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Surface thermodynamics, surface stress, equations at surfaces and triple lines for deformable bodies

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Abstract

The thermodynamics and mechanics of the surface of a deformable body are studied here, following and refining the general approach of Gibbs. It is first shown that the 'local' thermodynamic variables of the state of the surface are only the temperature, the chemical potentials and the surface strain tensor (true thermodynamic variables, for a viscoelastic solid or a viscous fluid). A new definition of the surface stress is given and the corresponding surface thermodynamics equations are presented. The mechanical equilibrium equation at the surface is then obtained. It involves the surface stress and is similar to the Cauchy equation for the volume. Its normal component is a generalization of the Laplace equation. At a (body–fluid–fluid) triple contact line, two equations are obtained, which represent: (i) the equilibrium of the forces (surface stresses) for a triple line fixed on the body; (ii) the equilibrium relative to the motion of the line with respect to the body. This last equation leads to a strong modification of Young's classical capillary equation.

1. Introduction

Thermodynamic, chemical and mechanical properties of the surfaces of deformable bodies, with various applications, e.g., on nanostructures, thin films, adhesions or coating, have been continually investigated, from the early work of Gibbs [1] until recent mechanical [2, 6] or thermodynamic [3–5, 7–9] approaches. However, some basic questions, such as the exact determination of the thermodynamic variables of state of the surface, still persist, as shown, e.g., in the recent expression of the work of deformation of the surface [3, 8]. This shows that there is a real need for a rigorous and general thermodynamic approach, in order to determine the thermodynamic variables of state and to obtain the corresponding equations of surface thermodynamics and mechanics. Another problem arises at a (body–fluid–fluid) triple contact line, where the classical elastic theory predicts a singularity of the deformation (namely, an infinite displacement). Generally, authors have assumed some finite thickness of the fluid–fluid interface [10, 11], only considered what occurs outside some neighbourhood of this line [12, 13], or proposed a new force derived from the volume stresses of the solid [14]. Nevertheless, the validity

of Young's classical capillary equation remains problematic and the equilibrium equations at the triple line are in fact completely unknown.

In this paper, the general thermodynamic approach of Gibbs is applied and refined, leading to (i) the determination of the 'local' thermodynamic variables of state of the surface, (ii) a new definition of the surface stress, (iii) the surface thermodynamics equations, (iv) the equilibrium equations at the surfaces and (v) the equilibrium equations at the triple lines, which imply a strong modification of Young's equation (as in [4, 5]).

2. Thermodynamic equilibrium conditions

Let us consider a general deformable body b in contact with various immiscible fluids f, f', \dots (figure 1). No mass exchange is assumed between the body and the fluids, but there may be mass exchanges between all the fluids and the body–fluid (bf, bf', \dots) and fluid–fluid (ff', \dots) surfaces. For simplicity's sake, we suppose that the body consists of a substance c , the fluids and the fluid–fluid surfaces are composed of the substances $1, 2, \dots, n$, with all these components $c, 1, 2, \dots, n$ being independent. We first recall

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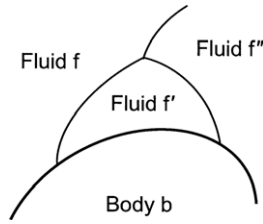


Figure 1. The studied system: a deformable body in contact with various fluids.

Gibbs’s definition of dividing surfaces, and then define the corresponding ‘ideal’ states and ‘ideal’ transformations.

2.1. Dividing surfaces, ideal states and ideal transformations

In the actual state, a body–fluid interface may be considered as a heterogeneous thin film across which the physical quantities may vary rapidly from their values in the homogeneous body to their values in the homogeneous fluid (‘homogeneous’ here means ‘with slow and continuous variations of the physical properties’). Following Gibbs [1], this actual state is replaced by an ideal state in which the body–fluid interface is replaced by a mathematical dividing surface (without thickness), the body and its physical properties being extrapolated (from their values in the homogeneous body) up to this dividing surface, and the same being made for the fluid on the other side of this surface. For any extensive physical quantity, the surface value of this quantity is then defined as the excess of this physical quantity in the actual state over that of the two homogeneous phases in the ideal state. It is expressed per unit area of the dividing surface, and its value depends on the exact position of this surface, which is arbitrary within (or very close to) the actual interface film. In the present paper, the position of the dividing surface is defined so that the surface mass density of the substance c of the body vanishes. Thus, the body–fluid dividing surfaces only contain (as mass excesses) the substances $1, 2, \dots, n$, as in the fluids and the fluid–fluid surfaces. In addition, for each component i ($= 1, 2, \dots, n$), all the fluid regions and the body–fluid and fluid–fluid surfaces which contain i are supposed to be connected. We also assume that, in the actual interface film, the physical quantities present slow and continuous variations (as those occurring in the homogeneous body or fluid) along the directions parallel to the interface (in contrast to the possible rapid variations of these quantities along the normal to the interface).

Let us now consider two arbitrary states of the body b , e.g., in contact with the fluid f , and call ‘initial’ and ‘final’ these two states. In the actual initial state, the body is homogeneous up to a surface S_{b1} , beyond which the bf interface film takes place (see figure 2). Note that a precise definition of S_{b1} is not necessary; in fact, we only need that the body is homogeneous up to S_{b1} and that this surface is close to the interface. On S_{b1} , the volume mass density ρ_c of the substance c of the body has some value $\rho_{c,b}$. Then, crossing the interface film, ρ_c varies rapidly, and finally vanishes in the homogeneous fluid region. We denote S_{b2} the surface such that ρ_c is generally $\neq 0$ between S_{b1} and S_{b2} , and $\rho_c = 0$ beyond S_{b2} (fluid side). The dividing

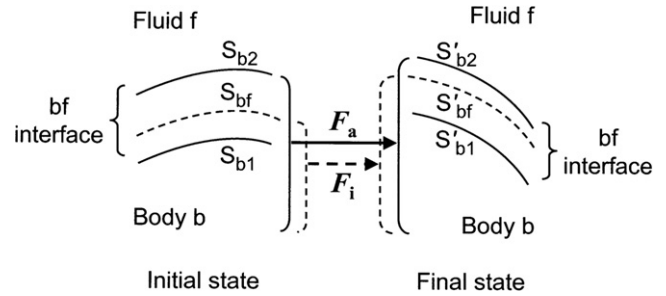


Figure 2. The various surfaces (S_{b1} , S_{b2} and S_{bf}) defined at the body–fluid interface, and the actual and ‘ideal’ transformations of the body (F_a and F_i) between the initial and final states (see definitions in the text).

bf surface, as defined above (no excess of mass of the substance c), is denoted S_{bf} . In a similar way, the surfaces S'_{b1} , S'_{b2} and S'_{bf} are defined in the final state. Between the initial and final states, there is an actual transformation F_a , defined in the initial state of the body up to S_{b2} , which maps the position x of a material point of the body in the actual initial state, to its position x' in the actual final state. Clearly, $S'_{b2} = F_a(S_{b2})$. In addition, S_{b1} and S'_{b1} may be chosen so that $S'_{b1} = F_a(S_{b1})$. Indeed, such a choice for S'_{b1} is justified if the surface $F_a(S_{b1})$ is not situated in the interface film region (in the final state). This last condition can always be satisfied, by choosing—if necessary—a surface S_{b1} slightly separated from the interface film (in the initial state).

If $x_1 \in S_{b1}$ and $x_2 \in S_{b2}$ are two points very close to each other (i.e., $\vec{x}_1 \vec{x}_2$ at a small angle from the normal to S_{b1}), we assume that $x'_1 = F_a(x_1)$ and $x'_2 = F_a(x_2)$ will also remain very close to each other. If $y_1 \in S_{b1}$ and $y_2 \in S_{b2}$ are two other such points (thus, $\vec{x}_1 \vec{y}_1 = \vec{x}_2 \vec{y}_2$; this equality and the other ones which follow, have to be considered as good approximations, when the thickness of the interface film is very small), this implies that $\vec{x}'_1 \vec{y}'_1 = \vec{x}'_2 \vec{y}'_2$. By taking infinitesimal vectors $\vec{x}_1 \vec{y}_1$, it means that $DF_a(x_1)|_P = DF_a(x_2)|_P$ (restrictions to P of the linear mappings $DF_a(x_i)$), where $P = T_{x_1}(S_{b1}) = T_{x_2}(S_{b2})$ is the plane tangent to the interface. More generally, we assume that $DF_a(x)|_P$ remains unchanged when x crosses the interface (from x_1 to x_2).

If the actual initial state is replaced by the ideal one, with respect to the dividing surface S_{bf} , an ideal transformation F_i may then be defined in the (ideal initial state of the) body up to S_{bf} , in the following way: it coincides with F_a in the homogeneous part of the body, up to S_{b1} , and its derivative DF_i (linear mapping) in the region between S_{b1} and S_{bf} is extrapolated from the value of the derivative DF_a in the homogeneous body. Three assertions will now be proved.

- (1) The surface S'_{bf} is generally not the image of S_{bf} by the actual transformation F_a . This may be shown by the following simple example. Let the interface be plane, x the normal axis, $x = 0$ and $x = d$ the respective positions of S_{b1} and S_{b2} , and ρ_c a linear decreasing function of x , with values $\rho_{c,b}$ at $x = 0$ and 0 at $x = d$, i.e. $\rho_c = \rho_{c,b}(1 - \xi)$ with $0 \leq \xi = x/d \leq 1$, which leads to the position $x = d/2$ of S_{bf} . Let the actual

transformation $F_a : x \rightarrow x'$ be a simple compression along the x axis, such that dx'/dx linearly decreases from the value 1 at $\xi = 0$ to the small value $\varepsilon > 0$ at $\xi = 1 - \varepsilon$ (i.e. $dx'/dx = 1 - \xi$), and then remains constant ($= \varepsilon$) for $1 - \varepsilon \leq \xi \leq 1$. Under this transformation, the volume mass density in the actual final state will be

$$\begin{aligned} \rho'_c &= \frac{\rho_c}{\frac{dx'}{dx}} = \rho_{c,b} && \text{for } 0 \leq \xi \leq 1 - \varepsilon \\ &= \rho_{c,b} \frac{1 - \xi}{\varepsilon} && \text{for } 1 - \varepsilon \leq \xi \leq 1. \end{aligned}$$

Since ρ'_c is constant for $0 \leq \xi \leq 1 - \varepsilon$, the dividing surface S'_{bf} in the final state will be situated at x' such that $1 - \varepsilon < \xi = x/d < 1$, i.e. ξ very close to 1. The surface S_{bf} being situated at $\xi = 1/2$, this shows that S'_{bf} cannot be the image of S_{bf} by F_a .

- (2) *The surface S'_{bf} is the image of S_{bf} by the ideal transformation F_i .* In order to prove this assertion, let us consider, in the actual initial state, $x_1 \in S_{b1}$, $x_2 \in S_{b2}$ (with $\overline{x_1x_2}$ at a small angle from the normal to S_{b1}), a small parallelepiped A with edge x_1x_2 , limited by S_{b1} and S_{b2} , and a similar parallelepiped A_1 limited by S_{b1} and S_{bf} (figure 3). In the final state, A is transformed into $A' = F_a(A)$, which is not a parallelepiped, since its (curved) ‘edge’ $x'_1x'_2$ suffered an heterogeneous deformation. Nevertheless, all the sections of A' by the planes parallel to $P' = T_{x'_1}(S'_{b1})$ represent the same parallelogram (up to a translation), since $DF_a(x)|_P$ remains unchanged when x moves from x_1 to x_2 (as noted above; $P = T_{x_1}(S_{b1})$). Let us consider the straight line $x'_1x''_2$ (with $x''_2 \in S'_{b2}$) tangent to the curved edge $x'_1x'_2$ at x'_1 , and the parallelepiped A'' with edge $x'_1x''_2$, having the same face on S'_{b1} as A' (see figure 3). By the definition of F_i , $DF_i(x)$ is constant and equal to $DF_a(x_1)$, between S_{b1} and S_{bf} , in A_1 , which implies that $A''_1 = F_i(A_1)$ is a parallelepiped which, like A'' , rests on the edge $x'_1x''_2$ and has the same face on S'_{b1} as A' .

By the definition of S_{bf} (no excess of mass of the constituent c), the mass of c contained in A (in the actual state) is equal to the mass of c contained in A_1 in the ideal state (i.e., if A_1 is filled with only the substance c , with a constant density ρ_c , equal to $\rho_{c,b} = \rho_c(x_1)$). Note that this property does not depend on the choice of the parallelepiped A (i.e., its face on S_{b1} and the orientation of $\overline{x_1x_2}$).

Under the transformation F_a , the mass of c contained in A is equal to that contained in A' (for the actual states). In addition, if A' is ‘cut up’ into very thin slices parallel to P' , then, by appropriate sliding of these slices (with respect to each other), we can obtain the parallelepiped A'' , which shows that the mass of c contained in A' is equal to that contained in A'' (for the actual state).

Now, let us transport by F_i the substance c contained in A_1 in the ideal state: $A''_1 = F_i(A_1)$ will thus contain the same mass of c as that contained in A_1 (in the ideal state). In addition, the density ρ'_c will be constant in A''_1 , and equal to $\rho'_c(x')$ (since ρ_c and DF_i are constant in A_1 , and respectively equal to $\rho_c(x_1)$ and $DF_a(x_1)$). The various

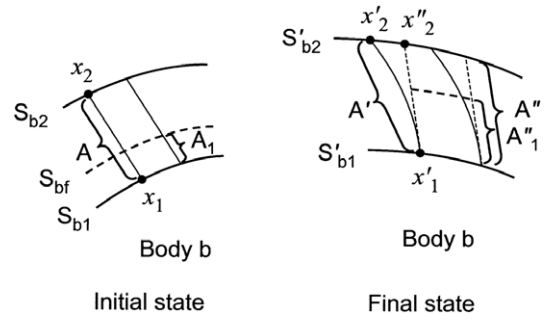


Figure 3. The image of S_{bf} by the ideal transformation F_i is equal to S'_{bf} (see proof, in the text).

preceding mass equalities finally lead to: the mass of c contained in A''_1 (filled with only the substance c , with a constant density ρ'_c , equal to $\rho'_c(x'_1)$) is equal to that contained in A'' in the actual state. This exactly means that the parallelepiped A''_1 is limited by the surface S'_{bf} (defined by: no excess of mass of the constituent c), i.e., that $S'_{bf} = F_i(S_{bf})$. We may also say that the mass density in A''_1 (resulting from the F_i transport) is that of the ideal final state (as defined at the beginning of the section).

- (3) *The volume mass density of the substance c of the body in the ideal final state results from the transport by the ideal transformation F_i of the mass density of this substance in the ideal initial state.* This is a consequence of the previous last conclusion.

Let us now consider a third arbitrary state of the body b , called the ‘reference state’, and define, as above for the initial and final states, the corresponding surfaces $S_{0,b1}$, $S_{0,b2}$ and $S_{0,bf}$ (subscript 0 for the reference state). The actual and ideal transformations are respectively denoted $F_{0,a}$ and $F_{0,i}$, between the reference and initial states, and $F'_{0,a}$ and $F'_{0,i}$, between the reference and final states. We have the new assertion:

- (4) *The ideal transformation $F'_{0,i}$ between the reference and final states is equal to the ideal transformation $F_{0,i}$ between the reference and initial states composed with the ideal transformation F_i between the initial and final states: $F'_{0,i} = F_i \circ F_{0,i}$.* Indeed, let x_0 be situated between $S_{0,b1}$ and $S_{0,bf}$, $x_{0,1} \in S_{0,b1}$ be very close to x_0 , and denote $x = F_{0,i}(x_0)$, $x_1 = F_{0,a}(x_{0,1})$, $x' = F_i(x)$, $x'_1 = F_a(x_1) = F'_{0,a}(x_{0,1})$. Then, $\overline{x'_1x'} = DF_a(x_1) \cdot \overline{x_1x} = DF_a(x_1) \cdot DF_{0,a}(x_{0,1}) \cdot \overline{x_{0,1}x_0} = DF'_{0,a}(x_{0,1}) \cdot \overline{x_{0,1}x_0}$, hence $x' = F'_{0,i}(x_0)$, i.e. $(F_i \circ F_{0,i})(x_0) = F'_{0,i}(x_0)$.

2.2. Thermodynamic equilibrium conditions

We consider that the system is closed and bounded by a closed surface Σ , and write the Gibbs equilibrium criterion

$$\delta U = \delta W_e$$

(U is the internal energy and δW_e the work of the external forces), for all variations δ of the system such that the entropy S and the masses m_i of the various components ($i = 1, \dots, n$)

are constant. If the bounding surface Σ , the points of the body which belong to this surface, and the lines in which the fluid–fluid surfaces meet this surface, are all fixed, then δW_e is reduced to the work of the forces of gravity (there is no work of the fluid pressures on Σ , since they are normal to Σ and the fluid displacements are tangent to Σ), and the criterion may be written

$$\delta(U + V) = 0,$$

where V is the potential energy of gravity. Note that, in this variation, we exclude the formation of new fluids or new (body–fluid or fluid–fluid) surfaces.

We thus have two states of the system: the present state and the (arbitrary) varied state, i.e., after the variation δ . Let us respectively call these two states ‘initial’ and ‘final’ and then apply the definitions and results of the preceding section. We may thus write the internal energy of the actual present state as

$$\begin{aligned} U &= U_b + \sum_f U_f + \sum_{ff'} U_{ff'} + \sum_{bf} U_{bf} \\ &= \int_b dU + \sum_f \int_f dU + \sum_{ff'} \int_{ff'} dU + \sum_{bf} \int_{bf} dU, \end{aligned}$$

where d refers to an element of volume or surface, U_b and U_f are the energies of the homogeneous phases in the ideal state (i.e., extrapolated up to the dividing surfaces), and $U_{ff'}$ and U_{bf} the excesses of the energy for the corresponding dividing surfaces ($S_{ff'}$ as defined by Gibbs; S_{bf} as defined above). Note that, in the present approach, we only take into account the volume and the surface effects (as a first approximation, intrinsic line effects, such as line energy, line tension, . . . are here neglected). Similarly, for the varied state,

$$\begin{aligned} U' &= U'_b + \sum_f U'_f + \sum_{ff'} U'_{ff'} + \sum_{bf} U'_{bf} \\ &= \int_b dU' + \sum_f \int_f dU' + \sum_{ff'} \int_{ff'} dU' + \sum_{bf} \int_{bf} dU', \end{aligned}$$

with respect to the dividing surfaces of this state, i.e., $S'_{ff'}$ (as defined by Gibbs) and S'_{bf} (as defined above). In the difference $\delta U = U' - U$, the first term is

$$\delta \int_b dU = \int_b dU' - \int_b dU.$$

In the last integral, we may consider that the body b , in its ideal present state (up to S_{bf}), has been divided into infinitesimal elements of volume (of energy dU). The assertions 2 and 3 of the preceding section show that the body b , in its ideal varied state (up to S'_{bf}), may be exactly divided into the elements which are the images of the preceding ones by the ideal transformation F_i (from the ideal present state to the ideal varied state). If $\delta dU = dU' - dU$ refers to an element of the ideal present state and its corresponding image by F_i , we may then write

$$\delta \int_b dU = \int_b \delta dU,$$

and since each element is a closed ‘system’ (with respect to the geometrical transformation F_i), for any infinitesimal reversible thermodynamic transformation δ :

$$\delta \int_b dU = \int_b (T \delta dS + \sigma \cdot \delta \varepsilon dv)$$

(in the ideal states; δ refers to F_i ; all the quantities are extrapolated up to the dividing surfaces), where T is the temperature, v the volume, σ the stress tensor at equilibrium and $\delta \varepsilon$ the strain tensor corresponding to F_i . According to assertion 4 of the preceding section, this may also be written in the Lagrangian representation, with respect to a given reference state of the body:

$$\delta \int_b dU = \int_b (T \delta dS + \pi \cdot \delta e dv_0),$$

where v_0 is the volume in the reference state, π the Piola–Kirchhoff stress tensor (relative to the reference state) at equilibrium, and e the Green–Lagrange strain tensor (relative to the reference state, i.e., associated to $F_{0,i}$; $\delta e = e(F'_{0,i}) - e(F_{0,i})$).

For the f and ff' terms in $\delta U = U' - U$, the expressions of Gibbs are used:

$$\begin{aligned} \delta \int_f dU &= \int_f (T \delta dS - p \delta dv + \sum_i \mu_i \delta dm_i) \\ \delta \int_{ff'} dU &= \int_{ff'} (T \delta dS + \gamma \delta da + \sum_i \mu_i \delta dm_i) \end{aligned} \quad (1)$$

(in the ideal states; in the integrals on f , the quantities are extrapolated up to the dividing surfaces; the ff' integrals refer to the dividing surfaces, dU , dS and dm_i being surface excesses and da an element of area), where p is the fluid pressure, γ the fluid–fluid surface tension and μ_i the chemical potential per unit mass of component i . Note that, in this case, each element of volume or surface is treated as an open ‘system’.

The above arguments may similarly be applied to the potential energy of gravity:

$$\begin{aligned} V &= V_b + \sum_f V_f + \sum_{ff'} V_{ff'} + \sum_{bf} V_{bf} \\ &= \int_b gz dm + \sum_f \int_f gz dm \\ &\quad + \sum_{ff'} \int_{ff'} gz dm + \sum_{bf} \int_{bf} gz dm, \end{aligned}$$

where V_b and V_f correspond to the homogeneous phases in the ideal state (i.e., extrapolated up to the dividing surfaces: $S_{ff'}$, S_{bf}), $V_{ff'}$ and V_{bf} are the excess quantities for these dividing surfaces, g is the gravity field (supposed constant), z the height and m the mass. In the ff' and bf integrals, dm represents the surface excess for the dividing surfaces (the excess of $\int_{vol} gz dm$ is equal to $\int_{surf} gz$ (excess of dm), since, crossing the interface film, z remains almost constant whereas the volume mass density varies rapidly). Then,

$$\delta \int_b gz dm = \int_b \delta(gz dm) = \int_b g \delta z dm,$$

each element being a closed ‘system’ with respect to the transformation F_i (δ refers to F_i), and

$$\begin{aligned} \delta \int_f g z \, dm &= \int_f (g \delta z \, dm + g z \delta \, dm) \\ \delta \int_{ff'} g z \, dm &= \int_{ff'} (g \delta z \, dm + g z \delta \, dm) \end{aligned}$$

(in the ideal states; the elements of volume or surface are here treated as open ‘systems’).

Finally, the Gibbs equilibrium criterion may be written

$$\begin{aligned} &\int_b (T \delta \, dS + \pi \cdot \delta e \, dv_0) + \int_b g \delta z \, dm \\ &+ \sum_f \int_f (T \delta \, dS - p \delta \, dv + \sum_i \mu_i \delta \, dm_i) \\ &+ \sum_f \int_f (g \delta z \, dm + g z \delta \, dm) \\ &+ \sum_{ff'} \int_{ff'} (T \delta \, dS + \gamma \delta \, da + \sum_i \mu_i \delta \, dm_i) \\ &+ \sum_{ff'} \int_{ff'} (g \delta z \, dm + g z \delta \, dm) \\ &+ \sum_{bf} \delta \int_{bf} dU + \sum_{bf} \delta \int_{bf} g z \, dm = 0, \end{aligned} \quad (2)$$

and the associated conditions of constant S and m_i are

$$\begin{aligned} &\int_b \delta \, dS + \sum_f \int_f \delta \, dS + \sum_{ff'} \int_{ff'} \delta \, dS + \sum_{bf} \delta \int_{bf} dS = 0 \quad (3) \\ &\sum_f \int_f \delta \, dm_i + \sum_{ff'} \int_{ff'} \delta \, dm_i + \sum_{bf} \delta \int_{bf} dm_i = 0 \\ &(i = 1, \dots, n). \end{aligned} \quad (4)$$

Note that these expressions, and all the following ones, refer to the ideal states, which means that all the quantities of the volume integrals are extrapolated up to the dividing surfaces (and, in the b integrals, δ refers to F_i), and the surface integrals refer to these dividing surfaces (dS , dU , dm and dm_i being surface excesses).

From this point, we may follow the proof given in [4] (extension of the approach of Gibbs [1]), here applied to the case of a general deformable body, which first shows that the equilibrium (2)–(4) of the system is equivalent to

(i) the thermal and chemical equilibrium equations:

$$T = \text{constant in space} \quad (5)$$

$$\mu_i + g z = M_i = \text{constant in space} \quad (i = 1, \dots, n). \quad (6)$$

(ii) The mechanical equilibrium equations concerning only the system of the fluids:

in each fluid f

$$\frac{dp}{dz} = -\rho g \quad (7)$$

in each ff' surface

$$\frac{d\gamma}{dz} = \rho_s g \quad (8)$$

$$p - p' = \gamma \left(\frac{1}{R_1} + \frac{1}{R_2} \right) + \rho_s g \cos \theta \quad (9)$$

in each $ff'f''$ triple line

$$\sum_{ff'} \gamma \nu = 0 \quad (10)$$

(ρ is the mass per unit volume, ρ_s the mass per unit area (surface excess); p refers to f , p' to f' ; R_1 and R_2 are the principal curvature radii of the ff' surface, considered positive when the centres are on the f side; θ is the angle between the Oz axis and the normal to the ff' surface, oriented from f to f' ; at the $ff'f''$ line, and for each ff' surface, ν is the unit vector normal to the $ff'f''$ line, tangent to the ff' surface, and oriented from the line to the interior of ff' ; in (7) and (8), p , γ , ρ and ρ_s only depend on z ; all these equations (5)–(10) were written by Gibbs [1] and

(iii) the following new mechanical equilibrium condition (of variational form) which concerns only the body, the body–fluid surfaces and the body–fluid–fluid lines:

$$\begin{aligned} &\int_b \pi \cdot \delta e \, dv_0 - \int_b \rho \bar{g} \cdot \delta x \, dv \\ &- \sum_{bf} \int_{bf} p n \cdot \delta x \, da - \sum_{bff'} \int_{bff'} \gamma_{ff'} \nu_{ff'} \cdot \delta X \, dl \\ &+ \sum_{bf} \left(\delta \int_{bf} dU - T \delta \int_{bf} dS \right. \\ &\left. - \sum_i M_i \delta \int_{bf} dm_i + \delta \int_{bf} g z \, dm \right) = 0, \end{aligned} \quad (11)$$

where \bar{g} is the (constant) gravity vector field, δx the displacement of a material point of the body (by F_i , up to the dividing surfaces S_{bf}), n the unit vector normal to the bf surface, oriented from f to b ($n \cdot \delta x$ also represents the normal displacement of the surface, from S_{bf} to S'_{bf} , positively measured from f to b), $\nu_{ff'}$ the unit vector normal to the bff' line, tangent to the ff' surface, and oriented from the line to the interior of ff' , dl the length of a bff' line element, and δX the (vector) displacement of the bff' line, perpendicular to the line (figure 4). Note that (7) and (8) are consequences of (5) and (6), since p and γ are functions of T and μ_i which satisfy [1]

$$\begin{aligned} dp &= S_v \, dT + \sum_i m_{i,v} \, d\mu_i \\ d\gamma &= -S_a \, dT - \sum_i m_{i,a} \, d\mu_i \end{aligned} \quad (12)$$

(the subscripts v and a respectively denote the volume density and the surface density).

The terms of the two last lines of (11) may be calculated in the (ideal) reference state of the body (i.e., on $S_{0,bf}$). With the help of the above assertions 2 ($S'_{bf} = F_i(S_{bf})$, $S_{bf} = F_{0,i}(S_{0,bf})$ and $S'_{bf} = F'_{0,i}(S_{0,bf})$) and 4 ($F'_{0,i} = F_i \circ F_{0,i}$), we may write, e.g., for the first term

$$\begin{aligned} \delta \int_{bf} dU &= \delta \int_{bf} U_{a_0} \, da_0 \\ &= \int_{bf} \delta U_{a_0} \, da_0 + \sum_{f'} \int_{bff'} U_{a_0,bf} \delta X_0 \, dl_0, \end{aligned}$$

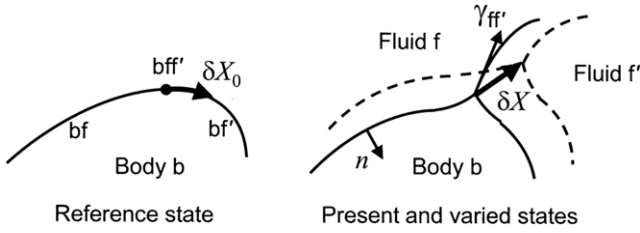


Figure 4. Displacement δX of the bff' triple line in space, between the present and the varied states, and displacement δX_0 of this line with respect to the body, in the reference state.

where the subscript 0 is used for the reference state, $U_{a_0} = dU/da_0$, δU_{a_0} is the variation at a fixed point of $S_{0,bf}$, and δX_0 the (scalar) displacement of the bff' line, measured in the reference state, perpendicular to that line in the reference state, and positively considered from bf to bf' (figure 4). Then,

$$\begin{aligned} \sum_{bf} \delta \int_{bf} dU &= \sum_{bf} \int_{bf} \delta U_{a_0} da_0 \\ &+ \sum_{bff'} \int_{bff'} (U_{a_0,bf} - U_{a_0,bf'}) \delta X_0 dl_0. \end{aligned}$$

The terms of the last line of (11) only depend on the variations of the masses and the geometrical positions. In particular, they do not depend on δM_i (or $\delta \mu_i$), and we may thus use, e.g., $\delta M_i = 0$ (i.e., $\delta \mu_i = -g\delta z$) to calculate these terms:

$$\begin{aligned} - \sum_i M_i \delta \int_{bf} dm_i + \delta \int_{bf} gz dm \\ = \delta \int_{bf} \left(- \sum_i M_i dm_i + gz dm \right) \\ = - \sum_i \delta \int_{bf} \mu_i dm_i = - \sum_i \delta \int_{bf} \mu_i m_{i,a_0} da_0. \end{aligned}$$

By applying the same method as above (with $\mu_i m_{i,a_0}$ instead of U_{a_0}), and according to $\delta \mu_i = -g\delta z$, we finally obtain for the two last lines of (11):

$$\begin{aligned} \sum_{bf} \left(\delta \int_{bf} dU - T \delta \int_{bf} dS - \sum_i M_i \delta \int_{bf} dm_i \right. \\ \left. + \delta \int_{bf} gz dm \right) = \sum_{bf} \int_{bf} g \delta z dm \\ + \sum_{bf} \int_{bf} \left(\delta U_{a_0} - T \delta S_{a_0} - \sum_i \mu_i \delta m_{i,a_0} \right) da_0 \\ + \sum_{bff'} \int_{bff'} (\gamma_{0,bf} - \gamma_{0,bf'}) \delta X_0 dl_0, \end{aligned}$$

where $\gamma_0 = U_{a_0} - T S_{a_0} - \sum_i \mu_i m_{i,a_0}$ is the excess of grand potential (on S_{bf} , for $\gamma_{0,bf}$), per unit area in the reference state (on $S_{0,bf}$). The equilibrium condition (11) may then be written as

$$\begin{aligned} \int_b \pi \cdot \delta e dv_0 - \int_b \rho \bar{g} \cdot \delta x dv \\ - \sum_{bf} \int_{bf} pn \cdot \delta x da - \sum_{bf} \int_{bf} \rho_s \bar{g} \cdot \delta x da \end{aligned}$$

$$\begin{aligned} + \sum_{bf} \int_{bf} \left(\delta U_{a_0} - T \delta S_{a_0} - \sum_i \mu_i \delta m_{i,a_0} \right) da_0 \\ - \sum_{bff'} \int_{bff'} \gamma_{ff'} \nu_{ff'} \cdot \delta X dl \\ + \sum_{bff'} \int_{bff'} (\gamma_{0,bf} - \gamma_{0,bf'}) \delta X_0 dl_0 = 0, \end{aligned} \quad (13)$$

in which δ is an arbitrary variation such that, on the surface Σ which bounds the system, the points of the body and the points of the body–fluid–fluid lines remain fixed. Note that δx is the displacement by F_i (up to the dividing surfaces S_{bf}).

3. Surface thermodynamics and surface stress

Now, let us take a bounding surface Σ which only encloses one fluid f and the body b . The S_{bf} surface enclosed in Σ is bounded by the closed curve $\Gamma = S_{bf} \cap \Sigma$. The above equilibrium condition (13) takes the form:

$$\begin{aligned} \int_b \pi \cdot \delta e dv_0 - \int_b \rho \bar{g} \cdot \delta x dv \\ - \int_{bf} pn \cdot \delta x da - \int_{bf} \rho_s \bar{g} \cdot \delta x da \\ + \int_{bf} \left(\delta U_{a_0} - T \delta S_{a_0} - \sum_i \mu_i \delta m_{i,a_0} \right) da_0 = 0, \end{aligned} \quad (14)$$

for any variation such that the points of the body which belong to Σ remain fixed (by the actual transformation F_a ; then, also, by the ideal transformation F_i , since F_i is the extrapolation of F_a , between S_{b1} and S_{bf}); b and bf respectively denote the parts of the body and the S_{bf} surface enclosed in Σ . Let us use the usual Eulerian representations of stress (σ) and strain ($\delta \varepsilon = \frac{1}{2}(Dw + (Dw)^*$), where $w = \delta x$), and Green's formula:

$$\begin{aligned} \int_b \pi \cdot \delta e dv_0 &= \int_b \sigma \cdot \delta \varepsilon dv \\ &= \int_b \frac{\sigma + \sigma^*}{2} \cdot \delta \varepsilon dv = \int_b \frac{\sigma + \sigma^*}{2} \cdot Dw dv \\ &= \int_b \sigma \cdot Dw dv - \int_b \frac{\sigma - \sigma^*}{2} \cdot Dw dv \\ &= - \int_b (\text{div } \sigma) \cdot w dv - \int_{bf} (\sigma \cdot n) \cdot w da \\ &\quad - \int_b \frac{\sigma - \sigma^*}{2} \cdot Dw dv. \end{aligned} \quad (15)$$

The preceding equilibrium condition is then equivalent to

(i) the mechanical equilibrium equations of the body

$$\text{div } \sigma + \rho \bar{g} = 0 \quad (16)$$

$$\sigma^* = \sigma \quad (17)$$

(obtained by fixing the points of the S_{bf} surface, and their thermodynamic state, in (14); note that, with the presence of volume couples of forces, of moment $M dv$ (M written as an antisymmetric tensor), the new term $-\int_b \frac{1}{2} M \cdot Dw dv$ would appear in (14), and (17) would become $\sigma - \sigma^* + M = 0$; in our case, $M = 0$, and σ and π are symmetric) and

(ii) the following mechanical equilibrium condition for S_{bf} :

$$-\int_{\text{bf}} (\sigma \cdot n) \cdot \delta x \, da - \int_{\text{bf}} pn \cdot \delta x \, da - \int_{\text{bf}} \rho_s \bar{g} \cdot \delta x \, da + \int_{\text{bf}} \left(\delta U_{a_0} - T \delta S_{a_0} - \sum_i \mu_i \delta m_{i,a_0} \right) da_0 = 0, \quad (18)$$

for any variation such that the points of the body which belong to Γ remain fixed.

From this condition, we are now able to determine the set of the ‘local’ (see below, after (21)) thermodynamic variables of state of the S_{bf} surface. The expression $\delta f_0 = \delta U_{a_0} - T \delta S_{a_0} - \sum_i \mu_i \delta m_{i,a_0}$ clearly depends on the variations of the thermodynamic variables of state of S_{bf} , for a given point $x_0 \in S_{0,\text{bf}}$. What is shown in the preceding condition (18) is that $\int_{\text{bf}} \delta f_0 \, da_0$, and then also δf_0 at a given point x_0 , only depend on the vector field δx defined on the S_{bf} surface, i.e., on the variation of only one geometrical variable: the field of the positions x of the points of the surface. Since a thermodynamic variable of state is geometrically local, this geometrical variable must be, in fact, $(x(x_0), \nabla x(x_0), \nabla^2 x(x_0), \dots)$ at the point x_0 (∇x is the covariant differential of x , on the surface $S_{0,\text{bf}}$; $x_0 \in S_{0,\text{bf}} \rightarrow x \in S_{\text{bf}}$ is the restriction of $F_{0,i}$ to $S_{0,\text{bf}}$). Obviously, $x(x_0)$ cannot be a variable of state, because the thermodynamic state of the surface may remain unchanged under any translation, $x' = x + a$, whereas $(x(x_0), \nabla x(x_0), \nabla^2 x(x_0), \dots)$ is changed into $(x(x_0) + a, \nabla x(x_0), \nabla^2 x(x_0), \dots)$. The variable is then reduced to $(\nabla x(x_0), \nabla^2 x(x_0), \dots)$, i.e., at the first order, $\nabla x(x_0)$. Let I_0 be an isometry of $T_x(S_{\text{bf}})$ onto $T_{x_0}(S_{0,\text{bf}})$, such that $I_0 \cdot \nabla x(x_0)$ is a direct linear mapping on $T_{x_0}(S_{0,\text{bf}})$, and use the classical decomposition $I_0 \cdot \nabla x(x_0) = R_0(x_0) \cdot S(x_0)$, where $S(x_0)$ is a positive symmetric tensor and $R_0(x_0)$ a rotation in $T_{x_0}(S_{0,\text{bf}})$. With respect to another isometry $I_1 : T_x(S_{\text{bf}}) \rightarrow T_{x_0}(S_{0,\text{bf}})$, such that $I_1 \cdot \nabla x(x_0)$ is direct, the decomposition would be $I_1 \cdot \nabla x(x_0) = R_1(x_0) \cdot S(x_0)$, with $R_1(x_0) = R_{1,0} \cdot R_0(x_0)$ and $R_{1,0} = I_1 \cdot I_0^{-1}$, which shows that the symmetric tensor $S(x_0)$ only depends on $\nabla x(x_0)$ (and not on I_0). We thus have the unique decomposition $\nabla x(x_0) = I(x_0) \cdot S(x_0)$, where $I(x_0) : T_{x_0}(S_{0,\text{bf}}) \rightarrow T_x(S_{\text{bf}})$ is an isometry. In addition, under a rotation (of the whole space), $x \rightarrow x'$, $\nabla x(x_0)$ is changed into $\nabla x'(x_0) = R \cdot \nabla x(x_0)$ (R being the associated vectorial rotation), but the symmetric tensor $S(x_0)$ remains unchanged, since $\nabla x'(x_0) = I'(x_0) \cdot S(x_0)$, with $I'(x_0) = R \cdot I(x_0)$. Since the thermodynamic state of the surface may remain unchanged under such an arbitrary rotation, whereas $\nabla x(x_0)$ is changed into $R \cdot \nabla x(x_0)$, but $S(x_0)$ remains unchanged, we may conclude that the true geometrical variable of state is $S(x_0)$. Other variables equivalent to $S = S(x_0)$ are S^2 (because S is symmetric and positive) or the (Lagrangian) surface strain $e_s = \frac{1}{2}(S^2 - I)$ ($I =$ identity operator), all these tensors being associated to the deformation of the surface (change of the scalar product), e.g., for e_s :

$$e_s(dx_0, dy_0) = \frac{1}{2}(dx \cdot dy - dx_0 \cdot dy_0), \quad (19)$$

for arbitrary vectors $dx_0, dy_0 \in T_{x_0}(S_{0,\text{bf}})$. In conclusion, we may take e_s (at x_0) as the geometrical variable of state and, as mentioned above (as a consequence of (18)), $\delta f_0 =$

$\delta U_{a_0} - T \delta S_{a_0} - \sum_i \mu_i \delta m_{i,a_0}$ is then proportional to its variation δe_s :

$$\delta U_{a_0} - T \delta S_{a_0} - \sum_i \mu_i \delta m_{i,a_0} = \pi_s \cdot \delta e_s. \quad (20)$$

The ‘coefficient’ π_s of δe_s will be called the (Lagrangian) surface stress tensor at equilibrium, and $\pi_s \cdot \delta e_s$ the work of deformation of the surface, expressed per unit area in the reference state. Note that (20) actually defines the symmetric part of the tensor π_s , because δe_s is symmetric. Here, we consider that the surface stress (π_s , and its Eulerian form σ_s , below) is symmetric, but this may not be always the case (e.g., in the presence of surface couples of forces, acting on the interface; as for the case of volume stress: see the comment after (17)). In an equivalent form,

$$\delta U_{a_0} = T \delta S_{a_0} + \pi_s \cdot \delta e_s + \sum_i \mu_i \delta m_{i,a_0}. \quad (21)$$

Finally, this expression gives us the set of the ‘local’ thermodynamic variables of state of the S_{bf} surface: S_{a_0} , e_s and m_{i,a_0} ($i = 1, \dots, n$). ‘Local’ here means: for the subset of the thermodynamic states which can be reached by reversible transformations from a given thermodynamic state. In such a subset of thermodynamic states, the surface stress π_s is then the partial derivative of U_{a_0} with respect to the surface strain e_s :

$$\pi_s^{\alpha\beta} = \frac{\partial U_{a_0}}{\partial e_{s,\alpha\beta}} \quad \text{with variables } (S_{a_0}, e_s, m_{i,a_0}) \quad (22)$$

(components $\alpha, \beta \in \{1, 2\}$, with arbitrary coordinates on the surface; the two variables $e_{s,12}$ and $e_{s,21}$ —although equal—being formally distinguished in (22)).

If the above subset of thermodynamic states of the surface is equal to the set of all thermodynamic states, then the above ‘local’ variables are the true (‘global’) thermodynamic variables of state of the surface. This occurs if any thermodynamic state can be reached by a reversible transformation from any other thermodynamic state. We know that such a property is valid for some volume bodies, such as viscoelastic solids or viscous fluids, for which any transformation becomes reversible when achieved at vanishing speed. We may assume that the surface of such bodies has the same property, in which case the above variables are the true thermodynamic variables of state of the surface.

From the definition of γ_0 and (20), we may also write

$$\delta \gamma_0 = -S_{a_0} \delta T + \pi_s \cdot \delta e_s - \sum_i m_{i,a_0} \delta \mu_i, \quad (23)$$

which gives another equivalent set of ‘local’ thermodynamic variables of state: T , e_s and μ_i ($i = 1, \dots, n$). The surface stress here appears as the partial derivative of γ_0 with respect to the surface strain:

$$\pi_s^{\alpha\beta} = \frac{\partial \gamma_0}{\partial e_{s,\alpha\beta}} \quad \text{with variables } (T, e_s, \mu_i) \quad (24)$$

(a Shuttleworth type equation [15]; its Eulerian version is expressed in (29), below).

As above, for the usual volume stress and strain tensors, we have a similar Eulerian representation for the surface stress and strain tensors (σ_s and $\delta\varepsilon_s$, respectively; $\delta\varepsilon_s(dx, dy) = \frac{1}{2}\delta(dx \cdot dy)$, for $dx, dy \in T_x(S_{bf})$), and the work of deformation of the surface:

$$\sigma_s \cdot \delta\varepsilon_s da = \pi_s \cdot \delta e_s da_0. \quad (25)$$

Equation (21) may also be written, with da_0 fixed:

$$\begin{aligned} \delta dU &= T\delta dS + \pi_s \cdot \delta e_s da_0 + \sum_i \mu_i \delta dm_i \\ &= T\delta dS + \sigma_s \cdot \delta\varepsilon_s da + \sum_i \mu_i \delta dm_i \end{aligned} \quad (26)$$

($dU = U_{a_0} da_0$, etc; compare with (1) for a fluid–fluid surface, where $\sigma_s = \gamma I$; I is the identity operator on $T_x(S_{bf})$) or

$$\delta U_a = T\delta S_a + (\sigma_s - \gamma I) \cdot \delta\varepsilon_s + \sum_i \mu_i \delta m_{i,a} \quad (27)$$

(since $dU = U_a da$, etc and $\delta da = \text{tr}(\delta\varepsilon_s) da$); and with da_0 variable:

$$\delta dU = T\delta dS + \pi_s \cdot \delta e_s da_0 + \gamma_0 \delta da_0 + \sum_i \mu_i \delta dm_i, \quad (28)$$

in which the surface stress π_s is associated with the deformation of a given element da_0 , and the surface grand potential γ_0 to the creation of a new element of surface δda_0 . The Eulerian form of (23) is, with da_0 fixed:

$$\delta\gamma = -S_a \delta T + (\sigma_s - \gamma I) \cdot \delta\varepsilon_s - \sum_i m_{i,a} \delta\mu_i, \quad (29)$$

since $\gamma da = \gamma_0 da_0$ and $\delta da = \text{tr}(\delta\varepsilon_s) da$ (compare with (12) for a fluid–fluid surface).

Note that, although the three variables $e_{s,\alpha\beta}$ are independent, it may occur, in some particular cases, that fewer variables are necessary. For example, if we a priori know that the tensor σ_s is isotropic (as for the isotropic pressure in a fluid, or the surface tension in a fluid–fluid surface), i.e., $\sigma_{s,\beta}^\alpha = \sigma_s \delta_\beta^\alpha$ (eigenvalue also denoted σ_s), then the expression (25) is reduced to $\sigma_s \delta\varepsilon_{s,\alpha}^\alpha da = \sigma_s \delta da$. In this case, we only need one variable, namely da .

Moreover, note that the expression (25) obtained for the work of deformation of the surface, differs from that proposed in [3, 8]:

$$(\bar{\sigma}_t \cdot \delta\varepsilon_t + \sigma_n \cdot \delta\bar{\varepsilon}_n) da, \quad (30)$$

where σ and $\delta\varepsilon$ are the volume stress and strain tensors, the subscripts t and n respectively refer to the tangential and normal components, and the symbol $\bar{}$ indicates an excess quantity on the surface. Since $\delta\varepsilon_s = \delta\varepsilon_t$, the comparison of the two expressions shows that the surface stress σ_s here defined differs from its usual definition as the excess of tangential stress $\bar{\sigma}_t$. There are, in fact, too many variables in (30): 3 variables $\delta\varepsilon_t$ + 3 variables $\delta\bar{\varepsilon}_n$. The above thermodynamic approach showed that there are only 3 geometrical (‘local’) variables of state for the surface, namely the 3 components of δe_s (or $\delta\varepsilon_s$). Note also that the continuity of the normal stress $\sigma_n = \sigma \cdot n$, when crossing the interface, is assumed in (30): however, the next section will show that there is generally a discontinuity of the normal stress, due to the presence of surface stress and gravity.

4. Equations at surfaces and triple lines

4.1. Surfaces

With (20) and (25), the mechanical equilibrium condition (18) for the bf surface takes the form:

$$\begin{aligned} - \int_{bf} (\sigma \cdot n) \cdot \delta x da - \int_{bf} pn \cdot \delta x da - \int_{bf} \rho_s \bar{g} \cdot \delta x da \\ + \int_{bf} \sigma_s \cdot \delta\varepsilon_s da = 0, \end{aligned} \quad (31)$$

for any variation such that $\delta x = 0$ on Γ . By application of Green’s formula to the last term, this leads to the mechanical equilibrium equation of the surface:

$$\text{div} \sigma_s + \rho_s \bar{g} + \sigma \cdot n + pn = 0. \quad (32)$$

With Cartesian coordinates (x^i) ($i = 1, 2, 3$) for the whole space and arbitrary curvilinear coordinates (x^α) ($\alpha = 1, 2$) for the surface (for $x \in S_{bf}$, (x^α) and (x^i) must be clearly distinguished), it may be written

$$\partial_\beta (\sigma_s^{\alpha\beta} \partial_\alpha x^i) + \Gamma_{\beta\gamma}^\beta \sigma_s^{\alpha\gamma} \partial_\alpha x^i + \rho_s \bar{g}^i + \sigma^{ij} n_j + pn^i = 0, \quad (33)$$

where $i, j \in \{1, 2, 3\}$ refer to space coordinates, $\alpha, \beta, \gamma \in \{1, 2\}$ to surface coordinates, summation is performed on repeated indices, $\partial_\alpha = \frac{\partial}{\partial x^\alpha}$ and $\Gamma_{\beta\gamma}^\alpha$ are Christoffel’s symbols. A similar equation was obtained in a purely mechanical approach [2]. Note the similarity of this equation (32) with the Cauchy volume one (16).

Note also that (32) may easily be generalized at the surface between two deformable bodies (b and b’):

$$\text{div} \sigma_s + \rho_s \bar{g} + \sigma \cdot n - \sigma' \cdot n = 0, \quad (34)$$

where σ' is the stress tensor in b’, and n is oriented from b’ to b.

Equation (32) may be separated into tangential and normal components. The tangential component is

$$\text{div}_s \sigma_s + \rho_s \bar{g}_t + (\sigma \cdot n)_t = 0, \quad (35)$$

where the subscript t indicates the vector component tangent to the surface and div_s is the surface divergence:

$$(\text{div}_s \sigma_s)^i = (\partial_\beta \sigma_s^{\alpha\beta} + \Gamma_{\gamma\beta}^\alpha \sigma_s^{\gamma\beta} + \Gamma_{\gamma\beta}^\beta \sigma_s^{\alpha\gamma}) \partial_\alpha x^i. \quad (36)$$

The normal component of (32) is

$$\sigma_s \cdot l_n + \rho_s \bar{g}_n + \sigma_{nn} + p = 0, \quad (37)$$

where $\bar{g}_n = \bar{g} \cdot n$, $\sigma_{nn} = (\sigma \cdot n) \cdot n = \sigma^{ij} n_i n_j$ and l_n is the ‘fundamental form’

$$l_{n,\alpha\beta} = (\partial_{\alpha\beta} x^i - \Gamma_{\alpha\beta}^\gamma \partial_\gamma x^i) n_i, \quad (38)$$

the eigenvalues of which are the principal curvatures, $\frac{1}{R_1}$ and $\frac{1}{R_2}$, of the surface (a curvature being considered positive, when its centre is on the side of n). This equation (37) generalizes the classical Laplace equation (9) for a fluid–fluid surface. Indeed, $\sigma_{nn} + p$ represents the difference of the normal pressures and, for isotropic surface stresses, $\sigma_s \cdot l_n = \sigma_s l_{n,\alpha}^\alpha = \sigma_s (\frac{1}{R_1} + \frac{1}{R_2})$ (eigenvalue also denoted σ_s).

Equation (32) also shows that there is a discontinuity of the normal stress at the interface, the jump of which, $\sigma \cdot n + pn$, is due both to surface stress (term $\text{div} \sigma_s$, with components $\text{div}_s \sigma_s$ and $\sigma_s \cdot l_n$) and to gravity (term $\rho_s \bar{g}$).

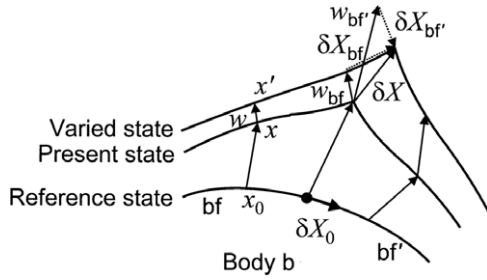


Figure 5. Displacement δX of the bff' triple line, expressed as $w_{bf} + \delta X_{bf}$ on the bf side, or $w_{bf'} + \delta X_{bf'}$ on the bf' side (δX_{bf} and $\delta X_{bf'}$ are indicated by dotted arrows; see text).

4.2. Triple lines

Let us now consider a bounding surface Σ which encloses two fluids (f and f') and the body b , and apply the general equilibrium condition (13), using the above expressions (15), (20) and (25). Note that Green's formula applied to the work of deformation of the bf surface leads to the new term $-\int_{bff'} (\sigma_s \cdot \nu) \cdot w \, dl$ at the triple line, where $w = \delta x$ and ν is the unit vector normal to the bff' line, tangent to the bf surface, and oriented from the line to the interior of bf (here, σ_s , ν and w refer to the bf side). With the help of the equilibrium equations (16)–(17) for b , and (32) for bf and bf' , the general equilibrium condition is then reduced to:

$$\begin{aligned}
 & - \int_{bff'} ((\sigma_{s,bf} \cdot \nu_{bf}) \cdot w_{bf} + (\sigma_{s,bf'} \cdot \nu_{bf'}) \cdot w_{bf'}) \, dl \\
 & - \int_{bff'} \gamma_{ff'} \nu_{ff'} \cdot \delta X \, dl \\
 & + \int_{bff'} (\gamma_{0,bf} - \gamma_{0,bf'}) \delta X_0 \, dl_0 = 0, \quad (39)
 \end{aligned}$$

for any variation such that the two points of the bff' line which belong to Σ remain fixed (both in space, and as points of the body).

The transformation $x_0 \rightarrow x$ restricted to the body–fluid surface, between the (ideal) reference and present states of the body, is continuous, but its differential ∇x is not continuous at the triple line, since the plane tangent to the bf surface and the plane tangent to the bf' surface (at the triple line) are different (figure 5). Its variation $w = \delta x$ will also be discontinuous at the triple line. From the bf side point of view, and if $\delta X_0 = 0$, the displacement of the bff' line would be equal to w_{bf} . On the other hand, if $w = 0$ on bf , and $\delta X_0 \neq 0$, this displacement would be $\delta X_{bf} = \nabla x(x_0)_{bf} \cdot \delta X_0$ (x_0 belongs to bff' ; δX_0 is here considered as a vector). In the general case, the displacement of the triple line will then be

$$\begin{aligned}
 \delta X & = w_{bf} + \delta X_{bf} = w_{bf} + \nabla x(x_0)_{bf} \cdot \delta X_0 \\
 & = w_{bf'} + \delta X_{bf'} = w_{bf'} + \nabla x(x_0)_{bf'} \cdot \delta X_0 \quad (40)
 \end{aligned}$$

(expression from the bf' side, in the second line; see figure 5; the component of this δX normal to bff' is the δX of (39), but this has no effect on $\nu_{ff'} \cdot \delta X$).

From (40) and the Eulerian form of the last term of (39) ($\gamma \, da = \gamma_0 \, da_0$; γ is the excess of grand potential on the

surface, per unit area in the present state), the equilibrium condition (39) takes the form

$$\begin{aligned}
 & - \int_{bff'} (\sigma_{s,bf} \cdot \nu_{bf} + \sigma_{s,bf'} \cdot \nu_{bf'} + \gamma_{ff'} \nu_{ff'}) \cdot \delta X \, dl \\
 & + \int_{bff'} ((\sigma_{s,bf} \cdot \nu_{bf}) \cdot \delta X_{bf} + (\sigma_{s,bf'} \cdot \nu_{bf'}) \cdot \delta X_{bf'}) \, dl \\
 & - \int_{bff'} (\gamma_{bf} \nu_{bf} \cdot \delta X_{bf} + \gamma_{bf'} \nu_{bf'} \cdot \delta X_{bf'}) \, dl = 0, \quad (41)
 \end{aligned}$$

which leads to two equilibrium equations at the triple line:

$$\sigma_{s,bf} \cdot \nu_{bf} + \sigma_{s,bf'} \cdot \nu_{bf'} + \gamma_{ff'} \nu_{ff'} = 0 \quad (42)$$

(by considering the triple line as fixed with respect to the body, i.e., $\delta X_0 = 0$, hence $\delta X_{bf} = \delta X_{bf'} = 0$) and

$$\begin{aligned}
 & - \gamma_{bf} \nu_{bf} \cdot \delta X_{bf} - \gamma_{bf'} \nu_{bf'} \cdot \delta X_{bf'} \\
 & + (\sigma_{s,bf} \cdot \nu_{bf}) \cdot \delta X_{bf} + (\sigma_{s,bf'} \cdot \nu_{bf'}) \cdot \delta X_{bf'} = 0. \quad (43)
 \end{aligned}$$

Equation (42) represents the equilibrium of the forces acting on the triple line, considered as fixed on the body ($\delta X_0 = 0$), whereas (43) expresses the equilibrium relative to the motion of the triple line with respect to the body ($\delta X_0 \neq 0$). A similar situation was found in the case of the thin plate [4, 5]. Note that it was proposed [14] that the equilibrium at the triple line involves not only the (bf , bf' and ff') surface forces, but also a force which originates from the volume stresses σ in the body and the singularity at the triple line. The obtained equation (42) shows that there is no body volume contribution, and that the equilibrium only involves the forces exerted by the three surfaces (bf , bf' and ff') on the triple line. This equation shows that surface stresses are forces acting on a line fixed on the body, and may easily be generalized to a line of contact between three deformable bodies (b , b' and b''):

$$\sigma_{s,bb'} \cdot \nu_{bb'} + \sigma_{s,b'b''} \cdot \nu_{b'b''} + \sigma_{s,bb''} \cdot \nu_{bb''} = 0 \quad (44)$$

(equilibrium of the forces acting on the triple line, considered as fixed with respect to the three bodies).

Let τ be a unit vector tangent to the triple line, ($\sigma_{bf, \nu\nu}$, $\sigma_{bf, \tau\nu}$) the components of $\sigma_{s,bf} \cdot \nu_{bf}$ in the basis (ν_{bf} , τ), and use similar notations for $\sigma_{s,bf'}$ with the basis ($\nu_{bf'}$, τ). Equation (42) may then be separated into its normal and tangential components (with respect to the line):

$$\sigma_{bf, \nu\nu} \nu_{bf} + \sigma_{bf', \nu\nu} \nu_{bf'} + \gamma_{ff'} \nu_{ff'} = 0 \quad (45)$$

$$\sigma_{bf, \tau\nu} + \sigma_{bf', \tau\nu} = 0. \quad (46)$$

Equation (43) may also be viewed as the expression of the equilibrium (41), when $\delta X = 0$ and $\delta X_0 \neq 0$: this means that the triple line is fixed in space, but moves with respect to the body; in other words, the body moves with respect to the triple line, which remains fixed in space (the body then also moves with respect to its singularity, attached to the triple line). Since $\delta X = 0$ implies that $w_{bf} = -\delta X_{bf} \in T_x(S_{bf})$ and $w_{bf'} = -\delta X_{bf'} \in T_x(S_{bf'})$, (43) may then be written as

$$\begin{aligned}
 & - \gamma_{bf} \nu_{bf} \cdot \delta X_{bf} - \gamma_{bf'} \nu_{bf'} \cdot \delta X_{bf'} \\
 & = (\sigma_{s,bf} \cdot \nu_{bf}) \cdot w_{bf} + (\sigma_{s,bf'} \cdot \nu_{bf'}) \cdot w_{bf'}. \quad (47)
 \end{aligned}$$

This equilibrium equation has a clear physical meaning: it states that the variation of surface energy (grand potential) due to the motion of the triple line with respect to the body (e.g., increase in bf area and decrease in bf' area) is equal to the work of the surface stresses acting on the triple line (although the triple line does not move in space, the points of the body situated at this line move by w_{bf} in the bf side, and by $w_{bf'}$ in the bf' side).

From the expressions (40) of δX_{bf} and $\delta X_{bf'}$, equation (43):

$$\begin{aligned} & ((\sigma_{s,bf} - \gamma_{bf}I) \cdot \nu_{bf}) \cdot \delta X_{bf} \\ & + ((\sigma_{s,bf'} - \gamma_{bf'}I) \cdot \nu_{bf'}) \cdot \delta X_{bf'} = 0 \end{aligned} \quad (48)$$

may be written as

$$\begin{aligned} & (\sigma_{s,bf} - \gamma_{bf}I) \cdot \nu_{bf} \cdot \nabla x(x_0)_{bf} \\ & + (\sigma_{s,bf'} - \gamma_{bf'}I) \cdot \nu_{bf'} \cdot \nabla x(x_0)_{bf'} = 0 \end{aligned} \quad (49)$$

(in this last equation, the covariant forms of the tensors $\sigma_{s,bf}$ and $\sigma_{s,bf'}$ are used, and I denotes the covariant metric tensors on S_{bf} and $S_{bf'}$, respectively).

In the reference state, let ν_0 be the unit vector normal to the bf' line, tangent to the bf or bf' surface (in the reference state, there is no singularity at the triple line, and the planes tangent to S_{bf} and $S_{bf'}$ are identical), and oriented from bf' to bf, and τ_0 the unit vector tangent to bf' , with the same orientation as τ . With the notations

$$\bar{\nu}_{bf} = \nabla x(x_0)_{bf} \cdot \nu_0 = a_{\nu\nu} \nu_{bf} + a_{\tau\nu} \tau$$

$$\bar{\nu}_{bf'} = \nabla x(x_0)_{bf'} \cdot \nu_0 = -a'_{\nu\nu} \nu_{bf'} + a'_{\tau\nu} \tau$$

$$\bar{\tau} = \nabla x(x_0) \cdot \tau_0 = a_{\tau\tau} \tau$$

($a_{\nu\nu}, a'_{\nu\nu}, a_{\tau\tau} > 0$), (48) or (49) is equivalent to the two equations

$$((\sigma_{s,bf} - \gamma_{bf}I) \cdot \nu_{bf}) \cdot \bar{\nu}_{bf} + ((\sigma_{s,bf'} - \gamma_{bf'}I) \cdot \nu_{bf'}) \cdot \bar{\nu}_{bf'} = 0 \quad (50)$$

$$\sigma_{bf,\tau\nu} + \sigma_{bf',\tau\nu} = 0. \quad (51)$$

The second equation is the same as (46) (which shows that (48) does not depend on the component of δX_0 along τ_0), and the first one may be written as

$$\begin{aligned} & (\sigma_{bf,\nu\nu} - \gamma_{bf})a_{\nu\nu} + \sigma_{bf,\tau\nu}a_{\tau\nu} \\ & - (\sigma_{bf',\nu\nu} - \gamma_{bf'})a'_{\nu\nu} + \sigma_{bf',\tau\nu}a'_{\tau\nu} = 0, \end{aligned} \quad (52)$$

i.e.,

$$\begin{aligned} & (\sigma_{bf,\nu\nu} - \gamma_{bf})a_{\nu\nu} - (\sigma_{bf',\nu\nu} - \gamma_{bf'})a'_{\nu\nu} \\ & + \sigma_{bf',\tau\nu}(a'_{\tau\nu} - a_{\tau\nu}) = 0. \end{aligned} \quad (53)$$

Another form of this equation is obtained after multiplication by $a_{\tau\tau}$:

$$\begin{aligned} & (\sigma_{bf,\nu\nu} - \gamma_{bf}) \left(\frac{da}{da_0} \right)_{bf} - (\sigma_{bf',\nu\nu} - \gamma_{bf'}) \left(\frac{da}{da_0} \right)_{bf'} \\ & + 2\sigma_{bf',\tau\nu}(e'_{\tau\nu} - e_{\tau\nu}) = 0, \end{aligned} \quad (54)$$

since

$$\left(\frac{da}{da_0} \right)_{bf} = a_{\nu\nu} a_{\tau\tau}$$

$$\left(\frac{da}{da_0} \right)_{bf'} = a'_{\nu\nu} a_{\tau\tau}$$

$$e_{\tau\nu} = e_{bf}(\tau_0, \nu_0) = \frac{1}{2} \bar{\tau} \cdot \bar{\nu}_{bf} = \frac{1}{2} a_{\tau\nu} a_{\tau\tau}$$

$$e'_{\tau\nu} = e_{bf'}(\tau_0, \nu_0) = \frac{1}{2} \bar{\tau} \cdot \bar{\nu}_{bf'} = \frac{1}{2} a'_{\tau\nu} a_{\tau\tau}.$$

Let us show that the preceding equations do not depend on the reference state. Since

$$\begin{aligned} \delta X_{bf'} &= \nabla x(x_0)_{bf'} \cdot \delta X_0 \\ &= \nabla x(x_0)_{bf'} \cdot (\nabla x(x_0)_{bf'})^{-1} \cdot \delta X_{bf} \\ &= \nabla x_{\tau} \cdot \delta X_{bf}, \end{aligned}$$

where

$$\nabla x_{\tau} = \nabla x(x_0)_{bf'} \cdot \nabla x(x_0)_{bf'}^{-1} \quad (55)$$

is the 'relative' differential of the transformation, on the bf' side with respect to the bf side (this concept was defined in [16]), the above equation (48) takes the form

$$(\sigma_{s,bf} - \gamma_{bf}I) \cdot \nu_{bf} + (\sigma_{s,bf'} - \gamma_{bf'}I) \cdot \nu_{bf'} \cdot \nabla x_{\tau} = 0 \quad (56)$$

(with the covariant forms of $\sigma_{s,bf}$, $\sigma_{s,bf'}$ and I , as above for (49)), which does not depend on the reference state. Indeed, if the previous reference state 0 (indicated by the subscript 0) is replaced by a new reference state 1 (subscript 1), such that $\nabla x_0(x_1)$ is continuous at the triple line, then

$$\nabla x(x_1)_{bf} = \nabla x(x_0)_{bf} \cdot \nabla x_0(x_1)$$

$$\nabla x(x_1)_{bf'} = \nabla x(x_0)_{bf'} \cdot \nabla x_0(x_1)$$

(at the triple line), hence

$$\begin{aligned} & \nabla x(x_1)_{bf'} \cdot \nabla x(x_1)_{bf'}^{-1} \\ &= \nabla x(x_0)_{bf'} \cdot \nabla x_0(x_1) \cdot \nabla x_0(x_1)^{-1} \cdot \nabla x(x_0)_{bf'}^{-1} \\ &= \nabla x(x_0)_{bf'} \cdot \nabla x(x_0)_{bf'}^{-1}, \end{aligned}$$

which shows that ∇x_{τ} does not depend on the reference state. Using the bases (ν_0, τ_0) , (ν_{bf}, τ) and $(-\nu_{bf'}, \tau)$, (55) may be written in the matrix form:

$$\begin{aligned} \begin{pmatrix} a_{\tau,\nu\nu} & 0 \\ a_{\tau,\tau\nu} & a_{\tau,\tau\tau} \end{pmatrix} &= \begin{pmatrix} a'_{\nu\nu} & 0 \\ a'_{\tau\nu} & a_{\tau\tau} \end{pmatrix} \begin{pmatrix} \frac{1}{a_{\nu\nu}} & 0 \\ -\frac{a_{\tau\nu}}{a_{\nu\nu}a_{\tau\tau}} & \frac{1}{a_{\tau\tau}} \end{pmatrix} \\ &= \begin{pmatrix} \frac{a'_{\nu\nu}}{a_{\nu\nu}} & 0 \\ \frac{a'_{\tau\nu} - a_{\tau\nu}}{a_{\nu\nu}} & 1 \end{pmatrix}, \end{aligned}$$

which shows that

$$a_{\tau,\nu\nu} = \frac{a'_{\nu\nu}}{a_{\nu\nu}}$$

$$a_{\tau,\tau\nu} = \frac{a'_{\tau\nu} - a_{\tau\nu}}{a_{\nu\nu}}$$

$$a_{\tau,\tau\tau} = 1,$$

and leads to another form of (56) or (53):

$$\sigma_{bf,\nu\nu} - \gamma_{bf} - (\sigma_{bf',\nu\nu} - \gamma_{bf'})a_{\tau,\nu\nu} + \sigma_{bf',\tau\nu}a_{\tau,\tau\nu} = 0. \quad (57)$$

4.3. Modified Young's equation

If the body is a rigid solid, (42) cannot be obtained from (41), because it is not possible to move the triple line in the space ($\delta X \neq 0$) while this line remains fixed to the solid ($\delta X_0 = 0$). In fact, (41) takes the form

$$-\int_{\text{bff}} (\gamma_{\text{ff}'} \nu_{\text{ff}'} + \gamma_{\text{bf}} \nu_{\text{bf}} + \gamma_{\text{bf}'} \nu_{\text{bf}'}) \cdot \delta X dl = 0 \quad (58)$$

($\delta X = \delta X_{\text{bf}} = \delta X_{\text{bf}'}$, since $w_{\text{bf}} = w_{\text{bf}'} = 0$), and leads to

$$\gamma_{\text{bf}} - \gamma_{\text{bf}'} + \gamma_{\text{ff}'} \cos \varphi_f = 0 \quad (59)$$

(since $\delta X \in T_x(\text{S}_{\text{bf}}) = T_x(\text{S}_{\text{bf}'})$ and $\nu_{\text{bf}'} = -\nu_{\text{bf}}$; φ_f is the angle of contact measured in the fluid f), which is Young's classical equation. This shows that Young's classical equation only refers to the surface energies γ (and not to the surface stresses σ_s) and is related to the displacement of the triple line with respect to the solid.

Then, in the present case of a deformable body, (42) cannot be compared with Young's classical equation (since it refers to the surface stresses and the triple line fixed on the body). The present generalization of Young's equation is in fact related to (43) (or (48), (49), (53), (56), (57)), because this equation contains the surface energies γ and is related to the displacement of the triple line with respect to the body. In order to eliminate the surface stresses $\sigma_{s,\nu\nu}$ in (57), we use the projections of (45) onto ν_{bf} and $\nu_{\text{bf}'}$:

$$\sigma_{\text{bf},\nu\nu} + \sigma_{\text{bf}',\nu\nu} \cos \varphi_b + \gamma_{\text{ff}'} \cos \varphi_f = 0$$

$$\sigma_{\text{bf},\nu\nu} \cos \varphi_b + \sigma_{\text{bf}',\nu\nu} + \gamma_{\text{ff}'} \cos \varphi_f = 0$$

(φ_f , $\varphi_{f'}$ and φ_b are the three angles of contact, respectively measured in f, f' and b), which give

$$\sigma_{\text{bf},\nu\nu} = \gamma_{\text{ff}'} \frac{\sin \varphi_{f'}}{\sin \varphi_b} \quad (60)$$

$$\sigma_{\text{bf}',\nu\nu} = \gamma_{\text{ff}'} \frac{\sin \varphi_f}{\sin \varphi_b} \quad (61)$$

(using $\varphi_b + \varphi_f + \varphi_{f'} = 2\pi$). By introducing these expressions in (57), we obtain the following modified form of Young's equation:

$$-\gamma_{\text{bf}} + \gamma_{\text{bf}'} a_{r,\nu\nu} + \gamma_{\text{ff}'} \frac{\sin \varphi_{f'} - a_{r,\nu\nu} \sin \varphi_f}{\sin \varphi_b} + \sigma_{\text{bf}',\tau\nu} a_{r,\tau\nu} = 0, \quad (62)$$

or

$$-\gamma_{\text{bf}} + \gamma_{\text{bf}'} a_{r,\nu\nu} - \gamma_{\text{ff}'} \cos \varphi_f - \gamma_{\text{ff}'} \sin \varphi_f \frac{\cos \varphi_b + a_{r,\nu\nu}}{\sin \varphi_b} + \sigma_{\text{bf}',\tau\nu} a_{r,\tau\nu} = 0 \quad (63)$$

(using $\sin \varphi_{f'} = -\sin(\varphi_b + \varphi_f)$). A modified form of Young's equation was previously presented in the case of the thin plate [4, 5]. Obviously, if $a_{r,\nu\nu} = 1$ and $a_{r,\tau\nu} = 0$ (or if $a_{r,\nu\nu} = 1$ and $\sigma_{\text{bf}',\tau\nu} = 0$), this equation takes the form

$$-\gamma_{\text{bf}} + \gamma_{\text{bf}'} - \gamma_{\text{ff}'} \cos \varphi_f - \gamma_{\text{ff}'} \sin \varphi_f \frac{1 + \cos \varphi_b}{\sin \varphi_b} = 0,$$

which leads to the Young's classical equation (59) when φ_b tends to π .

5. Conclusions

This paper deals with the thermodynamic (and mechanical) equilibrium of a deformable body in contact with fluids, specially at the surfaces and the triple contact lines of the body. We have applied the 'dividing surface' Gibbs approach [1], here refined with a new concept: the 'ideal transformation' between two 'ideal' states, which defines the 'ideal' displacement of the material points, within the interface film, up to the dividing surface. The approach is based on a careful application of the general thermodynamic equilibrium criterion of Gibbs. The classical thermal and chemical equilibrium equations (5), (6), and the mechanical equations concerning the fluids (7)–(10) and the (volume part of the) body (16), (17) are first separated. We thus obtain a new equilibrium condition which only refers to the surfaces and the triple contact lines of the body. As a first consequence of this condition, it is shown that the 'local' thermodynamic variables of state of the surface are only the temperature, the chemical potentials and the surface strain tensor (these are the true thermodynamic variables of state, if, e.g., the body is a viscoelastic solid or a viscous fluid). This leads to a new definition of the surface stress tensor (which differs from the usual definition as the excess of tangential stress) and to the corresponding surface thermodynamic equations (21)–(29), with the simple expression (25) for the work of deformation of the surface (which differs from the expression (30) of [3, 8]). The mechanical equilibrium equation of the surface (32) is then obtained. This equation, similar to the classical Cauchy one for the volume, may be separated into tangential (35) and normal (37) components. This normal component is in fact a generalization of the classical Laplace equation for a fluid–fluid surface. Finally, at the (body–fluid–fluid) triple contact lines, we show that there are two mechanical equilibrium equations. The first one (42) (or (45), (46)) represents the equilibrium of the forces which act on the triple line, considered as a line fixed on the body (these forces are the surface stresses; there is no contribution from the volume stresses of the body, as proposed in [14]). The very original second equation (48) (or (49), (53), (56), (57)) expresses the equilibrium relative to the motion of the triple line with respect to the body, while the line remains fixed in space: i.e., the body moves with respect to the triple line (and with respect to the singularity of the body, attached to this line), which remains fixed in space. This equation involves the surface energies, the surface stresses, and the 'relative deformation' [16] between the two sides of the body surface separated by the triple line. It leads to a strong modification of the Young's classical capillary equation, as shown in the equations (62) or (63). A similar situation was found in the case of the thin plate [4, 5]. An approximate solution of these equations, for an elastic solid, will be given in a future paper.

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References

- [1] Gibbs J W 1876 *Trans. Conn. Acad.* **III** 108–248
Gibbs J W 1878 *Trans. Conn. Acad.* **III** 343–524
- [2] Gurtin M E and Murdoch A I 1975 *Arch. Ration. Mech. Anal.* **57** 291–323
- [3] Nozières P and Wolf D E 1988 *Z. Phys. B* **70** 399–407
- [4] Olives J 1993 *J. Phys.: Condens. Matter* **5** 2081–94
- [5] Olives J 1996 *SIAM J. Appl. Math.* **56** 480–93
- [6] Gurtin M E, Weissmüller J and Larché F 1998 *Phil. Mag. A* **78** 1093–109
- [7] Sanfeld A and Steinchen A 2003 *J. Non-Equilib. Thermodyn.* **28** 115–40
- [8] Müller P and Saúl A 2004 *Surf. Sci. Rep.* **54** 157–258
- [9] Rusanov A I 2005 *Surf. Sci. Rep.* **58** 111–239
- [10] Lester G R 1961 *J. Colloid Sci.* **16** 315–26
- [11] Rusanov A I 1975 *Colloid J. USSR* **37** 614–22
- [12] Shanahan M E R and de Gennes P-G 1986 *C. R. Acad. Sci. Paris II* **302** 517–21
- [13] Shanahan M E R 1986 *C. R. Acad. Sci. Paris II* **303** 1537–40
- [14] Madasu S and Cairncross R A 2004 *Int. J. Num. Meth. Fluids* **45** 301–19
- [15] Shuttleworth R 1950 *Proc. R. Soc. A* **63** 444–57
- [16] Olives J and Bronner G 1984 *J. Struct. Geol.* **6** 599–601