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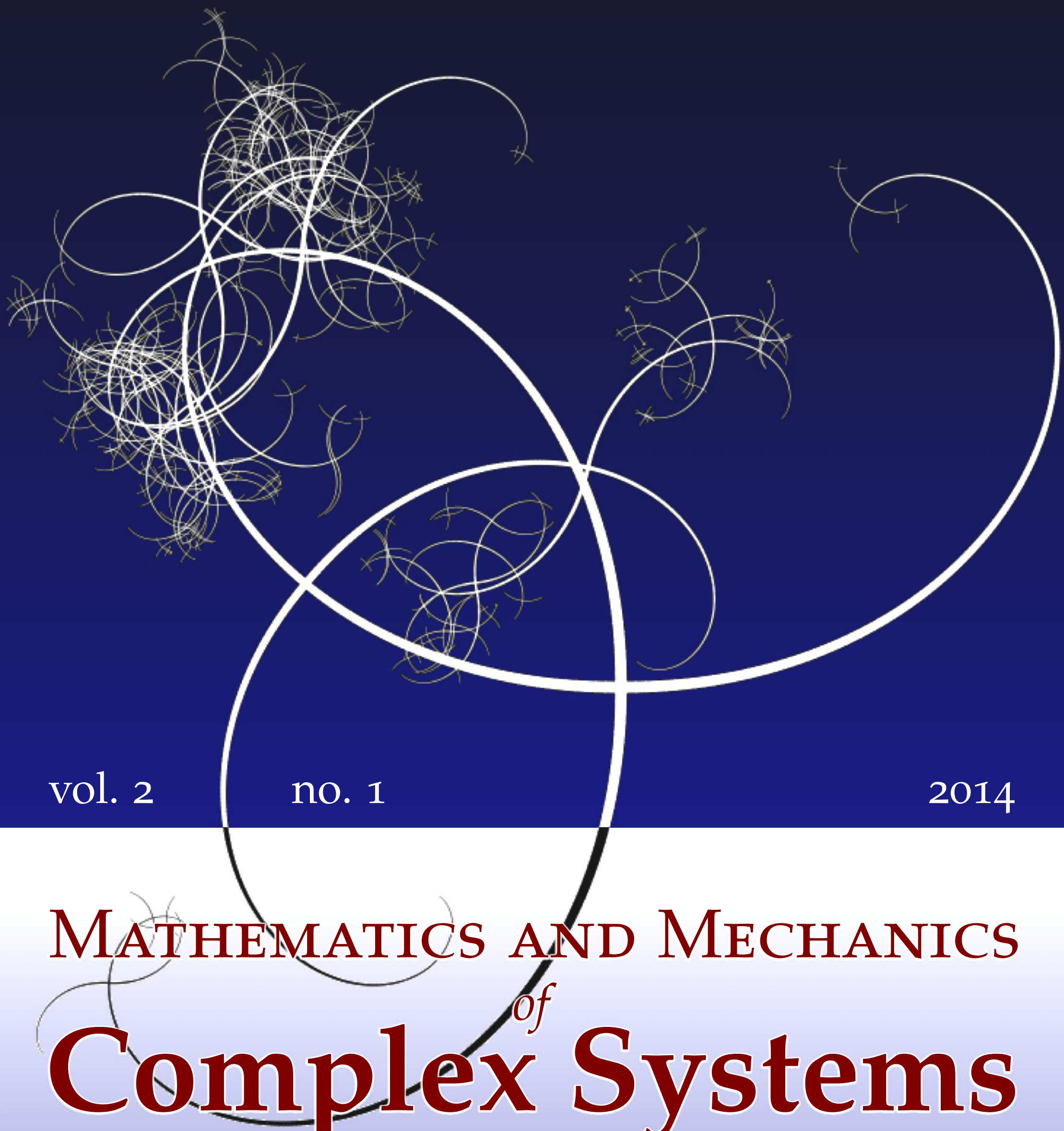

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INTERFACES ENDOWED WITH NONCONSTANT SURFACE ENERGIES REVISITED WITH THE D'ALEMBERT–LAGRANGE PRINCIPLE

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The equation of motion and the conditions on surfaces and edges between fluids and solids in the presence of nonconstant *surface energies*, as in the case of *surfactants* attached to fluid particles at the interfaces, are revisited under the principle of virtual work. We point out that adequate behaviors of surface concentrations may drastically modify the *surface tension* which naturally appears in the Laplace and the Young–Dupré equations. Thus, the principle of virtual work points out a strong difference between the two revisited concepts of surface energy and surface tension.

1. Introduction

This paper develops the principle of virtual work due to d'Alembert–Lagrange [Serrin 1959][1] when different phases of fluids are in contact through singular surfaces or interfaces. The study is first presented without a constitutive assumption for the surface energies, but the displacement fields are considered for a simple material corresponding to the first-gradient theory. The d'Alembert–Lagrange principle allows us to obtain the equation of motion and boundary conditions of mechanical nature and is able to be extended to more complex materials with microstructures [Daher and Maugin 1986] or to multigradient theories [Gouin 2007]. Here, we aim to emphasize the formulation of the principle of virtual work when the interfaces are endowed with nonconstant surface energies: the surfaces have their own material properties independent of the bulks and are embedded in the physical space, which is a three-dimensional metric space. The surface energy density is taken into account and naturally comes into the boundary conditions as the Laplace and the Young–Dupré equations by using variations associated with the virtual displacement fields. To do so, it is necessary to propose a constitutive equation of the surface energy; defining this is a main purpose of the paper. Such a

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[1] The principle of virtual work is also referred to in the literature as the *principle of virtual power* while virtual displacements are called virtual velocities [Germain 1973a; 1973b].

presentation is similar that of deformational and configurational mechanics [Steinmann 2008]; the method is analogous with the one employed in [Germain 1973a; 1973b; Daher and Maugin 1986] but with powerful differential geometry tools as in [Fosdick and Tang 2009]. However, the mathematical tools are adapted to the linear functional of virtual displacement fields and not to the integral balance laws over nonmaterial interfaces separating fluid phases as in [Cermelli et al. 2005].

Consequently, the main result of this paper is to propose a general form of the linear functional with interfaces in first-gradient theory which points out the significance of constitutive behaviors for the surface energies and highlights the clear difference between the notions of surface energy and surface tension. Fischer et al. [2008] emphasized a thermodynamical definition of surface energy, surface tension, and surface stress for which surface tension and surface stress are identical for fluids. Our presentation is not the same: without any thermodynamical assumptions, the difference between surface energy and surface tension is a natural consequence of the virtual work functional and the d'Alembert–Lagrange principle. The surface energy allows us to obtain the total energy of the interfaces and the surface tension is directly generated from the boundary conditions of the continuous medium.

In the simplest cases the two notions of surface energy and surface tension are mingled, but this is not generally the case when the surface energy is nonconstant along the interfaces. To prove this property, we first focus on the simplest case of Laplace's capillarity and obtain the well-known equations on interfaces and contact lines.

Surfaces endowed with surface matter, as in the case of surfactants, are a more complex case. Recent decades have seen the extension of surfactant applications in many fields including biology and medicine [Rosen 2004]; surfactants can also be expected to play a major mechanical role in the fluid and solid domains. The versatility of a surfactant mainly depends on its concentration at interfaces. It experimentally appears that a surfactant or surface-active agent is a substance present in liquids at a very low concentration rate and, when surface mass concentration is below the critical micelle concentration, it is mainly absorbed onto interfaces and alters only the interfacial free energies [de Gennes et al. 2004]. The interfacial free energy per unit area (generally called the *surface energy*) is the minimum amount of work required to create an interface at a given temperature [Edwards et al. 1991; Slattery et al. 2007]. The fact that surfactants can affect the mechanical behaviors of interfaces must be modelized in order to predict and control the properties of complete systems.

In fact, *our aim is not to study the general case of surfactants* proposed in the literature but to focus on the virtual work method to prove that simple behaviors of the surface energy depending on the mass concentration can drastically change the capillary effects. So, the concept of surface tension naturally appears in the equations on surfaces and on lines. In this paper, we call a *surfactant* the matter distributed only on the interfaces: we consider the special case when surfactant molecules are insoluble in the liquid bulk (the surface mass concentration is below the critical micelle concentration [Rosen 2004]) and are attached to fluid particles along the interfaces (without surface diffusion as in [McBride et al. 2011]).

The manuscript is organized as follows: Section 2 briefly reminds us of some results formally presenting the principle of virtual work in its more general form by using the kinematics of a continuous medium and the notion of virtual displacement. The simplest example of the Laplace model of capillarity concludes the section.

Section 3 deals with the case when the interfaces are endowed with nonconstant surface energy, whereby we essentially focus on liquid in contact with solid and gas. The special case of surfactants as interface matter attached to the fluid particles is considered. The surface energy depends on the surface matter concentration. Such a property drastically changes the boundary conditions on the interface by using surface tension instead of surface energy.

Section 4 deals with an explicit comparison between surface energy and surface tension only within deformational mechanics. And Section 5 is the conclusion in which some general extension can be forecast.

The main mathematics tools are collected in the large Appendix so that the presentation of the text is not cluttered with tedious calculations. The main mathematical tool is (15), which can be extended to more complex media.

2. Virtual work for a continuous medium

In continuum mechanics, motions can be equivalently studied with either the Newtonian model of a *system of forces* or the Lagrangian model of the *work of forces* [Germain 1973a; 1973b]. The Lagrangian model does not derive from a variational approach but, at equilibrium, the minimization of the energy coincides with the zero value of a linear functional. Generally, the linear functional expressing the work of forces is related to the theory of distributions; a decomposition theorem associated with displacements (as C^∞-test functions whose supports are compact manifolds) uniquely determines a canonical zero order form (a *separated form*) with respect to both the test functions and the transverse derivatives of the contact test functions [Schwartz 1966]. In the same way that the Newtonian principle is useless when we do not have any constitutive equation for the system of forces, the d'Alembert–Lagrange principle is useless when we do not have any constitutive assumption for the virtual work functional.

The equation of motion and boundary conditions of a continuous medium derive from the *d'Alembert–Lagrange principle of virtual work*, which is an extension of the same principle in the mechanics of systems with a finite number of degrees of freedom: *For any virtual displacement, the motion is such that the virtual work of forces is equal to the virtual work of mass accelerations* [Gouin 2007].

2.1. ***The background of the principle of virtual work.*** The motion of a continuous medium is classically represented by a continuous transformation $\boldsymbol{\varphi}$ of a three-dimensional space into the physical set. In order to describe the transformation analytically, the variables $\boldsymbol{X} = (X^1, X^2, X^3)$ which single out individual particles correspond to material or Lagrange variables; the variables $\boldsymbol{x} = (x^1, x^2, x^3)$ correspond to Euler variables. The transformation representing the motion of a continuous medium is of the form

$$\boldsymbol{x} = \boldsymbol{\varphi}(\boldsymbol{X}, t) \quad \text{or} \quad x^i = \varphi^i(X^1, X^2, X^3, t), \quad i \in \{1, 2, 3\}, \tag{1}$$

where t denotes the time. At a fixed time the transformation possesses an inverse and continuous derivatives up to the second order except on singular surfaces, curves, or points. Then, the diffeomorphism $\boldsymbol{\varphi}$ from the set D_0 of the particle references into the physical set D is an element of a functional space $\wp$ of the positions of the continuous medium considered as a manifold with an infinite number of dimensions.

To formulate the d'Alembert–Lagrange principle of virtual work in continuum mechanics, we recall the notion of *virtual displacements*. This notion is obtained by letting the displacements arise from variations in the paths of particles. Let a one-parameter family of varied paths or *virtual motions* denoted by $\{\boldsymbol{\varphi}_\eta\}$, and possessing continuous partial derivatives up to the second order, be analytically expressed by the transformation

$$\boldsymbol{x} = \boldsymbol{\Phi}(\boldsymbol{X}, t; \eta), \tag{2}$$

with $\eta \in O$, where O is an open real set containing 0, and such that $\boldsymbol{\Phi}(\boldsymbol{X}, t; 0) = \boldsymbol{\varphi}(\boldsymbol{X}, t)$ (the real motion of the continuous medium is obtained when $\eta = 0$). The derivative with respect to η at $\eta = 0$ is denoted by δ. In the literature, the derivative δ is named the *variation* and the virtual displacement is the variation of the position of the medium [Serrin 1959]. The virtual displacement is a tangent vector to $\wp$, the functional space of positions, at $\boldsymbol{\varphi}$ ($\delta\boldsymbol{\varphi} \in T_{\boldsymbol{\varphi}}(\wp)$). In the physical space, the virtual displacement $\delta\boldsymbol{\varphi}$ is determined by the variation of each particle: the *virtual displacement* $\boldsymbol{\zeta}$ *of the particle* $\boldsymbol{x}$ is such that $\boldsymbol{\zeta} = \delta\boldsymbol{x}$ when at $\eta = 0$, $\{\delta\boldsymbol{X} = 0, \delta t = 0, \delta\eta = 1\}$, and we associate the field of tangent vectors to D:

$$\boldsymbol{x} \in D \quad \to \quad \boldsymbol{\zeta} = \boldsymbol{\psi}(\boldsymbol{x}) \equiv \left.\frac{\partial \boldsymbol{\Phi}}{\partial \eta}\right|_{\eta=0} \in T_{\boldsymbol{x}}(D),$$

where $T_{\boldsymbol{x}}(D)$ is the tangent vector bundle to D at $\boldsymbol{x}$.

The virtual work concept, the dual of Newton's method, can be written in the following form:

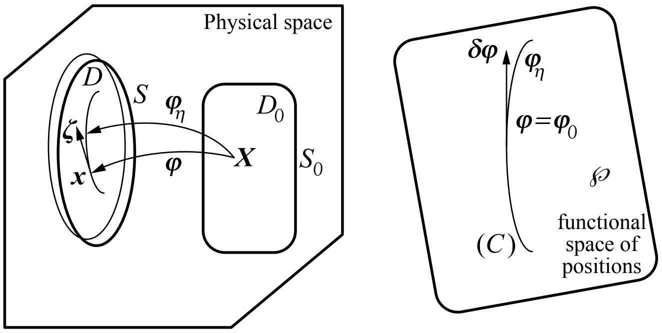
Physical space
D
S
$\boldsymbol{\varphi}_\eta$
D_0
ζ
$\boldsymbol{X}$
$\boldsymbol{x}$
$\boldsymbol{\varphi}$
S_0
$\delta\boldsymbol{\varphi}$
$\boldsymbol{\varphi}_\eta$
$\boldsymbol{\varphi}=\boldsymbol{\varphi}_0$
$\wp$
(C)
functional space of positions

Figure 1. The boundary S of D is represented by a thick curve and its variation by a thin curve. The variation $\delta\boldsymbol{\varphi}$ of the family $\{\boldsymbol{\varphi}_\eta\}$ of varied paths belongs to $T_{\boldsymbol{\varphi}}(\wp)$, tangent space of $\wp$ at $\boldsymbol{\varphi}$.

The virtual work $\delta\tau$ is a linear functional value of the virtual displacement,

$$\delta\tau = \langle \Im, \delta\boldsymbol{\varphi}\rangle, \tag{3}$$

where $\langle\,\cdot\,,\,\cdot\,\rangle$ denotes the inner product of $\Im$ and $\delta\boldsymbol{\varphi}$, with $\Im$ belonging to the cotangent space $T^*_{\boldsymbol{\varphi}}(\wp)$ of $\wp$ at $\boldsymbol{\varphi}$.

In (3), the medium in position $\boldsymbol{\varphi}$ is submitted to covector $\Im$ denoting all the "stresses" in mechanics. In the case of motion, we must add the inertial forces, corresponding to the accelerations of masses, to the volume forces.

The d'Alembert–Lagrange principle of virtual work is expressed as follows:

For all virtual displacements, the virtual work is null.

This principle leads to the analytic representation

$$\forall\ \delta\boldsymbol{\varphi} \in T_{\boldsymbol{\varphi}}(\wp), \qquad \delta\tau = 0.$$

Theorem. *If* (3) *is a distribution expressed in separated form* (see [Schwartz 1966]), *the d'Alembert–Lagrange principle yields the equation of motion and boundary conditions in the form* $\Im = 0$.

The virtual displacement is submitted to constraints coming from the constitutive equations and geometrical assumptions such as mass conservation. Consequently, the constraints are not expressed by Lagrange multipliers but are directly taken into account by the variations of the constitutive equations. The equation of motion and boundary conditions result from the explicit expression of $\delta\tau$ associated with the considered physical problem. As a first example, the simplest case of the theory of capillarity at equilibrium is considered.

2.2. ***The classical Laplace theory of capillarity.*** Liquid-vapor and two-phase interfaces are represented by material surfaces endowed with an energy related to the Laplace free energy of capillarity. When working far from critical conditions, the capillary layer has a thickness equivalent to a few molecular beams [Ono and Kondo 1960; Domb 1996] and the interface appears as a geometrical surface separating the two media, with its own characteristic behavior and energy properties [Levitch 1962]. The domain D of a compressible fluid (liquid) is immersed in a three Euclidean space. The boundary of the domain D is a surface S shared in N parts S_p of class C^2, $p = 1, \dots, N$ (Figure 2). We denote by $(R_m)^{-1}$ the mean curvature of S; the union of the limit edges Γ_{pq} between surfaces S_p and S_q is assumed to be of class C^2 and $\boldsymbol{t}_p$ is the tangent vector to $\Gamma_p = \bigcup \Gamma_{pq}$, $q = 1, \dots, N$ with $q \neq p$, oriented by the unit external vector to D denoted $\boldsymbol{n}_p$; $\boldsymbol{n}'_p = \boldsymbol{t}_p \times \boldsymbol{n}_p$ is the unit external normal vector to Γ_p in the tangent plane to S_p; the edge Γ of S is the union of the edges Γ_p of S_p.

To first verify the well-foundedness of the model, we consider the explicit expression of the functional $\delta\tau$ for compressible fluids with capillarity in the nondissipative case. The variation of the total energy E of such a fluid results from the variation of the sum of the local density of energy integrated on the domain D and the variation of the local density of surface energy integrated on its boundary S; to these variations, we must add the work of volume force $\rho \boldsymbol{f}$ in D, surface force $\boldsymbol{T}$ on S, and line force $\boldsymbol{L}$ on Γ. Such an amount represents, for the domain D, the virtual work of forces of the compressible fluid with capillarity.

The Laplace theory of capillarity introduces the notion of surface energy (or superficial energy) on surfaces such that, for a compressible liquid with capillary effects on the wall boundaries, the total energy of the fluid writes in the form

$$E = \iiint_D \rho\alpha(\rho)\, dv + \iint_S \sigma\, ds, \qquad \text{with} \quad \iint_S \sigma\, ds \equiv \sum_{p=1}^{N} \iint_{S_p} \sigma_p\, ds,$$

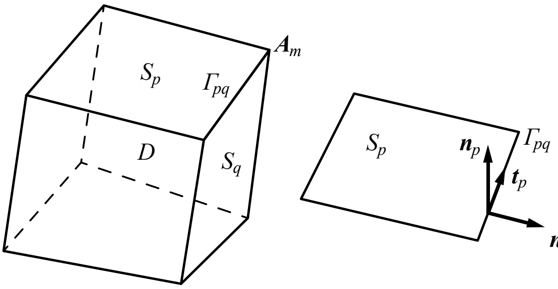

Figure 2. The set D has a surface boundary S divided into several parts. The edge of S is denoted by Γ which is also divided into several parts with endpoints $\boldsymbol{A}_m$.

where ρ is the matter density, $\alpha(\rho)$ is the fluid-specific energy ($\rho\alpha(\rho)$ is the volume energy), and the coefficients σ_p are the surface energy densities on each surface S_p represented — for the sake of simplicity — by σ on S.[2] Surface integrations are associated with the metric space. As proved in the Appendix, the variation of the deformation gradient tensor $F = \partial \boldsymbol{x}/\partial \boldsymbol{X}$ (with components $\{\partial x_i/\partial X_j\}$) of the mapping $\boldsymbol{\varphi}$ combined with the mass conservation and the variation of σ allow us to obtain the variation $-\delta E$ (see (A.3)); then the independent variables come from the position $\boldsymbol{x}$ of the continuous medium.

The virtual work of the volume forces defined on D is generally in the form

$$\iiint_D \rho \boldsymbol{f}^T \boldsymbol{\zeta}\, dv, \qquad \text{with } \boldsymbol{f} = -\operatorname{grad} U,$$

where $U(\boldsymbol{x})$ is a potential per unit mass and superscript T denotes transposition. The virtual work of surface and line forces defined on S and Γ are, respectively,

$$\iint_S \boldsymbol{T}^T \boldsymbol{\zeta}\, ds \quad \text{and} \quad \int_\Gamma \boldsymbol{L}^T \boldsymbol{\zeta}\, dl.$$

Consequently, the total virtual work of forces $\delta\tau$ is

$$\delta\tau = -\delta E + \iiint_D \rho \boldsymbol{f}^T \boldsymbol{\zeta}\, dv + \iint_S \boldsymbol{T}^T \boldsymbol{\zeta}\, ds + \int_\Gamma \boldsymbol{L}^T \boldsymbol{\zeta}\, dl.$$

From (A.3) and (A.6), we obtain

$$\begin{aligned}\delta\tau \equiv \iiint_D (-\operatorname{grad}^T p + \rho \boldsymbol{f}^T)\boldsymbol{\zeta}\, dv + \int_\Gamma (\boldsymbol{L}^T - \sigma \boldsymbol{n}'^T)\boldsymbol{\zeta}\, dl \\ + \iint_S \Big[-\delta\sigma + \Big\{\Big(p + \frac{2\sigma}{R_m}\Big)\boldsymbol{n}^T + \operatorname{grad}^T \sigma (\mathbf{1} - \boldsymbol{n}\boldsymbol{n}^T) + \boldsymbol{T}^T\Big\}\boldsymbol{\zeta}\Big]\, ds, \quad (4)\end{aligned}$$

where $p \equiv \rho^2 \alpha'(\rho)$ is the pressure of the liquid [Rocard 1952], $\delta\sigma$ denotes the variation of the surface energy σ, and $\mathbf{1}$ denotes the identity tensor. When σ is constant we get $\delta\sigma = 0$; then,

$$\begin{aligned}\delta\tau \equiv \iiint_D (-\operatorname{grad}^T p + \rho \boldsymbol{f}^T)\boldsymbol{\zeta}\, dv \\ + \iint_S \Big\{\Big(p + \frac{2\sigma}{R_m}\Big)\boldsymbol{n}^T + \boldsymbol{T}^T\Big\}\boldsymbol{\zeta}\, ds + \int_\Gamma (\boldsymbol{L}^T - \sigma \boldsymbol{n}'^T)\boldsymbol{\zeta}\, dl,\end{aligned}$$

and the d'Alembert–Lagrange principle yields the equation of equilibrium on D,

$$-p_{,i} + \rho f_i = 0 \qquad \text{or} \qquad -\operatorname{grad} p + \rho \boldsymbol{f} = 0. \qquad (5)$$

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[2] Our aim is not to consider the thermodynamics of interfaces. Consequently, α and σ are not considered as functions of thermodynamical variables such as temperature or entropy.

The condition on boundary surface S is

$$\Big(p+\frac{2\sigma}{R_m}\Big)n_i+T_i=0 \quad \text{or} \quad \Big(p+\frac{2\sigma}{R_m}\Big)\boldsymbol{n}+\boldsymbol{T}=0, \tag{6}$$

where, for an external fluid bordering D, $\boldsymbol{T}=-P\boldsymbol{n}$, with P the value of the pressure in the external fluid. On the lines, it is necessary to consider the partition of S such that the edge Γ_{pq} is common to S_p and S_q,

$$\sigma_p n'_{pi}+\sigma_q n'_{qi}-L_i=0 \quad \text{or} \quad \sigma_p \boldsymbol{n}'_p+\sigma_q \boldsymbol{n}'_q-\boldsymbol{L}=0. \tag{7}$$

Surface condition (6) is the *Laplace equation* and line condition (7) is the *Young–Dupré equation* with a line tension $\boldsymbol{L}$.

It is interesting to note that Steigmann and Li [1995] used the principle of virtual work by utilizing a system of line coordinates on boundary surfaces and lines. By introducing the free energy per unit area of interfaces and the free energy per unit of contact curve, they obtained Laplace's equation and a generalization of the Young–Dupré equation of equilibrium; moreover, by employing the necessary conditions for energy-minimizing states of fluid systems they got a demonstration that the line tension associated with a three-phase contact curve must be nonnegative.

When σ is not constant but $\delta\sigma=0$, we obtain the same equations for (5) and (7) but (6) on S is replaced by

$$\Big(p+\frac{2\sigma}{R_m}\Big)\boldsymbol{n}+(\boldsymbol{1}-\boldsymbol{n}\boldsymbol{n}^T)\operatorname{grad}\sigma+\boldsymbol{T}=0.$$

The additive term $(\boldsymbol{1}-\boldsymbol{n}\boldsymbol{n}^T)\operatorname{grad}\sigma=\operatorname{grad}_{tg}\sigma$ is the tangential part of $\operatorname{grad}\sigma$ to the surface S. This term corresponds to a shear stress necessarily balanced by the tangential component of $\boldsymbol{T}$. Such is the case when σ is defined on the S_0 image of S in the reference space D_0 (then, $\sigma=\sigma_0(\boldsymbol{X})$). We understand the importance of the surface energy constitutive behavior; this questioning is emphasized in the following section.

3. Capillarity of liquid in contact with solid and gas in the presence of nonconstant surface energy

We have seen in the previous section that the problem associated with the behavior of the surface energy is the key point to obtaining the boundary conditions on interfaces and contact lines bordering the fluid bulk. In this section we consider a very special case of surfactant: the interfaces are endowed with a concentration of matter which affects the surface energy. The surface matter is attached to the particles of the fluid such that they obey together to the same equations of motion (1) and of virtual motion (2). We consider a more general case than in Section 2.2:

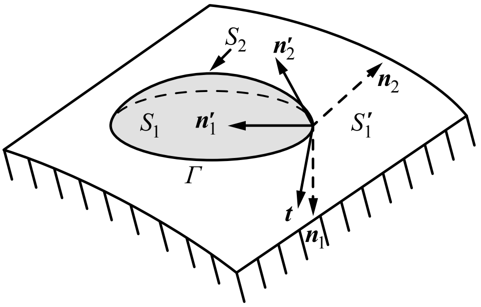

Figure 3. A liquid in drop form lies on a solid surface. The liquid is bordered by a gas and a solid; S_1 is the boundary between liquid and solid; S'_1 is the boundary between gas and solid; S_2 is the interface between liquid and gas; $\boldsymbol{n}_1$ and $\boldsymbol{n}_2$ are the unit normal vectors to S_1 and S_2, external to the domain of the liquid; the edge Γ (or contact line) is common to S_1 and S_2 and $\boldsymbol{t}$ is the unit tangent vector to Γ relative to $\boldsymbol{n}_1$; $\boldsymbol{n}'_1 = \boldsymbol{n}_1 \times \boldsymbol{t}$ and $\boldsymbol{n}'_2 = \boldsymbol{n}_2 \times (-\boldsymbol{t})$ are the binormals to Γ relative to S_1 and S_2, respectively.

we study the motion of the continuous medium with viscous forces. This viscosity affects not only the equation of motion but also the boundary conditions.

3.1. ***Geometrical description of the continuous medium.*** A drop of liquid fills the set D and lies on the surface of a solid. The liquid drop is also bordered by a gas. All the interfaces between liquid, solid and gas are assumed to be regular surfaces. We call σ_{S_1} and σ_{S_2} the values of the surface energies of S_1 and S_2, respectively (see Figure 3). These energies may depend on each point of the boundary of D. Afterwards, on the domain S'_1, the surface energy between gas and solid is neglected [Adamson 1967]. The liquid drop is submitted to a volume force $\rho \boldsymbol{f}$. The *external* surface force on D is modelized with two constraint vector fields, $\boldsymbol{T}_1$ on the solid surface, S_1, and $\boldsymbol{T}_2$ on the free surface, S_2. The line tension $\boldsymbol{L}$ is assumed to be null.

By using the principle of virtual work, we aim to write the equation of motion of the liquid drop and the conditions on the surfaces and line bordering the liquid drop.

3.2. ***Surfactant attached to interfacial fluid particles.*** To express the behavior of the surface energy, we need to represent first the equation of the surface matter density.

Under the mapping $\boldsymbol{\varphi}$, the set D_0 with boundary S_0 has image D with boundary S. We assume there exists an insoluble surfactant with a surface mass concentration c_0 defined on D_0 of image c in D [Levitch 1962; Adamson 1967; Defay 1971].

Let us consider the case when *the surfactant is attached to the fluid particles on the surface* S, that is,

$$c_0 = c_0(\boldsymbol{X}), \tag{8}$$

where $\boldsymbol{X} \in S_0$.

The mass conservation of the surfactant on the surface S requires that for any subset S_0^* of S_0, of image S^* subset of S,

$$\iint_{S^*} c\, ds = \iint_{S_0^*} c_0\, ds_0. \tag{9}$$

Relation (9) implies

$$c \det F\, \boldsymbol{n}_0^T F^{-1} \boldsymbol{n} = c_0 \quad \text{with } \boldsymbol{n}_0^T = \frac{\boldsymbol{n}^T F}{\sqrt{(\boldsymbol{n}^T F F^T \boldsymbol{n})}}, \tag{10}$$

where $\boldsymbol{n}_0$ denotes the unit normal vector to S_0. The proof of (10) is given in the Appendix.

From (10), we obtain the following: Firstly, the conservation of the surface concentration of the surfactant,

$$\frac{dc}{dt} + c(\operatorname{div} \boldsymbol{u} - \boldsymbol{n}^T \boldsymbol{D}\boldsymbol{n}) = 0, \tag{11}$$

where $\boldsymbol{u}$ is the fluid velocity vector and

$$\boldsymbol{D} = \tfrac{1}{2}(\partial \boldsymbol{u}/\partial \boldsymbol{x} + (\partial \boldsymbol{u}/\partial \boldsymbol{x})^T)$$

denotes the rate of the deformation tensor of the fluid. The term $\operatorname{div} \boldsymbol{u} - \boldsymbol{n}^T \boldsymbol{D}\boldsymbol{n}$ expresses the tangential divergence relative to the surface S.

Secondly, the variation of the mass concentration of the surfactant,

$$\delta c + c\Big[\operatorname{div} \boldsymbol{\zeta} - \boldsymbol{n}^T \frac{\partial \boldsymbol{\zeta}}{\partial \boldsymbol{x}} \boldsymbol{n}\Big] = 0. \tag{12}$$

The proofs of (11) and (12) are also given in the Appendix. In the case when the surface energy σ is a function of the surfactant concentration,

$$\sigma = \sigma(c),$$

we deduce $\delta\sigma = \sigma'(c)\, \delta c$. If we denote

$$\gamma = \sigma - c\sigma'(c), \tag{13}$$

which is the Legendre transformation of σ with respect to c, then by taking (A.3) into account we obtain, in the Appendix,

$$\delta E = -\iint_S \Big[\frac{2\gamma}{R_m} \boldsymbol{n}^T + \operatorname{grad}^T \gamma (\boldsymbol{1} - \boldsymbol{n}\boldsymbol{n}^T)\Big] \boldsymbol{\zeta}\, ds + \int_\Gamma \gamma \boldsymbol{n}'^T \boldsymbol{\zeta}\, dl. \tag{14}$$

As we shall see in Section 4, γ is the *surface tension* of the interface S. The variation δc of the concentration has an important consequence on the surfactant behavior and the surfactant behavior is essential to determining the virtual work of the liquid drop.

Relation (13) can easily be extended to several surfactants: if

$$\sigma = \sigma(c_1, \dots, c_n),$$

where the c_i, for $i \in \{1, \dots, n\}$, are the concentrations of the n surfactants, then

$$\gamma = \sigma - \sum_{i=1}^{n} c_i \frac{\partial \sigma}{\partial c_i},$$

corresponding to the Legendre transformation of σ with respect to c_i, $i \in \{1, \dots, n\}$ and (14) is always valid.

3.3. ***Governing equation of motion and boundary conditions.*** As previously indicated, we do not consider the thermodynamical problem of interfaces, but, for example, when the medium is isothermal, α can be considered as the specific free energy of the bulk and σ the free surface energy of the interface.

The use of virtual displacements yields a linear functional of virtual works, the sum of several partial works. To enumerate the works of forces, we have to consider how they are obtained in the literature [Germain 1973a; 1973b; Gouin 2007]. The virtual work expressions of volume force $\rho \boldsymbol{f}$, surface force $\boldsymbol{T}$, and liquid pressure p are the same as in Section 2.2.

(a) For fluid motion, the virtual work of mass impulsions is

$$-\iiint_D \rho \boldsymbol{a}^T \boldsymbol{\zeta}\, dv,$$

where $\boldsymbol{a}$ is the acceleration vector.

(b) For dissipative motion, we must add the virtual work of viscous stresses

$$-\iiint_D \operatorname{tr}\Big(\boldsymbol{\tau}_v \frac{\partial \boldsymbol{\zeta}}{\partial \boldsymbol{x}}\Big)\, dv,$$

where $\boldsymbol{\tau}_v$ denotes the viscous stress tensor usually written in Navier–Stokes form [Adamson 1967]. Taking account of the relation

$$\operatorname{tr}\Big(\boldsymbol{\tau}_v \frac{\partial \boldsymbol{\zeta}}{\partial \boldsymbol{x}}\Big) = \operatorname{div}(\boldsymbol{\tau}_v \boldsymbol{\zeta}) - (\operatorname{div} \boldsymbol{\tau}_v)\boldsymbol{\zeta},$$

an integration by parts using Stokes' formula in (14) for the virtual work of interfacial forces, together with the relations $\boldsymbol{n}'_1 = \boldsymbol{n}_1 \times \boldsymbol{t}$ and $\boldsymbol{n}'_2 = -\boldsymbol{n}_2 \times \boldsymbol{t}$, allows us to obtain the virtual work of forces applied to the domain D:

$$\begin{aligned}\delta\tau = &\iiint_D (-\operatorname{grad}^T p + \operatorname{div} \boldsymbol{\tau}_v + \rho \boldsymbol{f}^{\,T} - \rho \boldsymbol{a}^T)\boldsymbol{\zeta}\, dv\\ &+ \iint_{S_1}\left[\operatorname{grad}^T \gamma_1 (\mathbf{1} - \boldsymbol{n}_1\boldsymbol{n}_1^T) + \left(p + \frac{2\gamma_1}{R_{m_1}}\right)\boldsymbol{n}_1^T - \boldsymbol{n}_1^T\boldsymbol{\tau}_v + \boldsymbol{T}_1^T\right]\boldsymbol{\zeta}\, ds\\ &+ \iint_{S_2}\left[\operatorname{grad}^T \gamma_2 (\mathbf{1} - \boldsymbol{n}_2\boldsymbol{n}_2^T) + \left(p + \frac{2\gamma_2}{R_{m_2}}\right)\boldsymbol{n}_2^T - \boldsymbol{n}_2^T\boldsymbol{\tau}_v + \boldsymbol{T}_2^T\right]\boldsymbol{\zeta}\, ds\\ &+ \int_\Gamma (\gamma_1 \boldsymbol{n}_1'^T - \gamma_2 \boldsymbol{n}_2'^T)\boldsymbol{\zeta}\, dl,\end{aligned} \tag{15}$$

where R_{m_i} denotes the mean radius of curvature of S_i, γ_i denotes the surface tension of S_i, and $\boldsymbol{T}_i$ the surface force on S_i, $i \in \{1, 2\}$; $\boldsymbol{T}_2 = -P\boldsymbol{n}_2$, where P is the pressure in the external gas to the domain D.

The field of virtual displacement $\boldsymbol{x} \in D \longrightarrow \boldsymbol{\zeta}(\boldsymbol{x}) \in T_{\boldsymbol{x}}(D)$ must be tangent to the solid (rigid) surface S_1. The fundamental lemma of variational calculus yields the equation of motion associated with domain D, the conditions on surfaces S_1 and S_2, and the condition on contact line Γ.

Due to the fact that (15) is expressed in separate form in the sense of distributions [Schwartz 1966], the d'Alembert–Lagrange principle implies that $\forall\ \boldsymbol{\zeta}(\boldsymbol{x}) \in T_{\boldsymbol{x}}(D)$ tangent to S_1, each of the four integrals of (15) is null. Then, we obtain equations on D, S_1, S_2, and Γ, respectively.

- We get the *equation of motion* in D:

$$\rho\boldsymbol{a} + \operatorname{grad} p = (\operatorname{div} \boldsymbol{\tau}_v)^T + \rho\boldsymbol{f}. \tag{16}$$

Equation (16) is the Navier–Stokes equation for compressible fluids when $\boldsymbol{\tau}_v$ is written in the classical linear form by using the rate of the fluid deformation tensor, $\boldsymbol{\tau}_v = \lambda(\operatorname{tr} \boldsymbol{D})\mathbf{1} + 2\mu\boldsymbol{D}$. We may add a classical condition for the velocity on the boundary as the adherence condition.

- We get *the condition* on surface S_1. The virtual displacement is tangent to S_1; the constraint $\boldsymbol{n}_1^T\boldsymbol{\zeta} = 0$ implies there exists a scalar Lagrange multiplier $\boldsymbol{x} \in S_1 \longrightarrow \chi(\boldsymbol{x}) \in \Re$, such that

$$\left(p + \frac{2\gamma_1}{R_{m_1}}\right)\boldsymbol{n}_1 - \boldsymbol{\tau}_v\boldsymbol{n}_1 + (\mathbf{1} - \boldsymbol{n}_1\boldsymbol{n}_1^T)\operatorname{grad}\gamma_1 + \boldsymbol{T}_1 = \chi\boldsymbol{n}_1, \tag{17}$$

The normal and tangential components of (17) relative to S_1 are deduced from (17):

$$p + \frac{2\gamma_1}{R_{m_1}} - \boldsymbol{n}_1^T\boldsymbol{\tau}_v\boldsymbol{n}_1 + \boldsymbol{n}_1^T\boldsymbol{T}_1 = \chi, \tag{18}$$

$$(\mathbf{1} - \boldsymbol{n}_1\boldsymbol{n}_1^T)(-\boldsymbol{\tau}_v\boldsymbol{n}_1 + \operatorname{grad}\gamma_1 + \boldsymbol{T}_1) = 0. \tag{19}$$

Following (18), we obtain the value of χ along the surface S_1. The scalar field χ corresponds to the unknown value of the normal stress vector on the surface S_1; it corresponds to the difference between the mechanical and viscous normal stresses and a stress due to the curvature of S_1 taking into account the surface tension. Equation (19) represents the balance between the tangential components of the mechanical and viscous stresses and the tangential component of the surface tension gradient.

• We get *the condition* on surface S_2:

$$\left(p+\frac{2\gamma_2}{R_{m_2}}\right)\boldsymbol{n}_2-\boldsymbol{\tau}_v\boldsymbol{n}_2+(\mathbf{1}-\boldsymbol{n}_2\boldsymbol{n}_2^T)\operatorname{grad}\gamma_2-P\boldsymbol{n}_2=0. \tag{20}$$

The normal and tangential components of (20) relative to S_2 are deduced:

$$\frac{2\gamma_2}{R_{m_2}}-\boldsymbol{n}_2^T\boldsymbol{\tau}_v\boldsymbol{n}_2+p=P, \tag{21}$$

$$(\mathbf{1}-\boldsymbol{n}_2\boldsymbol{n}_2^T)(-\boldsymbol{\tau}_v\boldsymbol{n}_2+\operatorname{grad}\gamma_2)=0. \tag{22}$$

Equation (21) corresponds to the expression of the Laplace equation in the case of viscous motion; the normal component of viscous stresses is taken into account. Equation (22) is similar to (19) for the surface S_2 but without the component of the stress vector.

• We get *the condition* on line Γ. To get the line condition we must consider a virtual displacement tangent to S_1 and consequently in the form

$$\boldsymbol{\zeta}=\alpha\boldsymbol{t}+\beta\boldsymbol{t}\times\boldsymbol{n}_1,$$

where α and β are two scalar fields defined on Γ. From the last integral of (15), we get the following immediately: For any scalar field $\boldsymbol{x}\in\Gamma\longrightarrow\beta(\boldsymbol{x})\in\Re$,

$$\int_\Gamma \beta\gamma_1\boldsymbol{n}_1'^T(\boldsymbol{t}\times\boldsymbol{n}_1)\,dl-\int_\Gamma \beta\gamma_2\boldsymbol{n}_2'^T(\boldsymbol{t}\times\boldsymbol{n}_1)\,dl=0,$$

with $\boldsymbol{n}_1'=-\boldsymbol{t}\times\boldsymbol{n}_1$ and $\boldsymbol{n}_2'=\boldsymbol{t}\times\boldsymbol{n}_2$, and consequently,

$$-\gamma_1-\gamma_2\boldsymbol{n}_2^T\boldsymbol{n}_1=0.$$

Denoting by θ the angle $\langle\boldsymbol{n}_1,\boldsymbol{n}_2\rangle$, we obtain the well-known relation of Young–Dupré but adapted to γ_1 and γ_2 in place of σ_1 and σ_2:

$$\gamma_1+\gamma_2\cos\theta=0. \tag{23}$$

3.4. ***Remarks.*** For a motionless fluid, $\boldsymbol{\tau}_v=0$ and consequently, (19) yields

$$\operatorname{grad}_{tg}\gamma_1=-\boldsymbol{T}_{1tg},$$

where $\operatorname{grad}_{tg}\gamma_1$ and $\boldsymbol{T}_{1tg}$ denote the tangential parts of $\operatorname{grad}\gamma_1$ and $\boldsymbol{T}_1$, respectively. The tangential part of the vector stress is opposite to the surface tension gradient. Therefore, at a given value of $T_{1n} = \boldsymbol{n}_1^T\boldsymbol{T}_1$, (18) yields the value χ corresponding to the normal stress vector to the surface S_1, (21) yields $P = p + 2\gamma_2/R_{m_2}$ corresponding to the classical equation of Badshforth and Adams [Adamson 1967] but with the surface tension γ_2 instead of σ_2, and (22) implies $(\boldsymbol{1} - \boldsymbol{n}_2\boldsymbol{n}_2^T)\operatorname{grad}\gamma_2 = 0$. At equilibrium, along S_2, the surface tension γ_2 must be uniform.

In the case of motion, (22) represents the Marangoni effect as proposed in [Gibbs 1928; Defay 1971] but with the surface tension γ_2 instead of σ_2.

4. Surface energy and surface tension

A surface tension must appear on the boundary conditions as a force per unit of line. The Legendre transformation γ of σ with respect to c exactly corresponds to this property on the contact line Γ; then, surface tension γ differs from the surface energy; this important property was pointed out by Gibbs [1928] and Defay [1971] by means of thermodynamical considerations. The fundamental difference between surface tension and surface energy, in the presence of attached surfactants, is illustrated in the following cases corresponding to formal behaviors.

- If σ is independent of c, then $\gamma = \sigma$: the surface tension is equal to the surface energy. This is the classical case of capillarity for fluids considered in Section 2.2 and (23) is the classical Young–Dupré condition on the contact lines.
- In fact, σ is a decreasing function of c [Adamson 1967]; when c is small enough we consider the behavior

$$\sigma = \sigma_0 - \sigma_1 c, \qquad \text{where } \sigma_0 > 0 \text{ and } \sigma_1 > 0;$$

then, (13) implies $\gamma = \sigma_0$ and surface tension and surface energy are different.

- Now, we consider a formal case when the surface energy density model is written in the form

$$\sigma = \sigma_0 - \sigma_1 c - \sigma_2 c \sin\left(\frac{1}{c}\right),$$

where $\sigma_0 > 0$, $\sigma_1 > 0$, and $\sigma_2 > 0$. Then, (13) implies

$$\gamma = \sigma_0 - \sigma_2 \cos\left(\frac{1}{c}\right). \tag{24}$$

This case does not correspond to σ as a monotonic decreasing function of c. Nevertheless, when $c \to 0$, γ does not have any limit and we get

$$\gamma \in [\sigma_0 - \sigma_2, \sigma_0 + \sigma_2].$$

The surface tension may have a large scale of values. When the concentration c is low, a variation of the concentration c may generate strong fluctuations of the surface tension without significant change of the surface energy. Alternatively, the concentration behavior strongly affects the surface tension but not the surface energy. Relation (24) fits with the well-known physical case of hysteresis behavior for a drop lying on a horizontal plane (see, for example, [Gouin 2003] and the literature therein). So, *the surface roughness is not the only reason of the hysteresis of the contact angle even if the surface energy is nearly constant.*

5. Conclusion

The principle of virtual work allows us to deduce the equation of motion and the conditions on the surfaces and lines by means of a variational analysis. When capillary forces operate and surfactant molecules are attached to the fluid molecules at the interfaces, the conditions on the surfaces and lines point out a fundamental difference between the concepts of surface energy and surface tension. This fact was thermodynamically predicted in [Gibbs 1928; Defay 1971]. The hysteresis phenomenon may appear even if surface energy is almost constant on a planar substrate when the surface tension strongly varies.

In (23), γ_1 and γ_2 are not assumed to be constant, but are defined at each point of Γ. This expression of the Young–Dupré boundary condition on the contact line Γ is not true in more complex cases. For example, in the case when the surface tension is a nonlocal functional of surfactant concentration, the surface tension is no longer the classical Legendre transformation of the surface energy relative to surfactant concentration and more complex behaviors can be foreseen. These behaviors can change the variation of the integral of the free energy as in the case of shells or in second-gradient models for which boundary conditions become more complex [Cosserat and Cosserat 1909; Toupin 1962; Germain 1973b; Noll and Virga 1990; Dell'Isola and Seppecher 1997]. In a further article [Gouin $\geq$ 2014], we will see this is also the case when the surface energy depends on the surface curvature as in membranes and vesicles [Helfrich 1973; Seifert 1997; Agrawal and Steigmann 2011].

Appendix: Geometrical preliminaries
[Kobayashi and Nomizu 1963; Aris 1989; Gouin and Kosiński 1998]

A.1 ***Expression of the virtual work of forces in capillarity.*** The hypotheses and notations are presented in Section 2.2.

Lemma 1. *We have the following relations*:

$$\delta \det F = \det F \operatorname{div} \boldsymbol{\zeta}, \tag{A.1}$$

$$\delta(F^{-1}\boldsymbol{n}) = -F^{-1}\frac{\partial \boldsymbol{\zeta}}{\partial \boldsymbol{x}}\boldsymbol{n} + F^{-1}\delta \boldsymbol{n}. \tag{A.2}$$

The proof of (A.1) comes from the so-called Jacobi identity,

$$\delta(\det F) = \det F \operatorname{tr}(F^{-1}\delta F),$$

and from

$$\delta F = \delta\Big(\frac{\partial \boldsymbol{x}}{\partial \boldsymbol{X}}\Big) = \frac{\partial \boldsymbol{\zeta}}{\partial \boldsymbol{X}}.$$

Then,

$$\operatorname{tr}(F^{-1}\delta F) = \operatorname{tr}\bigg(\frac{\partial \boldsymbol{X}}{\partial \boldsymbol{x}}\,\frac{\partial \boldsymbol{\zeta}}{\partial \boldsymbol{X}}\bigg) = \operatorname{tr}\bigg(\frac{\partial \boldsymbol{\zeta}}{\partial \boldsymbol{X}}\,\frac{\partial \boldsymbol{X}}{\partial \boldsymbol{x}}\bigg) = \operatorname{tr}\bigg(\frac{\partial \boldsymbol{\zeta}}{\partial \boldsymbol{x}}\bigg) = \operatorname{div} \boldsymbol{\zeta}.$$

The proof of (A.2) comes as follows:

$$\delta(F^{-1}\boldsymbol{n}) = \delta(F^{-1})\boldsymbol{n} + F^{-1}\,\delta\boldsymbol{n}.$$

But $F^{-1}F = \mathbf{1}$ implies

$$\delta(F^{-1})F + F^{-1}\,\delta F = 0,$$

and so also

$$\delta(F^{-1}) = -F^{-1}\frac{\partial \boldsymbol{\zeta}}{\partial \boldsymbol{X}}F^{-1} = -F^{-1}\frac{\partial \boldsymbol{\zeta}}{\partial \boldsymbol{x}},$$

which yields (A.2).

Lemma 2. *Let us consider the surface integral*

$$E = \iint_S \sigma\, ds.$$

Then the variation of E is,

$$\delta E = \iint_S \Big[\delta\sigma - \Big(\frac{2\sigma}{R_m}\boldsymbol{n}^T + \operatorname{grad}^T \sigma\,(\mathbf{1} - \boldsymbol{n}\boldsymbol{n}^T)\Big)\boldsymbol{\zeta}\Big]\, ds + \int_\Gamma \sigma \boldsymbol{n}'^T \boldsymbol{\zeta}\, dl. \qquad \text{(A.3)}$$

Relation (A.3) points out the extreme importance of knowing the variation of $\delta\sigma$. The variation δE of E drastically changes following the different possible behaviors of the surface energy.

The proof can be found as follows. The external normal $\boldsymbol{n}(\boldsymbol{x})$ to S is locally extended in the vicinity of S by the relation $\boldsymbol{n}(\boldsymbol{x}) = \operatorname{grad} d(\boldsymbol{x})$, where d is the distance of point $\boldsymbol{x}$ to S; for any vector field $\boldsymbol{w}$, we obtain [Kobayashi and Nomizu 1963; Aris 1989]

$$\operatorname{rot}(\boldsymbol{n} \times \boldsymbol{w}) = \boldsymbol{n} \operatorname{div} \boldsymbol{w} - \boldsymbol{w} \operatorname{div} \boldsymbol{n} + \frac{\partial \boldsymbol{n}}{\partial \boldsymbol{x}}\boldsymbol{w} - \frac{\partial \boldsymbol{w}}{\partial \boldsymbol{x}}\boldsymbol{n}.$$

From $\boldsymbol{n}^T \dfrac{\partial \boldsymbol{n}}{\partial \boldsymbol{x}} = 0$ and $\operatorname{div} \boldsymbol{n} = -\dfrac{2}{R_m}$, we deduce on S,

$$\boldsymbol{n}^T \operatorname{rot}(\boldsymbol{n} \times \boldsymbol{w}) = \operatorname{div} \boldsymbol{w} + \frac{2}{R_m}\boldsymbol{n}^T \boldsymbol{w} - \boldsymbol{n}^T \frac{\partial \boldsymbol{w}}{\partial \boldsymbol{x}}\boldsymbol{n}. \qquad \text{(A.4)}$$

Due to

$$E = \iint_S \sigma \det(\boldsymbol{n}, d_1\boldsymbol{x}, d_2\boldsymbol{x}),$$

where $d_1\boldsymbol{x}$ and $d_2\boldsymbol{x}$ are differential vectors associated with two coordinate lines of S, we get

$$E = \iint_{S_0} \sigma \det F \det(F^{-1}\boldsymbol{n}, d_1\boldsymbol{X}, d_2\boldsymbol{X}),$$

where $d_1\boldsymbol{x} = F\, d_1\boldsymbol{X}$ and $d_2\boldsymbol{x} = F\, d_2\boldsymbol{X}$. Then,

$$\delta E = \iint_{S_0} \delta\sigma \det F \det(F^{-1}\boldsymbol{n}, d_1\boldsymbol{X}, d_2\boldsymbol{X}) + \iint_{S_0} \sigma\, \delta(\det F \det(F^{-1}\boldsymbol{n}, d_1\boldsymbol{X}, d_2\boldsymbol{X})).$$

Due to Lemma 1 and the fact that $\boldsymbol{n}^T\boldsymbol{n} = 1$ implies $\boldsymbol{n}^T \delta\boldsymbol{n} = 0$,

$$\begin{aligned}
&\iint_{S_0} \sigma\, \delta(\det F \det(F^{-1}\boldsymbol{n}, d_1\boldsymbol{X}, d_2\boldsymbol{X})) \\
&= \iint_S \left[\sigma \operatorname{div} \boldsymbol{\zeta} \det(\boldsymbol{n}, d_1\boldsymbol{x}, d_2\boldsymbol{x}) + \sigma \det(\delta\boldsymbol{n}, d_1\boldsymbol{x}, d_2\boldsymbol{x}) - \sigma \det\left(\frac{\partial \boldsymbol{\zeta}}{\partial \boldsymbol{x}}\boldsymbol{n}, d_1\boldsymbol{x}, d_2\boldsymbol{x}\right)\right] \\
&= \iint_S \left(\operatorname{div}(\sigma\boldsymbol{\zeta}) - (\operatorname{grad}^T \sigma)\boldsymbol{\zeta} - \sigma \boldsymbol{n}^T \frac{\partial \boldsymbol{\zeta}}{\partial \boldsymbol{x}}\boldsymbol{n}\right) ds.
\end{aligned}$$

Relation (A.4) yields

$$\operatorname{div}(\sigma\boldsymbol{\zeta}) + \frac{2\sigma}{R_m}\boldsymbol{n}^T\boldsymbol{\zeta} - \boldsymbol{n}^T \frac{\partial \sigma\boldsymbol{\zeta}}{\partial \boldsymbol{x}}\boldsymbol{n} = \boldsymbol{n}^T \operatorname{rot}(\sigma\boldsymbol{n} \times \boldsymbol{\zeta}).$$

Then,

$$\begin{aligned}
&\iint_{S_0} \sigma\, \delta(\det F \det(F^{-1}\boldsymbol{n}, d_1\boldsymbol{X}, d_2\boldsymbol{X})) \\
&\qquad = \iint_S \left(-\frac{2\sigma}{R_m}\boldsymbol{n}^T + \operatorname{grad}^T \sigma\,(\boldsymbol{n}\boldsymbol{n}^T - \mathbf{1})\right)\boldsymbol{\zeta}\, ds + \iint_S \boldsymbol{n}^T \operatorname{rot}(\sigma\boldsymbol{n} \times \boldsymbol{\zeta})\, ds,
\end{aligned}$$

where $\operatorname{grad}^T \sigma\,(\boldsymbol{n}\boldsymbol{n}^T - \mathbf{1})$ belongs to the cotangent plane to S and we obtain (A.3).

A.1.1 *Variation of the internal energy.* Let us note that

$$\delta \iiint_D \rho\alpha\, dv = \iiint_D \rho\, \delta\alpha\, dv, \qquad \text{where } \delta\alpha = \frac{\partial\alpha}{\partial\rho}\,\delta\rho.$$

Due to the mass conservation,

$$\rho \det F = \rho_0(\boldsymbol{X}), \tag{A.5}$$

where ρ_0 is defined on D_0, the differentiation of (A.5) yields

$$\delta\rho \det F + \rho\, \delta(\det F) = 0,$$

and from Lemma 1 we get

$$\delta\rho = -\rho \operatorname{div} \boldsymbol{\zeta}.$$

Consequently, from $p = \rho^2 \dfrac{\partial \alpha}{\partial \rho}$ and $\operatorname{div}(p\boldsymbol{\zeta}) = p \operatorname{div} \boldsymbol{\zeta} + (\operatorname{grad} p)^T \boldsymbol{\zeta}$, we get

$$\begin{aligned} \delta \iiint_D \rho\alpha \, dv &= \iiint_D \rho \frac{\partial \alpha}{\partial \rho}\, \delta\rho \, dv = \iiint_D -p \operatorname{div} \boldsymbol{\zeta} \, dv \\ &= \iiint_D (\operatorname{grad} p)^T \boldsymbol{\zeta} \, dv - \iint_S p\boldsymbol{n}^T \boldsymbol{\zeta} \, ds. \end{aligned} \tag{A.6}$$

By taking into account (A.3), we immediately get (4).

A.2 *Study of a surfactant attached to fluid particles.*

A.2.1 *Proof of* (10). Under the hypotheses and notations of Section 3.2,

$$\begin{aligned} \iint_{S^*} c \, ds &= \iint_{S^*} \det(\boldsymbol{n}c, d_1\boldsymbol{x}, d_2\boldsymbol{x}) = \iint_{S_0^*} \det(FF^{-1}\boldsymbol{n}c, F d_1\boldsymbol{X}, F d_2\boldsymbol{X}) \\ &= \iint_{S_0^*} c(\det F) \det(F^{-1}\boldsymbol{n}, d_1\boldsymbol{X}, d_2\boldsymbol{X}) = \iint_{S_0^*} c(\det F)\boldsymbol{n}_0^T F^{-1}\boldsymbol{n} \, ds_0, \end{aligned}$$

where $\boldsymbol{n}_0^T \boldsymbol{n}_0 = 1$. Moreover, $\boldsymbol{n}^T d\boldsymbol{x} = 0 \Rightarrow \boldsymbol{n}^T F d\boldsymbol{X} = 0$, then $\boldsymbol{n}_0'^T = \boldsymbol{n}^T F$ is normal to S_0^*, and consequently,

$$\boldsymbol{n}_0^T = \frac{\boldsymbol{n}^T F}{\sqrt{(\boldsymbol{n}^T F F^T \boldsymbol{n})}}, \qquad \boldsymbol{n}^T = \frac{\boldsymbol{n}_0^T F^{-1}}{\sqrt{(\boldsymbol{n}_0^T F^{-1}(F^{-1})^T \boldsymbol{n}_0)}},$$

and from (9),

$$c \det F \sqrt{\boldsymbol{n}_0^T F^{-1}(F^{-1})^T \boldsymbol{n}_0} = c_0. \tag{A.7}$$

A.2.2 *Proof of* (11) *and* (12). With the notations of Section 3.2, (A.7) yields

$$\frac{dc}{dt} = -\frac{c_0 \dfrac{d(\det F)}{dt}}{(\det F)^2 \sqrt{(\boldsymbol{n}_0^T F^{-1}(F^{-1})^T \boldsymbol{n}_0)}} - \frac{c_0 \dfrac{d}{dt}(\boldsymbol{n}_0^T F^{-1}(F^{-1})^T \boldsymbol{n}_0)}{2 \det F (\boldsymbol{n}_0^T F^{-1}(F^{-1})^T \boldsymbol{n}_0)^{3/2}}.$$

But, $\dfrac{d(\det F)}{dt} = (\det F) \operatorname{div} \boldsymbol{u}$ and $\dfrac{d}{dt}(F^{-1}(F^{-1})^T) = -2F^{-1}\boldsymbol{D}(F^{-1})^T$. Then,

$$\frac{dc}{dt} + c(\operatorname{div} \boldsymbol{u} - \boldsymbol{n}^T \boldsymbol{D}\boldsymbol{n}) = 0.$$

The same calculation with δ in place of $\dfrac{d}{dt}$ yields immediately

$$\delta c + c\left[\operatorname{div} \boldsymbol{\zeta} - \boldsymbol{n}^T \frac{\partial \boldsymbol{\zeta}}{\partial \boldsymbol{x}} \boldsymbol{n}\right] = 0.$$

A.2.3 *Proof of* (14). From (12) and $\sigma = \sigma(c)$ we get

$$\delta\sigma = \kappa\left[\operatorname{div}\boldsymbol{\zeta} - \boldsymbol{n}^T\frac{\partial\boldsymbol{\zeta}}{\partial\boldsymbol{x}}\boldsymbol{n}\right], \qquad \text{with } \kappa(c) = -c\sigma'(c).$$

Consequently,

$$\iint_S \delta\sigma = \iint_S\left(\operatorname{div}(\kappa\boldsymbol{\zeta}) - \operatorname{grad}^T\kappa\,\boldsymbol{\zeta} - \kappa\boldsymbol{n}^T\frac{\partial\boldsymbol{\zeta}}{\partial\boldsymbol{x}}\boldsymbol{n}\right)ds.$$

But (A.4) implies

$$\boldsymbol{n}^T\operatorname{rot}(\kappa\boldsymbol{n}\times\boldsymbol{\zeta}) = \operatorname{div}(\kappa\boldsymbol{\zeta}) + \frac{2\kappa}{R_m}\boldsymbol{n}^T\boldsymbol{\zeta} - \boldsymbol{n}^T\frac{\partial(\kappa\boldsymbol{\zeta})}{\partial\boldsymbol{x}}\boldsymbol{n},$$

and

$$\boldsymbol{n}^T\frac{\partial(\kappa\boldsymbol{\zeta})}{\partial\boldsymbol{x}}\boldsymbol{n} = (\boldsymbol{n}^T\boldsymbol{\zeta}).(\operatorname{grad}^T\kappa\,\boldsymbol{n}) + \kappa\boldsymbol{n}^T\frac{\partial\boldsymbol{\zeta}}{\partial\boldsymbol{x}}\boldsymbol{n} = \operatorname{grad}^T\kappa\,\boldsymbol{n}\boldsymbol{n}^T\boldsymbol{\zeta} + \kappa\boldsymbol{n}^T\frac{\partial\boldsymbol{\zeta}}{\partial\boldsymbol{x}}\boldsymbol{n}.$$

Then,

$$\operatorname{div}(\kappa\boldsymbol{\zeta}) - \operatorname{grad}^T\kappa\,\boldsymbol{\zeta} - \kappa\boldsymbol{n}^T\frac{\partial\boldsymbol{\zeta}}{\partial\boldsymbol{x}}\boldsymbol{n} = -\frac{2\kappa}{R_m}\boldsymbol{n}^T\boldsymbol{\zeta} - \operatorname{grad}^T\kappa\,(\boldsymbol{1} - \boldsymbol{n}\boldsymbol{n}^T)\boldsymbol{\zeta} + \boldsymbol{n}^T\operatorname{rot}(\kappa\boldsymbol{n}\times\boldsymbol{\zeta}).$$

Due to

$$\iint_S \boldsymbol{n}^T\operatorname{rot}(\kappa\boldsymbol{n}\times\boldsymbol{\zeta})\,ds = \int_\Gamma \kappa\boldsymbol{n}'^T\boldsymbol{\zeta}\,dl,$$

we get

$$\iint_S -\delta\sigma\,ds = \iint_S\left[\frac{2\kappa}{R_m}\boldsymbol{n}^T + \operatorname{grad}^T\kappa\,(\boldsymbol{1} - \boldsymbol{n}\boldsymbol{n}^T)\right]\boldsymbol{\zeta}\,ds - \int_\Gamma \kappa\boldsymbol{n}'^T\boldsymbol{\zeta}\,dl,$$

and (A.3) yields

$$\delta E = -\iint_S\left[\frac{2\gamma}{R_m}\boldsymbol{n}^T + \operatorname{grad}^T\gamma(\boldsymbol{1} - \boldsymbol{n}\boldsymbol{n}^T)\right]\boldsymbol{\zeta}\,ds + \int_\Gamma \gamma\boldsymbol{n}'^T\boldsymbol{\zeta}\,dl.$$

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