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MOTIONS IN LIQUID-VAPOUR INTERFACES BY USING A CONTINUOUS MECHANICAL MODEL

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ABSTRACT. By using a limit analysis for the motion equations of viscous fluid endowed with internal capillarity, we are able to propose a dynamical expression for the surface tension of moving liquid-vapour interfaces without any phenomenological assumption. The proposed relation extends the static case, yields the Laplace formula in cases of mass transfer across interfacial layers and allows to take the second coefficient of viscosity of compressible fluids into account. We generalize the Maxwell rule in dynamics and directly explain the Marangoni effect.

Dedicated to Professor Giuseppe Grioli on the occasion of his 100th birthday

1. Introduction

Far from the critical point of a fluid, experimental studies and spectrography measurements point out that liquid-vapour interfaces have a thickness of nanometer range and, in the vicinity of the layer, vapour and liquid are homogeneous [1, 2, 3, 4]. To model liquid-vapour interfaces, the kinetic theory of gases proposes fluid equations of state as, for example, van der Waals' [5, 6]. These equations are correct, more precisely they satisfy the Maxwell rule associated with the isothermal change of phases [7]. Nonetheless, they present two main defaults:
For fluid densities between vapour and liquid, the pressure can be negative, but simple experiments reveal the existence of pressures corresponding to traction in the fluid. In the domain between vapour and liquid, the internal energy cannot be represented as a convex surface of the density and entropy; this fact seems in contradiction with the existence of two-phase matter states in stable equilibria [8, 9].
To remove these disadvantages, the thermodynamics usually replaces the non-convex part of the surface energy by a plane domain; but the fluid is not any more a continuum: the interfacial domain is represented by a material surface without thickness. Numerous studies related as well to fluid mechanics as to thermodynamics interpret interfaces as surfaces of discontinuity between two media: a liquid-vapour interface is usually schematized by a material surface endowed with a superficial energy. This surface behaves as an autonomous one [10, 11, 12, 13]. But, this representation is not able to study the dynamical behavior of the interface more precisely than a surface of discontinuity and forgets its internal structure.

In equilibrium case, it is possible to correct the disadvantages by a convenient modification of the stress tensor; in the capillary layer its expression is anisotropic; the energy of the continuous medium must be modified. This *internal capillarity* model is a dynamical theory relevant of second gradient theory which came from van der Waals and Korteweg [14, 15] and was revisited by Cahn and Hilliard [16]. The model is compatible with the second law of thermodynamics [17]. The representation of the internal energy as a function of the entropy, density and density gradient allows to identify the isothermal case with a model deduced from molecular theories [18, 19]. The model is analog to the classical Landau-Ginzburg theory for second order transition [20]. Far from the critical point the model is qualitative. Nevertheless, it is a lot more advantageous than the model of Newtonian viscous fluids which is not able to take account of layers with a strong gradient of density. Because we do not consider bubbles and droplets of radius of some nanometers, the mean surface of interface is of large dimension with respect to its interfacial thickness [21]; it is necessary to take account of the different orders of lengths of our problem: the interfacial layer is of nanometer range, but the radii of curvature of interfaces are microscopic. The surface tension is obtained thanks to the integration across the capillary layer; it is not necessary uniform along the interface and depends on the dynamical distributions of density and temperature. These distributions take account of motion equations with a Navier-Stokes-like viscosity [22]. At a given temperature, the viscosity coefficients μ and η depend on the density (μ is the dynamic viscosity, and η is the second coefficient or shear coefficient of viscosity). For an incompressible fluid, the term involving η drops out from the equation; obviously it is not the case through fluid interfaces. We do not assume any special property on the viscosity coefficients which may strongly vary through the interface but they are bounded. The dissipative function must have a bounded integral through the capillary layer and the tangential components of the velocity field are continuous through the layer [23]. When the temperature distribution is non-uniform along the interface, the surface tension gradients create a motion along the capillary layer: this is the so-called Maragoni's effect [12]. Thanks to a limit analysis taking account of the length ranges of the interface, we are able to model the Marangoni effect along the interfaces. No special energy of interface is necessary. When the mass flow across interface is non-zero, we get a dynamical expression of the Laplace formula.

The proposed method is completely different from the classical calculation founded on balance equations through a surface of discontinuity where the variation of density appears only with a jump through the interface and when it is necessary to define physical surface quantities as mass or entropy per unit of area. Our study is related to interfaces with simple motions. The calculations are performed in the capillary layer as in a three-dimensional continuous medium; then, we consider the limit case when the interfacial thickness goes towards zero and consequently all the bounded expressions have a null integral through the layer [24]. We assume that the fluid velocity is bounded together with its partial derivatives with respect to the coordinates tangent to the interface.

The model of internal capillarity allows us to obtain a better understanding of dynamical liquid-vapour interfaces and answer to the question: is the fluid at the interface rigid or moving [25]? The fluid behavior is different from the classical thermodynamics of Newtonian fluids: a supplementary term similar to a heat flux one appears in the equation of

energy [26, 27]. An integral invariant for motions compatible with the interface consists in a generalization of the Maxwell rule for isothermal liquid-vapour phase transition.

In Section 2, we resume the properties of capillary fluids and we develop the fluid motions in liquid-vapour interfaces in Sections 3 to 5. A concluding remark focuses on the second coefficient of viscosity. For the sake of simplicity, all intermediate calculations are proposed in Appendices as well as some notations.

2. Equations of motions of viscous fluid endowed with internal capillarity

Recall the main results of a fluid with internal capillarity [18, 28]. We introduce only the specific free energy as a function of the density ρ, temperature T and $\operatorname{grad}\rho$

$$\varepsilon = \varepsilon\left(\rho, T, \beta\right) \quad \text{with} \quad \beta = \left(\operatorname{grad}\rho\right)^2 .$$

The specific free energy ε characterizes together fluid properties of *compressibility* and *molecular capillarity* of liquid-vapour interfaces. In accordance with the gas kinetic theory, $\lambda = 2\rho\,\varepsilon'_\beta(\rho,\beta)$ is assumed to be constant at a given temperature $\big(\lambda = a\,\kappa^2\gamma/(5\,m^2)$, where m is the molecular mass of the fluid, a the internal pressure, κ the molecular diameter and γ a factor associated with molecular potentials of interaction$\big)$ [5, 19], and

$$\rho\,\varepsilon = \rho\,\alpha(\rho) + \frac{\lambda}{2}\left(\operatorname{grad}\rho\right)^2,$$

where the term $(\lambda/2)\left(\operatorname{grad}\rho\right)^2$ is added to the volume free energy $\rho\,\alpha(\rho)$ of a compressible fluid. Specific free energy α enables to continuously connect liquid and vapour bulks such that the pressure $P(\rho) = \rho^2\alpha'_\rho(\rho)$ is similar to van der Waals' pressure. Thanks to experimental data, the λ value is $\lambda = 1.17\times10^{-5}$ c.g.s. for water at 20^o Celsius [29]. The equation of motion is

$$\rho\,\mathbf{a} = \operatorname{div}\,\left(\boldsymbol{\sigma} + \boldsymbol{\sigma}_v\right) - \rho\,\operatorname{grad}\Omega\,, \tag{1}$$

where $\mathbf{a}$ is the acceleration vector, Ω the body force potential and $\boldsymbol{\sigma}$ the generalization of the stress tensor:

$$\boldsymbol{\sigma} = -p\,\mathbf{1} - \lambda\,\operatorname{grad}\,\rho\,\otimes\,\operatorname{grad}\rho, \tag{2}$$

with $p = \rho^2\varepsilon'_\rho - \rho\,\operatorname{div}\,(\lambda\,\operatorname{grad}\rho)$; the viscous stress tensor is [20]

$$\boldsymbol{\sigma}_v = \eta\,(\operatorname{tr}\mathbf{D})\,\mathbf{1} + 2\mu\,\mathbf{D},$$

where $\mathbf{D}$ denotes the velocity strain tensor. Equation (1) can be written in the form

$$\rho\,\mathbf{a} + \operatorname{grad}P + \rho\operatorname{grad}\omega - \operatorname{div}\boldsymbol{\sigma}_v\ = 0, \tag{3}$$

where $\omega = \Omega - \lambda\,\Delta\rho$. The equation of motion must be completed by the balance of mass

$$\frac{\partial\rho}{\partial t} + \operatorname{div}\left(\rho\,\mathbf{u}\right) = 0, \tag{4}$$

where $\mathbf{u}$ is the velocity vector. Let us note that the equation of energy can be written in the form [26, 27]

$$\frac{\partial e}{\partial t} + \operatorname{div}\left[\left(e\,\mathbf{1} - \boldsymbol{\sigma} - \boldsymbol{\sigma}_v\right)\mathbf{u}\right] - \operatorname{div}\left(\lambda\,\frac{d\rho}{dt}\operatorname{grad}\rho\right) + \operatorname{div}\mathbf{q} - r - \rho\frac{\partial\Omega}{\partial t} = 0,$$

where $e = \rho\left(\frac{1}{2}\mathbf{u}^2 + \varepsilon + \Omega\right)$, $\mathbf{q}$ is the heat flux vector and r the heat supply, such that the model is compatible with the second law of thermodynamics [17].

3. The dynamical surface tension

Now, for the sake of simplicity, we neglect the body forces.

3.1. Case of a planar interface at equilibrium. The eigenvalues of the stress tensor in internal capillarity are deduced from Eq. (2):
$\lambda_1 = -p + \lambda \left(\mathrm{grad}\rho\right)^2$ is the eigenvalue associated with the plane orthogonal to $\mathrm{grad}\,\rho$,
$\lambda_2 = -p$ is the eigenvalue associated with the direction of $\mathrm{grad}\,\rho$.
The classical notations are presented in Appendix 1; in the system of coordinates associated with the interface, the stress tensor can be written

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

The equation of equilibrium of the planar interface is deduced from Eq. (1) and by neglecting the body forces, we get

$$\lambda_2 = -P_o,$$

where P_o denotes the common pressure in the vapour and liquid bulks. Per unit of length, the line force exerted on the edge of the interface is

$$F = \int_{x_3^v}^{x_3^l} \lambda_1 h_3 \, dx_3 = -P_o \, h + \int_{x_3^v}^{x_3^l} \lambda \left(\mathrm{grad}\,\rho\right)^2 h_3 \, dx_3,$$

where the subscript 3 denotes the normal component to the density surfaces of the capillary layer, h denotes the interface thickness and l, v indicate the liquid and vapour bulks. In the limit analysis of thin interfaces, the term $P_o\, h$ is negligible. Let us denotes $H = \int_{x_3^v}^{x_3^l} \lambda \left(\mathrm{grad}\,\rho\right)^2 h_3 dx_3$. The line force H exerted per unit of length corresponds to the surface tension.

3.2. The dynamical surface tension value. The notations are presented in Appendices 1 and 2. The equation of motion (3) is separated into normal and tangential components. In the orthogonal coordinate system presented in appendix 1,

$$\rho\, a_{tg} + \mathrm{grad}_{\mathrm{tg}}\, P = \rho\, \lambda\, \mathrm{grad}_{\mathrm{tg}}\, \Delta\rho + \mathrm{grad}_{\mathrm{tg}}\left(\eta\, \mathrm{div}\,\mathbf{u}\right) + 2\,\mathrm{div}\left(\mu\,\mathbf{D}\right)_{\mathrm{tg}}, \qquad (5)$$

$$\rho\, a_3 + \frac{1}{h_3}\frac{\partial P}{\partial x_3} = \rho\,\lambda \frac{1}{h_3}\frac{\partial \Delta\rho}{\partial x_3} + \frac{1}{h_3}\frac{\partial\left(\eta\,\mathrm{div}\mathbf{u}\right)}{\partial x_3} + 2\,\mathrm{div}\left(\mu\,\mathbf{D}\right)_3, \qquad (6)$$

where the subscript tg denotes the tangential component to the density surfaces of the capillary layer. The normal vector $\mathbf{e}_3$ corresponds to the direction of the increasing densities. An integration of Eq. (6) across the interface yields

$$\int_{x_3^v}^{x_3} \rho\, a_3\, h_3 dx_3 + \int_{x_3^v}^{x_3} \frac{\partial P}{\partial x_3}\, dx_3 = \int_{x_3^v}^{x_3} \rho\,\lambda\, \frac{\partial \Delta\rho}{\partial x_3}\, dx_3 + \int_{x_3^v}^{x_3} \frac{\partial\left(\eta\,\mathrm{div}\mathbf{u}\right)}{\partial x_3}\, dx_3 + 2\int_{x_3^v}^{x_3} \mathrm{div}\left(\mu\,\mathbf{D}\right)_3 \mathrm{h}_3 \mathrm{dx}_3.$$

The fluid is assumed to cross the capillary layer. Taking account of Eq. (29) and Eq. (33) proved in Appendix 2, we get,

$$P-P_v+Q^2\left(\frac{1}{\rho}-\frac{1}{\rho_v}\right)=\lambda\rho\,\Delta\rho-\lambda\int_{x_3^v}^{x_3}\Delta\rho\frac{\partial\rho}{\partial x_3}dx_3+[(\eta+2\mu)\,D_{33}]_{x_3^v}^{x_3}-\frac{2}{R_m}\left[\eta\,u_3\right]_{x_3^v}^{x_3},$$

where Q is the mass flow across the capillary layer, R_m the mean radius of curvature of the surfaces of equal density oriented following $\mathbf{e}_3$ and $[\,]$ denotes the difference of values through the interface. Taking account of Eqs. (22,25,26,27), we obtain

$$P-P_v+Q^2\left(\frac{1}{\rho}-\frac{1}{\rho_v}\right)=\lambda\,\rho\,\Delta\rho+\lambda\int_{x_3^v}^{x_3}\frac{2}{R_m}\frac{1}{h_3^2}\left(\frac{\partial\rho}{\partial x_3}\right)^2h_3dx_3$$
$$-\frac{\lambda}{2}\left[\frac{1}{h_3^2}\left(\frac{\partial\rho}{\partial x_3}\right)^2\right]_{x_3^v}^{x_3}-Q\left[(\eta+2\mu)\,\frac{1}{h_3}\frac{1}{\rho^2}\frac{\partial\rho}{\partial x_3}\right]_{x_3^v}^{x_3}-\frac{2}{R_m}\left[\eta u_3\right]_{x_3^v}^{x_3},$$

where u_3 is the third component of $\mathbf{u}$. The radius of curvature R_m is assumed to be constant across the capillary layer (see Appendix 1); then,

$$\begin{aligned}P-P_v+Q^2\left(\frac{1}{\rho}-\frac{1}{\rho_v}\right) &= \lambda\left\{\rho\,\Delta\rho-\frac{1}{2}\left(\mathrm{grad}\,\rho\right)^2\right\}+\frac{2\,\lambda}{R_m}\int_{x_3^v}^{x_3}\left(\mathrm{grad}\,\rho\right)^2h_3dx_3\\ &\quad -Q\left\{\left[(\eta+2\,\mu)\,\frac{\mathbf{e}_3.\mathrm{grad}\rho}{\rho^2}\right]_{x_3^v}^{x_3}+\frac{2}{R_m}\left[\frac{\eta}{\rho}\right]_{x_3^v}^{x_3}\right\}.\end{aligned}\tag{7}$$

The terms $\lambda\left\{\rho\,\Delta\rho-\frac{1}{2}\left(\mathrm{grad}\rho\right)^2\right\}$ and $Q\left\{\left[(\eta+2\mu)\left(\mathbf{e}_3.\mathrm{grad}\,\rho\right)/\rho^2\right]_{x_3^v}^{x_3^l}\right\}$ are null in the liquid and vapour bulks. Consequently, we get:

$$P_l-P_v=Q^2\left(\frac{1}{\rho_v}-\frac{1}{\rho_l}\right)+\frac{2\,K}{R_m},\tag{8}$$

where

$$K=H-Q\left(\frac{\eta_l}{\rho_l}-\frac{\eta_v}{\rho_v}\right)\qquad\text{with}\qquad H=\lambda\int_{x_3^v}^{x_3}\left(\mathrm{grad}\,\rho\right)^2h_3\,dx_3.\tag{9}$$

Equation (8) extends the Laplace formula which is obtained when $Q=0$. The term H can be interpreted as the *dynamical surface tension* of an interface crossed by a viscous fluid and K as the *viscous dynamical surface tension*. The surface tension depends on the dynamical distribution of the density through the interface and on the volume viscosity η, only. For a plane interface,

$$P_l-P_v=Q^2\left(\frac{1}{\rho_v}-\frac{1}{\rho_l}\right).\tag{10}$$

Equation (10) expresses the equality of normal stresses on an interface crossed by viscous fluid and classically obtained in the literature. In the case when $H=0$, Relations (8) and (10) cannot be identified with shock conditions. In a dissipative flow with a domain with strong gradients of density schematized in perfect fluid by a shock wave, the fluid is weakly dissipative and the relations of discontinuity are expressed in form of expansion with respect to the inverse of the Reynolds number [30].

4. Practical calculus of the surface tension

Let us consider the case when *the flux of mass is null across the interface*. The capillary layer is subject to tangential motions.

Definition : *A motion is compatible with the capillary layer if the surfaces of density are material surfaces.*
In the capillary layer $d\rho/dt = 0$ and consequently, $\operatorname{div} \mathbf{u} = 0$. Then, Eq. (3) can be written

$$\rho\, \mathbf{a} + \operatorname{grad} P = \lambda\, \rho \operatorname{grad} \Delta\rho + 2 \operatorname{div} (\mu\, \mathbf{D}) .$$

Equation (6) yields

$$a_{_3} + \frac{1}{\rho h_{_3}} \frac{\partial P}{\partial x_{_3}} = \frac{\lambda}{h_{_3}} \frac{\partial \Delta\rho}{\partial x_{_3}} + \frac{2}{\rho} \operatorname{div} (\mu\, \mathbf{D})_{_3} ,$$

and we get

$$\int_{x_{_3}^v}^{x_{_3}} a_{_3} h_{_3} dx_3 + \int_{x_{_3}^v}^{x_{_3}} \frac{1}{\rho} \frac{\partial P}{\partial x_{_3}}\, dx_{_3} = \int_{x_{_3}^v}^{x_{_3}} \lambda \frac{\partial \Delta\rho}{\partial x_{_3}}\, dx_3 + \int_{x_{_3}^v}^{x_{_3}} \frac{2}{\rho} \operatorname{div} (\mu\, \mathbf{D})_{_3}\, h_3 dx_3.$$

For the limit analysis of thin interfaces, two terms are null and Eqs. (31, 36) in Appendix 2 yield

$$\lambda\, \Delta\rho = \frac{P}{\rho} - \frac{P_v}{\rho_v} + \int_{\rho_v}^{\rho} \frac{P}{\rho^2}\, d\rho. \tag{11}$$

Consequently, in the liquid bulk,

$$\int_{\rho_v}^{\rho_l} \frac{P}{\rho^2}\, d\rho = \frac{P_v}{\rho_v} - \frac{P_l}{\rho_l}. \tag{12}$$

Relation (12) is an integral invariant associated with motions compatible with the capillary layer. In the special case of isothermal equilibrium, we get Eq. (4-11) from [7]. In the plane case, we are back to the Maxwell rule of equality of areas. Equation (11) writes

$$\lambda\, \Delta\rho = \frac{\partial}{\partial\rho} \left(\rho \int_{\rho_v}^{\rho} \frac{P - P_v}{\rho^2}\, d\rho \right). \tag{13}$$

To a constant temperature, $\rho \int_{\rho_v}^{\rho_l} (P - P_v) / \rho^2 d\rho$ is the Helmoltz free energy per unit volume of the fluid. If we assume a regular variation of the temperature in the capillary layer, $(\partial P/\partial\theta)\, (\partial\theta/\partial x_{_3})$ is negligible with respect to $(\partial P/\partial\rho)\, (\partial\rho/\partial x_{_3})$. By taking account of Eq. (22), Eq. (13) yields

$$-\frac{2}{R_m} \frac{\lambda}{h_{_3}} \left(\frac{\partial\rho}{\partial x_{_3}} \right)^2 + \lambda \left(\frac{1}{h_{_3}} \frac{\partial\rho}{\partial x_{_3}} \right) \left(\frac{1}{h_{_3}} \frac{\partial\rho}{\partial x_{_3}} \right)_{,3} = \frac{\partial}{\partial x_{_3}} \left(\rho \int_{\rho_v}^{\rho} \frac{P - P_v}{\rho^2}\, d\rho \right).$$

An integration across the capillary layer yields

$$\frac{\lambda}{2} (\operatorname{grad}\rho)^2 = \frac{2\,\lambda}{R_m} \int_{x_{_3}^v}^{x_{_3}} (\operatorname{grad}\rho)^2\, h_{_3} dx_{_3} + \rho \int_{\rho_v}^{\rho} \frac{P - P_v}{\rho^2}\, d\rho. \tag{14}$$

All the same,

$$\frac{\lambda}{2}\left(\mathrm{grad}\rho\right)^2 = \frac{2\,\lambda}{R_m}\int_{x_3^l}^{x_3}\left(\mathrm{grad}\rho\right)^2 h_3 dx_3 + \rho\int_{\rho_l}^{\rho}\frac{P-P_v}{\rho^2}\,d\rho.$$

Let us denote by x_3^i the third coordinate of a surface of density ρ_i, $(\rho_i \equiv \frac{1}{2}(\rho_v+\rho_l))$. Due to the fact we assume the radius of curvature of non-molecular size, for $x_3 \in \left[x_3^v, x_3^i\right]$ the quantity $(2\,\lambda/R_m)\int_{x_3^v}^{x_3}\left(\mathrm{grad}\rho\right)^2 h_3 dx_3$ is negligible with respect to $(\lambda/2)\left(\mathrm{grad}\rho\right)^2$. Then,

$$\text{for } \rho\in[\rho_v,\rho_i]\,,\ \frac{\lambda}{2}\left(\mathrm{grad}\rho\right)^2 = \rho\int_{\rho_v}^{\rho}\frac{P-P_v}{\rho^2}\,d\rho. \tag{15}$$

All the same,

$$\text{for } \rho\in[\rho_i,\rho_l]\,,\ \frac{\lambda}{2}\left(\mathrm{grad}\rho\right)^2 = \rho\int_{\rho_l}^{\rho}\frac{P-P_v}{\rho^2}\,d\rho. \tag{16}$$

Relations (9), (15) and (16) yield

$$H = 2\left\{\int_{x_3^v}^{x_3^i}\rho\left(\int_{\rho_v}^{\rho}\frac{P-P_v}{\rho^2}\,d\rho\right)h_3\,dx_3 + \int_{x_3^i}^{x_3^l}\rho\left(\int_{\rho_l}^{\rho}\frac{P-P_v}{\rho^2}\,d\rho\right)h_3\,dx_3\right\}.$$

Taking $d\rho = h_3\sqrt{\left(\mathrm{grad}\rho\right)^2}\,dx_3$ into account, we get

$$H = \sqrt{2\,\lambda}\left\{\int_{\rho_v}^{\rho_i}\left(u\sqrt{\int_{\rho_v}^{u}\frac{P-P_v}{\rho^2}\,d\rho}\right)du + \int_{\rho_i}^{\rho_l}\left(u\sqrt{\int_{\rho_l}^{u}\frac{P-P_l}{\rho^2}\,d\rho}\right)du\right\}. \tag{17}$$

Expression (17) allows to calculate the surface tension of a moving capillary layer; pressure P is a function of ρ and θ in each point of the layer.
Let us note that for the limit case when the capillary layer thickness is null, the viscosity of the fluid does not explicitly appear in Rel. (17). In the isothermal case of a planar interface at equilibrium, Rel. (17) is equivalent to

$$H = \sqrt{2\,\lambda}\int_{\rho_v}^{\rho_l}\sqrt{f(\rho)}\,d\rho,$$

where $f(\rho)$ is the free energy per unit volume which is null for $\rho=\rho_v$ and $P_v = P_l = P_o$. The H value of is numerically calculable by using thermodynamical pressure models through interfaces in the form $P = P(\rho,\theta)$.

5. Marangoni effect for liquid-vapour interfaces

The conditions of our study are the same than in Section 4: *the flux of mass across the interface is null; the surfaces of density are material surfaces*. Equation (7) yields

$$P - P_v = \lambda\left\{\rho\,\Delta\rho - \frac{1}{2}\left(\mathrm{grad}\rho\right)^2\right\} + \frac{2}{R_m}H_v\left(x_3\right),$$

where

$$H_v\left(x_3\right) = \lambda\int_{x_3^v}^{x_3}\left(\mathrm{grad}\rho\right)^2 h_3 dx_3.$$

All the same,

$$P - P_l = \lambda \left\{ \rho \, \Delta\rho - \frac{1}{2} \left(\mathrm{grad}\rho \right)^2 \right\} + \frac{2}{R_m} \, H_l \left(x_3 \right),$$

where

$$H_l \left(x_3 \right) = \lambda \int_{x_3}^{x_3^l} \left(\mathrm{grad}\rho \right)^2 h_3 dx_3 .$$

If we transfer these results into Eq. (5), we obtain for $j \in \{v, l\}$,

$$\rho \, a_{tg} = \frac{\lambda}{2} \, \mathrm{grad}_{\mathrm{tg}} \left(\mathrm{grad}\rho \right)^2 - \mathrm{grad}_{\mathrm{tg}} \left(\frac{2}{R_m} \, H_j \left(x_3 \right) \right) + \mathrm{grad}_{\mathrm{tg}} \left(P_j \right) + 2 \, \mathrm{div} \left(\mu \, \mathbf{D} \right)_{\mathrm{tg}} . \quad (18)$$

By integration of Eq. (18) across the capillary layer,

$$\begin{aligned} \int_{x_3^v}^{x_3^l} \rho \, a_{tg} h_3 dx_3 \quad = \quad & \int_{x_3^v}^{x_3^l} \frac{\lambda}{2} \, \mathrm{grad}_{\mathrm{tg}} \left(\mathrm{grad}\rho \right)^2 h_3 dx_3 - \int_{x_3^v}^{x_3^i} \mathrm{grad}_{tg} \left(\frac{2}{R_m} \, H_v \left(x_3 \right) \right) h_3 dx_3 \\ & - \int_{x_3^v}^{x_3^i} \mathrm{grad}_{\mathrm{tg}} \left(P_v \right) h_3 dx_3 - \int_{x_3^i}^{x_3^l} \mathrm{grad}_{\mathrm{tg}} \left(\frac{2}{R_m} H_l \left(x_3 \right) \right) h_3 dx_3 \\ & - \int_{x_3^i}^{x_3^l} \mathrm{grad}_{\mathrm{tg}} \left(P_l \right) h_3 dx_3 + 2 \int_{x_3^v}^{x_3^l} \mathrm{div} \left(\mu \, \mathbf{D} \right)_{\mathrm{tg}} \mathrm{h_3 dx_3} . \end{aligned} \quad (19)$$

Equation (14) yields

$$\frac{\lambda}{2} \left(\mathrm{grad} \, \rho \right)^2 = \frac{2}{R_m} \, H_v \left(x_3 \right) + \rho \int_{\rho_v}^{\rho} \frac{P - P_v}{\rho^2} \, d\rho,$$

and by integration,

$$H_v \left(x_3 \right) = \frac{4}{R_m} \int_{x_3^v}^{x_3} H_v \left(x_3 \right) \, h_3 dx_3 + 2 \int_{x_3^v}^{x_3} \rho \left(\int_{\rho_v}^{\rho} \frac{P \left(\theta, u \right) - P_v}{u^2} du \right) h_3 dx_3 .$$

For $x_3 \in \left[x_3^v, x_3^i \right]$, the quantity $\left(4/R_m \right) \int_{x_3^v}^{x_3} H_v \left(x_3 \right) \, h_3 dx_3$ is negligible with respect to $H_v \left(x_3 \right)$. Taking account of Rel. (15), we get:

$$\text{For } x_3 \in \left[x_3^v, x_3^i \right], \quad H_v \left(x_3 \right) = \sqrt{2 \, \lambda} \int_{\rho_v}^{\rho} \sqrt{u \int_{\rho_v}^{u} \frac{P \left(\theta, u \right) - P_v}{y^2} \, dy} \, du,$$

where ρ denotes the density associated with x_3. All the same,

$$\text{For } x_3 \in \left[x_3^i, x_3^l \right], \quad H_l \left(x_3 \right) = \sqrt{2 \, \lambda} \int_{\rho_l}^{\rho} \sqrt{u \int_{\rho_l}^{u} \frac{P \left(\theta, u \right) - P_l}{y^2} \, dy} \, du.$$

In the capillary layer, the pressure P is a function of θ depending on the coordinates x_1 and x_2; $\mathrm{grad}_{\mathrm{tg}} \theta$ is bounded as $\mathrm{grad}_{\mathrm{tg}} R_m$ and $\mathrm{grad}_{\mathrm{tg}} H_j \left(x_3 \right)$ where $j \in \{v, l\}$. In the liquid and vapour bulks, $\mathrm{grad}_{\mathrm{tg}} P_l$ and $\mathrm{grad}_{\mathrm{tg}} P_v$ are bounded. By taking account of Eqs. (28, 30, 32) in Appendices 1 and 2, and for the limit analysis of thin interfaces, Eq. (19) yields

$$\frac{\lambda}{2} \int_{x_3^v}^{x_3^l} \mathrm{grad}_{\mathrm{tg}} \left(\mathrm{grad}\rho \right)^2 h_3 dx_3 + 2 \left[\mu \, \mathbf{D} \, \mathbf{e}_3 \right]_{x_3^v}^{x_3^l} = 0.$$

But,

$$\begin{aligned}\frac{\lambda}{2}\int_{x_3^v}^{x_3^l}\mathrm{grad}_{\mathrm{tg}}\left(\frac{1}{h_3}\frac{\partial\rho}{\partial x_3}\right)^2 h_3\,dx_3 &= \lambda\int_{\rho_v}^{\rho_l}\mathrm{grad}_{\mathrm{tg}}\left(\frac{1}{h_3}\frac{\partial\rho}{\partial x_3}\right)d\rho\\ &= \mathrm{grad}_{\mathrm{tg}}\left(\lambda\int_{\rho_v}^{\rho_l}\frac{1}{h_3}\frac{\partial\rho}{\partial x_3}\,d\rho\right)\\ &= \mathrm{grad}_{\mathrm{tg}}\left(\lambda\int_{\rho_v}^{\rho_l}(\mathrm{grad}\rho)^2\,h_3\,dx_3\right).\end{aligned}$$

Then, $$\mathrm{grad}_{\mathrm{tg}}H + 2\,[\mu\,\mathbf{D}\,\mathbf{e}_3]_v^l = 0.$$

If we additively assume that the viscous stresses are negligible in the vapour bulk, we get

$$\mathrm{grad}_{\mathrm{tg}}H + 2\,\mu_l\,\mathbf{D}^l\,\mathbf{e}_3 = 0. \tag{20}$$

In the case when we consider the interface as a surface of discontinuity, the Marangoni condition is generally presented in the form of Eq. (20). The calculation is obtained without any approximation and with coefficients of viscosity non-constant across the capillary layer.

Let us note that we have obtained the interfacial energy by using a second gradient theory but without isothermal motions. That is the case when strong flows cross the capillary layer corresponding to important phase transitions. Moreover, the capillary layer is mobile and this fact answers to the Birkoff question [25].

6. Concluding remark

Equation (9) gives the value of the viscous dynamical surface tension. We assume that H-value in dynamics is closely the same that at equilibrium. If we consider the case of water at 20° Celsius, in c.g.s. units, $\nu_l = \mu_l/\rho_l = 0.01$ and $\nu_v = \mu_v/\rho_v = 0.15$. In the case of Stokes's hypothesis, $\eta = -(2/3)\mu$ and $K - H = -0.093 \times Q$.

For $u_l = 1\,cm/s$ corresponding to a very strong mass flow, the difference between K and H is not observable far from the critical point.

7. Appendix 1: Orthogonal line coordinates

7.1. Preliminaries [31, 32]**.** The effective thickness of a liquid-vapour interface is of nanometer range; the other dimensions are microscopic at least. The surfaces of equal mass density modeling the interfacial layer can be considered as parallel surfaces. In the interfacial layer, the surface of equal density and the normal lines are together a triple orthogonal system and the intersection of the associated surfaces of the system are the lines of curvature. The notations are the following: scalars x_1, x_2, x_3 denote the curvilinear coordinates; $\mathbf{x} \equiv (x_1, x_2, x_3)^T$, where superscript ^{T} denotes the transposition. At each point $\mathbf{M}$ of the interface, vectors $\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3$ denote the direct orthonormal vectors which are tangent to the coordinate lines. Vector $\mathbf{e}_3$ represents the unit normal vector collinear to $\mathrm{grad}\,\rho$ and directed along the increasing density. The elementary displacement of point $\mathbf{M}$ is such that

$$d\mathbf{M} = h_1 dx_1\,\mathbf{e}_1 + h_2 dx_2\,\mathbf{e}_2 + h_3 dx_3\,\mathbf{e}_3\,.$$

We deduce in classical derivative notations

$$\frac{\partial \mathbf{e}_1}{\partial x_1} = -\frac{h_{1,2}}{h_2}\,\mathbf{e}_2 - \frac{h_{1,3}}{h_3}\,\mathbf{e}_3 .$$

We denote $ds_i = h_i dx_i,\ \ i \in \{1,2,3\}$,

$$\frac{\partial \mathbf{e}_1}{\partial s_1} = r_{1,2}\mathbf{e}_2 + r_{1,3}\mathbf{e}_3 \ \text{ with } \ r_{1,2} = -\frac{h_{1,2}}{h_1 h_2} \ \text{ and } \ r_{1,3} = -\frac{h_{1,3}}{h_1 h_3}.$$

For surfaces $\Sigma_{1,2}$ generated by the two first coordinate lines, $r_{1,2}$ and $r_{1,3}$ are respectively the geodesic curvature and the normal curvature of the first coordinate line. Moreover,

$$\frac{\partial \mathbf{e}_2}{\partial s_1} = -r_{1,2}\mathbf{e}_1 \ \text{ and } \ \frac{\partial \mathbf{e}_3}{\partial s_1} = -r_{1,3}\mathbf{e}_2 .$$

In the same way, for $i \neq j$ and belonging to $\{1,2,3\}$, we denote $r_{i,j} = -h_{i,j}/(h_i h_j)$. We get analog relations for the partial derivatives with respect to the two last coordinates. Let us note that when surfaces $\Sigma_{1,2}$ are parallel surfaces, then $\partial \mathbf{e}_3/\partial s_3 = 0$ and consequently [33],

$$r_{3,1} = r_{3,2} = 0\,; \tag{21}$$

moreover, $\partial \mathbf{e}_1/\partial s_3 = \partial \mathbf{e}_2/\partial s_3 = 0$.
In the interfacial layer, $\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3$ are uniquely function of x_1, x_2. Vectors $\mathbf{e}_1, \mathbf{e}_2$ are the directions of the curvature lines of the surfaces of equal density. For $i \neq j$ and belonging to $\{1,2,3\}$, $r_{i,j}$ are continuous functions of coordinates x_1, x_2, x_3. For the limit analysis of thin interfaces, $h_1,\ h_2, \mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3, r_{i,j}$ can be assumed to be constant across the interfacial layer and along the coordinate line x_3.

7.2. Calculus of $\Delta\rho$. For all vector fields $\mathbf{v}$ and $\mathbf{w}$,

$$\mathrm{rot}\,(\mathbf{v}\times\mathbf{w}) = \mathbf{v}\,\mathrm{div}\mathbf{w} - \mathbf{w}\,\mathrm{div}\mathbf{v} + \frac{\partial \mathbf{v}}{\partial \mathbf{x}}\mathbf{w} - \frac{\partial \mathbf{w}}{\partial \mathbf{x}}\mathbf{v},$$

where $\partial/\partial\mathbf{x}$ is the gradient operator. Let us choose $\mathbf{v} = \mathbf{e}_3$ and $\mathbf{w} = \mathrm{grad}\,\rho$; then,

$$\mathrm{rot}\,(\mathbf{e}_3 \times \mathrm{grad}\rho) = \mathbf{e}_3\,\Delta\rho - \mathrm{grad}\,\rho\,\mathrm{div}\,\mathbf{e}_3 + \frac{\partial \mathbf{e}_3}{\partial \mathbf{x}}\mathrm{grad}\,\rho - \frac{\partial\,(\mathrm{grad}\,\rho)}{\partial \mathbf{x}}\,\mathbf{e}_3 ,$$

$\mathrm{div}\,\mathbf{e}_3 = -2/\mathrm{R_m}$ where R_m is the mean curvature radius of surfaces $\Sigma_{1,2}$ following the direction $\mathbf{e}_3$, orthonormal vector $\mathbf{e}_3$ is collinear to $\mathrm{grad}\,\rho$ and $\mathbf{e}_3^T\,\partial \mathbf{e}_3/\partial \mathbf{x} = \mathbf{0}$; consequently we get

$$\Delta\rho = -\frac{2}{R_m}\,\mathbf{e}_3^T\,\mathrm{grad}\rho + \mathbf{e}_3^{\mathrm{T}}\,\frac{\partial\,(\mathrm{grad}\rho)}{\partial \mathbf{x}}\mathbf{e}_3 ,$$

and finally

$$\Delta\rho = -\frac{2}{R_m}\frac{1}{h_3}\frac{\partial \rho}{\partial x_3} + \frac{1}{h_3}\left(\frac{1}{h_3}\frac{\partial \rho}{\partial x_3}\right)_{,3}. \tag{22}$$

For the limit analysis of thin interfaces, R_m is constant across the interfacial layer or along the coordinate line x_3.

7.3. Representation of the deformation velocity tensor. Scalars $u_1,\ u_2,\ u_3$ denote the components of the fluid velocity $\mathbf{u}$ in the system (x_1, x_2, x_3). The components of the deformation velocity tensor are

$$\begin{aligned}
D_{11} &= \frac{u_{1,1}}{h_1} - r_{1,2}u_2 - r_{1,3}u_3 , \\
D_{12} &= \frac{1}{2}\left(\frac{u_{1,2}}{h_2} + \frac{u_{2,1}}{h_1} + r_{1,2}u_1 + r_{2,1}u_2\right), \\
D_{13} &= \frac{1}{2}\left(\frac{u_{1,3}}{h_3} + \frac{u_{3,1}}{h_1} + r_{1,3}u_1 + r_{3,1}u_3\right).
\end{aligned} \tag{23}$$

There exist six other expressions obtained by circular permutation of indices 1,2,3. From Eq. (21), we get

$$D_{33} = \frac{u_{3,3}}{h_3}. \tag{24}$$

7.4. Kinematics of interfaces. We denote $u = u_3$ the fluid velocity with respect to a surface of iso-density and by Q the mass flow through the interface,

$$Q = \rho\, u. \tag{25}$$

In the capillary layer Q is only a function on x_1, x_2. Let us note that $Q = 0$ is equivalent to $\operatorname{div} \mathbf{u} = 0$. From relations (24) and (25), we get,

$$[\eta\, u_3]_{x_3^v}^{x_3} = Q \left[\frac{\eta}{\rho}\right]_{x_3^v}^{x_3}, \tag{26}$$

$$[(\eta + 2\,\mu)\, D_{33}]_{x_3^v}^{x_3} = \left[-\frac{1}{h_3}\frac{Q}{\rho^2}\,(\eta + 2\,\mu)\,\frac{\partial \rho}{\partial x_3}\right]_{x_3^v}^{x_3}. \tag{27}$$

When $Q = 0$, then $\operatorname{div} \mathbf{u} = 0$ and $D_{33} = 0$. Consequently,

$$[\mu\, \mathbf{D}\, \mathbf{e}_3]_{x_3^v}^{x_3^l} = [\mu D_{13}\, \mathbf{e}_1 + \mu\, D_{23}\, \mathbf{e}_2]_{x_3^v}^{x_3^l}. \tag{28}$$

8. Appendix 2: Conditions associated with the dissipative function

In the interfacial layer, we also assume that u_1, u_2, u_3 and $\eta,\ \mu$ are bounded and have partial derivative bounded with respect to x_1, x_2.

8.1. Property 1: *The tangential components of the fluid velocity are continuous through the interface. Consequently for the limit analysis of thin interfaces, we use the approximation that u_1 and u_2 are constant through the interface.*

The proof of this property comes from the dissipative function ψ associated with the viscous stress tensor.

$$\psi = \frac{1}{2}\left(\eta\ (\operatorname{tr}\mathbf{D})^2 + 2\,\mu \operatorname{tr}\left(\mathbf{D}^2\right)\right).$$

With the notations of Appendix 1,

$$\psi = \frac{(\eta + 2\,\mu)}{2}\left(D_{11}^2 + D_{22}^2 + D_{33}^2\right) + 2\,\mu\left(D_{12}^2 + D_{13}^2 + D_{23}^2\right) + \eta\left\{D_{11}\, D_{22} + D_{33}\,(D_{11} + D_{22})\right\}.$$

The dissipative function must have an integral $\int_{x_3^v}^{x_3^l}\left(\eta\,(\operatorname{tr}\mathbf{D})^2 + 2\,\mu \operatorname{tr}\left(\mathbf{D}^2\right)\right) h_3\, dx_3$ bounded in the layer. With the hypothesis of Section 7.3 on the partial derivatives of component velocity, we deduce that D_{11}, D_{12}, D_{22} are bounded across the interface and due to (Eq. (24)),

$$\int_{x_3^v}^{x_3^l} \eta\, D_{33}\,(D_{11} + D_{22})\, h_3 dx_3 = \int_{v_3^v}^{v_3^l} \eta\,(D_{11} + D_{22})\, du_3$$

is bounded. Moreover, Eq. (21) implies

$$D_{13} = \frac{1}{2}\left(\frac{u_{1,3}}{h_3} + \frac{u_{3,1}}{h_1} + r_{1,3}\, u_1\right).$$

Due to $\mu > 0$ and $\eta + 2\,\mu > 0$ [20], and the fact that in the integral of D_{13}^2, the term

$$\int_{x_3^v}^{x_3^l} \mu \frac{u_{1,3}}{h_3}\left(\frac{u_{3,1}}{h_1} + r_{1,3}\, u_1\right) h_3 dx_3 = \int_{u_1^v}^{u_1^l} \mu\left(\frac{u_{3,1}}{h_1} + r_{1,3}\, u_1\right) du_1$$

is bounded, the term $\int_{x_3^v}^{x_3^l} \mu \frac{u_{1,3}^2}{h_3} h_3 dx_3$ must be bounded. But $\int_{x_3^v}^{x_3^l} \frac{u_{1,3}^2}{h_3} h_3 dx_3$ is minimum when $u_{1,3}$ is independent of x_3, that is to say, $u_{1,3} = \frac{u_1^l - u_1^v}{h}$, where h is the interfacial thickness. Then,

$$\int_{x_3^v}^{x_3^l} \frac{u_{1,3}^2}{h_3} h_3\ dx_3 \geq \frac{\left(u_1^l - u_1^v\right)^2}{h}.$$

Additively, $\mu > 0$ implies

$$\int_{x_3^v}^{x_3^l} 2\,\mu \frac{u_{1,3}^2}{h_3} h_3\, dx_3 \geq 2\,\mu_{\min} \frac{\left(u_1^l - u_1^v\right)^2}{h}.$$

Consequently, for $u_1^l \neq u_1^v$, the dissipative function goes to infinity when h goes to zero. The component u_1 of the velocity is continuous across the interface and it is the same for component u_2.

8.2. Property 2: *For a motion normal to the interface,*

$$\int_{x_3^v}^{x_3} \left(\frac{\partial\left(\eta \,\mathrm{div}\mathbf{u}\right)}{\partial x_3} + 2\,h_3\left(\mathrm{div}\left(\mu\,\mathbf{D}\right)\right)_3 \right) dx_3 = \left[\left(\eta + 2\,\mu\right) D_{33}\right]_{x_3^v}^{x_3} - \frac{2}{R_m}\left[\eta\, u_3\right]_{x_3^v}^{x_3}. \tag{29}$$

We first get, $\displaystyle\int_{x_3^v}^{x_3} \frac{\partial\left(\eta \,\mathrm{div}\,\mathbf{u}\right)}{\partial x_3} dx_3 = \left[\eta\,\mathrm{div}\,\mathbf{u}\right]_{x_3^v}^{x_3}$.

Moreover, due to Property 1, $\dfrac{u_{1,1}}{h_1}$, $\dfrac{u_{2,1}}{h_1}$, $\dfrac{u_{1,2}}{h_2}$ and $\dfrac{u_{2,2}}{h_2}$ are null across the interface. From Rel. (23),

$$\begin{aligned}
\left[\eta\, D_{11}\right]_{x_3^v}^{x_3} &= \frac{u_{1,1}}{h_1}\left[\eta\right]_{x_3^v}^{x_3} - r_{1,2}u_2\left[\eta\right]_{x_3^v}^{x_3} - r_{1,3}\left[\eta\, u_3\right]_{x_3^v}^{x_3}, \\
\left[\eta\, D_{22}\right]_{x_3^v}^{x_3} &= \frac{u_{2,2}}{h_2}\left[\eta\right]_{x_3^v}^{x_3} - r_{2,1}u_1\left[\eta\right]_{x_3^v}^{x_3} - r_{2,3}\left[\eta\, u_3\right]_{x_3^v}^{x_3}
\end{aligned}$$

and consequently

$$\left[\eta\,\mathrm{div}\mathbf{u}\right]_{x_3^v}^{x_3} = -\frac{2}{R_m}\left[\eta\, u_3\right]_{x_3^v}^{x_3} + \left[\eta\right]_{x_3^v}^{x_3}\left(\frac{u_{1,1}}{h_1} + \frac{u_{2,2}}{h_2} - r_{1,2}u_2 - r_{2,1}u_1\right) + \left[\eta D_{33}\right]_{x_3^v}^{x_3}.$$

When $u_1 = u_2 = 0$,

$$\left[\eta\,\mathrm{div}\,\mathbf{u}\right]_{x_3^v}^{x_3} = \left[\eta\, D_{33} - \frac{2}{R_m}\eta\, u_3\right]_{x_3^v}^{x_3}.$$

Moreover,

$$\begin{aligned}
\left(\mathrm{div}\,\mu\,\mathbf{D}\right)_3 &= \frac{1}{h_1 h_2 h_3}\left(\left(h_1 h_2 \mu D_{33}\right)_{,3} + \left(h_2 h_3 \mu D_{31}\right)_{,1} + \left(h_3 h_1 \mu D_{32}\right)_{,2}\right) \\
&\quad + \mu D_{13}\frac{h_{3,1}}{h_3 h_1} + \mu D_{23}\frac{h_{3,2}}{h_3 h_2} - \mu D_{11}\frac{h_{1,3}}{h_1 h_3} - \mu D_{22}\frac{h_{2,3}}{h_2 h_3}.
\end{aligned}$$

Taking account of Eq. (21), we obtain

$$\begin{aligned}
\left(\mathrm{div}\,\mu\,\mathbf{D}\right)_3 &= \frac{1}{h_1 h_2 h_3}\left(\left(h_1 h_2\,\mu\, D_{33}\right)_{,3} + \left\{\frac{h_2 h_3}{2}\left(\frac{\mu\, u_{1,3}}{h_3} + \frac{\mu\, u_{3,1}}{h_1} + \mu\, u_1 r_{1,3} + \mu\, u_3 r_{3,1}\right)\right\}_{,1}\right. \\
&\quad \left. + \left\{\frac{h_3 h_1}{2}\left(\frac{\mu\, u_{3,2}}{h_2} + \frac{\mu\, u_{2,3}}{h_3} + \mu\, u_2 r_{2,3} + \mu\, u_3 r_{3,2}\right)\right\}_{,2}\right) \\
&\quad + r_{1,3}\left(\frac{\mu\, u_{1,1}}{h_1} - \mu\, u_2 r_{1,2} - \mu\, u_3 r_{1,3}\right) + r_{2,3}\left(\frac{\mu\, u_{2,2}}{h_2} - \mu\, u_3 r_{2,3} - \mu\, u_1 r_{2,1}\right).
\end{aligned}$$

The only non-bounded term across the interface is

$$\frac{1}{h_1 h_2 h_3}\left(\left(h_1 h_2 \mu D_{33}\right)_{,3} + \left\{\frac{h_2 h_3}{2}\frac{\mu\, u_{1,3}}{h_3}\right\}_{,1} + \left\{\frac{h_3 h_1}{2}\frac{\mu\, u_{2,3}}{h_3}\right\}_{,2}\right).$$

Consequently,

$$\begin{aligned}
\int_{x_3^v}^{x_3} \left(\mathrm{div}\,\mu\,\mathbf{D}\right)_3 h_3\, dx_3 &= \int_{x_3^v}^{x_3} \frac{1}{h_1 h_2}\left\{\left(h_1 h_2\,\mu\, D_{33}\right)_{,3} + \left(\frac{h_2}{2}\mu\, u_{1,3}\right)_{,1} + \left(\frac{h_1}{2}\mu\, u_{2,3}\right)_{,2}\right\} dx_3 \\
&= \left[\mu\, D_{33}\right]_{x_3^v}^{x_3} + \int_{x_3^v}^{x_3} \frac{1}{h_1 h_2}\left\{\left(\frac{h_2}{2}\mu\, u_{1,3}\right)_{,1} + \left(\frac{h_1}{2}\mu\, u_{2,3}\right)_{,2}\right\} dx_3.
\end{aligned}$$

When no tangential motion appears along the interface, $u_1 = u_2 = 0$ and $u_{1,3} = u_{2,3} = 0$. Consequently, $\int_{x_3^v}^{x_3} (\operatorname{div} \mu \mathbf{D})_3 \, h_3 \, dx_3 = [\mu \, D_{33}]_{x_3^v}^{x_3}$ and we get Rel. (29).

8.3. Property 3: *Across the interface,*

$$\int_{x_3^v}^{x_3^l} (\operatorname{div} \mu \mathbf{D})_{tg} \, h_3 dx_3 = [\mu \, D_{13} \, \mathbf{e}_1 + \mu \, D_{23} \, \mathbf{e}_2]_{x_3^v}^{x_3^l} . \tag{30}$$

This relation comes from the following calculations

$$\begin{aligned}
(\operatorname{div} \mu \mathbf{D})_1 \quad &= \quad \frac{1}{h_1 h_2 h_3} \Big((h_2 h_3 \mu \, D_{11})_{,1} + (h_3 h_1 \mu \, D_{12})_{,2} + (h_1 h_2 \mu \, D_{13})_{,3} \Big) \\
&\quad + \mu \, D_{21} \frac{h_{1,2}}{h_1 h_2} + \mu \, D_{31} \frac{h_{1,3}}{h_1 h_3} - \mu \, D_{22} \frac{h_{2,1}}{h_1 h_2} - \mu \, D_{33} \frac{h_{3,1}}{h_1 h_3} \\
= \quad & \frac{1}{h_1 h_2 h_3} \left(\left\{ \mu \, h_2 h_3 \left(\frac{u_{1,1}}{h_1} - r_{1,2} u_2 - r_{1,3} u_3 \right) \right\}_{,1} \right. \\
& + \left\{ \frac{\mu \, h_3 h_1}{2} \left(\frac{u_{1,2}}{h_2} + \frac{U_{2,1}}{h_1} + r_{1,2} u_1 + r_{2,1} u_2 \right) \right\}_{,2} + \{ \mu \, h_1 h_2 D_{13} \}_{,3} \Big) \\
& - \frac{\mu}{2} \left(\frac{u_{1,2}}{h_2} + \frac{u_{2,1}}{h_1} + r_{1,2} u_1 + r_{2,1} u_2 \right) r_{1,2} - \frac{\mu}{2} \left(\frac{u_{1,3}}{h_3} + \frac{u_{3,1}}{h_1} + r_{1,3} u_1 + r_{3,1} u_3 \right) r_{1,3} \\
& + \mu \left(\frac{u_{2,2}}{h_2} - r_{2,3} u_3 - r_{2,1} u_1 \right) r_{2,1} + \mu \left(\frac{u_{3,3}}{h_3} - r_{3,1} u_1 - r_{3,2} u_2 \right) r_{3,1} .
\end{aligned}$$

Taking account of Rel. (21), the non-bounded term across the interface is

$$\frac{(h_1 h_2 \mu \, D_{13})_{,3}}{h_1 h_2 h_3} - \mu \frac{r_{1,3}}{2} \frac{u_{1,3}}{h_3} .$$

Consequently,

$$\begin{aligned}
\int_{x_3^v}^{x_3^l} (\operatorname{div} \mu \mathbf{D})_1 \; h_3 dx_3 \quad &= \quad \int_{x_3^v}^{x_3^l} \frac{1}{h_1 h_2} (h_1 h_2 \mu D_{13})_{,3} \; dx_3 - \int_{x_3^v}^{x_3^l} \mu \frac{r_{1,3} u_1}{2} u_{1,3} dx_3 \\
&= \quad [\mu \, D_{13}]_{x_3^v}^{x_3^l} - \frac{r_{1,3}}{2} \int_{u_1^v}^{u_1^l} \mu \, u_1 du_1 .
\end{aligned}$$

With the hypothesis of the limit analysis of thin interfaces, the term $\frac{r_{1,3}}{2} \int_{u_1^v}^{u_1^l} \mu \, u_1 du_1$ is null and from an analogous calculation for $\int_{x_3^v}^{x_3^l} (\operatorname{div} \mu \mathbf{D})_2 \; h_3 \, dx_3$ we get Rel. (30).

8.4. Property 4: *For a null flow across the interface,*

$$\int_{x_3^v}^{x_3^l} \frac{(\operatorname{div} \mu \mathbf{D})_3}{\rho} \, h_3 \, dx_3 = 0. \tag{31}$$

When $Q = 0$, we get $D_{33} = 0$ (see Eqs. (23) and (24)); we deduce

$$\int_{x_3^v}^{x_3^l} \frac{(\operatorname{div} \mu \mathbf{D})_3}{\rho} \, h_3 \, dx_3 = \int_{x_3^v}^{x_3^l} \frac{1}{\rho \, h_1 h_2} \left(\left(\frac{\mu \, h_2}{2} u_{1,3} \right)_{,1} + \left(\frac{\mu \, h_1}{2} u_{2,3} \right)_{,2} \right) dx_3 .$$

For the limit analysis of thin interfaces, across the interface $u_{1,3} = u_{2,3} = 0$ and we get Rel. (31).

8.5. Property 5: *Across the interface,*

$$\int_{x_3^v}^{x_3^l} \rho\, a_{tg}\, h_3\, dx_3 = 0. \tag{32}$$

In fact, Rel. (21) implies

$$a_1 = \frac{\partial u_1}{\partial t} + \frac{u_1 u_{1,1}}{h_1} + \frac{u_2 u_{1,2}}{h_2} + \frac{u_3 u_{1,3}}{h_3} - u_1 u_2 r_{1,2} - u_1 u_3 r_{1,3} + u_2^2 r_{2,1}\,.$$

For $\partial u_1/\partial t$ bounded, we immediately deduce from the limit analysis of thin interfaces that $\int_{x_3^v}^{x_3^l} \rho\, a_1\, h_3 dx_3 = 0$ and the same result for a_2.

8.6. Property 6: *Through the interface,*

$$\int_{x_3^v}^{x_3} \rho\, a_3\, h_3\, dx_3 = Q^2 \left(\frac{1}{\rho} - \frac{1}{\rho_v}\right). \tag{33}$$

The only terms non bounded across the interface are: $\partial u_3/\partial t$ and $u_3 u_{3,3}/h_3$. Consequently,

$$\int_{x_3^v}^{x_3} \rho\, a_3\, h_3\, dx_3 = \int_{x_3^v}^{x_3} \rho \left(\frac{\partial u_3}{\partial t} + \frac{u_3 u_{3.3}}{h_3}\right) h_3 dx_3.$$

But $u_3 = Q/\rho$ and $\partial u_3/\partial t = (\partial Q/\partial t)\,(1/\rho) - \left(Q^2/\rho^2\right)(\partial\rho/\partial t)$. If we assume that $\partial Q/\partial t$ is bounded and

$$u_{3,3} = -\left(Q/\rho^2\right)\rho_{,3}, \tag{34}$$

then,

$$\int_{x_3^v}^{x_3} \rho\, a_3\, h_3\, dx_3 = \int_{x_3^v}^{x_3} \left(-\frac{Q}{\rho}\frac{\partial\rho}{\partial t} h_3 - \frac{u_3 Q}{\rho}\rho_{,3}\right) dx_3.$$

Taking account of Eq. (4), we get

$$\frac{\partial\rho}{\partial t} + \frac{\rho}{h_1 h_2 h_3}\left\{(u_1 h_2 h_3)_{,1} + (u_2 h_3 h_1)_{,2} + (u_3 h_1 h_2)_{,3}\right\} + \frac{\rho_{,3}}{h_3} u_3 = 0. \tag{35}$$

From Eq. (34), the only non bounded term of Eq. (35) is

$$\frac{\partial\rho}{\partial t} + \rho\frac{u_{3,3}}{h_3} + \frac{\rho_{,3}}{h_3} u_3 \equiv \frac{\partial\rho}{\partial t}.$$

Its integral across the interface is null. That is the same for the integral of $(Q/\rho)\,(\partial\rho/\partial t)$. Consequently,

$$\int_{x_3^v}^{x_3} \rho\, a_3\, h_3\, dx_3 = -\int_{x_3^v}^{x_3} \frac{u_3 Q}{\rho}\rho_{,3}\, dx_3 = -Q^2 \int_{x_3^v}^{x_3} \frac{\rho_{,3}}{\rho^2}\, dx_3 = Q^2\left(\frac{1}{\rho} - \frac{1}{\rho_v}\right).$$

8.7. Property 7: *For a null flow across the interface,*

$$\int_{x_3^v}^{x_3} a_3\, h_3 dx_3 = 0. \tag{36}$$

All the same, this result is an immediate consequence of the limit analysis of thin interfaces.

References

[1] V. Bongiorno, L.E. Scriven and H.T. Davis, Molecular theory of fluid interfaces, *J. Colloid Interf. Sci.* **57**, 462-475 (1976).

[2] R.C. Ball and R. Evans, The density profile of a confined fluid, *Molecular Physics* **63**, 159-163 (1988).

[3] B.V. Derjaguin, N.V. Churaev and V.M. Muller, *Surfaces Forces* (Plenum Press, New York, 1987).

[4] N.V. Churaev, Thin liquid layers, *Colloid J.* **58**, 681-693 (1996).

[5] Y. Rocard, *Thermodynamique* (Masson, Paris, 1952).

[6] J.S. Rowlinson and B. Widom, *Molecular theory of capillarity* (Clarendon Press, Oxford, 1984).

[7] E.C. Aifantis and J.B. Serrin, The mechanical theory of fluid interfaces and Maxwell's rule, *J. Colloid Interf. Sci.* **96**, 517-529 (1983).

[8] S. Ono and S. Kondo, *Molecular theory of surface tension in liquid*, Encyclopedia of Physics, X, (Springer, Berlin, 1960).
[9] R.E. Meyer, Ed., *Waves on fluid interfaces*, Math. Res. Center, Publ. **50** (Academic Press, New York, 1983).
[10] L.E. Scriven, Dynamics of a fluid interface equation of motion for Newtonian surface fluids, *Chem. Eng. Sci.* **12**, 98-108 (1960).
[11] M. Ishi, *Thermo-fluid dynamic theory of two-phase flow* (Eyrolles, Paris, 1975).
[12] R. Defay, I. Prigogine and A. Sanfeld, Surface thermodynamics, *J. Colloid Interf. Sci.* **58**, 498-510 (1977).
[13] B.J.A. Zielinska and P. Bedeaux, A hydrodynamic theory for fluctuations around equilibrium of a liquid-vapour interface, *Physica A* **112**, 265-286 (1982).
[14] J.D. van der Waals, Thermodynamique de la capillarité dans l'hypothèse d'une variation continue de la densité, *Archives Néerlandaises* **28**, 121-209 (1894-1895).
[15] D.J. Korteweg, Sur la forme que prennent les équations du mouvement des fluides si l'on tient compte des forces capillaires, *Archives Néerlandaises* **II 6**, 1-24 (1901).
[16] J.W. Cahn and J.E. Hilliard, Free energy of a nonuniform system. III. Nucleation in a two-component incompressible fluid, *J. Chem. Phys.* **31**, 688-699 (1959).
[17] C. Truesdell, *Rational thermodynamics* (Mac Graw Hill, London, 1969).
[18] H. Gouin, Utilization of the second gradient theory in continuum mechanics to study the motion and thermodynamics of liquid-vapour interfaces, *Physicochemical Hydrodynamics, Series B, Physics* **174**, 667-682 (1986) & arXiv:1108.2766.
[19] H. Gouin, Energy of interaction between solid surfaces and liquids, *J. Phys. Chem. B* **102**, 1212-1218 (1998) & arXiv:0801.4481.
[20] L. Landau and E. Lifschitz, *Fluid mechanics* (Mir, Moscow, 1958).
[21] F. dell'Isola, H. Gouin and G. Rotoli, Nucleation of shell-like interfaces by second gradient theory: numerical simulations, *Eur. J. Mech., B/Fluids* **15**, 545-568 (1996) & arXiv:0906.1897.
[22] A.K. Sen and S.H. Davis, Steady thermocapillary flows in two-dimensional slots, *J. Fluid Mech.* **121**, 163-186 (1982).
[23] D. Bedeaux, A.M. Alabano and P. Mazur, Boundary conditions and non-equilibrium thermodynamics, *Physica A*, **82**, 438-462 (1976).
[24] M. Slemrod, Admissibility criteria for propagating phase boundaries in a van der Waals fluid, *Arch. Rat. Mech. and Anal.* **81**, 301-315 (1983).
[25] G. Birkhoff, Numerical fluid dynamics, *SIAM Rev.* **25**, 1-34 (1983).
[26] P. Casal and H. Gouin, Connection between the energy equation and the motion equation in Korteweg's theory of capillarity, *Comptes rendus à l'Académie de Sciences, Paris* **300 II**, 231-234 (1985).
[27] J.E. Dunn and J. Serrin, On the thermodynamics of interstitial working, *Arch. Rat. Mech. and Anal.* **88**, 95-133 (1959).
[28] P. Casal and H. Gouin, Kelvin's theorem and potential equations in Korteweg's theory of capillarity, *Comptes rendus à l'Académie de Sciences, Paris* **300 II**, 301-304 (1985).
[29] H. Gouin, Liquid-solid interaction at nanoscale and its application in vegetal biology, *Coll. and Surf. A: Physicochemical and Engineering aspects* **393**, 17-22 (2011) & arXiv:1106.1275.
[30] P. Germain and J.P. Guiraud, Shock conditions and the structure of shock waves in a nonstationary flow of a dissipative fluid, *Journal de Mathématiques Pures et Appliquées* **45**, 311-358 (1966).
[31] P. Germain, *Mécanique des milieux continus, Ch. XVII* (Masson, Paris 1962).
[32] R. Aris, *Vectors, tensors and the basic equations of fluid mechanics* (Prentice Hall, New Jersey, 1962).
[33] S. Kobayashi and K. Nomizu, *Foundations of differential geometry* (Interscience Publ., New York, 1963).

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