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Capillarity and elasticity. The example of the thin plate

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Abstract. Following the method of Gibbs, the equilibrium equations for a solid and various fluids in contact, including capillarity and elasticity, are written for the general case. They are then applied to the example of a thin plate in contact with a drop of fluid. The classical Young's equation is modified.

1. Introduction

The equilibrium of a solid in contact with a drop of fluid (surrounded by another fluid), including capillarity and elasticity, has been mainly studied in the semi-infinite solid [1–4] (with a divergence problem at the solid–fluid–fluid contact line) and the thin-plate case [5–7]. Nevertheless, in all these studies, (i) it was assumed that either the solid–fluid–fluid line was fixed on the solid, or the volume of the drop of fluid was constant; (ii) the solid–fluid surfaces were treated exactly as if they were fluid–fluid surfaces. Assumption (i) is not justified (the true equilibrium variational condition must take into account a possible motion of the solid–fluid–fluid line and a variation of the volume—and the mass—of the drop of fluid), and assumption (ii) is incorrect, as known from the first thermodynamic approach of Gibbs [8]: it corresponds to a confusion between surface grand potential and surface stresses. An attempt to introduce the surface stresses was made in [9] (in the case of the thin plate), but with the erroneous starting assumption that the derivatives v'' and v''' of v (= elastic displacement perpendicular to the plate) were continuous at the solid–fluid–fluid line (the discontinuity jumps of v'' and v''' are precisely consequences of the equilibrium condition). There is then a real need to write the correct equilibrium equations for a general system involving capillarity and elasticity, together with the precise thermodynamics of a solid–fluid surface. These equations cannot be directly and rapidly obtained: we have followed a rigorous method similar to that of Gibbs [8], in which the various equilibrium equations are deduced from general thermodynamics. This method is presented in appendix A, and the equations in section 2. In addition to the above deficiencies, in the studies mentioned, the thin-plate case was treated without any stretching (of the middle plane) of the plate, then assuming that $u = 0$ (u = elastic displacement parallel to the plate). It was concluded that at the solid–fluid–fluid line, (i) the orientation of the plane tangent to the plate was continuous; (ii) v'' was continuous and v''' discontinuous and (iii) the classical Young's equation remained valid [7]. However, in contradiction with the above assumption, a stretching (of the middle plane) of the plate was clearly observed in a recent experiment [10].

Section 3 and appendix B are then devoted to the case of the elastic thin plate (with stretching, i.e. with both components u and v of the elastic displacement), by application of the general equilibrium conditions of section 2. This example illustrates perfectly: (i) the various discontinuities which occur at the solid–fluid–fluid line: discontinuities of the tangent plane, u', v'' and v'''; (ii) the influence of the surface stresses and (iii) how the classical capillary Young's equation is modified when elasticity is taken into account.

2. Equilibrium of a solid and various fluids in contact

Let us consider the general system formed by a solid s and various immiscible fluids f, f′, etc in contact, in which the solid can neither dissolve nor grow, but there may be mass exchanges between all the fluids and the solid–fluid and fluid–fluid surfaces. For simplicity's sake, we suppose that the solid consists of a substance c, the fluids and the solid–fluid and fluid–fluid surfaces are composed of the substances $1, 2, \ldots, n$, all these components $c, 1, 2, \ldots, n$ being independent (note that the solid–fluid dividing surfaces, as defined by Gibbs, are perfectly determined by the preceding condition that the surface density of the substance c vanish). In the derivation of appendix A, we also suppose that, for each component i, all the fluid regions and the fluid–fluid surfaces which contain i are connected to each other, and we exclude the formation of new fluids or new (solid–fluid or fluid–fluid) surfaces (in the variational equilibrium criterion). By carefully applying the method of Gibbs [8], we show, in appendix A, that the equilibrium of the system is equivalent to (i) the thermal and chemical equilibrium equations (A1, A2); (ii) the mechanical equilibrium equations (A6, A7) concerning only the system of the fluids (these equations (A1, A2, A6, A7) were written by Gibbs [8]) and (iii) the following new mechanical equilibrium condition (of variational form), which only concerns the solid, the solid–fluid surfaces and the solid–fluid–fluid lines

$$\delta_T F_s + \int g \delta z \, \mathrm{d}m + \sum_{\mathrm{sf}} \left[- \int_{\mathrm{sf}} p n \cdot \delta x \, \mathrm{d}a + \int_{\mathrm{sf}} g \delta z \, \mathrm{d}m + \int_{\mathrm{sf}} \left(\delta U_{a^0} - T \delta S_{a^0} - \sum_i \mu_i \delta m_{i,a^0} \right) \mathrm{d}a^0 \right] - \sum_{\mathrm{sff'}} \int_{\mathrm{sff'}} \gamma_{\mathrm{ff'}} \tau_{\mathrm{ff'}} \cdot \delta X \, \mathrm{d}l + \sum_{\mathrm{sff'}} \int_{\mathrm{sff'}} (\gamma^0_{\mathrm{sf}} - \gamma^0_{\mathrm{sf'}}) \delta X^0 \mathrm{d}l^0 \geqslant 0 \qquad (1)$$

in which δ is an arbitrary infinitesimal variation such that, on the closed surface which bounds the system, the points of the solid and the points of the solid–fluid–fluid lines remain fixed; see figures 1 and 2 for the geometrical notations; T is the temperature; $\delta_T F_s$ is the variation of the elastic Helmholtz free energy of the solid (at constant T); g is the gravity field; z the height; m the mass; p the fluid pressure; $\mathrm{d}a$, $\mathrm{d}a^0$ are areas of an sf surface element, in the present deformed state and in the 'undeformed' reference state of the solid, respectively; μ_i is the chemical potential per unit mass of component i; U_{a^0}, S_{a^0} and m_{i,a^0}, respectively, are the internal energy, the entropy and the mass of the component i per unit area in the reference state of the solid (these are surface excesses on sf, with the convention of Gibbs: no excess of mass for the component of the solid); $\gamma_{\mathrm{ff'}}$ is the ff′ surface tension; $\mathrm{d}l$, $\mathrm{d}l^0$ are lengths of an sff′

line element, in the present state and in the reference state of the solid, respectively; for an sf surface, $\gamma^0 = U_{a^0} - TS_{a^0} - \sum_i \mu_i m_{i,a^0}$ is the excess of grand potential on sf, per unit area in the reference state of the solid. It may be specified that the last summation $\sum_{\mathrm{sff'}}$ in (1) must also include similar terms for all other lines (of the surface of the solid) on which the thermodynamic (solid–fluid) surface quantities are discontinuous (if there are such lines which are not sff′ lines). Note that in expression (1), all the variations δ follow each material point of the solid, except $\delta \boldsymbol{X}$ and δX^0.

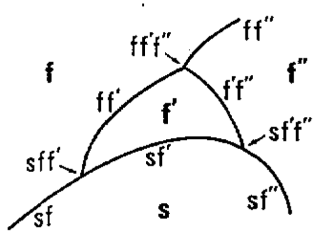

Figure 1. The system is formed by a solid s and various fluids f, f′, etc. The various surfaces sf, ff′, etc and lines sff′, ff′f″, etc are indicated.

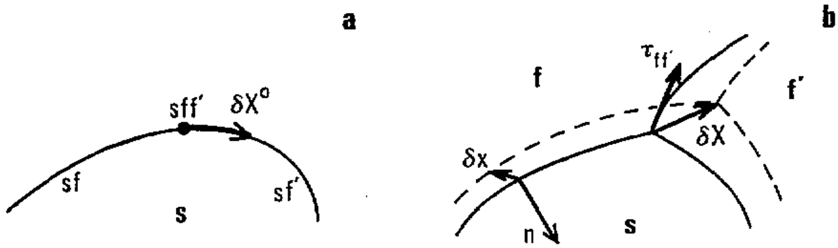

Figure 2. Geometrical notations. In the present state of the system (*b*), $\boldsymbol{n}$ is the unit vector, normal to sf, oriented from f to s; $\delta \boldsymbol{x}$ is the displacement of a material point of the solid; $\tau_{\mathrm{ff'}}$ is the unit vector, perpendicular to the sff′ line, tangential to the ff′ surface, and oriented from the sff′ line to the interior of ff′ and $\delta \boldsymbol{X}$ is the displacement of the sff′ line, perpendicular to the line. δX^0 is the displacement of the sff′ line, measured in the 'undeformed' reference state of the solid (*a*), perpendicular to that line in the reference state, positively considered from sf to sf′.

The term $\delta U_{a^0} - T\delta S_{a^0} - \sum_i \mu_i \delta m_{i,a^0}$ may be interpreted as the work of the 'surface stresses'. Indeed, if we consider that, for a solid–fluid surface, the variables are T, μ_i and the state of strain of the surface (see [11–14]), and represent the latter by the Green strain tensor $e_{\alpha\beta}$ $(\alpha, \beta = 1,2)$ of the surface (the coordinate system of the surface being fixed in the 'undeformed' reference state of the solid), then the application of (1), in the case of a unique fluid f, gives

$$\delta U_{a^0} - T\delta S_{a^0} - \sum_i \mu_i \delta m_{i,a^0} = 0 \qquad \text{at fixed } e_{\alpha\beta}(\alpha, \beta = 1,2)$$

(since the material points of the surface are fixed, and the sum of the two terms corresponding to the solid vanish, owing to the mechanical equilibrium in the solid).

We may then write, in the general case

$$\delta U_{a^0} - T\delta S_{a^0} - \sum_i \mu_i \delta m_{i,a^0} = \sum_{\alpha,\beta} \pi_{\alpha\beta} \delta e_{\alpha\beta} \tag{2}$$

(at each material point of sf; this surface stress tensor $\pi_{\alpha\beta}$ is taken to be symmetric because of the symmetry of $e_{\alpha\beta}$). This equation generalizes equation (24) of [14], in the case of a solid–fluid surface. As an immediate consequence, we have

$$\delta\gamma^0 = -S_{a^0}\delta T - \sum_i m_{i,a^0}\delta\mu_i + \sum_{\alpha,\beta} \pi_{\alpha\beta}\delta e_{\alpha\beta}. \tag{2'}$$

These expressions (2) (for each sf surface, and, in the case of a crystal, for each crystallographic orientation of the surface) may then be introduced in the equilibrium condition (1).

3. Example of the thin plate

3.1. *Equilibrium equations*

As a simple application of the above equilibrium condition (1) (with the expressions (2)), we now consider the example in which the solid s is a circular thin plate (with conditions of circular symmetry on its boundary circle), in contact with a drop of fluid f, centred on the plate, s and f being surrounded by another fluid f′. In order to simplify the equations, we suppose here that there is no gravity and no surface stresses (the more complete equations, including surface stresses, are given in appendix B). In this case, all the quantities T, μ_i, p_{f}, $p_{\mathrm{f}'}$, $\gamma_{\mathrm{ff}'}$, γ^0_{sf} and $\gamma^0_{\mathrm{sf}'}$ are constant in space at equilibrium (μ_i is constant because $g = 0$, according to (A2) of appendix A; p_{f}, $p_{\mathrm{f}'}$ and $\gamma_{\mathrm{ff}'}$ are constant because T and μ_i are constant; γ^0_{sf} and $\gamma^0_{\mathrm{sf}'}$ are constant, according to (2′), because T and μ_i are constant and $\pi_{\alpha\beta} = 0$). The geometry of the system is shown in figure 3. Let $u(r)$ and $v(r)$ respectively be the displacements, along Or and Oz, of a material point of the plate situated at the distance r from O (in the undeformed state). At equilibrium, the drop is spherical, with radius

$$R = 2\gamma_{\mathrm{ff}'}/(p_{\mathrm{f}} - p_{\mathrm{f}'}) \tag{3}$$

(according to (A6) of appendix A). We denote by τ_r and τ_z the components along Or and Oz respectively of the vector $\tau_{\mathrm{ff}'}$ (defined in section 2); we have the geometrical conditions

$$\tau_r^2 + \tau_z^2 = 1 \qquad \tau_z = -(r_1 + u(r_1))/R. \tag{4}$$

With the following expression of the free energy of the plate (at constant temperature)

$$F_{\mathrm{s}} = \int_0^{r_{\mathrm{P}}} \left\{ \frac{Eh^3}{24(1-\nu^2)} \left(\frac{v'^2}{r^2} + v''^2 + 2\nu \frac{v'}{r} v'' \right) 2\pi r + \frac{Eh}{2(1-\nu^2)} \right.$$
$$\left. \times \left[\frac{u^2}{r^2} + \left(u' + \frac{v'^2}{2} \right)^2 + 2\nu \frac{u}{r} \left(u' + \frac{v'^2}{2} \right) \right] 2\pi r \right\} \mathrm{d}r$$

deduced from [15] (in this expression, the first part represents the energy of flexion, and the second part the energy of stretching; r_p is the radius of the undeformed plate; E Young's modulus, ν Poisson's coefficient and h the thickness of the plate), the equilibrium condition (1) then leads to a variational problem with mobile discontinuities (for some derivatives of u and v at r_l). The variational calculus shows that the condition (1) is equivalent to the following equations

$$\frac{Eh}{2(1-\nu^2)}2\pi(2u/r - 2u' - 2ru'' - v'^2 - 2rv'v'' + \nu v'^2) = \begin{cases} -(p_f - p_{f'})v'2\pi(r+u) & \text{for all } r \in]0, r_l[\\ 0 & \text{for all } r \in]r_l, r_p[\end{cases} \tag{5}$$

$$\left.\begin{aligned} &\frac{Eh^3}{24(1-\nu^2)}2\pi 2(v'/r^2 - v''/r + 2v''' + rv^{(4)}) \\ &\frac{-Eh}{2(1-\nu^2)}2\pi[v'^3 + 3rv'^2v'' + 2u'v' + 2ru''v' + 2ru'v'' + 2\nu(u'v' + uv'')] \end{aligned}\right\} = \begin{cases} (p_f - p_{f'})(1+u')2\pi(r+u) & \text{for all } r \in]0, r_l[\\ 0 & \text{for all } r \in]r_l, r_p[\end{cases} \tag{6}$$

$$\frac{Eh}{2(1-\nu^2)}2[u'] + \gamma_{ff'}\{[r_l + u(r_l)]/r_l\}\tau_r = 0 \tag{7}$$

$$\frac{Eh^3}{24(1-\nu^2)}2[v'''] + \gamma_{ff'}\{[r_l + u(r_l)]/r_l\}(\tau_r v'(r_l) - \tau_z) = 0 \tag{8}$$

$v''$is continuous at r_l (9)

$$\left.\begin{aligned} &-\epsilon^{\otimes}\frac{(1-\nu^2)}{2Eh}\gamma_{ff'}^2\left(\frac{r_l + u(r_l)}{r_l}\right)^2\tau_r^2 \\ &-\gamma_{ff'}\frac{r_l + u(r_l)}{r_l}\{\tau_r(1 + u'(r_l^{\otimes})) + \tau_z v'(r_l)\} + \gamma_{sf}^0 - \gamma_{sf'}^0 \end{aligned}\right\} = 0 \tag{10}$$

in which $[u'] = u'(r_l^+) - u'(r_l^-) = \lim_{r\to r_l, r>r_l} u'(r) - \lim_{r\to r_l, r<r_l} u'(r)$; similarly, $[v'''] = v'''(r_l^+) - v'''(r_l^-)$; in (10), $\otimes = +$ or $-$, and $\epsilon^{\otimes} = +1$ if $\otimes = +$, $\epsilon^{\otimes} = -1$ if $\otimes = -$ (the two corresponding equations (10) are equivalent, according to (7)). These equations (3)–(10) (or (3)–(5) and (B1)–(B5) of appendix B) and the boundary conditions completely determine R, u, v, r_l, τ_r and τ_z.

3.2. *Physical meaning*

The equations (5), (6) or (5), (B1) (above and in appendix B) represent the elastic equilibrium of the plate (for $r \neq r_l$) subjected to the overpressure $p_f - p_{f'}$ in the interior of the circular solid–fluid–fluid line (for small deformations, $(r + u(r))/r \simeq 1$). There is of course a pressure effect due to the sum of the surface stresses when the plate is curved (in the right-hand side of (B1)).

There are four equilibrium equations (7)–(10) or (B2)–(B5) at the solid–fluid–fluid line. Equation (8) expresses the elastic reaction of the plate to the 'vertical' component of the tension of the fluid–fluid surface, acting on a fixed line of the solid

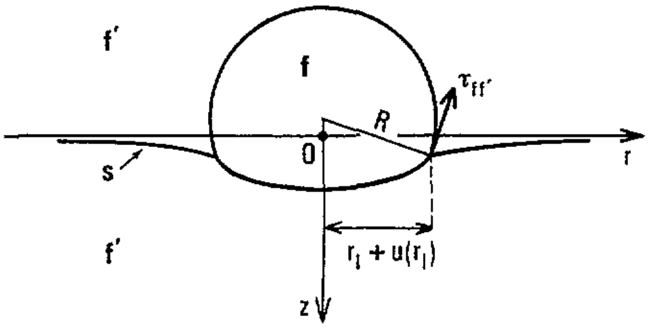

Figure 3. The solid thin plate s is in contact with a drop of fluid f and surrounded by another fluid f′. O is the centre of the undeformed plate; Or is a centrifugal radial axis (in the plane of the undeformed plate); Oz is the axis perpendicular to the undeformed plate, oriented from f to s and r_l is the radius of the circular sff′ line, in the undeformed state of the plate (it becomes $r_l + u(r_l)$ in the present state).

(the plane of the undeformed plate being horizontal): this reaction is a discontinuity jump of v''' at r_l (v is the vertical displacement of a point of the plate). This equation may be compared with equation (24) of [7]. In addition, there is a contribution of the surface stresses (in equation (B3)) by means of the jump of their moment $(\pi_{sf} - \pi_{sf'})h/2$ (see below, concerning (B4)).

Similarly, (7) or (B2) expresses the elastic reaction of the plate to (i) the horizontal component of the tension of the fluid–fluid surface, acting on a fixed line of the solid and (ii) the jump of the surface stresses $\pi_{sf'} - \pi_{sf} = (\pi_{sf'} + \pi_{sf'})$ (at r_l^+) $-(\pi_{sf} + \pi_{sf'})$ (at r_l^-). This elastic reaction is a discontinuity jump of u' at r_l (u is the horizontal displacement of a point of the plate). As a geometrical consequence, this discontinuity of u' at r_l implies a discontinuity of the orientation of the plane tangent to the plate.

Equation (9) or (B4) represents the equilibrium of the moments: the jump of the moment (at the middle plane of the plate) of the surface stresses $(\pi_{sf} - \pi_{sf'})h/2 = (\pi_{sf'} - \pi_{sf'})h/2$ (at r_l^+) $-(\pi_{sf'} - \pi_{sf})h/2$ (at r_l^-) is elastically equilibrated by a discontinuity jump of v'' at r_l. Note that the equations (7) or (B2), the discontinuity of the tangent plane and equations (B3) and (B4) are completely new with respect to the preceding work [7].

The last equation (10) or (B5) represents the equilibrium relative to the motion of the solid–fluid–fluid line with respect to the solid. This original equation generalizes the classical 'Young's equation' (which concerns the undeformable solid). Indeed, note that Young's equation, $\gamma_{ff'} \cos\varphi + \gamma_{sf} - \gamma_{sf'} = 0$ would correspond to equation (10) in which the first term (with coefficient $\epsilon^{\otimes}$) would be omitted and u' would be supposed continuous at r_l: with the help of $\{(r_l + u(r_l))/r_l\}\{\tau_r(1 + u'(r_l)) + \tau_z v'(r_l)\} = -(\mathrm{d}a/\mathrm{d}a^0)\cos\varphi$, where $\mathrm{d}a/\mathrm{d}a^0$ is taken at r_l and φ is the contact angle measured in the fluid f, and we use $\gamma = \gamma^0 \mathrm{d}a^0/\mathrm{d}a$ for sf and sf′. Then, in the case of the elastic thin plate, Young's equation is not valid and is explicitly replaced by equation (10) or (B5). To our knowledge, it is the first time that such a rigorous and explicit equation (which modifies Young's equation) has been written. Let us recall that the preceding work [7] concluded that Young's equation was valid. Note that this new equation (10) or (B5) involves all the parameters: fluid–fluid surface tension γ, solid–fluid surface grand potentials γ^0 (or $\bar{\gamma}$), surface stresses, geometry, strain and elasticity.

3.3. Magnitude of the effects

In addition to the interest of the above equations (and those of appendix B) as original theoretical equations, and as a very illustrative example of the equilibrium equations involving capillarity and elasticity, it is of course important to estimate the magnitude of their effects. As a first example, let us take typical elastic constants, $E \simeq 10^{11}$ Pa, $\nu \simeq 0.3$, and geometrical values suggested by experiment [10], $h \simeq 3 \times 10^{-8}$ m, $r_l \simeq 10^{-6}$ m, $v'(\text{minimum}) \simeq -6 \times 10^{-2}$, $v''(0) \simeq -6 \times 10^4$ m^{-1}. The respective elastic energies of flexion and stretching, estimated by means of the following terms (see, above, the expression of the elastic energy)

$$\text{flexion: } (Eh^3/24(1-\nu^2))v''^2 \simeq 0.5 \times 10^{-3} \text{ J m}^{-2}$$

$$\text{stretching: } (Eh/2(1-\nu^2))(v'^2/2)^2 \simeq 5 \times 10^{-3} \text{ J m}^{-2}$$

clearly show the importance of the stretching, in agreement with the direct observations of the stretching of the plate [10], and in opposition to the previous works [5–7] which did not take into account the energy of stretching.

Equation (8) generally produces an important negative jump of v'''. Thus, for a vertical fluid–fluid tension ($\tau_z = -1$), with a typical value $\gamma_{ff'} \simeq 0.5$ J m^{-2} (and other parameters as above), it gives $[v'''] \simeq -2 \times 10^{12}$ m^{-2}. As shown by the explicit profiles of [5], this discontinuity generally represents a jump from a high positive value $v'''(r_l^-) > 0$ to a negative one $v'''(r_l^+) < 0$, with the following visible effect: the (radial) curvature v'' rapidly increases ($v''' > 0$) from a negative value at $r = 0$ to a positive one at $r = r_l$ (v'' being supposed continuous at r_l), and then slowly decreases ($v''' < 0$) from this positive value to a lower one at $r = r_p$. The effect of the surface stresses (the last term in equation (B3)) is generally small since h/r_l is small. Nevertheless, this effect may be of the same magnitude as that of the fluid–fluid tension (the second term of (B3)) if $\tau_z \simeq 0$ (i.e. for contact angles $\simeq 0°$ or $180°$): in our example, $\gamma_{ff'}|\tau_r v'| \simeq 3 \times 10^{-2}$ J m^{-2} and $|\pi_{sf} - \pi_{sf'}|h/2r_l \simeq 1.5 \times 10^{-2}$ J m^{-2} if $|\pi_{sf} - \pi_{sf'}| \simeq 1$ J m^{-2}.

The effect of the surface stresses is very important in equation (B4). With $\pi_{sf} > \pi_{sf'}$ and a difference of surface stresses $\pi_{sf} - \pi_{sf'} \simeq 1$ J m^{-2}, the above example leads to the important positive jump $[v''] \simeq 6 \times 10^4$ m^{-1} (of the same magnitude as $|v''(0)|$). The consequence will be a high positive value of the curvature $v''(r_l^+)$, i.e. a rapid increase of the slope ($\simeq v'$) of the plate (from a negative value to nearly zero). This is probably the explanation of the rapid variation of the slope of the plate at $r \simeq r_l$, observed in [10].

With the preceding values, and according to equation (B2), the jump of u' may reach the value (with $\tau_r \simeq -1$) $[u'] \simeq 0.5 \times 10^{-3}$. This discontinuity jump is significant, compared with $u' \simeq v'^2/2 \simeq 1.8 \times 10^{-3}$ (if we consider, as a rough estimate, that $u/r \simeq u' \simeq v'^2/2$; these terms represent the global stretching of the plate, since $e_{11} + e_{22} \simeq u/r + u' + v'^2/2$ for the middle plane of the plate; see appendix B). The discontinuity of u' produces a discontinuity of the slope $v'/(1 + u')$ of the plate. The corresponding jump $[v'/(1 + u')] \simeq -v'[u']$ is generally small, but may be appreciable with more deformable solids. With $E \simeq 10^8$ Pa (the Young's modulus range 10^9–10^5 Pa is represented by polymers, elastomers and gels) and other parameters unchanged, the jump of the slope reaches the considerable value of $-0.5v'$.

The deviation from the classical Young's equation is mainly represented by the first term (with coefficient ϵ^{∞}) in (10) or (B5). With the previous numerical values and $E \simeq 10^9$ Pa, this term (in equation (B5)) is equal to 0.08 J m^{-2}, which is appreciable with respect to the second term $\simeq \gamma_{ff'} \simeq 0.5$ J m^{-2} of the equation. With $E \simeq 10^8$ Pa, it becomes of fundamental importance, its value (of 0.8 J m^{-2}) being greater than the second term $\gamma_{ff'}$.

4. Conclusions

By following the thermodynamic approach of Gibbs [8], we have obtained in section 2 and appendix A (i) the general thermodynamic equation (2) or (2′) for a solid–fluid surface, involving the surface grand potential and the surface stresses and (ii) the complete set of equilibrium equations for a solid and various immiscible fluids in contact, including elasticity of the solid and capillarity for all the solid–fluid and fluid–fluid surfaces. These equations are (a) the thermal and chemical equilibrium equations (A1, A2); (b) the mechanical equilibrium equations (A6, A7) concerning only the fluids (all these equations were written by Gibbs [8]) and (c) the new mechanical equilibrium condition (1) (with expressions (2)), of variational form, which only concerns the solid, the solid–fluid surfaces and the solid–fluid–fluid lines. This condition expresses the action on the solid of (i) the fluid pressure and the (solid–fluid) surface stresses, at each solid–fluid surface and (ii) the fluid–fluid surface tension and the difference of (solid–fluid) surface grand potentials, at each solid–fluid–fluid line.

As a very illustrative example of this general theory, the case of the elastic thin plate in contact with a drop of fluid (surrounded by another fluid) is treated in section 3 and appendix B. In this case, the equilibrium is equivalent to equations (3)–(5), (B1)–(B5) (or (6)–(10) in the absence of surface stresses) and the boundary conditions. The four original equations (B2)–(B5) at the solid–fluid–fluid line have a clear meaning: (B2)–(B4) express the equilibrium of the forces, corresponding to a solid–fluid–fluid line fixed on the solid; (B2) represents the 'horizontal' component of the equilibrium ('horizontal' refers to the plane of the undeformed plate), (B3) the vertical component and (B4) the equilibrium of the moments; whereas (B5) expresses the equilibrium relative to the motion of the solid–fluid–fluid line with respect to the solid.

Equations (B2)–(B4) perfectly illustrate the various discontinuities which occur at the solid–fluid–fluid line, caused by the action on the elastic solid of the fluid–fluid surface tension and the (solid–fluid) surface stresses: these are the discontinuity jumps of u', v'' and v''' (u and v respectively denote the horizontal and vertical components of the elastic displacement). The discontinuity of u' also implies a discontinuity of the orientation of the plane tangent to the plate. Note that, in the preceding work [7], (i) the surface stresses were ignored (the solid–fluid surfaces were treated as if they were fluid–fluid surfaces) and (ii) equation (B2) and the discontinuity of the tangent plane were unknown, since the horizontal displacement u (i.e. the stretching of the plate) was not taken into account (in opposition to the direct experimental observations [10]).

The original equation (B5) shows how the classical capillary Young's equation is modified when the solid is elastically deformable. To our knowledge, it is the first time that such a generalization of Young's equation has been proved and explicitly written (the preceding work [7] concluded that Young's equation was valid). In addition to the dependence of the (solid–fluid) surface grand potentials on the surface strain, and to the discontinuity of the plane tangent to the solid, this equation contains a new term directly related to the elasticity of the solid (and also involving the surface stresses and the fluid–fluid surface tension).

It is also shown that the magnitudes of these effects (i.e. the various discontinuities and the deviation from Young's equation) are measurable and may even be of prime importance, if the solid is sufficiently deformable.

Appendix A. The general equilibrium equations

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

$$\delta(U+V) \geqslant 0$$

(U is the internal energy and V the potential energy of gravity), for all variations of the system such that (i) the entropy S and the masses m_i of the various components ($i = 1, \ldots, n$) are constant and (ii) the bounding surface Σ, the points of the solid which belong to this surface, and the lines in which the fluid–fluid surfaces meet this surface, are all fixed. The above criterion may be written

$$\begin{aligned}
\int_{\mathrm{s}} \Big(T\delta\,\mathrm{d}S + \sum_{j,k} \pi_{jk}\delta e_{jk}\,\mathrm{d}v^0 \Big) + \sum_{\mathrm{f}} \int_{\mathrm{f}} \Big(T\delta\,\mathrm{d}S - p\delta\,\mathrm{d}v + \sum_i \mu_i \delta\,\mathrm{d}m_i \Big) \\
+ \sum_{\mathrm{ff}'} \int_{\mathrm{ff}'} \Big(T\delta\,\mathrm{d}S + \gamma\delta\,\mathrm{d}a + \sum_i \mu_i \delta\,\mathrm{d}m_i \Big) \\
+ \sum_{\mathrm{sf}} \delta \int_{\mathrm{sf}} \mathrm{d}U + \int_{\mathrm{s}} g\delta z\,\mathrm{d}m + \sum_{\mathrm{f}} \int_{\mathrm{f}} (g\delta z\,\mathrm{d}m + gz\delta\,\mathrm{d}m) \\
+ \sum_{\mathrm{ff}'} \int_{\mathrm{ff}'} (g\delta z\,\mathrm{d}m + gz\delta\,\mathrm{d}m) + \sum_{\mathrm{sf}} \delta \int_{\mathrm{sf}} gz\,\mathrm{d}m \geqslant 0
\end{aligned}$$

with the notations of the paper and v the volume; a the area; (π_{jk}) the Kirchhoff stress tensor; (e_{jk}) the Green strain tensor and $\mathrm{d}v^0$ an element of volume of the solid in its 'undeformed' reference state; note that, in the solid, the variation δ is attached to each material element, whereas this is not the case for the fluids and the ff′ surfaces. The equilibrium criterion, together with the conditions of constant S and m_i

$$\int_{\mathrm{s}} \delta\,\mathrm{d}S + \sum_{\mathrm{f}} \int_{\mathrm{f}} \delta\,\mathrm{d}S + \sum_{\mathrm{ff}'} \int_{\mathrm{ff}'} \delta\,\mathrm{d}S + \sum_{\mathrm{sf}} \delta \int_{\mathrm{sf}} \mathrm{d}S = 0$$

$$\sum_{\mathrm{f}} \int_{\mathrm{f}} \delta\,\mathrm{d}m_i + \sum_{\mathrm{ff}'} \int_{\mathrm{ff}'} \delta\,\mathrm{d}m_i + \sum_{\mathrm{sf}} \delta \int_{\mathrm{sf}} \mathrm{d}m_i = 0 \qquad (i = 1, \ldots, n)$$

lead to the thermal and chemical equilibrium equations

$$T = \text{constant in space} \tag{A1}$$

$$\mu_i + gz = M_i = \text{constant in space} \qquad (i = 1, \ldots, n). \tag{A2}$$

With the help of the preceding equations, the equilibrium condition reduces to the mechanical form

$$\delta_T F_s + \int_s g\delta z\,\mathrm{d}m + \sum_f \int_f (-p\delta\,\mathrm{d}v + g\delta z\,\mathrm{d}m) + \sum_{ff'} \int_{ff'} (\gamma\delta\,\mathrm{d}a + g\delta z\,\mathrm{d}m)$$
$$+ \sum_{sf} \left(\delta \int_{sf} \mathrm{d}U - T\delta \int_{sf} \mathrm{d}S - \sum_i M_i \delta \int_{sf} \mathrm{d}m_i + \delta \int_{sf} gz\,\mathrm{d}m \right) \geqslant 0 \tag{A3}$$

where $\delta_T F_s = \int_s \sum_{j,k} \pi_{jk}\delta e_{jk}\,\mathrm{d}v^0$.

Let us first transform the preceding terms Σ_f and $\Sigma_{ff'}$. Since the variation δ only concerns geometrical elements ($\mathrm{d}v$, $\mathrm{d}a$ and z), these terms will remain unchanged if arbitrary variations δp and $\delta\gamma$ are introduced. Following Gibbs, we take

$$\delta p = (\partial p/\partial x)(x, y, z)\delta x + (\partial p/\partial y)(x, y, z)\delta y + (\partial p/\partial z)(x, y, z)\delta z$$

$$\delta\gamma = (\partial\gamma/\partial x_1)(x_1, x_2)\delta x_1 + (\partial\gamma/\partial x_2)(x_1, x_2)\delta x_2$$

where $p(x, y, z)$ is the pressure in f as a function of spatial coordinates and $\gamma(x_1, x_2)$ the surface tension of ff' as a function of coordinates of the ff' surface (these functions refer to the present 'initial' state of the system, i.e. before the variation δ), and $(\delta x_1, \delta x_2)$ represents the component δx_t, tangent to ff', of the displacement of a point of ff'. Then

$$\int_f (-p\delta\,\mathrm{d}v + g\delta z\,\mathrm{d}m) = -\delta \int_f p\,\mathrm{d}v + \int_f (\delta p\,\mathrm{d}v + g\delta z\,\mathrm{d}m)$$
$$= -\int_{sf} p\delta N\,\mathrm{d}a - \sum_{f'} \int_{ff'} p\delta N\,\mathrm{d}a + \int_f (\delta p + g m_v \delta z)\,\mathrm{d}v$$

where $m_v = \mathrm{d}m/\mathrm{d}v$ and δN is the normal displacement of the sf (or ff') surface, positively measured from f to s (or from f to f'). Hence

$$\sum_f \int_f (-p\delta\,\mathrm{d}v + g\delta z\,\mathrm{d}m) = -\sum_{sf} \int_{sf} p\delta N\,\mathrm{d}a - \sum_{ff'} \int_{ff'} (p - p')\delta N\,\mathrm{d}a$$
$$+ \sum_f \int_f (\delta p + g m_v \delta z)\,\mathrm{d}v$$

in the term $\Sigma_{ff'}$, p refers to f, p' to f' and δN is positively measured from f to f'.

Similarly

$$\int_{ff'} (\gamma\delta\,\mathrm{d}a + g\delta z\,\mathrm{d}m) = \delta \int_{ff'} \gamma\,\mathrm{d}a + \int_{ff'} (-\delta\gamma\,\mathrm{d}a + g\delta z\,\mathrm{d}m)$$
$$= \begin{cases} \int_{ff'} \gamma \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \delta N\,\mathrm{d}a + \int_{sff'} -\gamma\boldsymbol{\tau} \cdot \delta\boldsymbol{X}\,\mathrm{d}l + \sum_{f''} \int_{ff'f''} -\gamma\boldsymbol{\tau} \cdot \delta\boldsymbol{X}\,\mathrm{d}l \\ + \int_{ff'} (-\delta\gamma\,\mathrm{d}a + g\delta z\,\mathrm{d}m) \end{cases}$$

in which R_1, R_2 are the principal curvature radii of the ff′ surface, positively considered when the centres are on the f side; for each ff′, τ is the unit vector, perpendicular to the sff′ (or ff′f″) line, tangent to the ff′ surface, and oriented from the line to the interior of ff′; in the above terms, $\gamma\tau$ refers to ff′; δX is the displacement of the sff′ (or ff′f″) line, perpendicular to the line and $\mathrm{d}l$ is the length element along the line.

Since

$$\delta z = \delta N \cos\theta + \delta z_t$$

(where θ is the angle between the Oz axis and the normal to the surface, oriented from f to f′, and δz_t is the component along Oz of δx_t), we may write:

$$\sum_{\mathrm{ff}'} \int_{\mathrm{ff}'} (\gamma\delta\,\mathrm{d}a + g\delta z\,\mathrm{d}m)$$

$$= \begin{cases} \displaystyle\sum_{\mathrm{ff}'} \int_{\mathrm{ff}'} \left\{ \left[\gamma\left(\frac{1}{R_1}+\frac{1}{R_2}\right) + g m_a \cos\theta \right] \delta N + (-\delta\gamma + g m_a \delta z_t) \right\} \mathrm{d}a \\ \displaystyle -\sum_{\mathrm{sff}'} \int_{\mathrm{sff}'} \gamma\boldsymbol{\tau}\cdot\delta \boldsymbol{X}\,\mathrm{d}l - \sum_{\mathrm{ff}'\mathrm{f}''} \int_{\mathrm{ff}'\mathrm{f}''} \left(\sum_{\mathrm{ff}'} \gamma\boldsymbol{\tau}\right)\cdot\delta\boldsymbol{X}\,\mathrm{d}l \end{cases}$$

in which $m_a = \mathrm{d}m/\mathrm{d}a$ and the summation $\sum_{\mathrm{ff}'} \gamma\tau$ concerns the various ff′ surfaces which meet in the ff′f″ line.

With the help of the preceding expressions, let us return to the condition (A3). By fixing the points of the solid, the sff′ lines and the thermodynamic state of the sf surfaces, this condition only refers to the fluids, the ff′ surfaces and the ff′f″ lines, and it is then equivalent to the following equations:

in each f

$$\mathrm{d}p/\mathrm{d}z = -g m_v \tag{A4}$$

in each ff′

$$\begin{cases} \mathrm{d}\gamma/\mathrm{d}z = g m_a & \text{(A5)} \\ p - p' = \gamma(1/R_1 + 1/R_2) + g m_a \cos\theta & \text{(A6)} \end{cases}$$

in each ff′f″

$$\sum_{\mathrm{ff}'} \gamma\boldsymbol{\tau} = \mathbf{0} \tag{A7}$$

(in (A4) and (A5), p, γ, m_v and m_a depend only on z). These equilibrium equations (A1), (A2), (A4)–(A7) were written by Gibbs [8]. Note that (A4) and (A5) are consequences of (A1) and (A2), since p and γ are functions of T and μ_i which satisfy

$$\mathrm{d}p = S_v\,\mathrm{d}T + \sum_i m_{i,v}\,\mathrm{d}\mu_i$$

$$\mathrm{d}\gamma = -S_a\,\mathrm{d}T - \sum_i m_{i,a}\,\mathrm{d}\mu_i$$

(as above for m, we use the subscripts v and a respectively to denote the volume density and the surface density).

With the help of (A4)–(A7), the above expressions may finally be written

$$\sum_{\mathrm{f}} \int_{\mathrm{f}} (-p\delta\,\mathrm{d}v + g\delta z\,\mathrm{d}m) + \sum_{\mathrm{ff'}} \int_{\mathrm{ff'}} (\gamma\delta\,\mathrm{d}a + g\delta z\,\mathrm{d}m)$$
$$= -\sum_{\mathrm{sf}} \int_{\mathrm{sf}} p\delta N\,\mathrm{d}a - \sum_{\mathrm{sff'}} \int_{\mathrm{sff'}} \gamma\boldsymbol{\tau}\cdot\delta\boldsymbol{X}\,\mathrm{d}l. \tag{A8}$$

The terms Σ_{sf} in (A3) are transformed in the following way

$$\delta\int_{\mathrm{sf}} \mathrm{d}U = \delta\int_{\mathrm{sf}} U_{a^0}\,\mathrm{d}a^0 = \int_{\mathrm{sf}} \delta U_{a^0}\,\mathrm{d}a^0 + \sum_{\mathrm{f'}} \int_{\mathrm{sff'}} U_{a^0,\mathrm{sf}}\,\mathrm{d}X^0\,\mathrm{d}l^0$$

the superscript 0 indicates that areas and lengths are taken in the 'undeformed' reference state of the solid; $U_{a^0} = \mathrm{d}U/\mathrm{d}a^0$; δU_{a^0} is attached to each material point of the solid; δX^0 is the displacement of the sff' line, measured in the reference state of the solid, perpendicular to that line in the reference state, positively considered from sf to sf'. Then

$$\sum_{\mathrm{sf}} \delta\int_{\mathrm{sf}} \mathrm{d}U = \sum_{\mathrm{sf}} \int_{\mathrm{sf}} \delta U_{a^0}\,\mathrm{d}a^0 + \sum_{\mathrm{sff'}} \int_{\mathrm{sff'}} (U_{a^0,\mathrm{sf}} - U_{a^0,\mathrm{sf'}})\delta X^0\,\mathrm{d}l^0.$$

More precisely, note that the last summation $\Sigma_{\mathrm{sff'}}$ must be performed for all the lines (of the surface of the solid) on which U_{a^0} is discontinuous (if there are such lines which are not sff' lines). With similar expressions and the help of (A1), (A2), we obtain

$$\sum_{\mathrm{sf}} \left(\delta\int_{\mathrm{sf}} \mathrm{d}U - T\delta\int_{\mathrm{sf}} \mathrm{d}S - \sum_i M_i\delta\int_{\mathrm{sf}} \mathrm{d}m_i + \delta\int_{\mathrm{sf}} gz\,\mathrm{d}m\right)$$
$$= \sum_{\mathrm{sf}} \left(\int_{\mathrm{sf}} (\delta U_{a^0} - T\delta S_{a^0} - \sum_i \mu_i\delta m_{i,a^0})\,\mathrm{d}a^0 + \int_{\mathrm{sf}} g\delta z\,\mathrm{d}m\right)$$
$$+ \sum_{\mathrm{sff'}} \int_{\mathrm{sff'}} (\gamma^0_{\mathrm{sf}} - \gamma^0_{\mathrm{sf'}})\delta X^0\,\mathrm{d}l^0 \tag{A9}$$

with the notations of the paper.

The introduction of expressions (A8) and (A9) into (A3) leads to the equilibrium condition (1) of the paper. The equilibrium of the system is then equivalent to equations (A1), (A2), (A6), (A7) and condition (1).

Appendix B. Equations for the thin plate with surface stresses

For simplicity's sake, we also suppose that there is no gravity. Then, T, μ_i, p_{f}, $p_{\mathrm{f'}}$ and $\gamma_{\mathrm{ff'}}$ are constant in space at equilibrium. Equations (3) and (4) of the paper remain valid. However, according to (2′), the surface grand potentials γ^0_{sf} and $\gamma^0_{\mathrm{sf'}}$ now depend on the surface strain $e_{\alpha\beta}$. The more simple case is that in which the surface stresses only depend on T and μ_i (and not on $e_{\alpha\beta}$), and are isotropic, i.e. $\pi_{sf,\alpha\beta} = \pi_{sf}\delta_{\alpha\beta}$ $(\alpha, \beta = 1, 2)$ where π_{sf} depends only on T and μ_i. As a consequence of (2′), we may then write

$$\gamma_{sf}^0 = \pi_{sf}(e_{11} + e_{22}) + \bar{\gamma}_{sf}$$

(and the same for sf′), in which π_{sf} and $\bar{\gamma}_{sf}$ depend only on T and μ_i (and are then constant in space, at the equilibrium). For small deformations, we use the following expression

$$e_{11} + e_{22} = u/r + u' + v'^2/2 + \epsilon(h/2)(v'/r + v'')$$

in which $\epsilon = +1$ for the surface of the plate corresponding to the side of the drop f and $\epsilon = -1$ for the other surface of the plate. The variational calculus here leads to the following equations: equation (5) unchanged

$$\left.\begin{array}{r}\dfrac{Eh^3}{24(1-\nu^2)}2\pi 2(v'/r^2 - v''/r + 2v''' + rv^{(4)}) \\ \dfrac{-Eh}{2(1-\nu^2)}2\pi(v'^3 + 3rv'^2v'' + 2u'v' + 2ru''v' + 2ru'v'' + 2\nu(u'v' + uv''))\end{array}\right\} = \begin{cases}(p_f - p_{f'})(1+u')2\pi(r+u) + 2\pi(\pi_{sf} + \pi_{sf'})(v' + rv'') & \text{for all } r \in]0, r-l[\\ 2\pi 2\pi_{sf'}(v' + rv'') & \text{for all } r \in]r_l, r_p[\end{cases} \quad \text{(B1)}$$

$$\frac{Eh}{2(1-\nu^2)}2[u'] + \gamma_{ff'}(r_l + u(r_l)/r_l)\tau_r + \pi_{sf'} - \pi_{sf} = 0 \quad \text{(B2)}$$

$$\frac{Eh^3}{24(1-\nu^2)}2[v'''] + \gamma_{ff'}\frac{r_l + u(r_l)}{r_l}(\tau_r v'(r_l) - \tau_z) + (\pi_{sf} - \pi_{sf'})h/2r_l = 0 \quad \text{(B3)}$$

$$\frac{Eh^3}{24(1-\nu^2)}2[v''] + (\pi_{sf'} - \pi_{sf})h/2 = 0 \quad \text{(B4)}$$

$$\left.\begin{array}{r}-\epsilon^{\otimes}\dfrac{1-\nu^2}{2Eh}\left\{3(\pi_{sf} - \pi_{sf'})^2 + \left(-\gamma_{ff'}\dfrac{r_l + u(r_l)}{r_l}\tau_r + \pi_{sf} - \pi_{sf'}\right)^2\right\} \\ -\gamma_{ff'}\dfrac{r_l + u(r_l)}{r_l}\{\tau_r(1 + u'(r_l^{\otimes})) + \tau_z v'(r_l)\} \\ +(\pi_{sf} - \pi_{sf'})\{u(r_l)/r_l + u'(r_l^{\otimes}) + (v'(r_l))^2/2 + (h/2)(v'(r_l)/r_l + v''(r_l^{\otimes}))\} \\ +\bar{\gamma}_{sf} - \bar{\gamma}_{sf'}\end{array}\right\} = 0 \quad \text{(B5)}$$

(notations as in the paper). Note that the terms of the two last lines of (B5) represent the value of $\gamma_{sf}^0 - \gamma_{sf'}^0$ at $r_l^{\otimes}$ and for the surface of the plate corresponding to the side of f. The two equations (B5) (for $\otimes = +$ and $\otimes = -$) are equivalent, according to (B2) and (B4).

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