Minimization of the Free Energy of Arbitrarily Curved Interfaces

Stig Ljunggren,* Jan Christer Eriksson,*,[1] and Peter A. Kralchevsky†

*Department of Chemistry/Physical Chemistry, Royal Institute of Technology, S-100 44 Stockholm, Sweden; and †Laboratory of Thermodynamics and Physico-Chemical Hydrodynamics, University of Sofia, Faculty of Chemistry, Sofia 1126, Bulgaria

The minimization of the free energy of a two-phase system with an interface of arbitrary curvature leads to an extremum (Laplace) condition containing the pressure difference, ΔP, between the two sides of the interface. The expression for ΔP is a function of the normal curvatures and of the resulting bending moments which are themselves functions of the normal curvatures, the mathematical form of which depends on the particular model for the interfacial bending energy that has been employed. On this basis, conclusions can be drawn about the equilibrium shape and curvatures of an interface, e.g., for bicontinuous microemulsions and vesicles. In addition, the pressure difference between the inside and the outside of surfactant-laden interfaces can be calculated. This pressure difference influences the work of formation of microemulsion droplets. A section devoted to the boundary conditions has also been included where in particular the case of a liquid meniscus attached to a cylindrically shaped solid surface is treated. © 1997 Academic Press

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INTRODUCTION

The reader no doubt recognizes that the proper way to proceed when deriving the equilibrium condition for an interface consists in minimizing the free energy, F, of the interface and its ambient bulk phases. The exact choice of this free energy, F, depends on the actual properties of the system and is not always equal to the Helmholtz free energy, F, as will be discussed under the section below entitled ''On the Choice of the Free Energy Function.''

For an ordinary fluid two-phase system minimization of the free energy results, first of all, in the well-known chemical potential condition for diffusive equilibrium with respect to the soluble components present. Further, the mathematical minimum condition for the free energy contains the pressure difference, ΔP, across the interface as a parameter. Solving for ΔP, this minimum condition takes the form of a Laplace equation.

In the present paper we discuss various forms of the generalized Laplace equation which are valid for interfaces with *variable curvature* and for an *arbitrary choice of dividing surface* between the two bulk phases. This rather complete surface-thermodynamic background is needed, especially when considering more exotic forms of surfactant aggregates for which the (curvature-dependent) interfacial free energy plays a key role.

On the basis of earlier works of Buff (1), Murphy (2), Melrose (3), and Eliassen (4), the first rigorous treatment of this kind was presented by Boruvka and Neumann (5) in 1977. Later on Kralchevsky (6) formulated an even more general thermodynamics of curved interfaces (encompassing the effect of elastic surface shear) subsequently commented by the present authors (7).

THE GENERALIZED LAPLACE EQUATION

The overall free energy, F, of the interface plus the adjacent bulk phases must, of course, have a minimum at equilibrium, i.e., the variation, δF, should be equal to zero when the surface is subject to an infinitesimal deformation from its equilibrium shape. Let the infinitesimal deformation vector be

$$\delta \mathbf{R} = \mathbf{s} + \psi \mathbf{n}, \quad [1]$$

where $\mathbf{s} = s^1 \mathbf{a}_1 + s^2 \mathbf{a}_2$ is in the tangent plane of the surface and $\mathbf{a}_1$ and $\mathbf{a}_2$ are the corresponding basis vectors, while $\psi \mathbf{n}$ is in the direction of the surface normal $\mathbf{n}$. After a complicated series of deduction steps Kralchevsky (6) arrived at the following expression for the variation of the free energy of a *closed* interfacial system with fixed overall volume comprising the interface and the adjacent phases, held at constant temperature, and for an arbitrary choice of dividing surface

$$\delta F = \Delta P \iint_S \psi dS + \iint_S (\gamma \delta \alpha + \zeta \delta \beta$$
$$+ B \delta H + \Theta \delta D) dS, \quad [2]$$

where the first integral represents the *pV*-work and where, apart from the term $\zeta d\beta$, the integrand of the second integral is identical to the expression for the infinitesimal work of surface deformation given by Gibbs (8). This expression for δF is valid both for the variation of the grand Ω-potential of an *open* interfacial system equilibrated at constant chemical potentials and for the variation of the Helmholtz free energy of an interface containing *insoluble* adsorbents provided that the chemical potentials of the components of the interface are constant throughout the interface so that there is no surface diffusion, and finally also for the mixed case, as shown in the Appendix. For completely *rigid* solid surfaces, however, Eq. [2] reduces to

$$\delta F = \iint_S (\gamma\delta\alpha + \zeta\delta\beta)dS \qquad [3]$$

because then we have to set ψ, δH, and δD equal to zero everywhere. This special case was treated earlier by Eriksson (9) and by Rusanov (10).

In Eq. [2] above, ΔP is the pressure difference between the two sides of the interface, $H = \frac{1}{2}(c_1 + c_2)$ the mean curvature, and $D = \frac{1}{2}(c_1 - c_2)$ the deviatoric curvature, c_1 and c_2 being the principal curvatures of the surface. All the variations, $\delta\alpha$, $\delta\beta$, δH, and δD are *local,* i.e., they are functions of the curvilinear surface coordinates (u^1 and u^2) with the following meaning: $\delta\alpha$ is the relative dilatation of the dividing surface element dS, and $\delta\beta$ is the shearing deformation, while δH and δD are the local variations of H and D, respectively. Further, γ is the ordinary (thermodynamic) surface tension, ζ the surface density of shearing free energy, while B and Θ are quantities related to the local bending moments of the interface which are defined below.

The sign conventions for the curvatures c_1 and c_2, and the pressure difference ΔP between the two sides of the interface are related to the direction of the surface normal, $\mathbf{n}$, which, as a rule, is assumed to be the outward normal in the case of a surfactant aggregate. This means that the surface normal is directed toward the phase on the (predominantly) convex side of the interface. Further, since according to differential geometry, $2H = -\nabla_s \cdot \mathbf{n}$, where $\nabla_s = \mathbf{a}^\alpha(\partial/\partial u^\alpha)$ is the surface gradient operator, it follows, e.g., that $H = -(1/R_1 + 1/R_2)/2$ (where R_1 and R_2 are curvature radii). More generally we adopt the convention that the curvatures c_i are negative when the corresponding principal curves of normal section are convex toward the phase to which the surface normal is pointing, and we define ΔP as the pressure jump when crossing the interface in the direction of the surface normal. This definition is the opposite of the more intuitive definition of ΔP, as, e.g., the pressure difference between the interior and the exterior of a droplet.

In terms of $\mathbf{s}$ and ψ the above variations may be written (6)

$$\delta\alpha = \mathbf{U}_S:\nabla_s\mathbf{s} - 2H\psi = \nabla_s\cdot\mathbf{s} - 2H\psi \qquad [4]$$

$$\delta\beta = \mathbf{q}:\nabla_s\mathbf{s} - 2D\psi \qquad [5]$$

$$\delta H = \mathbf{s}\cdot\nabla_s H + (H^2 + D^2)\psi + \tfrac{1}{2}\nabla_s^2\psi \qquad [6]$$

$$\delta D = \mathbf{s}\cdot\nabla_s D + 2HD\psi + \tfrac{1}{2}\mathbf{q}:\nabla_s\nabla_s\psi. \qquad [7]$$

Further, $\mathbf{U}_S = \mathbf{a}^1\mathbf{a}_1 + \mathbf{a}^2\mathbf{a}_2$ (where $\mathbf{a}_\alpha = \partial\mathbf{r}/\partial u^\alpha$ are basis vectors on the surface) is the surface identity tensor and $\mathbf{q}$, the surface deviatoric tensor, is defined by the relation

$$\mathbf{b} = H\mathbf{U}_S + D\mathbf{q}. \qquad [8]$$

Here, by definition, $\mathbf{b} = -\nabla_s\mathbf{n}$ is the curvature tensor (or second fundamental tensor) of the interface. Since the principal axes of the tensor $\mathbf{b}$ are identical to the principal axes of curvature, the same must hold for the tensor $\mathbf{q}$ as follows directly from its definition. These tensors obey the orthogonality relations

$$\mathbf{U}_S:\mathbf{U}_S = 2; \quad \mathbf{q}:\mathbf{q} = 2; \quad \mathbf{U}_S:\mathbf{q} = 0. \qquad [9]$$

Since $\mathbf{b}$ is, of course, diagonal in the basis of the principal curvatures (which are, in fact, the diagonal components, b_α^α of the curvature tensor $\mathbf{b}$), Eq. [8] tells us that the tensor $\mathbf{q}$ is also diagonal in the basis of the principal curvatures. This constitutes a certain limitation of the generality of Eq. [2], since the latter is based on the assumption that the rate of deformation tensor, $\mathbf{d}$, can be written in the form[2]

$$\mathbf{d}dt \equiv \nabla_s\delta\mathbf{R} \equiv \nabla_s\mathbf{s} - \psi\mathbf{b} = \tfrac{1}{2}\delta\alpha\mathbf{U}_S + \tfrac{1}{2}\delta\beta\mathbf{q} \qquad [10]$$

which, in turn, requires $\mathbf{d}$ to be diagonal in the basis of the principal curvatures. For symmetry reasons, however, this requirement is automatically satisfied in the case of cylindrical and spherical surfactant aggregates. Further, we note that Eqs. [4] and [5] follow from the definitions $\delta\alpha = \mathbf{U}_S:\mathbf{d}dt$ and $\delta\beta = \mathbf{q}:\mathbf{d}dt$. Equations [6] and [7] were derived by Eliassen (4) (Eq. [7] implicitly).

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[2] For a definition of $\mathbf{d}$, which is more general than Eq. [10], see Eq. [172] below.

The equilibrium condition, $\delta F = 0$ at constant T and overall volume V can now be written (irrespective of whether the system is closed, partially closed or completely open)

$$\delta F = \iint_S [\boldsymbol{\gamma}_S : \nabla_S \mathbf{s} + (B\nabla_S H + \Theta\nabla_S D) \cdot \mathbf{s}]dS$$
$$+ \iint_S [\Delta P - 2H\gamma - 2D\zeta + (H^2 + D^2)B$$
$$+ 2HD\Theta]\psi dS + \iint_S \tfrac{1}{2}(B\mathbf{U}_S + \Theta\mathbf{q}):\nabla_S\nabla_S\psi dS = 0,$$
[11]

where we have introduced the surface tension tensor

$$\boldsymbol{\gamma}_S = \gamma\mathbf{U}_S + \zeta\mathbf{q} \qquad [12]$$

which is likewise diagonal in the basis of the principal curvatures.

According to the ordinary procedure of variational calculus, ψ and $\nabla_S\nabla_S\psi$ (or $\mathbf{s}$ and $\nabla_S\mathbf{s}$) cannot be regarded as being independent of each other. On the contrary, a procedure equivalent to a partial integration has to be undertaken in order to convert the integrals in the expression for δF into integrals that contain only ψ (or $\mathbf{s}$) itself. Considering ψ and its derivatives as being independent would be similar to setting the terms containing the factors $\partial f/\partial y$ and $\partial f/\partial y'$ separately equal to zero in the expression for the variation of I obtained when minimizing the integral $I = \int f(x, y, y')dx$. For this very reason, the argument invoked by Neogi and Friberg (11) is false and their resulting ΔP expression of restricted validity. The same criticism is implicitly valid also for the derivation of an expression for ΔP by Melrose (3) using parallell displacements.

We now make use of a divergence theorem for curved surfaces due to Green, Gauss, and Ostrogradsky (cf. Weatherburn (12)) and obtain

$$\iint_S \boldsymbol{\gamma}_S:\nabla_S\mathbf{s}dS = \int_C \mathbf{m}\cdot\boldsymbol{\gamma}_S\cdot\mathbf{s}dl$$
$$- \iint_S [\nabla_S\cdot\boldsymbol{\gamma}_S + 2H\mathbf{n}\cdot\boldsymbol{\gamma}_S]\cdot\mathbf{s}dS, \quad [13]$$

where C denotes the boundary curve which limits the interface and where the last term in the last integral containing $2H$ vanishes because $\boldsymbol{\gamma}_S$ is a tensor in the tangent plane of the surface. The unit vector $\mathbf{m}$ is perpendicular both to the tangent of the boundary curve and to the normal vector of the surface at the boundary and it is directed outward. Thus,

$$\iint_S \boldsymbol{\gamma}_S:\nabla_S\mathbf{s}dS$$
$$= -\iint_S (\nabla_S\cdot\boldsymbol{\gamma}_S)\cdot\mathbf{s}dS + \int_C \mathbf{m}\cdot\boldsymbol{\gamma}_S\cdot\mathbf{s}dl. \quad [14]$$

We next introduce the surface bending moment tensor

$$\mathbf{M}_S = \tfrac{1}{2}(B\mathbf{U}_S + \Theta\mathbf{q}) \qquad [15]$$

which is also supposed to be diagonal in the basis of the principal curvatures. The corresponding eigenvalues are denoted by M_1 and M_2. Using another surface divergence theorem for curved surfaces, we obtain

$$\iint_S \tfrac{1}{2}(B\mathbf{U}_S + \Theta\mathbf{q}):\nabla_S\nabla_S\psi dS$$
$$\equiv \iint_S \mathbf{M}_S:\nabla_S\nabla_S\psi dS = \iint_S \psi\nabla_S\nabla_S:\mathbf{M}_S$$
$$+ \int_C \mathbf{m}\cdot\mathbf{M}_S\cdot\nabla_S\psi dl - \int_C \psi(\nabla_S\cdot\mathbf{M}_S)\cdot\mathbf{m}dl \quad [16]$$

and finally we get

$$\delta F = \iint_S [(B\nabla_S H + \Theta\nabla_S D) - \nabla_S\cdot\boldsymbol{\gamma}_S]\cdot\mathbf{s}dS$$
$$+ \iint_S \psi[\nabla_S\nabla_S:\mathbf{M}_S + \Delta P - 2H\gamma - 2D\zeta$$
$$+ (H^2 + D^2)B + 2HD\Theta]dS + \int_C \mathbf{m}\cdot\mathbf{M}_S\cdot\nabla_S\psi dl$$
$$- \int_C \psi(\nabla_S\cdot\mathbf{M}_S)\cdot\mathbf{m}dl + \int_C \mathbf{m}\cdot\boldsymbol{\gamma}_S\cdot\mathbf{s}dl = 0. \quad [17]$$

The expression within brackets in the first integral of Eq. [17] represents the tangential force acting on the surface element dS, and the expression within brackets in the second integral represents the corresponding normal force. These expressions are, in fact, nothing else than the functional derivatives $\delta F/\delta\mathbf{s}(\mathbf{r})$ and $\delta F/\delta\psi(\mathbf{r})$, respectively, with $\mathbf{r}$ denoting the coordinate of the surface element.

The scalar surface tension γ is related to the tensor $\boldsymbol{\gamma}_S$ in the following way:

$$\gamma = \tfrac{1}{2}\mathbf{U}_S:\boldsymbol{\gamma}_S = \tfrac{1}{2}\mathrm{Tr}(\boldsymbol{\gamma}_S) = \tfrac{1}{2}(\gamma_1 + \gamma_2), \qquad [18]$$

where γ_1 and $\boldsymbol{\gamma}_2$ (or more precisely γ_1^1 and γ_2^2) are the principal components of $\boldsymbol{\gamma}_S$. In an analogue way the shearing tension is given by the relation

$$\zeta = \tfrac{1}{2}\mathbf{q}:\boldsymbol{\gamma}_S = \tfrac{1}{2}(\gamma_1 - \gamma_2). \qquad [19]$$

From Eq. [16] we directly obtain the Euler–Lagrange equations for the variational problem with respect to the variations $\mathbf{s}$ and ψ. First,

$$\nabla_S\gamma + \nabla_S\cdot(\zeta\mathbf{q}) - B\nabla_S H - \Theta\nabla_S D = 0 \qquad [20]$$

which is the condition for lateral equilibrium, and, second,

$$\Delta P = 2H\gamma + 2D\zeta - (H^2 + D^2)B - 2HD\Theta - \nabla_S\nabla_S:\mathbf{M}_S$$

[21]

which is the condition for equilibrium in the direction perpendicular to the interface.

It is worth noting that the expression [21] for ΔP is nothing else than an *extremum condition for the free energy*. To calculate the equilibrium shape of the interface under given conditions, in addition, the numerical value of ΔP must be known. Equation [21] can also be regarded as a generalized Laplace equation. We stress that assigning a value to ΔP is an integral part of the minimization of the free energy and not an extra, unrelated condition. Moreover, Eq. [20] is the condition for the chemical potentials to be constant within the interface.

Upon choosing the surface of tension as the dividing surface for an isotropic interface with constant curvature, Eq. [21] reduces to the familiar form $\Delta P = 2H\gamma$.

THE BOUNDARY CONDITIONS

Let us now consider the integrals over the boundary, C, occurring in Eq. [17]:

$$\int_C \mathbf{m}\cdot\mathbf{M}_S\cdot\nabla_S\psi dl - \int_C \psi(\nabla_S\cdot\mathbf{M}_S)\cdot\mathbf{m} dl + \int_C \mathbf{m}\cdot\boldsymbol{\gamma}_S\cdot\mathbf{s} dl.$$

[22]

These integrals will, of course, be equal to zero if $\nabla_S\psi$, ψ, and $\mathbf{s}$ all vanish on the boundary.

The coefficients in front of these variables in the integrals over the boundary represent the *forces* or bending *moments* acting on the boundary. Thus, $\mathbf{m}\cdot\boldsymbol{\gamma}_S$ in principle yields the stretching force acting on the boundary in the tangent plane of the surface (not necessarily directed along $\mathbf{m}$), while $(\nabla_S\cdot\mathbf{M}_S)\cdot\mathbf{m}$ yields the force in the direction of the surface normal at the boundary, and, finally, $\mathbf{m}\cdot\mathbf{M}_S$ yields the bending moment acting on the boundary.

If any of these forces (moments) is equal to zero on the whole boundary (or part of it) this means that the corresponding variation can be let free on the same part of the boundary. This is what is referred to in variational calculus as *natural boundary conditions*.

The expression $\mathbf{m}\cdot\boldsymbol{\gamma}_S$ for the stretching force is a two-dimensional analogue to the expression $\boldsymbol{\sigma}\cdot\mathbf{n} = \mathbf{n}\cdot\boldsymbol{\sigma}$ in the three-dimensional case for the force acting at a planar surface with the unit normal vector $\mathbf{n}$, and $\boldsymbol{\sigma}$ being the bulk stress tensor. However, for reasons to be further discussed in a

following section, $\boldsymbol{\gamma}_S$ in this expression will have to be replaced by yet another surface tension tensor, $\boldsymbol{\sigma}_S$.

The meaning of the bending moment expression $\mathbf{m}\cdot\mathbf{M}_S$ is most simply understood if, for example, we assume that the vector $\mathbf{m}$ is directed along the basis vector $\mathbf{a}_2$ in the surface at the boundary. The relevant components of $\mathbf{m}\cdot\mathbf{M}_S$ will then be M_{21} and M_{22} of which M_{21} represents a torque on the boundary about the vector $\mathbf{m}$ and M_{22} a torque about the tangent vector of the boundary curve.

The meaning of the term $(\nabla_S\cdot\mathbf{M}_S)\cdot\mathbf{m}$ for the normal force on the boundary can be visualized as follows. Assume, for instance, that $\mathbf{m}$ points along the u^1 coordinate axis which, in turn, points in a principal direction of the

$$(\nabla_S\cdot\mathbf{M}_S)\cdot\mathbf{m} = (\nabla_S\cdot\mathbf{M}_S)\cdot\mathbf{a}_1 \qquad [23]$$

which is the two-dimensional analogue to the expression for the shearing stress in a loaded beam in the one-dimensional case.

The above considerations are of particular importance in connection with bicontinuous microemulsions and so-called L_3 phases with internal interfacial structures resembling infinite periodic minimal surfaces. The question about the external closure of such a lattice is, however, unsolved so far (cf. Ref. (13)).

ON THE CHOICE OF THE FREE ENERGY FUNCTION

The correct thermodynamic analysis of a system consists of two indispensable steps. First, the boundaries of the system must be carefully defined; i.e., it must be prescribed which parts of the universe that belong to the system and which do not. Second, the nature of the system must be clarified and it should be clearly stated which of the (independent) thermodynamic variables that are to be held constant and which will be allowed to vary. Surprisingly, these rather self-evident rules are often overlooked in the literature.

For a interface with components that are soluble in the adjacent bulk phases (as is often the case), the interface has to be treated as a completely open system, for which, at equilibrium, the chemical potentials are kept constant. Further, if the pressure on the two sides of the interface are not equal, a small displacement of the interface will always be accompanied by mechanical PV-work. In order to account for this, the system definition cannot be limited to the interface itself but portions of the bulk phases on both sides of the interface must also be included. Assuming the entire system to be an open one such that matter can pass through its borders, we can, without limitation, claim that it has a constant volume. It now follows that the variables to be held constant are μ_i, T, and V which are the characteristic variables of the grand canonical ensemble. The appropriate potential is thus the grand potential, $\Omega \equiv F - \Sigma_i N_i\mu_i$, of

the interface plus those parts of the bulk phases that belong to the system.

On the other hand, if there is no exchange at all of matter between the interfacial system and the adjacent bulk phases, the appropriate free energy to invoke is the overall Helmholtz free energy, F. In this case the appropriate variables are N_i, T, and V.

For *partially open* interfacial systems the appropriate free energy to consider is a mixed Ω-potential/Helmholtz free energy where the Ω-potential part refers to the soluble and the Helmholtz free energy part to the insoluble components.

THE GENERAL LAPLACE EQUATION IN THE FORM DUE TO BORUVKA AND NEUMANN

For a interface with components that are soluble in the bulk phases one can easily derive a generalized Gibbs surface tension equation (at constant temperature):

$$d\gamma = -\sum_i \Gamma_i \, d\mu_i + B\,dH + \Theta\,dD \qquad [24]$$

showing that the surface tension γ generally depends on the mean and deviatoric curvatures, H and D. Accordingly, by way of definition

$$B = (\partial\gamma/\partial H)_{T,\mu_i,D} \qquad [25]$$

and

$$\Theta = (\partial\gamma/\partial D)_{T,\mu_i,H} \qquad [26]$$

Switching to the Gaussian curvature $K = c_1 c_2 = H^2 - D^2$ as independent variable instead of the deviatoric curvature, D, we can write Eq. [24] in the form employed by Markin *et al.* (14)

$$d\gamma = -\sum_i \Gamma_i \, d\mu_i + C_1 \, dH + C_2 \, dK \qquad [27]$$

where

$$C_1 = (\partial\gamma/\partial H)_{T,\mu_i,K} \quad C_2 = (\partial\gamma/\partial K)_{T,\mu_i,H}. \qquad [28]$$

The coefficients B, Θ and C_1, C_2 are interrelated through the relationships

$$B = C_1 + 2C_2 H \qquad [29]$$

$$\Theta = -2C_2 D. \qquad [30]$$

In terms of the Gaussian curvature, K, and the new variables C_1 and C_2, the Euler–Lagrange Eqs. [20] and [21] can be written in the following alternative way

$$\nabla_S\gamma - C_1\nabla_S H - C_2\nabla_S K + \nabla_S \cdot (\zeta\mathbf{q}) = 0 \qquad [31]$$

and

$$\Delta P = 2H\gamma + 2\sqrt{H^2 - K}\,\zeta - C_1(2H^2 - K)$$
$$- 2C_2 HK - \tfrac{1}{2}\nabla_S^2 C_1 - 2H\nabla_S^2 C_2 + \mathbf{b}{:}\nabla_S\nabla_S C_2. \qquad [32]$$

This is just another way of writing the minimum free energy condition for the interface. It is easily shown (7) that Eq. [32] agrees with the corresponding generalized Laplace equation derived by Boruvka and Neumann (5) taking into account their differing definition of the (isotropic, $\zeta = 0$) interfacial tension.[3] It is also in agreement with a somewhat less general expression, more recently derived by Ou-Yang and Helfrich (15) by a variational method, for the Laplace pressure of a closed (in the geometrical sense) vesicle membrane.

DIFFERENT KINDS OF SURFACE TENSIONS

The local work of deformation per unit surface may be written (2)

$$\delta w_S = \gamma\delta\alpha + \zeta\delta\beta + B\delta H + \Theta\delta D. \qquad [33]$$

Apart from the term $\zeta\delta\beta$, this expression was already proposed by Gibbs (8). Gibbs tacitly assumed that $\gamma_1 = \gamma_2$ which yields $\zeta = 0$, that probably holds for most ordinary surfactant interfaces in the liquid state (as opposed to the gel state) but not necessarily for interfaces of a more complicated structure such as biological membranes or, for that part, rubber membranes and solid surfaces. Here, γ is the usual (thermodynamic) surface tension.

When the dividing surface is chosen to be coincident with the surface of tension (s.o.t.), the tensor $\boldsymbol{\gamma}_S$ will actually yield the ''hydrostatic'' mechanical tensions in the tangential plane of the surface. However, especially with the comparatively thick interfaces encountered in surfactant aggregates, the use of the s.o.t. is mostly nonfeasible. The reason for this is that for these thick interfaces the s.o.t. is usually located far away from any natural choice of the dividing surface such as the hydrocarbon/water interface, and sometimes even the calculation of the position of the s.o.t. represents a complicated mathematical problem in its own right. Under such circumstances the s.o.t. concept is rather useless for practical purposes.

At other dividing surfaces than the s.o.t. the ''hydrostatic'' tensions in the tangential plane of the surface at a given

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[3] The Boruvka and Neumann surface tension, γ^{BN}, is related to the γ we use by $\gamma^{BN} = \gamma - BH - \Theta D$ (6).

point of the surface are given by a surface tensor, $\boldsymbol{\sigma}_S$, different from $\boldsymbol{\gamma}_S$. The tensor $\boldsymbol{\sigma}_S$ can be written

$$\boldsymbol{\sigma}_S = \sigma \mathbf{U}_S + \eta \mathbf{q} \qquad [34]$$

with

$$\sigma = \tfrac{1}{2}\mathbf{U}_S{:}\boldsymbol{\sigma}_S = \tfrac{1}{2}(\sigma_1 + \sigma_2) \quad \eta = \tfrac{1}{2}\mathbf{q}{:}\boldsymbol{\sigma}_S = \tfrac{1}{2}(\sigma_1 - \sigma_2) \quad [35]$$

σ_1 and σ_2 (or more exactly σ_1^1 and σ_2^2) being the principal components of the surface tensor $\boldsymbol{\sigma}_S$, assuming, of course, that the tensor $\boldsymbol{\sigma}_S$ is diagonal in the basis of the principal curvatures.

The relation between σ and γ has been worked out by Gurkov and Kralchevsky (16). The result is that the infinitesimal work of surface deformation amounts to

$$\delta w_S = (\sigma + \tfrac{1}{2}BH + \tfrac{1}{2}\Theta D)\delta\alpha$$
$$+ (\eta + \tfrac{1}{2}BD + \tfrac{1}{2}\Theta H)\delta\beta + B\delta H + \Theta\delta D \quad [36]$$

A comparison with the previous expression [33] for δw_S then shows that

$$\gamma = \sigma + \tfrac{1}{2}BH + \tfrac{1}{2}\Theta D \qquad [37]$$

$$\zeta = \eta + \tfrac{1}{2}BD + \tfrac{1}{2}\Theta H \qquad [38]$$

with

$$B = \mathbf{U}_S{:}\mathbf{M}_S = M_1 + M_2 \qquad [39]$$

$$\Theta = \mathbf{q}{:}\mathbf{M}_S = M_1 - M_2, \qquad [40]$$

where M_1 and M_2 (or more exactly M_1^1 and M_2^2) are the principal values of the bending moment tensor $\mathbf{M}_S$ which is diagonal in the basis of the principal curvatures, i.e., in the principal axes of the curvature tensor, $\mathbf{b}$.

The basic reason for the difference between $\boldsymbol{\gamma}_S$ and $\boldsymbol{\sigma}_S$ is apparent already from the expression [33] for δw_S above which shows that $\delta w_S = \gamma\delta\alpha$ only holds if $\delta\beta$, δH, and δD are equal to zero, i.e., if H and D are kept constant. This means that a curved surface should result from the dilatation, which implies that the different layers of the interface parallel to the dividing surface will be stretched to different degrees, or differently stated, a dilatation is always accompanied by bending which gives rise to the extra terms in the expression for σ, which may also be written

$$\gamma = \sigma + \tfrac{1}{2}(M_1c_1 + M_2c_2). \qquad [41]$$

It is obvious that $\tfrac{1}{2}(M_1c_1 + M_2c_2)\delta\alpha$ is the work of bending

that accompanies the dilatation under conditions of constant H and D.

In terms of σ and η the generalized Laplace equation can now be written as

$$\Delta P = 2H\sigma + 2D\eta - \nabla_S\nabla_S{:}\mathbf{M}_S \qquad [42]$$

or, since $\sigma = (\sigma_1 + \sigma_2)/2$ and $\eta = (\sigma_1 - \sigma_2)/2$, even more simply as

$$\Delta P = c_1\sigma_1 + c_2\sigma_2 - \nabla_S\nabla_S{:}\mathbf{M}_S, \qquad [43]$$

where c_1 and c_2 are the two principal curvatures of the surface. Thus, even if σ_1 and σ_2 were both equal to zero, the bending moment alone might give rise to a ΔP different from zero, just as a construction beam can accept a distributed load although there is no longitudinal tension in the beam. On the other hand, if $\sigma_1 = \sigma_2$, and if $\mathbf{M}_S$ is constant we recover the usual Laplace equation.

From the argument above it should be clear that the pure stretching force acting on the boundary should equal $\mathbf{m}\cdot\boldsymbol{\sigma}_S$ and not $\mathbf{m}\cdot\boldsymbol{\gamma}_S$.

Finally, we note that Eq. [21] can also be written

$$\Delta P = 2H\gamma + 2D\zeta - (M_1c_1^2 + M_2c_2^2) - \nabla_S\nabla_S{:}\mathbf{M}_S, \quad [44]$$

where

$$\pi_c = -(M_1c_1^2 + M_2c_2^2) \qquad [45]$$

may be termed the *curvature pressure,* and we have

$$\Delta P = 2H\gamma + 2D\zeta + \pi_c - \nabla_S\nabla_S{:}\mathbf{M}_S. \qquad [46]$$

The curvature pressure is zero at the surface of tension where the tensor components M_1 and M_2 vanish. However, as was pointed out above, to employ the surface of tension as dividing surface is generally inconvenient for surfactant aggregates and surfactant-laden interfaces.

FURTHER DIGRESSION ON THE BOUNDARY CONDITIONS

Variational Derivation of the Young Equation

When deriving Eqs. [20] and [21] we used variations at *fixed* boundaries, i.e., we set $\mathbf{s} = 0$, $\psi = 0$, and $\nabla_S\psi = 0$ at the contour C in Eq. [17]. The next step is to derive the respective boundary conditions by using variations at *movable* boundaries.

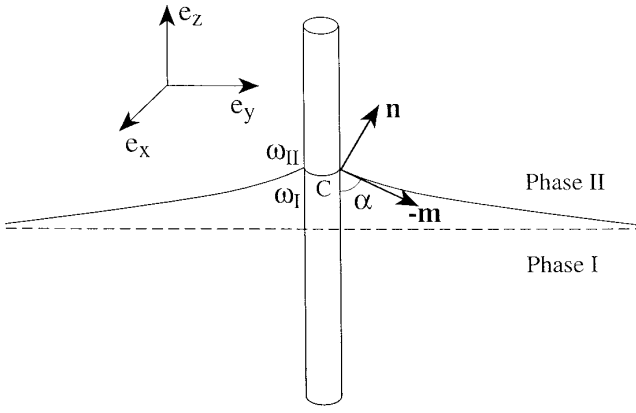This time we start by considering a meniscus attached to

FIG. 1. A liquid meniscus which is attached to a solid cylindrical needle. ω_I is the excess free energy of the solid/phase I interface, and, ω_{II}, correspondingly, of the solid/phase II interface.

a vertical solid cylinder (Fig. 1). (Later we will consider the general case.) The variation of points on the contact line, C, can be presented in the form

$$\delta \mathbf{R} = \varepsilon \mathbf{e}_z + \lambda \mathbf{t} \quad (\mathbf{R} \in C), \qquad [47]$$

where $\mathbf{e}_z$ is the unit vector along the vertical and $\mathbf{t}$ is the running tangent to the contact line; ε and λ denote two independent infinitesimal displacements. $\delta \mathbf{R}$ has a zero projection along the normal to the cylinder. Note also that

$$\mathbf{m} \cdot \mathbf{t} = 0 \quad \mathbf{n} \cdot \mathbf{t} = 0. \qquad [48]$$

From Eqs. [1], [47], and [48] one obtains

$$\mathbf{s}|_{\mathbf{R} \in C} = \varepsilon \mathbf{e}_z \cdot \mathbf{U}_S + \lambda \mathbf{t}, \quad \psi|_{\mathbf{R} \in C} = \varepsilon \mathbf{e}_z \cdot \mathbf{n}. \qquad [49]$$

The expression for the variation, δF, Eq. [17], now contains an additional term, *viz.*

$$\int_C (\omega_I - \omega_{II}) \varepsilon \, dl, \qquad [50]$$

where ω_I and ω_{II} are the surface densities of the grand thermodynamic potential for the solid–fluid I and solid–fluid II interfaces, respectively. In fact, Eq. [50] expresses the variation of the energy of wetting of the solid due to the variation in the position of the contact line. Since Eqs. [20] and [21] hold, the surface integrals disappear and from Eqs. [17] and [50] we get

$$\delta F = \int_C [\mathbf{m} \cdot \mathbf{M} \cdot \nabla_S \psi - \mathbf{m} \cdot (\nabla_S \cdot \mathbf{M}) \psi$$
$$+ \mathbf{m} \cdot \boldsymbol{\gamma}_S \cdot \mathbf{s} + (\omega_I - \omega_{II}) \varepsilon] \, dl = 0. \qquad [51]$$

To have $\delta F = 0$, the expressions multiplying the independent variations $\nabla_S \psi$, ε, and λ must be equal to zero. As $\nabla_S \psi$ represents the change of meniscus slope at the contact line at a fixed position of the contact line, one has

$$\mathbf{t} \cdot \nabla_S \psi = 0, \quad \mathbf{m} \cdot \nabla_S \psi \neq 0. \qquad [52]$$

Then from Eqs. [49], [51], and [52] we have the following conditions for equilibrium at the contact line

$$\mathbf{m} \cdot \mathbf{M} \cdot \mathbf{m} = 0 \qquad [53]$$

$$\mathbf{m} \cdot \boldsymbol{\gamma}_S \cdot \mathbf{e}_z - \mathbf{m} \cdot (\nabla_S \cdot \mathbf{M})(\mathbf{n} \cdot \mathbf{e}_z) + \omega_I - \omega_{II} = 0 \quad [54]$$

$$\mathbf{m} \cdot \boldsymbol{\gamma}_S \cdot \mathbf{t} = 0. \qquad [55]$$

The left-hand sides of Eqs. [53], [54], and [55] are the coefficients multiplying the independent variations $\nabla_S \psi$, ε, and λ, respectively. Below, we analyze the implications of these equations.

Let us start with Eq. [55]. In keeping with Eqs. [8] and [12] we derive from Eq. [55] that

$$\mathbf{m} \cdot \mathbf{b} \cdot \mathbf{t} = 0 \qquad [56]$$

showing that the curvature tensor, $\mathbf{b}$, must be diagonal in the basis formed by the vectors $\mathbf{m}$ and $\mathbf{t}$ at the contact line. In other words, we can write

$$\mathbf{b} = c_1 \mathbf{mm} + c_2 \mathbf{tt} \quad \text{for } \mathbf{R} \in C. \qquad [57]$$

Besides, from Eqs. [8] and [57] we can derive

$$\mathbf{m} \cdot \mathbf{q} \cdot \mathbf{m} = 1 \quad \text{for } \mathbf{R} \in C. \qquad [58]$$

Next we consider Eq. [53]. In accordance with Eqs. [15] and [58] we get from Eq. [53]

$$B + \Theta = 0 \quad \text{for } \mathbf{R} \in C. \qquad [59]$$

To elucidate the physical meaning of this equation we recall that according to Eqs. [39] and [40],

$$B = M_1 + M_2, \quad \Theta = M_1 - M_2, \qquad [60]$$

where M_1 and M_2 are eigenvalues of the tensor $\mathbf{M}$. By analogy with Eq. [57] one can write

$$\mathbf{M} = M_1 \mathbf{mm} + M_2 \mathbf{tt}, \quad \mathbf{R} \in C. \qquad [61]$$

Substitution of Eq. [60] into Eq. [59] yields

$$M_1 = 0, \quad \mathbf{R} \in C. \qquad [62]$$

For the mechanical meaning of the components of $\mathbf{M}$, see

Eq. [60] and Fig. 4c in Ref. (16). Equation [62] implies that the interfacial bending moment around the tangent **t** must be zero at the contact line.

Finally we consider Eq. [54]. Since $\mathbf{t} \cdot \mathbf{e}_z = 0$, one obtains

$$\mathbf{m} \cdot \boldsymbol{\gamma}_S \cdot \mathbf{e}_z = \mathbf{m} \cdot \boldsymbol{\gamma}_S \cdot \mathbf{m}(\mathbf{m} \cdot \mathbf{e}_z). \qquad [63]$$

Besides, $\mathbf{m} \cdot \mathbf{e}_z = \cos \alpha$, where α is the contact angle (see Fig. 1). Then, from Eqs. [12], [54], [58], and [63] we derive

$$(\gamma + \zeta)\cos \alpha - \mathbf{m} \cdot (\nabla_S \cdot \mathbf{M})\sin \alpha = \omega_{\mathrm{II}} - \omega_{\mathrm{I}}. \qquad [64]$$

If the stresses in the liquid interface are laterally isotropic, i.e., $\eta = 0$ in Eq. [34], then from Eqs. [37] and [38] we get

$$\gamma + \zeta = \sigma + \tfrac{1}{2}(B + \Theta)(H + D) = \sigma \quad \mathbf{R} \in C. \qquad [65]$$

At the last step we have utilized Eq. [59]. Moreover, it is known that

$$\sigma^{\alpha(n)} = -\mathbf{a}^{\alpha} \cdot (\nabla_S \cdot \mathbf{M}), \qquad [66]$$

where $\sigma^{\alpha(n)}$ is the transversal component of the surface stress tensor:

$$\boldsymbol{\sigma} = \boldsymbol{\sigma}_S + \mathbf{a}_{\alpha}\mathbf{n}\sigma^{\alpha(n)}. \qquad [67]$$

In view of Eqs. [65]–[67], Eq. [64] can be represented in the form

$$\mathbf{m} \cdot \boldsymbol{\sigma} \cdot \mathbf{e}_z = \omega_{\mathrm{II}} - \omega_{\mathrm{I}}. \qquad [68]$$

This equation will be useful when comparing with the mechanical approach to the boundary conditions treated below.

In the simplest case when the interfacial shearing and bending effects are negligible, one has $\zeta = 0$, $\gamma = \sigma$, and $\mathbf{M} = 0$, and Eq. [64] reduces to the classical Young equation:

$$\sigma \cos \alpha = \omega_{\mathrm{II}} - \omega_{\mathrm{I}}. \qquad [69]$$

For a Helfrich interface with curvature-dependent interfacial tension

$$\gamma = \gamma_0 + 2k_c(H - H_0)^2 + \overline{k}_c K \qquad [70]$$

we have

$$B = B_0 + 2(2k_c + \overline{k}_c)H, \quad \Theta = -2\overline{k}_c D, \qquad [71]$$

where k_c and $\overline{k}_c$ are the two curvature elastic moduli and B_0

is the bending moment of a flat interface, which is related to the spontaneous curvature, H_0:

$$B_0 = -4k_c H_0. \qquad [72]$$

Substitution of Eq. [71] in Eq. [59] yields

$$B_0 + 2k_c c_1 + 2(k_c + \overline{k}_c)c_2 = 0, \quad \mathbf{R} \in C. \qquad [73]$$

For the special case of axial symmetry, like the one depicted in Fig. 1, we can write

$$c_1 = \frac{u''}{[1 + (u')^2]^{3/2}} \quad c_2 = \frac{u'}{r[1 + (u')^2]^{1/2}}, \qquad [74]$$

where $z = u(r)$ determines the meniscus shape. Hence, Eq. [73] is a boundary condition relating the derivatives u' and u''. It is interesting to note that the boundary condition, Eq. [73] contains $\overline{k}_c$. Yet, $\overline{k}_c$ does not enter the generalized Laplace equation, cf. Ref. (17).

In addition, for a Helfrich interface (17), we have,

$$\nabla_S \cdot \mathbf{M} = 2k_c \nabla_S H. \qquad [75]$$

Then, in accordance with Eqs. [59], [64], and [65] one obtains the generalized Young equation for a Helfrich interface such that $\eta = 0$:

$$\sigma \cos \alpha + 2k_c \frac{\partial H}{\partial m} \sin \alpha = \omega_{\mathrm{II}} - \omega_{\mathrm{I}}, \qquad [76]$$

where $\partial H/\partial m$ denotes the directional derivative along $\mathbf{m}$.

Balances of the Linear and Angular Momenta at a Contact Line

Stresses and moments. Next we present a *hydrostatic* derivation of the balances of the linear and angular momenta at a three-phase contact line. This derivation is made after Podstrigach and Povstenko (18). In spite of being purely phenomenological, the hydrostatic approach is conceptually transparent and yields results in quite a general form.

Let us consider a volume, V, containing a part of the contact line, C, and portions of the adjacent three phases (see Fig. 2). V_1, V_2, and V_3 are the portions of phases 1, 2, and 3 confined in the volume V; L_{12}, L_{13}, and L_{23} are the intersection lines of the surface of volume V with the interfaces S_{12}, S_{13}, and S_{23}, respectively. The lines L_{12}, L_{13}, and L_{23} divide the surface of the volume V into three portions, called A_1, A_2, and A_3, whose outer normals are denoted by $\mathbf{n}_1$, $\mathbf{n}_2$, and $\mathbf{n}_3$, respectively (see Fig. 2).

Further, by $\boldsymbol{\sigma}_1$, $\boldsymbol{\sigma}_2$, and $\boldsymbol{\sigma}_3$ we denote the *bulk* stress tensors in the phases 1, 2, and 3. Similarly, let $\boldsymbol{\sigma}_{12}$, $\boldsymbol{\sigma}_{13}$, and $\boldsymbol{\sigma}_{23}$ be the *surface* stress tensors of the interfaces S_{12}, S_{13},
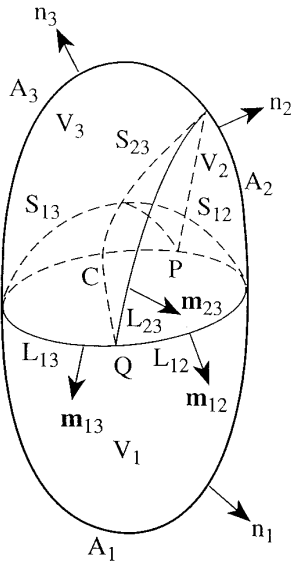
FIG. 2. Sketch of the volume V which entails a portion of the three-phase contact line, C, and is composeed of the volumes V_1, V_2, and V_3 of phases 1, 2, and 3, respectively. For additional information, see text.

and S_{23}, respectively. Note that each of the tensors $\boldsymbol{\sigma}_{12}$, $\boldsymbol{\sigma}_{13}$, and $\boldsymbol{\sigma}_{23}$ has both lateral and transversal components with respect to the interface, cf. Eq. [67]. Finally, by $\boldsymbol{\sigma}_L$ we denote the *linear* stress tensor at the contact line C.

The tensors of the interfacial moments in the surfaces S_{12}, S_{13}, and S_{23} are denoted by $\mathbf{M}_{12}$, $\mathbf{M}_{13}$, and $\mathbf{M}_{23}$; they are analogues of the symmetric tensor $\mathbf{M}$ defined by Eq. [15]. We will also use the tensors $\mathbf{N}_{12}$, $\mathbf{N}_{13}$, and $\mathbf{N}_{23}$ defined as follows (15):

$$\mathbf{N}_{12} = -\mathbf{M}_{12} \cdot \boldsymbol{\varepsilon}, \quad \mathbf{N}_{13} = -\mathbf{M}_{13} \cdot \boldsymbol{\varepsilon}, \quad \mathbf{N}_{23} = -\mathbf{M}_{23} \cdot \boldsymbol{\varepsilon}, \quad [77]$$

where the components of $\boldsymbol{\varepsilon} = \varepsilon_{\alpha\beta} \mathbf{a}^\alpha \mathbf{a}^\beta$ are alternators in the respective surfaces. The mechanical meaning of the components of the $\mathbf{M}$- and $\mathbf{N}$-type tensors is illustrated in Fig. 4 of Ref. (16). In addition we also introduce the *linear* tensor of moments exerted at the contact line, $\mathbf{N}_L$. In general, the linear tensors $\boldsymbol{\sigma}_L$ and $\mathbf{N}_L$ can be represented in the form (3)

$$\boldsymbol{\sigma}_L = \sigma_L^{(\gamma)k} \boldsymbol{\lambda} \mathbf{e}_k \quad \mathbf{N}_L = N_L^{(\gamma)k} \boldsymbol{\lambda} \mathbf{e}_k, \quad [78]$$

where $\mathbf{e}_1 \equiv \mathbf{e}_x$, $\mathbf{e}_2 \equiv \mathbf{e}_y$, and $\mathbf{e}_3 \equiv \mathbf{e}_z$ are the unit vectors of the Cartesian axes; $\boldsymbol{\lambda}$ is the running unit tangent to the contact line C.

Balance of the linear momentum. At hydrostatic equilibrium the net force and the net moment exerted at the volume V must be equal to zero. Let us start with the force balance. The force exerted on the volume V is a superposition of body force, bulk stresses exerted at the surface of the volume

V, interfacial stress exerted at the lines L_{12}, L_{13}, and L_{23}, and linear stresses exerted at the points P and Q in Fig. 2:

$$
\begin{aligned}
0 = \sum_{k=1}^{3} \int_{V_k} dV \rho_k \mathbf{f}_k + \sum_{1 \leq i < j \leq 3} \int_{S_{ij}} dS \rho_{ij} \mathbf{f}_{ij} \\
+ \int_C dl \rho_L \mathbf{f}_L + \sum_{k=1}^{3} \int_{A_k} dA \mathbf{n}_k \cdot \boldsymbol{\sigma}_k \\
+ \sum_{1 \leq i < j \leq 3} \int_{L_{ij}} dl \mathbf{m}_{ij} \cdot \boldsymbol{\sigma}_{ij} + (\boldsymbol{\lambda} \cdot \boldsymbol{\sigma}_L)^{\pm}. \quad [79]
\end{aligned}
$$

Here ρ_1, ρ_2, and ρ_3 are the mass densities of phases 1, 2, and 3; $\mathbf{f}_1$, $\mathbf{f}_2$, and $\mathbf{f}_3$ are the respective body forces per unit mass; ρ_{ij} and $\mathbf{f}_{ij}$ are the respective mass density and body force for the interface S_{ij}; likewise, ρ_L and $\mathbf{f}_L$ are mass density and body force for the contact line C; $\mathbf{m}_{ij}$ is a unit vector which is simultaneously tangential to the surface S_{ij} and normal to the contour encircling S_{ij}; finally

$$(\boldsymbol{\lambda} \cdot \boldsymbol{\sigma}_L)^{\pm} = \boldsymbol{\lambda} \cdot \boldsymbol{\sigma}_L|_P - \boldsymbol{\lambda} \cdot \boldsymbol{\sigma}_L|_Q$$

is the contribution of the linear stress to the net force exerted on the volume V. Similarly, the net force exerted on the volume V_1 reads

$$
\begin{aligned}
0 = \int_{V_1} dV \rho_1 \mathbf{f}_1 + \int_{A_1} dS \mathbf{n}_1 \cdot \boldsymbol{\sigma}_1 \\
+ \int_{S_{12}} dS \mathbf{n}_{12} \cdot \boldsymbol{\sigma}_1 + \int_{S_{13}} dS \mathbf{n}_{13} \cdot \boldsymbol{\sigma}_1, \quad [80]
\end{aligned}
$$

where $\mathbf{n}_{12}$ and $\mathbf{n}_{13}$ are the unit normals to the surfaces S_{12} and S_{13}. The balance of the forces exerted at the surface S_{12} yields

$$
\begin{aligned}
0 = \int_{S_{12}} dS \rho_{12} \mathbf{f}_{12} - \int_{S_{12}} dS \mathbf{n}_{12} \cdot (\boldsymbol{\sigma}_1 - \boldsymbol{\sigma}_2) \\
+ \int_{L_{12} \cup C} dl \mathbf{m}_{12} \cdot \boldsymbol{\sigma}_{12}. \quad [81]
\end{aligned}
$$

By using Eqs. [80] and [81] and analogous expressions for V_2, V_3, S_{13}, and S_{23} from Eq. [79] we get

$$
\begin{aligned}
0 = \int_C dl \rho_L \mathbf{f}_L - \int_C dl (\mathbf{m}_{12} \cdot \boldsymbol{\sigma}_{12} + \mathbf{m}_{13} \cdot \boldsymbol{\sigma}_{13} \\
+ \mathbf{m}_{23} \cdot \boldsymbol{\sigma}_{23}) + (\boldsymbol{\lambda} \cdot \boldsymbol{\sigma}_L)^{\pm}. \quad [82]
\end{aligned}
$$

Finally, by making use of the Newton–Leibnitz theorem, viz.

$$\int_C dl \nabla_L \cdot \boldsymbol{\sigma}_L = (\boldsymbol{\lambda} \cdot \boldsymbol{\sigma}_L)^{\pm}, \quad \nabla_L \equiv \boldsymbol{\lambda} \frac{\partial}{\partial l} \qquad [83]$$

we derive

$$\nabla_L \cdot \boldsymbol{\sigma}_L + \rho_L \mathbf{f}_L = \mathbf{m}_{12} \cdot \boldsymbol{\sigma}_{12} + \mathbf{m}_{13} \cdot \boldsymbol{\sigma}_{13} + \mathbf{m}_{23} \cdot \boldsymbol{\sigma}_{23}. \quad [84]$$

Hence, for the system depicted in Fig. 1 one derives from Eq. [82] (linear effects negligible)

$$0 = \mathbf{e}_z \cdot \boldsymbol{\sigma}_{12} \cdot \mathbf{e}_z - \mathbf{e}_z \cdot \boldsymbol{\sigma}_{13} \cdot \mathbf{e}_z + \mathbf{m} \cdot \boldsymbol{\sigma}_{23} \cdot \mathbf{e}_z \qquad [85]$$

where we have substituted $\mathbf{m}_{12} = -\mathbf{m}_{13} = \mathbf{e}_z$, $\mathbf{m}_{23} = +\mathbf{m}$; further, setting $\mathbf{e}_z \cdot \boldsymbol{\sigma}_{12} \cdot \mathbf{e}_z = \omega_I$; $\mathbf{e}_z \cdot \boldsymbol{\sigma}_{13} \cdot \mathbf{e}_z = \omega_{II}$ and $\boldsymbol{\sigma}_{23} = \boldsymbol{\sigma}$ one recovers the Young equation, Eq. [69].

If the linear body force term in Eq. [84] is negligible and if

$$\boldsymbol{\sigma}_{12} = \sigma_{12} \mathbf{U}_{12}, \quad \boldsymbol{\sigma}_{13} = \sigma_{13} \mathbf{U}_{13},$$

$$\boldsymbol{\sigma}_{23} = \sigma_{23} \mathbf{U}_{23}, \quad \boldsymbol{\sigma}_L = \sigma_L \boldsymbol{\lambda}\boldsymbol{\lambda} \quad [86]$$

with $\mathbf{U}_{ij}$ being the unit tensor of the surface S_{ij}, then Eq. [82] reduces to a generalized form of a Neumann triangle (16):

$$\mathbf{m}_{12} \cdot \boldsymbol{\sigma}_{12} + \mathbf{m}_{13} \cdot \boldsymbol{\sigma}_{13} + \mathbf{m}_{23} \cdot \boldsymbol{\sigma}_{23} = \kappa \sigma_L \boldsymbol{\mu} + \frac{\partial \sigma_L}{\partial l} \boldsymbol{\lambda}. \quad [87]$$

Here $\boldsymbol{\mu}$ is the unit normal vector of the contact line, C, and κ is the geodesic curvature of C; we have used the Frenet formula $\partial \boldsymbol{\lambda} / \partial l = \kappa \boldsymbol{\mu}$. Various special cases of Eq. [87] (with line tension terms) were derived and/or used by Veselovsky and Pertzov (19), Pethica (20), Torza and Mason (21), Pujado and Scriven (22), Lane (23), Ivanov *et al.* (24), etc. Note that in the general case Eq. [82] also contains a contribution from the interfacial bending moments hidden in the transversal components of $\boldsymbol{\sigma}_{ij}$, cf. Eq. [66].

Balance of the angular momentum. The net moment (torque) exerted on the volume V is

$$0 = \sum_{k=1}^{3} \int_{V_k} dV \rho_k \mathbf{f}_k \times \mathbf{r} + \sum_{1 \leq i < j \leq 3} \int_{S_{ij}} dS \rho_{ij} \mathbf{f}_{ij} \times \mathbf{r}$$

$$+ \int_C dl \rho_L \mathbf{f}_L \times \mathbf{r} + \sum_{k=1}^{3} \int_{A_k} dA (\mathbf{n}_k \cdot \boldsymbol{\sigma}_k) \times \mathbf{r}$$

$$+ \sum_{1 \leq i < j \leq 3} \int_{L_{ij}} dl [(\mathbf{m}_{ij} \cdot \boldsymbol{\sigma}_{ij}) \times \mathbf{r} + \mathbf{m}_{ij} \cdot \mathbf{N}_{ij}]$$

$$+ (\boldsymbol{\lambda} \cdot \boldsymbol{\sigma}_L \times \mathbf{r})^{\pm} + (\boldsymbol{\lambda} \cdot \mathbf{N}_L)^{\pm}. \quad [88]$$

In a similar way one can write expressions for the net moment exerted at the volume V_1 and the surface S_{12}:

$$0 = \int_{V_1} dV \rho_1 \mathbf{f}_1 \times \mathbf{r} + \int_{A_1} dS (\mathbf{n}_1 \cdot \boldsymbol{\sigma}_1) \times \mathbf{r}$$

$$+ \int_{S_{12}} dS (\mathbf{n}_{12} \cdot \boldsymbol{\sigma}_1) \times \mathbf{r} + \int_{S_{13}} dS (\mathbf{n}_{13} \cdot \boldsymbol{\sigma}_1) \times \mathbf{r} \quad [89]$$

$$0 = \int_{S_{12}} dS [\rho_{12} \mathbf{f}_{12} + \mathbf{n}_{12} \cdot (\boldsymbol{\sigma}_1 - \boldsymbol{\sigma}_2)] \times \mathbf{r}$$

$$+ \int_{L \cup C} dl \mathbf{m}_{12} \cdot (\boldsymbol{\sigma}_{12} \times \mathbf{r} + \mathbf{N}_{12}). \quad [90]$$

By using Eqs. [89] and [90] and similar expressions for V_2, V_3, S_{13}, and S_{23} from Eqs. [88], [83], and [84] one derives

$$\nabla_L \cdot \mathbf{N}_L + \boldsymbol{\lambda} \cdot \boldsymbol{\sigma}_L \times \boldsymbol{\lambda}$$

$$= \mathbf{m}_{12} \cdot \mathbf{N}_{12} + \mathbf{m}_{13} \cdot \mathbf{N}_{13} + \mathbf{m}_{23} \cdot \mathbf{N}_{23} \quad [91]$$

where we have used the identity

$$\nabla_L \cdot (\boldsymbol{\sigma}_L \times \mathbf{r}) = (\nabla_L \cdot \boldsymbol{\sigma}_L) \times \mathbf{r} + \boldsymbol{\lambda} \cdot \boldsymbol{\sigma}_L \times \boldsymbol{\lambda}. \quad [92]$$

Equation [91] expresses the local balance of the linear momentum. Let $\boldsymbol{\varepsilon}_{ij}$ be the alternator in the surface S_{ij}. Then

$$\boldsymbol{\varepsilon}_{ij} \cdot \boldsymbol{\lambda} = \mathbf{m}_{ij} \quad (\mathbf{R} \in C) \qquad [93]$$

Upon neglecting the line tension effects in Eq. [89] and multiplying by $\boldsymbol{\lambda}$ one obtains

$$\mathbf{m}_{12} \cdot \mathbf{M}_{12} \cdot \mathbf{m}_{12} + \mathbf{m}_{13} \cdot \mathbf{M}_{13} \cdot \mathbf{m}_{13} + \mathbf{m}_{23} \cdot \mathbf{M}_{23} \cdot \mathbf{m}_{23} = 0$$
$$[94]$$

where Eqs. [77] and [88] have been used. In fact, Eq. [92] is a more general form of Eq. [53].

Discussion

It is instructive to illustrate the application of the derived equations as boundary conditions for a specified problem. Let us consider the ''meniscus on a needle'' depicted in Fig. 1 for a small meniscus slope when the Laplace equation can be linearized:

$$\sigma \nabla_{II}^2 u - k_c \nabla_{II}^2 \nabla_{II}^2 u = g u \Delta \rho$$

$$\left(\nabla_{II}^2 \equiv \mathbf{e}_x \frac{\partial}{\partial x} + \mathbf{e}_y \frac{\partial}{\partial y} \right). \quad [95]$$

Here $\Delta \rho$ is the difference in density between the lower and upper phases and g is the gravity acceleration. To obtain Eq. [95] we have used that $\Delta P = g u \Delta \rho$ (flat interface at infinity) and we have assumed a Helfrich interface. In fact, this equation is a fourth-order ordinary differential equation (u

$= u(r))$ and four boundary conditions are needed. One of them is

$$\lim_{r \to \infty} u(r) = 0. \quad [96]$$

The second one stems from Eq. [76] where the term with $\sin \alpha$ is negligible in a linear approximation:

$$(du/dr)_{r=r_C} = -\cot \alpha; \quad \cos \alpha = (\omega_{II} - \omega_I)/\sigma. \quad [97]$$

The third boundary condition originates from Eq. [56]. In a linear approximation one has

$$\mathbf{n} = \frac{\mathbf{e}_z - \nabla_{II} u}{(1 + |\nabla_{II} u|^2)^{1/2}} \approx \mathbf{e}_z - \nabla_{II} u \quad [98]$$

$$\mathbf{b} = -\nabla_S \mathbf{n} \approx \nabla_{II} \nabla_{II} u \quad [99]$$

and consequently

$$0 = b_{r\varphi} = \frac{\partial^2 u}{\partial r \partial \varphi} - \frac{1}{r} \frac{\partial u}{\partial \varphi} \quad (\mathbf{R} \in C), \quad [100]$$

where (r, φ) are polar coordinates in the plane xy. This boundary condition is automatically satisfied in view of the axial symmetry. The last boundary condition stems from Eqs. [72]–[74]:

$$B_0 + 2k_c \frac{d^2 u}{dr^2} + 2(k_c + \bar{k}_c) \frac{1}{r} \frac{du}{dr} = 0 \quad (\mathbf{R} \in C) \quad [101]$$

where again the linear approximation was used.

Next, let us consider the problem from another point of view. One can represent Eq. [95] in the form

$$(\nabla_{II}^2 - \kappa_1^2)(\nabla_{II}^2 - \kappa_2^2)u = 0, \quad [102]$$

where

$$\kappa_{1,2}^2 = \frac{\sigma}{2k_c}[1 \pm (1 - 4k_c g \Delta\rho/\sigma^2)^{1/2}]. \quad [103]$$

In a first approximation to Eq. [103] one obtains

$$\kappa_1^2 \approx g\Delta\rho/\sigma; \quad \kappa_2^2 \approx \sigma/k_c. \quad [104]$$

κ_1^{-1} and κ_2^{-1} determine two characteristic decay lengths, which, in fact, are the decay lengths of the solutions of the equations $(\nabla_{II}^2 - \kappa_1^2)u = 0$ and $(\nabla_{II}^2 - \kappa_2^2)u = 0$. For a water/air interface we have $\sigma = 72$ mN/m, $\Delta\rho = 1000$ kg/m^3, $k_c = 4 \times 10^{-21}$ J and one calculates

$$\kappa_1^{-1} = 2.7 \times 10^{-3} \text{ m} \quad \kappa_2^{-1} = 2.4 \times 10^{-10} \text{ m} \quad [105]$$

showing that κ_2^{-1} is extremely small (molecular length scale). The physical meaning of the solutions of the macroscopic Laplace equation with a microscopic decay length is, of course, problematic.

If one disregards all solutions of Eq. [102] having a molecular decay length, it reduces to

$$(\nabla_{II}^2 - \kappa_1^2)u = 0. \quad [106]$$

This is a second-order differential equation which is to be solved in conjunction with the boundary conditions, Eqs. [96] and [97].

The bending moment effects, and the boundary conditions [100] and [101], can become important when the interfacial tension is very low and κ_2^{-1} is comparable to κ_1^{-1}, viz.,

$$\sigma \approx (gk_c\Delta\rho)^{1/2} \approx 6 \times 10^{-6} \text{ mN/m}. \quad [107]$$

Such low interfacial tensions may exist in critical emulsions and microemulsions.

MICROMECHANICAL EXPRESSIONS FOR SURFACE EXCESS QUANTITIES

All the relevant interfacial quantities can be expressed as integrals over the three-dimensional pressure tensor, $\mathbf{P}$, of the interface regarded as a three-dimensional body. The pressure tensor is simply the negative of the three-dimensional mechanical stress tensor $\boldsymbol{\sigma}$ (to be distinguished from the two-dimensional mechanical stress tensor, $\boldsymbol{\sigma}_S$). The pressure tensor must, of course, satisfy the mechanical equilibrium condition

$$\nabla \cdot \mathbf{P} = 0 \quad [108]$$

which for a spherical aggregate can be written

$$d(r^2 P_N)/d(r^2) = P_T \quad [109]$$

or

$$r^2[dP_N/d(r^2)] = P_T - P_N. \quad [110]$$

The corresponding equation for a cylindrical aggregate has the following form

$$d(rP_{rr})/dr = P_{\varphi\varphi}. \quad [111]$$

Next we introduce the excess pressure tensor

$$\mathbf{P}^s = \mathbf{P} - P_{\alpha\beta}\mathbf{U} \quad [112]$$

where $\mathbf{U}$ is the three-dimensional (or bulk) identity tensor, related to $\mathbf{U}_S$ in the following way

$$\mathbf{U} = \mathbf{U}_S + \mathbf{nn} \qquad [113]$$

bearing in mind that $\mathbf{U}_S = \mathbf{a}^1\mathbf{a}_1 + \mathbf{a}^2\mathbf{a}_2$. Further,

$$P_{\alpha\beta} = \begin{cases} P_\alpha & \text{if } \lambda < 0 \\ P_\beta & \text{if } \lambda > 0 \end{cases}$$

where λ is a coordinate along the surface normal and equal to zero at the dividing surface, and P_α is the homogeneous isotropic pressure ''below'' the interface and P_β the corresponding pressure ''above'' the interface. We then have the following micromechanical definitions of the surface tension tensors:

$$\boldsymbol{\gamma} = -\int_{\lambda_1}^{\lambda_2} \mathbf{P}^s\chi d\lambda \quad \boldsymbol{\sigma} = -\int_{\lambda_1}^{\lambda_2} \mathbf{L}\cdot\mathbf{P}^s d\lambda \quad [114]$$

The tensor $\mathbf{L}$ is defined as

$$\mathbf{L} = (1 - 2\lambda H)\mathbf{U}_S + \lambda\mathbf{b} \qquad [115]$$

It serves the following purpose. In order to calculate the tangential tensions and the bending moments we need to know the forces acting upon a vectorial surface element, $d\mathbf{S}_{\text{orth}}$, of a sectorial strip that is perpendicular to the dividing surface. Then, according to Eliassen (4)

$$d\mathbf{S}_{\text{orth}} = \boldsymbol{\nu}\cdot\mathbf{L}d\lambda dl, \qquad [116]$$

where $\boldsymbol{\nu}$ is a vector in the tangent plane of the dividing surface, normal to the above-mentioned perpendicular sectorial strip at values of λ different from zero. Then $\boldsymbol{\nu}\cdot\mathbf{L}$ is a vector perpendicular to the sectorial strip.

Further, since

$$\sigma = \tfrac{1}{2}\mathbf{U}_S{:}\boldsymbol{\sigma}; \quad \gamma = \tfrac{1}{2}\mathbf{U}_S{:}\boldsymbol{\gamma} \qquad [117]$$

$$\eta = \tfrac{1}{2}\mathbf{q}{:}\boldsymbol{\sigma}; \quad \zeta = \tfrac{1}{2}\mathbf{q}{:}\boldsymbol{\gamma} \qquad [118]$$

which, due to the orthogonality of $\mathbf{U}_S$ and $\mathbf{q}$, is consistent with Eqs. [12] and [34], i.e.,

$$\boldsymbol{\gamma}_S = \gamma\mathbf{U}_S + \zeta\mathbf{q} \qquad [119]$$

$$\boldsymbol{\sigma}_S = \sigma\mathbf{U}_S + \eta\mathbf{q} \qquad [120]$$

it follows that

$$\gamma = -\tfrac{1}{2}\int_{\lambda_1}^{\lambda_2} \mathbf{U}_S{:}\mathbf{P}^s\chi d\lambda; \quad \zeta = -\tfrac{1}{2}\int_{\lambda_1}^{\lambda_2} \mathbf{q}{:}\mathbf{P}^s\chi d\lambda \quad [121]$$

and

$$\sigma = -\tfrac{1}{2}\int_{\lambda_1}^{\lambda_2} \mathbf{L}{:}\mathbf{P}^s d\lambda; \quad \eta = -\tfrac{1}{2}\int_{\lambda_1}^{\lambda_2} (\mathbf{q}\cdot\mathbf{L}){:}\mathbf{P}^s d\lambda. \quad [122]$$

Further

$$\mathbf{M} = \tfrac{1}{2}\int_{\lambda_1}^{\lambda_2} \mathbf{L}\cdot\mathbf{P}^s\lambda d\lambda \qquad [123]$$

which is a tensor in three dimensions. The corresponding two-dimensional surface tensor equals

$$\mathbf{M}_S = \tfrac{1}{2}(\mathbf{U}_S\mathbf{U}_S + \mathbf{qq}){:}\mathbf{M} = \tfrac{1}{2}(B\mathbf{U}_S + \Theta\mathbf{q}) \quad [124]$$

as was already anticipated above. Since $B = \tfrac{1}{2}\mathbf{U}_S{:}\mathbf{M}$ and $\Theta = \tfrac{1}{2}\mathbf{q}{:}\mathbf{M}$ it follows that

$$B = \int_{\lambda_1}^{\lambda_2} \mathbf{L}{:}\mathbf{P}^s\lambda d\lambda; \quad \Theta = \int_{\lambda_1}^{\lambda_2} (\mathbf{q}\cdot\mathbf{L}){:}\mathbf{P}^s\lambda d\lambda. \quad [125]$$

In the equations for γ and ζ above, the variable

$$\chi = (1 - \lambda H)^2 - \lambda^2 D^2 = 1 - 2\lambda H + \lambda^2 K \quad [126]$$

is recognized as the local dilatation factor for the area of a parallel surface compared to that of the dividing surface.

In connection with the work of formation of the interface at constant chemical potentials we define another quantity

$$\delta w_f/\delta\alpha = -\tfrac{1}{2}\int_{\lambda_1}^{\lambda_2} \mathbf{U}_S{:}(\mathbf{P} - P_\beta\mathbf{U})\chi d\lambda$$

$$= \gamma - \int_{\lambda_1}^{0} (P_\alpha - P_\beta)\chi d\lambda = \gamma - \Delta P\int_{\lambda_1}^{0} \chi d\lambda$$

$$[127]$$

Then, per unit surface,

$$\delta w_f = \gamma\delta\alpha - \delta\alpha\Delta P\int_{\lambda_1}^{0} \chi d\lambda. \qquad [128]$$

Thus, the work of formation at constant chemical potentials is closely related to the deformation work for pure dilatation. As was pointed out above, the infinitesimal deformation work is the same in an open and in a closed system (in the thermodynamic sense). Finally, we note that if $\Delta P = 0$ it follows that $\delta w_f = \gamma\delta\alpha$. As to the interpretation of λ_1 we

remark that for a closed spherical or cylindrical aggregate $\lambda = \lambda_1$ corresponds to $r = 0$.

Below, we treat the special cases of spherical and cylindrical interfaces. Some of the formulas quoted have been published earlier, cf. Ref. (16).

Finally, it should be mentioned that Eqs. [121] and [125] were first published in Ref. (25).

The Spherical Interface

As an example of the application of the above relations we will take the case of a spherical interface. If the radius of the dividing surface is denoted by R, the following relations ensue

$$\gamma = \frac{1}{R^2} \int_0^\infty (P_{\alpha\beta} - P_T) r^2 dr; \quad \sigma = \frac{1}{R} \int_0^\infty (P_{\alpha\beta} - P_T) r dr$$

[129]

where, now,

$$P_{\alpha\beta} = \begin{cases} P_\alpha & \text{if } r < R \\ P_\beta & \text{if } r > R \end{cases}$$

Further,

$$B = -\frac{2}{R} \int_0^\infty (P_{\alpha\beta} - P_T) r(r - R) dr$$

[130]

Thus,

$$\gamma = \sigma + \tfrac{1}{2} BH.$$

[131]

The Laplace equation reads

$$\Delta P = 2H\gamma - BH^2 = 2H\sigma$$

[132]

with $H = -1/R$. The negative of curvature pressure, $-\pi_c$, equals $BH^2 = B/R^2$. The condition of lateral mechanical equilibrium requires that $\nabla_S \gamma$ and $B\nabla_S H$ should both be equal to zero, which is obviously satisfied on a sphere. Finally

$$M = M_1 = M_2 = -\frac{1}{R} \int_0^\infty (P_{\alpha\beta} - P_T) r(r - R) dr = B/2$$

[133]

whence

$$\gamma = \sigma + BH/2 = \sigma + Mc.$$

[134]

η is, of course, equal to zero for a spherical surface implying that γ and σ are equal at the s.o.t. where $M = 0$. The work of formation of a spherical aggregate at constant chemical potentials amounts to

$$w_f = 4\pi \int_0^\infty (P_\beta - P_T) r^2 dr = 4\pi R^2 \gamma$$

$$- 4\pi \int_0^R (P_\alpha - P_\beta) r^2 dr$$

$$= (4\pi R^2/3)(\gamma + BH^2/R)$$

$$= (4\pi R^2/3)(\gamma + B/R)$$

$$= (4\pi R^2/3)(\gamma + \pi_c R)$$

[135]

This work may be written in several different ways

$$w_f = 4\pi \int_0^\infty (P_\beta - P_T) r^2 dr = (4\pi/3) \int_0^\infty (P_N - P_T) r^2 dr$$

$$= 2\pi \int_0^\infty (P_N - P_\beta) r^2 dr.$$

[136]

The radius of the surface of tension, R_{sot}, is obtained by setting B and π_c equal to zero. We obtain

$$R_{sot}^3 = \frac{6}{P_\alpha - P_\beta} \int_0^\infty (P_\beta - P_T) r(r - R) dr$$

$$= \frac{6}{P_\alpha - P_\beta} \int_0^\infty (P_\beta - P_T) r^2 dr$$

$$= \frac{2}{P_\alpha - P_\beta} \int_0^\infty (P_N - P_T) r^2 dr$$

$$= \frac{3}{P_\alpha - P_\beta} \int_0^\infty (P_N - P_\beta) r^2 dr$$

[137]

where we have also used the condition of mechanical equilibrium

$$\int_0^\infty (P_\beta - P_T) r dr = 0.$$

[138]

Equation [138] can be obtained by substituting the Laplace equation $\sigma = (P_\alpha - P_\beta) R_{s.o.t.}/2$ in Eq. [129].

The Cylindrical Interface

For a cylindrical surface we have quite generally $H = D = -1/2R$ and $\lambda = r - R$ where R is the radius of the dividing surface, and

$$\mathbf{L} = (1 - 2\lambda H)\mathbf{U}_S + \lambda\mathbf{b}. \qquad [139]$$

We then have

$$\gamma = -\frac{1}{2}\int_0^\infty (P_{\varphi\varphi}^s + P_{zz}^s)\frac{r}{R}\,dr \qquad [140]$$

and

$$\zeta = -\frac{1}{2}\int_0^\infty (P_{\varphi\varphi}^s - P_{zz}^s)\frac{r}{R}\,dr \qquad [141]$$

and further

$$\sigma_{\varphi\varphi} = -\int_0^\infty P_{\varphi\varphi}^s\,dr; \quad \sigma_{zz} = -\int_0^\infty P_{zz}^s\frac{r}{R}\,dr \qquad [142]$$

$$M_{\varphi\varphi} = \int_0^\infty P_{\varphi\varphi}^s(r-R)\,dr; \quad M_{zz} = \int_0^\infty P_{zz}^s\frac{r}{R}(r-R)\,dr \qquad [143]$$

and

$$\sigma = -\frac{1}{2}\int_0^\infty \left(P_{\varphi\varphi}^s + \frac{r}{R}P_{zz}^s\right)dr = \frac{1}{2}(\sigma_{\varphi\varphi} + \sigma_{zz}) \qquad [144]$$

and

$$\eta = -\frac{1}{2}\int_0^\infty \left(P_{\varphi\varphi}^s - \frac{r}{R}P_{zz}^s\right)dr = \frac{1}{2}(\sigma_{\varphi\varphi} - \sigma_{zz}) \qquad [145]$$

and

$$B = \int_0^\infty \left(P_{\varphi\varphi}^s + \frac{r}{R}P_{zz}^s\right)(r-R)\,dr = M_{\varphi\varphi} + M_{zz} \qquad [146]$$

and

$$\Theta = \int_0^\infty \left(P_{\varphi\varphi}^s - \frac{r}{R}P_{zz}^s\right)(r-R)\,dr = M_{\varphi\varphi} - M_{zz}. \qquad [147]$$

It follows that

$$M_{\varphi\varphi} = \frac{1}{2}(B + \Theta); \quad M_{zz} = \frac{1}{2}(B - \Theta). \qquad [148]$$

Then Eqs. [37] and [38] reduce to

$$\gamma = \sigma + \frac{1}{2}(B + \Theta)H = \sigma - M\varphi\varphi/2R \qquad [149]$$

$$\zeta = \eta + \frac{1}{2}(B + \Theta)H = \eta - M\varphi\varphi/2R. \qquad [150]$$

Thus, for a cylindrical surface

$$\gamma - \zeta = \sigma - \eta. \qquad [151]$$

Cylindrical Micelles

Simple mechanical equilibrium considerations show that a freely floating cylindrical object must satisfy the condition $\sigma_{\varphi\varphi} = 2\sigma_{zz}$ as is shown in Eq. [155] below. On the other hand, a perfectly fluid interface must be isotropic in the tangent plan of the interface, i.e., $\sigma_{\varphi\varphi} = \sigma_{zz}$. We conclude that aggregates with a perfectly fluid surface cannot have a cylindrical shape.

A completely different case is presented by solid elastic interfaces, e.g., rubber membranes. Another interesting case is that of rod-shaped micelles which are considered to have at least an approximately cylindrical shape. We must, therefore, conclude that the entanglement of the hydrocarbon chains endows the interface (which comprises the whole of the micelle) with sufficient rigidity to support anisotropic tensions in the tangent plane of the dividing surface so that the condition $\sigma_{\varphi\varphi} = 2\sigma_{zz}$ is satisfied. Such interfaces are sometimes said to be fluid since the surfactant molecules are able to exchange places, but then mainly by reptation. In the following we exclusively treat the idealized case where this condition (i.e., $\sigma_{\varphi\varphi} = 2\sigma_{zz}$) is satisfied exactly.

Mechanical equilibrium with respect to two sections, one at right angles to the cylinder axis and another containing the axis, requires that

$$\int_0^\infty (P_{zz} - P_\beta)r\,dr = 0 \qquad [152]$$

$$\int_0^\infty (P_{\varphi\varphi} - P_\beta)\,dr = 0 \qquad [153]$$

The micromechanical definitions of $\sigma_{\varphi\varphi}$ and σ_{zz}, Eq. [142], then yield, after simple calculations,

$$\sigma_{\varphi\varphi} = R(P_\alpha - P_\beta); \quad \sigma_{zz} = \frac{1}{2}R(P_\alpha - P_\beta) \qquad [154]$$

whence

$$\sigma_{zz} = \frac{1}{2}\sigma_{\varphi\varphi}. \qquad [155]$$

Thus, according to Eq. [142]

$$\int_0^\infty P_{\varphi\varphi}^s\,dr = 2\int_0^\infty P_{zz}^s\frac{r}{R}\,dr. \qquad [156]$$

Finally, according to Eq. [141] we have

$$\zeta = -\frac{1}{2R} \int_0^\infty P_{\varphi\varphi}^s (r - R/2) dr. \qquad [157]$$

An important quantity in the thermodynamics of micelle solutions is the work of formation at chemical equilibrium, i.e., when the chemical potential of surfactant monomers in the solution is the same as for the surfactant molecules in the micelles. The work of formation of a cylindrical micelle can be written in two different ways corresponding to two different modes of formation at constant chemical potentials.

In the first mode, the cylindrical part is stretched very slowly in the z-direction so that chemical equilibrium is maintained all the time. Then,

$$w_f(z) = -2\pi\Delta L \int_0^\infty (P_{zz} - P_\beta) r dr. \qquad [158]$$

From Eq. [152] it follows directly that

$$w_f(z) = 0 \qquad [159]$$

In the second mode the cylindrical part is formed by letting a wedge-shaped cylindrical sector (like a piece of cake) grow from $\varphi = 0$ to $\varphi = 2\pi$ in analogy with the growing spherical cone generally used to calculate the work of formation of a spherical droplet. Thus,

$$w_f(\varphi) = -2\pi\Delta L \int_0^\infty (P_{\varphi\varphi} - P_\beta) r dr. \qquad [160]$$

From Eqs. [157], [158], and [160] it follows directly that

$$R\zeta = \frac{1}{4\pi\Delta L} [w_f(\varphi) - w_f(z)]. \qquad [161]$$

However, the right-hand side of Eq. [161] is manifestly independent of the radius R of the dividing surface. It follows that $R\zeta$ is invariant with respect to R. Further, since, for physical reasons, the work of formation must be the same in the two modes of formation, we must have $w_f(\varphi) = w_f(z) = 0$, and consequently

$$\zeta = 0. \qquad [162]$$

From Eqs. [18] and [19] it follows that $\gamma + \zeta = \gamma_1$ and $\gamma - \zeta = \gamma_2$. Hence,

$$\gamma_1 = \gamma_2 = \gamma \qquad [163]$$

Further, from Eqs. [140]–[142] we deduce that

$$\gamma_1 = \gamma_2 = \gamma = \sigma_{zz} \qquad [164]$$

Finally, Eq. [157] may be written

$$-2R\zeta = \int_0^\infty P_{\varphi\varphi}^s (r - R/2) dr \qquad [165]$$

from which we conclude that the integral on the right-hand side must be independent of R and equal to zero, although this may not be immediately apparent. However,

$$\int_0^\infty P_{\varphi\varphi}^s (r - R/2) dr = \int_0^\infty (P_{\varphi\varphi} - P_{\alpha\beta})(r - R/2) dr$$

$$= \int_0^\infty (P_{\varphi\varphi} - P_\beta)(r - R/2) dr + \int_0^R (P_\beta - P_\alpha)$$

$$\times (r - R/2) dr = \int_0^\infty (P_{\varphi\varphi} - P_\beta) r dr$$

$$- (R/2) \int_0^\infty (P_{\varphi\varphi} - P_\beta) dr + 0$$

$$= w_f(\varphi)/2\pi\Delta L - 0 + 0 = 0. \qquad [166]$$

which implies that the right-hand side of Eq. [165] is independent of R and equal to zero.

According to Eq. [43]

$$\Delta P = -\sigma_{\varphi\varphi}/R \qquad [167]$$

while according to Eq. [46]

$$\Delta P = -\gamma/R - \zeta/R + \pi_c = -\gamma_1/R + \pi_c \qquad [168]$$

where, according to Eq. [45] and the micromechanical equations, it is easy to show that

$$\pi_c = -M_{\varphi\varphi}/R^2 = \gamma_1/R - \sigma_{\varphi\varphi}/R.$$

Hence,

$$\Delta P = -\gamma_1/R + \gamma_1/R - \sigma_{\varphi\varphi}/R = -\sigma_{\varphi\varphi}/R \qquad [169]$$

as before, demonstrating full consistency.

GENERALIZATION TO SURFACE STRAIN AND STRESS TENSORS THAT ARE NOT DIAGONAL IN THE BASIS OF THE PRINCIPAL CURVATURES

The tensors $\mathbf{U}_S$ and $\mathbf{q}$ are mutually orthogonal but they do not form a complete set of basis tensors. Thus, only such tensors that are diagonal in the basis of the principal curvatures can be expressed as a linear combination of $\mathbf{U}_S$ and $\mathbf{q}$. If we take the analogous case of the Pauli spin matrices we know that four 2×2 basis matrices are required to express an arbitrary 2×2 matrix. They are the 2×2 unit matrix, e, and the Pauli spin matrices, σ_x, σ_y, and σ_z, of

which e and σ_z are diagonal, which means that only diagonal matrices can be expressed as linear combinations of e and σ_z alone. Thus, it was explicitly admitted in the theory of Gurkov and Kralchevsky (16) repeated above, that the rate of deformation tensor

$$\mathbf{d} = \tfrac{1}{2}\dot{\alpha}\mathbf{U}_S + \tfrac{1}{2}\dot{\beta}\mathbf{q} \qquad [170]$$

was assumed to be diagonal in the basis of the principal curvatures as follows directly from its form. This constitutes a limitation of the admissible deformations, $\delta\mathbf{R}$.

A completely general deformation rate can be represented in the basis of the principal curvatures as

$$2d = \dot{\alpha}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + \dot{\beta}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} + \dot{\beta}_1\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad [171]$$

where the three matrices correspond to e (the unit matrix), σ_z, and σ_x. The matrix

$$q_2 = \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}$$

proportional to σ_y is not included because it is antisymmetric (the deformation tensor being, by definition, symmetric) and because it would represent a pure rotation. In tensor form the above equation can be written in the following way (replacing Eq. [10])

$$2\mathbf{d} = \alpha\mathbf{U}_S + \dot{\beta}\mathbf{q} + \dot{\beta}_1\mathbf{q}_1, \qquad [172]$$

where $\mathbf{q}_1$ is obtained from $\mathbf{q}$ by rotation through an angle equal to 45° about the surface normal. Then Eq. [9] may be extended by the following relations

$$\mathbf{q}_1:\mathbf{q}_1 = 2; \quad \mathbf{U}_S:\mathbf{q}_1 = 0; \qquad \mathbf{q}:\mathbf{q}_1 = 0$$
$$\mathbf{q}\cdot\mathbf{q}_1 = \mathbf{q}_2; \quad \mathbf{q}\cdot\mathbf{q}_2 = \mathbf{q}_1; \quad \mathbf{q}_1\cdot\mathbf{q}_2 = \mathbf{q}. \qquad [173]$$

Further, it can be shown that

$$\mathbf{q}_1\cdot\mathbf{q}_1 = \mathbf{q}\cdot\mathbf{q} = \mathbf{U}_S \qquad [174]$$

In summary, we may say that from a qualitative point of view, Eq. [170] describes deformations of dilation and shear engendered by the bending and twisting of the interface. From this viewpoint the new term with the tensor $\mathbf{q}_1$ in Eq. [172] describes an additional (rate of) shear which is independent (or not coupled with) the changes in the interfacial shape. Such a shear deformation may, for instance, be due to a two-dimensional convective flow of the surface molecules.

Since there is, in general, for completely arbitrary mem-branes, no reason why $\boldsymbol{\sigma}_S$ should be diagonal in the basis of the normal curvatures, the definition equation, Eq. [34], will now be generalized to read

$$\boldsymbol{\sigma}_S = \sigma\mathbf{U}_S + \eta\mathbf{q} + \eta_1\mathbf{q}_1, \qquad [175]$$

where

$$\sigma = \tfrac{1}{2}\mathbf{U}_S:\boldsymbol{\sigma}_S; \quad \eta = \tfrac{1}{2}\mathbf{q}:\boldsymbol{\sigma}_S; \quad \eta_1 = \tfrac{1}{2}\mathbf{q}_1:\boldsymbol{\sigma}_S. \quad [176]$$

Then,

$$\boldsymbol{\sigma}_S:\mathbf{d} = \sigma\dot{\alpha} + \eta\dot{\beta} + \eta_1\dot{\beta}_1. \qquad [177]$$

Further, according to Gurkov and Kralchevsky (16), the rate of deformation work per unit surface equals

$$\frac{\delta w_s}{\delta t} = \boldsymbol{\sigma}_S:\mathbf{d} + \mathbf{M}_S:\left(\frac{\partial\mathbf{b}}{\partial t} - \mathbf{b}\cdot\mathbf{d}\right). \qquad [178]$$

The first term on the right-hand side has already been evaluated above. The second term obviously depends on the nature of $\mathbf{M}_S$. In the general case the calculus becomes extremely involved. However, in the special case where $\mathbf{M}_S$ is diagonal in the basis of the normal curvatures, which may possibly be a less stringent condition, at least for isotropic interfaces, than the corresponding condition applied to $\boldsymbol{\sigma}_S$, the second term in the above equation for $\delta w_s/\delta t$ will contain no contribution whatever from the term $\tfrac{1}{2}\dot{\beta}_1\mathbf{q}_1$ in the expression for $\mathbf{d}$ as is easily shown using the tensor relation

$$\mathbf{A}:(\mathbf{B}\cdot\mathbf{C}) = (\mathbf{A}\cdot\mathbf{B}):\mathbf{C}. \qquad [179]$$

This, in turn, implies that Eq. [A11] in the article by Gurkov and Kralchevsky (16) remains valid although the tensors $\boldsymbol{\sigma}_S$ and $\mathbf{d}$ are not diagonal in the basis of the principal curvatures. We thus obtain the following slightly modified form of Eq. [36]

$$\delta w_S = (\sigma + \tfrac{1}{2}BH + \tfrac{1}{2}\Theta D)\delta\alpha + (\eta + \tfrac{1}{2}BD + \tfrac{1}{2}\Theta H)\delta\beta$$
$$+ B\delta H + \Theta\delta D + \eta_1\delta\beta_1 \quad [180]$$

Thus, if Eq. [33] is modified to read

$$\delta w_S = \gamma\delta\alpha + \zeta\delta\beta + \zeta_1\delta\beta_1 + B\delta H + \Theta\delta D \quad [181]$$

we have the following relations

$$\gamma = \sigma + \tfrac{1}{2}BH + \tfrac{1}{2}\Theta D \qquad [182]$$

$$\zeta = \eta + \tfrac{1}{2}BD + \tfrac{1}{2}\Theta H \qquad [183]$$

$$\zeta_1 = \eta_1 \qquad [184]$$

Returning to the minimum conditions, we note again that

$$\mathbf{d}\,dt = \nabla_S\mathbf{s} - \psi\mathbf{b}. \qquad [185]$$

This means that in addition to the variations in Eqs. [4]–[7] we have the additional variation

$$\delta\beta_1 = \mathbf{q}_1{:}\mathbf{d}\,dt = \mathbf{q}_1{:}\nabla_S\mathbf{s}. \qquad [186]$$

From Eq. [185] it also follows that

$$\delta\alpha = \mathbf{U}_S{:}\mathbf{d}\,dt = \mathbf{U}_S{:}\nabla_S\mathbf{s} - 2H\psi$$

and

$$\delta\beta = \mathbf{q}{:}\mathbf{d}\,dt = \mathbf{q}{:}\nabla_S\mathbf{s} - 2D\psi,$$

i.e., we have recovered Eqs. [4] and [5].

In the integrand of the second integral in Eq. [2] we now have an additional term $\zeta_1\delta\beta_1$, and Eq. [12] should be replaced by

$$\boldsymbol{\gamma}_S = \gamma\mathbf{U}_S + \zeta\mathbf{q} + \zeta_1\mathbf{q}_1. \qquad [187]$$

Then, Eq. [19] should be replaced by the two equations

$$\zeta = \tfrac{1}{2}\mathbf{q}{:}\boldsymbol{\gamma}_S \qquad [188]$$

$$\zeta_1 = \tfrac{1}{2}\mathbf{q}_1{:}\boldsymbol{\gamma}_S \qquad [189]$$

Equation [21] for ΔP remains unaffected, but Eq. [20] should be replaced by

$$\nabla_S\cdot\boldsymbol{\gamma}_S - B\nabla_S H - \Theta\nabla_S D = 0 \qquad [190]$$

or

$$\nabla_S\gamma + \nabla_S\cdot(\zeta\mathbf{q} + \zeta_1\mathbf{q}_1) - B\nabla_S H - \Theta\nabla_S D = 0 \quad [191]$$

from which it follows that Eq. [42] remains valid as is also true for Eq. [44]. On the other hand, Eq. [43] does not hold any longer since $\eta = \tfrac{1}{2}\mathbf{q}{:}\boldsymbol{\sigma}_S$ is no longer equal to $\tfrac{1}{2}(\sigma_1 -$

σ_2). Instead, Eq. [43] should be replaced by the more general expression

$$\Delta P = \mathbf{b}{:}\boldsymbol{\sigma}_S - \nabla_S\nabla_S{:}\mathbf{M}_S \qquad [192]$$

which is always valid. Finally, we note that Eqs. [41], [44], and [45] remain valid, while the last membrum of Eq. [19] no longer holds. Equation [41] may also be written in the following way

$$\gamma = \sigma + \tfrac{1}{2}\mathbf{b}{:}\mathbf{M}_S \qquad [193]$$

and Eq. [45] as follows

$$\pi_c = \mathbf{U}_S{:}(\mathbf{b}\cdot\mathbf{M}_S\cdot\mathbf{b}). \qquad [194]$$

Finally, it should be pointed out that both $\mathbf{M}$ and $\boldsymbol{\sigma}$ of surfactant-laden interfaces in a fluid state at equilibrium are most likely to be diagonal in the basis of the principal curvatures, since, locally, there will be no preferential directions in the surface except the directions of principal curvature.

CONCLUSION

In the present paper several novel forms are derived of the Laplace equilibrium condition in the normal direction for a flexible interface of arbitrary curvature. Additionally, we have treated the associated boundary conditions in some depth. Finally, we have indicated the route along which an even more generally valid thermodynamics can be generated by refraining from making the assumption that the rate-of-strain $\mathbf{d}$ tensor is diagonal in the basis of the principal curvatures.

APPENDIX

According to Kralchevsky (6), Eq. [4.19], the variation of the Helmholtz free energy of an interface per unit surface equals

$$\delta f_s = -s_s\delta T + \sum_{k=1}^{N} \mu_k\delta\Gamma_k - (\gamma - \omega_s)\delta\alpha$$
$$+ \zeta\delta\beta + B\delta H + \Theta\delta D \qquad [195]$$

where ω_s is the grand Ω-potential of the interface per unit surface, i.e.,

$$\Omega_s = \iint_S \omega_s\,dS \qquad [196]$$

and the other quantities are those familiar from the extended Gibbs equation for the work of deformation (2)

$$\delta w_s = \gamma\delta\alpha + \zeta\delta\beta + B\delta H + \Theta\delta D. \qquad [197]$$

In the case where some of the components are insoluble in the bulk liquid phase(s), notably if the components ($i = 1, \ldots, M$) are soluble and at equilibrium with the environment, whence $\delta\mu_i = 0$ ($i = 1, \ldots, M$) and the components ($j = M + 1, \ldots, N$) are the insoluble, which means that in the absence of surface diffusion[4] we have $\delta\Gamma_i = -\Gamma_i\delta\alpha$, which in turn means that we have a mixed Helmholtz free energy and grand Ω-potential

$$F_s \equiv \hat{\Omega}_s = \iint_S \hat{\omega}_s dS \qquad [198]$$

and it follows from the above equations and

$$\hat{\omega}_s = \omega_s + \sum_{k=M+1}^{N} \Gamma_k\mu_k = f_s - \sum_{k=1}^{M} \Gamma_k\mu_k \qquad [199]$$

which is Eq. [4.24] of Ref. (6) that

$$\delta\hat{\omega}_s = -s_s\delta T - \sum_{k=1}^{M} \gamma_k\delta\mu_k + (\gamma - \hat{\omega}_s)\delta\alpha$$
$$+ \zeta\delta\beta + B\delta H + \Theta\delta D \qquad [200]$$

which is Eq. [4.23] of Ref. (6) and where the first two terms on the right-hand side vanish. Now,

$$\delta F_s = \delta \iint_S \hat{\omega}_s dS = \iint_S (\delta\hat{\omega}_s + \hat{\omega}_s\delta) dS \qquad [201]$$

where, by definition, $\delta dS = \delta\alpha dS$. Hence

$$\delta F_s = \iint_S (\delta\hat{\omega}_s + \hat{\omega}_s\delta\alpha) dS \qquad [202]$$

or

$$\delta F_s = \iint_S (\gamma\delta\alpha + \zeta\delta\beta + B\delta H + \Theta\delta D) dS. \qquad [203]$$

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[4] i.e., if the chemical potentials are constant within the interface.

Adding the contribution from the bulk phases we obtain Eq. [2].

REFERENCES

1. Buff, F. P., ''Handbuch der Physik,'' Vol. X, p. 281. Springer Verlag, Berlin, 1955.
2. Murphy, C. L., Ph.D. thesis, University of Minnesota, 1966; University Microfilms, Ann Arbor, Michigan, 1984.
3. Melrose, J. C., *Ind. Eng. Chem.* **60,** 53 (1968).
4. Eliassen, J. D., Ph.D. thesis, University of Minnesota, 1963; University Microfilms, Ann Arbor, Michigan, 1983.
5. Boruvka, L., and Neumann, A. W., *J. Chem. Phys.* **66,** 5464 (1977).
6. Kralchevsky, P. A., *J. Colloid Interface Sci.* **137,** 217 (1990).
7. Ljunggren, S., Eriksson, J. C., and Kralchevsky, P., *J. Colloid Interface Sci.* **161,** 133 (1993).
8. Gibbs, J. W., ''The Collected Works of J. Willard Gibbs,'' Vol. 1, p. 225. Longmans, Green, New York, 1928.
9. Eriksson, J. C., *Surf. Sci.* **14,** 221 (1969).
10. Rusanov, A. I., ''Phasengleichgewichte und Grenzflächenerscheinungen,'' p. 312. Akademie-Verlag, Berlin, 1978.
11. Neogi, P., and Friberg, S. E., *J. Chem. Phys.* **91,** 605 (1987).
12. Weatherburn, C. E., ''Differential Geometry of Three Dimensions.'' Cambridge, 1930.
13. Ljunggren, S., and Eriksson, J. C., *Langmuir* **8,** 1300 (1992).
14. Markin, V. S., Koslov, M. M., and Leikin, S. L., *J. Chem. Soc., Faraday Trans 2* **84,** 1149 (1988).
15. Ou-Yang, Z., and Helfrich, W., *Phys. Rev.* **A39,** 5280 (1989).
16. Gurkov, T. D., and Kralchevsky, P. A., *Colloids Surf.* **47,** 45 (1990).
17. Kralchevsky, P. A., Eriksson, J. C., and Ljunggren, S., *Adv. Colloid Interface Sci.* **49,** 19 (1994).
18. Podstrigach, Y. S., and Povstenko, Y. Z., ''Introduction to the Mechanics of Surface Phenomena in Deformable Solids.'' Naukova Dumka, Kiev, 1985.
19. Veselovsky, V. S., and Pertzov, V. N., *Z. Phys. Khim.* **8,** 245 (1936).
20. Pethica, B. A., *Rep. Progr. Appl. Chem.* **46,** 14 (1961).
21. Torza, S., and Mason, S. G., *Kolloid-Z. Z. Polym.* **246,** 593 (1971).
22. Pujado, P. R., and Scriven, L. E., *J. Colloid Interface Sci.* **40,** 82 (1972).
23. Lane, J. E., *J. Colloid Interface Sci.* **52,** 155 (1975).
24. Ivanov, I. B., Kralchevsky, P. A., and Nikolov, A. D., *J. Colloid Interface Sci.* **112,** 97 (1986).
25. Ivanov, I. B., and Kralchevsky, P. A., *in* ''Thin Liquid Films'' (I. B. Ivanov, Ed.), pp. 49–129. Dekker, New York, 1988.