde{\mathbf{v}}^i$ once and the terms $\mathbb{C}^i \vdots \nabla \, \nabla \, \tilde{\mathbf{v}}^i$ twice, and by taking virtual velocities which are zero on a neighbour of the boundary $\partial\mathcal{D}$ of $\mathcal{D}$ we obtain :

$$(9) \qquad \int_{\mathcal{D}} \left((\rho \, \Gamma - \mathbf{f}^{ext}).\tilde{\mathbf{v}} + \sum_{i=1}^{n} (\mathbf{a}^i - \nabla.\overline{\mathbb{B}}^i + \nabla \, \nabla : \overline{\mathbb{C}}^i).\tilde{\mathbf{v}}^i\right) dv = 0$$

where $\overline{\mathbb{B}}^i$ and $\overline{\mathbb{C}}^i$ are the tensors deduced from $\mathbb{B}^i$ and $\mathbb{C}^i$ by permuting the first and the last indices :

$$\overline{B}^i_{\alpha\beta} = B^i_{\beta\alpha} \quad , \quad \overline{C}^i_{\alpha\beta\gamma} = C^i_{\gamma\beta\alpha} \, .$$

We obtain the following local equations :

$$(10) \qquad \rho \, \Gamma = \mathbf{f}^{ext} + \nabla.\overline{\mathcal{T}} \quad \text{with} \quad \overline{\mathcal{T}} = \sum_{i=1}^{n} (\overline{\mathbb{B}}^i - \nabla.\overline{\mathbb{C}}^i)$$

(11)
$$a^i - \nabla.\overline{B}^i + \nabla \nabla : \overline{C}^i + \frac{\rho^i}{\rho} \nabla.\overline{C} = 0 \quad ; \quad i = 1,\ldots,n .$$

The equation (10) is obtained by taking all the virtual velocities $\tilde{V}^i$ as equal, and the equation (11) by taking all the velocities $\tilde{V}^i$ equal to zero except one of them. The equation (10) is the classical balance law for the momentum that we can also write :

(12)
$$\frac{d}{dt} g + g \nabla.V - \nabla.\mathcal{C} = f^{ext} \quad \text{with} \quad g = \rho V ;$$

the tensor $\mathcal{C}$ of order 2 is symmetrical and is called the stress tensor.

2.2 Application of the first and second principles of the thermodynamic

At every time the material derivative of the energy of a system is the sum of the power of the external forces and of the rate of the received heat $\dot{Q}$. Denoting by U the internal energy of the system $\mathcal{D}$ and using the kinetic energy theorem (obtained from the virtual power principle by taking the real velocities), this first principle can be written $(dU/dt) = \dot{Q} - P^{int}$. In a local form it becomes :

(13)
$$\frac{du}{dt} + u \nabla.V = r - \nabla.q + \sum_{i=1}^{n} (a^i.V^i + B^i : \nabla V^i + C^i \vdots \nabla \nabla V^i)$$

Here u denotes the internal energy per unit of volume, r the rate of energy source per unit of volume and q the heat current. By using the equation set (11), the equation (13) becomes :

(14)
$$\frac{du}{dt} + u \nabla.V = r - \nabla..q + \mathcal{C} : \nabla V + \nabla.E$$

(15)
$$E = \sum_{i=1}^{n} \left(\nabla V^i : C^i + \frac{1}{\rho^i} (\overline{B}^i - \nabla.\overline{C}^i).J^i\right)$$

We emphasize that in the energy equation (14), there appears an extra energy current denoted by E. To distinguish this extra energy current from the heat current q is absolutely necessary before defining the entropy current and before using the second principle of the thermodynamic.

Indeed we adopt for the entropy current the expression q/T related to the current q only ; here, as usual, T is the absolute temperature of the medium. We use the entropy balance in a classic form :

(16)
$$\frac{ds}{dt} + s \nabla.V + \nabla.(\frac{q}{T}) - \frac{r}{T} = \sigma \quad ; \quad \sigma \geq 0$$

where s is the massic entropy and σ the entropy production per unit of volume.

Now we assume that the internal energy u is an objective function depending on the entropy s, the densities ρ^i and their gradients $\nabla\rho^i$. Then we have

(17)
$$du = T ds + \sum_{i=1}^{n} \mu^i d\rho^i + \sum_{i=1}^{n} \sum_{j=1}^{n} \lambda^{ij} \nabla\rho^j.d(\nabla\rho^i)$$

with
$$\lambda^{ij} = \lambda^{ji} \quad \forall i,j \in \{1,\ldots,n\} .$$

The coefficients μ^i are called chemical potentials. The coefficients λ^{ij} might be

called "cocapillarity coefficients" ; in the case of one component only λ^{11} is the capillarity coefficient (21). The coefficients λ^{ij} are determined in a unique manner only if n is 3 at most. For n larger than 3, only the quantities $\sum\limits_{j=1}^{n} \lambda^{ij} \nabla^{j}\rho$ are uniquely determined.

2.3 Expression of the entropy production

Let us remark that the equations (3) imply

(18)
$$\sum_{j=1}^{n} \lambda^{ij} \nabla\rho^{i} \cdot \frac{d}{dt}(\nabla\rho^{i}) = \hat{a}^{i} \cdot J^{i} + \hat{B}^{i} : \nabla V^{i} + \hat{c}^{i} \vdots \nabla \nabla V^{i}$$

with
$$\hat{a}^{i} = - \sum_{j=1}^{n} \lambda^{ij} \nabla\rho^{j} \cdot \nabla \nabla\rho^{i}$$

$$\hat{B}^{i} = - \sum_{j=1}^{n} \lambda^{ij}(\nabla\rho^{i} \otimes \nabla\rho^{j} + \nabla\rho^{i} \cdot \nabla\rho^{j} \; \mathbb{I}_{2})$$

$$\hat{c}^{i} = - \sum_{j=1}^{n} \lambda^{ij} \rho^{i} \; \mathbb{I}_{2} \otimes \nabla\rho^{j}$$

where $\mathbb{I}_{2}$ denotes the unit tensor of order 2.

We assume that the equation (17) is always valid (Axiom of the local state). From the equation (17) and the equations (3), (13) and (16) we obtain the following expression for the dissipation $T\sigma$:

$$T\sigma = - \frac{q}{T} \cdot \nabla T + (Ts - u + \sum_{j=1}^{n} \rho^{j} \mu^{j})\nabla \cdot V + \sum_{j=1}^{n} (\mathbb{B}^{j} - \hat{B}^{j}) : \nabla V$$
$$- P^{int} - \sum_{i=1}^{n} \sum_{j=1}^{n} \lambda^{ij} \nabla\rho^{j} \cdot \frac{d}{dt}(\nabla\rho^{i})$$

By using (18) we arrive to

$$T\sigma = - \frac{q}{T} \cdot \nabla T + (Ts - u + \sum_{i=1}^{n} \rho^{i} \mu^{i})\nabla \cdot V + \sum_{i=1}^{n} (\mathbb{B}^{i} - \hat{B}^{i}) : \nabla V$$
$$+ \sum_{i=1}^{n} \left(\frac{a^{i} - \hat{a}^{i}}{\rho^{i}} + \frac{(\mathbb{B}^{i} - \hat{B}^{i}) \cdot \nabla\rho^{i}}{(\rho^{i})^{2}} \right) \cdot J^{i}$$
$$+ \sum_{i=1}^{n} \left(\frac{\mathbb{B}^{i} - \hat{B}^{i}}{\rho^{i}} + \mu^{i} \; \mathbb{I}_{2} : \nabla J^{i} \right)$$
$$+ \sum_{i=1}^{n} (c^{i} - \hat{c}^{i}) \vdots \nabla \nabla V^{i}$$

In order to go on, we make some simplifying assumptions. We restrict our study to a simple model in which the viscous stresses do not depend on the second gradient of the velocities V^{i} nor on the first gradient of the mass currents J^{i}. The first of these assumptions is proposed in the paper of Casal and Gouin in the case of one component only (21) ; the second assumption is usual in theory of the fluid mixtures. Therefore we assume that no dissipation may occur from the terms ∇J^{i} and $\nabla \nabla V^{i}$. Since the quantities $\nabla \nabla V^{i}$ are independent, we have

$$c^{i} - \hat{c}^{i} = 0 \qquad \forall \; i \in \{1,\dots,n\}$$

The quantities $\nabla \cdot J^{i}$ are related by the relation $\sum\limits_{i=1}^{n} \nabla \cdot J^{i} = 0$; so we have

$$\frac{1}{\rho^{i}} (\mathbb{B}^{i} - \hat{B}^{i}) + \mu^{i} \; \mathbb{I}_{2} = \mathbb{K} \qquad \forall \; i \in \{1,\dots,n\}$$

where $\mathbb{K}$ is a tensor which does not depend on the index i.

Let us denote

$$\mu'^i = \mu^i - \sum_{j=1}^{n} \mathbf{\nabla}.(\lambda^{ij} \mathbf{\nabla}\rho^j)$$

$$p = Ts - u + \sum_{i=1}^{n} \mu'^i \rho^i$$

$$\tau^N = - p \; \mathbb{I}_2 - \sum_{i=1}^{n} \sum_{j=1}^{n} \lambda^{ij} \; \mathbf{\nabla}\rho^i \otimes \mathbf{\nabla}\rho^j$$

$$\tau^D = \tau - \tau^N$$

The dissipation and the extra energy current involved in the equation (14) have the following expressions :

(20)
$$T\sigma = - \frac{\mathbf{q}}{T} . \mathbf{\nabla} T - \mathbf{\nabla}(\mu'^i) . \mathbf{J}^i + \tau^D : \mathbf{\nabla} \mathbf{V}$$

(21)
$$\mathbf{E} = - \sum_{i=1}^{n} u'^i \mathbf{J}^i - \sum_{i=1}^{n} \sum_{j=1}^{n} \lambda^{ij}(\mathbf{\nabla}.\mathbf{J}^i + \rho^i \mathbf{\nabla}.\mathbf{V})\mathbf{\nabla}\rho^j$$

In the limits of the linear thermodynamic of the irreversible processes (26), the study of the expression (20) for the dissipation leads to specify a set of constitutive laws for the considered mixture. The application of the objectivity principle (principle of Curie) is intricated due to the appearance of the vector parameters $\mathbf{\nabla}\rho^i$ among the thermostatic parameters. A complete study is given in Ref. (25).

The equation set (3), (10), (14), (16), (20) is different from the classic equation set for a mixture. On one hand we have the term $\sum_{i,j} \lambda^{ij}(\mathbf{\nabla}.\mathbf{J}^i +\rho^i \mathbf{\nabla}.\mathbf{V})\mathbf{\nabla}\rho^j$ in the energy current $\mathbf{E}$; this term corresponds to the extra energy term introduced by Dunn and Serrin (24). Moreover the stress tensor τ^N obtained without dissipation phenomenon is no longer spherical.

In the case of a medium with small gradients we have

$$\mu'^i = \mu^i \quad , \quad p = Ts - u + \sum_{i=1}^{n} \mu^i \rho^i \; ,$$

$$\tau^N = - p \; \mathbb{I}_2 \quad , \quad \mathbf{E} = \sum_{i=1}^{n} \mu^i \mathbf{J}^i \; .$$

We find the classic equations for a mixture with the following conventional difference : usually the quantity $\mathbf{q}' = \mathbf{q} + \sum_{i=1}^{n} \mu^i \mathbf{J}^i$ is called heat current, and consequently the entropy current is the quantity $(1/T)(\mathbf{q}' - \sum_{i} \mu^i \mathbf{J}^i)$.

In the case of a continuum with one constituent only we have

$$p = Ts - u + \rho\mathbf{\nabla}.(\lambda^{11} \mathbf{\nabla}\rho)$$

$$\tau^N = - p \; \mathbb{I}_2 - \lambda^{11} \mathbf{\nabla}\rho \otimes \mathbf{\nabla}\rho$$

$$\mathbf{E} = \lambda^{11} \rho (\mathbf{\nabla}.\mathbf{V})\mathbf{\nabla}\rho$$

We find the results of Casal and Gouin (21) and Dunn and Serrin (24).

Let us assume that the thermic and intrinsic dissipations are uncoupled. Then the theory of the linear thermodynamic of the irreversible proccesses leads to the following results for the viscous stress tensor

$$\tau^{D} = (\lambda \ tr \ D + \nu \ \xi.D.\xi) \ \mathbb{I}_2 + \mu \ D +$$

$$\beta (D.\xi \otimes \xi + \xi \otimes \xi.D)$$

$$+ (\nu \ tr \ D + \gamma \ \xi.D.\xi)\xi \otimes \xi$$

where
$$D = \frac{1}{2}(\nabla V + \overline{\nabla V}) \quad , \quad \xi = \frac{\nabla\rho}{|\nabla\rho|}$$

With five transport coefficients this last expression is more complete than the expression chosen by Casal and Gouin (21). Lastly we give the inequalities that these five coefficients must verify :

$$\mu \geq 0 \qquad \mu + \beta \geq 0 \qquad \lambda \geq 0$$

$$\lambda + \gamma + \mu + 2\nu \geq 0 \qquad \lambda(\gamma + \mu - 2\beta) - (\beta + \nu)^2 \geq 0$$

3. MODELISATION OF THE INTERFACIAL LAYER

Let us consider a three-dimensional region where we have a mixture with n components. Inside it the gradients of the volumic masses of some components are very much larger than outside. We assume that this region is small in the directions of these large gradients. We define an interfacial layer as being such a region, with in addition the property that all the considered gradients have a preferential direction ξ. The lines of the field ξ are assumed to be straight and to define the normals to the interfacial layer.

The interfacial layer has a small thickness in this direction. In the case where the large gradients have different directions we then have a contact line or a contact point the study of which is in Ref. (25).

Let ϵ be the ratio of the space scales, δ^o and L^o, of the rate of volumic masses inside and outside the layer respectively ($\epsilon \ll 1$). Let ξ be the common direction of the density gradients inside the layer. The surfaces normal to ξ are surfaces of equal density for each constituent, and appear as parallel surfaces Σ.

We delimit the interfacial layer by two extreme parallel surfaces Σ_- and Σ_+ (Fig. 1) on which the gradients are small and such as the distance between Σ_- and Σ_+ is of order $\delta^o = \epsilon L^o$. Let S be an isodensity surface located inside the layer. We denote by ξ the normal co-ordinate to the surfaces Σ ; the equations of S, Σ_- and Σ_+ are $\xi = 0$, $\xi = \xi_-$ and $\xi = \xi_+$.

In a dynamic problem the interfacial layer is in motion. We denote by W^S the displacement velocity of the moving surface S. Let us remark that only the normal component $W_\perp^S$ of W^S is well defined. But for some presentation convenience which will appear later on, we give to W^S a tangential component $W_{//}^S$ which defines a motion of S on itself.

To each physical quantity f defined in the interfacial layer, we associate two interfacial quantities $\langle f \rangle$ and (f) :

(22)
$$\langle f \rangle = \int_{\xi_-}^{\xi_+} f \, d\xi \quad , \quad (f) = \left(f(\xi^+) - f(\xi^-) \right)$$

We define the interfacial mass ρ^s per unit of area and the material velocity $\mathbf{V}^s$ of the particles on the interface (Ishii [12]) by :

(23)
$$\rho^s = \langle \rho \rangle \qquad \rho^s \mathbf{V}^s = \langle \rho \mathbf{V} \rangle$$

We write down the classical conservation law for a quantity ψ per unit of volume, firstly in a local form, and secondly in an integral form for a volume V limited by the surface ∂V :

(24)
$$\frac{\delta}{\delta t} \psi + \psi \, \nabla . \mathbf{W} + \nabla . \left(\psi(\mathbf{V} - \mathbf{W}) + \mathbf{J} \right) = \Phi$$

(25)
$$\frac{\delta}{\delta t} \int_V \psi \, dv + \int_{\partial V} \left(\psi(\mathbf{V} - \mathbf{W}) + \mathbf{J} \right) . \mathbf{n} \, ds = \int_V \Phi \, dv$$

where $\mathbf{J}$ is the current density associated with the quantity ψ, and Φ the rate of source density per unit of volume. In the equation (24), V is a volume moving with the velocity field $\mathbf{W}$ which is defined in the whole space and which is equal to $\mathbf{W}^s$ on S (cf. Annex). We have denoted by $\mathbf{n}$ the outward unit normal to ∂V, and by $\delta/\delta t$ the time derivative associated with the velocity $\mathbf{W}$ ($\delta/\delta t = \partial/\partial t + \mathbf{W}.\nabla$).
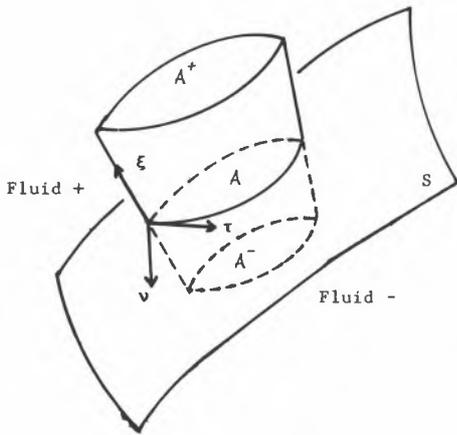
Let A be a piece of S moving with the velocity $\mathbf{W}^s$, and limited by the curve C. Along C we denote by ν the unit vector tangent to S, normal to C, and pointed outside of A, and by τ the tangent vector to C such as $\tau = \xi \wedge \nu$ (Fig. 4). We also introduce the surface A_ℓ generated by the normals to the surfaces of equal densities and leaning on C, and the pieces A_- and A_+ cutted on the surfaces Σ_- and Σ_+ by the lateral surface A_ℓ. We write the equation (24) for the thin volume V limited by the boundaries A_ℓ, A_- and A_+ :

Figure 4

(26)
$$\frac{\delta}{\delta t} \int_V \psi \, dv + \int_{A_\ell} \left(\psi(\mathbf{V} - \mathbf{W}) + \mathbf{J} \right) . \mathbf{n} \, ds$$
$$- \int_{A_-} \left(\psi(\mathbf{V} - \mathbf{W}) + \mathbf{J} \right) . \xi \, ds + \int_{A_+} \left(\psi(\mathbf{V} - \mathbf{W}) + \mathbf{J} \right) . \xi \, ds = \int_V \Phi \, dv$$

In order to introduce the interfacial quantities defined in (22), we are going to transform the integral expressions appearing in this last equation. In each point of the surface S we denote by $\mathbf{H}$ the three-dimensional tensor of order 2 associated with the second fundamental form (cf. Annex), and H the mean curvature. We shall limit our study to interfaces with a mean curvature of order L^o (or of order larger than L^o in order to consider plane inter-

faces). Let us remark that we have $\xi/L = 0(\varepsilon)$ at each point inside the interfacial layer. On these conditions we have :

(27)
$$\int_V f \, dv = \int_{\xi_-}^{\xi_+} d\xi \int_{A_\xi} f \, dA_\xi = \int_A \int_{\xi_-}^{\xi_+} f \, \det(\mathbb{1}_2 + \xi H) d\xi \, dA$$

$$= \int_A (\int_{\xi_-}^{\xi_+} f \, d\xi)(1 + 0(\varepsilon)) dA = (\int_A \langle f \rangle dA)(1 + 0(\varepsilon))$$

(28)
$$\int_{A_\ell} \mathbf{f.n} \, ds = \int_{\xi_-}^{\xi_+} d\xi \int_C \mathbf{f}.(\mathbb{1}_2 + \xi \, H).\nu \, d\ell$$

$$= \int_C ((\int_{\xi_-}^{\xi_+} \mathbf{f} \, d\xi).\nu) \, (1 + 0(\varepsilon)) d\ell = (\int_C \langle \mathbf{f}_{/\!/} \rangle.\nu \, d\ell)(1 + 0(\varepsilon))$$

(29)
$$\int_{A_\pm} \mathbf{f}.\xi \, ds = \int_{A_\pm} \mathbf{f}_\pm.\xi \, dA_\pm$$

$$= \int_A (\mathbf{f}_\pm.\xi) \, \det(\mathbb{1}_2 + \xi_\pm \, H) dA = (\int_A \mathbf{f}_\pm.\xi \, dA)(1 + 0(\varepsilon))$$

In the previous expressions, A_ξ is the section of the volume V by the S parallel surface of equation ξ = constante, dA_ξ and dA are the area elements on A_ξ and A, and $d\ell$ is the length element along C.

The scale for the space variations of the velocity field W is supposed of order L^0. Also we take $W = W^s \, (1 + 0(\varepsilon))$ in the interfacial layer. The time scales for the rate of variation of physical quantities are supposed to be of the same order inside and outside the layer. Finally, at the order 0 in ε, the equation (26) is written in the following form :

(30)
$$\frac{\delta}{\delta t} \int_A \langle \psi \rangle \, dA + \int_C \langle \psi(V - W^s) + J \rangle_{/\!/}.\nu \, d\ell$$

$$+ \int_A (\psi(V - W^s) + J)_\perp \, dA = \int_A \langle \Phi \rangle \, dA$$

where we denote the expression $(\mathbf{f}).\xi$ by $(\mathbf{f})_\perp$.

In the source term due to the adjacent media - and + (third term in the left hand) only the normal velocity $W_\perp^s$ of the displacement of the interface S does appear. On the other hand, in the curvilinear integral the velocity W^s appears through its tangential component $W_{/\!/}^s$ only. From now on, we specify $W_{/\!/}^s$ and we take it equal to the tangential component $V_{/\!/}^s$ of the material velocity V^s. This choice has been proposed by Ishii [12] for the first time. We have

(31)
$$\langle \psi(V - W^s) + J \rangle_{/\!/} = \langle \psi(V - V^s) + J \rangle_{/\!/}$$

This interfacial current density is a vector tangent to S. In $\langle \psi(V - V^s) + J \rangle_{/\!/}$ we have two contributions : the first one is related to the agitation of the fluid particles about the mean velocity $V_{s/\!/}$ and the second one corresponds to the mean value of $J_{/\!/}$ in the layer. This expression for the interfacial current will be validated in the next section when we shall present the interfacial mass balance law. The interfacial mass current density is zero only if $W_{/\!/}^s = V_{/\!/}^s$. This choice leading to a zero mass current is only possible because we approximate all the expressions at the order 0 in ε. Finally we write the interfacial balance equation in the following integral form :

(32)
$$\frac{\delta}{\delta t} \int_A \langle \psi \rangle \, dA + \int_C \langle \psi(\mathbf{V} - \mathbf{V}^S) + \mathbf{J} \rangle_{/\!/} \cdot \mathbf{v} \, d\ell$$

$$+ \int_A \left(\psi(\mathbf{V} - \mathbf{W}^S) + \mathbf{J} \right)_{\perp} dA = \int_A \langle \Phi \rangle \, dA$$

We obtain the local balance law by classical techniques using the surface divergence theorem and the surface transport theorem (we have recalled these theorems in Annex) :

(33)
$$\frac{\overset{\cdot}{\delta}_s}{\delta t} \langle \psi \rangle + \langle \psi \rangle \, \nabla_s \cdot \mathbf{W}^S + \nabla_s \cdot \langle \psi(\mathbf{V} - \mathbf{V}^S) + \mathbf{J} \rangle_{/\!/}$$

$$= - \left(\psi(\mathbf{V} - \mathbf{W}^S) + \mathbf{J} \right)_{\perp} + \langle \Phi \rangle$$

The new notations used in (33) are defined in Annex. This last balance law for the interfacial quantity $\langle \psi \rangle$ contains two source terms in the right hand ; the first one gives the contribution of the media - and + to the interfacial medium. We can read the equation (33) as an evolution equation for the quantity $\langle \psi \rangle$, but also as an equation for the jump $\left(\psi(\mathbf{V} - \mathbf{W}^S) + \mathbf{J} \right)_{\perp}$ between the two fluids - and +. In the latter case, we have boundary conditions for the two fluids, and these must be written on the surface S ; it is enough to know the macroscopic position of the surface S, an ε order term apart.

We already have said that in many works the interfacial balance laws are postulated in integral form (16), (17), (18) where the time derivative $\delta/\delta t$ is associated with the material velocity $\mathbf{V}^S$ instead of being defined with the velocity $\mathbf{W}^S$ as here.

An alternative method to obtain the equation (33) consists in multiplying each member of the local balance law (24) by the elementary volume $d\xi dA_\xi$, and in integrating the so deduced equation on the thickness of the layer (9).

Let us consider the local balance law (24) available in all the space. Let us substract from it the local balance law for the fluid - occupying all the region $R_- \cup R_-'$ and similarly the balance law for the fluid +. By integrating the corresponding result on the thickness of the layer, the interfacial quantities in excess, as defined in the introduction, then appear. Then we obtain balance laws for these quantities in excess (27).

4. INTERFACIAL BALANCE LAWS

In this section, by using the modelisation proccess presented in the last section, we write the interfacial balance laws for constituent masses, momentum, energy and entropy. We analyse the order of magnitude of the different terms in these equations and we construct a model for an interface without mass but possibly with accumulation of some surfactants.

First, we rewrite in a condensed form the two equations (24) and (33). Notice that the equation (24) is also valid on the both sides of the interfacial layer :

(34)
$$\frac{\delta}{\delta t} \psi + \psi \, \nabla \cdot \mathbf{W} + \nabla \cdot \Phi = \Phi$$

(35)
$$\frac{\delta_s}{\delta t} \langle \psi \rangle + \langle \psi \rangle \, \nabla_s \cdot \mathbf{W}^S + \nabla_s \cdot \langle \Phi \rangle_{/\!/} + \left(\Phi \right)_{\perp} = \langle \Phi \rangle$$

Let t^o be the characteristic time of the system, ψ^o the characteristic magnitude of ψ outside the interfacial layer, and L^o the characteristic length for the rates outside

the interfacial layer. We assume all the terms in the equation (34) to be of the same order ψ^o/t^o, so that ϕ is of order $\psi^o L^o/t^o$. We restrict our study to the order 0 in ε. So in the equation (35) we take no care of the terms of magnitude order lower than $\psi^o L^o/t^o$ (order of $\phi^+.\xi$ and $\phi^-.\xi$). We can neglect in $\langle\psi\rangle$ the terms of magnitude order lower than $\psi^o L^o$, in $\langle\phi\rangle_{/\!/}$ these of magnitude order lower than ψ^o/t^o and in $\langle\Phi\rangle$ these of magnitude order lower than $\psi^o L^o/t^o$. Particularly if ψ is also of order ψ^o inside the interfacial layer, then $\langle\psi\rangle$ is order $\varepsilon\psi^o L^o$ and is neglected. Similarly if Φ is everywhere of order ψ^o/t^o, then $\langle\Phi\rangle$ is order $\varepsilon\psi^o L^o/t^o$ and is neglected.

We do the following assumption : ψ is order ψ^o at one and the same time inside and outside the interfacial layer if the volumic quantity, ψ represents the total mass, the momentum, the kinetic energy and the external source densities. This assumption is released if ψ represents the internal energy, the entropy and a priori the partial volumic masses of each constituent.

4.1. Balance law of masses

From the equation (3) and by using the formalism of section III we obtain for the i-constituent :

$$(36) \qquad \frac{\delta_s}{\delta t}(\rho^{is}) + \rho^{is}\,\nabla_s.\mathbf{W}^s + \nabla_s.\mathbf{J}^{is} + \left(\rho^i(\mathbf{V} - \mathbf{W}^s) + \mathbf{J}^i\right)_\perp = 0$$

with
$$\rho^{is} = \langle\rho^i\rangle \quad , \quad \mathbf{J}^{is} = \langle\rho^i(\mathbf{V} - \mathbf{W}^s) + \mathbf{J}^i\rangle_{/\!/} \ .$$

By adding the equations (36) and by using the definition of $\mathbf{W}^s_{/\!/}$: $\langle\rho(\mathbf{V} - \mathbf{W}^s)\rangle_{/\!/} = 0$, we have

$$(37) \qquad \frac{\delta_s}{\delta t}\rho^s + \rho^s\,\nabla_s.\mathbf{W}^s + \left(\rho(\mathbf{V} - \mathbf{W}^s)\right)_\perp = 0$$

with $\rho^s = \langle\rho\rangle$.

Let ρ^o and c^{io} be the characteristic magnitude for the total mass density and the concentration of the i-component outside the interfacial layer. We assume ρ of order ρ^o everywhere. So we can consider that ρ^s is zero in the equation (37) : there is no accumulation for the total mass on the interface. For some components, c^{io} may be of order ε at least, and inside the layer c^i may be of order c^{io}/ε. Then ρ^i is of order $\rho^o c^{io}/\varepsilon$ inside the interfacial layer and it is not possible to neglect ρ^{is} in the equation (36). We can write the equation (37) in the classic form of a mass balance law through a discontinuity surface

$$(38) \qquad \left(\rho(\mathbf{V} - \mathbf{W}^s)\right)_\perp = 0$$

Then we denote by $\dot{m}$ the mass transfer per unit of area : $\dot{m} = \rho^+(\mathbf{V}^+ - \mathbf{W}^s).\xi = -\bar{\rho}(\mathbf{V}^- - \mathbf{W}^s).\xi$.

Lastly, according to whether the **interfacial** density ρ^{is} is neglected or not in the equation (36), the latter becomes either an equation for the jump of $\mathbf{J}^i$ or an equation for the evolution of the surfactant quantity ρ^{is}.

4.2. Interfacial balance of momentum

Integrating the equation (12) for the momentum balance we have :

(39)
$$\frac{\delta_s}{\delta t}(g^s) + g^s \nabla_s . w^s + \left(g \otimes (v - w^s) - \mathcal{T}\right)_\perp - \nabla_s . \overline{\mathcal{T}}^s = f^{sext}$$

with
$$g^s = \langle g \rangle = \langle \rho \ v \rangle \quad ; \quad f^{sext} = \langle f^{ext} \rangle$$

$$\mathcal{T}^s = \langle \mathcal{T} - g \otimes (v - v^s) \rangle_{/\!/}$$

We assume that v is of order L^o/t^o everywhere and f^{ext} of order $\rho^o L^o/t^{o2}$. Then

$$g = \frac{\rho^o L^o}{t^o} 0(1) \quad , \quad g^s = \varepsilon \frac{\rho^o L^{o2}}{t^o} 0(1) \quad , \quad f^{sext} = \varepsilon \frac{\rho^o L^{o2}}{t^{o2}} 0(1) \ ,$$

$$\langle g \otimes (v - w^s) = \varepsilon \frac{\rho^o L^{o3}}{t^{o2}} 0(1) \ .$$

So the equation (39) becomes :

(40)
$$\left(\mathcal{T} - g \otimes (v - w^s)\right)_\perp + \nabla_s . \overline{\mathcal{T}}^s = 0$$

with
$$\mathcal{T}^s = \langle \mathcal{T} \rangle_{/\!/}$$

Let 0 be a fixed point of the space and let $X = \overrightarrow{OM}$ be the position vector of every point M. With the notations defined in Annex, the three-dimensional balance law for the moment at the point 0 of momentum is :

(41)
$$\frac{\delta}{\delta t}(X \wedge g) + (X \wedge g) \nabla . w - \nabla . \overline{(X \wedge (\mathcal{T} - g \otimes (v - w)))} = X \wedge f^{ext}$$

This equation is equivalent to the symmetry of $\mathcal{T}$; it is integrated in :

(42)
$$\frac{\delta_s}{\delta t}\langle X \wedge g \rangle + \langle X \wedge g \rangle \nabla_s . w^s - \nabla_s . \overline{\langle X \wedge (\mathcal{T} - g \otimes (v - w)) \rangle}_{/\!/} =$$

$$\langle X \wedge f^{ext} \rangle + \left(X \wedge (\mathcal{T} - g \otimes (v - w^s))\right)_\perp$$

Let us choose a point 0 such that the distance between 0 and the interfacial layer is of order L^o. Retaining only the terms of order $\rho^o L^{o3}/t^{o2}$, the equation (42) becomes

(43)
$$\nabla_s . \langle X \wedge \mathcal{T} \rangle_{/\!/} + \left(X \wedge (\mathcal{T} - g \otimes (v - w^s))\right)_\perp = 0$$

Let M^s be the common point of the surface S and of the interface normal on which the integration is performed and let X^s be the vector $\overrightarrow{OM}^s$. We have $X = X^s + (X - X^s)$ with $X = L^o \ 0(1)$ and $X - X^s = \varepsilon L^o \ 0(1)$. So, at the order 0 in ε the last equation (43) is written

$$\nabla_s . \overline{(X^s \wedge \mathcal{T}^s)} + X^s \wedge \left(\mathcal{T} - g \otimes (v - w^s)\right)_\perp = 0$$

or if we use the equation (40)

$$\nabla_s . \overline{\mathbf{X}^s \wedge \tau^s} - \mathbf{X}^s \wedge \nabla_s . \overline{\tau^s} = 0$$

This last equation is equivalent to the symmetry of the tensor $\tau^s . \nabla_s \mathbf{X}^s$. In Annex we have introduced the projection tensor $\mathbb{P}$ on the surface S and we have $\nabla_s \mathbf{X}^s = \mathbb{P}$. Therefore

$$\tau^s = \tau^s . \mathbb{P} = \mathbb{P} . \tau^s$$

In conclusion, using the assumptions on the orders of magnitude for the volumic mass and for the velocity inside the interfacial layer, we have at the order 0 in ε :

$$\tau^s \quad \text{symmetric and} \quad \tau^s . \xi = \xi . \tau^s = 0$$

The tensor τ^s is called the interfacial stress tensor ; it is symmetric tensor and it transforms a vector tangent to S in a vector tangent to S. This form for τ^s is postulated in the book of Barrère and Prud'homme (16) ; a proof for it is given in the paper of Bedeaux, Albano and Mazur (20) in the case of a singular surface without mass, and also in the paper of Daher and Maugin (19).

Here this form of tensor τ^s is deduced for an interface without mass in an approximation of order 0 in ε. Let us notice that, when g^s is not neglected, this property for τ^s is no longer true, even in an approximation of order 0 in ε (25).

4.3. Interfacial balance of energy

We denote by e_c the kinetic energy per unit of volume ($e_c = \frac{1}{2} \rho \mathbf{V}^2$) and by e the total energy ($e = u + e_c$). By using the equations (3), (12) and (14) we can write the three dimensional balance law for the total energy e

(44) $$\frac{\delta}{\delta t} e + e \nabla . \mathbf{W} + \nabla . (\mathbf{q} - \tau . \mathbf{V} - \mathbf{E} + e(\mathbf{V} - \mathbf{W})) = r + \mathbf{f}^{ext} . \mathbf{V}$$

Let us recall the assumptions made on the orders of magnitude of ρ, $\mathbf{V}$, $\mathbf{f}^{ext}$, r inside the interfacial layer, namely that they are the same inside and outside the layer. In the associated interfacial balance law we can neglect the terms $\langle e_c \rangle$, $\langle e_c (\mathbf{V} - \mathbf{W}^s) \rangle$, $\langle r \rangle$, $\langle \mathbf{f}^{ext} . \mathbf{V} \rangle$.

We assume that at the order 0 in ε, the quantities $\sum_j \lambda^{ij} \nabla^j \rho$ are zero outside the interfacial layer. So we have

$$\left(\sum_{i=1}^{n} \sum_{j=1}^{n} \lambda^{ij} (\nabla . \mathbf{J}^i + \rho^i \nabla . \mathbf{V}) \nabla \rho^j \right)_{\perp} = 0$$

The gradients $\nabla \rho^i$ have been assumed to be parallel to the vector ξ normal to the interface :

$$\left\langle \sum_{i=1}^{n} \sum_{j=1}^{n} \lambda^{ij} (\nabla . \mathbf{J}^i + \rho^i \nabla . \mathbf{V}) \nabla \rho^j \right\rangle_{/\!/} = 0$$

Due to equation (15), the two last equations give :

$$(\mathbf{E})_{\perp} = \left(\sum_{i=1}^{n} \mu'^i \mathbf{J}^i \right)_{\perp} \quad , \quad \langle \mathbf{E} \rangle_{/\!/} = \left\langle \sum_{i=1}^{n} \mu'^i \mathbf{J}^i \right\rangle_{/\!/}$$

We put :

$$u^s = \langle u \rangle \quad , \quad \mu^{is} = \frac{1}{\rho^{is}} \langle \rho^i \mu'^i \rangle \quad , \quad \mathbf{V}^{is} = \frac{1}{\rho^{is}} \langle \rho^i \mathbf{V}^i \rangle$$

$$\mathbf{q}^s = \langle \mathbf{q} - \mathbf{\tau}.(\mathbf{V} - \mathbf{V}^s) + (u - \sum_{i=1}^{n} \mu'^i \rho^i)(\mathbf{V} - \mathbf{V}^s) + \sum_{i=1}^{n} \mu'^i \rho^i(\mathbf{V}^i - \mathbf{V}^{is}) \rangle_{//}$$

By integrating the equation (44) on the thickness of the interfacial layer, by using the approximations and the definitions previously given, and also the equations (38) and (40) we are led to the following result :

(45)
$$\frac{\delta_s}{\delta t} u^s + u^s \nabla_s.\mathbf{W}^s + \nabla_s.\mathbf{q}^s + \nabla_s.\sum_{i=1}^{n} (\mu^{is} J^{is}) - \mathbf{\tau}^s : \nabla_s \mathbf{W}^s +$$

$$\left(\mathbf{q} - \mathbf{\tau}.(\mathbf{V} - \mathbf{W}^s) + (u + \frac{1}{2} \rho(\mathbf{V} - \mathbf{W}^s)^2)(\mathbf{V} - \mathbf{W}^s) + \sum_{i=1}^{n} (\mu'^i J^i) \right)_{\perp} = 0$$

The vector $\mathbf{q}^s$ is called the interfacial heat current ; its definition takes into account the integrated value of $\mathbf{q}$ in the layer and the agitation of the fluid particles about the mean velocity $\mathbf{V}_{//}^s$. This agitation gives a contribution to $\mathbf{q}^s$ through the stresses, the internal energy and the chemical potentials of the continuum in the layer.

4.4. Interfacial balance of entropy. Dissipation

We put $s^s = \langle s \rangle$, $\sigma^s = \langle \sigma \rangle$. By integrating the equation (16) on the thickness of the interfacial layer we obtain the following interfacial balance for the entropy

(46)
$$\frac{\delta_s}{\delta t} (s^s) + s^s \nabla_s.\mathbf{W}^s + \nabla_s.\langle \frac{\mathbf{q}}{T} + s(\mathbf{V} - \mathbf{V}^s) \rangle_{//} +$$

$$\left(\frac{\mathbf{q}}{T} + s(\mathbf{V} - \mathbf{W}^s) \right)_{\perp} = \langle \frac{r}{T} \rangle + \sigma^s \quad ; \quad \sigma^s \geq 0$$

Let T^o be a characteristic temperature for the system. We assume T to be of order T^o inside and outside the layer. In the equation (46) we only retain the terms of order $\rho^o L^{o3}/(t^{o3} T^o)$, and so we neglect $\langle r/T \rangle$.

One meets some trouble to define the temperature T^s of the interface. Some tentative studies do exist (7), (20) but the discussion on this point is not closed. In general the existence of a value for the temperature is postulated (12), (16), (17) ; let us draw attention to the discussion given by Delhaye (17).

From now on we assume that there exists an interfacial temperature T^s such that $\langle (\mathbf{q}/T) + s(\mathbf{V} - \mathbf{V}^s) \rangle_{//} = (\mathbf{q}^s/T^s)$. Therefore the equation (46) is written

(47)
$$\frac{\delta_s}{\delta t} s^s + s^s \nabla^s.\mathbf{W}^s + \nabla^s.(\frac{\mathbf{q}^s}{T^s}) + \left(\frac{\mathbf{q}}{T} + s(\mathbf{V} - \mathbf{W}^s) \right)_{\perp} = \sigma^s$$

As usual we adopt the classical relation of Gibbs on the interface

(48)
$$du^s = T^s ds^s + \sum_i \mu^{is} d\rho^{is}$$

We are aware that this relation is suspicious even if it is very often used (12), (27) ... Let us notice that Gogosov et al. (13) deduce a more complicated relation than (48) from a microscopic analysis of the layer.

The adequate combination of the equations (38), (45), (47) and (48) gives the following

result for the interfacial dissipation

$$(49) \quad T^s \sigma^s = (\tau^s + p^s \, \mathbb{I}_2) : \nabla_s \, W^s + T^s \, q^s . \nabla_s (\frac{1}{T^s}) - \sum_{i=1}^{n} J^{is} . \nabla_s \, \mu^{is}$$

$$+ T^s (q(\frac{1}{T} - \frac{1}{T^s}))_\perp - \sum_{i=1}^{n} (J^i(\mu^i - \mu^{is}))_\perp$$

$$+ (\tau.(V - W^s))_\perp + ((T^s \, s - u + \sum_{i=1}^{n} \mu^{is} \rho^i + \frac{1}{2} \, (V - W^s)^2)(V - W^s))_\perp$$

with
$$p^s = T^s \, s^s - u^s + \sum_{i} \mu^{is} \rho^{is} \, .$$

We introduce the tensors of the viscous stresses on the both sides of the interface : $\Pi = \tau + p \, \mathbb{I}_2$ with $p = Ts - u + \sum_i \mu^i \rho^i$. Then the last two terms of the equation (49) are written in the form

$$(\Pi.(V - W^s)_{/\!/})_\perp + \dot{m} \, \frac{\xi.\Pi.\xi}{\rho} + \frac{s}{\rho}(T^s - T) + \sum_{i=1}^{n} \frac{\rho^i}{\rho} \, (\mu^{is} - \mu^i) + \frac{1}{2} \, (V - W^s)^2)_\perp$$

Finally we can take this expression for the dissipation and use the linear thermodynamic theory of the irreversible proccesses (26). So we can obtain general form for the interfacial constitutive laws (25). A similar work is found in the References (20) and (27).

4.5. __The equation set in a particular case__

We pay attention to the equation set in a particular case. Let us consider an interface dividing two immiscible fluids, the constituents 1 and 2. A small quantity of a surfactant (the constituent 3) is soluble in the two fluids 1 and 2. The fluids 1 and 2 occupy the regions + and - of the previous theory. The equations (38), (36) and (40) become

$$(50) \quad v^+_\perp = v^-_\perp = W^s_\perp \, ,$$

$$\dot{m} = 0 \quad \text{there is no mass transfer}$$

$$(51) \quad \frac{\delta_s}{\delta t} \rho^{3s} + \rho^{3s} \, \nabla_s . W^s + (J^3)_\perp + \nabla_s . J^{3s} = 0$$

$$(52) \quad (\tau)_\perp + \nabla_s . \tau^s = 0$$

Furthermore we assume the interface to be in thermal equilibrium with an uniform temperature and all the heat currents to be equal to zero. So the equation (49) becomes

$$(53) \quad T^s \sigma^s = (\tau^s + p^s \, \mathbb{I}_2) : \nabla_s \, W^s + J^{3s} . \nabla_s \, \mu^{3s}$$

$$+ (J^3(\mu^3 - \mu^{3s}))_\perp + (\Pi.(V - W^s)_{/\!/})_\perp$$

Moreover, if we suppose that the chemical and intrinsic dissipations are uncoupled, then the interfacial constitutive laws have the following form :

$$(54) \quad \tau^s = - p^s \, \mathbb{I}_2 + \lambda \, \nabla_s . W^s \, \mathbb{I}_2 + \mu(\nabla_s \, W^s + \overline{\nabla_s \, W^s})$$

$$(55) \quad \begin{aligned} (\mathbf{v}^+ - \mathbf{w}^s)_{/\!/} &= a \; \xi.\Pi^+_{/\!/} + b \; \xi.\Pi^-_{/\!/} \\[6pt] (\mathbf{v}^- - \mathbf{w}^s)_{/\!/} &= b \; \xi.\Pi^+_{/\!/} + c \; \xi.\Pi^-_{/\!/} \end{aligned}$$

$$\mathbf{J}^{3s} = K \; \nabla_s \; \mu^{3s}$$

$$(56) \quad \begin{aligned} \mathbf{J}^{3+}.\xi &= k^+(\mu^{3+} - \mu^{3s}) + \ell(\mu^{3-} - \mu^{3s}) \\[6pt] \mathbf{J}^{3-}.\xi &= \ell(\mu^{3+} - \mu^{3s}) + k^-(\mu^{3-} - \mu^{3s}) \end{aligned}$$

In the first law (54) we have two positive coefficients, μ is called the interfacial shear viscosity and $2\lambda + 2\mu$ the interfacial viscosity of surface dilatation. The equations (55) appear as the friction laws on the interface with the friction coefficients a, c and b ; the coefficients a and c are positive and the couple coefficient b is such that $b^2 \le ac$. At last the equations (56) are laws for the diffusion and the absorption of the surfactant and we have K, k^+, k^- positive and $\ell^2 \le k^+ k^-$.

5. CONCLUSION

In conclusion we recall that the interfaces are seen as three-dimensional layers with a small thickness. In order to shrink the layer and to obtain a discontinuity surface carrying material properties, we introduce an integration proccess through the layer. The true interfacial quantities are defined and it is easy to obtain the balance laws of masses, momentum, energy and entropy. Let us notice that we can introduce the excess interfacial quantities and that we can obtain the balance laws of masses, momentum and energy in a similar manner. But it is not possible to derive a balance law for entropy by the same way (we cannot substract two inequalities). This remark gives the reason why we have prefered the true interfacial quantities.

Lastly let us emphasize the yet unsolved difficulties related to the definition of an interfacial temperature. An other question concerns the validity of the usual interfacial Gibbs relation.

ANNEX

Notations

We use in a systematic way the dyadic notations as they are defined, for instance, in the book of Chapman and Cowling (28) that we recall here. In the oriented three-dimensional Cartesian space E we only use orthonormal frames of the same orientation. The components of tensor of order 1 (or vector) $\mathbf{A}$, of order 2, $\mathbb{A}$, or of order 2, $\mathbb{B}$, are denoted by A_i, A_{ij}, B_{ijk} where the indexes take the values 1, 2 or 3. The gradient operator is a formal vector with components $\partial_i = \partial/\partial x_i$, where $\mathbf{X}$ is the position vector in E.

The "simple product" of two tensors is denoted with one dot, the "double product" with two dots and the "triple product" with three dots :

$$\mathbf{A}.\mathbf{B} = A_i \; B_i \quad , \quad (\mathbb{A}.\mathbf{A})_i = A_{ij} \; A_j \quad ,$$

$$(\mathbf{A}.\mathbf{A}')_{ij} = A_{ik} A'_{kj} \quad , \quad \mathbf{A} : \mathbf{A}' = A_{ij} A'_{ji} \quad ,$$

$$\mathbf{B} : \mathbf{B}' = B_{ijk} B'_{kji} \quad , \quad \nabla.\mathbf{A} = \partial_i A_i \quad ,$$

$$(\nabla.\mathbf{A})_i = \partial_j A_{ji} \quad , \quad \nabla\nabla : \mathbf{A} = \partial_i(\partial_j A_{ji}) \; .$$

The tensorial product is denoted by the symbol $\otimes$ which is missed out when no confusion is possible. Let $\mathbf{A}$ be a tensor of order two. The conjugate tensor is denoted by $\overline{\mathbf{A}}$. Lastly $\mathbf{X} \wedge \mathbf{A}$ represents the tensor of order two with the components $\varepsilon_{i\ell k} x_k A_{\ell j}$ where ε_{ijk} are the components of the orientation tensor of the three-dimensional space.

Mean curvature of a surface

Let S be a surface in E defined by the equation $F(\mathbf{X}) = 0$. The surface S divides the space into two regions $F > 0$ and $F < 0$. The unit vector $\xi = \nabla F/|\nabla F|$ is normal to S and points toward the region $F > 0$. The mean curvature H satisfies $\nabla.\xi = -2H$ (H is negative when the surface S has its convex side in the direction of the region $F > 0$, and positive in the opposite case).

In each point of S we consider the curvature tensor associated with the second fundamental form ; its expression in the orthonormal frame defined by the principal directions of S, is the following

$$\begin{pmatrix} 1/R_1 & 0 \\ 0 & 1/R_2 \end{pmatrix}$$

where R_1 and R_2 are the two principal curvature radii. We construct a three-dimensional tensor $\mathbb{H}$ as being the tensor with the components

$$\begin{pmatrix} 1/R_1 & 0 & 0 \\ 0 & 1/R_2 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

in the orthonormal frame defined by the two principal directions of S and the normal vector ξ.

Surface divergence theorem

Let $\mathbf{B}$ be a vector field defined in E. Let A be a part of S limited by the curve C. Along C we denote by ν the unit vector tangent to S, normal to C and pointing out of A, and by τ the tangent vector to C such that $\tau = \xi \wedge \nu$ (Fig. 4). We have :

$$\int_C \mathbf{B}.\nu \; d\ell = \int_C \mathbf{B}.(\tau \wedge \xi)d\ell = \int_C (\xi \wedge \mathbf{B}).\tau \; d\ell = \int_A \{\nabla \wedge (\xi \wedge \mathbf{B})\}.\xi \; dA$$

where one uses the classical theorem of Stokes. If L represents the operator such that $L(\mathbf{B}) = \{\nabla \wedge (\xi \wedge \mathbf{B})\}.\xi$, it is easy to verify that :

$$L(\mathbf{B}) \;=\; (\mathbb{1}_2 - \xi\,\xi) : \nabla\,\mathbf{B} - (\nabla.\xi)(\mathbf{B}.\xi)$$

where $\mathbb{1}_2$ is the unit tensor of order two. Let us remark that the operator L is the operator denoted by X in Barrère and Prud'homme (16).

We introduce the following notation :

$$\mathbb{P} = \mathbb{1}_2 - \xi\,\xi \quad,\quad \text{projection operator on S } (\mathbb{P} = \overline{\mathbb{P}} = \mathbb{P}^2) \;,$$

$$\mathbf{B} = \mathbf{B}_{/\!/} + \mathbf{B}_{\perp} \quad \text{with} \quad \mathbf{B}_{/\!/} = \mathbb{P}.\mathbf{B} = \mathbf{B}.\mathbb{P} \quad,\quad \mathbf{B}_{\perp} = (\mathbf{B}.\xi)\xi \;,$$

$$\mathbf{A}_{/\!/} = \mathbf{A}.\mathbb{P} \quad \text{where} \quad \mathbf{A} \text{ is a tensor or order 2 or more,}$$

$$\nabla_s.\mathbf{B} = \mathbb{P} : \nabla\,\mathbf{B} \quad,\quad \text{surface divergence of } \mathbf{B}\;.$$

$$\nabla_s f = \mathbb{P}.\nabla f \quad,\quad \text{surface gradient of } f\;.$$

So we have

$$L(\mathbf{B}_{\perp}) \;=\; 0 \quad,\quad \nabla.\xi = \nabla_s.\xi$$

$$L(\mathbf{B}) \;=\; L(\mathbf{B}_{/\!/}) \;=\; \nabla_s.\mathbf{B}_{/\!/}$$

With the introduced notations the surface divergence is written :

$$\int_C \mathbf{B}.\nu\; d\ell \;=\; \int_A \nabla_s.\mathbf{B}_{/\!/}\; dA$$

Surface transport theorem

Let us suppose the surface S in motion and let us denote by $\mathbf{W}^S$ its displacement velocity. The equation of S is now $F(\mathbf{X},t) = 0$ and $\mathbf{W}^S$ satisfies the relation $\mathbf{W}^S.\xi = -(\partial F/\partial t)/|\nabla F|$. We define the velocity $\mathbf{W}$ in each point M of E by using the relation $\overrightarrow{OM} = \overrightarrow{OP} + PM\,\xi$ where the point P is the orthogonal projection of M on surface S.

Let us recall the transport theorem on a surface as it is given, for instance, in the book of Germain (29) and where the notation $\delta_s/\delta t$ is used to mention that the surface S is moving with the velocity $\mathbf{W}^S$:

$$\frac{\delta}{\delta t} \int_A \mathbf{B}.\xi\; dA = \int_A \left\{ \frac{\delta\mathbf{B}}{\delta t} + \mathbf{B}\,\nabla.\mathbf{W} - \mathbf{B}.\nabla\,\mathbf{W} \right\}.\xi\; dA$$

With $\mathbf{B} = f\,\xi$ it is easy to obtain

$$\frac{\delta}{\delta t} \int_A f\; dA \;=\; \int_A \left\{ \frac{\delta f}{\delta t} + f\,\nabla.\mathbf{W} - f\,\xi.(\nabla\,\mathbf{W}).\xi \right\}\; dA$$

or

$$\frac{\delta}{\delta t} \int_A f\; dA \;=\; \int_A \left(\frac{\delta_s t}{\delta t} + f\,\nabla_s.\mathbf{W}^S \right) dA$$

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