On the Geometry of Surface Stress

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Abstract

We present a fully general derivation of the Laplace–Young formula and discuss the interplay between the intrinsic surface geometry and the extrinsic one ensuing from the immersion of the surface in the ordinary euclidean three-dimensional space. We prove that the (reversible) work done in a general surface deformation can be expressed in terms of the surface stress tensor and the variation of the intrinsic surface metric.

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1 Introduction

The notion of surface tension in fluids dates back to the seminal writings of Laplace [1] and Young [2] where the famous formula relating the difference of the external and internal hydrostatic pressure of a spherical surface to the product of the mean curvature times the surface tension was first derived (see below eq. (3.13)).

The concept of surface stress (or interface stress) is of special importance for applications in the interdisciplinary areas of material science, physical chemistry and continuum mechanics [3]-[11] and it has been the subject of extensive studies since when it was introduced by Gibbs [12] [1]. A far for complete list of papers and books describing recent investigations in the field can be found in refs. from [13] to [25].

Despite this long history there seem to be still debatable issues and open questions on the subject, like the validity of the Shuttleworth [13] equation or the quest for an expression of the surface stress in terms of the microscopic degrees of freedom of the system (for instance, of the kind one can write for the bulk stress tensor, see [26, 27, 28, 29] and references therein).

In this paper we discuss some geometrical aspects of the notion of surface stress tensor, $\gamma^{\alpha\beta}$ ($\alpha, \beta = 1, 2$), associated to an arbitrarily shaped interfacial surface. Using methods borrowed from Riemannian geometry, that represents the natural tool to deal with a curved two-dimensional manifold embedded in a three-dimensional (flat) ambient, we derive in full generality a formula that in the isotropic and homogeneous case reduces to the Laplace–Young relation.

In order to make contact with Thermodynamics we give the expression of the (reversible) work done in the deformation of a generic two-dimensional interface, in terms of the surface stress tensor. The result is similar to the celebrated Shuttleworth [13] formula with the difference arising when deformations orthogonal to the surface are allowed (see eq. (4.8)).

The outline of the paper is as follows. In order to make the paper self-contained we start in sect. 2 by providing an introduction to the geometrical concepts needed for the present discussion. In sect. 3 we derive the generalized Laplace–Young formula that reduces to the *classical* one in the case of isotropic and homogeneous systems. Contact with Thermodynamics is made in sect. 4 where we provide the relation between the variation of the (Helmholtz) free energy per unit area under a surface deformation and the surface stress tensor. A few concluding remarks can be found in sect. 5. In Supplementary Material for completeness we provide a derivation of the Stokes theorem in intrinsic coordinates.

[1]For an interested and well documented summary of its historical development see [13].

2 Generalities

Let $\mathcal{S}$ be a two-dimensional surface embedded in a Euclidean three-dimensional ambient space, described by the parametric equations

$$\vec{x} \equiv x^k(u^\alpha)\vec{e}_k\,, \quad k = 1,2,3\,, \quad \alpha = 1,2 \tag{2.1}$$

with (u^1, u^2) ranging in a simply connected set, $U[\mathcal{S}]$, and $\vec{e}_k$ denoting the orthonormal vectors of a cartesian reference frame [2]. The two independent vectors

$$\vec{x}_\alpha(u) \equiv \frac{\partial \vec{x}(u)}{\partial u^\alpha}\,, \quad \alpha = 1,2 \tag{2.2}$$

span the tangent plane to $\mathcal{S}$ at the point $\vec{x} = \vec{x}\,(u^1, u^2)$. The unit normal to $\mathcal{S}$ is

$$\vec{n}_\mathcal{S} = \frac{\vec{x}_1 \wedge \vec{x}_2}{|\vec{x}_1 \wedge \vec{x}_2|}\,. \tag{2.3}$$

Given a vector $\vec{v}$ tangent to $\mathcal{S}$, eqs. (2.1) and (2.2) provide a correspondence between its Riemannian contravariant components, v^α, in the curvilinear coordinate system (u^1, u^2), and its cartesian components, v_k, in the ambient euclidean space, that reads

$$\vec{v} = v^k\vec{e}_k = v^\alpha\vec{x}_\alpha\,. \tag{2.4}$$

The embedding of the surface $\mathcal{S}$ defined by eq. (2.1) in the euclidean three-dimensional space induces on $\mathcal{S}$ the Riemannian metric, $g_{\alpha\beta}$, given by

$$g_{\alpha\beta} = \vec{x}_\alpha \cdot \vec{x}_\beta\,. \tag{2.5}$$

Use of this metric allows to express the scalar product of two vectors tangent to $\mathcal{S}$ in terms of their Riemannian contravariant components in the intrinsic form

$$\vec{v} \cdot \vec{w} = v^i w_i = g_{\alpha\beta}v^\alpha w^\beta\,. \tag{2.6}$$

2.1 Principal Curvature

Let $\mathcal{C}$ be a curve parametrized by $\vec{x}(\ell)$ with ℓ its arclength. The tangent vector $\vec{t}(\ell) = d\vec{x}(\ell)/d\ell$ has unit length, so that its derivative is orthogonal to $\vec{t}$. We have therefore

$$\frac{d\vec{t}}{d\ell} = K\vec{n}\,, \tag{2.7}$$

where the unit vector $\vec{n}$, orthogonal to $\vec{t}$, is the so-called principal normal. The proportionality factor, $K \equiv 1/R$, defines the curvature at any given point along

[2] As usual we use upper indices for contravariant components, e.g. $\vec{x} = (x^1, x^2, \ldots, x^N)$. Contravariant indices are lowered with the help of the metric tensor, $g_{ab} = (e_a, e_b)$ where $\{e_a, a = 1, 2, \ldots, N\}$ is the set of vectors spanning the basis of the vector space. Covariant components are then defined by the formula $x_a = g_{ab}x^b$.

the curve, with R the curvature radius. If the curve lies in a plane, its principal normal also lies on it.

With reference to the surface $\mathcal{S}$ parametrized by eqs. (2.1), we remark that any plane Π containing the normal $\vec{n}_{\mathcal{S}}$ (see eq. (2.3)) identifies a plane curve, $\mathcal{C}_\Pi$, on $\mathcal{S}$ called a normal section. Since $\mathcal{C}_\Pi$ is a plane curve, we have

$$\vec{t}(\ell) = \frac{d\vec{x}(\ell)}{d\ell} = \vec{x}_\alpha(u)\frac{du^\alpha(\ell)}{d\ell} \equiv \vec{x}_\alpha(u)\dot{u}^\alpha(\ell) \tag{2.8}$$

and eq. (2.7) becomes

$$\frac{d\vec{t}}{d\ell} = K\vec{n}_{\mathcal{S}}\,, \tag{2.9}$$

because the normal to $\mathcal{C}_\Pi$ is just $\vec{n}_{\mathcal{S}}$, yielding

$$K = \vec{n}_{\mathcal{S}} \cdot \frac{d\vec{t}}{d\ell}\,. \tag{2.10}$$

It is interesting to explicitly compute the derivative of $\vec{t}(\ell)$ with respect to the arclength parameter. One gets

$$\frac{d\vec{t}(\ell)}{d\ell} = \frac{d}{d\ell}\Big(\vec{x}_\alpha(u)\dot{u}^\alpha(\ell)\Big) = \frac{\partial^2\vec{x}(u)}{\partial u^\alpha\partial u^\beta}\dot{u}^\alpha(\ell)\dot{u}^\beta(\ell) + \vec{x}_\alpha(u)\ddot{u}^\alpha(\ell)\,. \tag{2.11}$$

Plugging eq. (2.11) into eq. (2.10) and taking into account the orthogonality of $\vec{x}_\alpha$ (and hence of $\vec{t}(\ell)$) to $\vec{n}_{\mathcal{S}}(\ell)$, one obtains

$$\begin{aligned} K(\ell) &= \vec{n}_{\mathcal{S}}(\ell) \cdot \Big(\frac{\partial^2\vec{x}(u)}{\partial u^\alpha\partial u^\beta}\dot{u}^\alpha(\ell)\dot{u}^\beta(\ell) + \vec{x}_\alpha(u)\ddot{u}^\alpha(\ell)\Big) = \\ &= \vec{n}_{\mathcal{S}}(\ell) \cdot \frac{\partial^2\vec{x}(u)}{\partial u^\alpha\partial u^\beta}\dot{u}^\alpha(\ell)\dot{u}^\beta(\ell) \equiv K_{\alpha\beta}(\ell)\dot{u}^\alpha(\ell)\dot{u}^\beta(\ell)\,, \end{aligned} \tag{2.12}$$

where we have introduced the definition

$$K_{\alpha\beta}(\ell) = \vec{n}_{\mathcal{S}}(\ell) \cdot \frac{\partial^2\vec{x}(u)}{\partial u^\alpha\partial u^\beta}\,. \tag{2.13}$$

$K(\ell)$ is the curvature of the normal section $\mathcal{C}_\Pi$ at the point $u^\alpha = u^\alpha(\ell)$, where the tangent vector has components $\dot{u}^\alpha(\ell)$, $\alpha = 1, 2$.

$K_{\alpha\beta}$ is a rank two tensor under surface coordinates transformations as it follows by a direct computation. Indeed, taking the derivative of the identity

$$\vec{n}_{\mathcal{S}}(u) \cdot \vec{x}_\alpha = 0\,, \tag{2.14}$$

with respect to u^β, we have

$$(\partial_\beta\vec{n}_{\mathcal{S}}) \cdot \vec{x}_\alpha + \vec{n}_{\mathcal{S}}(u) \cdot \frac{\partial^2\vec{x}(u)}{\partial u^\alpha\partial u^\beta} = 0\,, \tag{2.15}$$

implying the result

$$K_{\alpha\beta}(u) = -\vec{x}_\alpha \cdot \partial_\beta \vec{n}_{\mathcal{S}} \,. \tag{2.16}$$

Eq. (2.13) defines a real symmetric tensor, $K_{\alpha\beta} = K_{\beta\alpha}$, to which one can associate the two-dimensional eigenvalue problem

$$K_{\alpha\beta}{\tau_{(i)}}^\beta = k_i \tau_{(i)\alpha} \,. \tag{2.17}$$

The two eigenvalues $k_1 = 1/R_1$ and $k_2 = 1/R_2$ define the principal curvature radii R_1 and R_2 corresponding to the eigenvectors $\tau_{(i)\alpha}$, $i = 1, 2$, and are the smallest and the largest curvature radii among all the normal sections, as it follows from the elementary inequalities $k_{(2)}||\chi||^2 \leq \chi^\alpha K_{\alpha\beta}\chi^\beta \leq k_{(1)}||\chi||^2$ valid for any vector, χ^α, tangent to $\mathcal{S}$.

From eq. (2.17) and the symmetry of $K_{\alpha\beta}$ one gets

$${\tau_{(1)}}^\alpha K_{\alpha\beta}{\tau_{(2)}}^\beta = k_2\, {\tau_{(1)}}^\alpha \tau_{(2)\alpha} = k_1\, {\tau_{(2)}}^\alpha \tau_{(1)\alpha} \,, \tag{2.18}$$

which proves the orthogonality relation ${\tau_{(2)}}^\alpha\, \tau_{(1)\alpha} = {\tau_{(2)}}^\alpha g_{\alpha\beta}{\tau_{(1)}}^\beta = 0$ in the metric (2.5) and therefore also when they are considered as vectors in the three-dimensional ambient space, in accordance with eq. (2.4) [3]. The eigenvectors $\tau_{(1)}$ and $\tau_{(2)}$ obey the completeness relation

$${\tau_{(1)}}^\alpha\, {\tau_{(1)}}^\beta + {\tau_{(2)}}^\alpha\, {\tau_{(2)}}^\beta = g^{\alpha\beta} \,, \tag{2.19}$$

as can be checked by taking the scalar product of eq. (2.19) with $\tau_{(1)}$ and $\tau_{(2)}$. From eqs. (2.17) and (2.19) one obtains the well known geometrical result

$$\mathrm{Tr}[K] \equiv g^{\alpha\beta}K_{\alpha\beta} = \frac{1}{R_1} + \frac{1}{R_2} \,. \tag{2.20}$$

3 The Laplace–Young formula

3.1 The general case

The description of surface forces requires introducing the two-dimensional (surface) stress tensor $\gamma^{\alpha\beta}$ in analogy with what is done in the three-dimensional bulk when the stress tensor, τ_{ik}, $i, k = 1, 2, 3$, is introduced to describe volume forces [30].

Let $\mathcal{S}_\mathcal{C}$ be a surface separating two media bounded by the curve $\mathcal{C}$ with n_β the components of the unit vector orthogonal to $\mathcal{C}$, tangent to $\mathcal{S}_\mathcal{C}$ and directed towards the interior of $\mathcal{C}$. The force per unit length along $\mathcal{C}$ is given by the formula

$$f^\alpha = \gamma^{\alpha\beta} n_\beta \,. \tag{3.1}$$

This equation should be regarded as the definition of the surface stress tensor $\gamma^{\alpha\beta}$. Thus $\gamma^{\alpha\beta}$ represents the α component of the force per unit length exerted on a

[3] In the degenerate case $k_1 = k_2$ the corresponding two eigenvectors can always be orthogonalized.

line element whose normal (lying on the tangent plane to the surface) is n_β. The total force exerted on the interior of the curve $\mathcal{C}$ limiting $\mathcal{S}_\mathcal{C}$ is

$$\vec{F}(\mathcal{C}) = \oint_\mathcal{C} \vec{x}_\alpha \gamma^{\alpha\beta} n_\beta \, d\ell \, . \tag{3.2}$$

Using the Stokes theorem in intrinsic coordinates [31] (for which for completeness we provide a proof in Supplementary Material), one can rewrite eq. (3.2) as a flux integral over a surface, $\mathcal{S}_\mathcal{C}$, bounded by $\mathcal{C}$, in the form

$$\vec{F}(\mathcal{C}) = \oint_\mathcal{C} \vec{x}_\alpha \gamma^{\alpha\beta} n_\beta d\ell = \int_{U(\mathcal{S}_\mathcal{C})} \partial^\beta (\vec{x}^\alpha \gamma_{\alpha\beta}) \, d\sigma \, . \tag{3.3}$$

The equilibrium condition at the interface of two media takes then the expression

$$\int_{U(\mathcal{S}_\mathcal{C})} (\tau^{(2)}_{ik} - \tau^{(1)}_{ik}) \, n^k_\mathcal{S} \, d\sigma = \int_{U(\mathcal{S}_\mathcal{C})} \partial^\beta (\vec{x}^\alpha \gamma_{\alpha\beta}) \, d\sigma \, , \tag{3.4}$$

where $\tau^{(2)}_{ik}$ and $\tau^{(1)}_{ik}$ are the bulk stress tensors computed on the two sides of the separating surface. Eq. (3.4) leads to the local relation

$$(\tau^{(2)}_{ik} - \tau^{(1)}_{ik}) \, n^k_\mathcal{S} = \partial^\beta (x^\alpha_i \gamma_{\alpha\beta}) \, , \tag{3.5}$$

in agreement with the result derived in a number of papers [9, 10, 24].

Eq. (3.5) can be further elaborated by explicitly performing the derivative indicated in its r.h.s. One finds in this way

$$\begin{aligned} &(\tau^{(2)}_{ik} - \tau^{(1)}_{ik}) \, n^k_\mathcal{S} = \partial^\beta (x^\alpha_i \gamma_{\alpha\beta}) = \\ &= \frac{\partial^2 x_i}{\partial u^\alpha \partial u^\beta} \gamma^{\alpha\beta} + x^\alpha_i \partial^\beta \gamma_{\alpha\beta} = n^i_\mathcal{S} K^{\alpha\beta} \gamma_{\alpha\beta} + x^\alpha_i \nabla^\beta \gamma_{\alpha\beta} \, , \end{aligned} \tag{3.6}$$

where we have used the fact that, according to eq. (2.13), $K^{\alpha\beta}$ is the component of the tensor $\partial^2 \vec{x} / \partial u^\alpha \partial u^\beta$ along $\vec{n}_\mathcal{S}$ and we have introduced the covariant divergence of the surface stress tensor ???

$$\nabla_\beta \gamma^{\alpha\beta} = \partial_\beta \gamma^{\alpha\beta} + \Gamma^\alpha_{\beta\delta} \gamma^{\delta\beta} + \Gamma^\beta_{\beta\delta} \gamma^{\alpha\delta} \tag{3.7}$$

in terms of Christoffel symbols [32].

Projecting eq. (3.6) along the normal $\vec{n}_\mathcal{S}$ and on the plane orthogonal to it, we get the two relations (remember eq. (2.14))

$$n^i_\mathcal{S} (\tau^{(2)}_{ik} - \tau^{(1)}_{ik}) \, n^k_\mathcal{S} = \gamma_{\alpha\beta} K^{\alpha\beta} \, , \tag{3.8}$$

$$\nabla^\beta \gamma_{\alpha\beta} = 0 \, . \tag{3.9}$$

The first equation is the generalization of the equilibrium condition at the interface in the non homogeneous and isotropic case, i.e. the generalized Laplace–Young equation. The second says that the tensor $\gamma_{\alpha\beta}$ is covariantly constant on the surface $\mathcal{S}$.

3.2 The isotropic and homogeneous case

The *classical* Laplace–Young formula [1, 2] directly follows from eq. (3.3) in the case of isotropy and homogeneity. In this situation the surface stress tensor has the form $\gamma^{\alpha\beta} = \gamma\, g^{\alpha\beta}$, so the force acting on the surface element $d\sigma$ becomes

$$dF^i = -\Big[n^i_{\mathcal{S}} \mathrm{Tr}[K]\gamma + x^i_\alpha \partial^\alpha \gamma\Big]\, d\sigma\,, \tag{3.10}$$

where we used the relation ???

$$\nabla_\beta \gamma^{\alpha\beta} = \nabla_\beta[\gamma\, g^{\alpha\beta}] = \gamma \nabla_\beta g^{\alpha\beta} + g^{\alpha\beta}\partial_\beta \gamma = \partial^\alpha \gamma\,, \tag{3.11}$$

that follows from $\nabla_\beta g^{\alpha\beta} = 0$.

The surface element will be in equilibrium if the force dF^i is compensated by the force due to the (normal) pressure difference, $\Delta p = p^{(2)} - p^{(1)}$ of the two media at the interface, i.e. if

$$-\vec{n}_{\mathcal{S}} \Delta p + \vec{n}_{\mathcal{S}} \mathrm{Tr}[K]\gamma + \vec{x}_\alpha \partial^\alpha \gamma = 0\,. \tag{3.12}$$

Projecting out the component of this relation along the normal $\vec{n}_{\mathcal{S}}$ and on the plane orthogonal to it, we get the two scalar relations

$$\Delta p = \mathrm{Tr}[K]\gamma = \gamma \left(\frac{1}{R_1} + \frac{1}{R_2}\right)\,, \tag{3.13}$$

$$\partial_\alpha \gamma = 0\,. \tag{3.14}$$

The first is the *classical* Laplace–Young formula, as first formalized in ref. [33], and the second is the known result that says that the surface tension is a constant on the surface $\mathcal{S}$.

Naturally eqs. (3.13) and (3.14) are nothing but eqs. (3.8) and (3.9) in the isotropic and homogeneous limit.

4 Thermodynamic of a deformation

In this section we will consider the work done in a deformation of the equilibrium surface, a notion that is of paramount importance for every thermodynamic application. We start with a brief geometrical introduction.

4.1 Some geometrical considerations

An infinitesimal deformation of $\mathcal{S}$ can be described by a first order infinitesimal vector, $\delta\vec{x}(u)$, which gives rise to the displaced surface, $\mathcal{S}'$ described by the deformed parametric equations

$$\vec{x}\,'(u) = \vec{x}(u) + \delta\vec{x}(u)\,. \tag{4.1}$$

The infinitesimal vector $\delta\vec{x}(u)$ can be split in the form

$$\delta\vec{x}(u) = \epsilon(u)\vec{n}_{\mathcal{S}} + \eta^{\alpha}(u)\vec{x}_{\alpha}\,. \tag{4.2}$$

We are interested in computing the metric, $g'_{\alpha\beta}$, of the displaced surface, $\mathcal{S}'$. One finds from the definition (2.5)

$$g'_{\alpha\beta} \approx g_{\alpha\beta} + \vec{x}_{\alpha}\cdot\frac{\partial\delta\vec{x}}{\partial u^{\beta}} + \vec{x}_{\beta}\cdot\frac{\partial\delta\vec{x}}{\partial u^{\alpha}}\,. \tag{4.3}$$

Since from eq. (4.2) one finds

$$\frac{\partial\delta\vec{x}}{\partial u^{\beta}} = (\partial_{\beta}\epsilon(u))\vec{n}_{\mathcal{S}} + \epsilon(u)\partial_{\beta}\vec{n}_{\mathcal{S}} + (\partial_{\beta}\eta^{\gamma}(u))\vec{x}_{\gamma} + \eta^{\gamma}(u)\partial_{\beta}\vec{x}_{\gamma} \tag{4.4}$$

and

$$\vec{x}_{\alpha}\cdot\frac{\partial\delta\vec{x}}{\partial u^{\beta}} = \epsilon(u)\vec{x}_{\alpha}\cdot\partial_{\beta}\vec{n}_{\mathcal{S}} + (\partial_{\beta}\eta^{\gamma}(u))\vec{x}_{\alpha}\cdot\vec{x}_{\gamma} + \eta^{\gamma}(u)\vec{x}_{\alpha}\cdot\partial_{\beta}\vec{x}_{\gamma}\,, \tag{4.5}$$

one gets (see eq. (2.16) and eq. (20) of Supplementary Material)

$$\begin{aligned}\vec{x}_{\alpha}\cdot\frac{\partial\delta\vec{x}}{\partial u^{\beta}} &= -\epsilon(u)K_{\alpha\beta}(u) + g_{\alpha\gamma}\partial_{\beta}\eta^{\gamma}(u) + \eta^{\gamma}(u)\Gamma^{\delta}{}_{\beta\gamma}g_{\delta\alpha} = \\ &= -\epsilon(u)K_{\alpha\beta}(u) + \nabla_{\beta}\eta_{\alpha}(u)\,,\end{aligned} \tag{4.6}$$

where ∇_{β} is the covariant derivative ???

$$\nabla_{\beta}\eta_{\alpha}(u) = g_{\alpha\gamma}\partial_{\beta}\eta^{\gamma}(u) + \eta^{\gamma}(u)\Gamma^{\delta}{}_{\beta\gamma}g_{\delta\alpha}\,. \tag{4.7}$$

Eq. (4.6) finally yields

$$\delta g_{\alpha\beta} = g'_{\alpha\beta} - g_{\alpha\beta} \approx -2\epsilon(u)K_{\alpha\beta}(u) + \nabla_{\beta}\eta_{\alpha} + \nabla_{\alpha}\eta_{\beta}\,. \tag{4.8}$$

4.2 Work and free energy

We are now ready to compute the work, δW, performed by the surface stress under the infinitesimal deformation (4.2). Recalling that δW has two contributions, one from the stretching of the boundary curve, $\partial\mathcal{S}$, and another one from the "bulk" deformation of $\mathcal{S}$ itself, one gets (see the definition (3.1) and eq. (23) of Supplementary Material)

$$\begin{aligned}\delta W &= -\int_{\mathcal{S}}\left[\epsilon\,K_{\alpha\beta}\gamma^{\alpha\beta} + \eta_{\alpha}\nabla_{\beta}\gamma^{\alpha\beta}\right]d\sigma - \int_{\partial\mathcal{S}} f^{\alpha}\eta_{\alpha}d\ell = \\ &= -\int_{\mathcal{S}}\left[\epsilon\,K_{\alpha\beta}\gamma^{\alpha\beta} + \eta_{\alpha}\nabla_{\beta}\gamma^{\alpha\beta}\right]d\sigma - \int_{\partial\mathcal{S}}\gamma^{\alpha\beta}\,\eta_{\alpha}n_{\beta}d\ell\,,\end{aligned} \tag{4.9}$$

From the Stokes theorem in intrinsic coordinates [31] (see Appendix), we obtain

$$\int_{\partial\mathcal{S}}\gamma^{\alpha\beta}\eta_{\alpha}n_{\beta}d\ell = -\int_{\mathcal{S}}\nabla_{\alpha}(\gamma^{\alpha\beta}\eta_{\beta})d\sigma\,, \tag{4.10}$$

with the minus sign due to the orientation of the surface normal n, that in our convention is directed towards the interior of $\partial\mathcal{S}$. In virtue of eq. (4.10), eq. (4.9) becomes

$$\delta W = -\int_{\mathcal{S}} \left[\epsilon\, K_{\alpha\beta}\gamma^{\alpha\beta} + \eta_\alpha \nabla_\beta \gamma^{\alpha\beta}\right] d\sigma + \int_{\mathcal{S}} \nabla_\beta(\gamma^{\alpha\beta}\eta_\alpha) d\sigma =$$
$$= \int_{\mathcal{S}} \left[-\epsilon\, K_{\alpha\beta}\gamma^{\alpha\beta} + \gamma^{\alpha\beta}\nabla_\beta \eta_\alpha\right] d\sigma = \frac{1}{2}\int_{\mathcal{S}} \delta g_{\alpha\beta}\gamma^{\alpha\beta} d\sigma\,, \tag{4.11}$$

where $\delta g_{\alpha\beta}$ is the variation of the surface metric (eq. (4.8)) under the deformation (4.2). The final formula

$$\delta W = \frac{1}{2}\int_{\mathcal{S}} \delta g_{\alpha\beta}\gamma^{\alpha\beta} d\sigma\,, \tag{4.12}$$

is very interesting because it allows us to derive a thermodynamic definition of surface stress. In fact, under the assumption that the surface deformation (4.1) is carried out reversibly, one can identify δW with minus the (Helmholtz) free energy variation, $-\delta A$. Recalling eqs. (4) and (5) of Supplementary Material, one can derive from eq. (4.11) the local equation

$$-\frac{\delta A}{\delta g_{\alpha\beta}} = \frac{1}{2}\sqrt{|\det g|}\,\gamma^{\alpha\beta}\,. \tag{4.13}$$

If, as it is customary, one introduces the free energy per unit area, $a \equiv A/\sigma_{\mathcal{S}}$, from eq. (4.13) one obtains

$$\gamma^{\alpha\beta} = -\frac{2}{\sqrt{|\det g|}}\frac{\delta(a\sigma_{\mathcal{S}})}{\delta g_{\alpha\beta}} = -a\, g^{\alpha\beta} - 2\frac{\sigma_{\mathcal{S}}}{\sqrt{|\det g|}}\frac{\delta a}{\delta g_{\alpha\beta}}\,. \tag{4.14}$$

This equation is reminiscent of the Shuttleworth formula [13], but not identical with it. Apart from the trivial fact that eq. (4.14) correctly takes into account the general tensor nature of the surface stress, the crucial difference is that the derivative of the free energy per unit area is taken in eq. (4.14) with respect to the metric tensor $g_{\alpha\beta}$ and not with respect to the strain tensor $(\nabla_\alpha\eta_\beta + \nabla_\beta\eta_\alpha)/2$, as it is done in ref. [13] and in all the subsequent literature. As it is clear from eq. (4.8), (variations under the) metric tensor and strain tensor do not coincide, unless $\epsilon(u) = 0$.

Two comments are in order here. First of all, we notice that in the case of an isotropic medium, $\gamma^{\alpha\beta} = \gamma\, g^{\alpha\beta}$, eq. (4.11) can be written in the form

$$\delta W_{isotropic} = \int_{\mathcal{S}'} \gamma d\sigma - \int_{\mathcal{S}} \gamma d\sigma \tag{4.15}$$

which, in the case of a constant surface stress, γ, across $\mathcal{S}$, becomes

$$\delta W_{isotropic} = \gamma\left[\int_{\mathcal{S}'} d\sigma - \int_{\mathcal{S}} d\sigma\right] = \gamma\,\delta\sigma_{\mathcal{S}}\,, \tag{4.16}$$

$\delta\sigma_{\mathcal{S}}$ being the variation of the area of $\mathcal{S}$, in agreement with the usual definition of isotropic surface stress.

Secondly we remark that the idea of defining the bulk (three-dimensional) stress tensor as the response of the free energy under a deformation of the (three-dimensional) metric was advocated in refs. [28, 34]. In that case, however, it was shown [29, 35, 36] that derivatives with respect to the (three-dimensional) deformation tensor and derivatives with respect to the (three-dimensional) ambient space metrics give identical results.

5 Conclusions

Using elements of Riemannian tensor calculus, we have given a geometrical characterization of the surface stress tensor and rederived the Laplace–Young formula for an arbitrarily curved interfacial surface.

We have also discussed the expression of the (reversible) work done in a general surface deformation and we have shown that it is given by a two-dimensional integral where the surface stress tensor is saturated with the deformation of the surface intrinsic metric tensor (and not with the strain tensor). This allows us to derive the equation that relates $\gamma^{\alpha\beta}$ to the free energy per unit surface. We find that this relation differs from the classical Shuttleworth [13] formula because of the term that takes into account the possibility of a surface deformation in the direction orthogonal to it.

Physically the difference between eq. (4.14) and the Shuttleworth formula has to do with the fact that the total (reversible) work done in a generic deformation is the sum of a term related to the stretching of the surface, and a bulk contribution originating when the deformation extends in the normal direction. This last bit is what makes the situation different from the one it is encountered in the case of the stress tensor [29, 34, 35, 36]. There no out-of-three-dimension deformation is physically possible and the derivative of the free energy with respect to the deformation tensor coincide with the derivative with respect to the metric tensor. In the case of a two-dimensional system embedded in a three-dimensional ambient space this is not so, as it is clear from eq. (4.8)

As in the case of the bulk stress tensor, one would like to be able to write an explicit expression of $\gamma^{\alpha\beta}$ in terms of the microscopic degrees of freedom of the system. This is an open and difficult problem still under investigation. The main difficulty here lies in the fact that it is not clear how the standard notion of "thermodynamic limit" ($N \to \infty$, V = volume $\to \infty$ with V/N = fixed) should be extended (or modified) to discuss the Statistical Mechanics of a surface.

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