The Statics of Fluid Films with Bending Stiffness

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Based on the principles of rational mechanics, a general formulation for the bending of a fluid monolayer is given. The internal forces of the surface turn out to be by far more copious than for the classical theory of capillarity, in which case the energy density is independent of the local curvature. There are two striking consequences of the investigation: i) the membrane forces are not isotropic and hence cannot be characterized by one single surface tension and ii) the tangential component of the surface force must vanish if no torque density acts on the surface. The results should be noted in the study of amphiphiles.

1 Introduction

Amphiphilic monolayers, separating, e.g., oil and water within a microemulsion, are most interesting objects of physical chemistry (cf. Strey, 1994). Their mechanical behaviour has been treated by various theoretical techniques: microscopic models, Landau theories, and membrane models (cf. Gompper and Schick, 1994). We follow the last mentioned approach — also called phenomenological — which considers the monomolecular fluid film as a structureless two-dimensional curved sheet with bending stiffness. A free energy — also called bending energy — may be attributed to the actual (isothermal) shape of this material surface

$$W = \int_{A} w(\mathbf{C}) \, dA \tag{1}$$

The energy density w is assumed to be a function of the local curvature **C**. This concept was elaborated by Helfrich (1973) who considered the special case of a quadratic dependence of w on **C**. More general functions $w(\mathbf{C})$ have meanwhile been discussed (cf. Leitão *et al.*, 1996; Lade and Krawietz, 2001). In the paper in hand, we will not impose any restriction on the functional form of $w(\mathbf{C})$ in order to embrace the various proposals and to obtain results of utmost generality. Thus we are in accord with a central principle of rational mechanics (cf. Truesdell and Noll, 1965; Krawietz, 1986).

The curvature dependence of the energy density may be tuned, e.g., by the temperature so that a variety of structures — with typical lengths in the nanometer range — can be observed experimentally: lamellae, micelles as well as bicontinuous surfaces. These impose various volumetric constraints on the enclosed water or oil volumes. Therefore, the microemulsion of water, oil, and amphiphile may coexist with excess phases of pure water and oil. It was demonstrated by Lade and Krawietz (2001) how the postulate of a minimal free energy allows a prediction of the observed phase behaviour.

Although Helfrich (1973) pointed out that the dependence of the surface energy on the curvature gives rise to a variety of internal forces and torques within a fluid film, his arguments did not receive broad attention. While his concept of a bending energy is frequently cited, the internal forces of amphiphilic monolayers are even today treated by the inappropriate concept of a surface tension, taken from the classical theory of capillarity. The aim of the present paper is the clarification of the internal forces within an amphiphilic film and of its equilibrium conditions.

Since this article is intended to bridge the gap between experts of physical chemistry dealing with amphiphiles and experts of continuum mechanics studying elastic shells, the presentation is detailed and a knowledge of shell theory is not presupposed.

Symbolic vector and tensor notation is used throughout the paper (cf. Truesdell and Toupin, 1960; Lagally and Franz, 1959; Trostel, 1993, 1997; Krawietz, 1986). Bold face minuscules and majuscules **v**, **T** denote vectors and second-order tensors, respectively. The dot product, cross product and dyadic product of two vectors is written $\mathbf{a} \cdot \mathbf{b}$, $\mathbf{a} \times \mathbf{b}$, $\mathbf{a} \otimes \mathbf{b}$. A second-order tensor can be represented as a sum of

dyadic products, and the dot product of a dyadic product and a vector is defined by $\mathbf{a} \otimes \mathbf{b} \cdot \mathbf{v} = (\mathbf{b} \cdot \mathbf{v}) \mathbf{a}$. The dot product of two dyadic products is defined by $\mathbf{a} \otimes \mathbf{b} \cdot \mathbf{c} \otimes \mathbf{d} = (\mathbf{b} \cdot \mathbf{c}) \mathbf{a} \otimes \mathbf{d}$ and the double dot product by $\mathbf{a} \otimes \mathbf{b} : \mathbf{c} \otimes \mathbf{d} = (\mathbf{a} \cdot \mathbf{c})(\mathbf{b} \cdot \mathbf{d})$. Accents are sometimes used to indicate fields which are to be differentiated. So $\nabla_T (\mathbf{a} \cdot \mathbf{b})$ means that the differentiation of ∇_T acts on the vector field \mathbf{a} alone, while \mathbf{b} is treated as a constant vector. If there is no ambiguity, accents will be omitted.

2 Facts from Differential Geometry

The points of a material surface may uniquely be characterized by their position vector \mathbf{x}_0 in a reference placement of the surface in three-dimensional observer space V (e.g., the placement at time t = 0). Vectors $d\mathbf{x}_0$ from \mathbf{x}_0 to the reference positions of infinitesimally neighbouring material points constitute the tangential plane T_0 .

Given the actual placement of the material surface, the position vector of the material point is \mathbf{x} , and the vectors $d\mathbf{x}$ constitute the actual tangential plane T, the unit normal vector of which will be denoted by \mathbf{n} .

A field Φ that is defined on the material surface may be represented as a function of the vector **x** (Eulerian description) or as a function of the vector **x**₀ (Lagrangean description), i.e.,

$$\Phi = \bar{\Phi}(\mathbf{x}) = \tilde{\Phi}(\mathbf{x}_0) \tag{2}$$

It was Sommerfeld (1945) who pointed out that fluids as well as solids may be described in Eulerian as well as in Langrangean manner. When passing to an infinitesimally neighbouring material point the increment of Φ is

$$d\Phi = \Phi(\mathbf{x}) \otimes \nabla_T \cdot d\mathbf{x} = \Phi(\mathbf{x}_0) \otimes \nabla_{T_0} \cdot d\mathbf{x}_0 \tag{3}$$

The operators ∇_T and ∇_{T_0} denote tangential differentiation with respect to the position vectors **x** and **x**₀, respectively, and their algebraical behaviour is that of vectors in T and T₀, respectively.

Considering as a first choice $\Phi = \mathbf{x}$, we find

$$d\mathbf{x} = \mathbf{x} \otimes \nabla_T \cdot d\mathbf{x} = \mathbf{x} \otimes \nabla_{T_0} \cdot d\mathbf{x}_0 \tag{4}$$

The symbols ($\overline{)}$ and ($\widetilde{)}$ are omitted from now on. Obviously, $\mathbf{x} \otimes \nabla_T$ is the identical mapping on the tangential plane T,

$$\mathbf{x} \otimes \nabla_T = \mathbf{1}_T \tag{5}$$

while the transplacement

$$\mathbf{F} = \mathbf{x} \otimes \nabla_{T_0} \tag{6}$$

which is an invertible mapping from T_0 into T, connects the material line elements $d\mathbf{x}_0$ and $d\mathbf{x}$ of the reference and the actual placement according to

$$d\mathbf{x} = \mathbf{F} \cdot d\mathbf{x}_0 \tag{7}$$

The tensors $\mathbf{1}_T$ and \mathbf{F} may as well be interpreted as mappings of the observer space V into itself, but are then no longer invertible. The identical mappings on V and T are related by

$$\mathbf{1} = \mathbf{1}_T + \mathbf{n} \otimes \mathbf{n} \tag{8}$$

The second choice $\Phi = \mathbf{n}$ gives rise to

$$d\mathbf{n} = \mathbf{n} \otimes \nabla_T \cdot d\mathbf{x} = \mathbf{n} \otimes \nabla_{T_0} \cdot d\mathbf{x}_0$$

= $-\mathbf{C} \cdot d\mathbf{x} = -\mathbf{C} \cdot \mathbf{F} \cdot d\mathbf{x}_0$ (9)

with the definition of the curvature tensor ${f C}$ according to

$$\mathbf{C} = -\mathbf{n} \otimes \nabla_T \tag{10}$$

and a comparison shows

$$\mathbf{C} \cdot \mathbf{F} = -\mathbf{n} \otimes \nabla_{T_0} \tag{11}$$

The tensor **C**, connnecting $d\mathbf{x} \in T$ with $d\mathbf{n} \in T$ — note that differentiation of $\mathbf{n} \cdot \mathbf{n} = 1$ yields $d\mathbf{n} \cdot \mathbf{n} = 0$ — is a mapping of T into itself, and since it is symmetric (cf. the proof in Appendix A), it possesses a spectral representation

$$\mathbf{C} = c_1 \,\mathbf{e}_1 \otimes \mathbf{e}_1 + c_2 \,\mathbf{e}_2 \otimes \mathbf{e}_2 \tag{12}$$

with the principal curvatures c_1, c_2 and the principal axes given by the unit vectors $\mathbf{e}_1, \mathbf{e}_2 \in T$. Half of the trace and the second invariant of this tensor are called mean curvature H and Gaussian curvature K, respectively.

$$H = \frac{1}{2} \operatorname{tr} \mathbf{C} = \frac{1}{2} (c_1 + c_2) \qquad K = 2H^2 - \frac{1}{2} \mathbf{C} : \mathbf{C} = c_1 c_2$$
(13)

Next, we study the (temporal) rate of fields during a motion of the material surface. The velocity \mathbf{v} of a material point is simply the material time derivative of its actual position, i.e.,

$$\mathbf{v} = \dot{\mathbf{x}}$$
 (14)

and the rate of the transplacement \mathbf{F} is obtained by differentiation of equation (6)

$$\dot{\mathbf{F}} = \dot{\mathbf{x}} \otimes \nabla_{T_0} = \mathbf{v} \otimes \nabla_{T_0} \tag{15}$$

(Note that the material time derivative (), evaluated at fixed \mathbf{x}_0 , commutes with the spatial derivative ∇_{T_0} with respect to \mathbf{x}_0 — but not with ∇_T — according to Schwarz's theorem.)

The actual unit normal **n** is orthogonal to any $d\mathbf{x} \in T$. Thus we have

$$0 = \mathbf{n} \cdot d\mathbf{x} = \mathbf{n} \cdot \mathbf{F} \cdot d\mathbf{x}_0 \tag{16}$$

and hence

$$0 = \mathbf{n} \cdot \mathbf{F} \tag{17}$$

The time derivative of this equation yields a statement on the rate of the unit normal

$$\dot{\mathbf{n}} \cdot \mathbf{F} = -\mathbf{n} \cdot \dot{\mathbf{F}} \tag{18}$$

Differentiating equation (11), we get information on the rate of the curvature tensor

$$\dot{\mathbf{C}} \cdot \mathbf{F} + \mathbf{C} \cdot \dot{\mathbf{F}} = -\dot{\mathbf{n}} \otimes \nabla_{T_0} \tag{19}$$

From now on, it is appropriate to choose the actual placement as the reference placement. Then $T = T_0$, $\mathbf{F} = \mathbf{1}_{T_0} = \mathbf{1}_T$ and $\nabla_{T_0} = \nabla_T$. The tensor $\dot{\mathbf{F}}$, which is then called \mathbf{L} , turns out to be the tangential velocity gradient on the actual surface

$$\mathbf{L} = \dot{\mathbf{F}} \big|_{\mathbf{F} = \mathbf{1}_T} = \mathbf{v} \otimes \nabla_T \tag{20}$$

Since $\mathbf{n} \cdot \mathbf{n} = 1$ implies

$$\dot{\mathbf{n}} \cdot \mathbf{n} = 0 \quad \Rightarrow \quad \dot{\mathbf{n}} \in T \tag{21}$$

equation (18) reduces to

$$\dot{\mathbf{n}} \cdot \mathbf{1}_T = \dot{\mathbf{n}} = -\mathbf{n} \cdot \mathbf{L} \tag{22}$$

and equation (19) to

$$\dot{\mathbf{C}} \cdot \mathbf{1}_T + \mathbf{C} \cdot \mathbf{L} = -\dot{\mathbf{n}} \otimes \nabla_T \tag{23}$$

Another form of the rate of the curvature tensor can be derived from equation (12), giving

$$\dot{\mathbf{C}} = \dot{c}_1 \,\mathbf{e}_1 \otimes \mathbf{e}_1 + \dot{c}_2 \,\mathbf{e}_2 \otimes \mathbf{e}_2 + c_1 \left(\dot{\mathbf{e}}_1 \otimes \mathbf{e}_1 + \mathbf{e}_1 \otimes \dot{\mathbf{e}}_1 \right) + c_2 \left(\dot{\mathbf{e}}_2 \otimes \mathbf{e}_2 + \mathbf{e}_2 \otimes \dot{\mathbf{e}}_2 \right) \tag{24}$$

which allows to conclude

$$\mathbf{e}_1 \cdot \mathbf{C} \cdot \mathbf{e}_1 = \dot{c}_1, \qquad \mathbf{e}_2 \cdot \mathbf{C} \cdot \mathbf{e}_2 = \dot{c}_2 \tag{25}$$

The rate of a material line element is obtained by differentiating equation (7)

$$\overline{d\mathbf{x}} = \dot{\mathbf{F}} \cdot d\mathbf{x}_0 = \mathbf{L} \cdot d\mathbf{x} \tag{26}$$

Two material line elements $d\mathbf{x}_1 = ds_1\mathbf{e}_1$ and $d\mathbf{x}_2 = ds_2\mathbf{e}_2$ along the lines of principal curvatures determine a material surface element according to

$$d\mathbf{a} = d\mathbf{x}_1 \times d\mathbf{x}_2 = ds_1 ds_2 \, \mathbf{e}_1 \times \mathbf{e}_2 = dA \, \mathbf{n} \tag{27}$$

The rate of its area is given by — note equation (21), the fact that \mathbf{e}_1 , \mathbf{e}_2 , \mathbf{n} form a right-handed orthonormal basis, and the identity $\mathbf{a} \cdot (\mathbf{b} \times \mathbf{c}) = (\mathbf{a} \times \mathbf{b}) \cdot \mathbf{c}$ —

$$\mathbf{n} \cdot \overline{d\mathbf{a}} = \mathbf{n} \cdot \left(\overline{dA} \,\mathbf{n} + dA \,\dot{\mathbf{n}}\right) = \overline{dA}$$

$$= \mathbf{n} \cdot \left(\overline{d\mathbf{x}_{1}} \times d\mathbf{x}_{2} + d\mathbf{x}_{1} \times \overline{d\mathbf{x}_{2}}\right) = \mathbf{n} \cdot \left((\mathbf{L} \cdot d\mathbf{x}_{1}) \times d\mathbf{x}_{2} + d\mathbf{x}_{1} \times (\mathbf{L} \cdot d\mathbf{x}_{2})\right)$$

$$= ds_{1} ds_{2} \left((\mathbf{e}_{2} \times \mathbf{n}) \cdot \mathbf{L} \cdot \mathbf{e}_{1} + (\mathbf{n} \times \mathbf{e}_{1}) \cdot \mathbf{L} \cdot \mathbf{e}_{2}\right) = dA \left(\mathbf{e}_{1} \cdot \mathbf{L} \cdot \mathbf{e}_{1} + \mathbf{e}_{2} \cdot \mathbf{L} \cdot \mathbf{e}_{2}\right)$$

$$= dA \left(\mathbf{e}_{1} \otimes \mathbf{e}_{1} + \mathbf{e}_{2} \otimes \mathbf{e}_{2}\right) : \mathbf{L} = dA \,\mathbf{1}_{T} : \mathbf{L}$$
(28)

and hence

$$\frac{\overline{dA}}{dA} = \mathbf{1}_T : \mathbf{L} = \nabla_T \cdot \mathbf{v} \tag{29}$$

3 Internal and External Power

We assume the free energy W of the material surface to be a function of its actual shape. Therefore, the energy density w (free energy per actual unit area) is a function of the local shape, i.e., of the curvature tensor \mathbf{C} , and the free energy can be written

$$W = \int_{A} w \, dA = \int_{A} \tilde{w}(\mathbf{C}) \, dA = \int_{A} \check{w}(c_1, c_2) \, dA \tag{30}$$

The last (reduced) form is inferred from the fact that the free energy will not change during a rigid body motion of the surface, and hence w cannot depend on the principal axes — which change their orientation during a rotation — but only on the principal values c_1 , c_2 — or, equivalently, on the invariants H and K — of the curvature tensor **C** [cf. equations (12) and (13)]. This is a generalization of Helfrich's quadratic ansatz. Next, we study the rate of the free energy during a quasi-static isothermal motion of the material surface. According to equation (25), the rate of the energy density can be written

$$\dot{w} = \frac{\partial \tilde{w}}{\partial \mathbf{C}} : \dot{\mathbf{C}} = \frac{\partial \tilde{w}}{\partial c_1} \dot{c}_1 + \frac{\partial \tilde{w}}{\partial c_2} \dot{c}_2 = \frac{\partial \tilde{w}}{\partial c_1} \mathbf{e}_1 \cdot \dot{\mathbf{C}} \cdot \mathbf{e}_1 + \frac{\partial \tilde{w}}{\partial c_2} \mathbf{e}_2 \cdot \dot{\mathbf{C}} \cdot \mathbf{e}_2$$
$$= \left(\frac{\partial \tilde{w}}{\partial c_1} \mathbf{e}_1 \otimes \mathbf{e}_1 + \frac{\partial \tilde{w}}{\partial c_2} \mathbf{e}_2 \otimes \mathbf{e}_2\right) : \dot{\mathbf{C}}$$
(31)

and a comparison shows

$$\frac{\partial \tilde{w}}{\partial \mathbf{C}} = \frac{\partial \tilde{w}}{\partial c_1} \mathbf{e}_1 \otimes \mathbf{e}_1 + \frac{\partial \tilde{w}}{\partial c_2} \mathbf{e}_2 \otimes \mathbf{e}_2$$
(32)

The symbols $(\tilde{)}$ and $(\tilde{)}$ are henceforth omitted. The symmetric tensor

$$\mathbf{M} = -\frac{\partial w}{\partial \mathbf{C}} \tag{33}$$

later on interpreted as a tensor of moments, is a mapping of T into itself. It has the same principal axes as C and hence commutes with C, i.e., $\mathbf{M} \cdot \mathbf{C} = \mathbf{C} \cdot \mathbf{M}$ is a symmetric tensor. So — with equation (23) —

$$\frac{\partial w}{\partial \mathbf{C}} : \dot{\mathbf{C}} = -\mathbf{M} : \dot{\mathbf{C}} = -(\mathbf{M} \cdot \mathbf{1}_T) : \dot{\mathbf{C}} = -\mathbf{M} : (\dot{\mathbf{C}} \cdot \mathbf{1}_T)$$

$$= -\mathbf{M} : (-\mathbf{C} \cdot \mathbf{L} - \dot{\mathbf{n}} \otimes \nabla_T)$$

$$= (\mathbf{C} \cdot \mathbf{M}) : \mathbf{L} + \mathbf{M} : (\dot{\mathbf{n}} \otimes \nabla_T)$$
(34)

For brevity, we introduce the tensor

$$\mathbf{T} = w \, \mathbf{1}_T + \mathbf{C} \cdot \mathbf{M} \tag{35}$$

later on interpreted as a tensor of membrane forces, and obtain, from equations (30) with (20), (29)

$$\dot{W} = \int_{A} \left(\dot{w} \, dA + w \, \overline{dA} \right)$$

$$= \int_{A} \left(\frac{\partial w}{\partial \mathbf{C}} : \dot{\mathbf{C}} + w \, \frac{\overline{dA}}{dA} \right) \, dA$$

$$= \int_{A} \left((w \mathbf{1}_{T} + \mathbf{C} \cdot \mathbf{M}) : \mathbf{L} + \mathbf{M} : (\dot{\mathbf{n}} \otimes \nabla_{T}) \right) \, dA$$

$$= \int_{A} \left(\mathbf{T} : (\mathbf{v} \otimes \nabla_{T}) + \mathbf{M} : (\dot{\mathbf{n}} \otimes \nabla_{T}) \right) \, dA$$
(36)

From the last equation, the rate of the free energy is seen to be equivalent to the power of two kinds of internal forces: the first contribution is the power of the membrane forces \mathbf{T} and the second one is the power of the moments \mathbf{M} .

In the rest of this section, we will integrate the internal power by parts in order to construct an equivalence between the power of internal and external forces. (This equivalence is called the work theorem of mechanics. Integration by parts is usually applied to find the Euler-Lagrangean differential equations from a variational problem. As we will see, this technique can also be used without reference to a maximum or minimum principle.) First, we obtain

$$\dot{W} = \int_{A} \left(\dot{\mathbf{v}} \cdot \mathbf{T} + \dot{\mathbf{n}} \cdot \mathbf{M} \right) \cdot \nabla_{T} \, dA$$

$$= \int_{A} \overline{\left(\mathbf{v} \cdot \mathbf{T} + \dot{\mathbf{n}} \cdot \mathbf{M} \right)} \cdot \nabla_{T} \, dA$$

$$- \int_{A} \left(\mathbf{v} \cdot \mathbf{T} \cdot \nabla_{T} + \dot{\mathbf{n}} \cdot \mathbf{M} \cdot \nabla_{T} \right) \, dA$$
(37)

Next, we introduce the vector $\mathbf{q}_T \in T$, later on interpreted as a transverse force operator. Because of the equations (22) and (20), we find

$$-\dot{\mathbf{n}} \cdot \mathbf{q}_T = \mathbf{n} \cdot \mathbf{L} \cdot \mathbf{q}_T = \mathbf{n} \cdot \acute{\mathbf{v}} \otimes \nabla_T \cdot \mathbf{q}_T = \acute{\mathbf{v}} \cdot \mathbf{n} \otimes \mathbf{q}_T \cdot \nabla_T$$
(38)

and hence

$$-\int_{A} \dot{\mathbf{n}} \cdot \mathbf{q}_{T} \, dA = \int_{A} \acute{\mathbf{v}} \cdot \mathbf{n} \otimes \mathbf{q}_{T} \cdot \nabla_{T} \, dA$$
$$= \int_{A} \overbrace{\mathbf{v} \cdot \mathbf{n} \otimes \mathbf{q}_{T}} \cdot \nabla_{T} \, dA - \int_{A} \mathbf{v} \cdot \overbrace{\mathbf{n} \otimes \mathbf{q}_{T}}^{\prime} \cdot \nabla_{T} \, dA \tag{39}$$

Adding this identity to equation (37), we arrive at

$$\dot{W} = \int_{A} \overline{\left(\mathbf{v} \cdot \left(\mathbf{T} + \mathbf{n} \otimes \mathbf{q}_{T}\right) + \dot{\mathbf{n}} \cdot \mathbf{M}\right)} \cdot \nabla_{T} \, dA$$
$$- \int_{A} \left(\mathbf{v} \cdot \overline{\left(\mathbf{T} + \mathbf{n} \otimes \mathbf{q}_{T}\right)} \cdot \nabla_{T} + \dot{\mathbf{n}} \cdot \left(\mathbf{\dot{M}} \cdot \nabla_{T} - \mathbf{q}_{T}\right)\right) dA \tag{40}$$

Now, $\mathbf{v} \cdot \mathbf{n} \otimes \mathbf{q}_T = (\mathbf{v} \cdot \mathbf{n}) \mathbf{q}_T \in T$ and also $\mathbf{v} \cdot \mathbf{T} \in T$ and $\dot{\mathbf{n}} \cdot \mathbf{M} \in T$, because the (symmetric) tensors \mathbf{M} and \mathbf{T} are mappings of T into itself. Hence the divergence theorem (83) of Appendix B can be applied to the underlined integral in the last equation. To be precise, we consider the surface integrals extended over an arbitrary part of our material surface which we think cut out in the sense of Euler. The boundary of that part is then in general not a real boundary of the material surface but an imaginary cut through the surface. Therefore, the boundary forces and torques that we will identify have the meaning of contact interactions between adjacent regions of our material surface and actually represent internal forces and torques within the surface.

We get the result

$$\dot{W} = \oint \mathbf{v} \cdot (\mathbf{T} + \mathbf{n} \otimes \mathbf{q}_T) \cdot \mathbf{e} \, ds + \oint \dot{\mathbf{n}} \cdot \mathbf{M} \cdot \mathbf{e} \, ds - \int_A \mathbf{v} \cdot \overbrace{(\mathbf{T} + \mathbf{n} \otimes \mathbf{q}_T)} \cdot \nabla_T \, dA - \int_A \dot{\mathbf{n}} \cdot \left(\mathbf{\dot{M}} \cdot \nabla_T - \mathbf{q}_T \right) \, dA$$
(41)

and notice that the rate of the free energy of the considered part of the material surface is equivalent to the power of four external agents.

1) If a point on the boundary moves with the velocity \mathbf{v} , then the power of the boundary force (per unit length of the boundary) is

$$\mathbf{v} \cdot (\mathbf{T} + \mathbf{n} \otimes \mathbf{q}_T) \cdot \mathbf{e} \tag{42}$$

and hence the boundary force (per unit length) is given by

$$\mathbf{f} = (\mathbf{T} + \mathbf{n} \otimes \mathbf{q}_T) \cdot \mathbf{e} = \mathbf{T} \cdot \mathbf{e} + (\mathbf{q}_T \cdot \mathbf{e}) \,\mathbf{n} \tag{43}$$

Figure 1. The external and internal forces and torques acting on a (nearly) rectangular surface element bounded by orthogonal coordinate lines α and β . Arrows with one head: Normal, tangential and transverse components of contact forces per unit length. Arrows with two heads: Bending and twisting contact torques per unit length. Thick arrows with one head: Normal and tangential components of the surface force per unit area. In the case of a fluid film at rest without surface torques, the (dashed) tangential components must be zero. Thick arrows with two heads: Components of the surface torque per unit area. If α , β are lines of principal curvature then $T_{\alpha\beta} = T_{\beta\alpha} = 0$ and $M_{\alpha\beta} = M_{\beta\alpha} = 0$ hold.

It is composed of a membrane force $\mathbf{T} \cdot \mathbf{e} \in T$, which in general has components normal and parallel to the boundary, i.e., normal and shearing (or tangential) forces in the tangential plane, and a shearing (or transverse) force $(\mathbf{q}_T \cdot \mathbf{e}) \mathbf{n}$ perpendicular to the tangential plane, i.e., in the direction of \mathbf{n} (arrows with one head in Fig. 1).

2) Defining the angular velocity $\omega \in T$ of the tangential plane T by

$$\boldsymbol{\omega} = \mathbf{n} \times \dot{\mathbf{n}} \tag{44}$$

we find

$$\dot{\mathbf{n}} = \boldsymbol{\omega} \times \mathbf{n}$$
 (45)

If the tangential plane at a point of the boundary rotates with the angular velocity ω , then the power of the boundary torque (per unit length of the boundary) is

$$\dot{\mathbf{n}} \cdot \mathbf{M} \cdot \mathbf{e} = (\boldsymbol{\omega} \times \mathbf{n}) \cdot \mathbf{M} \cdot \mathbf{e} = \boldsymbol{\omega} \cdot (\mathbf{n} \times \mathbf{M} \cdot \mathbf{e})$$
(46)

and hence the boundary torque (per unit length) is given by

$$\mathbf{m} = \mathbf{n} \times \mathbf{M} \cdot \mathbf{e} \tag{47}$$

In general, it has components parallel and normal to the boundary, i.e. bending and twisting moments (arrows with two heads in Fig. 1).

3) If a point within the cut out part of our material surface moves with the velocity \mathbf{v} , then the power of the distributed surface force (per unit area of the surface) is

$$-\mathbf{v} \cdot \overline{(\mathbf{T} + \mathbf{n} \otimes \mathbf{q}_T)} \cdot \nabla_T \tag{48}$$

and hence the surface force (per unit area) is

$$\mathbf{p} = -(\mathbf{T} + \mathbf{n} \otimes \mathbf{q}_T) \cdot \nabla_T \tag{49}$$

Noting

$$\mathbf{n} \cdot \mathbf{\acute{T}} \cdot \nabla_T = \mathbf{\overbrace{n \cdot T}} \cdot \nabla_T - \mathbf{T} : \mathbf{\acute{n}} \otimes \nabla_T = \mathbf{T} : \mathbf{C}$$
(50)

and

$$\overrightarrow{\mathbf{n} \otimes \mathbf{q}_T} \cdot \nabla_T = \mathbf{n} \left(\nabla_T \cdot \dot{\mathbf{q}}_T \right) + \dot{\mathbf{n}} \otimes \nabla_T \cdot \mathbf{q}_T = \mathbf{n} \left(\nabla_T \cdot \dot{\mathbf{q}}_T \right) - \mathbf{C} \cdot \mathbf{q}_T$$
(51)

we can decompose the surface force into components tangential and normal to the surface (thick arrows with one head in Fig. 1).

$$\mathbf{1}_T \cdot \mathbf{p} = \mathbf{p}_T = -\mathbf{1}_T \cdot \mathbf{\hat{T}} \cdot \nabla_T + \mathbf{C} \cdot \mathbf{q}_T \tag{52}$$

$$\mathbf{n} \cdot \mathbf{p} = p_n = -\mathbf{T} : \mathbf{C} - \nabla_T \cdot \mathbf{q}_T \tag{53}$$

4) If the tangential plane at a point within the cut out part of our material surface rotates with the angular velocity ω , then the power of the distributed surface torque (per unit area of the surface) is

$$-\dot{\mathbf{n}}\cdot\left(\dot{\mathbf{M}}\cdot\nabla_{T}-\mathbf{q}_{T}\right)=-\left(\boldsymbol{\omega}\times\mathbf{n}\right)\cdot\left(\dot{\mathbf{M}}\cdot\nabla_{T}-\mathbf{q}_{T}\right)=-\boldsymbol{\omega}\cdot\mathbf{n}\times\left(\dot{\mathbf{M}}\cdot\nabla_{T}-\mathbf{q}_{T}\right)$$
(54)

and hence the surface torque (per unit area) is

$$\mathbf{t} = -\mathbf{n} \times \left(\mathbf{\hat{M}} \cdot \nabla_T - \mathbf{q}_T \right) \tag{55}$$

(thick arrows with two heads in Fig. 1) which implies

$$\mathbf{1}_T \cdot \mathbf{\hat{M}} \cdot \nabla_T - \mathbf{q}_T = \mathbf{n} \times \mathbf{t} \tag{56}$$

Using the abbreviations (43), (47), (49), (55), we can give the external power the illuminating form

$$\dot{W} = \oint (\mathbf{v} \cdot \mathbf{f} + \boldsymbol{\omega} \cdot \mathbf{m}) \, ds + \int_{A} (\mathbf{v} \cdot \mathbf{p} + \boldsymbol{\omega} \cdot \mathbf{t}) \, dA \tag{57}$$

The equations (52), (53), (56) are the local equilibrium conditions of forces and moments of a curved surface structure. Structures of that kind are called shells by the engineers and have been studied by them for a hundred years (cf. Flügge, 1960; Naghdi, 1972). However, the solid elastic shells of the engineering applications (pressure vessels, concrete domes) possess an energy density of the more general form $w(\mathbf{F}, \mathbf{C})$ so that their membrane forces mainly depend on the surface strains.

In our case, the energy density is assumed to be independent of the transplacement \mathbf{F} . Such a material model is applicable to an amphiphilic film, consisting of molecules which are arranged like needles in the direction of the normal \mathbf{n} . No work is required to perform a rearrangement of the molecules within the fixed shape of the surface. In the first instance, this interpretation of the film as a two-dimensional

fluid is surely correct as long as the area of the material surface element does not change. However, it will also be correct if the area changes but the mass μ per actual unit area remains constant due to a mass exchange with the surroundings; but this will only be possible in the limiting case of a quasi-static process, to which we restrict our attention. (If we would like to study rapid movements of a fluid film, we had to assume the energy density to be of the more general form $w(c_1, c_2, \mu)$. The treatment of such a kinetic process would require an evolution equation for μ .)

According to equation (35), the membrane forces of our model depend solely on the curvature. This allows us to prove an important theorem: The surface torque and the tangential component \mathbf{p}_T of the surface force cannot be prescribed independently of each other, but must satisfy the condition

$$\mathbf{p}_T + \mathbf{C} \cdot (\mathbf{n} \times \mathbf{t}) \equiv 0 \tag{58}$$

In order to see this, we introduce equations (35) and (56) into equation (52) and find

$$\mathbf{p}_{T} + \mathbf{C} \cdot (\mathbf{n} \times \mathbf{t}) = -\mathbf{1}_{T} \cdot \overline{\left(w \, \mathbf{1}_{T} + \mathbf{C} \cdot \mathbf{M}\right)} \cdot \nabla_{T} + \mathbf{C} \cdot \mathbf{1}_{T} \cdot \mathbf{\acute{M}} \cdot \nabla_{T}$$

$$= -\nabla_{T} w - w \, \underline{\mathbf{1}_{T} \cdot \mathbf{\acute{1}}_{T} \cdot \nabla_{T}}$$

$$-\mathbf{1}_{T} \cdot \mathbf{\acute{C}} \cdot \mathbf{M} \cdot \nabla_{T} - \mathbf{C} \cdot \mathbf{\acute{M}} \cdot \nabla_{T} + \mathbf{C} \cdot \mathbf{\acute{M}} \cdot \nabla_{T}$$
(59)

The last two underlined terms obviously cancel each other. The first underlined term is equal to zero, too, since the underlined terms in the following identity vanish:

$$\mathbf{1}_{T} \cdot \mathbf{\hat{1}}_{T} \cdot \nabla_{T} = \mathbf{1}_{T} \cdot \overline{(\mathbf{1} - \mathbf{n} \otimes \mathbf{n})} \cdot \nabla_{T} = -\mathbf{1}_{T} \cdot \mathbf{\hat{n}} \otimes \underline{\mathbf{n}} \cdot \nabla_{T} - \underline{\mathbf{1}_{T} \cdot \mathbf{n}} \otimes \mathbf{\hat{n}} \cdot \nabla_{T} = 0$$
(60)

Because of

$$\nabla_T w = \frac{\partial w}{\partial \mathbf{C}} : \left(\mathbf{\acute{C}} \otimes \nabla_T \right) \tag{61}$$

equation (59) with equation (33) reduces to

$$\mathbf{p}_T + \mathbf{C} \cdot (\mathbf{n} \times \mathbf{t}) = \mathbf{M} : \mathbf{\acute{C}} \otimes \nabla_T - \mathbf{1}_T \cdot \mathbf{\acute{C}} \cdot \mathbf{M} \cdot \nabla_T = \mathbf{M} : \mathbf{1}_T \cdot \mathbf{\acute{C}} \cdot \mathbf{1}_T \otimes \nabla_T - \mathbf{1}_T \cdot \mathbf{\acute{C}} \cdot \mathbf{1}_T \otimes \nabla_T : \mathbf{M}$$
(62)

But the right-hand side expression is, inded, equal to zero, since the third-order tensor $\mathbf{1}_T \cdot \mathbf{\acute{C}} \cdot \mathbf{1}_T \otimes \nabla_T$ is totally symmetric according to Appendix A.

4 Conclusions

Which is the physical meaning of our results?

As is to be expected, the classical theory of capillarity is included in our equations. It results if the surface does not possess any bending stiffness so that the energy density is actually independent of the curvature and hence constant. Moreover, no surface torques are admitted, which implies $\mathbf{p}_T = 0$. The equations (33), (56), (35) reduce to

$$w = \operatorname{const}, \quad \mathbf{M} = 0, \quad \mathbf{q}_T = 0, \quad \mathbf{T} = w \, \mathbf{1}_T$$
(63)

In this case, w does not only denote the energy density but also the surface tension which is the same in all directions. According to equations (43), (47), the boundary force and the boundary torque reduce to

$$\mathbf{f} = w \, \mathbf{e} \,, \qquad \mathbf{m} = 0 \tag{64}$$

while the surface force (53) normal to the surface becomes

$$p_n = -\mathbf{T} : \mathbf{C} = -w \, \mathbf{1}_T : \mathbf{C} = -2wH \tag{65}$$

In the general case where the energy density w actually depends on the curvature **C** of the surface, its internal forces are by far more copious (cf. Fig. 1). The equations (12), (32), (33), (35) yield the following representations of the tensors of membrane forces and of moments

$$\mathbf{T} = \left(w - c_1 \frac{\partial w}{\partial c_1}\right) \mathbf{e}_1 \otimes \mathbf{e}_1 + \left(w - c_2 \frac{\partial w}{\partial c_2}\right) \mathbf{e}_2 \otimes \mathbf{e}_2$$
(66)

$$\mathbf{M} = -\frac{\partial w}{\partial c_1} \mathbf{e}_1 \otimes \mathbf{e}_1 - \frac{\partial w}{\partial c_2} \mathbf{e}_2 \otimes \mathbf{e}_2$$
(67)

while the transverse forces are determined by the operator [cf. equation (56)]

$$\mathbf{q}_T = \mathbf{1}_T \cdot \mathbf{\hat{M}} \cdot \nabla_T - \mathbf{n} \times \mathbf{t} \tag{68}$$

The extensions, compared with the classical case, are the following ones.

- The membrane forces are not the same in all directions and hence cannot be characterized by the concept of one single surface tension. This implies that there are not only normal forces but also tangential forces on cuts which do not coincide with a principal axis of curvature.
- A tensor of moments exists which describes bending moments and twisting moments within the surface.
- According to equation (68), a tangential variability of the moments requires the existence of transverse forces (perpendicular to the surface). These assist the membrane forces in bearing the surface force p_n [cf. equation (53)].

Most of these features were already discussed by Helfrich (1973) in the context of a quadratic energy density and on the basis of physical arguments. (His use of the termini normal and tangential in the description of the internal forces is opposite to ours, since he refers them to the normal vector \mathbf{n} of the surface and not to the normal vector \mathbf{e} of the cut.)

In the special case $c_1 = c_2 = c$, the membrane forces are the same in all directions but, in general, are not identical with the energy density w. Let us illustrate this with an energy density of the special form

Figure 2. The dimensionless values of the energy density w, the membrane force T and the bending moment M, plotted as functions of the dimensionless curvature of a sphere with the special material behaviour given by equation (69).

$$w = k \left(\frac{c_1 + c_2}{2} - H_0\right)^2 + \hat{w} \left((c_1 - c_2)^2\right)$$
(69)

which satisfies the requirement $\check{w}(c_1, c_2) = \check{w}(c_2, c_1)$ and contains Helfrich's quadratic ansatz. We obtain from (66), (67)

$$w = k (c - H_0)^2 + \hat{w}(0)$$

T = T **1**_T with T = -k (c - H_0)H_0 + \hat{w}(0)
M = M **1**_T with M = -k (c - H_0) (70)

Fig. 2 gives the plots of w, T, M as functions of the curvature c of the sphere. The values of w and T coincide in the two cases c = 0 and M = 0, i.e., $c = H_0$.

The behaviour of our fluid material surfaces with bending stiffness is in two points more special than that of solid ones.

- The tensor of membrane forces \mathbf{T} shows a peculiar dependence on the curvature. If the actual tensor of moments \mathbf{M} or of curvature \mathbf{C} vanishes, then the tensor of membrane forces reduces to $\mathbf{T} = w \mathbf{1}_T$ as in the theory of capillarity.
- Due to this structure of \mathbf{T} , the surface force \mathbf{p} is subject to a severe restriction: Its tangential component \mathbf{p}_T must vanish in the absence of a surface torque \mathbf{t} so that \mathbf{p} is of the special form $\mathbf{p} = p_n \mathbf{n}$.

There are analogous restrictions in the theory of three-dimensional fluids at rest. First, the stress tensor is of the special form $\mathbf{T} = -p\mathbf{1}$ (p denotes the pressure) and second, the local equilibrium condition $\mathbf{T} \cdot \nabla + \mathbf{b} = 0$ reduces to $-\nabla p + \mathbf{b} = 0$ so that the body force field \mathbf{b} is subject to the condition $\nabla \times \mathbf{b} = 0$. Fortunately, the restrictions on fluid films and on bulk fluids fit together very well. If the material surface and the bulk fluids on both its sides are at rest, then the surface normal force p_n acting on the (extremely thin) fluid film is connected with the pressures p_i and p_o of the inner and outer bulk fluids, respectively, by

$$p_n = p_o - p_i \tag{71}$$

(We define the normal **n** to point to the inner side.) There is, indeed, no tangential force \mathbf{p}_T and no torque **t** acting on the surface since the bulk fluids at rest are free of shear stresses. (If the bulk fluids are in motion and possess a viscosity, then the fluid film will not remain at rest and inertial forces are to be incorporated into the surface force **p** and the surface torque **t**. The treatment of such a kinetic problem is out of the range of this paper.)

Finally, let us have a look at the equations which connect the shape of a material surface with its surface load.

1) Classical capillarity ($w = \text{const}, \mathbf{t} = 0$): The local mean curvature H is determined by the local surface force p_n according to equation (65).

2) Fluid film with bending stiffness ($w = w(\mathbf{C})$): The introduction of equation (68) into equation (53) gives a scalar differential equation which shows that the local surface force p_n is connected with the local curvature as well as with its first and second derivatives. The vector differential equation (52), however, need not be solved, since it either possesses no solution (if $\mathbf{p}_T + \mathbf{C} \cdot (\mathbf{n} \times \mathbf{t}) \neq 0$ is given) or is identically satisfied (in the case $\mathbf{p}_T + \mathbf{C} \cdot (\mathbf{n} \times \mathbf{t}) \equiv 0$).

3) Solid elastic shell ($w = w(\mathbf{F}, \mathbf{C})$): Not only the scalar equation (53) but also the vector equation (52) have to be considered.

Appendix A: The Symmetry of the Curvature Tensor and of its Gradient

We may characterize the points \mathbf{x}_3 within small layers on both sides of a surface by prescribing a point \mathbf{x} on the surface and a distance l from the surface in the direction of the unit normal $\mathbf{n}(\mathbf{x})$. Then $l(\mathbf{x}_3)$ may be considered a scalar field on a part of the three-dimensional space V, and its spatial gradient is just the unit normal vector \mathbf{n} , which does not change when l varies while \mathbf{x} is fixed. Hence

$$\mathbf{n} = \nabla l \quad \text{and} \quad \frac{\partial \mathbf{n}}{\partial l} = 0$$
(72)

On the surface, we have

$$\nabla = \nabla_T + \mathbf{n} \frac{\partial}{\partial l}, \qquad \nabla_T = \mathbf{1}_T \cdot \nabla \tag{73}$$

and therefore

$$\mathbf{C} = -\mathbf{n} \otimes \nabla_T = -\mathbf{n} \otimes \nabla + \frac{\partial \mathbf{n}}{\partial l} \otimes \mathbf{n} = -\nabla \otimes \nabla l \tag{74}$$

This reveals the symmetry of the curvature tensor **C**.

The gradient of \mathbf{C} along the surface is given by

$$\mathbf{C} \otimes \nabla_T = -\nabla \otimes \nabla \hat{l} \otimes \mathbf{1}_T \cdot \nabla = -\nabla \otimes \nabla \otimes \mathbf{1}_T \cdot \nabla \hat{l}$$
(75)

and therefore the third-order tensor

$$\mathbf{1}_T \cdot \mathbf{\acute{C}} \cdot \mathbf{1}_T \otimes \nabla_T = -\mathbf{1}_T \cdot \nabla \otimes \mathbf{1}_T \cdot \nabla \otimes \mathbf{1}_T \cdot \nabla \dot{l}$$
(76)

is obviously totally symmetric.

Appendix B: The Divergence Theorem of a Curved Surface

The integral theorem of Stokes is known from three-dimensional vector analysis

$$\int_{A} \mathbf{n} \cdot (\nabla \times \mathbf{w}) \, dA = \oint d\mathbf{x} \cdot \mathbf{w} \tag{77}$$

It allows us to transform an integral over a curved surface into a line integral along the boundary curves of the surface. Noting equation (73) and the identity $\mathbf{n} \times \mathbf{n} = 0$ we find

$$\mathbf{n} \cdot (\nabla \times \mathbf{w}) = (\mathbf{n} \times \nabla) \cdot \mathbf{\acute{w}} = (\mathbf{n} \times \nabla_T) \cdot \mathbf{\acute{w}} = \mathbf{n} \cdot (\nabla_T \times \mathbf{w})$$
(78)

so that only tangential derivatives enter the surface integral. In order to apply the Stokes theorem, it is therefore sufficient that the vector field \mathbf{w} is defined on the surface only and not in the neighbouring space. We restrict our attention to the case where \mathbf{w} is defined by means of a tangential vector field \mathbf{z}_T (i.e., $\mathbf{z}_T \cdot \mathbf{n} \equiv 0$) according to

$$\mathbf{w} = \mathbf{n} \times \mathbf{z}_T \tag{79}$$

With the identity

$$\nabla_T \times (\mathbf{\acute{n}} \times \mathbf{\acute{z}}_T) = (\nabla_T \cdot \mathbf{\acute{z}}_T) \,\mathbf{\acute{n}} - (\nabla_T \cdot \mathbf{\acute{n}}) \,\mathbf{\acute{z}}_T \tag{80}$$

and the product rule, we find

$$\mathbf{n} \cdot (\nabla_T \times \mathbf{w}) = \mathbf{n} \cdot (\nabla_T \times (\mathbf{n} \times \mathbf{z}_T))$$
$$= \mathbf{n} \cdot \left((\nabla_T \cdot \mathbf{\dot{z}}_T) \mathbf{n} + \mathbf{z}_T \cdot (\nabla_T \otimes \mathbf{\dot{n}}) - (\nabla_T \cdot \mathbf{\dot{n}}) \mathbf{z}_T - \mathbf{n} \cdot (\nabla_T \otimes \mathbf{\dot{z}}_T) \right) = \nabla_T \cdot \mathbf{z}_T$$
(81)

(Note $\nabla_T \otimes \mathbf{n} \cdot \mathbf{n} = -\mathbf{C} \cdot \mathbf{n} = 0$, $\mathbf{n} \cdot \mathbf{z}_T = 0$ and $\mathbf{n} \cdot \nabla_T = 0$.) We put

$$d\mathbf{x} = \mathbf{g} \, ds$$
 and $\mathbf{e} = \mathbf{g} \times \mathbf{n}$ (82)

so that the tangent vector \mathbf{g} , the normal to the surface \mathbf{n} and the external normal $\mathbf{e} \in T$ of the boundary represent a natural orthonormal basis. Thus we arrive at the divergence (or Gauss integral) theorem of the curved surface:

$$\int_{A} \nabla_T \cdot \mathbf{z}_T \, dA = \oint \mathbf{e} \cdot \mathbf{z}_T \, ds \tag{83}$$

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