Deduction of thermodynamic balance laws for bidimensional nonmaterial directed continua modelling interphase layers

Francesco Dell'Isola, W. Kosinski

Arch. Mech., 45, 3, pp. 333–359, Warszawa 1993

Deduction of thermodynamic balance laws for bidimensional nonmaterial directed continua modelling interphase layers

F. DELL'ISOLA (ROMA) and W. KOSIŃSKI (WARSZAWA)

Ϗ Ἄφρων δ', ϲ ὅς κ' Ϗ εὐ ἔλῃ πρὸς χρείσσονας Ϗ αὐτιφερίζειν
ὑίχης τε στέρεται πρὸς τ' Ϗ αἴσχεσιν Ϗ ἄλγεα πάσχει
ϲ Ὡς Ϗ ἔφατ' Ϗ ὠκυπέτης Ϗ ἶρηξ, ταυσίπτερος Ϗ ὄρνις
Hesiod, Op vv. 210–212

AN HEURISTIC METHOD for the solution of some contradictions arising in the formulation of direct models for nonmaterial interphase layers is proposed. The novelty of the method consists in its use as a guide for the formulation of the right balance laws for a pretty new object: nonmaterial bidimensional continua. By means of an integration across the thickness of the layer starting from balance laws which are valid for $3D$ nonpolar continua, new $2D$ balance laws are derived. In modelling surface phenomena associated with interfaces between phases a notion of "interfacial thickness" that could vary both with respect to time and along the interface itself, is recognized, even when the interphase layer is modeled as a $2D$ continuum. The quantities — together with their evolution equations — necessary to describe surface phenomena, heuristically assuming that the $2D$ continuum actually models a three-dimensional interfacial continuum, are indicated. Surface balance laws for all h-moments with respect to the thickness of the interface, where suitable surface extra-fluxes naturally appear, are deduced with quoted heuristic method and therefore postulated. Preliminary considerations aiming to prove that Tolmann's formula cannot be improved — in order to match all experimental evidence — without introducing at least a first order model for the interface between two phases, are developed.

1. Introduction

THE SURFACE phenomena play an essential role in the border land between the chemistry, physics and mechanics of fluids and solids. Since the days of Young [51] mechanical phenomena associated with fluid interface regions in equilibrium are well-described in terms of a surface tension: indeed, the interface between two fluids — say, a liquid and its vapor — has been considered from the mechanical point of view as if it were a uniformly stretched mass-less membrane of zero thickness.

When a system in equilibrium is composed of two or more phases, the interface region between any two phases has a small but perceptible contribution to the mechanical and thermodynamic behavior of the system. An extensive description of thermostatic behavior of multi-component interfaces was established by GIBBS [20]; it used the method of the dividing surface. However, non-equilibrium situations are more complex. Any comprehensive theory must accommodate the possibility of transport phenomena both within and across the interface; bulk motions may be induced by inhomogeneities of fields and of the matter in the interfacial region (cf. BUFF [9], LEVINE [33], LEVICH and KRYLOV [32], MURREL and BOUCHER [37], ONO and KONDO [41], OŚCIK [42], SCRIVEN [44]) and moreover, physical adsorption and evaporation can occur there.

The use of the classical method of the dividing surface of Gibbs has been preferred by many authors (cf. ONO and KONDO [41]) to avoid the necessity of assigning

some thickness to the interface zone. In that method the surface tension is not only a quantity strictly defined with reference to the dividing surface since the excess contributions to the densities and fluxes (currents) appear there in the form of superficial quantities.

The above method for treating surface tension and description of the excess contributions to the densities and fluxes (currents) at the dividing surface in the form of superficial quantities, is simple, intuitive and often useful but:

i) it is of approximate nature from the molecular point of view (cf. ONO and KONDO [41]), for the structure of the fluid undergoes not a discontinuous but progressive modification across the actual interface.

ii) it does not seem to be easily extendible to describe non-equilibrium phenomena (for a full discussion of this point see DELL'ISOLA and KOSIŃSKI [11]).

In the majority of known models of interfaces a surface or a layer of singularity of bulk fields appear, which in the case of models dealing with a $3D$ layer become additionally carriers of interfacial fields; the latter being defined as mean quantities of either true or excess bulk localized fields. In the both approaches: the singular dividing surface and the interfacial layer of finite thickness, the resulting systems of universal balance laws of mechanics and thermodynamics have in principle similar forms. The differences concern interpretations of the terms appearing in the resulting balance equations ([1]).

At this point one should underline the difference appearing between two models based on the concept of the interface $3D$ layer: the first referring to the excess quantities and the second referring to the true ones. In the first model one introduces a dividing surface located somewhere in the transition (interface) zone, and then the bulk quantities are extrapolated up to this surface by stipulating (cf. DREEMER and SLATTERY [15], DUMAIS [16], ALTS and HUTTER [5], GOGOSOV *et al.* [21]) that they must satisfy the typical $3D$ balance equations and the bulk constitutive relations (whatever these may be). The main problem of this model consists in introducing surface excess densities (quantities) to compensate the error introduced by replacing the exact (true) quantities by the extrapolated quantities in the transition zone.

In the second model no extrapolation is made ([2]), instead two dividing surfaces are introduced (cf. GATIGNOL [17]), which make the boundary between the single phase bulk media and the interface zone; in the latter multi-phase behavior is observed, in which the confining matter possess constitutive properties different from the surrounding bulk phases.

In both models the averaging procedure is applied in which the integration along the thickness is performed thus yielding mean quantities defined as surface fields. In the first model one relates those quantities to the deviations between exact and extrapolated quantities in the layer, in the second one the mean quantities are defined as the line integrals of the exact fields on some reference (e.g. mean) surface located between the previous two ones. Here no physical meaning is ascribed to that surface as it simply models the "geometry" of the interface layer: however, for the convenience one can call it the dividing surface (like in the first model).

([1]) A slightly different point of view represents BLINOWSKI [7].

([2]) For seek of selfconsistence we describe here the deduction procedure formally introduced in DELL'ISOLA and KOSIŃSKI [11], and KOSIŃSKI and ROMANO [29].

In the present paper as well as in the second approach the interface is modeled as a shell-like Eulerian region composed in principle of different material points at different time instants. ([3])

Having, without any extrapolations, the exact integral relations for the surface true fields in terms of the bulk quantities of the layer, one tries to make constitutive description, that takes into account the interface and its interaction with the bulk phases as a whole, without retaining those "microscopical" details of its structure which could be regarded (for a certain class of phenomena) as irrelevant. A more detailed description ([4]) for the interface can be given by developing theories in which higher order moments of the true fields appear (cf. DUMAIS [16] and DELL'ISOLA and KOSIŃSKI [12]) as proposed in the last section of this paper.

In the phenomenological approach we are presenting the interface is modelled as a finite slab, and more detailed information about the structure of the dividing surface is introduced by relating the interfacial quantities to their $3D$ counterparts.

It should be pointed out at this place that both the approaches lead finally to equations which are similar to those of the thermodynamics with surface field singularities. In this way one can find a common point with the singular surface approach well developed in the literature (cf. SCRIVEN [44], GHEZ [19], MOECKEL [35], ROMANO [43], DELL'ISOLA and IANNECE [10], ALBANO, BEDEAUX and VLIEGER [2], KOSIŃSKI [24]).

It is one of our aims to draw attention that by localizing the surface phenomena to their carrier, namely to the moving surfaces, we are loosing some information necessary in the constitutive modelling (cf. MURDOCH [36].) To get it back we can explore the results of our exact derivation and the formula in which the interfacial quantities appearing in the interfacial balance laws are defined in terms of the corresponding $3D$ quantities. In this way we get some "hints" and "compatibility" conditions to be taken into account even when $2D$ balance laws are to be postulated, in that which is usually called the *direct* approach for the development of the theory of $2D$ nonmaterial continua. The reasoning developed in this paper could be considered in such a direct approach as "heuristic" in nature.

2. Moving shell-like Eulerian region in a continuum

Let us now assume that the effect of the interface in a continuous material system $\mathcal{B}$ occupying at time t in a motion χ a simply-connected region $\mathcal{B}_t$ in $3D$ space E^3 may be localized in a three-dimensional *moving region* $\mathcal{Z}_t$ of finite (and in a sense to be made precise "small" when compared with its "area") thickness. The region $\mathcal{B}_t$ consists of two phases $\mathcal{B}_t^+$ and $\mathcal{B}_t^-$. In addition there exists a narrow layer $\mathcal{Z}_t$ which divides the volume phases $\mathcal{B}_t^{\pm}$.

The boundaries between $\mathcal{Z}_t$ and both $\mathcal{B}_t^{\pm}$ are regular surfaces Σ_t^+ and Σ_t^-; between them a reference (mean) surface Σ_t is located to which the mean, interfacial, fields will be referred. (Note the subscript t appearing in the sets introduced, which reflects the fact

([3]) This is unavoidable in the case of phase transition, while the case of adsorption may be also modeled by a material region with extra mass supply sources, cf. OŚCIK [42].

([4]) Another approach can be developed by introducing two different scales: micro- and macro-coordinates, the former responsible for the inner structure of the layer. The nonstandard analysis tool could be helpful here.

that the sets are not fixed in the time, they change ([5]) with time.) In the case when the excess quantities are used the reference surface Σ_t plays the role of the dividing surface (cf. DEEMER and SLATTERY [15] or ALTS and HUTTER [4–6]).

The model with a shell-like interfacial region, whose geometry was described above, is aimed to formulate an initial boundary-value problem in terms of the bulk field equations valid in the regions $\mathcal{B}_t^{\pm}$ and the interfacial field equations valid on Σ_t: indeed in the present formulation of the problem the motion of the region $\mathcal{Z}_t$ will be determined by means of (free-moving) boundary conditions, since the conditions primitively (and physically) formulated on the lateral boundary of $\mathcal{Z}_t$, i.e on $\Omega_t := \partial\mathcal{Z}_t \setminus \Sigma_t^{\pm}$, once recalculated (read: integrated along the thickness) will lead to boundary conditions for the interface equations.

2.1. Geometry and kinematics of the interfacial layer

2.1.1. Normal coordinate system. In the case of layers of constant thickness $z = z^+ - z^-$ and the boundary surfaces $\Sigma_t^{\pm}$ are equidistant (parallel) and the parallel surface coordinate system (NAGHDI [38], NAPOLITANO [40]) is most convenient for the description of an arbitrary point in the layer $\mathcal{Z}_t$. If the position of the reference surface at time t is given by

$$y = \mathbf{r}(l^1, l^2, t), \tag{2.1}$$

where l^1 and l^2 are Gauss parameters of the surface, then an arbitrary point $\mathbf{x}$ in $\mathcal{Z}_t$ can be represented as

$$\mathbf{x} = \mathbf{r}(l^1, l^2, t) + l\mathbf{n}(\mathbf{r}(l^1, l^2, t)), \tag{2.2}$$

where $l \in [z^-, z^+]$ is the third coordinate, measuring the distance of the point x from Σ_t along the unit normal $\mathbf{n}$. Here points of the region $\mathcal{Z}_t$ are referred to a fixed rectangular Cartesian coordinate system.

The representation (2.2) means that the zone $\mathcal{Z}_t$ is *delineated* by the surfaces Σ_t^l, at the distance of l from Σ_t and represented by Eq. (2.2) with fixed l, and is delimited by the surfaces Σ_t^+ and Σ_t^-, at the distance of $l = z^+$ and $l = z^-$ from Σ_t, respectively, where to the surfaces lying between Σ_t and $\mathcal{B}_t^-$ the negative values of the coordinate l are attributed. We will see in the next subsections that Eq. (2.2) allows us to "delineate" the interfacial layer also when its "thickness" is variable.

2.1.2. Geometrical properties of parallel surfaces. Let

$$\frac{\partial \mathbf{r}(l^\alpha, t)}{\partial l^1} =: \mathbf{a}_1, \qquad \frac{\partial \mathbf{r}(l^\alpha, t)}{\partial l^2} =: \mathbf{a}_2 \tag{2.3}$$

denote two linearly independent vectors $\mathbf{a}_1$ and $\mathbf{a}_2$ *tangent* to Σ_t at $\mathbf{r}$, then $\mathbf{a}^\alpha$, where $\alpha = 1, 2$, denote the co-tangent vectors of the surface Σ_t defined by the relation $\mathbf{a}_\beta \cdot \mathbf{a}^\alpha = \delta_\beta^\alpha$, where $\beta = 1, 2$ and $\mathbf{a}^\alpha \cdot \mathbf{n} = 0$. If we define the *surface gradient* $\operatorname{grad}_s(\cdot)$ by the formula

$$\operatorname{grad}_s \mathbf{u}(l^\beta, t) := \frac{\partial \mathbf{u}(l^\beta, t)}{\partial l^\alpha} \otimes \mathbf{a}^\alpha, \tag{2.4}$$

([5]) Only Eulerean formalism is possible in modeling surface phenomena at phase interfaces in phase transition problems (c.f. DELL'ISOLA and ROMANO [13, 14].

for an arbitrary vector (or tensor)-valued smooth field $\mathbf{u}$, then Eq. (2.4) allows us to define the tensor field on (the tangent space of) the surface Σ_t, called the *curvature or second fundamental tensor*, by

$$\mathbf{b} := -\operatorname{grad}_s \mathbf{n}, \tag{2.5}$$

for which $b_{\alpha\beta}$ are its components in the tensor basis $\{\mathbf{a}^\alpha \otimes \mathbf{a}^\beta\}$. The components of the curvature tensor in the basis $\{\mathbf{a}_\alpha \otimes \mathbf{a}_\beta\}$ or in the mixed basis $\{\mathbf{a}_\alpha \otimes \mathbf{a}^\beta\}$, are $b^{\alpha\beta}$ and b^α_β, respectively. As we will need it when manipulating the expressions where $\mathbf{b}$ appears, we recall here the *Cayley–Hamilton theorem* for 2×2 matrices, from which the identity follows

$$\mathbf{d}^2 - \mathbf{d}\operatorname{tr}\mathbf{d} + \mathbf{1}_s \det \mathbf{d} = \mathbf{0} \tag{2.6}$$

for any surface tensor $\mathbf{d}$, where $\mathbf{1}_s$ denotes the unit (metric) tensor of Σ_t.

Obviously Eq. (2.2) allows us to use for the parallel surface Σ_t^l the same Gauss parameters used for Σ_t: in this way all geometric differential objects we have introduced for Σ_t are naturally inherited by all Σ_t^l. To underline that except for the field of the normal vector $\mathbf{n}$, the intrinsic as well as the embedded geometries of the surfaces Σ_t^l can be different, we shall explicitly consider the dependence of the objects $\mathbf{a}^\alpha$, $\mathbf{a}_\beta$ and $\mathbf{b}$ on the third coordinate l (if l differs from zero).

Using the representation (2.2), together with Eq. (2.3), we have, after performing the necessary differentiation, the relation

$$\mathbf{a}_\alpha(l) = (\mathbf{1}_s - l\mathbf{b})\mathbf{a}_\alpha . \tag{2.7}$$

In what follows we shall need the expansion formula for the second invariant of the surface tensor $(\mathbf{1}_s - l\mathbf{b})$, denoted by $j(l)$, i.e. for the determinant of the matrix $[\delta^\beta_\alpha - lb^\beta_\alpha]$,

$$j(l) := \det[\delta^\beta_\alpha - lb^\beta_\alpha] = 1 - 2Hl + Kl^2 , \tag{2.8}$$

where H and K are invariants of $\mathbf{b}$, i.e. the mean and Gauss curvatures, respectively. If we put $k_1(\mathbf{r})$ and $k_2(\mathbf{r})$, for principal curvatures at $\mathbf{r} \in \Sigma_t$, then to avoid loss of regularity of the representation of the layer, we have to restrict the thickness z of the layer to the value

$$z < \inf\{\min(|k_1(\mathbf{r})^{-1}|, |k_2(\mathbf{r})^{-1}|) : \mathbf{r} \in \Sigma_t\} .$$

The relationships (2.7) between the basis of a typical surface Σ_t^l and Σ_t allows to calculate its surface metric tensor components $a_{\alpha\beta}(l)$, and the area element $\sqrt{a(l)}$; we obtain

$$a_{\alpha\beta}(l) := \mathbf{a}_\alpha(l) \cdot \mathbf{a}_\beta(l) = \mathbf{a}_\alpha \cdot (\mathbf{1}_s - l\mathbf{b})^2 \mathbf{a}_\beta .$$

Hence $a(l) := \det[a_{\alpha\beta}(l)] = \det[a_{\alpha\beta}] \det(\mathbf{1}_s - l\mathbf{b})^2 = aj(l)^2$.

It means that the ratio of the surface area elements of Σ_t^l to Σ_t is given by

$$j(l) = \sqrt{a(l)a^{-1}} . \tag{2.9}$$

The last formula is particularly useful in splitting the volume measure dv in the layer $\mathcal{Z}_t$ into the product of two measures: dl and da_l. Here dl represents the line measure (element) of a typical segment $\{\mathbf{r} + l\mathbf{n}(\mathbf{r}) : l \in [z^-, z^+], \mathbf{r} \in \Sigma_t\}$ in the layer, orthogonal to each surface Σ_t^l, while da_l is the the surface measure (element) of Σ_t^l. The last measure can be written as $da_l = \sqrt{a(l)}dl^1 dl^2$. From the orthogonality of segments and

the surfaces Σ_t^l, and the formula for $j(l)$, follows

$$dv = dl da_l = j(l) dl\, da\,, \tag{2.10}$$

where da is the the surface measure (element) of Σ_t. We can proceed further to get relations for other geometrical objects in the layer. Due to Eqs (2.2), (2.5) and (2.8) we obtain

$$\mathbf{b}(l) = j(l)^{-1}(\mathbf{b} - lK\mathbf{1}_s) = j(l)^{-1}\mathbf{b}(\mathbf{1}_s + l(\mathbf{b} - 2H\mathbf{1}_s)\,. \tag{2.11}$$

The surface tensors appearing under the sign of the last bracket, will play an important role in the further derivation, they satisfy the relation

$$j(l)\mathbf{1}_s = (\mathbf{1}_s - l\mathbf{b})\mathbf{A}_s(l)\,, \tag{2.12}$$

where

$$\mathbf{A}(l) := \mathbf{1}_s + l\tilde{\mathbf{b}}, \quad \tilde{\mathbf{b}} := \mathbf{b} - 2H\mathbf{1}_s\,. \tag{2.13}$$

Note that at a spherical point of the surface Σ_t, where $\mathbf{b} = H\mathbf{1}_s$, the tensor $\tilde{\mathbf{b}}$ is of opposite sign to $\mathbf{b}$, i.e. $\tilde{\mathbf{b}} = -\mathbf{b}$. To determine $\mathbf{a}^\beta(l)$ we use the relation $\mathbf{a}(l)\cdot\mathbf{a}^\beta(l) = \delta_\alpha^\beta$, valid for any l, to get

$$\mathbf{a}^\beta(l) = j(l)^{-1}(\mathbf{1}_s + l\tilde{\mathbf{b}})\mathbf{a}^\beta = j(l)^{-1}\mathbf{A}_s(l)\mathbf{a}^\beta\,. \tag{2.14}$$

The expressions (2.7), (2.11), (2.14) relate the geometry of a typical surface Σ_t^l to the geometry of Σ_t, quite similarly to the thin shell theory. What differs this derivation from that in the shell theory is the fact that here the region $\mathcal{Z}_t$ is not material, in general. To finish the derivation of geometrical relationships in the layer let us transform the oriented surface element $\mathbf{N}(l)da$ of the ruled surface Ω_t formed of segments

$$\{\mathbf{r} + l\mathbf{n}(\mathbf{r}) : l \in [z^-, z^+],\ \mathbf{r} \in \mathcal{C}_t \subset \Sigma_t\}\,,$$

where $\mathcal{C}_t$ is a curve (6) on Σ_t. Here $\mathbf{N}(l)$ is the outward unit normal to Ω_t, given by

$$\mathbf{N}(l) := \mathbf{t}_l \times \mathbf{n}\|\mathbf{t}_l \times \mathbf{n}\|^{-1}\,, \tag{2.15}$$

where $\mathbf{t}_l$ is a tangent vector to the curve $\mathcal{C}_t^l$ which is the lifting of the curve $\mathcal{C}_t$ to Σ_t^l; the vector tangent to the latter we shall denote by $\mathbf{t}_0$. Due to (2.2) and the fact that each of $\mathbf{t}_l$ and $\mathbf{t}_0$ are orthogonal to $\mathbf{n}$, and $\mathbf{n}$ has the unit length, we get (cf. Appendix)

$$\mathbf{N}(l)da = j(l)(\mathbf{a}^\gamma(l) \otimes \mathbf{a}_\gamma)\tilde{\mathbf{n}}dl\, ds\,, \tag{2.16}$$

where we have put $\tilde{\mathbf{n}} := \mathbf{t}_0 \times \mathbf{n}/\|\mathbf{t}_0\|$ for the unit normal to the curve $\mathcal{C}_t$ that is both tangent and outwardly directed with respect to Σ_t, and by ds we denote the line element of the curve $\mathcal{C}_0$.

2.1.3. Kinematics of a family of parallel surfaces. To describe the kinematics of $\mathcal{Z}_t$ we employ the vector

$$\mathbf{c} := \frac{\partial \mathbf{r}(l^\alpha, t)}{\partial t} \tag{2.17}$$

which represents the *velocity of the displacement* of the point

$$l^\alpha = \text{const}\,.$$

(6) If $\mathcal{C}_t = \Sigma_t \cap \overline{\mathcal{Z}}_t$, then the ruled surface will be the lateral boundary of $\mathcal{Z}_t$, i.e. $\partial\mathcal{Z}_t \setminus (\Sigma_t^- \cup \Sigma_t^+)$.

It is obvious that in another parametric representation of the moving surface, say $x = \mathbf{r}'(k^\alpha, t)$, the calculated time derivative will lead in general to another value

$$\mathbf{c}' = \frac{\partial \mathbf{r}(k^\alpha, t)}{\partial t}.$$

However, the normal component of both the derivatives $\mathbf{c}$ and $\mathbf{c}'$,

$$\mathbf{n} \cdot \mathbf{c} = \mathbf{n} \cdot \mathbf{c}' = c_n \tag{2.18}$$

are equal. That is easy to see, if one starts with the implicit representation of the hypersurface $\mathcal{S} := \bigcup \Sigma_t \times \{t\}$ in terms of some nontrivial differentiable function g by the equation

$$\mathcal{S} \subseteq \{(x, t) : g(x, t) = 0\}.$$

Then substituting $\mathbf{r}$ or $\mathbf{r}'$ into the equation $g(x, t) = 0$ and performing the differentiation under the identity sign, we get

$$\frac{\partial g(\mathbf{r}, t)}{\partial t} / \| \operatorname{grad} g \| = -c_n, \tag{2.19}$$

due to the expression for the normal vector $\mathbf{n}$. The normal component c_n of the velocity of the displacement of the point $l^\alpha = \text{const}$ is called the *normal speed of displacement of the surface*, since it is independent of the parameterization. On the contrary, the tangential component $c^\alpha := \mathbf{c} \cdot \mathbf{a}^\alpha$ is strictly related to the parameterization (l^α), for in another parameterization $c'^\alpha = \mathbf{c}' \cdot \mathbf{a}^\alpha$. Let us notice that if the both are related by a time-dependent transformation

$$k^\alpha = \hat{k}^\alpha(l^\beta, t) \quad \text{then} \quad c'^\alpha = c^\alpha + \frac{\partial \hat{k}^\alpha(l^\beta, t)}{\partial t}.$$

Now, if we choose the transformation $\hat{k}^\alpha(l^\beta, t)$ such that its time derivative is equal to $-c^\alpha$, then in the parameterization k^α the tangential velocity c'^α vanishes. That particular parameterization of the moving surface is called the *convected parameterization* (BOWEN and WANG [8], KOSIŃSKI [27]), in that parameterization $\mathbf{c}'$ is equal to $c_n\mathbf{n}$. The integral curve of the field $\mathbf{u} = c_n\mathbf{n}$, i.e. the spatial projection of a solution of the vector differential equation

$$\frac{dx}{ds} = c_n\mathbf{n}(x), \qquad \frac{dt}{ds} = 1,$$

is called the *normal trajectory* of the moving surface $\{\mathcal{S}_t\}$ if at $t_0 = t(0)$ it begins at a certain point of the initial surface Σ_{t_0}; each point of Σ_{t_0} is the starting point for a certain normal trajectory; moreover, through different points of Σ_t different normal trajectories are passing. In the convected parameterization the normal trajectory is a locus of the surface point $k^\alpha = \text{const}$. The choice of the convected parameterization in the description is of particular convenience in the derivation of any formula of a general nature.

Moreover, no final formula should depend on the particular choice of the parameterization of the moving surface, consequently it should be independent of the tangential component of the velocity field $\mathbf{c}$, only its normal component c_n has the geometrical meaning.

In the literature, however, one can find a discussion concerning the form of the $c^\alpha \mathbf{a}_\alpha$. In our opinion this velocity has no physical meaning, unless a fictitious point $l^\alpha = \text{const}$ will be equipped with an additional structure.

2.2. Displacement and other time derivatives

In the derivation of the local balance laws in the interfacial layer, an invariant time derivative has to appear, which is independent of the chosen parameterization of the moving surface Σ_t. Introducing the velocity of displacement $\mathbf{c}$ of the moving surface in a particular parameterization, namely in the convected parameterization, and following THOMAS [47, 48] and HAYES [22], the so-called

$$\textit{displacement time derivative } \frac{\delta}{\delta t}\mathbf{u}$$

of a quantity (a C^1-smooth field) $\mathbf{u}$ can be defined on the hypersurface $\mathcal{S}$ as the time derivative of $\mathbf{u}$ at fixed convected parameters of the moving surface $\{\Sigma_t\}$, i.e. by the formula

$$\frac{\delta}{\delta t}\mathbf{u} := \frac{\partial \mathbf{u}(k^\alpha, t)}{\partial t}, \tag{2.20}$$

where (k^α, t) is the convected parameterization of $\mathcal{S}$. It is a direct consequence of Eq. (2.20) that in any (not necessarily convected) parameterization (l^α, t) the operation formula for this derivative is

$$\frac{\delta}{\delta t}\mathbf{u} = \frac{\partial \mathbf{u}(l^\alpha, t)}{\partial t} - \operatorname{grad}_s \mathbf{u}\,\mathbf{c}. \tag{2.21}$$

Together with displacement (or Thomas) derivative we need to introduce other time derivatives of fields defined on a moving surface . To this aim we begin to apply the representation (2.2) of the surface Σ_t^l so that the velocity of displacement of Σ_t^l can be calculated as

$$\mathbf{c}(l) = \mathbf{c} - l(\operatorname{grad}_s c_n + \mathbf{bc}). \tag{2.22}$$

Here the explicit dependence of the fields on the coordinate l is written only, neither dependence on l^α nor on t is represented. To get Eq. (2.22) we have to differentiate (2.2) with respect to time t keeping l^α and l constant. Hence we need the time derivative of the normal vector field $\mathbf{n}$ (note that here $\mathbf{n}$ is the same for each l in the zone $\mathcal{Z}_t$). Due to the fact that $\mathbf{n} \cdot \mathbf{a}_\alpha = 0$, where the dot $\cdot$ denotes the inner product in E^3 and $\alpha = 1, 2$, we get

$$\frac{\partial \mathbf{n}}{\partial t} = -\mathbf{n} \cdot \frac{\partial \mathbf{c}(l^\alpha, t)}{\partial l^\beta} \otimes \mathbf{a}^\beta = -\mathbf{n} \operatorname{grad}_s \mathbf{c} = -(\operatorname{grad}_s c_n + \mathbf{bc}). \tag{2.23}$$

The derived formula (2.22) for the velocity is exact and can be compared with that proposed by GATIGNOL and SEPPECHER [18] and others. Additionally to the derivative related to the motion of the reference surface Σ_t and due to the derived representation for $\mathbf{c}(l)$ in Eq. (2.22), we may introduce the time derivative following the displacement of the whole region (layer) $\mathcal{Z}_t$. We denote this derivative by d_c/dt and define it by

$$\frac{d_c}{dt}\psi := \frac{\partial \psi(x, t)}{\partial t} + \operatorname{grad} \psi(x, t)\mathbf{c}(x), \tag{2.24}$$

where, according to Eq. (2.2), we put $x = \mathbf{r}(l^1, l^2, t) + l\mathbf{n}(\mathbf{r}(l^1, l^2, t))$ and ψ is an arbitrary (C^1-smooth field) defined (at least) on $\mathcal{S}$

$$\mathcal{S} := \cup\{\mathcal{Z}_t \times \{t\} : t \in I\},$$

2.3. Moving regions of variable thickness

The assumption about the constant thickness of the layer is rather reasonable when very thin layer of the interfacial medium is modeled. However, the constant in time (and in the surface coordinates) interfacial layer restricts the class of physical problems successfully treated by both the models based upon Gibbs' excess or true quantities. Consequently in this section to overcome this drawback we shall try to drop this assumption and to check its consequences on the formulae derived till now.

We consider a narrow layer $\mathcal{Z}_t$ dividing the volume phases $\mathcal{B}_t^{\pm}$: the boundaries between $\mathcal{Z}_t$ and both $\mathcal{B}_t^{\pm}$ are regular surfaces Σ_t^+ and Σ_t^-, which, however, are not in general any more equidistant (parallel). As before we use the parallel surface coordinate system describing an arbitrary point in the layer $\mathcal{Z}_t$: if the position of the reference surface is given by Eq. (2.1), then an arbitrary point x in $\mathcal{Z}_t$ can be represented as in Eq. (2.2), where the third coordinate l measuring the distance of the point x from Σ_t does not run over a fixed interval. Indeed, two scalar fields ζ^- and ζ^+ on the hypersurface $\mathcal{S}$ are defined such that their values give the distance of the boundary surfaces $\Sigma_t^{\pm}$ from Σ_t. The thickness z of the layer can then change according to the difference of both the functions, depending on the point and time, i.e.

$$z(\mathbf{r}, t) := \zeta^+(\mathbf{r}, t) - \zeta^-(\mathbf{r}, t). \tag{2.25}$$

The interfacial zone $\mathcal{Z}_t$ is therefore *delineated* by the surfaces Σ_t^l, at distance l from Σ_t and represented by Eq. (2.2) with fixed l, and is *delimited* by the surfaces Σ_t^+ and Σ_t^- given by

$$\Sigma_t^{\pm} \equiv \{y \in \mathcal{Z}_t : y = \mathbf{r} + \zeta^{\pm}(\mathbf{r}, t)\mathbf{n}(\mathbf{r}),\ \mathbf{r} \in \Sigma_t\} \tag{2.26}$$

which are not parallel to Σ_t, unless $\zeta^{\pm}(\mathbf{r}, t)$ is independent of the position $\mathbf{r}$. Let us notice that under the present weaker assumptions the layer can shrink locally to a surface if $\zeta^{\pm} = 0$. Moreover, it is possible now to describe the situation when the lateral boundary of the whole layer is not a ruled surface.

To avoid any singularities in the representation of the layer described in terms of the parallel surface coordinates, the assumption similar to that made in Sec. 2.2 and concerning the maximal thickness of the layer

$$\zeta := \sup\{\max(|\zeta^-(\mathbf{r}, t)|, |\zeta^+(\mathbf{r}, t)|) : (\mathbf{r}, t) \in \mathcal{S}\}$$

should be done. The geometry of the boundary surfaces $\Sigma_t^{\pm}$ will be related to that of Σ_t as follows. If $\mathbf{a}_\alpha^{\pm}$, $\alpha = 1, 2$, denote the natural base vectors of either surface, then due to Eq. (2.26), we get

$$\mathbf{a}_\alpha^{\pm} = (\mathbf{1}_s - \zeta^{\pm}\mathbf{b})\mathbf{a}_\alpha + \frac{\partial \zeta^{\pm}(\mathbf{r}, t)}{\partial l^\alpha}\mathbf{n}. \tag{2.27}$$

For the components of the metric tensor we then obtain

$$a_{\alpha\beta}^{\pm} := \mathbf{a}_\alpha^{\pm} \cdot \mathbf{a}_\beta^{\pm} = \mathbf{a}_\alpha \cdot (\mathbf{1}_s - \zeta^{\pm}\mathbf{b})^2\mathbf{a}_\beta + \frac{\partial \zeta^{\pm}}{\partial l^\alpha}\frac{\partial \zeta^{\pm}}{\partial l^\beta}. \tag{2.28}$$

The directed surface element of $\Sigma^{\pm}$ is given by (cf. Appendix)

$$\mathbf{n}^{\pm}(\mathbf{r})da^{\pm} := \mathbf{a}_1^{\pm} \times \mathbf{a}_2^{\pm} dl^1 dl^2 = (j(\zeta^{\pm}, \mathbf{r})\mathbf{n}(\mathbf{r}) - \mathbf{A}(\zeta^{\pm}) \operatorname{grad}_s \zeta^{\pm}) da\,, \tag{2.29}$$

where on the RHS the surface element $da = \sqrt{a} dl^1 dl^2$. In what follows the ratio $da^{\pm}/da$ we denote by $j^{\pm}$; it is a function of $\mathbf{r}$ and t.

The boundary surfaces $\Sigma_t^{\pm}$ move now with a velocity different than that calculated by Eq. (2.22). In fact, performing the time differentiation in Eq. (2.26) we obtain the following velocities $\mathbf{c}^{\pm}$ of displacement of $\Sigma^{\pm}$:

$$\mathbf{c}^{\pm} = \mathbf{c} - \zeta^{\pm}(\operatorname{grad}_s c_n + \mathbf{bc}) + \frac{\partial \zeta^{\pm}}{\partial t}\mathbf{n}\,. \tag{2.30}$$

To finish the geometrical preparation to the next section concerning the general balance law for $3D$ fields we write the product of $j^{\pm}$ and the normal speed of displacement of either boundary surface $\Sigma^{\pm}$ (cf. Appendix)

$$j^{\pm}\mathbf{c}^{\pm} \cdot \mathbf{n}^{\pm}(\mathbf{r}) = j(\zeta^{\pm}, \mathbf{r})\left(c_n + \frac{\delta \zeta^{\pm}}{\delta t}\right) + \zeta^{\pm} \operatorname{grad}_s \zeta^{\pm} \mathbf{A}_s(\zeta^{\pm}) \cdot \operatorname{grad}_s c_n\,. \tag{2.31}$$

3. Balance laws for a moving non-material shell-like region

The tools we developed in the previous sections will be now applied to derive the general and particular balance laws of thermomechanics. It will be done for the case of interfacial layer with nonvanishing thickness and for true, not excess, quantities.

3.1. General balance law

In one of previous papers (cf. DELL'ISOLA and ROMANO [14] or KOSIŃSKI and ROMANO [2]) it was assumed that the lateral boundary of the whole interface (transition) region, i.e.

$$\mathcal{Z}_t \setminus \Sigma_t^+ \cup \Sigma_t^-$$

is a ruled "lifted from a curve" surface .

It turns out that this assumption can be disregarded out on the global level keeping, however, this assumption, on the local level, i.e. during the passage from global to local forms of balance laws. It can be done assuming the integral form of the laws to be valid for any sub-layer, which is a proper subset of the whole layer bounded by subsurfaces of $\Sigma_t^{\pm}$ and a lateral boundary which is a ruled surface. In such a case the natural boundary conditions given on the lateral boundary of $\mathcal{Z}_t$ need to be recalculated in an appropriate way, also by introducing lines with material properties.

According to our notation the normal unit vector of $\Sigma_t^{\pm}$ will point from the region "$-$" to "$+$". The question how to choose the surfaces $\Sigma_t^{\pm}$ and the reference surface Σ_t lying between $\Sigma_t^{\pm}$ will not be discussed here (cf. DELL'ISOLA and KOSIŃSKI [11]). The choice of its position should be based on the mathematical convenience in the process of modelling and solving; this convenience is especially evident in the case of variable thickness of the layer.

The surface field ρ^s defined by

$$\rho^s(\mathbf{r}(l^1, l^2, t), t) = \int_{\zeta^-}^{\zeta^+} \rho(\mathbf{r}(l^\alpha, t) + l\mathbf{n}(\mathbf{r}), t) j(l, \mathbf{r}(l^\alpha, t)) dl \tag{3.1}$$

with $j(l, \mathbf{r}(l^\alpha, t))$, $\alpha = 1, 2$, given by Eq. (2.8), will be called the *surface mass density*. Here and in what follows both the cases of constant and variable thickness are discussed, for the former $\zeta^\pm$ should be identified with $z^\pm$.

Notice that in terms of the surface mass density ρ^s the mass of the matter contained at instant t in the zone $\mathcal{Z}_t$ is

$$\mathcal{M}(\mathcal{Z}_t) := \int_{\mathcal{Z}_t} \rho(x, t) d\nu = \int_{\Sigma_t} \rho^s da .$$

Therefore our definition of "surface" density is such that introduction of the $2D$ continuum Σ_t as a model for the interface $\mathcal{Z}_t$ does not cause a *loss* of the quantity $\mathcal{M}$. On the other hand, let us notice, that the definition of the surface mass does not take into account the type and the form of the $3D$ motion governed by the particle velocity field $\mathbf{v}$ in the layer (especially its tangential components): as a consequence we shall get an extra term in the flux of the mass in the $2D$ continuity equation (3.21). However, confining the velocity field to a particular form we could define the surface mass density in a different way appropriate to this form. Particular examples of $3D$ motions in a material zone are discussed in KOSIŃSKI and WĄSOWSKI [30].

After choosing the moving reference surface Σ_t as a geometrical object the remaining material structure of $\mathcal{Z}_t$ is preserved by equipping the surface Σ_t with a structure of $2D$ continuum. It is done by defining, in addition to ρ^s, next surface densities and fluxes of physical quantities as suitable integrals of the corresponding volume ones along the thickness of $\mathcal{Z}_t$. Hence, following the definition of the mass density, we can define for f, representing the density of a bulk quantity (i.e. a $3D$ density field) in the layer $\mathcal{Z}_t$, the corresponding surface field f^s as

$$f^s = \int_{\zeta^-}^{\zeta^+} j(l, \mathbf{r}) f(\mathbf{r} + l\mathbf{n}(\mathbf{r}), t) dl =: \langle jf \rangle . \tag{3.2}$$

The procedure makes possible the identification of interfacial quantities which appear in surface balance laws, even when we are dealing with non-material continua. Moreover, a more careful discussion of the *Galilean invariance* of the derived interfacial balance laws is possible when dealing with the explicit representations of the interfacial densities and fluxes (cf. Eq. (3.2) and (3.11)), respectively. This was the subject of the previous papers of DELL'ISOLA and ROMANO [14], KOSIŃSKI and ROMANO [29], DELL'ISOLA and KOSIŃSKI [11].

Referring to this last paper for a more detailed discussion, we remark here that, in our opinion, to the *geometrical* surface speed field c_n, describing how $\mathcal{Z}_t$ moves in E^3, no physically meaningful tangential component can be added. In the literature, however, such a component is searched for, which is "reasonable" from the physical point of view, thus getting a "complete" velocity field to be used in the balance of linear momentum (cf. ISHII [23], GATIGNOL and SEPPECHER [18], MOECKEL [35]): in DELL'ISOLA and

ROMANO [14] it is proved that these reasonable reasonings are valid only in the case of perfectly viscous interfaces as defined by Ishii.

On the other hand, in phase transition problems the material particles constituting the interfacial matter at instant t differ from those at another instant t'. Hence, together with the field $c_n\mathbf{n}$, we have to introduce an average velocity $\mathbf{V}^s$ of particles belonging to the layer. In terms of the $3D$ material (particle) velocity field $\mathbf{v}$, the densities ρ and ρ^s, the *"surface" material point velocity* $\mathbf{V}^s$ is given by the relation for the *surface momentum density*

$$\rho^s\mathbf{V}^s = \int_{\zeta^-}^{\zeta^+} \rho\mathbf{v}j(l,\mathbf{r})dl\,, \tag{3.3}$$

together with Eq. (3.1). A continuous $2D$ system modelled by Σ_t will be called *non-material* if ([7])

$$c_n \equiv \mathbf{c}\cdot\mathbf{n} \neq \mathbf{V}^s\cdot\mathbf{n}\,,$$

which means that in the mean the material points (particles) occupying the interface layer will not stay in it all the time. The difference

$$d_n := (\mathbf{c}-\mathbf{V}^s)\cdot\mathbf{n} \tag{3.4}$$

is a Galilean invariant and it is relevant to phase transition and adsorption processes if it does not vanish. It can be regarded as a quantity which needs to be determined by a constitutive equation (cf. DELL'ISOLA and ROMANO [11] and KOSIŃSKI [28]).

The classical balance law for the quantity ψ with its Galilean invariant flux (current) $\mathbf{w}$ and the source (supply + production) term p in the material volume $\mathcal{P}_t \subseteq \mathcal{B}_t$ is of the form

$$\frac{d}{dt}\int_{\mathcal{P}_t}\psi d\nu = -\int_{\partial\mathcal{P}_t}\mathbf{w}\cdot\mathbf{N}da + \int_{\mathcal{P}_t} p d\nu\,, \tag{3.5}$$

where $\mathbf{N}$ is the outward unit normal to $\partial\mathcal{P}_t$. Using the derivative d_c/dt , we get the following integral balance law for ψ in the non-material, in general, region $\mathcal{Z}_t$ moving with the velocity $\mathbf{c}$,

$$\frac{d_c}{dt}\int_{\mathcal{Z}_t}\psi dv = -\int_{\partial\mathcal{Z}_t}(\psi(\mathbf{v}-\mathbf{c})+\mathbf{w})\cdot\mathbf{N}da + \int_{\mathcal{Z}_t} p dv\,. \tag{3.6}$$

After the partition of both volumetric and surface measures into the product measures (cf. Eqs. (2.10) and (2.16)) we get ([8])

$$\frac{d_c}{dt}\int_{\Sigma}\psi^s da = -\int_{\mathcal{C}_t}(\mathbf{W}^{s'}\{\psi\} - \psi^s\mathbf{P}\mathbf{c})\tilde{\mathbf{n}}ds - \int_{\Sigma_t}((\tilde{\mathbf{w}}j\mathbf{n})^- + (\tilde{\mathbf{w}}j\mathbf{n})^+)da + \int_{\Sigma_t} p^s da\,. \tag{3.7}$$

The "weighted" limiting bulk-field values $(\tilde{\mathbf{w}}j\mathbf{n})^\pm$ are

$$(\tilde{\mathbf{w}}j\mathbf{n})^\pm := \tilde{\mathbf{w}}(\mathbf{r}+\zeta^\pm\mathbf{n}(\mathbf{r}),t)(j\mathbf{n})^\pm\,, \tag{3.8}$$

([7]) The surface is p-material if the equality holds (KOSIŃSKI [27]).

([8]) Here $\mathbf{P}$ denotes the tangent projection operator, i.e. $\mathbf{Pc} = \mathbf{c}_\tau$.

where

$$\tilde{\mathbf{w}} := \psi \otimes (\mathbf{v} - \mathbf{c}) + \mathbf{w} \tag{3.9}$$

is the new flux in Eq. (3.6) appearing under the surface integral over $\partial \mathcal{Z}_t$, and we have used the fact that $\mathbf{N}da = (j\mathbf{n})^{\pm}da$ on $\Sigma_t^{\pm}$. Let us notice that in the case of a constant thickness $\zeta^{\pm} = z^{\pm}$ is independent of $\mathbf{r}$ and t, and

$$(j\mathbf{n})^{\pm} = \pm j(z^{\pm}, \mathbf{r})\mathbf{n}\,, \tag{3.10}$$

while the case of a variable thickness is governed by Eq. (2.29) with $\zeta^{\pm}$ depending on $\mathbf{r}$ and t, in general. Since the definition of a general surface density has been given by Eq. (3.2) we have the definition of the surface flux in place of $\tilde{\mathbf{w}}$. To the flux $\tilde{\mathbf{w}}$ in Eq. (3.9) the corresponding surface flux $\mathbf{W}^{s'}\{\psi\}$ (note the prime over s) is defined as

$$\mathbf{W}^{s'}\{\psi\} \equiv \langle \psi \otimes (\mathbf{v} + l\,\mathrm{grad}_s\, c_n)\mathbf{A}_s(l)\rangle + \langle \mathbf{w}\mathbf{A}_s(l)\rangle\,. \tag{3.11}$$

The above definition together with Eq. (3.2) give at the same time the only possible relationships between the surface quantities and their bulk counterparts (better to say — their primitives), in order to make the interfacial balance law localized on the surface Σ_t compatible and derivable from the $3D$ law. The latter is postulated for ψ in the integral form Eq. (3.5). Let us notice that the surface flux $\mathbf{W}^{s'}\{\psi\}$ is Galilean invariant (due to the Cayley–Hamilton identity (2.6)). Now, we can get the final form of the integral balance law for layer $\mathcal{Z}_t$

$$\int_{\Sigma_t} \left(\frac{d_c}{dt}\psi^s + \psi^s \,\mathrm{div}_s\, \mathbf{c}_\tau\right) da + \int_{\mathcal{C}_t} (\mathbf{W}^{s'}\{\psi\} - \psi^s \otimes \mathbf{c}_\tau)\tilde{\mathbf{n}}\, ds$$
$$= -\int_{\Sigma_t} ((\tilde{\mathbf{w}}j\mathbf{n})^- + (\tilde{\mathbf{w}}j\mathbf{n})^+) da + \int_{\Sigma_t} p^s da\,.$$

Here we have used $\mathbf{c}_\tau$ to denote the tangential part of $\mathbf{c}$. However, in order to obtain the local, differential form of the law we have to perform the localization procedure by applying the integral law to an arbitrary *subzone* $\mathcal{Z}_t'$ of $\mathcal{Z}_t$. Here by *a subzone* we mean an arbitrary (shell-like) subregion $\mathcal{Z}_t'$ of $\mathcal{Z}_t \subset \mathcal{P}_t$ bounded by subsurfaces $\Sigma_t'^{\pm}$ of $\Sigma_t^{\pm}$ with a subsurface Σ_t' of Σ_t and with a nonvanishing lateral boundary being a ruled surface, for which the Stokes and Green-Gauss theorems can be applied.

After calculating the time derivative of the first integral and applying the obtained integral law to the arbitrary Σ_t' (supporting, by means the lifting along its normal field the subzone $\mathcal{Z}_t'$ of the layer $\mathcal{Z}_t$), we get under the continuity of the integrand ([9]), the following local equations:

$$\frac{d_c}{dt}\psi^s + \psi^s \,\mathrm{div}_s\, \mathbf{c} + \mathrm{div}_s(\mathbf{W}^{s'}\{\psi\} - \psi^s \otimes \mathbf{c}_\tau)$$
$$= -(\{\psi \otimes (\mathbf{v} - \mathbf{c}) + \mathbf{w}\}j\mathbf{n})^- + (\{\psi \otimes (\mathbf{v} - \mathbf{c}) + \mathbf{w}\}j\mathbf{n})^+\} + p^s\,. \tag{3.12}$$

([9]) If weaker conditions were assumed, like measurability of the integrand, the derived equation (3.12) should hold except for a set of H^2-measure zero, (i.e. at most on curves) where H^2-measure represents the $2D$ Hausdorff measure. This more general case leads to additional equations responsible for contact line effects.

Using the Thomas displacement derivative $\delta_n/\delta t$ (cf. (2.20)), together with the relationship

$$\frac{d_c}{dt}\psi^s + \psi^s \operatorname{div}_s \mathbf{c} - \operatorname{div}_s(\psi^s \mathbf{c}_\tau) = \frac{\delta_n}{\delta t}\psi^s - 2Hc_n\psi^s,$$

we arrive at

$$\frac{\delta_n}{\delta t}\psi^s - 2Hc_n\psi^s + \operatorname{div}_s \mathbf{W}^{s'}\{\psi\} = -\{(\{\psi \otimes (\mathbf{v}+\mathbf{c}) + \mathbf{w}\}j\mathbf{n})^- + (\{\psi \otimes (\mathbf{v}-\mathbf{c}) + \mathbf{w}\}j\mathbf{n})^+\} + p^s. \tag{3.13}$$

In *the constant thickness case* we obtain the following formula, which we quote here for the sake of completeness:

$$\frac{\delta_n}{\delta t}\psi^s - 2Hc_n\psi^s + \operatorname{div}_s \mathbf{W}^{s'}\{\psi\} = [\![\psi(\mathbf{v}-\mathbf{c}) + \mathbf{w}]\!]\cdot\mathbf{n} + \tilde{p}^s, \tag{3.14}$$

where

$$[\![g]\!] := g(\mathbf{r} + \zeta^-\mathbf{n}(\mathbf{r}), t) - g(\mathbf{r} + \zeta^+\mathbf{n}(\mathbf{r}), t) \tag{3.15}$$

for an arbitrary field g defined on $\mathcal{B}_t$.

The last equation is very well known in thermodynamics with surface singularities (called also: thermodynamics with singular surfaces, cf. MOECKEL [35], ISHII [23], KOSIŃSKI [24, 26, 27], ROMANO [43], ALTS [3], DELL'ISOLA and ROMANO [13]). The surface term $\tilde{p}^s$, called there a *surface supply*, is equal here to

$$\tilde{p}^s = p^s + [\![h\{\psi(\mathbf{v}-\mathbf{c}) + \mathbf{w}\}]\!]\cdot\mathbf{n}, \tag{3.16}$$

where $h(z^\pm, \mathbf{r}) := (K(\mathbf{r})z^\pm - 2H(\mathbf{r}))z^\pm$, and as previously $\mathbf{r} \in \Sigma_t$.

ALTS [3], ALTS and HUTTER [5, 6] gave a boundary layer model for curved phase boundaries and compared it with the model employing a singular surface. In their derivation, however, the surface quantities are identified with the so-called *excess* interfacial quantities in contrast with the definition given in the present paper. Moreover, they made use of balance laws for fields which are "extensions" of the bulk-field values at the boundary layer edges, i.e. at $\Sigma_t^\pm$, in our notation. In this way their definition of the surface quantities depends on the method of continuation of the bulk fields into the layer. The same definition of surface quantities has been used by DUMAIS [16], who performed the derivation for the case of a fixed material volume, not taking into account the diffusion terms. Partial results under the similar definition was obtained by Deemer and SLATTERY [18] together with the structural models for interface employing local area averages dealing with excess quantities. The present results could be compared with those of GATIGNOL and SEPPECHER [18], where dimensional and quantitive analyses of an approximation were performed. The present derivations are rather close to the results of the $2D$ approximation theory of shells. A comparison will be done in the other paper by KOSIŃSKI and WĄSOWSKI [30].

The variable thickness case ends with the law similar to Eq. (3.14), in which however the surface supply term $\tilde{p}^s$ is different and if we denote it by $\tilde{p}^s_v$, then due to Eqs. (2.29) and (2.31) it is equal to

$$\tilde{p}^s_v = p^s + [\![h\{\psi(\mathbf{v}-\mathbf{c}) + \mathbf{w}\}]\!]\cdot\mathbf{n} - [\![\psi \otimes (\mathbf{v} + \zeta^\pm \operatorname{grad}_s c_n)\mathbf{A}_s(\zeta^\pm)\operatorname{grad}_s \zeta^\pm]\!] - [\![\mathbf{w}\mathbf{A}_s(\zeta^\pm)\operatorname{grad}_s \zeta^\pm]\!] - \left[\!\left[\frac{\delta_n}{\delta t}\zeta^\pm \psi j\right]\!\right]. \tag{3.17}$$

Brief inspection of this term (in view of the previous one) shows the contribution of a new tangential part. This can be particularly important even in the case of the equilibrium equation for the interfacial stress tensor. The change of the thickness of the soap film on the bubble could be explained by means of those new terms.

3.2. Particular balance laws

Let us consider the particular quantities to be balanced by Eq. (3.14).

a. *Mass balance equation*: ψ is equal to ρ, and if the mass is conserved in the bulk medium, the flux of mass $\mathbf{w}$ and supply p of ρ (compare notation in (3.11)) are zero. The surface flux $\mathbf{W}^{s'}\{\rho\}$ is given by

$$\mathbf{W}^{s'}\{\rho\} = \langle \rho(\mathbf{v} + l \operatorname{grad}_s c_n)\mathbf{A}_s(l)\rangle =: \langle \mathbf{m}(l)\rangle , \tag{3.18}$$

which can be split into two parts

$$\mathbf{W}^{s'}\{\rho\} = \rho^s \mathbf{V}_\tau^s + \mathbf{W}_\rho = \rho^s \mathbf{V}_\tau^s + \langle \rho(\mathbf{A}_s(l) - j(l)\mathbf{1}_s)\mathbf{v} + l\rho \operatorname{grad}_s c_n \mathbf{A}_s(l)\rangle . \tag{3.19}$$

In the obvious way this equation leads to the definition of the extra mass flux $\mathbf{W}_\rho$. Hence the local balance equation for the mass is

$$\frac{\delta_n}{\delta t}\rho^s - 2Hc_n\rho^s + \operatorname{div}_s(\rho^s \mathbf{V}_\tau^s) + \operatorname{div}_s \mathbf{W}_\rho = [\![j\rho(\mathbf{v} - \mathbf{c})]\!] \cdot \mathbf{n} + [\![\rho(\mathbf{v} + \zeta^{\pm} \operatorname{grad}_s c_n)\mathbf{A}_s \ (\zeta^{\pm}) \cdot \operatorname{grad}_s \zeta^{\pm}]\!] - \left[\!\!\left[\frac{\delta_n}{\delta t}\zeta^{\pm}\rho j \right]\!\!\right] , \tag{3.20}$$

where from (3.18) and (3.19) follows the explicit form of the surface extra mass flux $\mathbf{W}_\rho$

$$\mathbf{W}_\rho := \langle l\rho\mathbf{v}\rangle \mathbf{b} - K\langle l^2\rho \mathbf{P}\mathbf{v}\rangle + \{\langle l\rho\rangle \mathbf{1}_s + \langle l^2\rho\rangle \tilde{\mathbf{b}}\} \operatorname{grad}_s c_n . \tag{3.21}$$

The last two terms on the RHS of Eq. (3.20) disappear in the *constant thickness case*. The simple inspection of Eq. (3.21) shows that the first two moments of the mass (i.e. $\langle l\rho\rangle$ and $\langle l^2\rho\rangle$) and of the momenta (i.e. $\langle l\rho\mathbf{v}\rangle$ and $\langle l^2\rho\mathbf{v}\rangle$) lead to the nonvanishing, in general, extra flux of the mass. Dealing with a p-material interface and the excess mass density field $\rho - \rho^{\pm}$, in the constant thickness case, ALTS [3] and then ALTS and HUTTER [4, 5] put the term corresponding to our $\mathbf{W}_\rho$ equal to zero. They chose, however, the surface coordinates as lines that are frozen to the motion of the surface "particles" (where the particles are defined in terms of the excess mass density). They should however distinguish between the density of surface particles defined in terms of the true mass distribution and that defined in terms of the excess fields, since their mass density can be negative. Moreover, their choice is local in l^β, and the disappearing of $\mathbf{W}_\rho$ cannot be interpreted as a constraint on the thickness of the layer which, in the constant thickness case, is a material intrinsic quantity, independent of l^β.

On the other hand, assuming that a reference surface should be chosen in the layer so that the quantity on RHS in Eq. (3.3) could represent the flux of mass, one cannot regard the same quantity as the surface linear momentum density, independently of the kinematics and the geometry of the surface, due to the K and $\operatorname{grad}_s c_n$ appearing in it. It follows that in the exact theory of interfaces one should expect the additional term $\mathbf{W}_\rho$ in the balance of mass, as compared with the form of this law given by the singular surface approach.

Let us notice that in the present model of an interface layer, the appearance of the non-vanishing extra flux of the mass $\mathbf{W}_\rho$ means that the flux of the surface mass is different from the density of interfacial linear momentum density; this observation has been already made by DELL'ISOLA and ROMANO [14] and SEPPECHER [45], using however an approximate theory.

b. *Linear momentum balance equation*: $\psi = \rho\mathbf{v}$ and the Cauchy stress $\mathbf{T}$ with the minus sign serves as the flux of linear momentum, and the body force $\rho\mathbf{f}$ is the supply term (no production in the bulk medium is admitted). For the surface flux $\mathbf{W}^{s'}\{\rho\mathbf{v}\}$ we have

$$\mathbf{W}^{s'}\{\rho\mathbf{v}\} \equiv \langle \rho\mathbf{v} \otimes (\mathbf{v} + l \operatorname{grad}_s c_n)\mathbf{A}_s(l)\rangle - \langle \mathbf{T}\mathbf{A}_s(l)\rangle , \tag{3.22}$$

which can be split into two parts

$$\mathbf{W}^{s'}\{\rho\mathbf{v}\} = \mathbf{V}^s \otimes \mathbf{W}^{s'}\{\rho\} + \mathbf{T}_s . \tag{3.22'}$$

The Galilean invariant *interfacial surface stress tensor* $\mathbf{T}_s$ can be written as the sum of two invariant parts $\mathbf{S}$ and $\mathbf{W}_{\rho v}$, where the definition of the first part imitates exactly that known in the continuum mixture theory (with the integration across the thickness instead of summing up over mixture constituents), and the second part can be called the extra surface linear momentum flux, i.e.

$$\begin{aligned} -\mathbf{S}(\mathbf{r},t) &:= \langle \mathbf{T}\mathbf{A}_s(l)\rangle - \langle \rho(\mathbf{v}-\mathbf{V}^s)\otimes(\mathbf{v}-\mathbf{V}^s)\mathbf{A}_s(l)\rangle , \\ \mathbf{W}_{\rho v}(\mathbf{r},t) &:= \langle \rho(\mathbf{v}-\mathbf{V}^s)\otimes((\mathbf{A}_s(l) - j(l)\mathbf{1}_s)\mathbf{V}^s + l\rho \operatorname{grad}_s c_n \mathbf{A}_s(l))\rangle . \end{aligned} \tag{3.23}$$

The other splitting can be made by defining two new components contributing to $\mathbf{T}_s$ as $\mathbf{S}^1$ and $\mathbf{S}^2$, where we put

$$\begin{aligned} \mathbf{S}^1(\mathbf{r},t) &:= -\langle \mathbf{T}\mathbf{A}_s(l)\rangle , \\ \mathbf{S}^2(\mathbf{r},t) &:= \langle (\mathbf{v}-\mathbf{V}^s)\otimes \mathbf{m}(l)\rangle , \\ \mathbf{T}_s &= \mathbf{S}^1 + \mathbf{S}^2 . \end{aligned} \tag{3.24}$$

Using the last formula we can write the local balance equation for the linear momentum as below, where the superscript $\pm$ is omitted,

$$\begin{aligned} \frac{\delta_n}{\delta t}(\rho^s\mathbf{V}^s) - 2Hc_n\rho^s\mathbf{V}^s + \operatorname{div}_s(\mathbf{V}^s\otimes(\rho^s\mathbf{V}_\tau^s + \mathbf{W}_\rho) + \mathbf{T}_s) &= \rho^s\mathbf{f}^s \\ + [\![(\rho\mathbf{v}\otimes(\mathbf{v}\cdot\mathbf{n} - c_n) - \mathbf{T}\mathbf{n})j]\!] - [\![\rho\mathbf{v}\otimes(\mathbf{v} + \zeta \operatorname{grad}_s c_n)\mathbf{A}_s(\zeta)\operatorname{grad}_s\zeta]\!] & \\ + [\![\mathbf{T}\mathbf{A}_s(\zeta)\operatorname{grad}_s\zeta]\!] - \left[\!\!\left[\frac{\delta_n}{\delta t}\zeta\rho\mathbf{v}j\right]\!\!\right] . & \end{aligned} \tag{3.25}$$

The last three terms on the RHS of Eq. (3.25) disappear in the *constant thickness case*. The above expressions for the interfacial stress tensor $\mathbf{T}_s$ show that even in the equilibrium case, when the diffusion terms $\mathbf{S}^2$ and $\mathbf{W}_{\rho v}$ are put equal to zero, the symmetry of the tangential components of $\mathbf{S}$ cannot hold automatically. Moreover, the normal component $\mathbf{n}\mathbf{T}_s$ of the surface stress tensor $\mathbf{T}_s$ contains a contribution from the diffusion terms unless

the tangential component $\mathbf{v}_\tau$ of the velocity field $\mathbf{v}$ is constant along each segment of the layer ([10]), i.e. is independent of l.

The last but not the least important proposition concerning the interfacial stress tensor concerns the explicit dependence of $\mathbf{S}$ on the curvature of the interface Σ_t. The dependence will be present even in the case when the contribution due to the diffusion is neglected. Consequently, in formulating a constitutive equation for the surface stress tensor one should not forget that $\mathbf{S}$ is a function of $\mathbf{b}$ as well. In particular, if the interface is modelled as a two-phase Korteweg fluid, then

$$-\mathbf{T} = \mathbf{p}\mathbf{1} + \alpha \mathbf{n} \otimes \mathbf{n}, \quad ([11])$$

with a scalar p as the pressure, then even in equilibrium (i.e. when $\mathbf{v} - \mathbf{V}^s = \mathbf{0}$), the surface stress will be different from the spherical tensor because of the term $-\langle lp \rangle \tilde{\mathbf{b}}$. Note that in the case of a spherical interface with non-vanishing thickness (e.g. a soap bubble) under equilibrium conditions $\mathbf{v} - \mathbf{V}^s = \mathbf{0}$, the surface stress will be

$$\mathbf{T}_s = \langle \mathbf{p}(1 + l/r) \rangle \mathbf{1}_s, \tag{3.26}$$

where r is a radius of the bubble. We can interpret the term $\langle p \rangle$ as the classical surface tension, here the additional part $\langle pl/r \rangle$ appears, which is normally very small, unless the thickness of the bubble is comparable with the radius r. This will be the case of very small bubbles. In our opinion, a deeper investigation of the consequences of (3.26) will lead to the improvement of Tolmann's formula which is considered necessary by ADAMSON [17] to match the experimental evidence. The quoted investigation will be made possible by means of the introduction of a first order model for the interface (cf. the following section).

It is seen from the above derivation that the local balance equations known in the singular surface approach are limited to very particular cases of the present approach and are valid under a particular set of assumptions.

c. *Angular momentum balance equation*: $\psi = \mathbf{x} \times \rho \mathbf{v}$. We restrict ourselves only to nonpolar continua. The master angular momentum balance law is well known in the $3D$ theory; its interfacial counterpart requires to define two quantities, namely

$$\Psi^s := \langle j(\mathbf{r} + l\mathbf{n}) \times \rho \mathbf{v} \rangle, \quad \Psi_2^s := \langle jl\mathbf{n} \times \rho \mathbf{v} \rangle \tag{3.27}$$

and the corresponding flux and production terms

$$\begin{aligned} \mathbf{w}(l) &= -(\mathbf{r} + l\mathbf{n}) \times \mathbf{T}, \quad \mathbf{w}_2(l) = -l\mathbf{n} \times \mathbf{T}, \\ \mathbf{p}^s &= \langle j(\mathbf{r} + l\mathbf{n}) \times \rho \mathbf{f} \rangle, \quad \mathbf{p}_2^s = \langle jl\mathbf{n} \times \rho \mathbf{f} \rangle - \langle j\mathbf{F} \rangle, \end{aligned} \tag{3.28}$$

where

$$j\mathbf{F} := (j\mathbf{1} + l(\mathbf{b} - Kl\mathbf{1}_s) \times \mathbf{T}) - j\mathbf{n} \times \mathbf{T} \cdot \mathbf{n} - \mathbf{m}(l) \times (\mathbf{v} \cdot \mathbf{n})\mathbf{n} + j\rho \mathbf{v} \times c_n \mathbf{n}.$$

Making use of the balance law (3.14), replacing ψ^s with those defined in Eqs. (3.27) together with the corresponding terms from Eqs. (3.28), we arrive at a pair of equations.

([10]) In that case $\langle f\mathbf{v} \rangle_\tau = \langle f \rangle \mathbf{v}_\tau$ for an arbitrary field f, and $\mathbf{v}_\tau = \mathbf{v}_\tau^\pm = \mathbf{V}_\tau^s$. Such condition has been admitted by DELL'ISOLA and ROMANO [14] and interpreted as the perfect viscosity consequence of the viscosity of the $3D$ matter contained in the layer.

([11]) We are assuming here that inside the layer i) $\nabla \rho$ is parallel to the field $\mathbf{n}$ inside the layer, ii) α is a nonvanishing scalar field.

Subtracting the second from the first one and using the cross product of $\mathbf{r}$ with the linear momentum equation (3.25), we end up with

$$\langle j(\mathbf{1} \times \mathbf{T}) \rangle = \mathbf{0} \tag{3.29}_1$$

which is automatically satisfied if $\mathbf{T}$ is symmetric. On the other hand, the last equation, which represents the *zero* order condition of non-polarity of the layer, leads to the following one:

$$\mathbf{l}_0 + \mathbf{l}_1 + (\mathbf{1} - \mathbf{n} \otimes \mathbf{n}) \underset{1,3}{\times} \mathbf{T}_s = \mathbf{b} \underset{1,3}{\times} {}^1\mathbf{T}_\sigma \tag{3.29}_2$$

where:

i. The product

$$\mathbf{N} \underset{1,3}{\times} \mathbf{M}$$

between 3-3 double tensors $\mathbf{N}$ and $\mathbf{M}$, whose components in a given basis are $N^j{}_m$ and M^{km}, respectively, is a 3-vector whose i-th component in the same basis is:

$$\varepsilon_{ijk} N^j{}_m M^{km} ,$$

with ε_{ijk} being the components of the three-dimensional Levi–Civita tensor.

Similarly the $\underset{1,3}{\times}$ product between 3-2 tensors is introduced; if $\mathbf{N}$ and $\mathbf{M}$ are 3-2 tensors whose components are $N^j{}_\alpha$ and $M^{k\alpha}$, respectively, with a fixed basis $\mathbf{e}_i$ for E^3 and another one $\mathbf{a}_\alpha$ for the tangent plane to Σ_t, then we denote with the symbol $\mathbf{N} \underset{1,3}{\times} \mathbf{M}$ a three-dimensional vector whose i-th component in the basis $\mathbf{e}_i$ is given by:

$$\varepsilon_{ijk} N^j{}_\alpha M^{k\alpha} .$$

ii. The quantities $\mathbf{l}_0$, $\mathbf{l}_1$ and ${}^1\mathbf{T}_\sigma$ have to be determined by means of constitutive equations. The quantities $\mathbf{l}_0$ and $\mathbf{l}_1$ represent, respectively, the *zero* and *higher order sources of kinetical couples*, and are introduced in order to describe those features of the kinematics of the layer which cannot be completely neglected even in the case of very thin layers. Indeed they can be represented, in terms of $3D$ fields, as follows:

$$\mathbf{l}_0 := \langle \rho(v_n - c_n)\mathbf{n} \times (\mathbf{v}_\mathrm{T} - \mathbf{V}^s_\mathrm{T}) \rangle ,$$

$$\mathbf{l}_1 := \langle (1 - j)\rho(v_n - c_n)\mathbf{n} \times (\mathbf{v}_\mathrm{T} - \mathbf{V}^s_\mathrm{T}) \rangle + \langle \mathbf{w}_\rho \times (\mathbf{V} \cdot \mathbf{n})\mathbf{n} \rangle + \mathbf{b}\, {}^1\mathbf{M}^s \times {}^1\mathbf{V}^s - \langle \mathrm{grad}_s\, c_n \times l\rho j\mathbf{v} \rangle ,$$

where

$${}^1\mathbf{M}^s := \langle {}^1\mathbf{m}(l) \rangle \equiv \langle jl\rho\mathbf{v}\mathbf{1}_s \rangle + {}^1\mathbf{w}_\rho$$

is the flux of the first moment of mass, ${}^1\mathbf{V}^s$ is defined by

$${}^1\rho^s\, {}^1\mathbf{V}^s = \langle \rho l j \mathbf{v} \rangle , \qquad {}^1\rho^s := \langle \rho j l \rangle ,$$

and

$${}^1\mathbf{w}_\rho := \langle l\rho(\mathbf{A}_s(l) - j\mathbf{1}_s)\mathbf{v} + l^2 \rho\, \mathrm{grad}_s\, c_n \mathbf{A}_s(l) \rangle .$$

Finally the quantity

$${}^1\mathbf{T}_\sigma := {}^1\mathbf{S}_1 + {}^1\mathbf{S}_2$$

represents the *interfacial first moment of stress tensor*, where

$${}^1\mathbf{S}_1\{\rho\mathbf{v}\} := \langle (\mathbf{v} - {}^1\mathbf{V}^s) \otimes {}^1\mathbf{m}(l) \rangle , \qquad {}^1\mathbf{S}_2\{\rho\mathbf{v}\} := -\langle l\mathbf{T}\mathbf{A}_s(l) \rangle .$$

Before closing the discussion of the equation of motion we shall write the explicit relation for the normal and antisymmetric parts of the surface stress tensor $\mathbf{T}_s$ in the natural basis $\{\mathbf{a}_\alpha, \mathbf{n}\}$. They are

$$T_s^{n\alpha} = -\langle jT^{n\alpha}\rangle + \langle j\rho(\mathbf{v}\cdot\mathbf{n} - c_n)(v^\alpha - V^{s\alpha})\rangle + \langle(\mathbf{v}-\mathbf{V}^s)\cdot\mathbf{n}w_\rho^\alpha\rangle - \langle jlb_\delta^\alpha T^{n\delta}\rangle\rangle\,, \tag{3.30}$$

$$T_s^{12} - T_s^{21} = -\langle jl(b_2^1(T^{22} - T^{11}) + (b_1^1 - b_2^2)T^{12})\rangle\,,$$

where

$$T_s^{n\alpha} := \mathbf{n}\cdot\mathbf{T}_s\mathbf{a}^\alpha, \quad T^{12} := \mathbf{a}^1\cdot\mathbf{T}\,\mathbf{a}^2, \quad \text{etc.}$$

d. *Energy balance equation*: $\psi = \rho(e + 0.5\mathbf{v}\cdot\mathbf{v}) =: \rho E$, where e represents the specific internal energy, the sum $-\mathbf{v}\mathbf{T} + \mathbf{q}$ serves as the flux of the total energy, where $\mathbf{q}$ is the heat flux vector, the sum $\rho(\mathbf{f}\cdot\mathbf{v} + r)$ is the supply term, where r represents the body heat supply density. For the surface flux $\mathbf{W}^{s'}\{\rho E\}$ we have

$$\mathbf{W}^{s'}\{\rho E\} \equiv \langle E\mathbf{m}(l)\rangle - \langle(\mathbf{v}\mathbf{T} - \mathbf{q})\mathbf{A}_s(l)\rangle\,. \tag{3.31}$$

If we define

$$\begin{aligned}
&\rho^s e^s := \langle j\rho\tilde{e}\rangle, \quad \tilde{e} := e + 0.5(\mathbf{v}-\mathbf{V}^s)^2, \quad \rho^s\tilde{r}^s := \langle j\rho(r + \mathbf{f}\cdot(\mathbf{v}-\mathbf{V}^s))\rangle\,,\\
&\mathbf{q}^s := \langle(\rho\tilde{e}(\mathbf{v}-\mathbf{V}^s) + \mathbf{q} - (\mathbf{v}-\mathbf{V}^s)\mathbf{T})\mathbf{A}_s(l)\rangle\,,\\
&\mathbf{W}_E := \langle\rho\tilde{e}(\mathbf{A}_s(l) - j(l)\mathbf{1}_s)\mathbf{V}^s + l\rho\tilde{e}\,\mathrm{grad}_s\, c_n\mathbf{A}_s(l)\rangle\,,
\end{aligned} \tag{3.32}$$

then the local energy balance equation will be

$$\begin{aligned}
\frac{\delta_n}{\delta t}(\rho^s(e^s + 0.5\mathbf{V}^s\cdot\mathbf{V}^s)) - 2Hc_n\rho^s(e^s + 0.5\mathbf{V}^s\cdot\mathbf{V}^s)&\\
+ \mathrm{div}_s(\rho^s(e^s + 0.5\mathbf{V}^s\cdot\mathbf{V}^s)\mathbf{V}_\tau^s + \mathbf{q}^s + \mathbf{W}_E + \mathbf{V}^s\mathbf{T}_s + 0.5\mathbf{V}^s\cdot\mathbf{V}^s\mathbf{W}_\rho)&\\
= \rho^s\mathbf{f}^s\cdot\mathbf{V}^s + \rho^s\tilde{r}^s + [\![(\rho(e + 0.5\mathbf{v}\cdot\mathbf{v})(\mathbf{v}-\mathbf{c}) + \mathbf{q} - \mathbf{v}\mathbf{T})j]\!]\cdot\mathbf{n}&\\
-[\![\rho(e + 0.5\mathbf{v}\cdot\mathbf{v})(\mathbf{v} + \zeta\,\mathrm{grad}_s\, c_n)\mathbf{A}_s(\zeta)\,\mathrm{grad}_s\,\zeta]\!] + [\![(\mathbf{v}\mathbf{T} - \mathbf{q})\mathbf{A}_s(\zeta)\,\mathrm{grad}_s\,\zeta]\!]&\\
-\left[\!\!\left[\frac{\delta_n}{\delta t}\zeta\rho(e + 0.5\mathbf{v}\cdot\mathbf{v})j\right]\!\!\right]\,.&
\end{aligned} \tag{3.33}$$

The last three terms on the RHS of Eq. (3.33) disappear in the *constant thickness case*. The above expressions for the interfacial heat flux $\mathbf{Q}^s$ and the supply terms $\rho^s\tilde{r}^s$ lead to the following relations:

$$\begin{aligned}
\mathbf{Q}^s &= \mathbf{q}^s + \mathbf{W}_E\,,\\
\rho^s r^s &\neq \rho^s\tilde{r}^s\,,
\end{aligned} \tag{3.34}$$

which mean that even the case of a nonconductor of heat at the $3D$ level leads to the nonvanishing interfacial heat flux, and the vanishing heat supply term ρr at the $3D$ level leads to the interfacial heat supply $\rho^s\tilde{r}^s$ equal to $\langle j\rho\mathbf{f}\cdot(\mathbf{v}-\mathbf{V}^s)\rangle$, which does not need to vanish if $\mathbf{f}$ is different from zero.

f. *Thermodynamic inequality*

The second law of thermodynamics for the $3D$ material continuum is assumed in the form of the entropy production inequality

$$\frac{d}{dt}\int_{\mathcal{P}_t}\rho\eta d\nu \geq -\int_{\partial\mathcal{P}_t}(\mathbf{q}/\vartheta + \mathbf{k})\cdot\mathbf{N}da + \int_{\mathcal{P}_t}\rho r/\vartheta d\nu\,, \tag{3.35}$$

where η and ϑ represent the specific entropy and the absolute temperature, respectively, while $\mathbf{k}$ is the so-called extra entropy flux. Performing the usual localization for the interfacial layer we get the inequality

$$\frac{\delta_n}{\delta t}\rho^s\eta^s - 2Hc_n\rho^s\eta^s + \operatorname{div}_s(\rho^s\eta^s\mathbf{V}_\tau^s + \tilde{\mathbf{k}}^s + \mathbf{W}_\eta) \geq \rho^s r_\eta^s + [\![(\rho\eta(\mathbf{v}-\mathbf{c}) + \mathbf{q}/\vartheta + \mathbf{k})j]\!]\cdot\mathbf{n} - [\![\rho\eta(\mathbf{v} + \zeta\operatorname{grad}_s c_n)\mathbf{A}_s(\zeta)\operatorname{grad}_s\zeta]\!] - [\![(\mathbf{q}/\vartheta + \mathbf{k})\mathbf{A}_s(\zeta)\operatorname{grad}_s\zeta]\!] - \left[\!\left[\frac{\delta_n}{\delta t}\zeta\rho\eta j\right]\!\right], \tag{3.36}$$

where

$$\mathbf{W}^{s'}\{\rho\eta\} \equiv \langle\rho\eta\mathbf{m}(l)\rangle + \langle(\mathbf{q}/\vartheta + \mathbf{k})\mathbf{A}_s(l)\rangle,$$

and we have defined

$$\rho^s\eta^s := \langle j\rho\eta\rangle, \quad \rho^s r_\eta^s := \langle j\rho(r/\vartheta)\rangle,$$
$$\tilde{\mathbf{k}}^s := \langle(\rho(\mathbf{q}/\vartheta + \mathbf{k})\mathbf{A}_s(l) + (\rho\eta(\mathbf{v}-\mathbf{V}^s))\mathbf{A}_s(l)\rangle, \tag{3.37}$$
$$\mathbf{W}_\eta := \langle\rho\eta(\mathbf{A}_s(l) - j(l)\mathbf{1}_s)\mathbf{V}^s + l\rho\eta\operatorname{grad}_s c_n\mathbf{A}_s(l)\rangle.$$

The last three terms on the RHS of (3.36) disappear in the *constant thickness case*. The above expressions for the interfacial entropy flux cannot be simple related to the interfacial heat flux $\mathbf{Q}^s$, even in the case of the vanishing extra-term $\mathbf{k}$. However, under particular set of assumptions concerning the kinematics and the constitutive properties of the matter in the layer, some simplification can be made in order to derive such a relation. This will be the subject of a future paper.

4. H-order models for nonmaterial twodimensional continua

Using the model developed in the previous sections one could not completely take into account the influence of the thickness of the layer on the thermomechanical behaviour of phase interfaces. The quoted model will be called a *0-th order model*.

On the other hand the considerations preceding and following formula for (3.26) clearly point out the following circumstance: if one wants to account the influence of surface effects in the formation of small drops, one has to consider (at least) the first moment of the interfacial tension field.

In order to provide a guide to the introduction of a more complex structure to nonmaterial bidimensional continua, an H-th order model can be developed (cf. DELL'ISOLA and KOSIŃSKI [12] for the case of the constant thickness) the idea of which comes from DUMAIS [16]. Similarly to the previous sections we will assume that the interfacial layer has a variable thickness, in the sense made precise in Sec. 2.

4.1. H-th order model

One introduces the k-th moment field ($k \leq H$) of a typical interfacial quantity f by

$$^k f \equiv l^k(x,t^*)f \quad \text{when } x \in \mathcal{Z}_t. \tag{4.1}$$

Here l^k means the k-th power of l.

Then for every k the following k-th local balance equation for the physical quantity represented by the field ψ can be easily derived by evaluating partial time derivative of

the k-th moment ${}^k\psi$, using the properties of the function $l(x, t^*)$ and using the local balance equation for the field ψ (see Eqs. (3.17)–(3.20) in KOSIŃSKI [31]):

$$\frac{\partial}{\partial t}\,{}^k\psi + \operatorname{div}({}^k\psi \otimes \mathbf{v} + {}^k\mathbf{w}) = {}^kp + k({}^{k-1}\psi \otimes (\mathbf{v}\cdot\mathbf{n} - c_n) + {}^{k-1}\mathbf{w}\cdot\mathbf{n}). \tag{4.2}$$

Regarding Eq. (4.2) as the local form of a particular case of Eq. (3.5) and recalling the form (3.14) we get the following surface balance equation:

$$\begin{aligned}\frac{\delta_n}{\delta t}\,{}^k\psi^s - 2Hc_n\,{}^k\psi^s + \operatorname{div}_s(\langle {}^k\psi \otimes (\mathbf{v} + l\operatorname{grad}_s c_n)\mathbf{A}_s(l)\rangle + \langle {}^k\mathbf{w}\mathbf{A}_s(l)\rangle) \\ = [\![({}^k\psi \otimes (\mathbf{v} - \mathbf{c}) + {}^k\mathbf{w}]\!]\cdot\mathbf{n} + {}^k\tilde{p}_v^s + \langle jk({}^{k-1}\psi \otimes (\mathbf{v}\cdot\mathbf{n} - c_n) + {}^{k-1}\mathbf{w}\cdot\mathbf{n})\rangle,\end{aligned} \tag{4.3}$$

where the following definition has been used:

$$\begin{aligned}{}^k\tilde{p}_v^s := {}^kp^s + [\![h\{{}^k\psi \otimes (\mathbf{v} - \mathbf{c}) + {}^k\mathbf{w}\}]\!]\cdot\mathbf{n} \\ -[\![{}^k\psi \otimes (\mathbf{v} + \zeta^{\pm}\operatorname{grad}_s c_n)\mathbf{A}_s(\zeta^{\pm})\operatorname{grad}_s\zeta^{\pm}]\!] - [\![{}^k\mathbf{w}\mathbf{A}_s(\zeta^{\pm})\operatorname{grad}_s\zeta^{\pm}]\!] - \left[\!\!\left[\frac{\delta_n}{\delta t}\zeta^{\pm}\,{}^k\psi j\right]\!\!\right].\end{aligned} \tag{4.4}$$

Equation (4.3) is valid for any $k \geq 1$.

We remark that when $k = 0$ the primitive interfacial balance law (3.14) with (3.17) yields Eq. (4.3) as a particular case.

However, a question may arise concerning the completeness of a k-th order model, formulated by postulating, for the interface, the first $k + 1$ surface balance equations of the type (4.3) and assuming that all the higher order quantities appearing in them are determined by means of constitutive equations.

To answer this question one should first notice that the k-th moment of a typical function f in Eq. (4.1) (regarded as a function of l only) defines the projection of f on the polynomial l^k belonging to the basis formed by all polynomials of the function space

$$L^2([z^-, z^+], d\mu = j\,dl).$$

The measure μ is positive and absolutely continuous with respect to the Lebesgue measure as long as j is positive and H and K are finite; this corresponds to the assumed hypothesis on the thickness of the layer $\mathcal{Z}_t$. Therefore the H-order theory deals with truncated expansions across the thickness of the layer of the physical quantities to be balanced.

4.2. H-th order thermomechanical balance equations

We present here the balance equations of k-th moments of mass, linear momentum, energy and entropy.

We explicitly remark that balance of angular momentum leads to some surface equations which simply generalize either Eq. $(3.29)_1$ or its different formulation $(3.29)_2$.

a. *Balance of mass*

$$\begin{aligned}\frac{\delta_n}{\delta t}\,{}^k\rho^s - 2Hc_n\,{}^k\rho^s + \operatorname{div}_s({}^k\rho^s\,{}^k\mathbf{V}_\tau^s) + \operatorname{div}_s\,{}^k\mathbf{W}_\rho \\ = \langle jk\,{}^{k-1}\rho(\mathbf{v} - \mathbf{c})\rangle\cdot\mathbf{n} + [\![j\,{}^k\rho(\mathbf{v} - \mathbf{c})]\!]\cdot\mathbf{n} \\ -[\![{}^k\rho(\mathbf{v} + \zeta^{\pm}\operatorname{grad}_s c_n)\mathbf{A}_s(\zeta^{\pm})\cdot\operatorname{grad}_s\zeta^{\pm}]\!] - \left[\!\!\left[\frac{\delta_n}{\delta t}\zeta^{\pm}\,{}^k\rho j\right]\!\!\right],\end{aligned} \tag{4.5}$$

where we have used the following notation:

$$ {}^{k}\rho^{s}\,{}^{k}\mathbf{V}^{s} := \langle j\,{}^{k}\rho\mathbf{v}\rangle\,. $$

b. *Balance of linear momentum*

$$ \begin{aligned} (4.6)\quad & \frac{\delta_n}{\delta t}({}^{k}\rho^{s}\,{}^{k}\mathbf{V}^{s}) - 2Hc_n\,{}^{k}\rho^{s}\,{}^{k}\mathbf{V}^{s} + \operatorname{div}_s({}^{k}\mathbf{V}^{s}\otimes{}^{k}\mathbf{M}^{s} + {}^{k}\mathbf{S}^{1} + {}^{k}\mathbf{S}^{1}) \\ &= {}^{k}(\rho\mathbf{f})^{s} + [\![({}^{k}\rho\mathbf{v}\otimes(\mathbf{v}\cdot\mathbf{n}-c_n) - {}^{k}\mathbf{T}\mathbf{n})j]\!] + \langle k({}^{k-1}\rho\mathbf{v}\otimes(\mathbf{v}\cdot\mathbf{n}-c_n) - {}^{k-1}\mathbf{T}\mathbf{n})j\rangle \\ &\quad -[\![{}^{k}\rho\mathbf{v}\otimes(\mathbf{v}+\zeta\operatorname{grad}_s c_n)\mathbf{A}_s(\zeta)\operatorname{grad}_s\zeta]\!] + [\![{}^{k}\mathbf{T}\mathbf{A}_s(\zeta)\operatorname{grad}_s\zeta]\!] - \left[\!\!\left[\frac{\delta_n}{\delta t}\zeta\,{}^{k}\rho\mathbf{v}j\right]\!\!\right], \end{aligned} $$

where we have omitted the superscript $\pm$ and used the following notations:

$$ \begin{aligned} \langle {}^{k}\rho(\mathbf{v}+l\operatorname{grad}_s c_n)\mathbf{A}_s(l)\rangle =: \langle {}^{k}\mathbf{m}(l)\rangle &\equiv {}^{k}\mathbf{M}^{s}\,, \\ {}^{k}\mathbf{S}^{1}(\mathbf{r},t) &:= -\langle {}^{k}\mathbf{T}\mathbf{A}_s(l)\rangle\,, \\ {}^{k}\mathbf{S}^{2}(\mathbf{r},t) &:= \langle(\mathbf{v}-{}^{k}\mathbf{V}^{s})\otimes{}^{k}\mathbf{m}(l)\rangle\,. \end{aligned} $$

c. *Balance of energy*

$$ \begin{aligned} (4.7)\quad & \frac{\delta_n}{\delta t}({}^{k}\rho^{s}({}^{k}e^{s} + 0.5\,{}^{k}\mathbf{V}^{s}\cdot{}^{k}\mathbf{V}^{s})) - 2Hc_n\,{}^{k}\rho^{s}({}^{k}e^{s} + 0.5\,{}^{k}\mathbf{V}^{s}\cdot{}^{k}\mathbf{V}^{s}) \\ &\quad + \operatorname{div}_s({}^{k}\rho^{s}({}^{k}e^{s} + 0.5\,{}^{k}\mathbf{V}^{s}\cdot\mathbf{V}^{s})\,{}^{k}\mathbf{V}_{\tau}^{s} + {}^{k}\mathbf{q}^{s} + {}^{k}\mathbf{W}_{E} \\ &\quad + {}^{k}\mathbf{V}^{s}\,{}^{k}\mathbf{T}_{s} + 0.5\,{}^{k}\mathbf{V}^{s}\cdot{}^{k}\mathbf{V}^{s}\,{}^{k}\mathbf{W}_{\rho}) = {}^{k}(\rho\mathbf{f})^{s}\cdot{}^{k}\mathbf{V}^{s} + {}^{k}\rho^{s}\,{}^{k}\tilde{r}^{s} \\ &\quad + [\![({}^{k}\rho(e+0.5\mathbf{v}\cdot\mathbf{v})(\mathbf{v}-\mathbf{c}) + {}^{k}\mathbf{q} - {}^{k}\mathbf{v}\mathbf{T})j]\!]\cdot\mathbf{n} \\ &\quad + \langle k({}^{k-1}\rho(e+0.5\mathbf{v}\cdot\mathbf{v})(\mathbf{v}-\mathbf{c}) + {}^{k-1}\mathbf{q} - {}^{k-1}\mathbf{v}\mathbf{T})j\rangle\cdot\mathbf{n} \\ &\quad - [\![{}^{k}\rho(e+0.5\mathbf{v}\cdot\mathbf{v})\otimes(\mathbf{v}+\zeta\operatorname{grad}_s c_n)\mathbf{A}_s(\zeta)\operatorname{grad}_s\zeta]\!] \\ &\quad [\![({}^{k}\mathbf{v}\mathbf{T} - {}^{k}\mathbf{q})\mathbf{A}_s(\zeta)\operatorname{grad}_s\zeta]\!] - \left[\!\!\left[\frac{\delta_n}{\delta t}\zeta\,{}^{k}\rho(e+0.5\mathbf{v}\cdot\mathbf{v})j\right]\!\!\right], \end{aligned} $$

where we have used the notations:

$$ \begin{aligned} {}^{k}\rho^{s}\,{}^{k}e^{s} &:= \langle j\rho\,{}^{k}\tilde{e}\rangle, \quad \rho^{s}\tilde{r}^{s} := \langle j^{k}\rho(r+\mathbf{f}\cdot(\mathbf{v}-\mathbf{V}^{s}))\rangle\,, \\ {}^{k}\mathbf{T}_{s} &:= {}^{k}\mathbf{S}_{1} + {}^{k}\mathbf{S}_{2}\,. \end{aligned} $$

d. *Thermodynamic inequality*

$$ \begin{aligned} (4.8)\quad & \frac{\delta_n}{\delta t}\,{}^{k}\rho^{s}\,{}^{k}\eta^{s} - 2Hc_n\,{}^{k}\rho^{s}\,{}^{k}\eta^{s} + \operatorname{div}_s({}^{k}\rho^{s}\,{}^{k}\eta^{s}\,{}^{k}\mathbf{V}_{\tau}^{s} + {}^{k}\tilde{\mathbf{k}}^{s} + {}^{k}\mathbf{W}_{\eta}) \\ &\quad \geq {}^{k}\rho^{s}\,{}^{k}r_{\eta}^{s} + [\![({}^{k}\rho\eta(\mathbf{v}-\mathbf{c}) + {}^{k}\mathbf{q}/\vartheta + {}^{k}\mathbf{k})j]\!]\cdot\mathbf{n} \\ &\quad -[\![{}^{k}\rho\eta(\mathbf{v}+\zeta\operatorname{grad}_s c_n)\mathbf{A}_s(\zeta)\operatorname{grad}_s\zeta]\!] - [\![({}^{k}\mathbf{q}/\vartheta + {}^{k}\mathbf{k})\mathbf{A}_s(\zeta)\operatorname{grad}_s\zeta]\!] \\ &\quad -\left[\!\!\left[\frac{\delta_n}{\delta t}\zeta\,{}^{k}\rho\eta j\right]\!\!\right] + \langle k({}^{k}\rho\eta(\mathbf{v}-\mathbf{c}) + {}^{k}\mathbf{q}/\vartheta + {}^{k}\mathbf{k})j\rangle\cdot\mathbf{n}\,, \end{aligned} $$

where we have used the following notations:

$$ {}^{k}\rho^{s}\,{}^{k}\eta^{s} := \langle j^{k}\rho\eta\rangle, \quad {}^{k}\rho^{sk}r_{\eta}^{s} := \langle j^{k}\rho(r/\vartheta)\rangle\,, $$

$$ {}^{k}\tilde{\mathbf{k}}^{s} := \langle ({}^{k}\rho(\mathbf{q}/\vartheta + \mathbf{k})\mathbf{A}_s(l) + ({}^{k}\rho\eta(\mathbf{v} - \mathbf{V}^s))\mathbf{A}_s(l)\rangle , $$

$$ \mathbf{W}_\eta := \langle {}^{k}\rho\eta(\mathbf{A}_s(l) - j(l)\mathbf{1}_s)\mathbf{V}^s + l\, {}^{k}\rho\eta \operatorname{grad}_s c_n \mathbf{A}_s(l)\rangle . $$

4.3. Epilogue: future developments towards a constitutive theory for nonmaterial twodimensional continua

The problem which has to be faced at this stage of the development of our model concerns Constitutive Modelling of the interfacial layers.

Self-consistence arguments will lead us to try to deduce, exactly so as it was done for balance equations, the constitutive relations for nonmaterial bidimensional continua from the corresponding threedimensional ones.

One observation is immediately possible: let us look, for instance, at the previously obtained expression for surface stress tensor: the deduction of the surface constitutive relations is not straightforward from the threedimensional ones. Indeed, in the expression for $2D$ quantities the $3D$ velocity field $\mathbf{v}$ appears: this means that the particular kinematical situations inside the layer affect the behaviour of the twodimensional continuum modelling it.

The last circumstance, while giving reasonable chances to yield the right framework for modelling Marangoni effects, renders the constitutive description of bidimensional nonmaterial continua more complex.

A possible way of avoiding such a difficulty is suggested in the classical *"Theory of Shells"* (material bidimensional continua) by LOVE [34]: some physically reasonable assumptions about the kinematics inside the thin continua are made, what leads to sufficiently accurate bidimensional models.

This procedure proved itself to be fruitful also in the theory of nonmaterial bidimensional continua: indeed, for the so-called *perfectly viscous interfacial layers* (introduced by ISHII [23]) even the deduction of surface balance laws is greatly simplified (for more details see DELL'ISOLA and ROMANO [13, 14] or SEPPECHER [45]).

For this reasons we are led to define the *Kirchhoff–Love type interfaces*.

We call the Kirchhoff–Love type interfaces such interfaces $\mathcal{Z}_t$ that:

i) $\mathcal{Z}_t$ is delineated (in the sense of our Sec. 2) by a surface Σ_t and surface fields $\zeta^{\pm}$ (or $z^{\pm}$),

ii) the material $3D$ field $\mathbf{v}$ has the following particular form:

$$ \mathbf{v}(l; \mathbf{r}, t) = \mathbf{v}_0(\mathbf{r}, t) - l(\operatorname{grad}_s w_n + \mathbf{b}_0 \mathbf{v}_\tau) , \tag{4.9} $$

where $\mathbf{v}_0$, $\mathbf{v}_\tau$ and w_n are the suitable vectors, tangent (to Σ_t) and scalar fields defined on Σ_t and on every Σ_t^l, respectively.

Previous definition can be interpreted as follows:

a) all the particles belonging to the line

$$ \mathbf{l}_t := \{\mathbf{z} \in \mathcal{Z}_t / \exists l \in [\zeta^-, \zeta^+] \quad \mathbf{z} = \mathbf{r} + l\mathbf{n}\} $$

move with the same normal (i.e. along the vector field $\mathbf{n}$) speed: $\mathbf{v}_0 \cdot \mathbf{n}$;

b) when the fields w_n and $\mathbf{v}_\tau$ are independent of the variable l, then the tangential velocity field along the same $\mathbf{l}_t$ depends linearly upon the variable l;

c) when the following equalities

$$\forall l \in [\zeta^-, \zeta^+] \quad w_n = c_n, \quad (\mathbf{1} - \mathbf{n} \otimes \mathbf{n})\mathbf{v}_0 = \mathbf{v}_\tau \tag{4.10}$$

hold, then all the particles belonging to the same $\mathbf{l}_t$ at a given instant t will belong (if they still belong to $\mathcal{Z}_\tau$) to the same line $\mathbf{l}_\tau$, for every different instant τ,

d) when, togheter with the relations (4.10), also the following equality

$$\mathbf{v}_0 \cdot \mathbf{n} = c_n ,$$

holds, then the layer $\mathcal{Z}_t$ is material,

The case d) was considered by Love, in his classical treatment of the theory of material shells.

Appendix

Here the derivation of the transformation of the oriented surface element $\mathbf{N}(l)da$ of the ruled surface Ω_t formed by segments $\{\mathbf{r} + l\mathbf{n}(\mathbf{r}) : l \in [z^-, z^+], \mathbf{r} \in \mathcal{C}_t \subset \Sigma_t\}$, where $\mathcal{C}_t$ is a curve ([12]) on Σ_t, will be given. Here $\mathbf{N}(l)$ is the outward unit normal to Ω_t, given by

$$\mathbf{N}(l) := \mathbf{t}_l \times \mathbf{n} \| \mathbf{t}_l \times \mathbf{n} \|^{-1} , \tag{A.1}$$

where $\mathbf{t}_l$ is a vector tangent to the curve $\mathcal{C}_t^l$ which is lifting of the curve $\mathcal{C}_t$ to Σ_t^l; the tangent vector to the latter we shall denote by $\mathbf{t}_0$. Due to Eq. (2.2) and to the fact that each of $\mathbf{t}_l$ and $\mathbf{t}_0$ is orthogonal to $\mathbf{n}$, and $\mathbf{n}$ has a unit length, we get

$$\mathbf{t}_l = (\mathbf{1}_s - l\mathbf{b})\mathbf{t}_0 \quad \text{and} \quad \mathbf{t}_l \times \mathbf{n} = (\mathbf{1}_s - l\mathbf{b})\mathbf{t}_0 \times \mathbf{n}$$

and

$$\| \mathbf{t}_l \times \mathbf{n} \| = \| \mathbf{t}_l \| = j(l) \| \mathbf{t}_0 \| . \tag{A.2}$$

If by ds_l and ds we denote the line element of the curves $\mathcal{C}_t^l$ and $\mathcal{C}_t$, respectively, then from Eq. (A.2) it follows that its ratio $ds_l/ds := \|\mathbf{t}_l\|/\|\mathbf{t}_0\|$ is equal to $j(l)$. If the tangent vector $\mathbf{t}_0$ has ([13]) the splitting $d^\alpha \mathbf{a}_\alpha$, then $\mathbf{t}_l = d^\alpha \mathbf{a}_\alpha(l)$, and denoting components of the alternation tensor $\varepsilon(l)$ of the surface Σ_t^l by $\varepsilon_{\alpha\beta}(l) = j(l)\varepsilon_{\gamma\alpha}$ (cf. one formula above Eq. (2.9) and the next one, i.e. (2.10)), we obtain

$$\begin{aligned} \mathbf{t}_l \times \mathbf{n} = d^\alpha \mathbf{a}_\alpha(l) \times \mathbf{n} &= d^\alpha \varepsilon_{\gamma\alpha}(l)\mathbf{a}^\gamma(l) = d^\alpha j(l)\varepsilon_{\gamma\alpha}\mathbf{a}^\gamma(l) \\ &= d^\alpha j(l)\varepsilon_{\beta\alpha}\delta_\gamma^\beta \mathbf{a}^\gamma(l) = d^\alpha j(l)\varepsilon_{\beta\alpha}(\mathbf{a}^\beta \cdot \mathbf{a}_\gamma)\mathbf{a}^\gamma(l) \\ &= d^\alpha j(l)(\mathbf{a}_\alpha \times \mathbf{n}) \cdot \mathbf{a}_\gamma \mathbf{a}^\gamma(l) = j(l)(\mathbf{a}^\gamma(l) \otimes \mathbf{a}_\gamma)\mathbf{t}_0 \times \mathbf{n} . \end{aligned}$$

If we put $\tilde{\mathbf{n}} := \mathbf{t}_0 \times \mathbf{n}/\|\mathbf{t}_0\|$ for the unit normal to the curve $\mathcal{C}_t$ that is both tangent and outwardly directed with respect to Σ_t, then the last expression, together with Eqs. (A.1) and (A.2), will lead to relation

$$\mathbf{N}(l)da = \mathbf{N}(l)dl\, ds_l = j(l)(\mathbf{a}^\gamma(l) \otimes \mathbf{a}_\gamma)\tilde{\mathbf{n}} dl\, ds . \tag{A.3}$$

The componentwise derivation of the last formula can be found in ALT and HUTTER [4].

([12]) If $\mathcal{C}_t = \Sigma_t \cap \overline{\mathcal{Z}}_t$, then the ruled surface will be the lateral boundary of $\mathcal{Z}_t$, i.e. $\partial\mathcal{Z}_t \backslash (\Sigma_t^- \cup \Sigma_t^+)$.

([13]) If λ, running along some interval of the real line, is a parameter of the curve $\mathcal{C}_t$ and each of $\mathcal{C}_t^l$, then $d^\alpha := dl^\alpha/d\lambda$.

The normal (not unit) vector to either surface $\Sigma_t^{\pm}$ in Eq. (2.26) will be given by

$$\begin{aligned}(A.4)\quad \mathbf{a}_1^{\pm}\times\mathbf{a}_2^{\pm} &= \mathbf{a}_1\times\mathbf{a}_2-\zeta^{\pm}(\mathbf{b}\mathbf{a}_1\times\mathbf{a}_2+\mathbf{a}_1\times\mathbf{b}\mathbf{a}_2)+(\zeta^{\pm})^2\mathbf{b}\mathbf{a}_1\times\mathbf{b}\mathbf{a}_2\\ &\quad+\mathbf{a}_1\times\mathbf{n}\frac{\partial\zeta^{\pm}}{\partial l^2}+\mathbf{n}\times\mathbf{a}_2\frac{\partial\zeta^{\pm}}{\partial l^1}-\zeta^{\pm}\left(\mathbf{b}\mathbf{a}_1\times\mathbf{n}\frac{\partial\zeta^{\pm}}{\partial l^2}+\mathbf{n}\times\mathbf{b}\mathbf{a}_2\frac{\partial\zeta^{\pm}}{\partial l^1}\right)\\ &= \varepsilon_{12}(1-\zeta^{\pm}\operatorname{tr}\mathbf{b}+(\zeta^{\pm})^2\det\mathbf{b})\mathbf{n}+\varepsilon_{12}\zeta^{\pm}\left(b_1^1\frac{\partial\zeta^{\pm}}{\partial l^2}-b_2^1\frac{\partial\zeta^{\pm}}{\partial l^1}\right)\mathbf{a}^2\\ &\quad-\varepsilon_{12}\zeta^{\pm}\left(b_1^2\frac{\partial\zeta^{\pm}}{\partial l^2}-b_2^2\frac{\partial\zeta^{\pm}}{\partial l^1}\right)\mathbf{a}^1-\varepsilon_{12}\operatorname{grad}_s\zeta^{\pm}.\end{aligned}$$

Inspecting the contents of the first bracket we can see the value of the Jacobian j at $l=\zeta^{\pm}$, while the next two brackets give minus $\zeta^{\pm}(\mathbf{b}-2H\mathbf{1}_s)\operatorname{grad}_s\zeta^{\pm}$ equal (cf. Eq. (2.12)) to $-\zeta^{\pm}\tilde{\mathbf{b}}\operatorname{grad}_s\zeta^{\pm}$. With this at hand and remembering the tensor $\mathbf{A}_s(l)$ from Eq. (2.13), we write the final relationship

$$(A.5)\qquad \mathbf{n}^{\pm}(\mathbf{r})da^{\pm}:=\mathbf{a}_1^{\pm}\times\mathbf{a}_2^{\pm}dl^1dl^2=(j(\zeta^{\pm},\mathbf{r})\mathbf{n}(\mathbf{r})-\mathbf{A}(\zeta^{\pm})\operatorname{grad}_s\zeta^{\pm})da,$$

where on RHS the surface element $da=\sqrt{a}dl^1dl^2$. In what follows the ratio $da^{\pm}/da$ is denoted by $j^{\pm}$; it is a function of $\mathbf{r}$ and t.

The boundary surfaces $\Sigma_t^{\pm}$ move now with a velocity different than that calculated by Eq. (2.22). In fact, performing the time differentiation in Eq. (2.26) we obtain the following velocities $\mathbf{c}^{\pm}$ of displacement of $\Sigma_t^{\pm}$:

$$(A.6)\qquad \mathbf{c}^{\pm}=\mathbf{c}-\zeta^{\pm}(\operatorname{grad}_s c_n+\mathbf{b}\mathbf{c})+\frac{\partial\zeta^{\pm}}{\partial t}\mathbf{n}.$$

Now we are making the final calculation of the product of $j^{\pm}$ and the normal speed of displacement of either boundary surface $\Sigma_t^{\pm}$. It will proceed as follows

$$\begin{aligned}(A.7)\quad & j^{\pm}\mathbf{c}^{\pm}\cdot\mathbf{n}^{\pm}(\mathbf{r})\\ &=\left(\mathbf{c}-\zeta^{\pm}(\operatorname{grad}_s c_n+\mathbf{b}\mathbf{c})+\frac{\partial\zeta^{\pm}}{\partial t}\mathbf{n}\right)\cdot(j(\zeta^{\pm},\mathbf{r})\mathbf{n}(\mathbf{r})-\mathbf{A}(\zeta^{\pm})\operatorname{grad}_s\zeta^{\pm})\\ &=j(\zeta^{\pm},\mathbf{r})\left(c_n+\frac{\partial\zeta^{\pm}}{\partial t}-\operatorname{grad}_s\zeta^{\pm}\mathbf{c}\right)+\zeta^{\pm}\operatorname{grad}_s\zeta^{\pm}\mathbf{A}_s(\zeta^{\pm})\cdot\operatorname{grad}_s c_n.\end{aligned}$$

Using the formula (2.21) for the displacement derivative we can rewrite Eq. (A.7) to get

$$(A.8)\qquad j^{\pm}\mathbf{c}^{\pm}\cdot\mathbf{n}^{\pm}(\mathbf{r})=j(\zeta^{\pm},\mathbf{r})\left(c_n+\frac{\delta\zeta^{\pm}}{\delta t}\right)+\zeta^{\pm}\operatorname{grad}_s\zeta^{\pm}\mathbf{A}_s(\zeta^{\pm})\cdot\operatorname{grad}_s c_n.$$

Hence follows the expression for $j^{\pm}$

$$j^{\pm}:=\|\mathbf{a}_1^{\pm}\times\mathbf{a}_2^{\pm}\|=\sqrt{a}(j^2((\zeta^{\pm},\mathbf{r})+\operatorname{grad}_s\zeta^{\pm}\cdot\mathbf{A}_s^2(\zeta^{\pm})\operatorname{grad}_s\zeta^{\pm})^{0.5},$$

which can be useful in some derivations.

Acknowledgements

This research was sponsored by the Polish Academy of Sciences (Research Project CPBP 02.01) and Italian CNR, GNFM.

References

1. A. W. ADAMSON, *Physical chemistry of surfaces*, Interscience, New York-London, 1982.
2. A. M. ALBANO, D. BEDEAUX and J. VLIEGER, *On the description of interfacial properties using singular densities and currents at a dividing surface*, Physica, **99** A, 293–304, 1979.
3. T. ALTS, *Some results of a boundary-layer theory for curved phase interfaces* [in:] Lectures Notes in Physics, vol.249: Trends in Applications of Pure Mathematics to Mechanics, Proc. of 6-th Symp. Bad Honnef, October 21-25, 1985, E. KRÖNER and K. KIRCHGÄSSNER [Eds.], Springer, Berlin – Heidelberg – New York – Tokyo, pp. 500–512, 1986.
4. T. ALTS and K. HUTTER, *Towards a theory of temperate glacier. Part I. Dynamics and thermodynamics of phase boundaries between ice and water*, Mitteilungen No. 82 der Versuchtsanstalt für Wasserbau, Hydrologie und Glaziologie, ETH, Zürich, 1986.
5. T. ALTS and K. HUTTER, *Continuum description of the dynamics and thermodynamics of phase boundaries between ice and water. Parts I and II*, J. Non-Equilib. Thermodyn., **13**, 221–280, 1988.
6. T. ALTS and K. HUTTER, *Continuum description of the dynamics and thermodynamics of phase boundaries between ice and water. Parts III and IV*, J. Non-Equilib. Thermodyn., **13**, 301–329, **14**, 1–22, 1989.
7. A. BLINOWSKI, *On the surface behaviour of gradient-sensitive liquids*, Arch. Mech., **25**, 2, 259–2268, 1973.
8. R. M. BOWEN and C. -C. WANG, *On displacement derivatives*, Quart. Appl. Math., **29**, 1, 29–39, 1971.
9. F. P. BUFF, *The theory of capillarity* [in:] Handbuch der Physik. vol. X, Springer, Berlin-Heidelberg-New York, pp.281–304, 1960.
10. F. DELL'ISOLA and D. IANNECE, *On phase transition in classical fluid mixtures with surface adsorption*, Int. J. Engng. Sci., **27**, 9, 1069–1078, 1989.
11. F. DELL'ISOLA and W. KOSIŃSKI, *The interface between phases as a layer. Part I*, Preprint Dipartimento di Matematica Universitá di Napoli n. 16 July 1989.
12. F. DELL'ISOLA and W. KOSIŃSKI, *The interface between phases as a layer. Part II* [in:] Proc. of the V-th Meeting: Waves and Stability in Continuous Media, Sorrento, October1989, S. RIONERO [Ed.], World Scientific, Singapore, New Jersey, London, Hong Kong, pp.108-113, 1991.
13. F. DELL'ISOLA and A. ROMANO, *On a general balance law for continua with an interface*, Ricerche di Matematica, **35**, 2, 325–337, 1986.
14. F. DELL'ISOLA and A. ROMANO, *On the derivation of thermomechanical balance equations for continuous systems with a nonmaterial interface*, Int. J. Engng Sci. **25**, 11/12, 1459–1468, 1987.
15. A. R. D. DREEMER and J. C. SLATTERY, *Balance equations and structural models for phase interfaces*, Int. J. Multiphase Flow, **4**, 171–192, 1978.
16. J. -F. DUMAIS, *Two and three-dimensional interface dynamics*, Physica, **104** A, 143–180, 1980.
17. R. GATIGNOL, *Liquid-vapour interfacial conditions*, Rev. Romaine des Sci. Tèchn. Méc. Appl., **32**, **3**, 255–271, 1987.
18. R. GATIGNOL and P. SEPPECHER, *Modelization of fluid-fluid interfaces with material properties*, J. Méc. Theor. et Appl., Numero special, 225–247, 1986.
19. R. GHEZ, *A generalized Gibbsian surface*, Surface Science, **4**, 125–140, 1966.
20. J. W. GIBBS, *The scientific papers of J. Willard Gibbs*, vol. I. Dover Publications, New York, 1961.
21. V. V. GOGOSOV, V. A. NALETOVA, CHUNG ZA BING and G. A. SHAPOSHNIKOVA, *Conservation laws for the mass, momentum, and energy on a phase interface for true and excess surface parameters*, Izvest. Akad. Nauk SSSR-Mekh. Zhidk. Gaz, **18**, 6, 107, (Engl. transl. in Fluid Dynamics **6**, 923–930, 1983).
22. W. D. HAYES, *The vorticity jump across a gasdynamic discontinuity*, J. Fluid Mech., **2**, 6, 595–600, 1957.
23. M. ISHII, *Thermo-fluid dynamic theory of two phase flow*, Eyroles, Paris, 1975.
24. W. KOSIŃSKI, *Introduction to the theory of field singularities and wave analysis* [in Polish], PWN, Warszawa-Poznań, 1981.
25. W. KOSIŃSKI, *Evolution equations of disssipative bodies* [in Polish], Habilitation Thesis, IFTR-Reports, 36, IPPT PAN, Warszawa, 1983.
26. W. KOSIŃSKI, *Thermodynamics of singular surfaces and phase transitions* [in:] Free Moving Boundary Problems: Applications and Theory. vol. III, A. BOSSAVIT, A. DAMLAMIAN and A. M. FREMOND [Eds.], Pitman, Boston–London–Melbourne, pp. 140–151, 1985.
27. W. KOSIŃSKI, *Field singularities and wave analysis in continuum mechanics*, Ellis Horwood Ltd, Chichester and PWN-Polish Scientific Publishers, Warsaw, 1986.

28. W. KOSIŃSKI, *Characteristics in phase transition problems*. Inter. Workshop on Nonlinear Hyperbolic Equations for Applied Sciences, ISI, Villa Gualino, Torino,June 1987, also Rend. Sem. Math. Univ. Pol. Torino, Fasciolo Speciale, Hyperbolic Problems (1987), 138–144 1988.
29. W. KOSIŃSKI and A. ROMANO, *Evolution balance laws in two-phase problems*, XVIIth IUTAM Congress in Grenoble, August 1988, also Arch. Mech., **41**, 2–3, 255–266, 1989.
30. W. KOSIŃSKI and A. O. WĄSOWSKI, *On shell theory equations* [under preparation] 1993.
31. W. KOSIŃSKI, *A phenomenological approach to fluid-phase interfaces* [in:] Modelling Macroscopic Phenomena at Liquid Boundaries, W. Kosiński and I. Murdoch (eds.), CISM Courses and Lectures, No. 318, Springer, Wien-New York, pp.65–105, 1991.
32. V. G. LEVICH and V. S. KRYLOV, *Surface tension-driven phenomena* [in:] Annual Review in Fluid Mechanics **1**, Annual Review, New York, 1969.
33. I. N. LEVINE, *Physical chemistry*, McGraw-Hill, New York, 1978.
34. J. LOVE, *Note on the present state of the theory of thin elastic shells*, Proc. Roy. Soc. London Ser. A **49** 100–102, 1891.
35. G. P. Moeckel, *Themodynamics of an interface*, Arch. Rational Mech. Analysis, **57**, 3, 255–280, 1974.
36. A. I. MURDOCH, *A remark on the modelling of thin three-dimensional regions* [in:] Elasticity: Mathematical Methods and Applications. (The Ian Sneddon 70th Birthday Volume), G. E. EASON and R. W. OGDEN [Eds.], Ellis Horwood Ltd., Chichester, 1990.
37. J. N. MURREL and E. A. BOUCHER, *Properties of liquids and solutions*, John Wiley & Sons, Chichester 1982.
38. P. M. NAGHDI, *The theory of shells and plates* [in:] Handbuch der Physik, vol. VIa/2, 425–640, Springer Verlag, Berlin-Heidelberg-New York, 1972.
39. L. G. Napolitano, *Thermodynamics and dynamics of pure interfaces*, Acta Astronautica, **5**, 655–670, 1978.
40. L. G. NAPOLITANO, *Properties of parallel-surface coordinate systems*, Meccanica, **17**, 107–118, 1982.
41. S. ONO and S. KONDO, *Molecular theory of surface tension in liquids* [in:] Handbuch der Physik, vol. X, 135–280, Springer Verlag, Berlin-Goettingen-Heidelberg, 1960.
42. J. OŚCIK, *Adsorption*, PWN, Warszawa and Ellis Horwood, Chichester, 1982.
43. A. ROMANO, *Thermodynamics of a continuum with an interface and Gibbs' rule*, Ricerche di Matematica, **31**, 2, 277–294, 1983.
44. L. E. SCRIVEN, *Dynamics of a fluid interface*, Chem. Engng., Sci., **12**, 98–108, 1960.
45. P. SEPPECHER, *Étude d'une modélisation des zones capillares fluides interfaces et lignes de contact*, Thèse, Univerisité Paris VI et E.N.S.T.A., 1987.
46. J. C. SLATTERY, *General balance equation for a phase interface*, Ind. Engng. Chem. Fundamentals, **6**, 1, 108–115, 1967.
47. T. Y. THOMAS, *Extended compatibility conditions for the study of surface of discontinuity in continuum mechanics*, J. Maths. Mech., **6**, 311–322, 907–908, 1957.
48. T. Y. THOMAS, *Plastic flow and fracture in solids*, Academic Press, New York-London, 1961.
49. T. Y. THOMAS, *Concepts from tensor analysis and differential geometry*, 2nd Edition, Academic Press, New York-London, 1965.
50. C. A. TRUESDELL and R. A. TOUPIN, *The classical field theories* [in:] Handbuch der Physik, vol. III/1, 226–793, Springer Verlag, Berlin-Göttingen-Heidelberg, 1960.
51. T. YOUNG, *An essay on the cohesion of fluids*, Phil. Trans. Roy. Soc. **95**, 67–87, 1805.

UNIVERSITA' DEGLI STUDI DI ROMA "LA SAPIENZA"
DIPARTIMENTO DI INGEGNERIA STRUTTURALE E GEOTECNICA, ROMA, ITALY
and
POLISH ACADEMY OF SCIENCES
INSTITUTE OF FUNDAMENTAL TECHNOLOGICAL RESEARCH.

Received May 28, 1993.