Surface Tension and Surface Energy of Curved Interfaces and Membranes

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ABSTRACT

In this work we develop the basic idea that the mechanical properties of a curved Gibbsian dividing surface are characterized, not only by the surface tension, but also by surface moments. It is shown that an additional surface bending moment term is to be introduced in the interfacial balance of the force moments at a spherical dividing surface. The existence of surface bending moment leads to a difference between the dilational surface energy and the surface tension. These two quantities are expressed in terms of integrals over the components of the pressure tensor for an arbitrarily chosen spherical dividing surface (not necessarily the surface of tension). The relation between dilational surface energy and surface tension is generalized for interfaces with an arbitrary curvature. A similar relationship was derived for a surface shearing energy, which is important for interfaces exhibiting shearing elasticity, like biomembranes. The relation between the dilational surface energy and the interfacial density of the grand potential is discussed. The results can be useful for the analysis of data for microemulsions, interfacial waves, vesicles and biomembranes.

INTRODUCTION

The effect of the curvature on the interfacial tension can affect the occurrence of many processes in microheterogeneous systems, such as formation of microemulsions and phase nucleation. During the last decade the interest in curvature effects has increased due to the intensive studies of microemulsions.

The purpose of the present work is to demonstrate the difference between surface tension and surface dilational energy for curved interfaces. These two quantities coincide for a flat interface or for the so called "surface of tension", introduced by Gibbs [1]. For interfaces with low surface tension (like microemulsions) the thermodynamic surface of tension can be located away from the real transition zone between the two neighbouring phases. In this case it is more appropriate to use other dividing surfaces, different from the surface of tension. Then one has to account for the difference between surface tension and surface dilational energy, which is due to the presence of surface moments.

In the first part of this paper we will consider the simpler case of spherical interfaces. The difference between surface tension and surface energy is more pronounced for arbitrarily curved interfaces; in this case the surface tension is, in general, a tensorial quantity, whereas the surface energy is a scalar quantity, connected with the invariants of the tensors of the surface tension, surface moments and surface curvature. The resulting relationships are the subject of the second part of this paper. The thermodynamic aspect of the results (and especially the connection between surface dilational energy and surface density of the grand thermodynamic potential) is discussed at the end of the paper.

Many works have been devoted to the mechanics and the thermodynamics of curved fluid interfaces [1–13], but because of the diversity of approaches and notations an outline is needed.

The theory of curved interfaces originates from the work of Gibbs [1]. According to him the work of deformation of an elementary parcel, ΔA, of an interface, can be written in the form

$$\delta w_s = \gamma \delta \alpha + B \delta H + \theta \delta D \tag{1}$$

Here δw_s is surface mechanical work per unit area, $\delta \alpha = \delta(\Delta A)/\Delta A$ is the relative dilation of the element ΔA from the dividing surface, and

$$H = \tfrac{1}{2}(c_1 + c_2), \qquad D = \tfrac{1}{2}(c_1 - c_2) \tag{2}$$

where c_1 and c_2 are the two principal curvatures of this surface; H and D are the mean and the deviative curvatures (the latter being a measure for the local deviation of the surface from spherical shape). One sees from Eqn (1) that $\gamma \delta \alpha$ is the work for simple dilation ($\delta c_1 = \delta c_2 = 0$) of the interface, $B \delta H$ is the work for simple bending of the interface ($\delta c_1 = \delta c_2$, $\delta \alpha = 0$), and $\theta \delta D$ is the work for simple torsion of the interface ($\delta c_1 = -\delta c_2$, $\delta \alpha = 0$) — see Fig. 1. B and θ are called bending and torsion moments, respectively [2]. When all chemical components are soluble in at least one of the bulk phases, γ equals the density of the surface excess of the grand thermodynamic potential (see, e.g., Eqn (158) in Ref. [3]). In other words, γ can be perceived as the surface energy per unit area. When the Gibbsian dividing surface is chosen to be the surface of tension, the respective value γ_s of γ can be interpreted as the mechanical surface tension.

Some authors [2,13] have used in Eqn (1) variables H and $K = H^2 - D^2$ instead of the variables H and D in the Gibbs approach; the variables H and D have the advantage of providing simple geometrical interpretation (cf. Fig. 1), and moreover, the bending and torsion moments B and θ have the same physical dimension.

For isotropic deformations of a spherical interface $\delta D = 0$ and the other quantities in Eqn (1) do not depend on the position in the surface. Then an integrated form of Eqn (1) reads
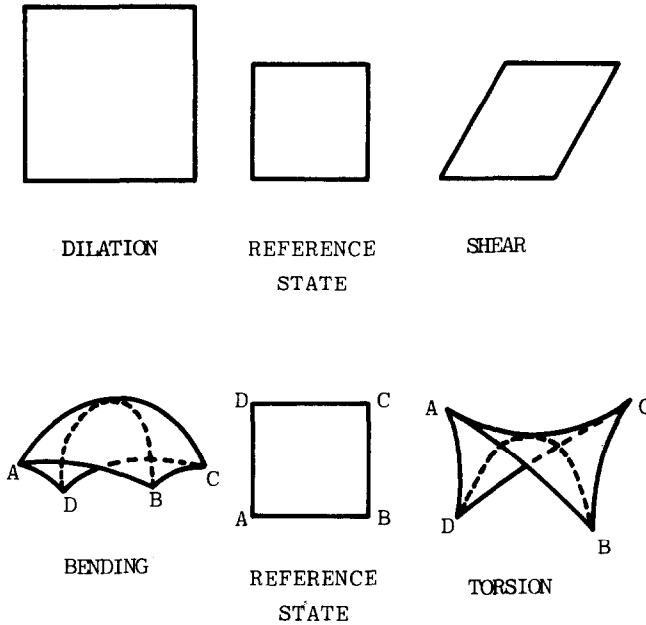
Fig. 1. Independent modes of surface deformation.

$$\delta W_s = \gamma \delta A + AB \delta H \tag{3}$$

where $\delta W_s = A\delta w_s$, A being the surface area. On the other hand, Kondo [4,5] and Rusanov [6] have derived (by using different approaches) an alternative expression for δW_s

$$\delta W_s = \gamma \delta A + A\left[\frac{\partial \gamma}{\partial a}\right]\delta a \tag{4}$$

where a is the radius of the spherical dividing surface and the derivative $[\partial \gamma / \partial a]$ corresponds to a change of a at a fixed physical state of the system. For a spherical surface $H = -1/a$ and from Eqns (3) and (4) one finds [3]

$$B = a^2\left[\frac{\partial \gamma}{\partial a}\right] \tag{5}$$

γ and B can be expressed as integrals over the components of the pressure tensor by the so called "hydrostatic approach", developed in Refs [5–7]. Our analysis below is based mainly on this approach and therefore we will consider its physical basis in more detail.

Imagine a spherical drop or bubble, phase α, surrounded by another fluid phase, β. Due to the symmetry of the system the pressure tensor has only three nonzero components; P_{rr} and $P_{\theta\theta} = P_{\varphi\varphi}$, where r, θ and φ are polar coordinates

(r is the distance to the center of curvature). The force (per unit area), acting normally to any surface, $r=$ constant, is P_{rr} and it is called the normal component of the pressure tensor $P_N(r)$; tangentially to the same surface acts $P_T(r) = P_{\theta\theta} = P_{\varphi\varphi}$, which is called the tangential component of the pressure tensor.

Let us consider a portion of the system, enclosed between two spheres of radii r_α and r_β. The total force acting on the surface, hatched in Fig. 2, in a direction, perpendicular to it, is [5]

$$d\theta \int_{r_\alpha}^{r_\beta} P_T r \, dr \tag{6}$$

The respective force moment is given by

$$d\theta \int_{r_\alpha}^{r_\beta} P_T r^2 \, dr \tag{7}$$

Following Gibbs [1] one can define an idealized system by introducing two bulk phases, α and β, homogeneous up to the spherical dividing surface of radius a_s. Then one can consider the dividing surface as a membrane (of zero thickness) with surface tension γ_s. Then the counterparts of Eqns (6) and (7) for the idealized system are
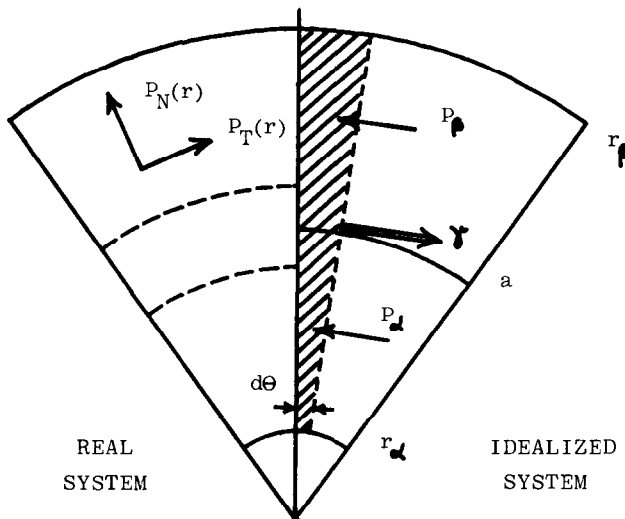

Fig. 2. Real and idealized two-phase system of spherical symmetry.

$$d\theta \int_{r_\alpha}^{r_\beta} \bar{P}_s r \, dr - \gamma_s a_s \, d\theta \qquad (8)$$

$$d\theta \int_{r_\alpha}^{r_\beta} \bar{P}_s r^2 \, dr - \gamma_s a_s^2 \, d\theta \qquad (9)$$

where

$$\bar{P}_s(r) = \begin{cases} P_\alpha \text{ for } r < a_s \\ P_\beta \text{ for } r > a_s \end{cases}$$

is the pressure in the idealized system. The requirement for the idealized system to be mechanically equivalent (in terms of force and moment) to the real one, yields [5]

$$\gamma_s a_s = \int_{r_\alpha}^{r_\beta} (\bar{P}_s - P_T) \, r \, dr \qquad (10)$$

$$\gamma_s a_s^2 = \int_{r_\alpha}^{r_\beta} (\bar{P}_s - P_T) \, r^2 \, dr \qquad (11)$$

where Eqns (6)–(9) have been utilized. Equations (10) and (11) can be considered as a set of two equations determining γ_s and a_s [9]. In particular,

$$a_s = \left(\int_{r_\alpha}^{r_\beta} (\bar{P}_s - P_T) r^2 \, dr \right) \bigg/ \left(\int_{r_\alpha}^{r_\beta} (\bar{P}_s - P_T) r \, dr \right)$$

is the radius of the surface of tension.

The condition for equivalence between the idealized and the real systems with respect to the mechanical moment can be analogously derived for an arbitrary spherical dividing surface of radius a (not necessarily the surface of tension) [6,9]:

$$\gamma a^2 = \int_{r_\alpha}^{r_\beta} (\bar{P} - P_T) r^2 \, dr \qquad (12)$$

where

$$\bar{P} = \begin{cases} P_\alpha \text{ for } r < a \\ P_\beta \text{ for } r > a \end{cases} \qquad (13)$$

Note that γ in Eqn (12) is, in general, different from γ_s, which satisfies not only Eqn (12) but also the force balance, Eqn (10).

The differentiation of Eqn (12) with respect to a for a constant physical state of the system (fixed P_T, P_α, P_β, r_α and r_β) leads to [4,6]

$$\left[\frac{\partial \gamma}{\partial a}\right]+\frac{2\gamma}{a}=P_\alpha-P_\beta \tag{14}$$

which is the generalized form of the Laplace equation, first derived by Kondo [4]. On the other hand, the condition for hydrostatic equilibrium [5,8,9]

$$\frac{d(r^2 P_N)}{dr}=2\,r\,P_T \tag{15}$$

integrated between r_α and r_β, along with the force balance Eqn (10), yields

$$\frac{2\gamma_s}{a_s}=P_\alpha-P_\beta \tag{16}$$

(here it is supposed that $P_N(r_\alpha)=P_\alpha$ and $P_N(r_\beta)=P_\beta$). The comparison between Eqn (14) (which is valid for every dividing surface) and Eqn (16) shows that

$$\left[\frac{\partial \gamma}{\partial a}\right]_{a=a_s}=0 \tag{17}$$

at the surface of tension. The latter result, in conjunction with Eqn (5) implies that the bending moment, B, is zero at the surface of tension. By eliminating $P_\alpha-P_\beta$ between Eqns (14) and (16) one derives the equation

$$\frac{dy}{dx}+\frac{2}{x}y-2=0 \tag{18}$$

where

$$x=a/a_s, \qquad y=\gamma/\gamma_s \tag{19}$$

The solution of Eqn (18) along with the boundary condition $y(1)=1$, reads

$$y(x)=\frac{1}{3x^2}+\frac{2}{3}x \tag{20}$$

This equation, first derived by Kondo [4], represents the dependence of the interfacial tension on the choice of the dividing surface for a given physical state. Then from Eqns (5), (19) and (20) one can find the respective dependence for the bending moment B [3]

$$\bar{B}=\frac{B}{2\gamma a}=\frac{x^3-1}{2x^3+1} \tag{21}$$

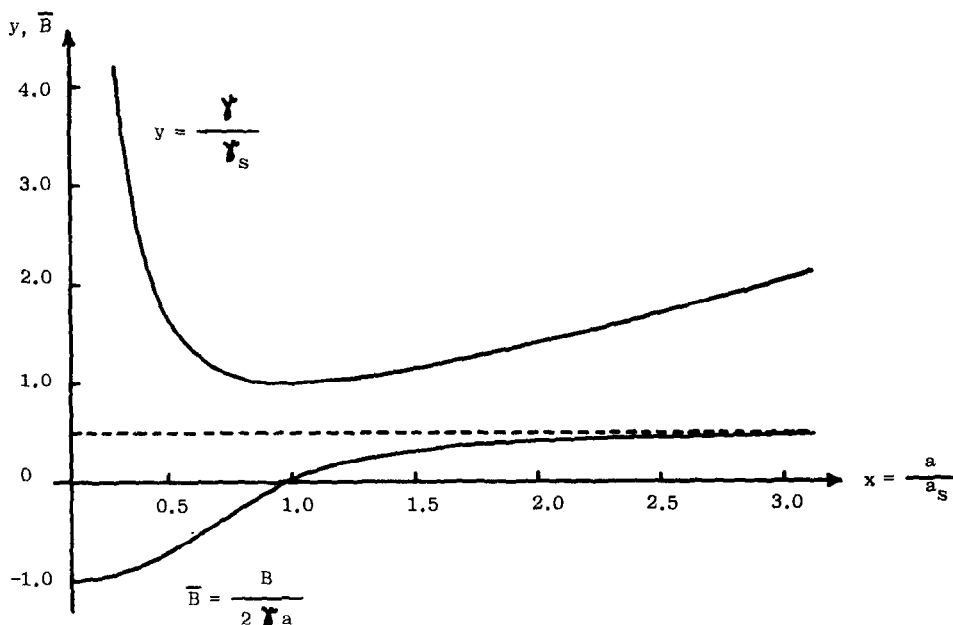Equations (20) and (21) are illustrated graphically in Fig. 3. Equation (20)

Fig. 3. Dependence of the dilational energy γ and surface moment B on the position of an arbitrarily chosen spherical dividing surface under constant physical state.

lies on the basis of the thermodynamic analysis of the curvature dependence of the surface tension (see Ref. [5] for details).

In summary, according to the existing hydrostatic theory of spherical interfaces the idealized system is mechanically equivalent to the real one [with respect both to the acting forces and to the force moments — see Eqns (10) and (11)] only for one specially chosen dividing surface, the surface of tension. In spite of the fact that γ can be defined properly for each spherical dividing surface, it can be interpreted as the hydrostatic surface tension only for the surface of tension. Indeed, the moment balance, Eqn (12), [giving as a corollary Eqn (14)], holds for all dividing surfaces, whereas the force balance, Eqn (10), is satisfied only at the surface of tension. However, as pointed out by Miller [10], for interfaces of low surface tension (like critical emulsions and micro-emulsions), the mathematical surface of tension can be located far away from the real transition region between the two phases; then it is more appropriate to use dividing surfaces, other than the surface of tension.

Our aim in this paper is to construct the idealized system in such a way, that the condition for mechanical equivalence to the real system (with respect both to the forces and to the force moments), be fulfilled for every dividing surface (not necessarily the surface of tension.) In this way a hydrostatic surface tension, σ, which is different from γ, is defined for every dividing surface. The

difference between σ and γ turns out to be proportional to the surface bending moment, B. The resulting extended theory contains as a special case all equations quoted above in this section. In addition, some equations, which are known to hold at the surface of tension, are generalized for every dividing surface and some new relationships are derived. We believe this analysis will be useful for the studies of microemulsions, where the use of the surface of tension is not convenient and bending moment effect [10,11] as well as the effect due to the entropy of mixing [12] is important. The problem about the difference between interfacial tension and interfacial excess free energy [13] is discussed at the end of the paper.

BENDING MOMENT OF A SPHERICAL INTERFACE

We postpone consideration of the general formalism to the next section and here we will restrict our treatment to uniform spherical interfaces. In this case, besides the surface tension (denoted now by σ), we will ascribe to the idealized system a surface bending moment M, acting on the dividing surface in Fig. 2. Then instead of Eqns (8) and (9) one can write for the force and moment in the idealized system

$$d\theta \int_{r_\alpha}^{r_\beta} \bar{P}r\, dr - \sigma a d\theta \tag{22}$$

$$d\theta \int_{r_\alpha}^{r_\beta} \bar{P}r^2\, dr - \sigma a^2 d\theta + M a d\theta \tag{23}$$

In view of Eqns (6) and (7), the conditions for mechanical equivalence between the idealized and the real system now read

$$\sigma a = \int_{r_\alpha}^{r_\beta} (\bar{P} - P_T)r\, dr \tag{24}$$

$$\sigma a^2 - M a = \int_{r_\alpha}^{r_\beta} (\bar{P} - P_T)r^2\, dr \tag{25}$$

Comparison of Eqns (12) and (25) leads to the following connection between γ, σ and M

$$\gamma = \sigma - \frac{M}{a} \tag{26}$$

Therefore, γ but not σ will satisfy the generalized Laplace Eqn (14). Remem-

bering that γ in Eqn (1) multiplies the elementary interfacial dilation $\delta\alpha$, we will call γ "dilational surface energy", in order to distinguish between it and the proper surface tension, σ.

On the other hand, by integration of Eqn (15) one can derive from Eqn (24) a counterpart of Eqn (16)

$$\frac{2\sigma}{a} = P_\alpha - P_\beta \tag{27}$$

(In contrast to Eqn (16), Eqn (27) holds for every choice of the spherical dividing surface.) Then it follows from Eqns (5), (14), (26) and (27), that

$$B = 2M \tag{28}$$

(As demonstrated in the next section, B is the trace and M is one of the two (equal) eigenvalues of the surface tensor of moments.) In view of Eqn (28) the connection between the surface dilational energy and surface tension, Eqn (26), can be transformed to read

$$\gamma = \sigma - \frac{B}{2a} = \sigma + \tfrac{1}{2}BH \tag{29}$$

where $H = -1/a$ is the mean curvature of the sphere. In the next section Eqn (29) will be generalized for arbitrarily shaped interfaces. It is seen from Eqn (29) that γ and σ coincide only at the surface of tension, where $B = 0$

$$\gamma_s = \sigma_s \tag{30}$$

As mentioned earlier, Eqns (10) and (11) uniquely determine the two parameters γ_s and a_s. However, in the present approach Eqns (12) and (24) do not determine the three parameters γ, σ and a. Then a can be considered as a free parameter, connected with the choice of the dividing surface. Hence σ, similarly to γ, depends on the choice of the dividing surface. From Eqn (27) it follows that

$$\sigma = \tfrac{1}{2}\,(P_\alpha - P_\beta)a = \frac{\sigma_s}{a_s}a = \frac{\gamma_s}{a_s}a \tag{31}$$

The formal dependence of σ on a (at a fixed physical state) is linear, i.e., it is much simpler than the analogous dependence of γ on a, exhibiting a minimum — see Fig. 3.

Whereas Eqn (10) holds only for the surface of tension, Eqn (24) is valid for every choice of the dividing surface. Then Eqn (24) can be differentiated with respect to a at a given physical state. The result reads

$$\sigma + a\left[\frac{\partial\sigma}{\partial a}\right] = (P_\alpha - P_\beta)a$$

The latter equation is satisfied identically due to Eqn (31). This fact can serve as an indication for the self-consistency of the approach developed in this section. One can easily check, that the dependence on B on a

$$B = \frac{2}{3}\gamma_s a_s \left(\frac{a^2}{a_s^2} - \frac{a_s}{a} \right) \tag{32}$$

following from Eqns (19)–(21), satisfies the differential equation

$$\left[\frac{\partial B}{\partial a} \right] = 2\gamma \tag{33}$$

which is a counterpart of Eqn (5). Buff [7] and Goodrich [15] have derived the equations

$$\gamma_s = \int_{r_\alpha}^{r_\beta} (P_N - P_T) \frac{r^2}{a_s^2} \, dr \tag{34}$$

$$\gamma_s = \int_{r_\alpha}^{r_\beta} (P_N - P_T) \frac{a_s}{r} \, dr \tag{35}$$

which are valid only for the surface of tension. Our purpose below is to generalize Eqns (34) and (35) for an arbitrarily chosen dividing surface.

An equivalent form of Eqn (15) is

$$\frac{dP_N}{dr} = \frac{2}{r}(P_T - P_N) \tag{36}$$

Upon integration it leads to

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

Then in view of Eqn (27) one obtains

$$\sigma = \int_{r_\alpha}^{r_\beta} (P_N - P_T) \frac{a}{r} \, dr \tag{37}$$

On the other hand, from Eqn (12) one derives

$$\gamma a^2 = \tfrac{1}{3} a^3 (P_\alpha - P_\beta) - \tfrac{1}{3} (P_\alpha r_\alpha^3 - P_\beta r_\beta^3) - \int_{r_\alpha}^{r_\beta} P_T r^2 \, dr \tag{38}$$

Besides, by means of Eqn (15) one can easily prove that

$$2 \int\limits_{r_\alpha}^{r_\beta} P_\mathrm{T} r^2 \, \mathrm{d}r = P_\beta r_\beta^3 - P_\alpha r_\alpha^3 - \int\limits_{r_\alpha}^{r_\beta} P_\mathrm{N} r^2 \, \mathrm{d}r \tag{39}$$

Thus, from Eqns (38) and (39), along with Eqns (27) and (37) one obtains

$$\gamma = \frac{1}{3} \int\limits_{r_\alpha}^{r_\beta} \left(P_\mathrm{N} - P_\mathrm{T} \right) \left(\frac{2a}{r} + \frac{r^2}{a^2} \right) \mathrm{d}r \tag{40}$$

Equations (40) and (37) are in fact the generalizations sought for Eqns (34) and (35). A new expression for B follows from Eqns (5) and (40)

$$B = \frac{2}{3} \int\limits_{r_\alpha}^{r_\beta} \left(P_\mathrm{N} - P_\mathrm{T} \right) \left(\frac{a^2}{r} - \frac{r^2}{a} \right) \mathrm{d}r \tag{41}$$

The last equation can also be derived by means of Eqns (29), (37) and (40).

Equations (37), (40) and (41) can be used for calculation of the surface tension, σ, surface dilational energy, γ, and surface bending moment, B, if some model expression for $(P_\mathrm{N} - P_\mathrm{T})$ is available.

At the end of this section we will briefly discuss the problem about the position of the surface of tension with respect to other dividing surfaces and the interfacial transition zone.

Let a_v be the radius of a given dividing surface, located somewhere in the interfacial transition zone, say the radius of the equimolecular dividing surface — see Ref. [5]. Besides, let γ_v, σ_v and B_v be the values of the respective quantities at this specified surface. Then Eqns (19) and (20) yield

$$\frac{\gamma_\mathrm{v}}{a_\mathrm{v}} = \frac{\gamma_\mathrm{s}}{a_\mathrm{s}} \left(\frac{2}{3} + \frac{1}{3} \frac{a_\mathrm{s}^3}{a_\mathrm{v}^3} \right) \tag{42}$$

For $a = a_\mathrm{v}$ one obtains from Eqns (5), (14) and (16)

$$\frac{2\gamma_\mathrm{v}}{a_\mathrm{v}} + \frac{B_\mathrm{v}}{a_\mathrm{v}^2} = \frac{2\gamma_\mathrm{s}}{a_\mathrm{s}} \tag{43}$$

The elimination of $\gamma_\mathrm{s}/a_\mathrm{s}$ between Eqns (42) and (43) leads to

$$\frac{a_\mathrm{s}^3}{a_\mathrm{v}^3} = \frac{\gamma_\mathrm{v} - B_\mathrm{v}/a_\mathrm{v}}{\gamma_\mathrm{v} + \frac{1}{2} B_\mathrm{v}/a_\mathrm{v}} \tag{44}$$

Then with

$$\delta = a_\mathrm{v} - a_\mathrm{s} \tag{45}$$

one finally obtains

$$\delta = a_{\mathrm{v}} \left\{ 1 - \left(\frac{\gamma_{\mathrm{v}} - B_{\mathrm{v}}/a_{\mathrm{v}}}{\gamma_{\mathrm{v}} + \frac{1}{2}B_{\mathrm{v}}/a_{\mathrm{v}}} \right)^{1/3} \right\}$$
$$= a_{\mathrm{v}} \left\{ 1 - \left(\frac{\sigma_{\mathrm{v}} - \frac{3}{2}B_{\mathrm{v}}/a_{\mathrm{v}}}{\sigma_{\mathrm{v}}} \right)^{1/3} \right\} \tag{46}$$

(at the last step Eqn (29) was used). Equation (46) shows that the sign of δ is connected with the sign of B_{v}: $\delta_{\mathrm{v}} > 0$ when $B_{\mathrm{v}} > 0$ and vice versa. Some calculations, based on the statistical mechanics [5,9] show, that $\delta > 0$ for a drop of pure liquid. Hence some conclusions for the bending moment can be made. It can be expected that $B_{\mathrm{v}} > 0$ for drops and $B_{\mathrm{v}} < 0$ for bubbles.

Equation (46) also suggests, that for low surface tensions ($\sigma_{\mathrm{v}} \lesssim |B_{\mathrm{v}}/a_{\mathrm{v}}|$) the surface of tension can be located away from the real interfacial zone, in agreement with the suggestion of Miller [10].

GENERALIZATION FOR AN INTERFACE OR MEMBRANE OF ARBITRARY CURVATURE

Our purpose below is to find a generalized version of Eqn (29), relating the surface dilational energy, γ, with the surface tension, σ, and the surface bending moment, B, for arbitrarily shaped interfaces. The adequate formalism for this case is provided by the differential geometry of surfaces — see, e.g., Refs [14,16–20].

Let (u^1, u^2) be curvilinear coordinates on the surface, and let $\mathbf{R}(u^1, u^2, t)$ be the running-radius vector of the dividing surface. Then

$$\mathbf{a}_{\mu} = \frac{\partial \mathbf{R}}{\partial u^{\mu}}, \qquad V_{\mathrm{II}} = \mathbf{a}^{\mu} \frac{\partial}{\partial u^{\mu}} \tag{47}$$

are the vectors of the surface basis and the surface gradient operator. Here and hereafter the Greek indices take values 1 and 2, and summation over the repeating indices is carried out. It is known that the curvature tensor

$$\underline{b} = -V_{\mathrm{II}} \mathbf{n} \tag{48}$$

($\mathbf{n}$ is the unit normal to the surface), is a symmetrical surface tensor, whose eigenvalues are the two principal curvatures, c_1 and c_2. Then it is clear that the trace of $\underline{b}$ is equal to $2H$ (cf. Eqn (2)) and the determinant of $\underline{b}$ is the Gaussian curvature $K = c_1 c_2$.

$$\underline{U}_{\mathrm{II}} = \mathbf{a}^{\mu} \mathbf{a}_{\mu} \text{ and } \underline{q} = \frac{1}{D} (\underline{b} - H \underline{U}_{\mathrm{II}}) \tag{49}$$

are the surface idemfactor and the curvature deviatoric tensor. The eigenvalues of $\mathbf{q}$ are 1 and -1, whereas both eigenvalues of $\underline{U}_{II}$ are equal to 1. Therefore $\underline{U}_{II}$ and $\mathbf{q}$ are constant surface tensors, i.e., the covariant derivatives of their components are zero

$$a_{\lambda\mu,\nu} = q_{\lambda\mu,\nu} = 0 \tag{50}$$

In particular, the components of $\underline{U}_{II}$

$$a_{\mu\nu} = \mathbf{a}_\mu \cdot \mathbf{a}_\nu \tag{51}$$

are in fact the components of the surface metric tensor. In view of Eqn (49) the curvature tensor can be expressed as a sum of isotropic and deviatoric parts

$$b_{\lambda\mu} = Ha_{\lambda\mu} + Dq_{\lambda\mu} \tag{52}$$

Let us suppose in addition that (u^1, u^2) are the material surface coordinates. Then

$$\mathbf{v} = \left(\frac{\partial \mathbf{R}}{\partial t}\right)_{u^1, u^2} \tag{53}$$

is the velocity of the surface material points. According to Eliassen [18], the surface rate-of-strain (stretching) tensor, $d_{\mu\nu}$, is defined by the expression

$$d_{\mu\nu} = \frac{1}{2}\frac{\partial a_{\mu\nu}}{\partial t} = \tfrac{1}{2}(v_{\mu,\nu} + v_{\nu,\mu} - 2b_{\mu\nu}v^{(n)}) \tag{54}$$

where

$$v_\mu = \mathbf{a}_\mu \cdot \mathbf{v} \text{ and } v^{(n)} = \mathbf{n} \cdot \mathbf{v} \tag{55}$$

In spite of the fact that we will finally arrive at some quasistatic relationships, it is convenient to work in the beginning with the rates of changing of some quantities with time. Then it is easy to obtain the respective infinitesimal increments of these quantities during an elementary quasistatic process. For example, if δt is a time increment, then $d_{\mu\nu}\delta t$ are the components of the surface strain tensor. Similarly, if $\dot{H}$ is the time derivative of the mean curvature, then $\delta H = \dot{H}\delta t$ is the differential of H, which enters Eqn (1).

As shown in Ref. [21] the scalar quantities

$$\dot{\alpha} = a^{\mu\nu}d_{\mu\nu} \text{ and } \dot{\beta} = q^{\mu\nu}d_{\mu\nu} \tag{56}$$

characterize the local rates of dilation and shearing, respectively. The corresponding differentials are

$$\delta\alpha = \dot{\alpha}\delta t \text{ and } \delta\beta = \dot{\beta}\delta t \tag{57}$$

in particular, $\delta\alpha$ takes part in Eqn (1). For purely fluid interfaces the shearing deformation $\delta\beta$ does not contribute to the work of interfacial deformation,

expressed by Eqn (1). However, as pointed out in Refs [21–23], if the interface is a biomembrane, an additional term accounting for the shearing elastic energy should be included in Eqn (1)

$$\delta w_\mathrm{s} = \gamma\delta\alpha + \xi\delta\beta + B\delta H + \theta\delta D \tag{58}$$

ξ in Eqn (58) accounts for the surface density of the shearing energy in the same way as γ accounts for the energy of dilation. Benson and Yun [24] demonstrated that the shearing elasticity can also lead to a difference between surface energy and surface tension. That is why we will work below with the more general Eqn (58) instead of Eqn (1).

We will restrict our considerations to quasistatic processes, for which the rate-of-strain tensor $d_{\mu\nu}$ is diagonal in the basis of the principal curvatures all the time. (This is so, for example, in the familiar case of axisymmetric deformations of an axisymmetric membrane — see Ref. [22].) In this case, having in mind Eqn (56), one can write

$$d_{\mu\nu} = \tfrac{1}{2}\,\dot\alpha a_{\mu\nu} + \tfrac{1}{2}\,\dot\beta q_{\mu\nu} \tag{59}$$

Due to the physical relation between stress and strain, one can present the surface stress tensor (the tensor of the surface tension) in the form

$$\sigma_{\mu\nu} = \sigma a_{\mu\nu} + \eta q_{\mu\nu} \tag{60}$$

If σ_1 and σ_2 are the eigenvalues of the tensor $\sigma_{\mu\nu}$ (in our case they are the tensions acting along the lines of curvature), then it follows from Eqn (60)

$$\sigma = \tfrac{1}{2}\,(\sigma_1 + \sigma_2) \text{ and } \eta = \tfrac{1}{2}\,(\sigma_1 - \sigma_2) \tag{61}$$

According to Refs [3,22,24] σ is the hydrostatic surface tension (generalizing σ in Eqn (27) for arbitrarily curved interfaces) and η is the shearing tension. The meaning of the components of $\sigma_{\mu\nu}$ in an arbitrary surface basis is illustrated in Fig. 4a.

Let us consider a tensorial field of the surface moments

$$M_{\mu\nu} = \tfrac{1}{2}\,(M_1 + M_2)a_{\mu\nu} + \tfrac{1}{2}\,(M_1 - M_2)q_{\mu\nu} \tag{62}$$

defined throughout the dividing surface. (In other words we consider the interface as a two-dimensional continuum of Cosserat [14].) Obviously, M_1 and M_2 are the eigenvalues of the tensor $M_{\mu\nu}$ as well as σ_1 and σ_2 are the eigenvalues of $\sigma_{\mu\nu}$. Sometimes [14] the surface moments are characterized by another tensor

$$N_{\mu\nu} = M_\mu{}^\lambda \epsilon_{\nu\lambda} \tag{63}$$

where $\epsilon_{\mu\nu}$ is the surface alternator defined as in Refs [14,16–18]. The meaning of the components of the tensors $N_{\mu\nu}$ and $M_{\mu\nu}$ is illustrated in Fig. 4b and c. It is seen that N_{11} (and N_{22}) represents normal moment (it causes torsion of the surface element), whereas N_{12} (and N_{21}) represents tangential moment (it causes bending of the surface element). Hence the mechanical interpretation
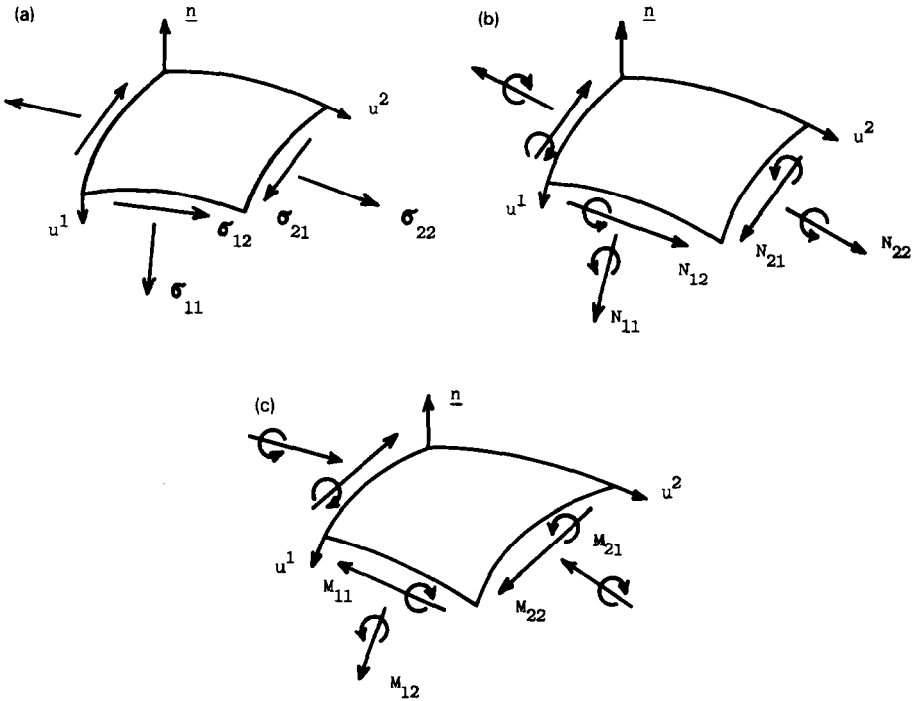
Fig. 4. (a) Components of the surface stress tensor σ. (b) Components of the surface moment tensor $\underline{N}$. (c) Components of the surface moment tensor $\underline{M}$.

of $N_{\mu\nu}$ is similar to that of $\sigma_{\mu\nu}$ (cf. Fig. 4a and b). However, $N_{\mu\nu}$ is not a symmetrical surface tensor and that is why the symmetrical tensor $M_{\mu\nu}$ is preferably used in the works devoted to shells [19] and biomembranes [22].

A necessary condition for equilibrium (see, e.g., Eqn (3.45) in Ref. [14]) is

$$b^{\mu\nu}N_{\mu\nu} = \epsilon^{\mu\nu}\sigma_{\mu\nu} \tag{64}$$

A substitution from Eqns (60), (62) and (63) shows that Eqn (64) is identically satisfied by the above expressions for $\sigma_{\mu\nu}$ and $M_{\mu\nu}$.

According to Eqn (4.26) in Ref. [14] the mechanical work of surface deformation per unit area and per unit time can be expressed as

$$\frac{\delta w_{\mathrm{s}}}{\delta t} = \underline{\sigma}: (V_{\mathrm{II}}\mathbf{v} + U_{\mathrm{II}}\times\mathbf{w}) + \underline{N}: (V_{\mathrm{II}}\mathbf{w}) \tag{65}$$

where the double scalar product of two dyadics is defined according to Gibbs

$$(\mathbf{ab}):(\mathbf{cd}) = (\mathbf{a}\cdot\mathbf{c})(\mathbf{b}\cdot\mathbf{d})$$

and $\mathbf{w}$ is the angular velocity. In our case $\mathbf{w}$ is a vector field, defined on the surface, characterizing the rotation of the unit normal, $\mathbf{n}$, during the bending

of the surface. As illustrated in Fig. 5, $|\mathbf{w}| = \Delta\varphi/\Delta t = |\Delta\mathbf{n}|/(|\mathbf{n}|\Delta t)$ at $\Delta t \to 0$. Accounting for the fact that $|\mathbf{n}| = 1$ and that $\mathbf{w}$ is perpendicular to the plane, defined by the vectors $\mathbf{n}$ and $\Delta\mathbf{n}/\Delta t$, one obtains an explicit expression for $\mathbf{w}$:

$$\mathbf{w} = \mathbf{n} \times \frac{d\mathbf{n}}{dt} \tag{66}$$

As shown in the Appendix to this paper, a substitution from Eqns (60), (62), (63) and (66) into Eqn (65), along with Eqns (54) and (59), leads to the result

$$\frac{\delta w_s}{\delta t} = \sigma\dot{\alpha} + \eta\dot{\beta} + (M_1 + M_2)(\dot{H} + \tfrac{1}{2}H\dot{\alpha} + \tfrac{1}{2}D\dot{\beta})$$
$$+ (M_1 - M_2)(\dot{D} + \tfrac{1}{2}D\dot{\alpha} + \tfrac{1}{2}H\dot{\beta}) \tag{67}$$

Having in mind that $\delta H = \dot{H}\delta t$, $\delta D = \dot{D}\delta t$ and Eqn (57) one finally obtains

$$\delta w_s = [\sigma + \tfrac{1}{2}(M_1 + M_2)H + \tfrac{1}{2}(M_1 - M_2)D]\delta\alpha$$
$$+ [\eta + \tfrac{1}{2}(M_1 + M_2)D + \tfrac{1}{2}(M_1 - M_2)H]\delta\beta \tag{68}$$
$$+ (M_1 + M_2)\delta H + (M_1 - M_2)\delta D$$

The coefficients multiplying the independent differentials in Eqns (58) and (68) must be equal. Hence one obtains:
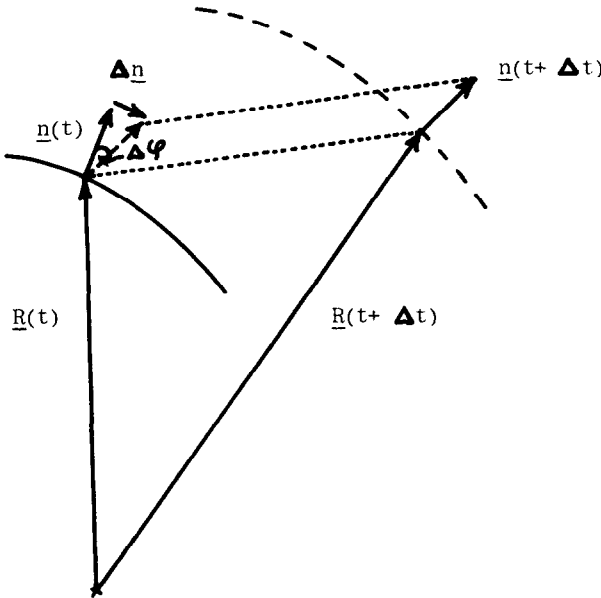

Fig. 5. Rotation of the unit normal during the surface deformation.

$$B = M_1 + M_2 \tag{69}$$

$$\theta = M_1 - M_2 \tag{70}$$

$$\gamma = \sigma + \tfrac{1}{2}BH + \tfrac{1}{2}\theta D \tag{71}$$

$$\xi = \eta + \tfrac{1}{2}BD + \tfrac{1}{2}\theta H \tag{72}$$

For a spherical interface $D = 0$ and $M_1 = M_2 = M$. Then Eqns (69) and (71) will reduce to Eqns (28) and (29), respectively. In other words, Eqn (71) is the generalization of the connection between the dilational surface energy, γ, and the surface tension, σ, sought for. In addition we obtained a similar relationship, Eqn (72), connecting the shearing surface energy, ξ, with the shearing tension, η.

DISCUSSION

All the coefficients in the right-hand side of Eqn (58) (γ, ξ, B and θ) are surface excess quantities and can be expressed as integrals over the excess pressure tensor

$$\underline{P}^s = \underline{P} - \bar{P}\underline{U}$$

($\underline{U}$ is the bulk idemfactor). Indeed, as shown in Refs [3,21] their values at each point of an arbitrarily curved dividing surface are:

$$\gamma = -\tfrac{1}{2} \int_{\lambda_1}^{\lambda_2} \underline{U}_{II} : \underline{P}^s \chi d\lambda \quad ; \quad \xi = -\tfrac{1}{2} \int_{\lambda_1}^{\lambda_2} \underline{q} : \underline{P}^s \chi d\lambda \tag{73}$$

$$B = \int_{\lambda_1}^{\lambda_2} \underline{L} : \underline{P}^s \lambda d\lambda \quad ; \quad \theta = \int_{\lambda_1}^{\lambda_2} (\underline{q} \cdot \underline{L}) : \underline{P}^s \lambda d\lambda \tag{74}$$

where

$$\chi = (1 - \lambda H)^2 - \lambda^2 D^2 \text{ and } \underline{L} = (1 - 2\lambda H)\underline{U}_{II} + \lambda \mathbf{b} \tag{75}$$

and the integration is carried out along the normal to the surface at the respective point. λ has the meaning of distance to the dividing surface and the limits of integration, λ_1 and λ_2, correspond to points placed in the bulk of the neighbouring fluid phases. For a spherical dividing surface with radius a, one has $H = -1/a$, $D = 0$ and

$$\underline{P} = P_T \underline{U}_{II} + P_N \mathbf{nn}$$

Then Eqn (73) for γ reduces to Eqn (12), and Eqn (74) for B reads

$$B = 2 \int\limits_{\lambda_1}^{\lambda_2} (P_T - \bar{P})(1 + \frac{\lambda}{a})\lambda \mathrm{d}\lambda$$

The last equation, known as the Tolman–Buff equation [5], can be derived simply by substitution of Eqns (12) and (24) into Eqn (29) with $\lambda = r - a$.

While Eqn (73) elucidates the meaning of γ from a hydrostatic viewpoint, the thermodynamic interpretation of γ calls for additional discussion. A question of special interest is how the surface energy, γ, is related to the surface density of the excess grand thermodynamic potential, ω_s. In order to answer this question, let us consider an elementary portion, $\mathrm{d}A$, of the curved dividing surface. Let the excess values of the internal energy, entropy, grand potential and number of adsorbed molecules of the ith component on that portion be

$$\mathrm{d}U_s = u_s \mathrm{d}A, \quad \mathrm{d}S_s = s_s \mathrm{d}A, \quad \mathrm{d}\Omega_s = \omega_s \mathrm{d}A, \quad \mathrm{d}N_i^s = \Gamma_i \mathrm{d}A \tag{76}$$

where u_s, s_s, ω_s and Γ_i are the respective surface densities ($i = 1, 2, ..., k$).

Let the area $\mathrm{d}A$ of the portion under consideration be changed during a thermodynamic process by

$$\delta(\mathrm{d}A) = \frac{\delta(\mathrm{d}A)}{\mathrm{d}A} \mathrm{d}A = \delta\alpha \, \mathrm{d}A \tag{77}$$

According to Gibbs [1] the changes of the thermodynamic parameters in Eqn (76) are related by the fundamental equation

$$\delta(\mathrm{d}U_s) = T\delta(\mathrm{d}S_s) + \sum_{i=1}^{k} \mu_i \delta(\mathrm{d}N_i^s) + \delta W_s \tag{78}$$

where δW_s is the mechanical work of deformation of the surface element $\mathrm{d}A$. (One sees that the essence of the Gibbs approach is to apply the fundamental equations of an uniform surface locally, i.e., for each elementary portion, $\mathrm{d}A$, of the curved interface.) Since δw_s in Eqn (58) is mechanical work per unit area, then

$$\delta W_s = (\gamma \delta\alpha + \xi \delta\beta + B \delta H + \theta \delta D)\mathrm{d}A \tag{79}$$

Besides, due to Eqns (76) and (77)

$$\delta(\mathrm{d}U_s) = (\delta u_s + u_s \delta\alpha)\mathrm{d}A \tag{80}$$

and so on for the other differentials in Eqn (78). Thus Eqn (78) can be transformed to read

$$\delta u_s = T\delta s_s + \sum_{i=1}^{k} \mu_i \delta\Gamma_i + (\gamma - \omega_s)\delta\alpha + \xi\delta\beta + B\delta H + \theta\delta D \tag{81}$$

where

$$\omega_s = u_s - Ts_s - \sum_{i=1}^{k} \mu_i \Gamma_i \tag{82}$$

is the interfacial density of the grand thermodynamic potential. It is demonstrated in Ref. [21] that Eqn (81) can be derived from the (local) fundamental equations of the two neighbouring phases.

The number of the independent differentials in the right-hand side of Eqn (81) is related to the type of the interface and of the quasistatic process. If the internal energy of the interface does not depend on its quasistatic dilation, then

$$\left(\frac{\partial u_s}{\partial \alpha} \right)_{s_s, \Gamma_i, \beta, H, D} = 0 \tag{83}$$

and it follows from Eqn (81) that

$$\gamma = \omega_s \tag{84}$$

Hence the surface energy γ equals the interfacial density of the grand potential, ω_s, for processes of equilibrium interfacial dilation, which do not change the surface density of the internal energy, u_s. For example, such is the case when all components present at the interface are soluble at least in one of the neighbouring bulk phases.

Now, let Γ_i be the interfacial density of a component, which is *insoluble* in the bulk phases and for which the interfacial mass balance reads [17,18,21,25]

$$\frac{\delta \Gamma_i}{\delta t} + \Gamma_i V_{II} \cdot \mathbf{v} = 0 \tag{85}$$

As pointed out in Ref. [21], Eqn (85) holds only in the case, when there is no surface diffusion of the respective component. A multiplication of Eqn (85) by δt, along with Eqn (57) and the identity $\dot{\alpha} = V_{II} \cdot \mathbf{v}$, leads to [21]

$$\delta \Gamma_i = -\Gamma_i \delta \alpha, \qquad i = m+1, m+2, ..., k \tag{86}$$

It is supposed here that the components with $i = m+1, m+2, ..., k$, are insoluble in the bulk phases. Then not all $\delta \Gamma_i$ in the right-hand side of Eqn (81) are independent differentials and by using Eqns (82) and (86) one can bring Eqn (81) in the form [21]

$$\delta \hat{\omega}_s = -s_s \delta T + \sum_{i=1}^{m} \Gamma_i \delta \mu_i + (\gamma - \hat{\omega}_s) \delta \alpha + \xi \delta \beta + B \delta H + \theta \delta D \tag{87}$$

here $1 \leq i \leq m$ corresponds to soluble components and

$$\hat{\omega}_s = \omega_s + \sum_{i=m+1}^{k} \Gamma_i \mu_i = u_s - Ts_s - \sum_{i=1}^{m} \Gamma_i \mu_i \tag{88}$$

is the surface density of the modified grand potential. Then the surface energy, γ, is expressed by the equation

$$\gamma = \hat{\omega}_s + \left(\frac{\partial \hat{\omega}_s}{\partial \alpha}\right)_{T,\beta,H,D,\mu_1,\mu_2,...,\mu_m} \tag{89}$$

By combining Eqns (71) and (89), one obtains

$$\sigma = \hat{\omega}_s + \left(\frac{\partial \hat{\omega}_s}{\partial \alpha}\right)_{T,\beta,H,D,\mu_1,\mu_2,...,\mu_m} - \tfrac{1}{2}BH - \tfrac{1}{2}\theta D \tag{90}$$

which is a generalization of the Shuttleworth equation [26] for curved interfaces.

Boruvka et al. [13] followed another (different but equivalent) way in the thermodynamics of the curved interfaces. In Ref. [13] they postulated the local fundamental equations

$$\delta u_s = T\delta s_s + \sum_i \mu_i \delta \Gamma_i + 2C_1 \delta H + C_2 \delta K \tag{91}$$

$$u_s = Ts_s + \sum_i \mu_i \Gamma_i + \gamma^B + 2C_1 H + C_2 K \tag{92}$$

which are to be compared with our equations

$$\delta u_s = T\delta s_s + \sum_i \mu_i \delta \Gamma_i + B\delta H + \theta \delta D \tag{93}$$

$$u_s = Ts_s + \sum_i \mu_i \Gamma_i + \gamma \tag{94}$$

[Eqn (94) follows from Eqns (82) and (84), and Eqn (93) — from Eqns (81) and (84) for *fluid* interfaces: $\xi = 0$.] We introduced the subscript "B" in order to distinguish between γ's in Eqns (92) and (94). The comparison of Eqns (92) and (94) yields the equation

$$\gamma = \gamma^B + 2C_1 H + C_2 K$$

which in view of Eqn (84) coincides with Eqn (20) in the work of Boruvka et al. [13]. Due to the identity $K = H^2 - D^2$, a comparison of Eqns (91) and (93) gives

$$C_1 = \frac{1}{2}B + \frac{1}{2}\frac{H}{D}\theta, \qquad C_2 = -\frac{1}{2}\frac{1}{D}\theta \tag{95}$$

Hence, the difference between Eqns (91) and (93) rests in the choice of the independent variables: (H,K) in Eqn (91) and (H,D) in Eqn (93). We preferred to use the couple (H,D) because of the simple geometric interpretation of δH and δD — see Fig. 1, and because of the fact that the coefficients B and θ have the same dimension and are simply connected with the eigenvalues of

the surface moment tensor — see Eqns (69) and (70). Besides, $\delta D = 0$ for a spherical interface ($\delta K \neq 0$ in this case) and all the equations for surfaces of arbitrary curvature automatically reduce to the respective equations for spherical surfaces in Refs [5,6,9,20].

CONCLUSIONS

In this work we have followed the general idea of Gibbs [1] and Buff [20], that the mechanical properties of a curved Gibbsian dividing surface are characterized not only by the surface tension, σ, but also by bending and torsion moments, B and θ. Special attention is paid to the most simple (but important) case of a spherical interface. It is demonstrated that in order to make the idealized system mechanically equivalent to the real one, an additional surface bending moment term must be introduced in the moment balance equation, Eqn (25). The existence of surface bending moment leads to a difference between the surface dilational energy, γ, and the surface tension, σ, — see Eqn (29). Two new expressions [Eqns (40) and (41)] are derived, allowing the calculation of γ and B if some model expression for the distribution of the pressure tensor across the interface is available. For the surface of tension ($B = 0$) all derived equations reduce to relationships known in the literature. It is also demonstrated that for interfaces of low surface tension the surface of tension can be located far away from the interfacial zone (i.e., far away from one of the different equimolecular dividing surfaces used in the thermodynamics of microemulsions) — see Eqn (46).

The idea that not only the surface of tension, but also every dividing surface must correspond to mechanical equivalence between the idealized and the real system is supported and generalized by the treatment of an arbitrarily curved interface as a two-dimensional continuum of Cosserat. This means, that tensorial fields of the surface tension, Eqn (60), and of the surface moments, Eqn (62), are distributed throughout the dividing surface. Such an analysis shows that the bending moment, B, equals the trace of the surface moment tensor [Eqn (69)], whereas the torsion moment, θ, equals the deviator of the same tensor, Eqn (70). The difference between surface tension and surface energy is more pronounced in this case: the surface tension, σ, is in general a tensorial quantity, whereas the surface energy, γ, is a scalar quantity, connected with the invariants of the tensors of surface tension, surface moments and surface curvature, according to Eqn (71). In addition, we derived a similar relationship for the surface shearing energy, ξ, which is important for interfaces exhibiting shearing elasticity, like biomembranes [22,23].

The mechanical meaning of γ, ξ, B and θ, revealed by Eqns (73) and (74), is determined by the different distribution of the pressure tensor in the real and idealized systems. It turns out that a curved interface behaves as a two-dimensional continuum of Cosserat even if the bulk phases are not three-di-

mensional continua of Cosserat (absence of internal moments in the bulk phases). The thermodynamical meaning of the dilational surface energy γ is discussed. When an isothermal surface dilation (at fixed curvature) does not change the local composition of the interface, γ equals the interfacial density of the grand thermodynamic potential, ω_s, see Eqn (84). When the deformation of the interface is accompanied by extension of an insoluble surface layer, the surface energy γ can be expressed as a sum of the reduced grand potential $\hat{\omega}_s$ and its derivative with respect to the dilation α — see Eqn (89).

We believe that the study presented will be useful when analyzing experimental data for emulsions, microemulsions, interfacial waves, vesicles and biological membranes.

ACKNOWLEDGMENTS

APPENDIX

According to Eqns (60) and (66) σ and $\mathbf{w}$ are pure surface tensor and vector, respectively. Then $\underline{\sigma} : (\underline{\mathbf{U}}_{II} \times \mathbf{w}) = \bar{0}$ and Eqn (65) reduces to

$$\frac{\delta w_s}{\delta t} = \underline{\sigma} : (\nabla_{II} \mathbf{v}) + \underline{\mathbf{N}} : (\nabla_{II} \mathbf{w}) \tag{A.1}$$

Because σ is a symmetric surface tensor one obtains

$$\underline{\sigma} : (\nabla_{II} \mathbf{v}) = \tfrac{1}{2} \underline{\sigma} : [\nabla_{II} \mathbf{v} + (\nabla_{II} \mathbf{v})^+] = \sigma^{\mu\nu} d_{\mu\nu} \tag{A.2}$$

where "$+$" denotes conjugation (cf. Ref. [18]). The substitution from Eqns (59) and (60) in Eqn (A.2) yields

$$\underline{\sigma} : (\nabla_{II} \mathbf{v}) = \sigma \dot{\alpha} + \eta \dot{\beta} \tag{A.3}$$

In view of Eqns (47) and (66) the last term in Eqn (A.1) can be transformed in the following way

$$\underline{\mathbf{N}} : (\nabla_{II} \mathbf{w}) = \underline{\mathbf{N}} : \left\{ \mathbf{a}^\mu \left[\frac{\partial \mathbf{n}}{\partial u^\mu} \times \frac{\partial \mathbf{n}}{\partial t} + \mathbf{n} \times \frac{\partial}{\partial t} \left(\frac{\partial \mathbf{n}}{\partial u^\mu} \right) \right] \right\} \tag{A.4}$$

Having in mind the fact, that the vector $(\partial \mathbf{n}/\partial u^\mu) \times (\partial \mathbf{n}/\partial t)$ is directed along $\mathbf{n}$ and the Weingarten equation [16,18]

$$\frac{\partial \mathbf{n}}{\partial u^\mu} = -b_{\mu\nu} \mathbf{a}^\nu$$

one then derives

$$\underline{\mathbf{N}}: (V_{\mathrm{II}}\mathbf{w}) = -\underline{\mathbf{N}}: \{\mathbf{a}^\mu \mathbf{n} \times (\mathbf{a}^\nu \frac{\partial b_{\mu\nu}}{\partial t} + \frac{\partial \mathbf{a}^\nu}{\partial t} b_{\mu\nu})\} \tag{A.5}$$

With the help of Eqn (63) and the relations

$$\mathbf{n} \times \frac{\partial \mathbf{a}^\nu}{\partial t} = -\mathbf{n} \times \mathbf{a}_\lambda (v^{\nu,\lambda} - b^{\nu\lambda} v^{(n)}), \quad \mathbf{n} \times \mathbf{a}_\lambda = \epsilon_{\lambda\sigma} \mathbf{a}^\sigma$$

(see, e.g., Ref. [18], Eqns (B.3.38) and (B.5.35)), one obtains

$$\underline{\mathbf{N}}: (V_{\mathrm{II}}\mathbf{w}) = M^{\mu\nu} \{ \frac{\partial b_{\mu\nu}}{\partial t} - (v_{\sigma,\nu} - b_{\sigma\nu} v^{(n)}) b_\mu^\sigma \} \tag{A.6}$$

Making use of the fact that the symmetric tensors $M^{\mu\nu}$ and $b^{\mu\nu}$ are both diagonal in the basis of the principal curvatures, along with Eqn (54), one easily transforms Eqn (A.6) to read

$$\underline{\mathbf{N}}: (V_{\mathrm{II}}\mathbf{w}) = M^{\mu\nu} \left\{ \frac{\partial b_{\mu\nu}}{\partial t} - b_\mu^\sigma d_{\sigma\nu} \right\} \tag{A.7}$$

Besides [14,18],

$$\frac{\partial b_{\mu\nu}}{\partial t} = v^\sigma_{,\mu} b_{\sigma\nu} + v^\sigma_{,\nu} b_{\sigma\mu} + v^\sigma b_{\mu\nu,\sigma} - b_\mu^\sigma b_{\sigma\nu} v^{(n)} + v^{(n)}_{,\mu\nu} \tag{A.8}$$

$$b_\mu^\sigma b_{\sigma\nu} = 2H b_{\mu\nu} - (H^2 - D^2) a_{\mu\nu} \tag{A.9}$$

and (see Refs [3,14,18,21])

$$\dot{H} = H_{,\sigma} v^\sigma + (H^2 + D^2) v^{(n)} + \tfrac{1}{2} a^{\mu\nu} v^{(n)}_{,\mu\nu}$$
$$\dot{D} = D_{,\sigma} v^\sigma + 2HD v^{(n)} + \tfrac{1}{2} q^{\mu\nu} v^{(n)}_{,\mu\nu} \tag{A.10}$$

A substitution from Eqns (59), (62) and (A.8) into Eqn (A.7), in view of Eqns (54), (A.9) and (A.10), leads to

$$\underline{\mathbf{N}}: (V_{\mathrm{II}}\mathbf{w}) = (M_1 + M_2)(\dot{H} + \tfrac{1}{2}H\dot{\alpha} + \tfrac{1}{2}D\dot{\beta}) +$$
$$+ (M_1 - M_2)(\dot{D} + \tfrac{1}{2}D\dot{\alpha} + \tfrac{1}{2}H\dot{\beta}) \tag{A.11}$$

Finalling, a combination of Eqns (A.1), (A.3) and (A.11) gives directly Eqn (67).

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