Non-Linear Continuum Mechanics of Microemulsions and Amphiphilic Monolayers

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Abstract

Microemulsions are objects of chemical physics with great theoretical and practical importance. They consist of curved monomolecular fluid films of amphiphiles in the nano range, which separate oil from water. One way of understanding the variety of shapes and phases is the application of the continuum mechanical theory of surfaces with bending stiffness. The present monograph tries to give a comprehensive treatment within the framework of full non-linearity in the spirit of rational mechanics. Incorporated are bending and stretching of the film, the monomeric solubility of the amphiphile within the bulk fluids, and the influence of the pressures in the cavities. While the experimentally confirmed three-phase coexistence of a microemulsion with an oil and a water excess cannot be explained on the basis of a linear bending elasticity approach, the nonlinear setting can predict this phenomenon. In a former paper, this has already been shown on the basis of a phenomenological *ad hoc* assumption, which allows symmetry breaking. In the present study, it is proved that a possible explanation is the existence of a state of prestress within the amphiphilic film.

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Preface

The reader may be surprised that an engineer is engaged in a topic from chemical physics. In 1998, Oliver Lade, at that time occupied with his thesis[8] on amphiphiles at the University of Cologne, pointed out to me, that the behaviour of microemulsions had recently been understood to be governed by the bending elasticity of monomolecular amphiphilic films (Gompper and Schick[2], Strey[17]). As I had been involved since decades in the mechanics of structures, where bending plays a central role, I became interested in this field of chemical research.
Soon I realized that the statics of such a fluid film differs markedly from that of the solid shells of engineering (pressure vessels, concrete domes) ([6]). Oliver Lade and I exploited the idea of symmetry breaking of the bending energy density function, originating in [9], and succeeded in explaining the occurence of an X point in phase maps of microemulsions ([7]).

But these two papers left some questions open:

- How can the monomeric solubility of the amphiphile in oil and water be incorporated?
- Which is the influence of a stretching of the film in addition to bending?
- How can the pressures in the cavities be obtained?
- Which is the deeper cause of the symmetry breaking, beyond a phenomenological *ad hoc* assumption?
- Which are the conditions of a coexistence of different structures within the microemulsion?
- Is it admissible to interpret the spinning drop test on the basis of the concept of a surface tension although Helfrich already pointed out that the internal forces of a film are much more copious?

The answer to these questions is the topic of this monograph.

I thank Oliver Lade for helpful comments.

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1 Objectives and Main Results

This monograph tries to bridge the gap between nonlinear continuum mechanics and the theory of microemulsions, which is an object of chemical physics. Therefore, it starts with two separate introductions. The first is intended to communicate the basic facts of microemulsions to researchers in the field of mechanics. The second seeks to clarify concepts of modern continuum mechanics to researchers in chemistry. So the investigation is expected to be of use to scientists of both disciplines.

The list of references is restricted. Useful survey articles, describing experimental findings and containing extensive bibliographies are [17], [2], [12], [4], [16], [19].

1.1 Information for the Reader with a Background in Mechanics

It is well known, that oil and water do not mix. However, the addition of a sufficient amount of amphiphile gives rise to the formation of a microemulsion, which looks homogeneous, at least macroscopically. If the amount of amphiphile is too small, then a decomposition into two or three separate phases will be observed: A microemulsion, which is rich of amphiphile, and above and/or below it excesses of oil and water, respectively, with a rather low content of amphiphile. Then, the efficiency of the amphiphile is too low, or otherwise speaking, the amphiphile is to weak to bring all of the oil and the water together. This phenomenon is also termed emulsification failure.

The macroscopic behaviour is meanwhile well understood on the basis of various experiments which give insight into the microemulsion on a mesoscopic level. They reveal that oil and water are separated by a monomolecular amphiphilic film which may form a variety of structures: lamellae, micelles as well as bi-continuous surfaces. We will restrict our attention to non-ionic amphiphiles. Such a film possesses preferred curvatures which are strongly influenced by the temperature ([17]). It tries to occupy these curvatures but is constrained by the fact that no structure — except planes, spheres and cylinders — has constant curvatures everywhere. Moreover, additional restrictions arise, if there is not enough oil or water to fill the cavities of the preferred structure so that a less desirable structure must be formed.

The self-assembly of the films is understood by an inspection of the microscopic level. The molecule chain of the amphiphile consists of a hydrophilic head (which prefers a water environment) and a hydrophobic tail (which prefers oil). This double preference gives rise to the name amphiphile. Therefore, these molecules lie side by side like pencils thus forming a surface which separates oil from water with each end having its preferred environment, and are therefore also called surfactants.

If we try to describe the mechanics of such a curved film by the theory of shells, we get unexpected results since the film has the character of a two-dimensional fluid with bending stiffness.

Of utmost practical importance is the fact that the surface tension of a plane oil-water interface which is endowed with a surfactant film reaches ultra-low values in a small temperature range.

Applications of microemulsions can be found in nanotechnology where use is made of the small structures of the amphiphilic film.

1.2 Information for the Reader with a Background in Chemical Physics

Although matter consists of atoms and molecules, the continuum approach has been rather successful in the description of natural phenomena and the prediction of the behaviour of engineering structures and processes. The method, dating back to Euler and Cauchy, is applicable to both solid and fluid matter. While investigations were often based on special constitutive assumptions, *e.g.* linear ones, the modern rational mechanics, extended in the famous encyclopedia article of Truesdell and Noll[18] —*cf.* also Krawietz[5]— and resuscitating ideas of Euler, tries to embrace an utmost generality of the assumptions.

We will apply the continuum approach on three levels. On the macroscopic level, the single phases of a mixture of oil, water, and amphiphile are treated as homogeneous fluids. On the mesoscopic level, the monomolecular film is considered as a surface endowed with a free energy. The continuum mechanics of such a surface is well known to engineers ([1],[10]). They discern surfaces with bending stiffness, called shells, *e.g.* a pipe made of steel, and surfaces without bending stiffness, called membranes, *e.g.* canvas. (While the monolayers are usually referred to as membranes with bending stiffness in the literature on microemulsions, this is not in accord with the nomenclature of mechanics.) In the theory of capillarity, a surface tension is attributed to the surface of a bulk fluid, and this surface tension is isotropic in contrast to the membrane forces within a shell or membrane.

It was Helfrich[3] who applied the concepts of shell theory to fluid surfaces, especially bilayers. He studied the effects of bending, stretching, and tilt. Since he was interested in vesicles, he could neglect stretching and tilt and restrict himself to linear constitutive laws of bending, since the curvatures are small.

Although his paper is cited frequently, it seems that hardly anyone ever studied it in detail. So only the quadratic bending energy is extracted and applied to monolayers. The internal forces of such a layer are then described by the concept of a surface tension and hence the equilibrium by the membrane equation, also called Laplace equation (mean curvature related to the pressure difference). In Helfrich's original paper, however, the correct internal forces and the correct derivation of the equilibrium conditions can be found.

In this monograph, tilt is disregarded (this corresponds to Bernoulli's hypothesis in the theory of beams and Kirchhoff's hypothesis in the theory of plates), but bending and stretching are taken into account in a fully nonlinear manner. Therefore, the familiar curvature and saddle-splay moduli do not appear anywhere.

A very important task is the explanation of the presence of the so-called X point in the phase diagram which allows a three phase coexistence (microemulsion, oil excess and water excess simultaneously). This is not possible within a purely linear mechanical theory, *i.e.* with a quadratic bending energy. Nevertheless, explanations have been given, but with the help of additional features like thermal undulations and statistical models ([11]). It was shown, however in [7], that an explanation can be found on the basis of a symmetry breaking which may be introduced by a non-quadratic bending energy.

The radii of curvature of the monolayer are often of the order of magnitude of its thickness. So the film may not be treated as thin, and the computation of volumes must be done accurately. Therefore, we finally descend to the microscopic level and even apply the continuum approach there, *i.e* we consider the film as a thick layer consisting of an infinite number of sublayers. We assume the existence of plane states of stress and strain within these sublayers. They give rise to a streching of the middle surface and a bending of the layer.

It is a common misunderstanding, that each of the sublayers should have the character of a lateral fluid, *i.e.* it should possess equal stresses in all directions of the tangential plane. This is best discussed by temporarily adopting the molecular model. The idea is correct if the film is actually plane. Then the molecules will, in the mean, achieve equal distances in all directions, as is to be expected with a fluid. But consider, *e.g.* a cylindrical shape of the film. The upper and lower ends of the molecules have the same distance in the axial direction. In the circumferential direction, however, the distance of neighbouring molecules is larger at the upper end and smaller at the lower end. So the distances are not identical in the axial and the circumferential directions. If it is conceded that the mutual forces between the molecules are influenced by their distance, then it is necessary to allow different stresses in different directions in the continuum model.

There may be doubts wether a continuum treatment is admissible on the microscopic level, since there is only a limited number of atoms over the thickness of the layer, which is identical with the length of the molecule of the amphiphile. Moreover, we only discuss states of rest, although there is surely a vivid thermal motion of the molecules.

Now, this question can only be answered *a posteriori* on the basis of the results. At least we will see that this approach is flexible enough to predict a symmetry breaking of the mesoscopic bending energy and hence an X point in the macroscopic phase maps.

It would be desirable, of course, to have a description of mutual interactions of the atoms and to compare its expense and its predictions with those of the continuum model.

In the following, extensive quantities of the bulk fluids are referred not to the volume, but to the mass. The reason is, that compressibility is allowed in order to clarify the role of the pressure. The incompressible case is afterwards obtained by a limit process.

1.3 Organization of the Investigation

We start in chapter 2 with the mesoscopic approach. The amphiphilic monomolecular film is regarded as a curved surface. Only when computing volumes, we do not ignore the finite thickness h of the film. The total free energy of the system consists of the elastic energy of bending and stretching of the film, the energy of the monomeric solution of the amphiphile within oil or water, and the potential energy of the environmental pressure. We derive the necessary conditions of a minimum of that free energy and gain insight into the variety of internal forces and moments within the film. (The details are elaborated in appendix G.) The classical concept of a surface tension turns out to be only applicable with plane or nearly plane surfaces. Moreover, we see that the surface tension is identical neither with the surface energy density nor with the membrane forces.

In chapter 3, the microscopic approach treats the film as a thick layer. Not only stress resultants but the stress distribution over the thickness itself is considered. The development is restricted to the case where the principal axes of curvature and of the elastic stretch of the middle surface coincide. (The discussion of the general case is postponed to appendix I.)

Chapter 4 demonstrates the transition from the microscopic to the mesoscopic level by means of a special constitutive assumption. A quadratic dependence of the strain energy on the logarithmic strains is postulated for any layer of the film. Integration over the thickness yields constitutive relations of the mesoscopic level, which are no longer quadratic. These are compared with the familiar quadratic form of the bending energy proposed by Helfrich.

Special surfaces (spheres, cylinders, and triply periodic bi-continuous structures) are the object of chapter 5. The pressures within the cavities and the mass fractions of the monomerically solved amphiphile are derived without assuming any special functional form of the free energy of the film or of the solutions.

The description of our mixtures is essentially simplified if three assumptions are laid down: The plane surfaces which separate different phases are negligible, the solubility of the amphiphile is identical in small cavities and in the excess oil or water, and the compressibility of the bulk fluids can be disregarded. These simplifications, the constitutive assumption of chapter 4 and another assumption on the solubility together are used in chapter 6 in order to perform the transition from the mesoscopic to the macroscopic level. Numerical computations allow the construction of phase maps, some of which possess a characteristic X point. It is shown, that this X point only exists if a positive prestress of the outer layers of the thick film is incorporated into the constitutive model, which causes a symmetry breaking. Finally, it is demonstrated that the coexistence of different types of structures may achieve a smaller value of the total free energy than each of the structures alone.

The six chapters of the main part of this monograph present all essential results without making use of tensor arguments.

The detailed development by means of advanced tensor calculus can be found in the appendices. They contain a short introduction into symbolic tensor notation, facts from the differential geometry of curved surfaces, the derivation of the Euler-Lagrangean differential equations of our minimum problem (in appendix F), the construction of a class of bi-continuous surfaces (in appendix H), and, last not least, an investigation of the spinning drop test (in appendix J). There it is explained why, in general, the evaluation of this test on the basis of the simple concept of a surface tension gives useful results, although we have pointed out, that the correct description of the internal forces of a film is much more sophisticated.

1.4 The Main Results

The central messages of this monograph are:

- The internal forces and moments of an amphiphilic monomolecular film are the same as those of a solid shell. The simple concept of a surface tension, originating from the theory of capillarity, is not sufficient. That concept can, however, be used in the treatment of plane or almost plane surfaces between different phases. The bearing capacity of a fluid film is much more restricted than that of a solid shell: If external torques are not present, then tangential forces cannot be applied to a surface in a relaxed state. Fortunately, this does not cause problems, since the only loads on the film are the pressures of the bulk fluids.

- The local energy density of an amphiphilic film is not determined by the local curvatures alone, but depends on the properties of the whole system through the chemical potential, which dominates the apportioning of the amphiphile content to the different subsystems.
- The pressures within the cavities may be related with the monomeric solubility of the amphiphile.
- A numerical example gives the most important result that the continuum approach on the microscopic level is able to explain a symmetry breaking on the mesoscopic level and hence the existence of an X point in the macroscopic phase map. This phenomenon is evoked by a positive prestress (*i.e.* a tension) in the outer layers of the thick amphiphilic film.

Important remark: The results of this investigation are of a theoretical nature. They give qualitative insight into possible phenomena. A quantitative adjustment to experimental data of special microemulsions is not included and should be the object of future activity.

2 The Mesoscopic Approach

2.1 Composition of the Mixture

A mixture of water, oil, and amphiphile gives rise to a microemulsion and perhaps to oil and water excesses above and below that microemulsion, respectively. The dominant part of the amphiphile forms a monomolecular film separating regions of oil and water within the microemulsion and plane layers separating the microemulsion from the excesses. The rest is solved as monomers within the oil or the water. We allow that different film structures coexist. The structure with the number k is assumed to be composed of n_k identical cells (*e.g.* single spheres, single cylinders or the elementary unit from which a triply periodic surface is built up.) The indices O, W, A, C, E, F will denote oil, water, amphiphile, cell, excess, and film, respectively.

The masses of oil and water can be decomposed according to

$$m_{\mathrm{O}} = \sum_k n_k m_{\mathrm{OC}k} + m_{\mathrm{OE}}, \qquad m_{\mathrm{W}} = \sum_k n_k m_{\mathrm{WC}k} + m_{\mathrm{WE}} \tag{2.1}$$

into parts which are contained within the cells of the film structures and others which form the excesses.

The mass of the amphiphile can be decomposed as follows

$$m_{\mathrm{A}} = \sum_k n_k \big(m_{\mathrm{A,FC}k} + m_{\mathrm{A,OC}k} + m_{\mathrm{A,WC}k}\big) + m_{\mathrm{A,OE}} + m_{\mathrm{A,WE}} + \sum_{j=\mathrm{O,\,W}} m_{\mathrm{A},j} \tag{2.2}$$

The single contributions denote those parts of the amphiphile which form the film of the cells of some structure, the monomers which are solved in the oil and the water within these cells or in the oil and the water excess, and that part which forms the plane layers separating the microemulsion from the oil and the water excess.

We define the following solution parameters which characterize the mass fraction of the solution of the amphiphile within the cells of the different structures

$$k_{\mathrm{O}k} = \frac{m_{\mathrm{A,OC}k}}{m_{\mathrm{OC}k}}\,, \qquad k_{\mathrm{W}k} = \frac{m_{\mathrm{A,WC}k}}{m_{\mathrm{WC}k}} \tag{2.3}$$

and within the excesses

$$k_{\mathrm{OE}} = \frac{m_{\mathrm{A,OE}}}{m_{\mathrm{OE}}}\,, \qquad k_{\mathrm{WE}} = \frac{m_{\mathrm{A,WE}}}{m_{\mathrm{WE}}} \tag{2.4}$$

We denote by μ_j ($j = \mathrm{O}$, W) the mass density (mass referred to the unit area) of the plane layers (their area A_j is determined by the geometric situation), and by μ the mass density of the curved film (not necessarily constant over the film). Neither the number of cells n_k nor the area of the middle surface of a cell $A_{\mathrm{C}k}$ nor the total area $n_k A_{\mathrm{C}k}$ of a structure is known *a priori*.

Equation (2.2) becomes

$$\begin{aligned} g \quad \equiv \quad & m_{\mathrm{A}} - \sum_k n_k \left(\int_{A_{\mathrm{C}k}} \mu \, dA + k_{\mathrm{O}k} m_{\mathrm{OC}k} + k_{\mathrm{W}k} m_{\mathrm{WC}k} \right) \\ & \qquad -k_{\mathrm{OE}} m_{\mathrm{OE}} - k_{\mathrm{WE}} m_{\mathrm{WE}} - \sum_{j=\mathrm{O,\,W}} \mu_j A_j = 0 \end{aligned} \tag{2.5}$$

The free energy F of the system consists of contributions of the curved film, of the oil (with solved amphiphile), of the water (with solved amphiphile), of the plane layers, and of the environmental pressure p_{e}. The total volume of the system (microemulsion, oil and water excess) is denoted by V.

$$F = \sum_k n_k \big(F_{\mathrm{FC}k} + F_{\mathrm{OC}k} + F_{\mathrm{WC}k} \big) + F_{\mathrm{OE}} + F_{\mathrm{WE}} + \sum_{j=\mathrm{O,\,W}} F_j + p_{\mathrm{e}} V \tag{2.6}$$

We introduce the energy density of oil and water as the ratio of the energy and the mass of the solvent. It depends, of course, on the local values of the solution parameter and of the pressure. The pressure of the excesses is the environmental pressure p_{e}, while there may be different pressures $p_{\mathrm{O}k}$ and $p_{\mathrm{W}k}$ of the oil and water within the cells.

$$F_{\mathrm{OE}} = f_{\mathrm{OE}}(k_{\mathrm{OE}}, p_{\mathrm{e}}) \, m_{\mathrm{OE}} \,, \qquad F_{\mathrm{WE}} = f_{\mathrm{WE}}(k_{\mathrm{WE}}, p_{\mathrm{e}}) \, m_{\mathrm{WE}} \tag{2.7}$$

$$F_{\mathrm{OC}k} = f_{\mathrm{O}k}(k_{\mathrm{O}k}, p_{\mathrm{O}k}) \, m_{\mathrm{OC}k} \,, \qquad F_{\mathrm{WC}k} = f_{\mathrm{W}k}(k_{\mathrm{W}k}, p_{\mathrm{W}k}) \, m_{\mathrm{WC}k} \tag{2.8}$$

We further define the energy densities w_{O} and w_{W} of the plane layers and w of the curved film as the energy referred to the actual unit area. We assume that w_{O} and w_{W} depend on the mass densities μ_{O} and μ_{W}, respectively, and that w depends on the local mass density μ and on the local principal curvatures c_1 and c_2. So one aspect of w is that of a bending energy.

$$F_j = w_j(\mu_j) \, A_j \,, \qquad F_{\mathrm{FC}k} = \int_{A_{\mathrm{C}k}} w(c_1, c_2, \mu) \, dA \tag{2.9}$$

Introduction into (2.6) yields

$$
\begin{aligned}
F \;=\; & \sum_k n_k \Bigg(\int_{A_{\mathrm{C}k}} w(c_1, c_2, \mu)\, dA \\
& \qquad + f_{\mathrm{O}k}(k_{\mathrm{O}k}, p_{\mathrm{O}k})\, m_{\mathrm{OC}k} + f_{\mathrm{W}k}(k_{\mathrm{W}k}, p_{\mathrm{W}k})\, m_{\mathrm{WC}k} \Bigg) \\
& + f_{\mathrm{OE}}(k_{\mathrm{OE}}, p_{\mathrm{e}})\, m_{\mathrm{OE}} + f_{\mathrm{WE}}(k_{\mathrm{WE}}, p_{\mathrm{e}})\, m_{\mathrm{WE}} + \sum_{j=\mathrm{O,W}} w_j(\mu_j)\, A_j + p_{\mathrm{e}} V
\end{aligned}
\tag{2.10}
$$

2.2 Computation of Volumes

Let us consider a bi-continuous structure or spheres or cylinders which contain oil. Moreover, let ϱ_{O} and ϱ_{A} denote the mass density (mass per unit volume) of the oil and the monomeric amphiphile within it, respectively. These densities depend on the oil pressure within the cell. Then, with (2.3), we obtain the following relation between the volume $V_{\mathrm{OC}k}$ of the cavity and the mass $m_{\mathrm{OC}k}$ of the enclosed oil.

$$
V_{\mathrm{OC}k} = \frac{m_{\mathrm{OC}k}}{\varrho_{\mathrm{O}}(p_{\mathrm{O}k})} + \frac{m_{\mathrm{A,OC}k}}{\varrho_{\mathrm{A}}(p_{\mathrm{O}k})} = \left(\frac{1}{\varrho_{\mathrm{O}}(p_{\mathrm{O}k})} + \frac{k_{\mathrm{O}k}}{\varrho_{\mathrm{A}}(p_{\mathrm{O}k})} \right) m_{\mathrm{OC}k} \tag{2.11}
$$

With the abbreviation

$$
\upsilon_{\mathrm{O}k} = \frac{1}{\varrho_{\mathrm{O}}(p_{\mathrm{O}k})} + \frac{k_{\mathrm{O}k}}{\varrho_{\mathrm{A}}(p_{\mathrm{O}k})} \tag{2.12}
$$

we arrive at

$$
V_{\mathrm{OC}k} = \upsilon_{\mathrm{O}k}\, m_{\mathrm{OC}k} \tag{2.13}
$$

Introducing this into (2.1) we obtain the mass of the oil excess

$$
m_{\mathrm{OE}} = m_{\mathrm{O}} - \sum_k n_k \upsilon_{\mathrm{O}k}^{-1} V_{\mathrm{OC}k} \tag{2.14}
$$

In a similar manner, we define

$$
\upsilon_{\mathrm{OE}} = \frac{1}{\varrho_{\mathrm{O}}(p_{\mathrm{e}})} + \frac{k_{\mathrm{OE}}}{\varrho_{\mathrm{A}}(p_{\mathrm{e}})} \tag{2.15}
$$

and arrive at a relation between the mass and the volume of the oil excess

$$
V_{\mathrm{OE}} = \upsilon_{\mathrm{OE}} m_{\mathrm{OE}} \tag{2.16}
$$

If O is replaced by W everywhere, then the corresponding formulae for water arise.

The volume of the film material (of thickness h) of one cell amounts to

$$V_{\mathrm{FC}k} = \int_{A_{\mathrm{C}k}} \left(h + c_1 c_2 \frac{h^3}{12} \right) dA \tag{2.17}$$

according to equation (D.11) in appendix D.

The total volume of the system is

$$V = \sum_k n_k \Big(V_{\mathrm{FC}k} + V_{\mathrm{OC}k} + V_{\mathrm{WC}k} \Big) + V_{\mathrm{OE}} + V_{\mathrm{WE}} + \sum_{j=\mathrm{O,\,W}} h A_j \tag{2.18}$$

or

$$\begin{aligned} V \;=\; & \sum_k n_k \Bigg(\int_{A_{\mathrm{C}k}} \left(h + c_1 c_2 \frac{h^3}{12} \right) dA \\ & \qquad + \big(1 - \upsilon_{\mathrm{OE}} \upsilon_{\mathrm{O}k}^{-1}\big) V_{\mathrm{OC}k} + \big(1 - \upsilon_{\mathrm{WE}} \upsilon_{\mathrm{W}k}^{-1}\big) V_{\mathrm{WC}k} \Bigg) \\ & + \upsilon_{\mathrm{OE}} m_{\mathrm{O}} + \upsilon_{\mathrm{WE}} m_{\mathrm{W}} + \sum_{j=\mathrm{O,\,W}} h A_j \end{aligned} \tag{2.19}$$

Introducing this and (2.14) into (2.10) we obtain

$$\begin{aligned} F \;=\; & \sum_k n_k \Bigg(\int_{A_{\mathrm{C}k}} \left(w(c_1, c_2, \mu) + p_{\mathrm{e}} \Big(h + c_1 c_2 \frac{h^3}{12} \Big) \right) dA \\ & + \Big(f_{\mathrm{O}k}(k_{\mathrm{O}k}, p_{\mathrm{O}k}) - f_{\mathrm{OE}}(k_{\mathrm{OE}}, p_{\mathrm{e}}) + p_{\mathrm{e}} \big(\upsilon_{\mathrm{O}k} - \upsilon_{\mathrm{OE}} \big) \Big) \upsilon_{\mathrm{O}k}^{-1} V_{\mathrm{OC}k} \\ & + \Big(f_{\mathrm{W}k}(k_{\mathrm{W}k}, p_{\mathrm{W}k}) - f_{\mathrm{WE}}(k_{\mathrm{WE}}, p_{\mathrm{e}}) + p_{\mathrm{e}} \big(\upsilon_{\mathrm{W}k} - \upsilon_{\mathrm{WE}} \big) \Big) \upsilon_{\mathrm{W}k}^{-1} V_{\mathrm{WC}k} \Bigg) \\ & + \big(f_{\mathrm{OE}}(k_{\mathrm{OE}}, p_{\mathrm{e}}) + p_{\mathrm{e}} \upsilon_{\mathrm{OE}} \big) m_{\mathrm{O}} + \big(f_{\mathrm{WE}}(k_{\mathrm{WE}}, p_{\mathrm{e}}) + p_{\mathrm{e}} \upsilon_{\mathrm{WE}} \big) m_{\mathrm{W}} \\ & + \sum_{j=\mathrm{O,W}} \big(w_j(\mu_j) + p_{\mathrm{e}} h \big) A_j \end{aligned} \tag{2.20}$$

2.3 Elastic Behaviour of the Fluids

We assume the fluids to be elastic. If the mass of the fluid within a cell — say, oil with solved amphiphile — remains constant and only the volume changes, then the rate of the free energy of the fluid is equal to the isothermal power

$$\Big(f_{\mathrm{O}k}(k_{\mathrm{O}k}, p_{\mathrm{O}k}) m_{\mathrm{OC}k} \Big)^{\bullet} = -p_{\mathrm{O}k} \dot{V}_{\mathrm{OC}k} \tag{2.21}$$

and hence, with (2.13),

$$\frac{\partial f_{\mathrm{O}k}}{\partial p_{\mathrm{O}k}} m_{\mathrm{OC}k}\, \dot{p}_{\mathrm{O}k} = -p_{\mathrm{O}k} \frac{\partial \upsilon_{\mathrm{O}k}}{\partial p_{\mathrm{O}k}} m_{\mathrm{OC}k}\, \dot{p}_{\mathrm{O}k} \tag{2.22}$$

or

$$\frac{\partial f_{\mathrm{O}k}}{\partial p_{\mathrm{O}k}} = -p_{\mathrm{O}k} \frac{\partial \upsilon_{\mathrm{O}k}}{\partial p_{\mathrm{O}k}} = -p_{\mathrm{O}k} \frac{\partial}{\partial p_{\mathrm{O}k}} \left(\frac{1}{\varrho_{\mathrm{O}}(p_{\mathrm{O}k})} + \frac{k_{\mathrm{O}k}}{\varrho_{\mathrm{A}}(p_{\mathrm{O}k})} \right) \tag{2.23}$$

Integration by parts yields

$$\begin{aligned} f_{\mathrm{O}k}(k_{\mathrm{O}k}, p_{\mathrm{O}k}) = & \int_{p=0}^{p_{\mathrm{O}k}} \left(\frac{1}{\varrho_{\mathrm{O}}(p)} - \frac{1}{\varrho_{\mathrm{O}}(p_{\mathrm{O}k})} \right) dp \\ & + k_{\mathrm{O}k} \int_{p=0}^{p_{\mathrm{O}k}} \left(\frac{1}{\varrho_{\mathrm{A}}(p)} - \frac{1}{\varrho_{\mathrm{A}}(p_{\mathrm{O}k})} \right) dp + f_{\mathrm{O}k}(k_{\mathrm{O}k}, p_{\mathrm{O}k} = 0) \end{aligned} \tag{2.24}$$

which reveals the dependence of the energy on the pressure.

2.4 The Extended Energy

If there is no oil excess, then (2.14) with $m_{\mathrm{OE}} = 0$ yields the constraint

$$h_{\mathrm{O}} \equiv m_{\mathrm{O}} - \sum_k n_k \upsilon_{\mathrm{O}k}^{-1} V_{\mathrm{OC}k} = 0 \tag{2.25}$$

If there is no water excess then there exists a similar constraint

$$h_{\mathrm{W}} \equiv m_{\mathrm{W}} - \sum_k n_k \upsilon_{\mathrm{W}k}^{-1} V_{\mathrm{WC}k} = 0 \tag{2.26}$$

Moreover, the side condition (2.5) ($g = 0$) is valid in any case. We multiply the three conditions with Lagrangean parameters and add them to the free energy, thus obtaining the extended energy

$$E = F + f\, g + y_{\mathrm{O}}\, h_{\mathrm{O}} + y_{\mathrm{W}}\, h_{\mathrm{W}} \tag{2.27}$$

In the absence of constraints, we define $y_{\mathrm{O}} = 0$ and/or $y_{\mathrm{W}} = 0$. Otherwise we have $h_{\mathrm{O}} = 0$, $k_{\mathrm{OE}} = 0$, $f_{\mathrm{OE}}(k_{\mathrm{OE}}, p_{\mathrm{e}}) + p_{\mathrm{e}} \upsilon_{\mathrm{OE}} = 0$, $A_{\mathrm{O}} = 0$ and/or $h_{\mathrm{W}} = 0$, $k_{\mathrm{WE}} = 0$, $f_{\mathrm{WE}}(k_{\mathrm{WE}}, p_{\mathrm{e}}) + p_{\mathrm{e}} \upsilon_{\mathrm{WE}} = 0$, $A_{\mathrm{W}} = 0$. Since also $g = 0$ in any case, the value of E is the same as that of F for a real system.

We obtain

$$
\begin{aligned}
E \;=\; & \sum_k n_k \Bigg(\int_{A_{\mathrm{C}k}} \Big(w(c_1, c_2, \mu) + p_\mathrm{e}\Big(h + c_1 c_2 \frac{h^3}{12}\Big) - f\mu \Big)\, dA \\
& + \Big(f_{\mathrm{O}k}(k_{\mathrm{O}k}, p_{\mathrm{O}k}) - f_\mathrm{OE}(k_\mathrm{OE}, p_\mathrm{e}) + p_\mathrm{e}\big(\upsilon_{\mathrm{O}k} - \upsilon_\mathrm{OE}\big) \\
& \qquad - f\, \big(k_{\mathrm{O}k} - k_\mathrm{OE}\big) - y_\mathrm{O} \Big) \upsilon_{\mathrm{O}k}^{-1} V_{\mathrm{OC}k} \\
& + \Big(f_{\mathrm{W}k}(k_{\mathrm{W}k}, p_{\mathrm{W}k}) - f_\mathrm{WE}(k_\mathrm{WE}, p_\mathrm{e}) + p_\mathrm{e}\big(\upsilon_{\mathrm{W}k} - \upsilon_\mathrm{WE}\big) \\
& \qquad - f\, \big(k_{\mathrm{W}k} - k_\mathrm{WE}\big) - y_\mathrm{W} \Big) \upsilon_{\mathrm{W}k}^{-1} V_{\mathrm{WC}k} \Bigg) \\
& + \big(f_\mathrm{OE}(k_\mathrm{OE}, p_\mathrm{e}) + p_\mathrm{e} \upsilon_\mathrm{OE} - f\, k_\mathrm{OE} \big) m_\mathrm{O} \\
& + \big(f_\mathrm{WE}(k_\mathrm{WE}, p_\mathrm{e}) + p_\mathrm{e} \upsilon_\mathrm{WE} - f\, k_\mathrm{WE} \big) m_\mathrm{W} \\
& + \sum_{j=\mathrm{O},\mathrm{W}} \big(w_j(\mu_j) + p_\mathrm{e} h - f \mu_j \big)\, A_j + f\, m_\mathrm{A} + y_\mathrm{O}\, m_\mathrm{O} + y_\mathrm{W}\, m_\mathrm{W}
\end{aligned}
\tag{2.28}
$$

We want to find the minimum of the free energy F of the system under the mentioned side conditions. This means that the extended energy E is minimal with respect to unconstrained variations. Now, we can vary the degrees of freedom f, $k_{\mathrm{O}k}$, $k_{\mathrm{W}k}$, $p_{\mathrm{O}k}$, $p_{\mathrm{W}k}$, n_k, the field μ and the shape of the cells, which determines the fields c_1, c_2 of the principal curvatures, the oil-sided and water-sided cavity volumes $V_{\mathrm{OC}k}$, $V_{\mathrm{WC}k}$, and the area $A_{\mathrm{C}k}$. In the case of constraints, there are, in addition, the degrees of freedom y_O and y_W, in the case of excesses, we have instead k_OE, k_WE and μ_O, μ_W. If the energy takes its minimal value then the derivatives of E with respect to the degrees of fredom and the variation of E under any variation of the unknown fields must vanish.

2.5 Necessary Conditions of a Minimum

The postulate that the derivatives of E with respect to $k_{\mathrm{O}k}$ and $p_{\mathrm{O}k}$ must vanish yields the following two equations for the structure with number k — note (2.12).

$$
\begin{aligned}
& \frac{\partial f_{\mathrm{O}k}}{\partial k_{\mathrm{O}k}} - f - \Big(f_{\mathrm{O}k}(k_{\mathrm{O}k}, p_{\mathrm{O}k}) - f_\mathrm{OE}(k_\mathrm{OE}, p_\mathrm{e}) - p_\mathrm{e} \upsilon_\mathrm{OE} \\
& \qquad - f\, \Big(k_{\mathrm{O}k} - k_\mathrm{OE}\Big) - y_\mathrm{O} \Big) \frac{1}{\upsilon_{\mathrm{O}k}\, \varrho_\mathrm{A}(p_{\mathrm{O}k})} = 0
\end{aligned}
\tag{2.29}
$$

$$\frac{\partial f_{\mathrm{O}k}}{\partial p_{\mathrm{O}k}} - \Bigg(f_{\mathrm{O}k}(k_{\mathrm{O}k}, p_{\mathrm{O}k}) - f_{\mathrm{OE}}(k_{\mathrm{OE}}, p_{\mathrm{e}}) - p_{\mathrm{e}} \upsilon_{\mathrm{OE}} - f \Big(k_{\mathrm{O}k} - k_{\mathrm{OE}} \Big) - y_{\mathrm{O}} \Bigg) \frac{1}{\upsilon_{\mathrm{O}k}} \frac{\partial \upsilon_{\mathrm{O}k}}{\partial p_{\mathrm{O}k}} = 0 \qquad (2.30)$$

The last equation together with (2.23) leads to

$$p_{\mathrm{O}k} = - \Bigg(f_{\mathrm{O}k}(k_{\mathrm{O}k}, p_{\mathrm{O}k}) - f_{\mathrm{OE}}(k_{\mathrm{OE}}, p_{\mathrm{e}}) - p_{\mathrm{e}} \upsilon_{\mathrm{OE}} - f \Big(k_{\mathrm{O}k} - k_{\mathrm{OE}} \Big) - y_{\mathrm{O}} \Bigg) \frac{1}{\upsilon_{\mathrm{O}k}} \qquad (2.31)$$

and insertion into (2.29) gives

$$f = \frac{\partial f_{\mathrm{O}k}}{\partial k_{\mathrm{O}k}}(k_{\mathrm{O}k}, p_{\mathrm{O}k}) + \frac{p_{\mathrm{O}k}}{\varrho_{\mathrm{A}}(p_{\mathrm{O}k})} \qquad (2.32)$$

(2.31) with (2.32), (2.12) and (2.15) implies

$$\begin{aligned} y_{\mathrm{O}} &= f_{\mathrm{O}k}(k_{\mathrm{O}k}, p_{\mathrm{O}k}) - f_{\mathrm{OE}}(k_{\mathrm{OE}}, p_{\mathrm{e}}) - \big(k_{\mathrm{O}k} - k_{\mathrm{OE}} \big) \frac{\partial f_{\mathrm{O}k}}{\partial k_{\mathrm{O}k}}(k_{\mathrm{O}k}, p_{\mathrm{O}k}) \\ &\quad + \left(\frac{1}{\varrho_{\mathrm{O}}(p_{\mathrm{O}k})} + \frac{k_{\mathrm{OE}}}{\varrho_{\mathrm{A}}(p_{\mathrm{O}k})} \right) p_{\mathrm{O}k} - \left(\frac{1}{\varrho_{\mathrm{O}}(p_{\mathrm{e}})} + \frac{k_{\mathrm{OE}}}{\varrho_{\mathrm{A}}(p_{\mathrm{e}})} \right) p_{\mathrm{e}} \end{aligned} \qquad (2.33)$$

In case of a constraint, the last condition acts as a prescription for the calculation of y_{O}, which shrinks to

$$y_{\mathrm{O}} = f_{\mathrm{O}k}(k_{\mathrm{O}k}, p_{\mathrm{O}k}) - k_{\mathrm{O}k} \frac{\partial f_{\mathrm{O}k}}{\partial k_{\mathrm{O}k}}(k_{\mathrm{O}k}, p_{\mathrm{O}k}) + \frac{p_{\mathrm{O}k}}{\varrho_{\mathrm{O}}(p_{\mathrm{O}k})} \qquad (2.34)$$

If the dimensions of the cells of two structures — which we think numbered by $k = 1$ and $k = 2$ — are of the same order of magnitude, then it will be reasonable to assume $f_{\mathrm{O}1} = f_{\mathrm{O}2}$. If, moreover, the two variables $k_{\mathrm{O}k}$ and $p_{\mathrm{O}k}$ can uniquely be calculated from the two non-linear equations (2.32) and (2.33), then we must have $k_{\mathrm{O}1} = k_{\mathrm{O}2}$ and $p_{\mathrm{O}1} = p_{\mathrm{O}2}$. So the mass fractions and the pressures within the different structures must be identical. (If, however, the cells of structure 1 are much smaller than those of structure 2 — maybe the diameter of its cavities is of the order of magnitude of the length of the amphiphilic molecule —, then it seems imaginable that $f_{\mathrm{O}1}$ differs from $f_{\mathrm{O}2}$ and so the mass fractions of the amphiphilic monomers and the pressure may differ between the two structures.)

If an oil excess is present, then the postulate that the derivative of E with respect to k_{OE} must vanish, yields the equation — note (2.15) —

$$f = \frac{\partial f_{\mathrm{OE}}(k_{\mathrm{OE}}, p_{\mathrm{e}})}{\partial k_{\mathrm{OE}}} + \frac{p_{\mathrm{e}}}{\varrho_{\mathrm{A}}(p_{\mathrm{e}})} \qquad (2.35)$$

Moreover, we have to put $y_{\mathrm{O}} = 0$, and (2.33) then represents a connexion between $k_{\mathrm{O}k}$, $p_{\mathrm{O}k}$ and k_{OE}. If (2.32) and (2.35) are introduced, then this connexion may be given the form

$$\begin{aligned} & f_{\mathrm{O}k}(k_{\mathrm{O}k}, p_{\mathrm{O}k}) - k_{\mathrm{O}k}\frac{\partial f_{\mathrm{O}k}}{\partial k_{\mathrm{O}k}}(k_{\mathrm{O}k}, p_{\mathrm{O}k}) + \frac{p_{\mathrm{O}k}}{\varrho_{\mathrm{O}}(p_{\mathrm{O}k})} \\ = \; & f_{\mathrm{OE}}(k_{\mathrm{OE}}, p_{\mathrm{e}}) - k_{\mathrm{OE}}\frac{\partial f_{\mathrm{OE}}}{\partial k_{\mathrm{OE}}}(k_{\mathrm{OE}}, p_{\mathrm{e}}) + \frac{p_{\mathrm{e}}}{\varrho_{\mathrm{O}}(p_{\mathrm{e}})} \end{aligned} \tag{2.36}$$

If a plane layer between the microemulsion and the oil excess is present, then we must have

$$f = \frac{dw_{\mathrm{O}}(\mu_{\mathrm{O}})}{d\mu_{\mathrm{O}}} \tag{2.37}$$

Analogous conditions result if O is replaced by W.

The derivatives of E with respect to f and — if there is no excess — to y_{O} and y_{W} are zero, if the conditions $g = 0$ and $h_{\mathrm{O}} = 0$, $h_{\mathrm{W}} = 0$ according to (2.5), (2.25), (2.26) are satisfied.

The sum over k in the extended energy (2.28) may considerably be simplified by means of (2.31) to read

$$\begin{aligned} \sum_k n_k \Bigg(\int_{A_{\mathrm{C}k}} \Big(w(c_1, c_2, \mu) + p_{\mathrm{e}}\Big(h + c_1 c_2 \frac{h^3}{12}\Big) - f\mu \Big)\, dA \\ -\big(p_{\mathrm{O}k} - p_{\mathrm{e}}\big)V_{\mathrm{OC}k} - \big(p_{\mathrm{W}k} - p_{\mathrm{e}}\big)V_{\mathrm{WC}k} \Bigg) \end{aligned} \tag{2.38}$$

The postulate that the derivative of E with respect to n_k must vanish yields the following condition for each structure k.

$$f = \frac{\int_{A_{\mathrm{C}k}} \Big(w + p_{\mathrm{e}}\big(h + c_1 c_2 \frac{h^3}{12}\big)\Big)\, dA - \big(p_{\mathrm{O}k} - p_{\mathrm{e}}\big)V_{\mathrm{OC}k} - \big(p_{\mathrm{W}k} - p_{\mathrm{e}}\big)V_{\mathrm{WC}k}}{\int_{A_{\mathrm{C}k}} \mu\, dA} \tag{2.39}$$

Actually, n_k is a discrete and not a continouous variable, so that differentiation seems inappropriate. But since the number n_k will be rather large, our approximate approach will hardly cause a serious error.

The minimum of E requires also that the variation of E with respect to the field μ vanishes.

$$\delta E = \sum_k n_k \int_{A_{\mathrm{C}k}} \Big(\frac{\partial w(c_1, c_2, \mu)}{\partial \mu} - f\Big)\delta\mu\, dA = 0 \tag{2.40}$$

Since the field $\delta\mu$ is arbitrary, the condition

$$f = \frac{\partial w(c_1, c_2, \mu)}{\partial \mu} \tag{2.41}$$

must hold all over the film.

2.6 The Physical Meaning of these Conditions

The Lagrangean parameter f allows an illuminating interpretation. It gives the amount of free energy which is required in order to import a unit mass of the amphiphile into one of the subsystems. Equation (2.32) describes the energy needed for the solution of additional monomers within the cells, (2.35) for the solution within the excesses, (2.37) for the implementation in the plane layers between the microemulsion and the excesses, and (2.41) for the insertion into the curved film. (2.39) represents the energy which is needed to create the film of additional cells while the fluid content within the totality of the cells remains constant. The volume of this content is therefore increasing, and work is done by its pressure. Our necessary conditions state, that all these amounts of energy must equal the same value of f, so that the exchange of mass between any two subsystems does not alter the minimum value of the free energy of the whole system. The physical quantity f is closely related to the concept of a chemical potential. However, the chemical potential is defined as the molar free enthalpy, while f denotes the density of the free energy (per unit mass).

The Lagrangean parameter y_{O} may also be given a physical interpretation. According to (2.34), it is equal to an amount of free energy which can be seen to be required in order to import a unit mass of oil into a cell. If an oil excess exists, then equation (2.36) states that this energy must equal the energy which is needed to import a unit mass of oil into the excess. So an exchange of oil between the cell and the excess does not alter the energy of the whole system.

2.7 Equilibrium of the Film

Finally, E must also be a minimum with respect to any change of the shape of the film. The evaluation of this condition requires some knowledge of advanced tensor calculus and is worked out in the appendices F and G. The Euler-Lagrangean differential equations of our variational problem can be found in (G.29) and (G.30) with (F.18). The condition

$$\mathbf{q}_T = \mathbf{1}_T \cdot \acute{\mathbf{M}} \cdot \nabla_T \tag{2.42}$$

states that the operator of transverse forces $\mathbf{q}_T$ equals the tangential part of the divergence of the tensor of moments $\mathbf{M}$. This ensures the equilibrium of moments around any axis within the tangential plane. The condition

$$\begin{aligned} &-\mathbf{T} : \mathbf{C} - \nabla_T \cdot \mathbf{q}_T = \\ &p_{\mathrm{W}k}\left(1 + \mathrm{tr}\mathbf{C}\frac{h}{2} + \det\mathbf{C}\frac{h^2}{4}\right) - p_{\mathrm{O}k}\left(1 - \mathrm{tr}\mathbf{C}\frac{h}{2} + \det\mathbf{C}\frac{h^2}{4}\right) \end{aligned} \tag{2.43}$$

ensures the equilibrium of forces normal to the middle surface. The first term on the left-hand side represents the contribution of the tensor of membrane forces **T** due to the curvature **C**, while the second one, the divergence of the transverse forces, originates in bending. On the right-hand side, we see the difference of the pressures on the two sides of the film, both reduced to the middle surface. The equilibrium of forces in any tangential direction is automatically satisfied, since the membrane forces of the film have the special form

$$\begin{aligned}\mathbf{T} &= (w - f\mu)\,\mathbf{1}_T + \mathbf{C}\cdot\mathbf{M} \\ &= (w - f\mu + c_1 m_1)\,\mathbf{e}_1\otimes\mathbf{e}_1 + (w - f\mu + c_2 m_2)\,\mathbf{e}_2\otimes\mathbf{e}_2 \qquad (2.44)\end{aligned}$$

according to (F.20), while (F.19) shows the tensor of moments to be given by

$$\mathbf{M} = -\frac{\partial w}{\partial C} = -\frac{\partial w}{\partial c_1}\mathbf{e}_1\otimes\mathbf{e}_1 - \frac{\partial w}{\partial c_2}\mathbf{e}_2\otimes\mathbf{e}_2 \qquad (2.45)$$

Here $\mathbf{e}_1$ and $\mathbf{e}_2$ denote directions of principal curvatures. Hence the principal membrane forces and moments are obtained from

$$t_1 = w - f\mu + c_1 m_1 = w - f\mu - c_1\frac{\partial w}{\partial c_1}\,, \quad t_2 = w - f\mu + c_2 m_2 = w - f\mu - c_2\frac{\partial w}{\partial c_2} \qquad (2.46)$$

$$m_1 = -\frac{\partial w}{\partial c_1}\,, \qquad m_2 = -\frac{\partial w}{\partial c_2} \qquad (2.47)$$

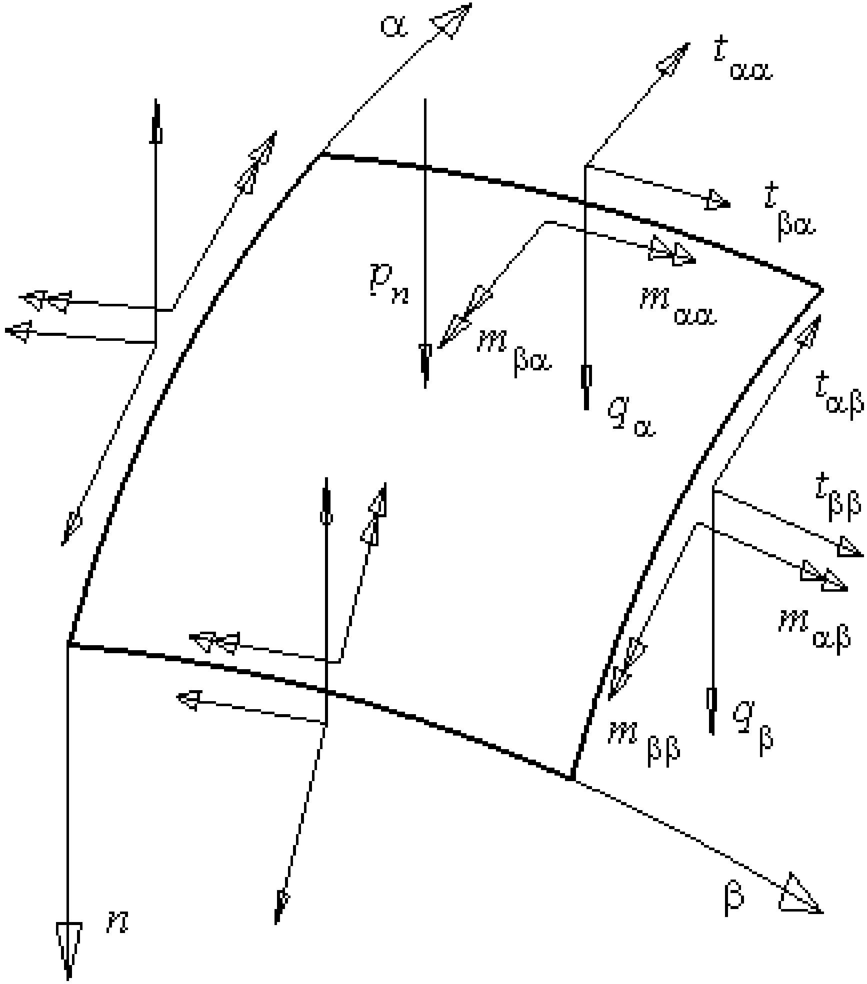
If the surface energy density w would not depend on the curvature, then we had $\mathbf{M} = 0$ and hence $\mathbf{q}_T = \mathbf{0}$ according to (2.42). Moreover, according to (2.44), $\mathbf{T} = (w - f\mu)\,\mathbf{1}_T$ would be isotropic and the left-hand side of (2.43) would become $-(w - f\mu)\mathrm{tr}\mathbf{C}$. If, in addition, $f = 0$, then the energy density w equals the isotropic surface tension and we arrive at the classical theory of capillarity.

However, since w depends on the curvature, the internal forces of the amphiphilic film turn out to be much more copious than those of the classical theory of capillarity. Actually they are as diverse as those of a solid shell. On the other hand, the load carrying behaviour of our fluid film is much more special than that of a solid shell. As is shown in appendix G.2, tangential forces cannot be applied to the film unless also an external torque density acts on the surface.

2.8 The Internal Forces of a Fluid Film

Figure 2.1 illustrates the internal forces in the case where α and β are not lines of principal curvatures. Let **e** be a unit vector normal to a cut and **g** a unit vector parallel to the cut (*cf.* appendix E, especially (E.6)). For example,

Fig. 2.1 The internal forces of a shell



$\mathbf{e} = \mathbf{e}_\alpha$, $\mathbf{g} = \mathbf{e}_\beta$, if the cut is characterized by a constant value of α. The unit normal $\mathbf{n}$ of the surface is orthogonal to these two tangential vectors.

The vector of boundary force (per unit length) on the cut is

$$\mathbf{f} = (\mathbf{T} + \mathbf{n} \otimes \mathbf{q}_T) \cdot \mathbf{e} = \Big(\mathbf{e} \cdot \mathbf{T} \cdot \mathbf{e}\Big)\mathbf{e} + \Big(\mathbf{g} \cdot \mathbf{T} \cdot \mathbf{e}\Big)\mathbf{g} + (\mathbf{q}_T \cdot \mathbf{e})\,\mathbf{n} \tag{2.48}$$

It possesses components $t_{\alpha\alpha} = \mathbf{e} \cdot \mathbf{T} \cdot \mathbf{e}$, $t_{\alpha\beta} = t_{\beta\alpha} = \mathbf{g} \cdot \mathbf{T} \cdot \mathbf{e}$, and $q_\alpha = \mathbf{q}_T \cdot \mathbf{e}$ in the directions of $\mathbf{e}$, $\mathbf{g}$, and $\mathbf{n}$, respectively, called membrane normal force, membrane shear force, and transverse force.

The vector of boundary torque (per unit length) is given by

$$\mathbf{m} = \mathbf{n} \times \mathbf{M} \cdot \mathbf{e} = \Big(\mathbf{e} \cdot \mathbf{M} \cdot \mathbf{e}\Big)\mathbf{g} - \Big(\mathbf{g} \cdot \mathbf{M} \cdot \mathbf{e}\Big)\mathbf{e} \tag{2.49}$$

It possesses components $m_{\alpha\alpha} = \mathbf{e} \cdot \mathbf{M} \cdot \mathbf{e}$, and $m_{\alpha\beta} = m_{\beta\alpha} = \mathbf{g} \cdot \mathbf{M} \cdot \mathbf{e}$ in the directions of $\mathbf{g}$ and $-\mathbf{e}$, respectively, called bending moment and torsional moment.

If the cut is orthogonal to a direction of principal curvature, then no membrane shear force and no torsional moment exists, as is seen from equations (2.44) and (2.45).

Since the description of fluid films with the concept of surface tension is rather popular (*e.g.* [4]), the deviations from classical capillarity shall be summarized once more:

- 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 shear forces on cuts which do not coincide with a principal direction of curvature.
- A tensor of moments exists which describes bending moments and torsional moments within the surface.
- According to equation (2.42), 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 loading.

Most of these features were already discussed by Helfrich (1973) [3] 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.)

However, we must be aware of the following fact. Helfrich assumed the energy density of a film to depend on the local curvatures alone, *i.e.* $w(c_1, c_2)$. Our energy density, however has the more general structure $w(c_1, c_2, \mu)$. Now, as (2.41) shows, μ is not simply a function of c_1 and c_2 but depends on the value of the variable f, too, which has the character of a chemical potential and reflects the environment into which the film is embedded.

2.9 Global Equilibrium

The differential equations (2.42) and (2.43) describe the local equilibrium of the film. They were obtained by admitting an arbitrary change of the geometry of the film structure. A statement on global equilibrium results if we restrict the change of geometry to an affine magnification of the middle surface. We notice that the actual geometry — with characteristic length L — may be obtained by affine magnification from the surface with characteristic length 1, the properties of which will be denoted by a hat. We write that part of the extended energy which is related with the geometry of a single cell in the form — *cf.* (2.38), (F.1), (F.2) —

$$\begin{aligned}\Phi &= \int_{A_\mathrm{C}} \Big(w(c_1, c_2, \mu) + p_\mathrm{e}\Big(h + c_1 c_2 \frac{h^3}{12}\Big) - f\mu \Big)\, dA \\ &\qquad -(p_\mathrm{O} - p_\mathrm{e})V_\mathrm{OC} - (p_\mathrm{W} - p_\mathrm{e})V_\mathrm{WC} \\ &= \int_{\hat{A}_\mathrm{C}} \Big(w\Big(\frac{\hat{c}_1}{L}, \frac{\hat{c}_2}{L}, \mu\Big) + p_\mathrm{e}\Big(h + \frac{\hat{c}_1 \hat{c}_2}{L^2}\frac{h^3}{12}\Big) - f\mu \Big) d\hat{A}\, L^2 \\ &\qquad -(p_\mathrm{O} - p_\mathrm{e})V_\mathrm{OC}(L) - (p_\mathrm{W} - p_\mathrm{e})V_\mathrm{WC}(L) \end{aligned} \tag{2.50}$$

We find

$$\frac{\partial c_j}{\partial L} = -\frac{\hat{c}_j}{L^2} = -\frac{c_j}{L} \tag{2.51}$$

and, with (2.46), (2.47), obtain the necessary condition of a minimum

$$\begin{aligned} 0 &= \frac{\partial \Phi}{\partial L} = -\int_{\hat{A}_\mathrm{C}} \Big(\frac{\partial w}{\partial c_1} c_1 + \frac{\partial w}{\partial c_2} c_2\Big)\, d\hat{A}\, L + \int_{\hat{A}_\mathrm{C}} \big(w + p_\mathrm{e} h - f\mu\big)\, d\hat{A}\, 2L \\ &\qquad -(p_\mathrm{O} - p_\mathrm{e})\frac{dV_\mathrm{OC}}{dL} - (p_\mathrm{W} - p_\mathrm{e})\frac{dV_\mathrm{WC}}{dL} \end{aligned} \tag{2.52}$$

or

$$\begin{aligned} &\int_{A_\mathrm{C}} \Big(2\big(w + p_\mathrm{e} h - f\mu\big) + c_1 m_1 + c_2 m_2\Big)\, dA = \int_{A_\mathrm{C}} \big(t_1 + t_2 + 2p_\mathrm{e} h\big)\, dA \\ &\qquad = (p_\mathrm{O} - p_\mathrm{e})\, L\, \frac{dV_\mathrm{OC}}{dL} + (p_\mathrm{W} - p_\mathrm{e})\, L\, \frac{dV_\mathrm{WC}}{dL} \end{aligned} \tag{2.53}$$

This is a global relation between the internal forces of the film and the pressures in the oil and the water, whereas (2.43) represents a local relation. On the other hand, (2.39) may be given the form

$$\int_{A_\mathrm{C}} \big(w + p_\mathrm{e} h - f\mu\big)\, dA + p_\mathrm{e}\frac{h^3}{12}\int_{A_\mathrm{C}} c_1 c_2\, dA = (p_\mathrm{O} - p_\mathrm{e})V_\mathrm{OC} + (p_\mathrm{W} - p_\mathrm{e})V_\mathrm{WC} \tag{2.54}$$

If the geometry of the middle surface and the field μ and hence also f — note (2.41) — is known, then (2.53) and (2.54) constitute two linear equations for the computation of the pressures p_O and p_W.

2.10 The Surface Tension

While the concept of a surface tension is not meaningful in the context of a curved amphiphilic film, it may well be applied in the case of a plane surface which separates two phases. The contribution of the last two terms in (2.10) to the free energy of such a surface is

$$F = \big(w_j(\mu_j) + p_{\mathrm{e}}h\big)A_j \tag{2.55}$$

If the tube with the mixture is tilted, then the area will increase. If the starting state is relaxed, then we may assume, without loss of generality (*cf.* appendix I.6), the conservation of the mass of the surface

$$m = \mu_j A_j = const \quad \Longrightarrow \quad \mu_j \delta A_j + \delta\mu_j A_j = 0 \tag{2.56}$$

Then we can define the surface tension t_{S} by

$$\delta F = \big(w_j + p_{\mathrm{e}}h\big)\delta A_j + \frac{dw_j}{d\mu_j}\delta\mu_j A_j = \big(w_j + p_{\mathrm{e}}h - \mu_j\frac{dw_j}{d\mu_j}\big)\delta A_j = t_{\mathrm{S}}\delta A_j \tag{2.57}$$

Since the surface is plane, we have $c_1 = c_2 = 0$, and (2.46), (2.37) yield equal principal membrane forces

$$t_1 = t_2 = w_j - f\mu_j = w_j - \mu_j\frac{dw_j}{d\mu_j} = t_{\mathrm{S}} - p_{\mathrm{e}}h \tag{2.58}$$

So the surface tension describes the isotropic state of the membrane forces apart from a contribution of the environmental pressure. Note that, generally, neither the surface tension nor the membrane forces are equal to the surface energy density w_j. Moreover, there will be an isotropic state of bending moments, too, in the plane amphiphilic surface. The quantity or even the existence of the bending moments cannot be inferred from the concept of the surface tension.

It is important to take the environmental pressure p_{e} into account, at least in the case of ultra-low surface tensions, where the last two terms in (2.58) may be of the same order of magnitude.

The surface tension will reappear in appendix J, where the spinning drop test is investigated, since the film around the drop can be regarded as almost plane, as will be demonstrated.

2.11 Special theories

In the papers [6] and [7], two special theories were exploited that did not care for the variable mass density of the film or the monomeric solubility of the amphiphile. It may be interesting, to clarify the relation to the more general setting presented above.

The framework of [6] is obtained, if we do not consider f as a quantity that has to be determined but simply put $f = 0$. Then the conditions (2.32), (2.35), which concern the solubility, are not applicable, while (2.39) could not be considered, since the paper discussed states of equilibrium and not states of minimal free energy. (The condition that the derivative of the free energy with respect to the number n of cells be zero is not a condition of equilibrium!) According to (2.41), we can compute the mass density of the relaxed state from

$$0 = f = \frac{\partial w(c_1, c_2, \mu)}{\partial \mu} \qquad \Longrightarrow \qquad \mu_{\text{rel}} = \mu_{\text{rel}}(c_1, c_2) \tag{2.59}$$

So the energy density could, indeed, be expressed as a function of the local curvatures alone.

$$w(c_1, c_2, \mu) = w(c_1, c_2, \mu_{\text{rel}}(c_1, c_2)) = w_{\text{rel}}(c_1, c_2) \tag{2.60}$$

The framework of [7] is obtained, if we neglect the monomeric solubility, the environmental pressure p_{e}, the compressibility of the bulk fluids, the mass and energy of the separating surfaces between the microemulsion and the excesses, and consider the mass density μ as a fixed quantity, thus excluding an elastic area stretch. Moreover, only one kind of structure is allowed simultaneously. The free energy (2.10) reduces to

$$F = n \int_{A_{\text{C}}} w(c_1, c_2)\, dA \tag{2.61}$$

the mass of the amphiphile is given by

$$m_{\text{A}} = n\mu \int_{A_{\text{C}}} dA \tag{2.62}$$

while the constraints (2.25), (2.26), when present, simplify to

$$m_{\text{O}} - n\varrho_{\text{O}} V_{\text{OC}} = 0 \tag{2.63}$$

$$m_{\text{W}} - n\varrho_{\text{W}} V_{\text{WC}} = 0 \tag{2.64}$$

In addition, the film is regarded as thin and hence a simplified computation of the volumes performed.

In the mentioned paper, various structures are discussed and that with the actual minimum ratio

$$\frac{F}{m_{\text{A}}} = \frac{\int_{A_{\text{C}}} w(c_1, c_2)\, dA}{\mu \int_{A_{\text{C}}} dA} \tag{2.65}$$

eventually subject to the constraints (2.63), (2.64), is used for the construction of phase maps. A non-quadratic energy density $w(c_1, c_2)$ is used which implies symmetry breaking and allows the description of the coexistence of a microemulsion with both a water and an oil excess.

3 The Microscopic Approach

3.1 Deformation of a Thick Layer

The mesoscopic approach, discussed in the preceding chapter, treats a monomolecular film as a material surface endowed with a free energy. The thickness of the film is used only to obtain correct values of volumes.

In contrast to this, the microscopic approach treats a monomolecular amphiphilic film as a layer of thickness h and studies the distribution of the stresses over the thickness. The co-ordinate normal to the middle surface is denoted by z, and the matter fills the space between $z = -h/2$ and $z = h/2$. (A fixed neutral surface, popular in the linear theory, does not exist in a non-linear context.) An even more refined approach would be to model the molecules as pencils of length h lying side by side in the z-direction with interaction forces between them. The intensity of these forces will depend on the mutual distance of the molecules. Since the film is curved, this distance varies with z. But even in a plane film, where the distance is constant, the forces will surely not be constant along z. For each z, there will be a characteristic distance of the molecules such that the forces vanish.

Now going back to our layer model we see that we must admit a state of elastic prestress. Moreover, deformations of the film may be elastic, corresponding to a change of distance of the molecules, or inelastic, due to a rearrangement of the molecules or an exchange of molecules with the environment. Furthermore it is helpful to imagine the thick layer to consist of a deck of infinitesimally thin layers, each characterized by its value of the coordinate z. We simply refer to any one of them as to the layer at z.

In the beginning, we consider the thick layer in a placement, where the middle surface is plane. We cut out a brick with length $ds_{1\mathrm{b}}$ and $ds_{2\mathrm{b}}$, and height h. The area element of the middle surface is then $dA_{\mathrm{b}} = ds_{1\mathrm{b}}\, ds_{2\mathrm{b}}$. Moreover, we assume that the layer at $z = 0$ is free of stress in this basic placement. Then the layers with $z \neq 0$ will usually not be free of stress. We assume, however, that their prestress is isotropic. So we could think of applying an isotropic unloading stretch $\lambda_{1\mathrm{u}}(z) = \lambda_{2\mathrm{u}}(z) = \lambda_{\mathrm{p}}^{-1}(z)$, which changes the length and width of the brick into

$$ds_{1\mathrm{b}z} = \lambda_{\mathrm{p}}^{-1}(z)\, ds_{1\mathrm{b}}\,, \qquad ds_{2\mathrm{b}z} = \lambda_{\mathrm{p}}^{-1}(z)\, ds_{2\mathrm{b}} \tag{3.1}$$

and makes the layer at z free of stress. But we can also say, that, in the basic placement, the layer at z possesses already elastic prestretches λ_{p} in the directions 1 and 2, which cause the prestress.

Next, we apply elastic stretches $\lambda_{\rm e1}$ and $\lambda_{\rm e2}$ which change the length and width of the brick into

$$ds_1 = \lambda_{\rm e1}\, ds_{1\rm b}\,, \qquad ds_2 = \lambda_{\rm e2}\, ds_{2\rm b} \tag{3.2}$$

and the area element into $dA = ds_1\, ds_2 = \lambda_{\rm e1}\lambda_{\rm e2}\, dA_{\rm b}$.

Finally, the plane layer is bent in the directions 1 and 2. The principal curvatures and the corresponding radii of curvature of the middle surface are

$$c_1 = \frac{1}{R_1}\,, \qquad c_2 = \frac{1}{R_2} \tag{3.3}$$

The radii of curvature of a layer at z are then $R_1 - z$ and $R_2 - z$, respectively, so that we obtain

$$ds_{1z} = \frac{R_1 - z}{R_1}\, ds_1 = (1 - c_1\, z)\, ds_1\,, \quad ds_{2z} = \frac{R_2 - z}{R_2}\, ds_2 = (1 - c_2\, z)\, ds_2 \tag{3.4}$$

and the area element becomes $dA_z(z) = ds_{1z} ds_{2z} = (1 - c_1\, z)(1 - c_2\, z)\, dA$.

The elastic stretch of the layer at z is therefore seen to be the succession of an isotropic prestretch of this layer, the elastic stretch of the middle surface and a stretch due to bending.

$$\lambda_{z\rm e1}(z) = \lambda_{\rm p}(z)\, \lambda_{\rm e1}\, (1 - c_1\, z)\,, \qquad \lambda_{z\rm e2}(z) = \lambda_{\rm p}(z)\, \lambda_{\rm e2}\, (1 - c_2\, z) \tag{3.5}$$

We assume for the sake of simplicity that the thickness h of the layer does not change during a deformation process. Other assumptions would be possible, *e.g.* conservation of the local volume.

The crucial point of our procedure is that 1 and 2 are principal directions of both the stretch of the middle surface and the bending of the layer.

The more general case, where the tensors of stretching and bending are not co-axial, is treated in appendix I. That investigation reveals that the co-axial case is one which gives the free energy a stationary value. Since we are interested in structures with minimal free energy, the co-axial case turns out to be a promising candidate.

It will be useful to introduce the logarithmic elastic principal strains

$$\epsilon_1(z) = \ln \lambda_{z\rm e1}(z)\,, \quad \epsilon_2(z) = \ln \lambda_{z\rm e2}(z) \tag{3.6}$$

of the layer at z, the logarithmic prestrain

$$\epsilon_{\rm p}(z) = \ln \lambda_{\rm p}(z) \tag{3.7}$$

— with $\epsilon_{\rm p}(0) = 0$ — and the logarithmic elastic principal strains of the middle surface

$$\epsilon_{\rm e1} = \ln \lambda_{\rm e1}\,, \quad \epsilon_{\rm e2} = \ln \lambda_{\rm e2} \tag{3.8}$$

as well as their sum and difference

$$\epsilon_{\mathrm{es}} = \epsilon_{\mathrm{e1}} + \epsilon_{\mathrm{e2}}\,, \quad \epsilon_{\mathrm{ed}} = \epsilon_{\mathrm{e1}} - \epsilon_{\mathrm{e2}} \tag{3.9}$$

Then the logarithm of (3.5) yields

$$\begin{aligned} \epsilon_1(z) &= \epsilon_{\mathrm{p}}(z) + \frac{1}{2}(\epsilon_{\mathrm{es}} + \epsilon_{\mathrm{ed}}) + \ln\big(1 - c_1 z\big) \\ \epsilon_2(z) &= \epsilon_{\mathrm{p}}(z) + \frac{1}{2}(\epsilon_{\mathrm{es}} - \epsilon_{\mathrm{ed}}) + \ln\big(1 - c_2 z\big) \end{aligned} \tag{3.10}$$

We will make use of the following two elastic strain invariants

$$I_1(z) = \epsilon_1(z) + \epsilon_2(z) = 2\epsilon_{\mathrm{p}}(z) + \epsilon_{\mathrm{es}} + \ln(1 - c_1\, z) + \ln(1 - c_2\, z) \tag{3.11}$$

$$I_2(z) = \big(\epsilon_1(z) - \epsilon_2(z)\big)^2 = \Big(\epsilon_{\mathrm{ed}} + \ln(1 - c_1\, z) - \ln(1 - c_2\, z)\Big)^2 \tag{3.12}$$

Hitherto we restricted our attention to elastic deformations. But inelastic ones are also possible. They change the length and width $ds_{1\mathrm{b}}$ and $ds_{1\mathrm{b}}$ of the basic placement (where the middle surface is free of stress). We define

$$\delta_{\mathrm{s}} = \frac{\dot{\overline{ds_{1\mathrm{b}}}}}{ds_{1\mathrm{b}}} + \frac{\dot{\overline{ds_{2\mathrm{b}}}}}{ds_{2\mathrm{b}}}\,, \qquad \delta_{\mathrm{d}} = \frac{\dot{\overline{ds_{1\mathrm{b}}}}}{ds_{1\mathrm{b}}} - \frac{\dot{\overline{ds_{2\mathrm{b}}}}}{ds_{2\mathrm{b}}} \tag{3.13}$$

Now, according to (3.2), (3.8), we have

$$ds_1 = \lambda_{\mathrm{e1}}\, ds_{1\mathrm{b}} = \exp(\epsilon_{\mathrm{e1}})\, ds_{1\mathrm{b}}\,, \quad ds_2 = \lambda_{\mathrm{e2}}\, ds_{2\mathrm{b}} = \exp(\epsilon_{\mathrm{e2}})\, ds_{2\mathrm{b}} \tag{3.14}$$

and hence with (3.9)

$$\frac{\dot{\overline{ds_1}}}{ds_1} = \frac{1}{2}\big(\dot\epsilon_{\mathrm{es}} + \dot\epsilon_{\mathrm{ed}} + \delta_{\mathrm{s}} + \delta_{\mathrm{d}}\big)\,, \qquad \frac{\dot{\overline{ds_2}}}{ds_2} = \frac{1}{2}\big(\dot\epsilon_{\mathrm{es}} - \dot\epsilon_{\mathrm{ed}} + \delta_{\mathrm{s}} - \delta_{\mathrm{d}}\big) \tag{3.15}$$

Moreover, since

$$dA_{\mathrm{b}} = ds_{1\mathrm{b}} ds_{2\mathrm{b}}\,, \qquad dA = ds_1 ds_2 = \exp(\epsilon_{\mathrm{es}})\, dA_{\mathrm{b}} \tag{3.16}$$

we obtain

$$\frac{\dot{\overline{dA_{\mathrm{b}}}}}{dA_{\mathrm{b}}} = \frac{\dot{\overline{ds_{1\mathrm{b}}}}}{ds_{1\mathrm{b}}} + \frac{\dot{\overline{ds_{2\mathrm{b}}}}}{ds_{2\mathrm{b}}} = \delta_{\mathrm{s}} \tag{3.17}$$

and

$$\frac{\dot{\overline{dA}}}{dA} = \frac{\dot{\overline{ds_1}}}{ds_1} + \frac{\dot{\overline{ds_2}}}{ds_2} = \dot\epsilon_{\mathrm{es}} + \delta_{\mathrm{s}} \tag{3.18}$$

If $\delta_{\mathrm{s}} \neq 0$, then the area dA_{b} of the basic placement changes. On the other hand, the condition $\delta_{\mathrm{s}} = 0,\ \delta_{\mathrm{d}} \neq 0$ characterizes a shear of the basic placement alone. If we adopt the model of the pencil-like molecules, then a change of dA_{b} requires the exchange of matter with the environment so that the number of molecules per unit area of the basic placement is always constant. The shear, however, represents a mere rearrangement of the molecules. The possibility of such a rearrangement characterizes the fluidic nature of the monomolecular film. Both kinds of inelastic deformation do not change the average mutual distance of the molecules and hence the stresses, as long as the elastic strains remain constant.

3.2 Mass

The mass of our brick is given by

$$\begin{aligned} dm &= \int_{z=-h/2}^{h/2} \varrho(z)\, dA_z(z)\, dz = \int_{z=-h/2}^{h/2} (1-c_1 z)(1-c_2 z)\, \varrho(z)\, dz\, dA \\ &\equiv \mu\, dA = \mu \exp\big(\epsilon_{\mathrm{es}}\big)\, dA_{\mathrm{b}} = \mu_{\mathrm{b}}\, dA_{\mathrm{b}} \end{aligned} \tag{3.19}$$

Here $\varrho(z)$ denotes the mass density (referred to the actual unit volume) of the layer at z, $(1-c_1 z)(1-c_2 z)\,\varrho(z)$ would be the density before bending, μ shall be called the mass density of the thick layer (referred to the actual unit area of the middle surface) and μ_{b} the mass density in the basic placement of the thick layer. Note also that, during a bending, the mass density μ does not change while $\varrho(z)$, of course, does.

Although the basic placement may change with time, its mass density must always be the same. The derivative of (3.19) therefore gives

$$\dot{\mu}_{\mathrm{b}} = \Big(\mu \exp\big(\epsilon_{\mathrm{es}}\big)\Big)^{\bullet} = \Big(\dot{\mu} + \mu\, \dot{\epsilon}_{\mathrm{es}}\Big) \exp\big(\epsilon_{\mathrm{es}}\big) = 0 \quad \Longrightarrow \quad \frac{\dot{\mu}}{\mu} = -\, \dot{\epsilon}_{\mathrm{es}} \tag{3.20}$$

The mass which is supplied from the environment per unit time and unit area of the actual middle surface shall be denoted by $\tilde{\mu}$. Then the rate of mass can, with (3.18), be written

$$\dot{\overline{dm}} = \tilde{\mu}\, dA = \big(\mu\, dA\big)^{\bullet} = \left(\frac{\dot{\mu}}{\mu} + \frac{\dot{\overline{dA}}}{dA}\right) \mu\, dA = \delta_{\mathrm{s}}\ \mu\, dA \tag{3.21}$$

from which we infer, with (3.17),

$$\frac{\tilde{\mu}}{\mu} = \delta_{\mathrm{s}} = \frac{\dot{\overline{dA_{\mathrm{b}}}}}{dA_{\mathrm{b}}} \tag{3.22}$$

A positive mass supplement is seen to increase the area of the basic placement.

3.3 Power and Energy

The elastic behaviour of all layers is assumed to be isotropic. Thus our brick contains the strain energy

$$
\begin{aligned}
& \int_{z=-h/2}^{h/2} w_z\big(I_1(z), I_2(z)\big)\, dA_z(z)\, dz \\
= \; & \int_{z=-h/2}^{h/2} (1-c_1 z)(1-c_2 z)\, w_z\big(I_1(z), I_2(z)\big)\, dz\, dA \\
= \; & w\big(c_1, c_2, \epsilon_{\text{es}}, \epsilon_{\text{ed}}\big)\, dA \qquad (3.23)
\end{aligned}
$$

While w_z denotes the energy per unit volume of the layer at z, w refers the energy of the thick layer to the actual unit area of the middle surface.

The rate of energy can be written, with (3.18),

$$
\begin{aligned}
\big(w\, dA\big)^{\bullet} &= \left(\dot{w} + w\,\frac{\dot{\overline{dA}}}{dA}\right) dA \\
&= \left(\frac{\partial w}{\partial c_1}\dot{c_1} + \frac{\partial w}{\partial c_2}\dot{c_2} + \frac{\partial w}{\partial \epsilon_{\text{es}}}\dot{\epsilon}_{\text{es}} + \frac{\partial w}{\partial \epsilon_{\text{ed}}}\dot{\epsilon}_{\text{ed}} + w\left(\dot{\epsilon_{\text{es}}} + \delta_{\text{s}}\right)\right) dA \qquad (3.24)
\end{aligned}
$$

with

$$
\begin{aligned}
\frac{\partial w}{\partial c_1} &= -\int_{z=-h/2}^{h/2} (1-c_1 z)(1-c_2 z)\left(w_z + \frac{\partial w_z}{\partial I_1} + I_0(z)\frac{\partial w_z}{\partial I_2}\right)\frac{z}{1-c_1 z}\, dz \\
\frac{\partial w}{\partial c_2} &= -\int_{z=-h/2}^{h/2} (1-c_1 z)(1-c_2 z)\left(w_z + \frac{\partial w_z}{\partial I_1} - I_0(z)\frac{\partial w_z}{\partial I_2}\right)\frac{z}{1-c_2 z}\, dz \\
\frac{\partial w}{\partial \epsilon_{\text{es}}} &= \int_{z=-h/2}^{h/2} (1-c_1 z)(1-c_2 z)\,\frac{\partial w_z}{\partial I_1}\, dz \\
\frac{\partial w}{\partial \epsilon_{\text{ed}}} &= \int_{z=-h/2}^{h/2} (1-c_1 z)(1-c_2 z)\, I_0(z)\frac{\partial w_z}{\partial I_2}\, dz \qquad (3.25)
\end{aligned}
$$

and the abbreviation

$$
I_0(z) = 2\Big(\epsilon_{\text{ed}} + \ln(1-c_1\, z) - \ln(1-c_2\, z)\Big) \qquad (3.26)
$$

Let $\sigma_1(z)$ and $\sigma_2(z)$ denote the normal stresses (force per unit area) on the surfaces of the brick which are normal to the directions 1 and 2. The power exerted during a deformation of the brick is, with (3.4), (3.15),

$$\begin{aligned}
P\,dA &= \int_{z=-h/2}^{h/2} \Big(\sigma_1(z)\,ds_{2z}\dot{\overline{ds_{1z}}} + \sigma_2(z)\,ds_{1z}\dot{\overline{ds_{2z}}}\Big)\,dz \\
&= \int_{z=-h/2}^{h/2} \Big(\sigma_1(z)\,ds_2(1-c_2z)\Big(\dot{\overline{ds_1}}(1-c_1z) - ds_1\dot{c_1}z\Big) \\
&\qquad\qquad +\sigma_2(z)\,ds_1(1-c_1z)\Big(\dot{\overline{ds_2}}(1-c_2z) - ds_2\dot{c_2}z\Big)\Big)\,dz \\
&= \Big(-m_1\dot{c_1} - m_2\dot{c_2} + (\tilde{t}_\mathrm{s}+\tilde{t}_\mathrm{d})\frac{\dot{\overline{ds_1}}}{ds_1} + (\tilde{t}_\mathrm{s}-\tilde{t}_\mathrm{d})\frac{\dot{\overline{ds_2}}}{ds_2}\Big)\,dA \\
&= \Big(-m_1\dot{c_1} - m_2\dot{c_2} + \tilde{t}_\mathrm{s}\big(\dot{\epsilon}_\mathrm{es}+\delta_\mathrm{s}\big) + \tilde{t}_\mathrm{d}\big(\dot{\epsilon}_\mathrm{ed}+\delta_\mathrm{d}\big)\Big)\,dA
\end{aligned} \tag{3.27}$$

with

$$\begin{aligned}
m_1 &= \int_{z=-h/2}^{h/2} (1-c_1z)(1-c_2z)\,\sigma_1(z)\,\frac{z}{1-c_1z}\,dz \\
m_2 &= \int_{z=-h/2}^{h/2} (1-c_1z)(1-c_2z)\,\sigma_2(z)\,\frac{z}{1-c_2z}\,dz
\end{aligned} \tag{3.28}$$

$$\begin{aligned}
\tilde{t}_\mathrm{s} &= \int_{z=-h/2}^{h/2} (1-c_1z)(1-c_2z)\,\frac{\sigma_1(z)+\sigma_2(z)}{2}\,dz \\
\tilde{t}_\mathrm{d} &= \int_{z=-h/2}^{h/2} (1-c_1z)(1-c_2z)\,\frac{\sigma_1(z)-\sigma_2(z)}{2}\,dz
\end{aligned} \tag{3.29}$$

We observe that m_1 is nothing but the moment of the stresses which act in the direction 1 with respect to the middle surface and referred to the unit length on the middle surface. It is known as the bending moment in the theory of shells.

$$m_1 = \frac{1}{ds_2}\int_{z=-h/2}^{h/2} z\,\sigma_1(z)\,ds_{2z}\,dz \tag{3.30}$$

In a similar manner, we can refer the resulting force of these stresses to the unit length on the middle surface and obtain what is called the membrane normal force in the theory of shells. The following relation with the quantities of (3.28), (3.29) exists

$$t_1 = \frac{1}{ds_2}\int_{z=-h/2}^{h/2} \sigma_1(z)\,ds_{2z}\,dz = \tilde{t}_\mathrm{s} + \tilde{t}_\mathrm{d} + c_1m_1 \tag{3.31}$$

There act, of course, also stresses in the z-direction within the thick layer: Normal stresses $\sigma_3(z)$ and transverse shear stresses $\tau_{13}(z)$, $\tau_{23}(z)$ — and, of course, we also have the associate stresses $\tau_{31}(z) = \tau_{13}(z)$ and $\tau_{32}(z) = \tau_{23}(z)$. They are caused by the pressures on the upper and lower boundary and by the transverse forces — *cf.* chapter 2. However, we do not attribute any deformation to them, neither a strain normal to the layer, since we assume the thickness of all sublayers to be constant, nor a shear strain, since tilt is excluded. So these stresses do no work — they are pure reactions — and hence need not be considered in the actual context.

3.4 Relaxation

The mass $\tilde{\mu}\, dA$ which is absorbed from the environment per unit time carries with itself the energy

$$f\tilde{\mu}\, dA \tag{3.32}$$

Usually mechanisms of dissipation are present in any system. Therefore we postulate that the sum of the external power and the energy supply of the absorbed mass together must be greater than or at least equal to the rate of the elastic strain energy.

$$P\, dA + f\tilde{\mu}\, dA \geq \big(w\, dA\big)^{\bullet} \tag{3.33}$$

Introduction of (3.22), (3.24), (3.27) yields

$$\begin{aligned} &-\underline{\left(m_1 + \frac{\partial w}{\partial c_1}\right)}\dot{c_1} - \underline{\left(m_2 + \frac{\partial w}{\partial c_2}\right)}\dot{c_2} \\ &+\underline{\left(\tilde{t}_\mathrm{s} - \frac{\partial w}{\partial \epsilon_\mathrm{es}} - w\right)}\dot{\epsilon}_\mathrm{es} + \underline{\left(\tilde{t}_\mathrm{d} - \frac{\partial w}{\partial \epsilon_\mathrm{ed}}\right)}\dot{\epsilon}_\mathrm{ed} \\ &+\big(\tilde{t}_\mathrm{s} + f\mu - w\big)\ \delta_\mathrm{s} + \tilde{t}_\mathrm{d}\ \delta_\mathrm{d} \quad \geq \quad 0 \end{aligned} \tag{3.34}$$

Since this inequality must be satisfied for arbitrary values of $\dot{c_1}$, $\dot{c_2}$, $\dot{\epsilon}_\mathrm{es}$, $\dot{\epsilon}_\mathrm{ed}$, the underlined terms must vanish, and we infer the potential relations

$$m_1 = -\frac{\partial w}{\partial c_1}\,, \qquad m_2 = -\frac{\partial w}{\partial c_2} \tag{3.35}$$

$$\tilde{t}_\mathrm{s} = w + \frac{\partial w}{\partial \epsilon_\mathrm{es}}\,, \qquad \tilde{t}_\mathrm{d} = \frac{\partial w}{\partial \epsilon_\mathrm{ed}} \tag{3.36}$$

and the remaining inequality

$$\big(\tilde{t}_\mathrm{s} + f\mu - w\big)\ \delta_\mathrm{s} + \tilde{t}_\mathrm{d}\ \delta_\mathrm{d} \geq 0 \tag{3.37}$$

The simplest ansatz which guarantees the fulfilment of this inequality is one within the framework of linear viscosity. So we set

$$\delta_{\rm s} = \frac{2}{\eta_1}(\tilde{t}_{\rm s} + f\mu - w)\,, \qquad \delta_{\rm d} = \frac{2}{\eta_2}\tilde{t}_{\rm d} \tag{3.38}$$

with two positive viscosities η_1 and η_2. (We shall not investigate the question whether this approach is realistic, because a discussion of the kinetics of monomolecular films is beyond the scope of this monograph.)

What we are interested in is the relaxed state, which will asymptotically be reached. It is characterized by $\delta_{\rm s} = 0$, $\delta_{\rm d} = 0$ and hence by

$$\tilde{t}_{\rm s} = w - f\mu\,, \qquad \tilde{t}_{\rm d} = 0 \tag{3.39}$$

Now, according to (3.19), we have

$$\mu = \mu_{\rm b}\exp(-\epsilon_{\rm es}) \quad \Longrightarrow \quad \frac{d\mu}{d\epsilon_{\rm es}} = -\mu \tag{3.40}$$

and hence

$$\frac{\partial w}{\partial \epsilon_{\rm es}} = \frac{\partial w}{\partial \mu}\frac{d\mu}{d\epsilon_{\rm es}} = -\mu\frac{\partial w}{\partial \mu} \tag{3.41}$$

and, with (3.36), (3.39),

$$\tilde{t}_{\rm s} = w + \frac{\partial w}{\partial \epsilon_{\rm es}} = w - \mu\frac{\partial w}{\partial \mu} = w - f\mu \tag{3.42}$$

A comparison shows that

$$\frac{\partial w}{\partial \mu} = f \tag{3.43}$$

is valid in the relaxed state. The prescription for the calculation of the bending moments

$$m_1 = -\frac{\partial w}{\partial c_1}\,, \qquad m_2 = -\frac{\partial w}{\partial c_2} \tag{3.44}$$

was already given by (3.35), while (3.31) with (3.39) yields the membrane normal forces of the relaxed state

$$t_1 = w - f\mu + c_1 m_1\,, \qquad t_2 = w - f\mu + c_2 m_2 \tag{3.45}$$

These results were already derived in chapter 2 from the mesoscopic theory — *cf.* equations (2.41), (2.46), (2.47).

A more detailed discussion of the relation between the microscopical point of view and the mesoscopical approach can be found in appendix I.6.

4 A Constitutive Assumption

4.1 The Energy Density of the Film

In this chapter, we want to illustrate the transition from the microscopic to the mesoscopic scale by means of an example. We incorporate a state of prestress on the microscopic level and will see in chapter 6 that this allows a symmetry breaking of the mesoscopic energy density function of the fluid film. Our example is based on two special constitutive assumptions.

• **First constitutive assumption:** The energy density (per unit mass) of each layer has the following dependence on the elastic strains.

$$W_z = W_{z0} + W_{z1}\left(I_1^2 + \kappa I_2\right) = W_{z0} + W_{z1}\left((1+\kappa)(\varepsilon_1^2 + \varepsilon_2^2) + 2(1-\kappa)\varepsilon_1\varepsilon_2\right) \tag{4.1}$$

Here, W_{z0}, W_{z1}, and κ are material constants of the layer under discussion. The chosen functional form is the most general polynomial of second order, which satisfies the condition that the state with $\varepsilon_1 = \varepsilon_2 = 0$ be free of stress. Therefore, linear terms must be absent, as can be inferred from (I.64). In the case of small elastic strains, our ansatz may be regarded as a truncated Taylor expansion. In the limit of very large magnitudes of the strains ($|\varepsilon_1| \to \infty$ or $|\varepsilon_2| \to \infty$), the energy density tends to infinity. Moreover, the use of the strain invariants I_1 and I_2 allows the separation of the influences of an elastic volume change and a volume-preserving elastic shear, respectively. The choice $\kappa = 0$ would eliminate the shear stiffness and thus characterize each sublayer as a lateral fluid.

We introduce the mass density (per unit volume) ϱ_{b} of the layer at z in the basic placement which results from (3.16)

$$\varrho_{\mathrm{b}}\, dA_{\mathrm{b}} = \varrho\, dA_z = \varrho\,(1 - c_1\, z)(1 - c_2\, z)\, dA = \varrho_{\mathrm{b}} \exp\big(-\epsilon_{\mathrm{es}}\big)\, dA \tag{4.2}$$

The energy density (per actual unit volume) of the layer at z is then $w_z = \varrho W_z$, and integration over all the layers yields, with (3.23),

$$w\, dA = \int_{z=-h/2}^{h/2} \varrho W_z\, dA_z\, dz = \int_{z=-h/2}^{h/2} \varrho_{\mathrm{b}} W_z\, dz \exp\big(-\epsilon_{\mathrm{es}}\big)\, dA \tag{4.3}$$

whence we infer

$$w = \int_{z=-h/2}^{h/2} \varrho_{\mathrm{b}}(z)\Big(W_{z0}(z) + W_{z1}(z)\,\big(I_1(z)^2 + \kappa(z) I_2(z)\big)\Big)\, dz \exp\big(-\epsilon_{\mathrm{es}}\big) \tag{4.4}$$

• **Second constitutive assumption:** The following simple interrelations exist between the material properties of the single layers.

$$\begin{aligned} \varrho_{\mathrm{b}}(z)\, W_{z0}(z) &= \frac{w_0}{h} = const\,, \\ \varrho_{\mathrm{b}}(z)\, W_{z1}(z) &= \frac{w_1}{h} = const\,, \\ \kappa(z) &= \kappa = const\,, \end{aligned} \tag{4.5}$$

(More realistic relations could surely be obtained, if information on the molecular substructure were available.) This yields the energy density (referred to the actual unit area of the middle surface)

$$w = \left(w_0 + w_1 \frac{1}{h} \int_{z=-h/2}^{h/2} \big(I_1(z)^2 + \kappa I_2(z)\big)\, dz \right) \exp\big(-\epsilon_{\mathrm{es}}\big) \tag{4.6}$$

The invariants (3.11), (3.12) may be written

$$I_1(z) = \epsilon_{\mathrm{es}} + g_{\mathrm{s}}(z)\,, \qquad I_2(z) = \big(\epsilon_{\mathrm{ed}} + g_{\mathrm{d}}(z)\big)^2\,, \tag{4.7}$$

with

$$g_{\mathrm{s}}(z) = 2\epsilon_{\mathrm{p}}(z) + \ln(1-c_1\, z) + \ln(1-c_2\, z)\,, \qquad g_{\mathrm{d}}(z) = \ln(1-c_1\, z) - \ln(1-c_2\, z) \tag{4.8}$$

and we obtain

$$\begin{aligned} w &= \Bigg(w_0 + w_1 \frac{1}{h} \int_{z=-h/2}^{h/2} \Big(\epsilon_{\mathrm{es}}^2 + 2 g_{\mathrm{s}}(z)\, \epsilon_{\mathrm{es}} + g_{\mathrm{s}}(z)^2 \\ &\qquad\qquad + \kappa\big(\epsilon_{\mathrm{ed}}^2 + 2 g_{\mathrm{d}}(z)\, \epsilon_{\mathrm{ed}} + g_{\mathrm{d}}(z)^2\big)\Big)\, dz \Bigg) \exp(-\epsilon_{\mathrm{es}}) \\ &= \Big(w_0 + w_1 \Big(\epsilon_{\mathrm{es}}^2 + 2G_{\mathrm{s}}\, \epsilon_{\mathrm{es}} + G_{\mathrm{ss}} + \kappa\big(\epsilon_{\mathrm{ed}}^2 + 2G_{\mathrm{d}}\, \epsilon_{\mathrm{ed}} + G_{\mathrm{dd}}\big)\Big)\Big) \exp(-\epsilon_{\mathrm{es}}) \\ &= \Big(w_0 + w_1 \Big(\big(\epsilon_{\mathrm{es}} + G_{\mathrm{s}}\big)^2 + \kappa\big(\epsilon_{\mathrm{ed}} + G_{\mathrm{d}}\big)^2 + G \Big)\Big) \exp(-\epsilon_{\mathrm{es}}) \end{aligned} \tag{4.9}$$

with the abbreviations

$$\begin{aligned} G_{\mathrm{s}} &= \frac{1}{h}\int_{z=-h/2}^{h/2} g_{\mathrm{s}}(z)\,dz\,, \qquad G_{\mathrm{ss}} = \frac{1}{h}\int_{z=-h/2}^{h/2} g_{\mathrm{s}}(z)^2\,dz\,, \\ G_{\mathrm{d}} &= \frac{1}{h}\int_{z=-h/2}^{h/2} g_{\mathrm{d}}(z)\,dz\,, \qquad G_{\mathrm{dd}} = \frac{1}{h}\int_{z=-h/2}^{h/2} g_{\mathrm{d}}(z)^2\,dz\,. \end{aligned} \tag{4.10}$$

and

$$G = G_{\mathrm{ss}} - G_{\mathrm{s}}^2 + \kappa\big(G_{\mathrm{dd}} - G_{\mathrm{d}}^2\big) \tag{4.11}$$

Since

$$G = \frac{1}{h}\int_{z=-h/2}^{h/2} \left(\Big(g_{\mathrm{s}}(z) - G_{\mathrm{s}}\Big)^2 + \kappa\Big(g_{\mathrm{d}}(z) - G_{\mathrm{d}}\Big)^2\right) dz \tag{4.12}$$

the expression G, obviously, cannot be negative (if $\kappa \geq 0$ is presupposed).

The second equations of (3.36), (3.39) become

$$0 = \tilde{t}_{\mathrm{d}} = \frac{\partial w}{\partial \epsilon_{\mathrm{ed}}} = 2\,\kappa\,w_1\big(\epsilon_{\mathrm{ed}} + G_{\mathrm{d}}\big)\exp(-\epsilon_{\mathrm{es}}) \tag{4.13}$$

and so we must have

$$\epsilon_{\mathrm{ed}} = -G_{\mathrm{d}} \tag{4.14}$$

in the relaxed state. Moreover, we introduce the mass density (per actual unit area of the film) according to (3.40)

$$\mu = \mu_{\mathrm{b}}\exp(-\epsilon_{\mathrm{es}}) \tag{4.15}$$

and make use of (3.41). Then the condition (3.43) of the relaxed state takes the form

$$\begin{aligned} f &= \frac{\partial w}{\partial \mu} = -\frac{1}{\mu}\frac{\partial w}{\partial \epsilon_{\mathrm{es}}} = -\frac{1}{\mu_{\mathrm{b}}}\exp(\epsilon_{\mathrm{es}})\frac{\partial w}{\partial \epsilon_{\mathrm{es}}} \\ &= \frac{w_0}{\mu_{\mathrm{b}}} + \frac{w_1}{\mu_{\mathrm{b}}}\Big(\big(\epsilon_{\mathrm{es}} + G_{\mathrm{s}}\big)^2 - 2\big(\epsilon_{\mathrm{es}} + G_{\mathrm{s}}\big) + \kappa\big(\epsilon_{\mathrm{ed}} + G_{\mathrm{d}}\big)^2 + G\Big) \end{aligned} \tag{4.16}$$

and introduction of (4.14) yields the quadratic equation

$$f = \frac{w_0}{\mu_{\mathrm{b}}} + \frac{w_1}{\mu_{\mathrm{b}}}\left(\Big(G_{\mathrm{s}} - 1 + \epsilon_{\mathrm{es}}\Big)^2 + G - 1\right) \tag{4.17}$$

with the solution

$$\epsilon_{\mathrm{es}} = -\ln\frac{\mu}{\mu_{\mathrm{b}}} = 1 - G_{\mathrm{s}} - \sqrt{1 - G + \frac{f\mu_{\mathrm{b}}}{w_1} - \frac{w_0}{w_1}} \tag{4.18}$$

The sign of the square root is chosen so that $\epsilon_{\mathrm{es}} = 0$ results in the case $g_{\mathrm{s}}(z) \equiv 0$, $g_{\mathrm{d}}(z) \equiv 0$ and $f\mu_{\mathrm{b}} - w_0 = 0$.

The energy density (4.9) of the relaxed state becomes

$$w(c_1, c_2, \mu) = \frac{\mu}{\mu_{\mathrm{b}}} \left(w_0 + w_1 \left(\left(G_{\mathrm{s}}(c_1, c_2) - \ln \frac{\mu}{\mu_{\mathrm{b}}} \right)^2 + G(c_1, c_2) \right) \right) \tag{4.19}$$

and the mass density may be obtained from (4.18) in the form

$$\mu = \mu_{\mathrm{b}} \exp \left(G_{\mathrm{s}}(c_1, c_2) - 1 + \sqrt{1 - G(c_1, c_2) + \frac{f\mu_{\mathrm{b}}}{w_1} - \frac{w_0}{w_1}} \right) \tag{4.20}$$

Thus the local value of μ is expressed by the local curvatures c_1, c_2 and the parameter f. The value of f, however, is the same at all points of the film and hence also at some distinguished point P.

$$f = \frac{w_0}{\mu_{\mathrm{b}}} + \frac{w_1}{\mu_{\mathrm{b}}} \left(\left(G_{\mathrm{s}}(c_{1\mathrm{P}}, c_{2\mathrm{P}}) - 1 - \ln \frac{\mu_{\mathrm{P}}}{\mu_{\mathrm{b}}} \right)^2 + G(c_{1\mathrm{P}}, c_{2\mathrm{P}}) - 1 \right) \tag{4.21}$$

If we introduce (4.21) into (4.20) then we find μ at any point expressed by the local curvatures c_1, c_2 and the mass density μ_{P} at the distinguished point P.

$$\ln \frac{\mu}{\mu_{\mathrm{b}}} = G_{\mathrm{s}}(c_1, c_2) - 1 + \sqrt{G(c_{1\mathrm{P}}, c_{2\mathrm{P}}) - G(c_1, c_2) + \left(1 - G_{\mathrm{s}}(c_{1\mathrm{P}}, c_{2\mathrm{P}}) + \ln \frac{\mu_{\mathrm{P}}}{\mu_{\mathrm{b}}} \right)^2} \tag{4.22}$$

4.2 Evaluation

The elastic prestrain is chosen in the form

$$\epsilon_{\mathrm{p}}(z) = H_0 z + Q z^2 \,, \tag{4.23}$$

which satisfies the condition $\epsilon_{\mathrm{p}}(0) = 0$ of chapter 3. The coefficient H_0 describes a skew prestrain, which causes a preferred isotropic curvature of the film, while Q takes into account a symmetric prestrain of the outer layers of the film. We will need

$$w - \mu \frac{\partial w}{\partial \mu} = \frac{\mu}{\mu_{\mathrm{b}}} 2 w_1 \left(G_{\mathrm{s}} - \ln \frac{\mu}{\mu_{\mathrm{b}}} \right) \tag{4.24}$$

and

$$\begin{aligned} -m_j &= \frac{\partial w}{\partial c_j} = \frac{\mu}{\mu_{\mathrm{b}}} w_1 \left(2 \left(G_{\mathrm{s}} - \ln \frac{\mu}{\mu_{\mathrm{b}}} \right) \frac{\partial G_{\mathrm{s}}}{\partial c_j} + \frac{\partial G}{\partial c_j} \right) \\ &= \frac{\mu}{\mu_{\mathrm{b}}} w_1 \left(-2 \ln \frac{\mu}{\mu_{\mathrm{b}}} \frac{\partial G_{\mathrm{s}}}{\partial c_j} + \frac{\partial G_{\mathrm{ss}}}{\partial c_j} + \kappa \left(\frac{\partial G_{\mathrm{dd}}}{\partial c_j} - 2 G_{\mathrm{d}} \frac{\partial G_{\mathrm{d}}}{\partial c_j} \right) \right) \end{aligned} \tag{4.25}$$

If the following dimensionless variables are introduced

$$\tilde{z} = \frac{2z}{h}\,, \quad \lambda = \frac{2L}{h}\,, \quad \bar{h}_0 = \frac{h}{2}\,H_0\,, \quad q = \frac{h^2}{4}\,Q\,, \quad \tilde{c}_1 = c_1\,L\,, \quad \tilde{c}_2 = c_2\,L \tag{4.26}$$

then the integrals become

$$G_{\mathrm{s}} = \frac{1}{2}\int_{\tilde{z}=-1}^{1} \left(2\bar{h}_0\tilde{z} + 2q\tilde{z}^2 + \ln\left(1 - \frac{\tilde{c}_1\tilde{z}}{\lambda}\right) + \ln\left(1 - \frac{\tilde{c}_2\tilde{z}}{\lambda}\right)\right) d\tilde{z} \tag{4.27}$$

$$G_{\mathrm{ss}} = \frac{1}{2}\int_{\tilde{z}=-1}^{1} \left(2\bar{h}_0\tilde{z} + 2q\tilde{z}^2 + \ln\left(1 - \frac{\tilde{c}_1\tilde{z}}{\lambda}\right) + \ln\left(1 - \frac{\tilde{c}_2\tilde{z}}{\lambda}\right)\right)^2 d\tilde{z} \tag{4.28}$$

$$G_{\mathrm{d}} = \frac{1}{2}\int_{\tilde{z}=-1}^{1} \left(\ln\left(1 - \frac{\tilde{c}_1\tilde{z}}{\lambda}\right) - \ln\left(1 - \frac{\tilde{c}_2\tilde{z}}{\lambda}\right)\right) d\tilde{z} \tag{4.29}$$

$$G_{\mathrm{dd}} = \frac{1}{2}\int_{\tilde{z}=-1}^{1} \left(\ln\left(1 - \frac{\tilde{c}_1\tilde{z}}{\lambda}\right) - \ln\left(1 - \frac{\tilde{c}_2\tilde{z}}{\lambda}\right)\right)^2 d\tilde{z} \tag{4.30}$$

$$\frac{\partial G_{\mathrm{s}}}{\partial c_j} = -\frac{L}{2\lambda}\int_{\tilde{z}=-1}^{1} \tilde{z}\left(1 - \frac{\tilde{c}_j\tilde{z}}{\lambda}\right)^{-1} d\tilde{z} \tag{4.31}$$

$$\begin{aligned}\frac{\partial G_{\mathrm{ss}}}{\partial c_j} = {} & -\frac{L}{\lambda}\int_{\tilde{z}=-1}^{1} \left(2\bar{h}_0\tilde{z} + 2q\tilde{z}^2 + \ln\left(1 - \frac{\tilde{c}_1\tilde{z}}{\lambda}\right) + \ln\left(1 - \frac{\tilde{c}_2\tilde{z}}{\lambda}\right)\right) \times \\ & \qquad \tilde{z}\left(1 - \frac{\tilde{c}_j\tilde{z}}{\lambda}\right)^{-1} d\tilde{z}\end{aligned} \tag{4.32}$$

$$\frac{\partial G_{\mathrm{d}}}{\partial c_j} = (-1)^j\,\frac{L}{2\lambda}\int_{\tilde{z}=-1}^{1} \tilde{z}\left(1 - \frac{\tilde{c}_j\tilde{z}}{\lambda}\right)^{-1} d\tilde{z} \tag{4.33}$$

$$\frac{\partial G_{\mathrm{dd}}}{\partial c_j} = (-1)^j\,\frac{L}{\lambda}\int_{\tilde{z}=-1}^{1} \left(\ln\left(1 - \frac{\tilde{c}_1\tilde{z}}{\lambda}\right) - \ln\left(1 - \frac{\tilde{c}_2\tilde{z}}{\lambda}\right)\right)\tilde{z}\left(1 - \frac{\tilde{c}_j\tilde{z}}{\lambda}\right)^{-1} d\tilde{z} \tag{4.34}$$

Although an analytic evaluation of these integrals is possible, it yields involved expressions containing logarithms and dilogarithms. Therefore a numeric integration with, say, ten Gauss points over the thickness is more efficient.

However, a Taylor expansion of the integrals with respect to the curvatures can easily be obtained and gives good qualitative information. If we make use of the quantities H, D and K as derived from the curvature tensor in appendix C, introduce the dimensionless quantities

$$\bar{h} = \frac{h}{2}\,H = \frac{h}{2}\,\frac{c_1 + c_2}{2}\,, \qquad \bar{d} = \frac{h}{2}\,D = \frac{h}{2}\,\frac{c_1 - c_2}{2} \tag{4.35}$$

and note

$$\bar{h}^{\,2} - \bar{d}^{\,2} = \frac{h^2}{4}\left(H^2 - D^2\right) = \frac{h^2}{4}\,c_1 c_2 = \frac{h^2}{4}\,K \tag{4.36}$$

then the expansion of G up to fourth order terms in the curvatures may be written

$$\begin{aligned} G \;\approx\;& \frac{16}{45}q^2 + \frac{4}{3}\bar{h}_0^2 - \frac{8}{3}\bar{h}_0\bar{h} + \frac{4}{3}\left(1 - \frac{4}{15}q\right)\bar{h}^{\,2} + \frac{4}{3}\left(\kappa - \frac{4}{15}q\right)\bar{d}^{\,2} \\ & - \frac{8}{15}\bar{h}_0\bar{h}^{\,3} - \frac{8}{5}\bar{h}_0\bar{h}\bar{d}^{\,2} + \frac{4}{15}\left(\frac{7}{3} - \frac{4}{7}q\right)\bar{h}^{\,4} \\ & + \left(\frac{16}{9} + \frac{88}{45}\kappa - \frac{32}{35}q\right)\bar{h}^{\,2}\bar{d}^{\,2} + \frac{4}{15}\left(\frac{1}{3} + 2\kappa - \frac{4}{7}q\right)\bar{d}^{\,4} \end{aligned} \tag{4.37}$$

We will learn in the next section that G describes the energy density — to a first approximation. In the paper [7], we proposed an energy density with the additive structure $w_1(\bar{h}) + w_2(\bar{d}\,)$. Now, the seventh and the ninth term in (4.37) show that our function G does not possess such a simple form. Its properties will be discussed in detail in section 6.9, where we will also need the following Taylor approximations.

$$G_{\mathrm{s}} \approx \frac{2}{3}q - \frac{1}{3}\left(\,\bar{h}^{\,2} + \bar{d}^{\,2}\,\right) - \frac{1}{10}\left(\,\bar{h}^{\,4} + 6\,\bar{h}^{\,2}\bar{d}^{\,2} + \bar{d}^{\,4}\,\right) \tag{4.38}$$

$$\left(1 + \frac{h^2}{12}\,K\right)\exp(-G_{\mathrm{s}}) \approx \exp\left(-\frac{2}{3}q\right)\left(1 + \frac{2}{3}\,\bar{h}^{\,2} + \frac{4}{15}\,\bar{h}^{\,4} + \frac{32}{45}\,\bar{h}^{\,2}\bar{d}^{\,2} + \frac{2}{45}\,\bar{d}^{\,4}\right) \tag{4.39}$$

4.3 Helfrich's Bending Energy Density

(4.19) with (4.18) yields

$$\begin{aligned} \frac{w}{\mu} &= \frac{w_0}{\mu_{\mathrm{b}}} + \frac{w_1}{\mu_{\mathrm{b}}}\left(\left(1 - \sqrt{1 - G + \frac{f\mu_{\mathrm{b}}}{w_1} - \frac{w_0}{w_1}}\,\right)^2 + G\right) \\ &= \frac{w_0}{\mu_{\mathrm{b}}} + \frac{w_1}{\mu_{\mathrm{b}}}\left(2\left(1 - \sqrt{1 - G + \frac{f\mu_{\mathrm{b}}}{w_1} - \frac{w_0}{w_1}}\,\right) + \frac{f\mu_{\mathrm{b}}}{w_1} - \frac{w_0}{w_1}\right) \end{aligned} \tag{4.40}$$

If we replace the square root by the first three terms of its Taylor series, then we obtain the approximation

$$\frac{w}{\mu} \approx \underline{\frac{w_0}{\mu_{\mathrm{b}}} + \frac{w_1}{\mu_{\mathrm{b}}}\,G} + \frac{w_1}{4\mu_{\mathrm{b}}}\left(G - \frac{f\mu_{\mathrm{b}}}{w_1} + \frac{w_0}{w_1}\right)^2 \tag{4.41}$$

The underlined leading terms of this representation of the energy per unit mass of the amphiphilic film are seen to depend only on the expression G

and hence on the local curvatures, while the remaining term depends also on the properties of the whole system through the parameter f. If we only retain the underlined terms and introduce the Taylor representation (4.37) up to second order terms in the curvatures, we arrive at

$$\frac{3}{4}\frac{w}{w_1}\frac{\mu_\mathrm{b}}{\mu} = \frac{3}{4}\frac{w_0}{w_1} + \frac{4}{15}q^2 + \bar{h}_0^2 - 2\bar{h}_0\bar{h} + \Big(1 - \frac{4}{15}q\Big)\bar{h}^2 + \Big(\kappa - \frac{4}{15}q\Big)\bar{d}^2 \tag{4.42}$$

The bending of amphiphilic films is often discussed on the basis of the following quadratic form of the bending energy per unit area

$$w = \frac{1}{2}k_\mathrm{c}\big(2H - c_0\big)^2 + \bar{k}_\mathrm{c}K \tag{4.43}$$

taken from a famous paper of Helfrich [3], where k_c, $\bar{k}_\mathrm{c}$, and c_0 are material constants at a given temperature. With (4.35), (4.36) and with

$$\bar{c}_0 = \frac{h}{2}c_0 \tag{4.44}$$

it can be rewritten as

$$\frac{h^2}{8k_\mathrm{c}}w = \frac{1}{4}\bar{c}_0^2 - \bar{c}_0\bar{h} + \left(1 + \frac{\bar{k}_\mathrm{c}}{2k_\mathrm{c}}\right)\bar{h}^2 - \frac{\bar{k}_\mathrm{c}}{2k_\mathrm{c}}\bar{d}^2 \tag{4.45}$$

If we define

$$\bar{c}_0 = \frac{2\bar{h}_0}{C}\,, \qquad \frac{\bar{k}_\mathrm{c}}{2k_\mathrm{c}} = \frac{1}{C}\left(\frac{4}{15}q - \kappa\right) \tag{4.46}$$

with the abbreviation

$$C = 1 + \kappa - \frac{8}{15}q \tag{4.47}$$

we obtain

$$\frac{C\,h^2}{8k_\mathrm{c}}w = \frac{1}{C}\bar{h}_0^2 - 2\bar{h}_0\bar{h} + \Big(1 - \frac{4}{15}q\Big)\bar{h}^2 + \Big(\kappa - \frac{4}{15}q\Big)\bar{d}^2 \tag{4.48}$$

Then (4.42) and (4.48) become identical if we further choose

$$w_1 = \frac{1}{1 + \kappa - \frac{8}{15}q}\,\frac{\mu_\mathrm{b}}{\mu}\,\frac{6}{h^2}\,k_\mathrm{c} \tag{4.49}$$

$$\frac{w_0}{w_1} = -\frac{16}{45}q^2 + \frac{4}{3}\,\frac{\frac{8}{15}q - \kappa}{1 + \kappa - \frac{8}{15}q}\,\bar{h}_0^2 \tag{4.50}$$

We observe several important differences between the two approaches:

- Our energy density (4.19) depends not only on the local curvatures but also on the local mass density, *i.e.* on the elastic stretch of area, and that mass density, according to (4.20), is a function of the curvatures and of the properties of the whole system, which enter through the parameter f.

- If we only retain the underlined terms in (4.41), then the energy density per unit mass, but not the energy density per unit area, is only dependent on the curvatures. On the other hand, the quadratic form (4.43) assumes the energy per unit area to depend on the curvatures alone. However, if the stretch of the area is small, *i.e.* the ratio $\mu/\mu_{\rm b}$ near to 1, then the distinction between the two kinds of energy density may be disregarded. Otherwise, formula (4.49) is inconsistent since w_1 and $k_{\rm c}$ cannot both be material constants.

- According to (4.46), there is no equality between the characteristic curvatures $\bar{c}_0/2$ and $\bar{h}_0$ of the two approaches.

- Our energy density is not a quadratic expression of the curvatures. The correspondence between the two approaches was discussed on the basis of a truncated Taylor series of our expression. We will see, however, in section 6.9, that higher order terms are essential for the explanation of symmetry breaking and hence for the existence of an X point in the phase diagram.

- Since (4.45) implies $w = 0$, if $\bar{h} = \bar{d} = \bar{c}_0/2$, our material constant w_0 cannot be arbitrary but must have the special value given by (4.50). Moreover, since $\bar{h}_0$ is known to show a strong dependence on the temperature, the same must be true with w_0. These properties are not required in our setting.

5 Evaluation for Special Surfaces

5.1 The Basic Variables

We consider the case that all of the amphiphilic film forms only one kind of structure with uniform characteristic length L. The index k, discerning different structures in the formulae of chapter 2, is then unnecessary and will be omitted. To be more precise, we will discuss lamellae, spheres, cylinders, and a class of bi-continuous surfaces depending on a shape parameter ζ as constructed in appendix H.2.

Surfaces with constant principal curvatures c_1, c_2, *i.e.* lamellae, spheres and cylinders, will have a constant mass density μ, and so the parameter

$$f = \frac{\partial w}{\partial \mu}\big(c_1, c_2, \mu\big) \tag{5.1}$$

according to (2.41) is trivially constant over the surface.

In contrast to this, the principal curvatures as well as the mass density of all other surfaces will constitute fields on the surface. These fields, however, are interrelated in such a way, that the parameter f according to (5.1) must have the same value at each point. Let us single out one such point P. If we compare it with an arbitrary point, we must have

$$f = \frac{\partial w}{\partial \mu}\big(c_1, c_2, \mu\big) = \frac{\partial w}{\partial \mu}\big(c_{1\mathrm{P}}, c_{2\mathrm{P}}, \mu_{\mathrm{P}}\big) \tag{5.2}$$

We assume that this relation can be solved for μ to give

$$\mu = \mu(c_1, c_2, \mu_{\mathrm{P}}) \tag{5.3}$$

After all, a surface of any type is fully characterized by two basic variables, the length L and the mass density μ_{P}. (The index P may be omitted in the case of surfaces with constant principal curvatures.) Once L and μ_{P} are given, then the fields c_1, c_2, μ and, according to (2.41), (2.46), (2.47), also f and the internal forces t_1, t_2, m_1, m_2 are known.

5.2 Areas and Volumes

5.2.1 Spheres

If the amphiphilic film of thickness h forms spheres with uniform radius L, which enclose oil, then the area of the middle surface of one sphere is

$$A_\mathrm{C} = 4\pi L^2 \tag{5.4}$$

and the volume of the oil-sided cavity is

$$V_\mathrm{OC} = \frac{4}{3}\pi \left(L - \frac{h}{2}\right)^3 \tag{5.5}$$

If the spheres are not in contact, then no water volume will be attributed to them, *i.e.* $V_\mathrm{WC} = 0$, and all of the water is interpreted as an excess. On the other hand, if the spheres are arranged in their closest position then we consider all of the water as being attached to them, and the water-sided volume per sphere is given by

$$V_\mathrm{WC} = \chi_\mathrm{S} \frac{4}{3}\pi \left(L + \frac{h}{2}\right)^3 \tag{5.6}$$

with Kepler's coefficient

$$\chi_\mathrm{S} = \frac{3\sqrt{2}}{\pi} - 1 = 0.350 \tag{5.7}$$

5.2.2 Cylinders

Now we consider the case that the amphiphilic film forms cylinders, which enclose oil. Let the ratio of the length l and the radius L of the cylinder be denoted by α, so that $l = \alpha L$. The area of the middle surface of one cylinder is

$$A_\mathrm{C} = 2\pi L\, l = 2\pi\alpha L^2 \tag{5.8}$$

and the volume of the oil-sided cavity is

$$V_\mathrm{OC} = \pi \left(L - \frac{h}{2}\right)^2 l = \pi\alpha \left(L - \frac{h}{2}\right)^2 L \tag{5.9}$$

If the cylinders are not in contact, then no water volume will be attributed to them, *i.e.* $V_\mathrm{WC} = 0$, and all of the water is interpreted as an excess. On the other hand, if the cylinders are arranged in their closest position then we consider all of the water as being attached to them, and the water-sided volume per cylinder is given by

$$V_\mathrm{WC} = \chi_\mathrm{C}\, \pi \left(L + \frac{h}{2}\right)^2 l = \chi_\mathrm{C}\, \pi\alpha \left(L + \frac{h}{2}\right)^2 L \tag{5.10}$$

with

$$\chi_{\mathrm{C}} = \frac{2\sqrt{3}}{\pi} - 1 = 0.103 \tag{5.11}$$

5.2.3 Bi-continuous Structures

In appendix H.2, a class of triply periodic surfaces is constructed. Each surface is characterized by its shape parameter ζ and its characteristic length L. Let us consider the Gaussian curvature as an example of a typical field on the surface. Then its value at a point on the special surface with $L = 1$ and $\zeta = 0$ is denoted by $\bar{K}$ and the value at the corresponding point on the surface with $L = 1$ and arbitrary ζ by $\hat{K}$, while K denotes the value on a surface with any L. With (H.46), we find the interrelations

$$H = \frac{\hat{H}}{L} = -\,\frac{1}{L}\,\frac{\zeta\bar{K}}{1+\zeta^2\bar{K}}\,, \qquad K = \frac{\hat{K}}{L^2} = \frac{1}{L^2}\,\frac{\bar{K}}{1+\zeta^2\bar{K}} \tag{5.12}$$

and hence

$$H = -\,\zeta\,L\,K \tag{5.13}$$

The corresponding principal curvatures are

$$c_{1,2} = \frac{\sqrt{-\,\bar{K}}}{L\Big(-\,\zeta\sqrt{-\,\bar{K}} \pm 1\Big)} \tag{5.14}$$

as is easily checked, since the conditions $c_1 + c_2 = 2H$, $c_1 c_2 = K$ are satisfied.

According to (H.55), the area of one patch is

$$A = \hat{A}\,L^2 = \Big(\bar{A} - \frac{\pi}{6}\,\zeta^2\Big)\,L^2 \tag{5.15}$$

and hence the area of the middle surface of one cell is

$$A_{\mathrm{C}} = 6A = \big(6\bar{A} - \pi\,\zeta^2\big)\,L^2 \tag{5.16}$$

With (H.53), (H.54), the integral of the Gaussian curvature over one patch becomes

$$\int_A K\,dA = \int_{\hat{A}} K\,d\hat{A}L^2 = \int_{\bar{A}} K\big(1+\zeta^2\,\bar{K}\big)\,d\bar{A}\,L^2 = \int_{\bar{A}} \bar{K}\,d\bar{A} = -\frac{\pi}{6} \tag{5.17}$$

and the integral over the mean curvature

$$\int_A H\,dA = -\,\zeta\,L\int_A K\,dA = \frac{\pi}{6}\,\zeta\,L \tag{5.18}$$

The volume of one cell is $V_{\mathrm{C}} = 8L^3$, and hence (H.56) gives the oil-sided volume of the cell as

$$V_{\mathrm{O}} = \left(\frac{1}{2} - \frac{3}{4}\bar{A}\,\zeta + \frac{\pi}{24}\,\zeta^3\right)\,8\,L^3 \tag{5.19}$$

With (D.10) and (H.47), we obtain the volume of the oil-sided cavity by

$$V_{\mathrm{OC}} = V_{\mathrm{O}} - 6V_{+} \tag{5.20}$$

with

$$\begin{aligned} V_{+} &= \int_A \left(\frac{h}{2} - H\frac{h^2}{4} + K\frac{h^3}{24} \right) dA \\ &= \frac{h}{2}\Big(\bar{A} - \frac{\pi}{6}\,\zeta^2\Big)\, L^2 - \frac{h^2}{4}\frac{\pi}{6}\,\zeta\, L - \frac{h^3}{24}\frac{\pi}{6} \\ &= \left(\bar{A}\,\frac{h}{2L} - \frac{\pi}{18}\left(\Big(\zeta + \frac{h}{2L}\Big)^3 - \zeta^3 \right) \right) L^3 \end{aligned} \tag{5.21}$$

and hence

$$V_{\mathrm{OC}} = 4\,L^3 - 6\bar{A}\,L^2\Big(\zeta\,L + \frac{h}{2}\Big) + \frac{\pi}{3}\Big(\zeta\,L + \frac{h}{2}\Big)^3 \tag{5.22}$$

and

$$V_{\mathrm{WC}} = 4\,L^3 + 6\bar{A}\,L^2\Big(\zeta\,L - \frac{h}{2}\Big) - \frac{\pi}{3}\Big(\zeta\,L - \frac{h}{2}\Big)^3 \tag{5.23}$$

5.3 Oil and Water Pressures

5.3.1 Spheres

We note $c_1 = c_2 = 1/L$ and hence $t_1 = t_2 = t$, $m_1 = m_2 = m$. We consider the case that the spheres are in their closest position and introduce (5.4), (5.5), (5.6) into (2.53) and (2.54). These equations may be solved for p_{W} and p_{O} to give

$$\begin{aligned} p_{\mathrm{O}} &= \frac{1}{h\left(L - \frac{h}{2}\right)^2} \left(-L\,(L-h)\,(w - f\mu) + \Big(L + \frac{h}{2}\Big) 2m \right) \\ p_{\mathrm{W}} &= \frac{1}{\chi_{\mathrm{S}}\, h\left(L + \frac{h}{2}\right)^2} \left(L\,(L+h)\,(w - f\mu) - \Big(L - \frac{h}{2}\Big) 2m \right) \\ &\qquad + \left(1 + \frac{1}{\chi_{\mathrm{S}}} \right) p_{\mathrm{e}} \end{aligned} \tag{5.24}$$

Thus the oil and water pressures are represented as functions of L and μ.

5.3.2 Cylinders

We note $c_1 = 1/L$, $c_2 = 0$ and hence $c_2 m_2 = 0$. We consider the case that the cylinders are in their closest position and introduce (5.8), (5.9), (5.10) into

(2.53) and (2.54). These equations may be solved for p_W and p_O to give

$$\begin{aligned} p_\mathrm{O} &= \frac{1}{h\,L\,\left(L-\frac{h}{2}\right)}\left(-L\Big(L-\frac{h}{2}\Big)\,(w-f\mu)+\Big(L+\frac{h}{2}\Big)m_1\right) \\ p_\mathrm{W} &= \frac{1}{\chi_\mathrm{C}\,h\,L\,\left(L+\frac{h}{2}\right)}\left(L\Big(L+\frac{h}{2}\Big)\,(w-f\mu)-\Big(L-\frac{h}{2}\Big)m_1\right) \\ &\quad +\left(1+\frac{1}{\chi_\mathrm{C}}\right)p_\mathrm{e} \end{aligned} \tag{5.25}$$

5.3.3 Bi-continuous Structures

We introduce (5.16), (5.22), (5.23) into (2.53) and (2.54) and arrive at

$$\begin{aligned} p_\mathrm{O} &= \frac{N_1(\zeta)}{D(\zeta)}\left(\int_{A_\mathrm{C}}\big(w-f\mu\big)\,dA+8\,p_\mathrm{e}L^3\right) \\ &\quad +\frac{N_2(\zeta)}{D(\zeta)}\left(\int_{A_\mathrm{C}}\big(c_1m_1+c_2m_2\big)\,dA+8\,p_\mathrm{e}L^3\right) \end{aligned} \tag{5.26}$$

$$\begin{aligned} p_\mathrm{W} &= \frac{N_1(-\zeta)}{D(-\zeta)}\left(\int_{A_\mathrm{C}}\big(w-f\mu\big)\,dA+8\,p_\mathrm{e}L^3\right) \\ &\quad +\frac{N_2(-\zeta)}{D(-\zeta)}\left(\int_{A_\mathrm{C}}\big(c_1m_1+c_2m_2\big)\,dA+8\,p_\mathrm{e}L^3\right) \end{aligned} \tag{5.27}$$

with the abbreviations

$$N_1(\zeta)=\frac{\pi}{3}\Big(\zeta\,L+h\Big)\Big(\zeta\,L-\frac{h}{2}\Big)^2-(4+6\bar{A}\,\zeta)L^3\,,\quad N_2(\zeta)=V_\mathrm{WC} \tag{5.28}$$

$$D(\zeta)=\zeta\,L\,h\left(\frac{\pi^2}{3}\Big(\zeta\,L+\frac{h}{2}\Big)^2\Big(\zeta\,L-\frac{h}{2}\Big)^2-4\pi\big(L^3h+2\bar{A}\,\zeta^2L^4\big)+36\bar{A}^2\,L^4\right) \tag{5.29}$$

The pressures p_O and p_W are dependent on the basic variables L and μ_P.

The solution is not applicable in the isometric case $\zeta=0$, since the denominator D vanishes. Finite values of p_O and p_W require that the numerator is also equal to zero, *i.e.*

$$\begin{aligned} 0 &= N_1(0)\left(\int_{A_\mathrm{C}}\big(w-f\mu\big)\,dA+8\,p_\mathrm{e}L^3\right) \\ &\quad +N_2(0)\left(\int_{A_\mathrm{C}}\big(c_1m_1+c_2m_2\big)\,dA+8\,p_\mathrm{e}L^3\right) \end{aligned} \tag{5.30}$$

with

$$N_1(0) = \frac{\pi}{12}h^3 - 4L^3\,, \quad N_2(0) = 4L^3 - 3\bar{A}L^2h + \frac{\pi}{24}h^3 \tag{5.31}$$

This implies that the equations (2.53) and (2.54) are linearly dependent. Hence the sum of the pressures can be derived from equation (2.54) alone, which takes the form — note (5.16), (5.17), (5.23) —

$$\int_{A_\mathrm{C}} \big(w - f\mu\big)\,dA + p_\mathrm{e}\left(h\int_{A_\mathrm{C}} dA + \frac{h^3}{12}\int_{A_\mathrm{C}} K\,dA + 2V_\mathrm{WC}\right) = \big(p_\mathrm{O} + p_\mathrm{W}\big)\,V_\mathrm{WC}$$

$$= \int_{A_\mathrm{C}} \big(w - f\mu\big)\,dA + 8p_\mathrm{e}L^3 = \big(p_\mathrm{O} + p_\mathrm{W}\big)\,N_2(0) \tag{5.32}$$

We obtain

$$p_\mathrm{O} + p_\mathrm{W} = \frac{1}{N_2(0)}\left(\int_{A_\mathrm{C}} \big(w - f\mu\big)\,dA + 8p_\mathrm{e}L^3\right) \tag{5.33}$$

Thus the sum of p_O and p_W is determined by the basic variables L and μ_P, but not their difference. We have, however, the additional equation (5.30), which constitutes a relation between L and μ_P.

5.4 Four Possible Cases

5.4.1 Case 1: Neither Oil nor Water Excess

The condition (2.32) must be valid for the enclosed oil and water. So

$$f = \frac{\partial f_\mathrm{O}}{\partial k_\mathrm{O}}(k_\mathrm{O}, p_\mathrm{O}) + \frac{p_\mathrm{O}}{\varrho_\mathrm{A}(p_\mathrm{O})} = \frac{\partial f_\mathrm{W}}{\partial k_\mathrm{W}}(k_\mathrm{W}, p_\mathrm{W}) + \frac{p_\mathrm{W}}{\varrho_\mathrm{A}(p_\mathrm{W})} \tag{5.34}$$

Now, f, p_O, and p_W have already been expressed as functions of the basic variables L and μ_P. Therefore the last equations allow us to express k_O and k_W as functions of L and μ_P, too.
(The case $\zeta = 0$ has to be treated in a somewhat different manner, but this shall not be detailed here but in chapter 6.)

The two constraints $h_\mathrm{O} = 0$ and $h_\mathrm{W} = 0$ according to (2.25) and (2.26) may be rewritten — note (2.12) —

$$v_\mathrm{O} m_\mathrm{O} \equiv \left(\frac{1}{\varrho_\mathrm{O}(p_\mathrm{O}(L,\mu_\mathrm{P}))} + \frac{k_\mathrm{O}(L,\mu_\mathrm{P})}{\varrho_\mathrm{A}(p_\mathrm{O}(L,\mu_\mathrm{P}))}\right) m_\mathrm{O} = nV_\mathrm{OC}(L) \tag{5.35}$$

and

$$v_\mathrm{W} m_\mathrm{W} \equiv \left(\frac{1}{\varrho_\mathrm{W}(p_\mathrm{W}(L,\mu_\mathrm{P}))} + \frac{k_\mathrm{W}(L,\mu_\mathrm{P})}{\varrho_\mathrm{A}(p_\mathrm{W}(L,\mu_\mathrm{P}))}\right) m_\mathrm{W} = nV_\mathrm{WC}(L) \tag{5.36}$$

where V_OC, V_WC have to be taken from section 5.2.

The number n of cells can be inferred from equation (2.5), which specializes to

$$m_\mathrm{A} - n\int_{A_\mathrm{C}} \mu\, dA - k_\mathrm{O} m_\mathrm{O} - k_\mathrm{W} m_\mathrm{W} = 0 \tag{5.37}$$

and yields

$$n(L,\mu_\mathrm{P}) = \frac{1}{\int_{A_\mathrm{C}} \mu\, dA\big(L,\mu_\mathrm{P}\big)}\Big(m_\mathrm{A} - k_\mathrm{O}(L,\mu_\mathrm{P})\, m_\mathrm{O} - k_\mathrm{W}(L,\mu_\mathrm{P})\, m_\mathrm{W}\Big) \tag{5.38}$$

So n is also represented as a function of L and μ_P.

Inserting this expression into (5.35) and (5.36) we may compute the unknowns L and μ_P from these two nonlinear equations and, afterwards, get the number n from (5.38).

5.4.2 Case 2: Oil Excess but no Water Excess

Not only an oil excess but also a plane layer of separation between the excess and the microemulsion exists. Therefore (2.35) and (2.37) must hold

$$f = \frac{\partial f_\mathrm{OE}(k_\mathrm{OE}, p_\mathrm{e})}{\partial k_\mathrm{OE}} + \frac{p_\mathrm{e}}{\varrho_\mathrm{A}(p_\mathrm{e})} = \frac{d w_\mathrm{O}(\mu_\mathrm{O})}{d\mu_\mathrm{O}} \tag{5.39}$$

They allow us to express k_OE and μ_O as functions of L and μ_P. Moreover, (2.36) must be valid

$$\begin{aligned} &f_\mathrm{OE}\big(k_\mathrm{OE}(L,\mu_\mathrm{P}), p_\mathrm{e}\big) - k_\mathrm{OE}(L,\mu_\mathrm{P})\frac{\partial f_\mathrm{OE}}{\partial k_\mathrm{OE}}\big(k_\mathrm{OE}(L,\mu_\mathrm{P}), p_\mathrm{e}\big) + \frac{p_\mathrm{e}}{\varrho_\mathrm{O}(p_\mathrm{e})} \\ &= f_\mathrm{O}\big(k_\mathrm{O}(L,\mu_\mathrm{P}), p_\mathrm{O}(L,\mu_\mathrm{P})\big) - k_\mathrm{O}(L,\mu_\mathrm{P})\frac{\partial f_\mathrm{O}}{\partial k_\mathrm{O}}\big(k_\mathrm{O}(L,\mu_\mathrm{P}), p_\mathrm{O}(L,\mu_\mathrm{P})\big) \\ &\quad + \frac{p_\mathrm{O}(L,\mu_\mathrm{P})}{\varrho_\mathrm{O}\big(p_\mathrm{O}(L,\mu_\mathrm{P})\big)} \end{aligned} \tag{5.40}$$

This equation represents a relation between the basic variables L and μ_P.

Equation (2.5) reads

$$m_\mathrm{A} - n\Big(\int_{A_\mathrm{C}} \mu\, dA + (k_\mathrm{O} - k_\mathrm{OE}) v_\mathrm{O}^{-1} V_\mathrm{OC}\Big) - k_\mathrm{OE} m_\mathrm{O} - k_\mathrm{W} m_\mathrm{W} - \mu_\mathrm{O} A_\mathrm{O} = 0 \tag{5.41}$$

and yields

$$n = \frac{m_\mathrm{A} - k_\mathrm{OE} m_\mathrm{O} - k_\mathrm{W} m_\mathrm{W} - \mu_\mathrm{O} A_\mathrm{O}}{\int_{A_\mathrm{C}} \mu\, dA + (k_\mathrm{O} - k_\mathrm{OE}) v_\mathrm{O}^{-1} V_\mathrm{OC}} \tag{5.42}$$

Thus n is represented as a function of L and μ_P. Introducing this into (5.36) we obtain a relation between these two basic variables. This relation and the relation (5.40) form a set of two nonlinear equations for the computation of the unknowns L and μ_{P}. Afterwards, the number n is obtained from (5.42).

Our solution is only valid, if an oil excess actually exists, *i.e.* if n is so small that we have

$$m_{\mathrm{O}} > n\, v_{\mathrm{O}}^{-1} V_{\mathrm{OC}} \tag{5.43}$$

5.4.3 Case 3: Water Excess but no Oil Excess

In general this case is obtained from case 2 by simply interchanging the indices O and W.

The situation is different if we are concerned with spheres or cylinders which enclose oil. If there is much water then the single surfaces are not in their closest position and do not touch each other. The microemulsion appears diluted, all of the water is regarded as an excess, but a separating surface between the excess and the microemulsion does not exist.

Equation (5.34) is replaced by

$$f = \frac{\partial f_{\mathrm{O}}}{\partial k_{\mathrm{O}}}(k_{\mathrm{O}}, p_{\mathrm{O}}) + \frac{p_{\mathrm{O}}}{\varrho_{\mathrm{A}}(p_{\mathrm{O}})} = \frac{\partial f_{\mathrm{WE}}(k_{\mathrm{WE}}, p_{\mathrm{e}})}{\partial k_{\mathrm{WE}}} + \frac{p_{\mathrm{e}}}{\varrho_{\mathrm{A}}(p_{\mathrm{e}})} \tag{5.44}$$

and these equations allow us to express k_{O} and k_{WE} as functions of L and μ.

The water pressure equals the environmental pressure $p_{\mathrm{W}} = p_{\mathrm{e}}$, so that the last terms in the equations (2.53) and (2.54) vanish. (Moreover, $V_{\mathrm{WC}} = 0$.) Thus p_{O} is the only remaining unknown in these two equations which therefore must be linearly dependent. If we put $p_{\mathrm{W}} = p_{\mathrm{e}}$ on the left-hand side of the solutions (5.24) and (5.25), respectively, we indeed obtain an interrelation between L and μ, namely

$$L(L+h)\big(w - f\mu\big) - \left(L - \frac{h}{2}\right) 2m + h\left(L + \frac{h}{2}\right)^2 p_{\mathrm{e}} = 0 \tag{5.45}$$

in the case of spheres and

$$L\left(L + \frac{h}{2}\right)\big(w - f\mu + p_{\mathrm{e}} h\big) - \left(L - \frac{h}{2}\right) m_1 = 0 \tag{5.46}$$

in the case of cylinders.

Since the membrane force of the sphere may be written

$$t = w - f\mu + \frac{m}{L} \tag{5.47}$$

according to (2.46), the condition (5.45) may be given the form

$$3m = (L+h)\, t + p_{\mathrm{e}} \frac{h}{L}\left(L + \frac{h}{2}\right)^2 \tag{5.48}$$

of a relation between the membrane force t and the bending moment m.

The membrane forces of the cylinder are

$$t_1 = w - f\mu + \frac{m_1}{L}\,, \qquad t_2 = w - f\mu \tag{5.49}$$

and the condition (5.46) can be given the form

$$2m_1 = \left(L + \frac{h}{2}\right)\,\bigl(t_1 + p_\mathrm{e}\,h\bigr) \tag{5.50}$$

of a relation between the membrane force t_1 and the bending moment m_1.

Equation (2.5) specializes to

$$m_\mathrm{A} - n\,\mu\,A_\mathrm{C} - k_\mathrm{O} m_\mathrm{O} - k_\mathrm{WE} m_\mathrm{W} = 0 \tag{5.51}$$

whence follows the number n

$$n(L,\mu) = \frac{1}{\mu\,A_\mathrm{C}(L)}\Bigl(m_\mathrm{A} - k_\mathrm{O}(L,\mu)\,m_\mathrm{O} - k_\mathrm{WE}(L,\mu)\,m_\mathrm{W}\Bigr) \tag{5.52}$$

Introducing this into (5.35) gives one equation, while (5.45) or (5.46) is the second one from which L and μ have to be computed. The number n is then obtained from (5.52).

Our solution is only valid if the surfaces are not in their closest position. The amount of water must therefore satisfy

$$m_\mathrm{W} > n\,\upsilon_\mathrm{W}^{-1} V_\mathrm{WC} \equiv n\,\left(\frac{1}{\varrho_\mathrm{W}(p_\mathrm{e})} + \frac{k_\mathrm{WE}(L,\mu)}{\varrho_\mathrm{A}(p_\mathrm{e})}\right)^{-1} V_\mathrm{WC} \tag{5.53}$$

where the minimum water volume of one cell V_WC is taken from (5.6) or (5.10), respectively.

5.4.4 Case 4: Water Excess and Oil Excess

We need two equations for the determination of the basic variables L and μ_P. One of them is equation (5.40). The second one is generally obtained by replacing the index O by W in (5.40), and the number n of cells results from

$$n = \frac{m_\mathrm{A} - k_\mathrm{OE} m_\mathrm{O} - k_\mathrm{WE} m_\mathrm{W} - \mu_\mathrm{O} A_\mathrm{O} - \mu_\mathrm{W} A_\mathrm{W}}{\int_{A_\mathrm{C}} \mu\,dA + (k_\mathrm{O} - k_\mathrm{OE})\upsilon_\mathrm{O}^{-1} V_\mathrm{OC} + (k_\mathrm{W} - k_\mathrm{WE})\upsilon_\mathrm{W}^{-1} V_\mathrm{WC}} \tag{5.54}$$

However, if we are considering spheres or cylinders which contain oil, then the second equation is instead given by (5.45) or (5.46), respectively, and the number n is given by

$$n = \frac{m_\mathrm{A} - k_\mathrm{OE} m_\mathrm{O} - k_\mathrm{WE} m_\mathrm{W} - \mu_\mathrm{O} A_\mathrm{O}}{\int_{A_\mathrm{C}} \mu\,dA + (k_\mathrm{O} - k_\mathrm{OE})\upsilon_\mathrm{O}^{-1} V_\mathrm{OC}} \tag{5.55}$$

The number n must be so small that we have

$$m_\mathrm{O} > n\,\upsilon_\mathrm{O}^{-1} V_\mathrm{OC}\,, \qquad m_\mathrm{W} > n\,\upsilon_\mathrm{W}^{-1} V_\mathrm{WC} \tag{5.56}$$

where V_{WC} denotes the minimum water volume of one cell in the case of spheres and cylinders which contain oil.

On the other hand, n must not be negative, *i.e.* the numerator of (5.54) or (5.55) must be positive. Otherwise no film exists but only a separating surface between oil and water, and the rest of the amphiphile is solved as monomers. Then we have

$$m_{\mathrm{A}} = k_{\mathrm{OE}} m_{\mathrm{O}} + k_{\mathrm{WE}} m_{\mathrm{W}} + \mu_{\mathrm{OW}} A_{\mathrm{OW}} \tag{5.57}$$

where A_{OW} and μ_{OW} denote the area and the mass density of the separating surface. Moreover, we must have

$$f = \frac{\partial f_{\mathrm{OE}}(k_{\mathrm{OE}}, p_{\mathrm{e}})}{\partial k_{\mathrm{OE}}} + \frac{p_{\mathrm{e}}}{\varrho_{\mathrm{A}}(p_{\mathrm{e}})} = \frac{\partial f_{\mathrm{WE}}(k_{\mathrm{WE}}, p_{\mathrm{e}})}{\partial k_{\mathrm{WE}}} + \frac{p_{\mathrm{e}}}{\varrho_{\mathrm{A}}(p_{\mathrm{e}})} = \frac{d w_{\mathrm{OW}}(\mu_{\mathrm{OW}})}{d\mu_{\mathrm{OW}}} \tag{5.58}$$

The equations (5.57), (5.58) allow us to compute k_{OE}, k_{WE} and μ_{OW}.

5.5 Local Equilibrium

The local equilibrium conditions (2.42), (2.43) will, in general, not be satisfied by our structures. That means: Neither the spheres nor the cylinders nor the bi-continuous structures are exact solutions of the Euler-Lagrange equations of our minimum problem. On the contrary, they are test functions in the sense of Rayleigh-Ritz and satisfy only one global equilibrium condition (2.53). So there will be neighbouring shapes which yield smaller values of the free energy.

There are, however, two exceptions. They concern spheres and cylinders which are not in contact with each other. They are uniformly loaded by the oil and the water pressure.

The condition of global equilibrium (2.53) yields in the case of spheres, with (5.4), (5.5),

$$t = (p_{\mathrm{O}} - p_{\mathrm{e}}) \frac{1}{2L} \left(L - \frac{h}{2} \right)^2 - p_{\mathrm{e}} h \tag{5.59}$$

which can be rearranged to read

$$0 = t\, 2\pi L + p_{\mathrm{e}}\, \pi \left(L + \frac{h}{2} \right)^2 - p_{\mathrm{O}}\, \pi \left(L - \frac{h}{2} \right)^2 \tag{5.60}$$

and may be interpreted as the equilibrium condition of a hemisphere. The first term is the resultant of the membrane forces over the perimeter of the cut, the second one is the resultant of the water pressure over the circular area with radius $L + h/2$ and the third the resultant of the oil pressure over the circular area with radius $L - h/2$ and, of course, acting in the opposite direction.

We arrive at the same result if we refer to the local equilibrium conditions. With (C.23) and $\mathbf{C} = L^{-1}\,\mathbf{1}_T$, we have

$$\mathbf{1}_T \cdot \acute{\mathbf{M}} \cdot \nabla_T = \mathbf{1}_T \cdot m\overline{\mathbf{1}_T}^{\,\prime} \cdot \nabla_T = \mathbf{1}_T \cdot \frac{2m}{L}\,\mathbf{n} = 0 \tag{5.61}$$

and the equilibrium condition of moments (2.42) is hence satisfied with arbitrary m but vanishing transverse force, *i.e.* $\mathbf{q}_T = 0$. The equilibrium condition of forces (2.43) reads

$$\begin{aligned} -\mathbf{T} : \mathbf{C} &= p_{\mathrm{e}} \left(1 + \mathrm{tr}\mathbf{C}\frac{h}{2} + \det\mathbf{C}\frac{h^2}{4}\right) - p_{\mathrm{O}} \left(1 - \mathrm{tr}\mathbf{C}\frac{h}{2} + \det\mathbf{C}\frac{h^2}{4}\right) \\ = -\frac{2\,t}{L} &= p_{\mathrm{e}} \left(1 + \frac{h}{L} + \frac{h^2}{4L^2}\right) - p_{\mathrm{O}} \left(1 - \frac{h}{L} + \frac{h^2}{4L^2}\right) \end{aligned} \tag{5.62}$$

and the last equation is, indeed, equivalent to (5.60).

In the case of cylinders, the condition of global equilibrium (2.53) yields with (5.8), (5.9), (5.49), (5.50)

$$t_1 = p_{\mathrm{O}} \left(L - \frac{h}{2}\right) - p_{\mathrm{e}} \left(L + \frac{h}{2}\right) \tag{5.63}$$

This may be interpreted as the equilibrium condition of a hemicylinder. The left-hand side gives the membrane force per unit length, the right-hand side is the resultant of the oil pressure over the area of unit width and height $L - h/2$ minus the resultant of the water pressure over the area of unit width and height $L + h/2$.

We arrive at the same result if we refer to the local equilibrium conditions. The tensor of moments reads $\mathbf{M} = m_1\,\mathbf{e}_1 \otimes \mathbf{e}_1 + m_2\,\mathbf{e}_2 \otimes \mathbf{e}_2$. We have

$$\mathbf{1}_T \cdot \acute{\mathbf{M}} \cdot \nabla_T = \mathbf{1}_T \cdot m_1\overline{\mathbf{e}_1}^{\,\prime}\,\big(\mathbf{e}_1 \cdot \nabla_T\big) = \mathbf{1}_T \cdot \frac{m_1}{L}\,\mathbf{n} = 0 \tag{5.64}$$

and the equilibrium condition of moments (2.42) is hence satisfied with arbitrary constant values m_1 and m_2 but vanishing transverse force, *i.e.* $\mathbf{q}_T = 0$.

The tensor of membrane forces reads $\mathbf{T} = t_1\,\mathbf{e}_1 \otimes \mathbf{e}_1 + t_2\,\mathbf{e}_2 \otimes \mathbf{e}_2$ and the equilibrium condition of forces (2.43) becomes

$$\begin{aligned} -\mathbf{T} : \mathbf{C} &= p_{\mathrm{e}} \left(1 + \mathrm{tr}\mathbf{C}\frac{h}{2} + \det\mathbf{C}\frac{h^2}{4}\right) - p_{\mathrm{O}} \left(1 - \mathrm{tr}\mathbf{C}\frac{h}{2} + \det\mathbf{C}\frac{h^2}{4}\right) \\ = -\frac{t_1}{L} &= p_{\mathrm{e}} \left(1 + \frac{h}{2L}\right) - p_{\mathrm{O}} \left(1 - \frac{h}{2L}\right) \end{aligned} \tag{5.65}$$

The last equation is, indeed, equivalent to (5.63).

Note: If the spheres or cylinders are in contact, then $p_{\mathrm{W}} \neq p_{\mathrm{e}}$ and the local equilibrium conditions are not satisfied, since the interaction at the contact points is not modelled in detail.

6 A Simplified Approach

6.1 The Assumptions

Our results become more transparent if we adopt two simplifications.

- The areas A_{O}, A_{W} of the separating surfaces are small and so these surfaces are neglected.
- The fluid within a cavity and the excess fluid have the same energy density function. This seems reasonable if the cavities are large, *i.e.* if $L/h \gg 1$. If they are small, then the solubility of monomers may be reduced, but we ignore such an effect.

The solution parameters and pressures of a fluid, say oil, within a cavity and within the excess are interrelated by equation (2.36). Now, if the energy density functions are equal ($f_{\mathrm{O}} \equiv f_{\mathrm{O}k} = f_{\mathrm{OE}}$) then $k_{\mathrm{O}} \equiv k_{\mathrm{O}k} = k_{\mathrm{OE}}$ and $p_{\mathrm{O}k} = p_{\mathrm{e}}$ describe an obvious solution of this equation. The condition (2.32) is no longer needed since it is identical to (2.35). The equation (2.36) does not constitute a relation between L and μ_{P} any more and has to be replaced by the new equation $p_{\mathrm{O}k} = p_{\mathrm{e}}$.

Next we introduce the mass of the film of one cell

$$m_{\mathrm{A,FC}} = \int_{A_{\mathrm{C}}} \mu \, dA \tag{6.1}$$

and the ratios

$$\alpha_{\mathrm{O}} = \frac{m_{\mathrm{O}}}{m_{\mathrm{A}}}, \qquad \alpha_{\mathrm{W}} = \frac{m_{\mathrm{W}}}{m_{\mathrm{A}}} \tag{6.2}$$

We restrict our attention to the case that there are only cells of one type of structure and of equal characteristic length L. Due to our simplifications, equation (2.2) reduces to

$$m_{\mathrm{A}} = n \, m_{\mathrm{A,FC}} + k_{\mathrm{O}} m_{\mathrm{O}} + k_{\mathrm{W}} m_{\mathrm{W}} \tag{6.3}$$

and yields the number of cells

$$n = \frac{m_{\mathrm{A}}}{m_{\mathrm{A,FC}}} \big(1 - k_{\mathrm{O}} \alpha_{\mathrm{O}} - k_{\mathrm{W}} \alpha_{\mathrm{W}}\big) \tag{6.4}$$

The oil and water masses must satisfy the inequalities — *cf.* (5.35), (5.36) —

$$\left(\frac{1}{\varrho_{\mathrm{O}}(p_{\mathrm{O}})}+\frac{k_{\mathrm{O}}}{\varrho_{\mathrm{A}}(p_{\mathrm{O}})}\right)m_{\mathrm{O}}\geq nV_{\mathrm{OC}}\,,\quad \left(\frac{1}{\varrho_{\mathrm{W}}(p_{\mathrm{W}})}+\frac{k_{\mathrm{W}}}{\varrho_{\mathrm{A}}(p_{\mathrm{W}})}\right)m_{\mathrm{W}}\geq nV_{\mathrm{WC}} \tag{6.5}$$

which may be given the form

$$\left(\Big(\frac{1}{\varrho_{\mathrm{O}}(p_{\mathrm{O}})}+\frac{k_{\mathrm{O}}}{\varrho_{\mathrm{A}}(p_{\mathrm{O}})}\Big)\frac{m_{\mathrm{A,FC}}}{V_{\mathrm{OC}}}+k_{\mathrm{O}}\right)\alpha_{\mathrm{O}}\geq 1-k_{\mathrm{W}}\alpha_{\mathrm{W}} \tag{6.6}$$

$$\left(\Big(\frac{1}{\varrho_{\mathrm{W}}(p_{\mathrm{W}})}+\frac{k_{\mathrm{W}}}{\varrho_{\mathrm{A}}(p_{\mathrm{W}})}\Big)\frac{m_{\mathrm{A,FC}}}{V_{\mathrm{WC}}}+k_{\mathrm{W}}\right)\alpha_{\mathrm{W}}\geq 1-k_{\mathrm{O}}\alpha_{\mathrm{O}} \tag{6.7}$$

Of course, the number of cells cannot be negative so that (6.4) implies the inequality

$$1-k_{\mathrm{O}}\alpha_{\mathrm{O}}-k_{\mathrm{W}}\alpha_{\mathrm{W}}\geq 0 \tag{6.8}$$

6.2 Consequences

If there is an oil excess then we have $p_{\mathrm{O}}=p_{\mathrm{e}}$, and (2.53), (2.54) imply

$$\begin{aligned} &V_{\mathrm{WC}}\int_{A_{\mathrm{C}}}\Big(2(w-f\mu+p_{\mathrm{e}}h)+c_1m_1+c_2m_2\Big)\,dA\\ &=L\frac{dV_{\mathrm{WC}}}{dL}\int_{A_{\mathrm{C}}}\left(w-f\mu+p_{\mathrm{e}}h+p_{\mathrm{e}}\frac{h^3}{12}K\right)\,dA \end{aligned} \tag{6.9}$$

If there is a water excess then we have $p_{\mathrm{W}}=p_{\mathrm{e}}$, and (2.53), (2.54) imply

$$\begin{aligned} &V_{\mathrm{OC}}\int_{A_{\mathrm{C}}}\Big(2(w-f\mu+p_{\mathrm{e}}h)+c_1m_1+c_2m_2\Big)\,dA\\ &=L\frac{dV_{\mathrm{OC}}}{dL}\int_{A_{\mathrm{C}}}\left(w-f\mu+p_{\mathrm{e}}h+p_{\mathrm{e}}\frac{h^3}{12}K\right)\,dA \end{aligned} \tag{6.10}$$

If there is an oil and a water excess (our former **case 4**), then (2.53), (2.54) imply

$$\int_{A_{\mathrm{C}}}(w-f\mu)\,dA=-p_{\mathrm{e}}\left(h\int_{A_{\mathrm{C}}}dA+\frac{h^3}{12}\int_{A_{\mathrm{C}}}K\,dA\right) \tag{6.11}$$

$$\int_{A_{\mathrm{C}}}(c_1m_1+c_2m_2)\,dA=p_{\mathrm{e}}\frac{h^3}{6}\int_{A_{\mathrm{C}}}K\,dA \tag{6.12}$$

so that both (6.9) and (6.10) are valid. These are two equations for the computation of L and μ_{P}. We denote the result by L^* and μ_{P}^*. Then V_{OC},

V_{WC}, and $m_{\mathrm{A,FC}}$ are also fixed. Moreover, f is known from (2.41), and the solution parameters k_{O} and k_{W} are obtained from (2.35)

$$f = \frac{\partial w}{\partial \mu}(L^*, \mu_{\mathrm{P}}^*) = \frac{\partial f_{\mathrm{O}}}{\partial k_{\mathrm{O}}}(k_{\mathrm{O}}, p_{\mathrm{e}}) + \frac{p_{\mathrm{e}}}{\varrho_{\mathrm{A}}(p_{\mathrm{e}})} = \frac{\partial f_{\mathrm{W}}}{\partial k_{\mathrm{W}}}(k_{\mathrm{W}}, p_{\mathrm{e}}) + \frac{p_{\mathrm{e}}}{\varrho_{\mathrm{A}}(p_{\mathrm{e}})} \tag{6.13}$$

So each of the inequalities (6.6), (6.7), and (6.8) describes a half-plane in the $\alpha_{\mathrm{O}}, \alpha_{\mathrm{W}}$-plane. All the pairs ($\alpha_{\mathrm{O}}$,$\alpha_{\mathrm{W}}$) within the intersection of these three half-planes (region E in fig. 6.1.) give rise to the same film structure (with $L = L^*$ and $\mu = \mu_{\mathrm{P}}^*$) as that of the point P* but differ in the number of cells and the amounts of excess oil and excess water. Note that the extension of the region E is considerably underestimated in the figure.

If (6.8) is violated then no monomolecular film exists and all of the amphiphile is solved as monomers. The solution parameters are obtained from the last equation of (6.13) and from the equality which results from (6.8) when $\geq$ is replaced by $=$.

If there is a water excess but no oil excess (our former **case 3**), then (6.10) constitutes a relation between L and μ_{P}. Since the equations (2.53) and (2.54) are then linearly dependent, it is possible to obtain the oil pressure from (2.54) alone as a function of L and μ_{P} as follows.

$$p_{\mathrm{O}} = p_{\mathrm{e}} + \frac{1}{V_{\mathrm{OC}}} \int_{A_{\mathrm{C}}} \left(w - f\mu + p_{\mathrm{e}} h + p_{\mathrm{e}} \frac{h^3}{12} K \right) dA \tag{6.14}$$

Then the solution parameters k_{O} and k_{W} may be obtained as functions of L and μ_{P} from

$$f = \frac{\partial w}{\partial \mu} = \frac{\partial f_{\mathrm{O}}}{\partial k_{\mathrm{O}}}(k_{\mathrm{O}}, p_{\mathrm{O}}) + \frac{p_{\mathrm{O}}}{\varrho_{\mathrm{A}}(p_{\mathrm{O}})} = \frac{\partial f_{\mathrm{W}}}{\partial k_{\mathrm{W}}}(k_{\mathrm{W}}, p_{\mathrm{e}}) + \frac{p_{\mathrm{e}}}{\varrho_{\mathrm{A}}(p_{\mathrm{e}})} \tag{6.15}$$

Moreover, (6.6) must hold as an equality so that

$$\alpha_{\mathrm{O}} = \left(\Big(\frac{1}{\varrho_{\mathrm{O}}(p_{\mathrm{O}})} + \frac{k_{\mathrm{O}}}{\varrho_{\mathrm{A}}(p_{\mathrm{O}})} \Big) \frac{m_{\mathrm{A,FC}}}{V_{\mathrm{OC}}} + k_{\mathrm{O}} \right)^{-1} (1 - k_{\mathrm{W}} \alpha_{\mathrm{W}}) \tag{6.16}$$

This equation describes points on a straight line in the $\alpha_{\mathrm{O}}, \alpha_{\mathrm{W}}$-plane (line W in figure 6.1). Insertion of (6.16) into (6.7) gives

$$\begin{aligned} \alpha_{\mathrm{W}} \quad \geq \quad & \left(\Big(\frac{1}{\varrho_{\mathrm{W}}(p_{\mathrm{e}})} + \frac{k_{\mathrm{W}}}{\varrho_{\mathrm{A}}(p_{\mathrm{e}})} \Big) \frac{m_{\mathrm{A,FC}}}{V_{\mathrm{WC}}} + k_{\mathrm{W}} \right. \\ & \left. + k_{\mathrm{O}} \Big(\frac{1}{\varrho_{\mathrm{W}}(p_{\mathrm{e}})} + \frac{k_{\mathrm{W}}}{\varrho_{\mathrm{A}}(p_{\mathrm{e}})} \Big) \Big(\frac{1}{\varrho_{\mathrm{O}}(p_{\mathrm{O}})} + \frac{k_{\mathrm{O}}}{\varrho_{\mathrm{A}}(p_{\mathrm{O}})} \Big)^{-1} \frac{V_{\mathrm{OC}}}{V_{\mathrm{WC}}} \right)^{-1} \end{aligned} \tag{6.17}$$

The equality characterizes the point $\mathrm{P_W}$ without water excess. Other pairs (α_{O},α_{W}) on the line W give rise to the same film structure as that of the point $\mathrm{P_W}$ but differ in the number of cells and the amount of excess water.

In section 5.4, spheres and cylinders had to be treated separately due to the lack of attached water in the presence of a water excess. This problem does no longer exist, since the properties of the two kinds of water are now assumed to be the same.

If we interchange the indices O and W in (6.16) and (6.17), we obtain a line O, the points of which characterize states with an oil excess but no water excess (our former **case 2**).

If there is neither a water excess nor an oil excess (our former **case 1**), then two distinct procedures are needed.

1. If we regard the isometric bi-continuous structure (with $\zeta = 0$), then we can prescribe the characteristic length L and the pressure difference $p_\Delta = p_\text{O} - p_\text{W}$. The value of μ_P is then determined by (5.30) and the sum of the pressures $p_\Sigma = p_\text{O} + p_\text{W}$ by (5.33) so that the pressures are given by
$$p_\text{O} = \frac{1}{2}\big(p_\Sigma + p_\Delta\big) \qquad p_\text{W} = \frac{1}{2}\big(p_\Sigma - p_\Delta\big) \tag{6.18}$$
2. In case of any other structure, we can prescribe L and μ_P, and the pressures p_O and p_W are obtained from (2.53) and (2.54).

Afterwards the solution parameters k_O and k_W are inferred from

$$f = \frac{\partial w}{\partial \mu} = \frac{\partial f_\text{O}}{\partial k_\text{O}}(k_\text{O}, p_\text{O}) + \frac{p_\text{O}}{\varrho_\text{A}(p_\text{O})} = \frac{\partial f_\text{W}}{\partial k_\text{W}}(k_\text{W}, p_\text{W}) + \frac{p_\text{W}}{\varrho_\text{A}(p_\text{W})} \tag{6.19}$$

The inequalities (6.6) and (6.7) now hold as equalities and allow to compute the pair (α_O, α_W). Only such values of L and p_Δ or μ_P, respectively, are to be considered which yield pairs (α_O, α_W) that can be found in the region N in figure 6.1. The width of that region is exaggerated in the figure. Actually, the two bounding lines almost coincide and only differ noticeably in the range of small α_O and α_W , where the length L is of the magnitude of the thickness h.

6.3 The Total Energy Density

According to (2.20), (2.54), (6.1), (6.3), (2.12) and (6.19), the minimal free energy of our system simplifies to

$$\begin{aligned} F &= n \int_{A_\text{C}} \left(w + p_\text{e}\Big(h + \frac{h^3}{12}K\Big)\right) dA \\ &\qquad + \big(f_\text{O} + p_\text{e}\upsilon_\text{O}\big)m_\text{O} + \big(f_\text{W} + p_\text{e}\upsilon_\text{W}\big)m_\text{W} \end{aligned}$$

$$\begin{aligned}
&= f\,n \int_{A_\mathrm{C}} \mu\, dA + \big(f_\mathrm{O} + p_\mathrm{O}\upsilon_\mathrm{O}\big) m_\mathrm{O} + \big(f_\mathrm{W} + p_\mathrm{W}\upsilon_\mathrm{W}\big) m_\mathrm{W} \\
&\qquad \underline{+\big(p_\mathrm{O} - p_\mathrm{e}\big)\big(nV_\mathrm{OC} - \upsilon_\mathrm{O} m_\mathrm{O}\big) + \big(p_\mathrm{W} - p_\mathrm{e}\big)\big(nV_\mathrm{WC} - \upsilon_\mathrm{W} m_\mathrm{W}\big)} \\
&= f m_\mathrm{A} + \big(f_\mathrm{O} - f k_\mathrm{O} + p_\mathrm{O}\upsilon_\mathrm{O}\big) m_\mathrm{O} + \big(f_\mathrm{W} - f k_\mathrm{W} + p_\mathrm{W}\upsilon_\mathrm{W}\big) m_\mathrm{W} \\
&= f m_\mathrm{A} + \left(f_\mathrm{O}(k_\mathrm{O}, p_\mathrm{O}) - k_\mathrm{O} \frac{\partial f_\mathrm{O}}{\partial k_\mathrm{O}}(k_\mathrm{O}, p_\mathrm{O}) + \frac{p_\mathrm{O}}{\varrho_\mathrm{O}(p_\mathrm{O})} \right) m_\mathrm{O} \\
&\qquad + \left(f_\mathrm{W}(k_\mathrm{W}, p_\mathrm{W}) - k_\mathrm{W} \frac{\partial f_\mathrm{W}}{\partial k_\mathrm{W}}(k_\mathrm{W}, p_\mathrm{W}) + \frac{p_\mathrm{W}}{\varrho_\mathrm{W}(p_\mathrm{W})} \right) m_\mathrm{W} \qquad (6.20)
\end{aligned}$$

The underlined terms vanish because either $p_\mathrm{O} - p_\mathrm{e} = 0$ (if there is an oil excess) or $nV_\mathrm{OC} - \upsilon_\mathrm{O} m_\mathrm{O} = 0$ (if no oil excess exists). We refer the free energy of the system to the mass of the amphiphile and obtain what may be called the total energy density.

$$\begin{aligned}
\frac{F}{m_\mathrm{A}} &= f + \left(f_\mathrm{O}(k_\mathrm{O}, p_\mathrm{O}) - k_\mathrm{O} \frac{\partial f_\mathrm{O}}{\partial k_\mathrm{O}}(k_\mathrm{O}, p_\mathrm{O}) + \frac{p_\mathrm{O}}{\varrho_\mathrm{O}(p_\mathrm{O})} \right) \alpha_\mathrm{O} \\
&\qquad + \left(f_\mathrm{W}(k_\mathrm{W}, p_\mathrm{W}) - k_\mathrm{W} \frac{\partial f_\mathrm{W}}{\partial k_\mathrm{W}}(k_\mathrm{W}, p_\mathrm{W}) + \frac{p_\mathrm{W}}{\varrho_\mathrm{W}(p_\mathrm{W})} \right) \alpha_\mathrm{W} \qquad (6.21)
\end{aligned}$$

On each of the lines W and O as well as in the region E of figure 6.1, the values of f, k_O, k_W, p_O, p_W are constant. So the total energy density is a linear function on those straight lines and in that region.

6.4 Solubility

In order to get numerical results, we need some assumption on the monomeric solubility of the amphiphile in oil and water. Starting from the linear ansatz

$$f_\mathrm{O}(k_\mathrm{O}, p_\mathrm{O}) - k_\mathrm{O} \frac{\partial f_\mathrm{O}}{\partial k_\mathrm{O}}(k_\mathrm{O}, p_\mathrm{O}) \equiv -\, k_\mathrm{O}^2 \frac{\partial}{\partial k_\mathrm{O}} \left(\frac{f_\mathrm{O}}{k_\mathrm{O}} \right) = \hat{a}_\mathrm{O}(p_\mathrm{O}) - a_\mathrm{O}(p_\mathrm{O})\, k_\mathrm{O} \qquad (6.22)$$

we find by integration

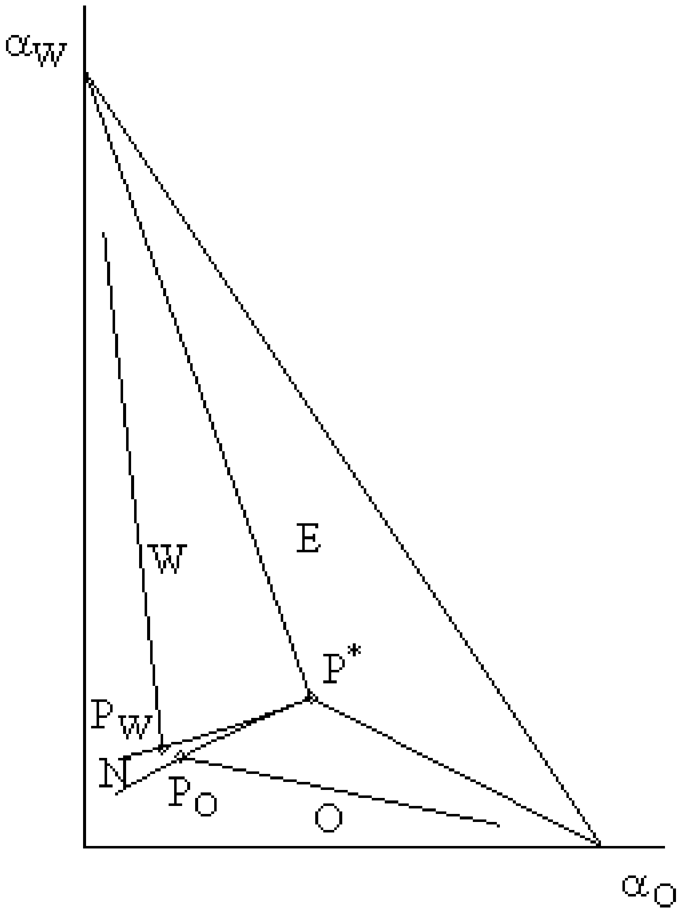
$$f_\mathrm{O}(k_\mathrm{O}, p_\mathrm{O}) = \hat{a}_\mathrm{O}(p_\mathrm{O}) + a_\mathrm{O}(p_\mathrm{O})\, k_\mathrm{O} \ln k_\mathrm{O} + \bar{a}_\mathrm{O}(p_\mathrm{O})\, k_\mathrm{O} \qquad (6.23)$$

The condition (6.19) yields

$$f = \frac{\partial f_\mathrm{O}}{\partial k_\mathrm{O}}(k_\mathrm{O}, p_\mathrm{O}) + \frac{p_\mathrm{O}}{\varrho_\mathrm{A}(p_\mathrm{O})} = a_\mathrm{O}(p_\mathrm{O})\big(\ln k_\mathrm{O} + 1\big) + \bar{a}_\mathrm{O}(p_\mathrm{O}) + \frac{p_\mathrm{O}}{\varrho_\mathrm{A}(p_\mathrm{O})} \qquad (6.24)$$

A comparison of (6.23) with (2.24) shows that a_O actually cannot depend on p_O.

Fig. 6.1 Dependence of excesses on mass ratios



In the following, we adopt a third simplifying assumption.

- The oil, the water and the solved amphiphile are incompressible.

Then not only the densities ϱ_{O} and ϱ_{A} but — according to (2.24) — also the function f_{O} and hence $\hat{a}_{\mathrm{O}}$ and $\bar{a}_{\mathrm{O}}$ do not depend on the pressure p_{O}. Using the abbreviation

$$\hat{f} = \frac{f\,\mu_{\mathrm{b}} - w_0}{w_1} = \left(1 - G_{\mathrm{s}}(c_{1\mathrm{P}}, c_{2\mathrm{P}}) + \ln\frac{\mu_{\mathrm{P}}}{\mu_{\mathrm{b}}}\right)^2 + G(c_{1\mathrm{P}}, c_{2\mathrm{P}}) - 1 \qquad (6.25)$$

according to (4.21), we obtain from (6.24) the solution parameter

$$k_{\mathrm{O}} = \exp\left(\frac{w_1}{\mu_{\mathrm{b}} a_{\mathrm{O}}}\Big(\hat{f} - \frac{\mu_{\mathrm{b}}\bar{a}_{\mathrm{O}} - w_0}{w_1} - \frac{\mu_{\mathrm{b}}}{h\varrho_{\mathrm{A}}}\frac{p_{\mathrm{O}} h}{w_1}\Big) - 1\right) \qquad (6.26)$$

and from (6.21), (6.22) what may be called the dimensionless total energy density

$$\begin{aligned}\frac{\mu_{\mathrm{b}}}{w_1}\frac{F}{m_{\mathrm{A}}} \quad &= \quad \hat{f} \;+\; \frac{w_0}{w_1} \;+\; \left(\frac{\mu_{\mathrm{b}}\hat{a}_{\mathrm{O}}}{w_1} - \frac{\mu_{\mathrm{b}} a_{\mathrm{O}}}{w_1} k_{\mathrm{O}} + \frac{\mu_{\mathrm{b}}}{h\varrho_{\mathrm{O}}}\frac{p_{\mathrm{O}} h}{w_1}\right)\alpha_{\mathrm{O}} \\ &\quad + \left(\frac{\mu_{\mathrm{b}}\hat{a}_{\mathrm{W}}}{w_1} - \frac{\mu_{\mathrm{b}} a_{\mathrm{W}}}{w_1} k_{\mathrm{W}} + \frac{\mu_{\mathrm{b}}}{h\varrho_W}\frac{p_{\mathrm{W}} h}{w_1}\right)\alpha_{\mathrm{W}} \qquad (6.27)\end{aligned}$$

6.5 Lamellae as a Reference

The comparison of the total energy density of different structures is simplified, if we discuss their deviation from the total energy density of a reference structure, which we choose to be the lamella, *i.e.* a plane surface. Water and oil between the lamellae have to be considered as excesses so that we have $p_{\mathrm{O}} = p_{\mathrm{W}} = p_{\mathrm{e}}$. Since $c_1 = c_2 = 0$, equation (6.12) is trivially satisfied while (6.11) with (6.19) yields

$$w(0,0,\mu) - \mu\frac{\partial w}{\partial \mu}(0,0,\mu) + p_{\mathrm{e}} h = 0 \qquad (6.28)$$

from which the mass density μ_{L} of the lamella and afterwards also $\hat{f}_{\mathrm{L}}$, k_{OL}, and k_{WL} can be computed. The surplus of the dimensionless total energy density of any structure over that of the lamellae is given by

$$\begin{aligned}R \quad &= \quad \frac{\mu_{\mathrm{b}}}{w_1}\left(\frac{F}{m_{\mathrm{A}}} - \frac{F}{m_{\mathrm{A}}}\bigg|_{\mathrm{L}}\right) \\ &= \quad \hat{f} - \hat{f}_{\mathrm{L}} \;-\; \left(\frac{\mu_{\mathrm{b}} a_{\mathrm{O}}}{w_1}\big(k_{\mathrm{O}} - k_{\mathrm{OL}}\big) + \frac{\mu_{\mathrm{b}}}{h\varrho_{\mathrm{O}}}\frac{(p_{\mathrm{e}} - p_{\mathrm{O}})h}{w_1}\right)\alpha_{\mathrm{O}} \\ &\quad - \left(\frac{\mu_{\mathrm{b}} a_{\mathrm{W}}}{w_1}\big(k_{\mathrm{W}} - k_{\mathrm{WL}}\big) + \frac{\mu_{\mathrm{b}}}{h\varrho_{\mathrm{W}}}\frac{(p_{\mathrm{e}} - p_{\mathrm{W}})h}{w_1}\right)\alpha_{\mathrm{W}} \qquad (6.29)\end{aligned}$$

and shall be called the rating function. In contrast to the total energy density, the rating function does not depend on the material constants w_0, $\hat{a}_{\mathrm{O}}$, and $\hat{a}_{\mathrm{W}}$. (Note that k_{O} depends not on w_0 but only on the difference $\mu_{\mathrm{b}}\bar{a}_{\mathrm{O}} - w_0$.)

6.6 A Numerical Example

We choose the following values of the dimensionless constants of our model:

$$\frac{\mu_{\mathrm{b}}}{h\varrho_{\mathrm{O}}} = \frac{1}{0.9} \qquad \frac{\mu_{\mathrm{b}}}{h\varrho_{\mathrm{W}}} = 1.0 \qquad \frac{\mu_{\mathrm{b}}}{h\varrho_{\mathrm{A}}} = 1.0 \tag{6.30}$$

$$\frac{\mu_{\mathrm{b}}\bar{a}_{\mathrm{O}} - w_0}{w_1} = 3.0 \qquad \frac{\mu_{\mathrm{b}}\bar{a}_{\mathrm{W}} - w_0}{w_1} = 4.0 \tag{6.31}$$

$$\frac{\mu_{\mathrm{b}}a_{\mathrm{O}}}{w_1} = 1.0 \qquad \frac{\mu_{\mathrm{b}}a_{\mathrm{W}}}{w_1} = 1.0 \tag{6.32}$$

$$\kappa = 0.02 \qquad q = 0.12 \qquad \frac{p_{\mathrm{e}}h}{w_1} = 0.1 \tag{6.33}$$

Important remark: It is not the intention of the following computation to produce a quantitative agreement with any experiment. It shall rather be demonstrated that the model is versatile enough to predict qualitative phase behaviour which resembles that of real mixtures.

We restrict our attention to the case of equal volumes of water and oil,

$$\frac{\alpha_{\mathrm{W}}}{\alpha_{\mathrm{O}}} = \frac{m_{\mathrm{W}}}{m_{\mathrm{O}}} = \frac{\varrho_{\mathrm{W}}V_{\mathrm{W}}}{\varrho_{\mathrm{O}}V_{\mathrm{O}}} = \frac{\varrho_{\mathrm{W}}}{\varrho_{\mathrm{O}}} = \frac{1.0}{0.9} \tag{6.34}$$

The mixture can then be characterized, for example, by the variable

$$\alpha = \frac{m_{\mathrm{O}} + m_{\mathrm{W}}}{m_{\mathrm{A}}} = \alpha_{\mathrm{O}} + \alpha_{\mathrm{W}} \quad \big(= 2.11\,\alpha_{\mathrm{O}} \big) \tag{6.35}$$

In order to construct the following diagrams point by point we let a loop run over an increasing sequence of values of L. Each of them determines the fields of the curvatures c_1, c_2 while the field μ still depends on the unknown value μ_{P}. Let us consider spheres or cylinders which enclose oil or bi-continuous structures with negative ζ as examples. Because of (6.34), there must be a water excess. However, if L is small enough, no oil excess is present. Then μ_{P} may be computed by iteration from the nonlinear equation (6.10), and, afterwards, p_{O} from (6.14). (Both (6.10) and (6.14) are elaborated for the different types of structures in chapter 5.) The values of $\hat{f}$, k_{O}, and k_{W} result from (6.25), (6.26). Finally, α_{O} and α_{W} can be obtained from (6.16) and (6.34), α from (6.35) and R from (6.29). If the sign of $p_{\mathrm{O}} - p_{\mathrm{e}}$ changes from one value of L to the next, then we have passed L^*, where not only $p_{\mathrm{W}}{=}p_{\mathrm{e}}$ but also $p_{\mathrm{O}}{=}p_{\mathrm{e}}$ holds. Beyond that point, which we will later call point **b**, the film is said to be saturated, (6.29) yields a linear dependence of R on α, since $\hat{f}$, k_{O}, k_{W}, p_{O}, and p_{W} remain constant, and not only the water excess but also an oil excess is present.

6.7 Graphs of the Rating Functions

First, we choose $\bar{h}_0 = 0$. That means that the prestrain of the film is symmetric with respect to its middle surface and no preferred curvature towards the oil or the water side exists. Figure 6.2 gives the rating functions of various bi-continuous structures over α. (The values of the rating functions of spheres and cylinders are so large that their graphs are above the represented area.) Of all the bi-continuous structures, the isometric one (with $\zeta = 0$) yields the lowest curve and hence requires the least amount of energy. However, if α is small enough (on the left of point **a**) then lamellae, the rating function of which is zero by definition, become more favoured. If α is large (on the right of point **b**) then we have an oil and a water excess with equal volumes and hence three phases. Our pair $(\alpha_{\mathrm{O}}, \alpha_{\mathrm{W}})$ then lies in the region E of fig. 6.1. On the left of point **b**, there is neither an oil nor a water excess and we have only one phase. Outside of the represented area, on the right-hand side of some point **c** at about $\alpha = 82.0$, the amount of amphiphile is so small that it is totally solved as monomers and no film exists.

Remark: Our interpretation is based on a simplification. Actually the monomeric solubility of the amphiphile in oil and water will not be identical. (Our numerical example gives values of $k_{\mathrm{O}} \approx 0.018$ and $k_{\mathrm{W}} \approx 0.007$.) Therefore, if the volumes of pure oil and water are the same, then the oil-sided and water-sided volumes of a bi-continuous structure must be different, if no excess is allowed. This means that the value of ζ cannot be exactly equal to 0. However, since the values of both k_{O} and k_{W} are small, that deviation was ignored.

Next we allow a non-symmetric prestrain of the film and study the consequences of the resulting preferred curvature.

In the case $\bar{h}_0 = 0.04$ (fig. 6.4), we again identify the limiting points **a** and **b**. However, the lowest values of the rating function are obtained by the bi-continuous structure with $\zeta = 0.05$ on the right-hand side of point **a** and with $\zeta = 0.15$ at point **b**. From **a** to **b**, the value of ζ of the lowest graph is continuously increasing. The positive sign of $\bar{h}_0$ implies that the film possesses a preferred curvature towards the oil side. Since bi-continuous structures with positive ζ show this property, they are favoured. But their oil-sided volume is smaller than the water-sided one. If all of the existing water is enclosed (on the left of point **b**), then there must be an oil excess, and we have two phases. On the right of point **b**, we have, in addition, a water excess and hence three phases.

Going back to the case of the smaller preferred curvature $\bar{h}_0 = 0.005$ (fig. 6.3), we note that a new important point d causes a more diverse behaviour. Between **d** and **b**, the lowest graphs represent again bi-continuous structures with positive ζ. But between **a** and **d**, the isometric structure, with $\zeta = 0$, requires the least energy. Hence all of the oil and the water is enclosed, no excesses exist, and we have just one phase.

Fig. 6.2 Rating functions, h0=0.00

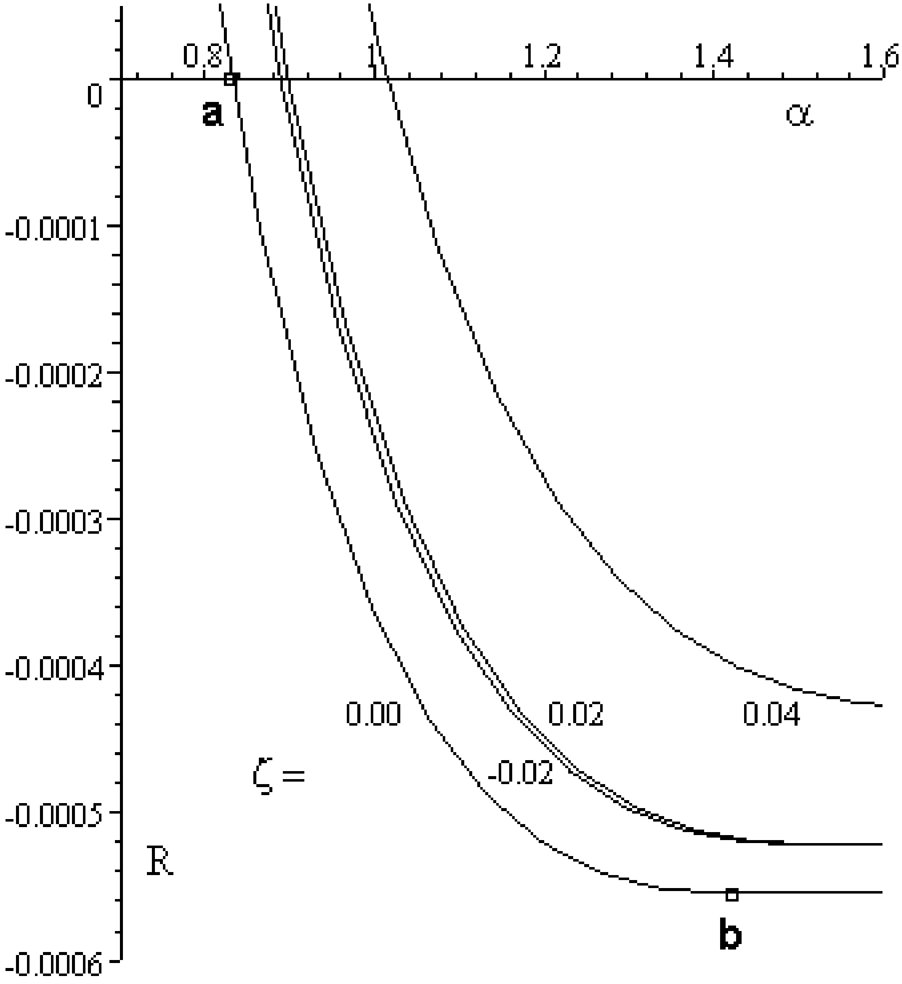


Fig. 6.3 Rating functions, h0=0.005

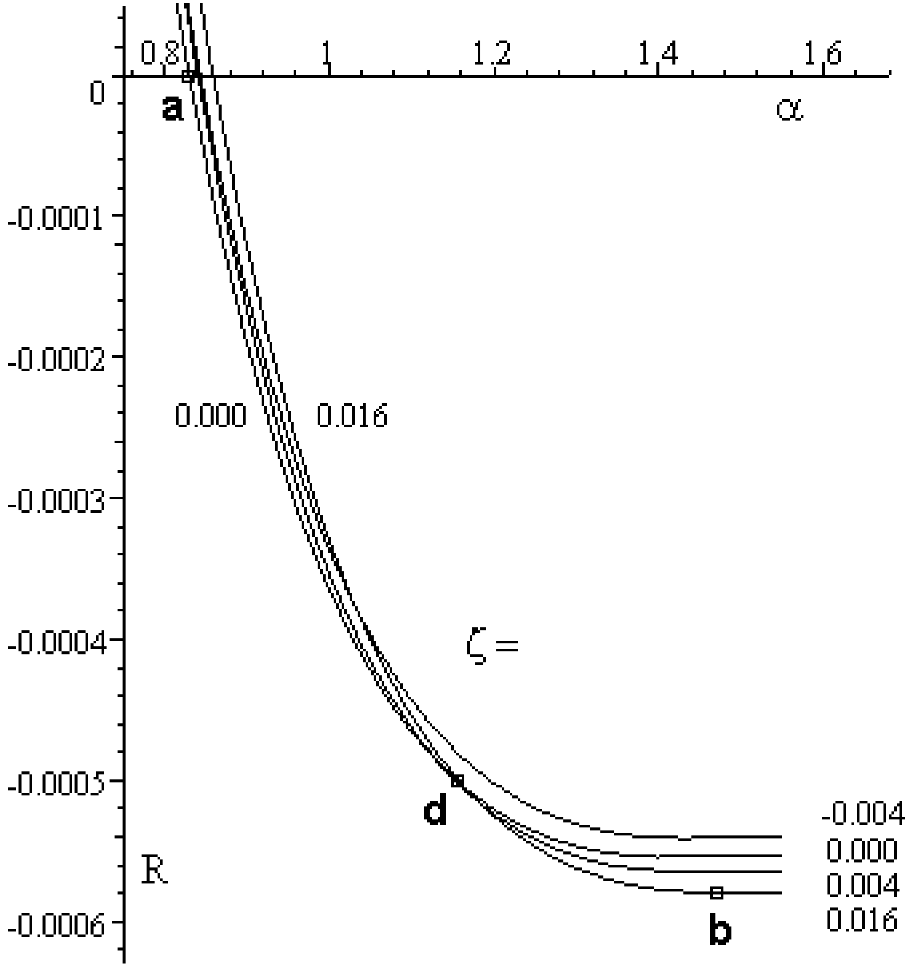


Fig. 6.4 Rating functions, h0=0.04

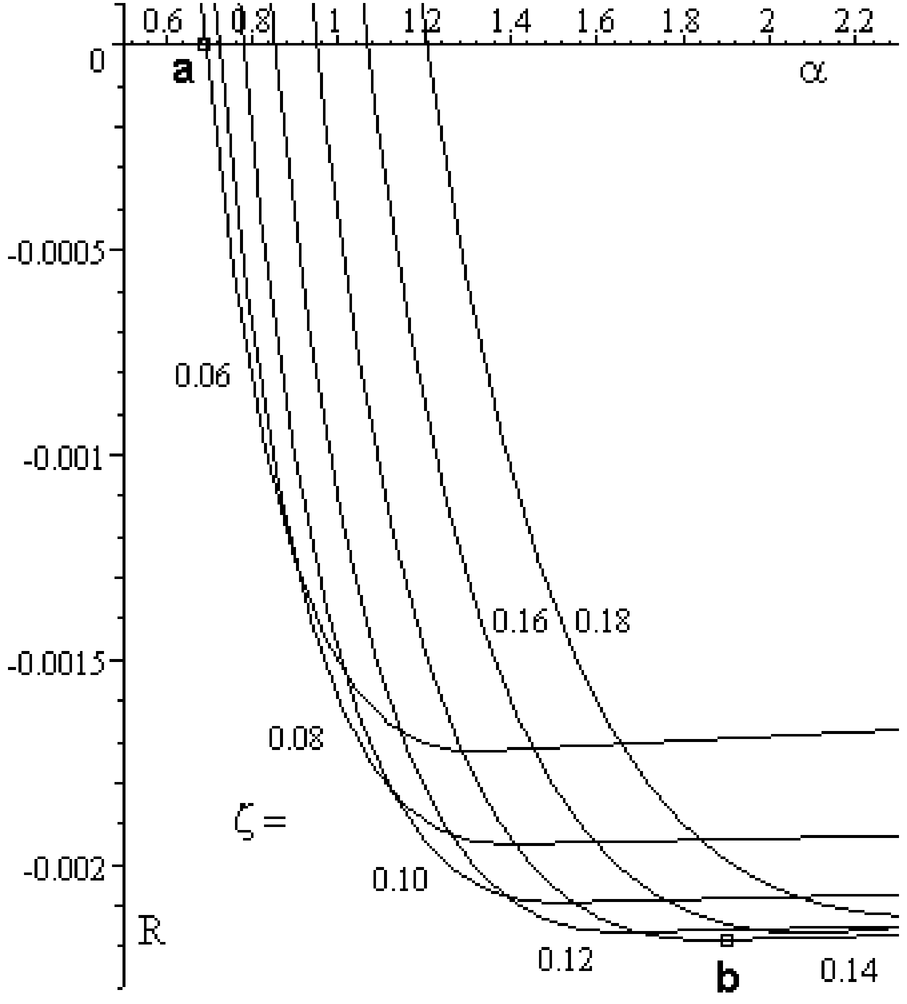
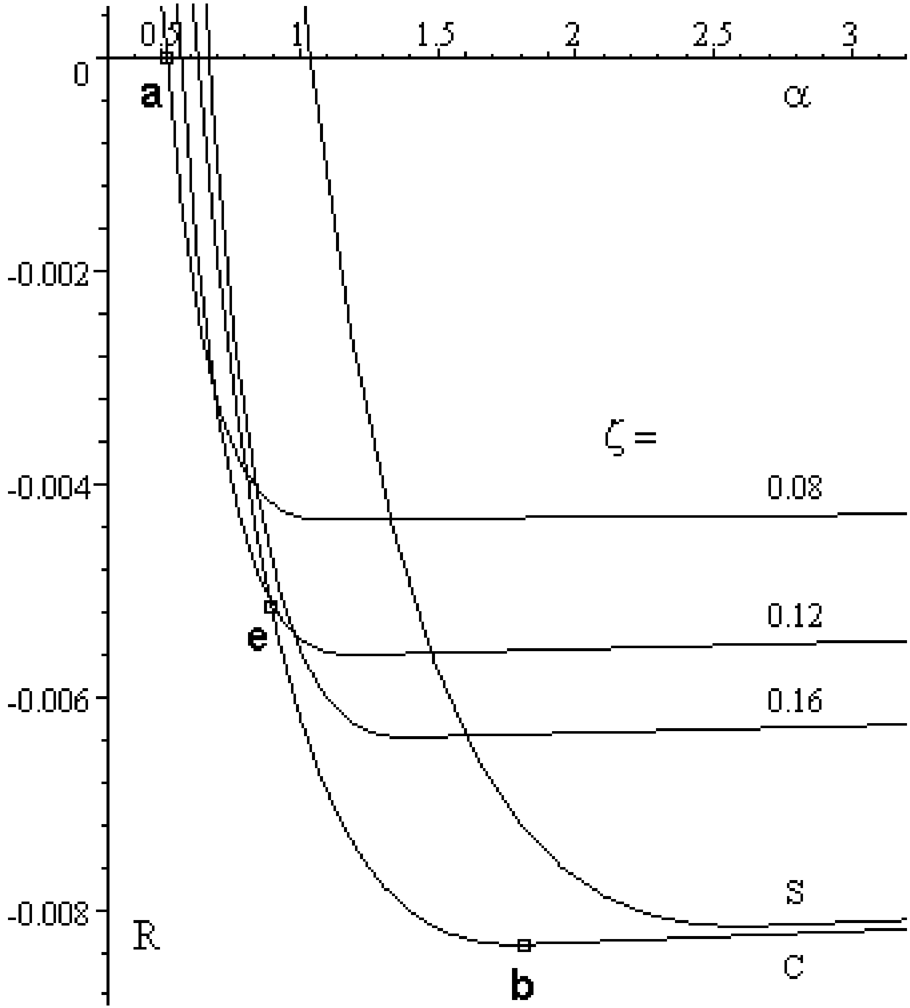


Fig. 6.5 Rating functions, h0=0.08



The case $\bar{h}_0 = 0.08$ (fig. 6.5) reveals a further phenomenon. On the right-hand side, the graphs of cylinders (C) and spheres (S) enclosing oil are below those of the bi-continuous structures, characterized by their values of ζ. Point **b** separates states where all of the oil is enclosed (to the left) from states with an oil excess (to the right). There is always excess water which dilutes the microemulsion. Thus we have a transition from one phase to two phases. The new point **e** separates the reign of the bi-continuous structures, where we have an oil excess, from the reign of the cylinders and hence marks a transition from two phases to one phase.

6.8 The Phase Map

The points **a**, **b**, *etc.* which we have constructed mark phase transitions corresponding to different values of $\bar{h}_0$. If we introduce them into a map (fig. 6.6) and connect them, then we obtain boundaries of the various phase regions of a mixture. The preferred curvature of an amphiphilic film can be tuned, for example, by the temperature. Often, low temperatures induce a curvature towards the oil. In this case, the vertical axis of fig. 6.6 may be interpreted as an axis of decreasing temperature. On the horizontal axis, we do not use the variable α but — in accord with familiar representations — its inverse

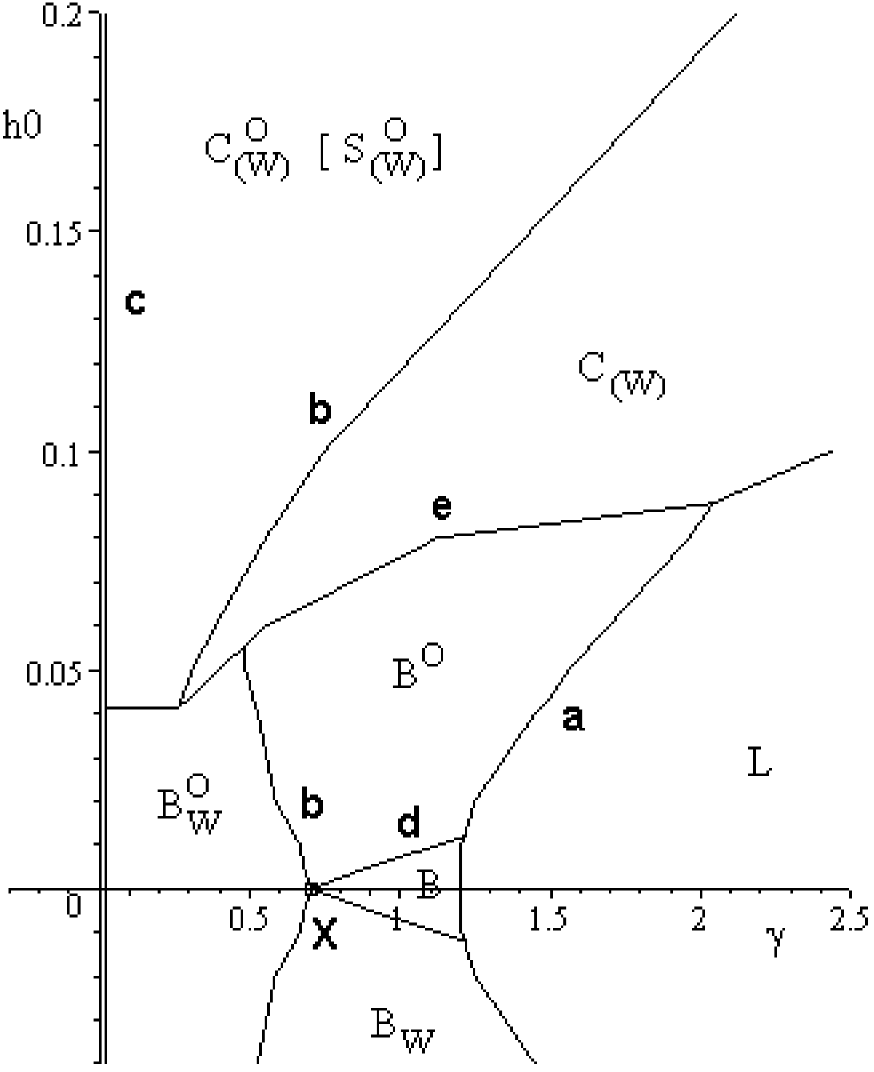
$$\gamma = \frac{1}{\alpha} = \frac{m_\mathrm{A}}{m_\mathrm{O} + m_\mathrm{W}} \tag{6.36}$$

which increases with an increasing amount of amphiphile.

It is sufficient to present the upper half of the map. If the properties of oil and water were the same, then the lower half would be obtained by a mere reflexion and an interchange of the indices O and W. Now, the distinction between the properties of oil and water leads to somewhat different numerical results but does not alter the qualitative picture. The regions are denoted by L, B, C, or S, if the structures which give the mixture its lowest energy are lamellar, bi-continuous, cylindrical or spherical. If excess oil or water is present in addition to the microemulsion, then this is indicated by an upper index O and a lower index W, respectively. An index in brackets means that no separate excess phase exists but that the excess outside of cylinders or spheres merely dilutes the microemulsion.

Observing fig. 6.5 we notice that the graphs of the rating functions of cylinders and spheres almost coincide in case of large α. So it will be a matter of chance whether cylinders or spheres are actually formed. Therefore this possibility is bracketed in fig. 6.6.

Fig. 6.6 Phase map



6.9 The X Point

Of great practical importance is the existence of the so-called X point on the horizontal axis within the region where bi-continuous structures are preferred. It characterizes the minimum amount of amphiphile necessary to enclose all of the oil and the water. If more amphiphile is present then there will also be only one phase. If, however, the amount of amphiphile is smaller, then not all of the oil and the water is contained within the microemulsion and we find an oil excess and a water excess. If we only change the temperature and hence the preferred curvature of the amphiphile, then an oil excess in the case of a positive curvature and a water excess in the case of a negative one appears.

The existence of the X point is only guaranteed if a sufficient prestrain of the outer layers of the film is present. Only then, the energy of an isometric bi-continuous structure is smaller than that of lamellae. To prove this, we first use the abbreviation

$$\omega_{\mathrm{O}} = \exp\left(- \frac{w_1}{\mu_{\mathrm{b}} a_{\mathrm{O}}} \Big(\frac{\mu_{\mathrm{b}} \bar{a}_{\mathrm{O}} - w_0}{w_1} + \frac{\mu_{\mathrm{b}}}{h \varrho_{\mathrm{A}}} \frac{p_{\mathrm{O}} h}{w_1} \Big) - 1 \right) \tag{6.37}$$

and write (6.26) in the form

$$k_{\mathrm{O}} = \omega_{\mathrm{O}} \exp\left(\frac{w_1}{\mu_{\mathrm{b}} a_{\mathrm{O}}} \hat{f} \right) \approx \omega_{\mathrm{O}} \left(1 + \frac{w_1}{\mu_{\mathrm{b}} a_{\mathrm{O}}} \hat{f} \right) \tag{6.38}$$

The replacement of the exponential function by a truncated Taylor series is admissible because our numerical computations have revealed that the absolute value of the argument of the exponential function is small.

If we note in addition that $p_{\mathrm{O}} = p_{\mathrm{W}} = p_{\mathrm{e}}$ is valid at the X point, since we have an oil and a water excess on the left of it , the rating function (6.29) reduces to

$$R = \big(\hat{f} - \hat{f}_{\mathrm{L}} \big) \left(1 - \omega_{\mathrm{O}} \alpha_{\mathrm{O}} - \omega_{\mathrm{W}} \alpha_{\mathrm{W}} \right) \tag{6.39}$$

Now, the numerical investigation has proved ω_{O} and ω_{W} to be rather small. Therefore the expression in the second bracket will be positive even in the case of large α_{O} and α_{W}. We arrive at the conclusion: The existence of the X point requires — note (6.25) —

$$\hat{f} - \hat{f}_{\mathrm{L}} = \frac{\mu_{\mathrm{b}}}{w_1} \big(f - f_{\mathrm{L}} \big) < 0 \tag{6.40}$$

So the isometric bi-continuous structure must have a smaller value of f than the lamella.

6.10 Symmetry Breaking

In order to evaluate the last condition, we first introduce (4.20) into (4.24)

$$w - f\mu = w - \mu \frac{\partial w}{\partial \mu} = 2 w_1 \exp\big(G_{\mathrm{s}} \big) \exp\big(-1 + \sqrt{1-\nu} \big) \big(1 - \sqrt{1-\nu} \big) \tag{6.41}$$

with the abbreviation — note (6.25) —

$$\nu = G - \frac{f\,\mu_\mathrm{b} - w_0}{w_1} = G - \hat{f} \tag{6.42}$$

Next we notice that the absolute value of ν is small so that the lengthy function of ν may be replaced by the first term of its Taylor series.

$$2\exp\big(-1+\sqrt{1-\nu}\big)\big(1-\sqrt{1-\nu}\big) \approx \nu \tag{6.43}$$

Thus we arrive at

$$w - f\mu = w_1 \exp\big(G_\mathrm{s}\big)\nu = w_1 \exp\big(G_\mathrm{s}\big)\big(G - \hat{f}\,\big) \tag{6.44}$$

The condition (6.11) must hold at the X point and reads

$$\begin{aligned} 0 &= \int_{A_\mathrm{C}} \left(w - f\mu + p_\mathrm{e}\Big(h + \frac{h^3}{12}K\Big)\right) dA \\ &= \int_{A_\mathrm{C}} \left(w_1 \exp\big(G_\mathrm{s}\big)\big(G-\hat{f}\,\big) + p_\mathrm{e}\Big(h + \frac{h^3}{12}K\Big)\right) dA \end{aligned} \tag{6.45}$$

Thus we obtain

$$\hat{f} \int_{A_\mathrm{C}} \exp\big(G_\mathrm{s}\big)\,dA = \int_{A_\mathrm{C}} G\exp\big(G_\mathrm{s}\big)\,dA + \frac{p_\mathrm{e}h}{w_1}\int_{A_\mathrm{C}}\Big(1+\frac{h^2}{12}K\Big)\,dA \tag{6.46}$$

which simplifies in the case of a lamella to

$$\hat{f}_\mathrm{L}\exp\big(G_\mathrm{s\,L}\big) = G_\mathrm{L}\exp\big(G_\mathrm{s\,L}\big) + \frac{p_\mathrm{e}h}{w_1} \tag{6.47}$$

and leads to

$$\begin{aligned} &\hat{f}_\mathrm{L}\int_{A_\mathrm{C}} \exp\big(G_\mathrm{s}\big)\,dA \\ &= \int_{A_\mathrm{C}} G_\mathrm{L}\exp\big(G_\mathrm{s}\big)\,dA + \frac{p_\mathrm{e}h}{w_1}\int_{A_\mathrm{C}} \exp\big(-G_\mathrm{s\,L}\big)\exp\big(G_\mathrm{s}\big)\,dA \end{aligned} \tag{6.48}$$

Finally the difference of (6.46) and (6.48) yields

$$\begin{aligned} &\big(\hat{f} - \hat{f}_\mathrm{L}\,\big)\int_{A_\mathrm{C}} \exp\big(G_\mathrm{s}\big)\,dA = \int_{A_\mathrm{C}} \Bigg(\underline{G - G_\mathrm{L}} \\ &\underline{+\frac{p_\mathrm{e}h}{w_1}\bigg(\Big(1+\frac{h^2}{12}K\Big)\exp\big(-G_\mathrm{s}\big) - \exp\big(-G_\mathrm{s\,L}\big)\bigg)}\Bigg)\exp\big(G_\mathrm{s}\big)\,dA \end{aligned} \tag{6.49}$$

The integrals are taken over one cell of the isomorphic bi-continuous structure. The condition (6.40) can by no means be satisfied unless the underlined expression is negative somewhere on that structure. In order to check this, we use the truncated Taylor series (4.37) and (4.39). We must put $\bar{h}_0 = 0$ and, in the case of a lamella, $\bar{h} = 0$, $\bar{d} = 0$, while we have $\bar{h} = 0$, but $\bar{d} \neq 0$ in the case of the isometric bi-continuous structure. So the underlined expression of (6.49) is approximated by

$$\frac{4}{3}\left(\kappa - \frac{4}{15}\,q\right)\bar{d}^{\,2} + \frac{4}{15}\left(\frac{1}{3} + 2\kappa - \frac{4}{7}\,q + \frac{1}{6}\frac{p_{\mathrm{e}}h}{w_1}\exp\Big(-\frac{2}{3}\,q\Big)\right)\bar{d}^{\,4} \tag{6.50}$$

Neither of the two terms can be negative, if

$$q \leq \frac{7}{2}\,\kappa \tag{6.51}$$

is valid, since κ represents an elastic shear stiffness of the film and is surely positive. On the other hand, a positive value of q indicates a positive prestrain (and a positive prestress, *i.e.* a tension) in the outer layers. Therefore, if we have a negative prestrain, no prestrain at all, or a positive prestrain which is not strong enough, then the existence of an X point is excluded.

On the contrary, if the positive prestrain of the outer layers satisfies the condition

$$q > \frac{15}{4}\,\kappa \tag{6.52}$$

then the first term in the expression (6.50) is obviously negative and the corresponding graph looks as shown in fig. 6.7 (solid line). So the underlined expression in (6.49) becomes negative on those parts of the bi-continuous structure where $|\bar{d}|$ is not too large.

Our choice (6.33) of the values of κ and q satisfies (6.52) and, indeed, produces a phase map with an X point and yields the solid line of fig. 6.7. On the other hand, if the numerical computation is performed without a prestrain, *i.e.* with $q = 0$, then we obtain the dashed line of fig. 6.7, the rating functions of all bi-continuous structures turn out to be positive and an X point does not exist.

The influence of the environmental pressure is rather weak, it only modifies the second term in (6.50) but not the first one. If we ignore it, then the underlined expression in (6.49) reduces to $G - G_{\mathrm{L}}$ which approximately measures the difference of the energy density (per unit mass) of the bi-continuous structure and the lamella. This is seen from the underlined terms of (4.41), while the remaining term contains the small quantity ν^2.

If no prestrain is present, then we have a convex function with its minimum at $\bar{d} = 0$, and the energy of the lamella is smaller than that of a bi-continuous structure. If there is enough prestrain, however, then we find a phenomenon of symmetry breaking, namely two minima according to fig. 6.7, and the energy of a bi-continuous structure is less than that of the lamella. Although the film is isotropic (has no preferred material directions), it prefers

Fig. 6.7 Symmetry breaking

Solid: positive prestrain

Dashed: no prestrain

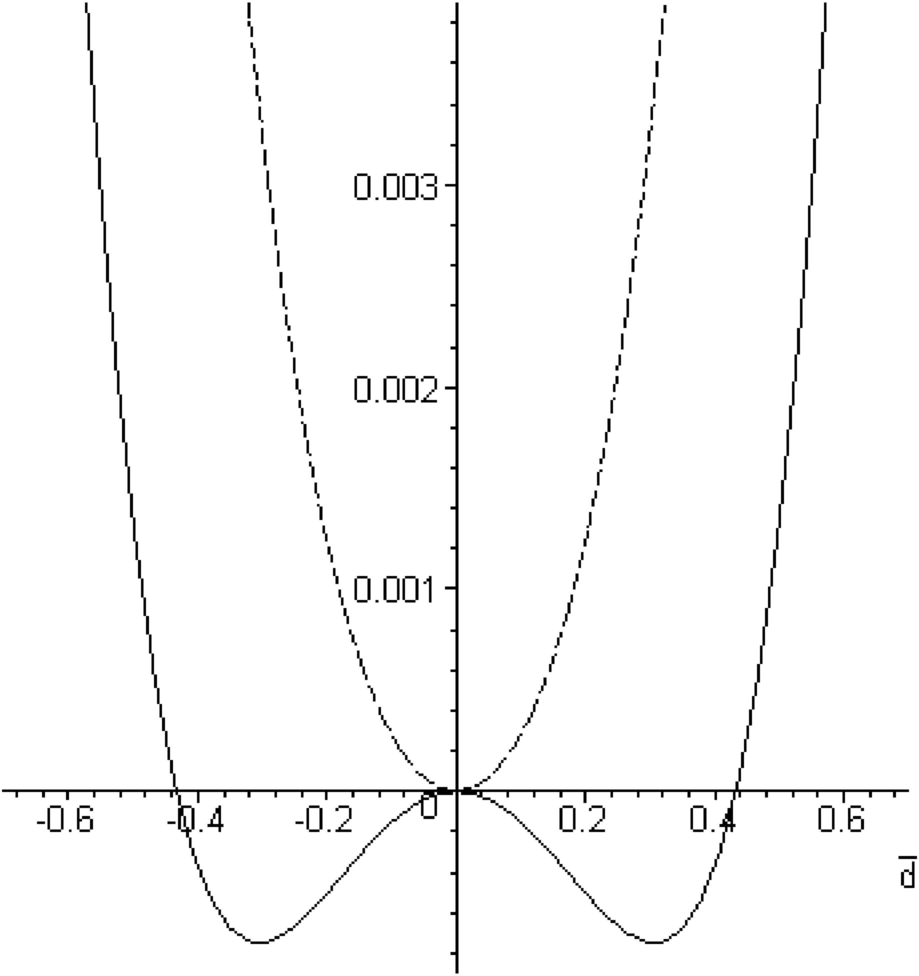
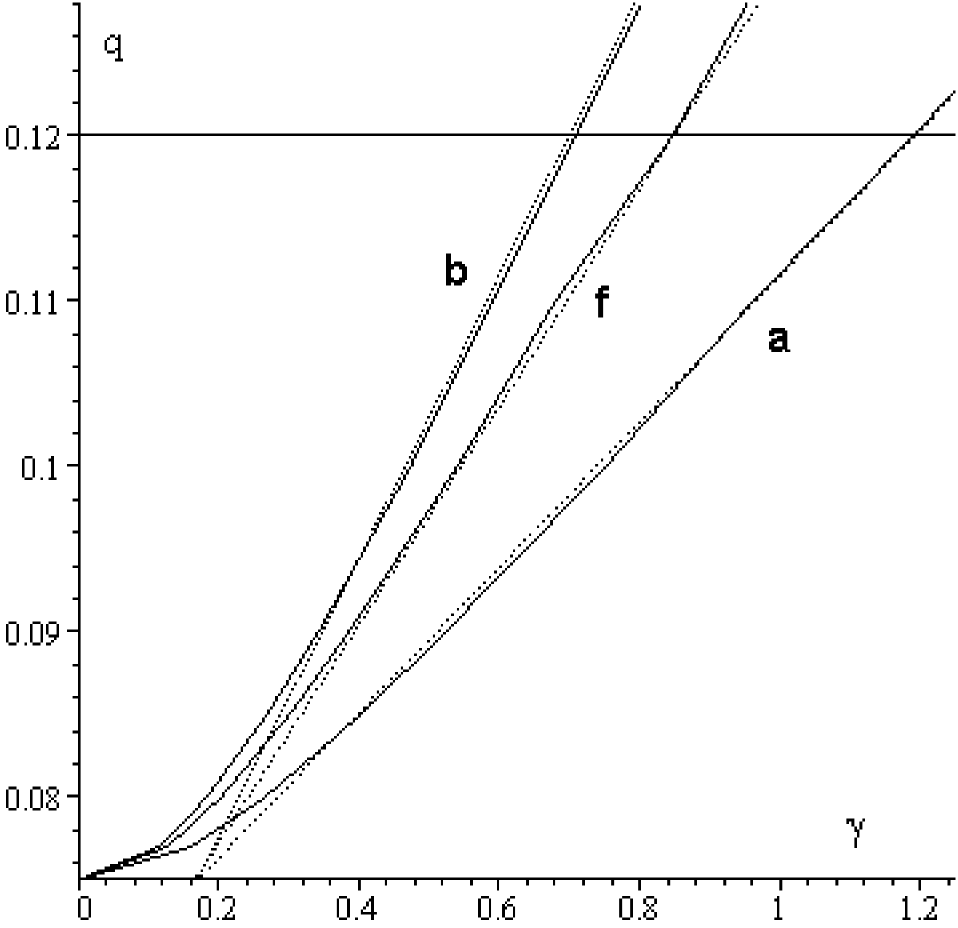


Fig. 6.8 Desiccated slice of bread

Fig. 6.9 Influence of the prestrain parameter q



an anisotropic configuration (with the distinguished local directions of the principal curvatures of opposite sign). A similar phenomenon is well known from everyday life: A desiccating slice of bread takes the form of a hyperboloid (fig. 6.8), presumably since a state of tension develops in the outer layers.

The influence of the prestrain parameter q is illustrated in fig. 6.9. Line **b** indicates the position of the X point and line **a** the boundary between the isomorphic bi-continuous phase and the lamellar phase. It will be shown, however, in subsection 6.11.4 that a coexistence of both phases will develop on the right-hand side of line **f**. The horizontal line indicates the value $q = 0.12$, on which our numerical treatment and hence the construction of fig. 6.2 was based. When q drops to $q = 0.075 = 15 \cdot 0.02/4 = 15\kappa/4$, then the lines approach $\gamma = 0$, since smaller values of q exclude the existence of an X point. If $\gamma > 0.35$ then the three lines are well approximated by the linear expressions (dotted lines in fig. 6.9)

$$q_{\mathbf{b}} = 0.0605 + 0.085\,\gamma\,, \quad q_{\mathbf{f}} = 0.0640 + 0.066\,\gamma\,, \quad q_{\mathbf{a}} = 0.0675 + 0.044\,\gamma \tag{6.53}$$

6.11 Coexistence of Two Structures

6.11.1 The Mixing Rules

We consider two tubes with two different mixtures containing different structures. Let the total mass of amphiphile m_{A} be partitioned among the two tubes according to

$$m_{\mathrm{A}\,1} = (1-\psi)\,m_{\mathrm{A}}\,, \qquad m_{\mathrm{A}\,2} = \psi\,m_{\mathrm{A}} \qquad \text{with} \quad \psi \in [0,1] \tag{6.54}$$

Moreover, we have

$$m_{\mathrm{O}} = \alpha_{\mathrm{O}}\,m_{\mathrm{A}} = m_{\mathrm{O}\,1} + m_{\mathrm{O}\,2} = \alpha_{\mathrm{O}\,1}\,m_{\mathrm{A}\,1} + \alpha_{\mathrm{O}\,2}\,m_{\mathrm{A}\,2} \tag{6.55}$$

Dividing by m_{A} we obtain

$$\alpha_{\mathrm{O}} = (1-\psi)\,\alpha_{\mathrm{O1}} + \psi\,\alpha_{\mathrm{O2}} \tag{6.56}$$

and, analogously,

$$\alpha_{\mathrm{W}} = (1-\psi)\,\alpha_{\mathrm{W1}} + \psi\,\alpha_{\mathrm{W2}} \tag{6.57}$$

With the abbreviation

$$\bar{y}_{\mathrm{O}} \equiv f_{\mathrm{O}}(k_{\mathrm{O}}, p_{\mathrm{O}}) - k_{\mathrm{O}} \frac{\partial f_{\mathrm{O}}}{\partial k_{\mathrm{O}}}(k_{\mathrm{O}}, p_{\mathrm{O}}) + \frac{p_{\mathrm{O}}}{\varrho_{\mathrm{O}}(p_{\mathrm{O}})} = f_{\mathrm{O}}(k_{\mathrm{O}}) - k_{\mathrm{O}} \frac{df_{\mathrm{O}}}{dk_{\mathrm{O}}}(k_{\mathrm{O}}) + \frac{p_{\mathrm{O}}}{\varrho_{\mathrm{O}}} \tag{6.58}$$

— where the last form is valid under the assumption of incompressibility —

the minimal free energy of each of the two systems may be written (note (6.20))

$$F_k = f_k\, m_{\mathrm{A}k} + \bar{y}_{\mathrm{O}k}\, m_{\mathrm{O}k} + \bar{y}_{\mathrm{W}k}\, m_{\mathrm{W}k} = \Big(f_k + \bar{y}_{\mathrm{O}k}\, \alpha_{\mathrm{O}k} + \bar{y}_{\mathrm{W}k}\, \alpha_{\mathrm{W}k}\Big) m_{\mathrm{A}k} \quad k = 1, 2 \tag{6.59}$$

and the free energy — not necessarily minimal — of the whole system is therefore

$$F = F_1 + F_2 = \Big((1-\psi)\, f_1 + \psi\, f_2\Big) m_{\mathrm{A}}$$
$$+ \Big((1-\psi)\, \bar{y}_{\mathrm{O}1}\, \alpha_{\mathrm{O}1} + \psi\, \bar{y}_{\mathrm{O}2}\, \alpha_{\mathrm{O}2}\Big) m_{\mathrm{A}} + \Big((1-\psi)\, \bar{y}_{\mathrm{W}1}\, \alpha_{\mathrm{W}1} + \psi\, \bar{y}_{\mathrm{W}2}\, \alpha_{\mathrm{W}2}\Big) m_{\mathrm{A}} \tag{6.60}$$

whence follows

$$\frac{F}{m_{\mathrm{A}}} = (1-\psi)\, \frac{F_1}{m_{\mathrm{A}\,1}} + \psi\, \frac{F_2}{m_{\mathrm{A}\,2}} \tag{6.61}$$

The minimal free energies of the corresponding lamellae are

$$F_{\mathrm{L}k} = \Big(f_{\mathrm{L}} + \bar{y}_{\mathrm{OL}}\, \alpha_{\mathrm{O}k} + \bar{y}_{\mathrm{WL}}\, \alpha_{\mathrm{W}k}\Big) m_{\mathrm{A}k} \quad k = 1, 2 \tag{6.62}$$

and this implies

$$R = (1-\psi)\, R_1 + \psi\, R_2 \tag{6.63}$$

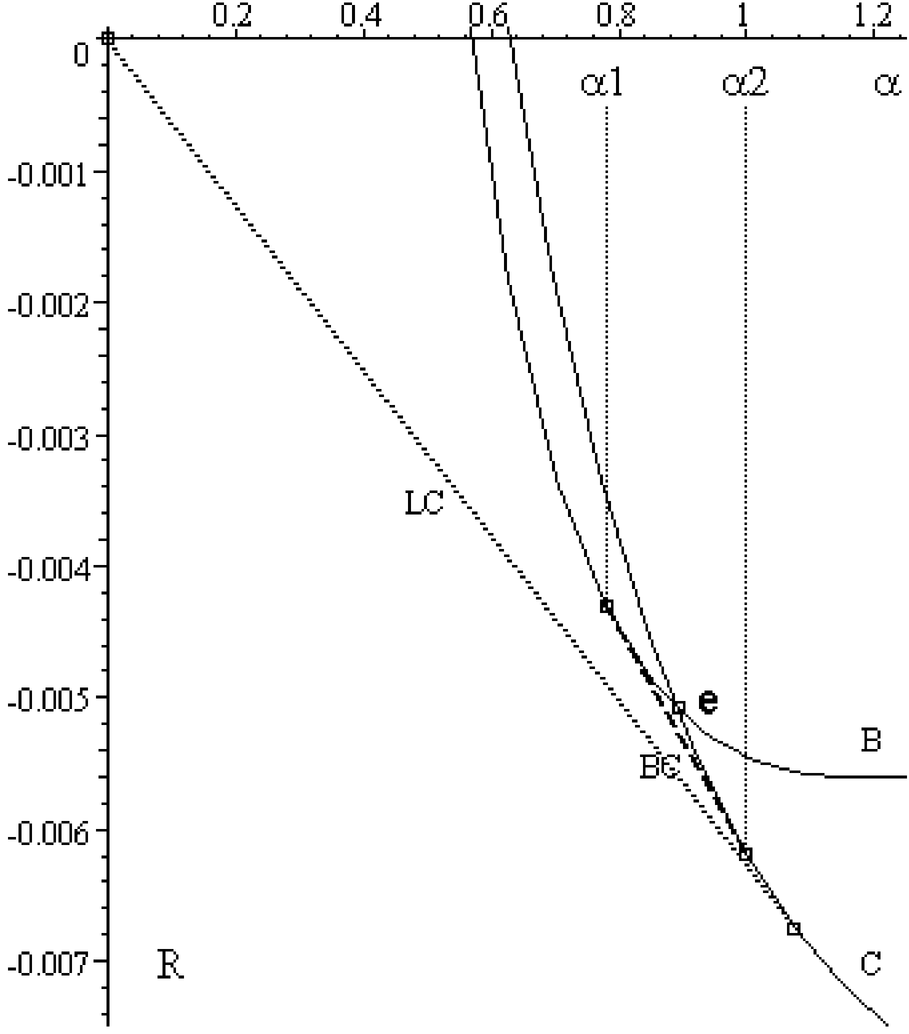
If we bring the two mixtures together in one tube, then we get a resulting mixture with two coexisting structures. Its parameters α_{O} and α_{W} as well as its total energy density and its rating function are obtained from those of the original two systems by the mixing rules (6.56), (6.57), (6.61), (6.63).

6.11.2 A Coarse Treatment of the Coexistence

Let us go back to fig. 6.5 and single out the graphs of R of the mixture with a bi-continuous structure of ζ=0.12 (referred to as B) and of the mixture with cylinders which enclose oil (referred to as C). We can generate a resulting mixture with the parameter α by combining the two mixtures B and C with the parameters α_1 and α_2, respectively. The graph of the corresponding rating function according to the rule (6.63) is given by the straight line BC in the interval $\alpha_1 \leq \alpha \leq \alpha_2$ in fig. 6.10. The rating function and hence the free energy of the two coexisting structures is obviously less then that of any of the single structures. Moreover, we have chosen the values of α_1 and α_2 of our example in such a manner as to give the straight line its lowest possible position.

In a similar manner, the straight line LC describes the coexistence of a mixture with lamellae (with $\alpha = 0$) and a mixture with cylinders. We see

Fig. 6.10 Coexistence, coarse treatment



that the corresponding rating function is lower than that of a mixture of B and C or of bi-continuous structures alone.

So fig. 6.6 must obviously be reinterpreted. The lines **a** and **e** do not separate regions with totally distinct structures. Instead, they are surrounded by bands of coexisting structures.

6.11.3 A Refined Treatment

According to section 2.5, a coexistence can only persist, if the additional conditions

$$p_{\mathrm{O}} \equiv p_{\mathrm{O1}} = p_{\mathrm{O2}}\,, \qquad p_{\mathrm{W}} \equiv p_{\mathrm{W1}} = p_{\mathrm{W2}} \tag{6.64}$$

$$k_{\mathrm{O}} \equiv k_{\mathrm{O1}} = k_{\mathrm{O2}}\,, \qquad k_{\mathrm{W}} \equiv k_{\mathrm{W1}} = k_{\mathrm{W2}} \tag{6.65}$$

are satisfied and hence also

$$f \equiv f_1 = f_2 = \frac{\partial w}{\partial \mu} = \frac{\partial f_{\mathrm{O}}}{\partial k_{\mathrm{O}}} + \frac{p_{\mathrm{O}}}{\varrho_{\mathrm{A}}} = \frac{\partial f_{\mathrm{W}}}{\partial k_{\mathrm{W}}} + \frac{p_{\mathrm{W}}}{\varrho_{\mathrm{A}}} \tag{6.66}$$

and

$$\bar{y}_{\mathrm{O}} \equiv \bar{y}_{\mathrm{O1}} = \bar{y}_{\mathrm{O2}}\,, \qquad \bar{y}_{\mathrm{W}} \equiv \bar{y}_{\mathrm{W1}} = \bar{y}_{\mathrm{W2}} \tag{6.67}$$

This implies that the total energy density of a system with coexisting structures may be calculated by the same formula

$$\frac{F}{m_{\mathrm{A}}} = f + \bar{y}_{\mathrm{O}}\,\alpha_{\mathrm{O}} + \bar{y}_{\mathrm{W}}\,\alpha_{\mathrm{W}} \tag{6.68}$$

as in the case (6.21) with only one kind of structure.

In the example of the coexistence of B and C, the mixture B possesses an oil excess, which implies $p_{\mathrm{O}} = p_{\mathrm{e}}$, $p_{\mathrm{W}} \neq p_{\mathrm{e}}$, while the mixture C is diluted by excess water, which implies $p_{\mathrm{O}} \neq p_{\mathrm{e}}$, $p_{\mathrm{W}} = p_{\mathrm{e}}$. So the conditions (6.64) to (6.67) are not satisfied. This means that the coexistence of B and C in the described manner cannot be stable since it does not satisfy the necessary conditions of minimal free energy. Therefore, the construction of fig. 6.10 is too simple and only gives an upper bound of the minima of R.

In order to obtain a more general result, we consider the quantities α_{O} and α_{W} as given and determine α_{O1}, α_{O2}, α_{W1}, α_{W2}, and ψ from the condition that the rating function R be minimal under the side conditions (6.56) and (6.57). Introducing the Lagrangean parameters λ_{O} and λ_{W}, we arrive at

$$\begin{aligned}&(1-\psi)\,R_1(\alpha_{\mathrm{O1}},\alpha_{\mathrm{W1}}) + \psi\,R_2(\alpha_{\mathrm{O2}},\alpha_{\mathrm{W2}})\\ &+\lambda_{\mathrm{O}}\Big(\alpha_{\mathrm{O}} - (1-\psi)\,\alpha_{\mathrm{O1}} - \psi\,\alpha_{\mathrm{O2}}\Big) + \lambda_{\mathrm{W}}\Big(\alpha_{\mathrm{W}} - (1-\psi)\,\alpha_{\mathrm{W1}} - \psi\,\alpha_{\mathrm{W2}}\Big) = \min\end{aligned} \tag{6.69}$$

The postulate that the derivatives with respect to λ_{O} and λ_{W} must vanish yields the equations (6.56) and (6.57). The derivatives with respect to $\alpha_{\mathrm{O}1}$, $\alpha_{\mathrm{O}2}$, $\alpha_{\mathrm{W}1}$, and $\alpha_{\mathrm{W}2}$ are zero, if

$$\frac{\partial R_1}{\partial \alpha_{\mathrm{O}1}} = \frac{\partial R_2}{\partial \alpha_{\mathrm{O}2}} = \lambda_{\mathrm{O}}\,, \qquad \frac{\partial R_1}{\partial \alpha_{\mathrm{W}1}} = \frac{\partial R_2}{\partial \alpha_{\mathrm{W}2}} = \lambda_{\mathrm{W}} \tag{6.70}$$

holds, and the derivative with respect to ψ is zero, if we have

$$R_2 - R_1 = \lambda_{\mathrm{O}}\big(\alpha_{\mathrm{O}2} - \alpha_{\mathrm{O}1}\big) + \lambda_{\mathrm{W}}\big(\alpha_{\mathrm{W}2} - \alpha_{\mathrm{W}1}\big) \tag{6.71}$$

In order to obtain the derivatives of (6.70) we go back to (6.59)

$$F_k = f_k\, m_{\mathrm{A}k} + \bar{y}_{\mathrm{O}k}\, m_{\mathrm{O}k} + \bar{y}_{\mathrm{W}k}\, m_{\mathrm{W}k} \tag{6.72}$$

This expression gives the minimal free energy of a mixture with the fixed masses $m_{\mathrm{A}k}$, $m_{\mathrm{O}k}$, $m_{\mathrm{W}k}$ under the restriction to one kind of structure. If another mixture with slightly different masses is considered, then the parameters of the structure, the pressures *etc.* and hence also the values of f_k, $\bar{y}_{\mathrm{O}k}$, and $\bar{y}_{\mathrm{W}k}$ will be different. Therefore the increment of the minimal free energy is obtained from

$$dF_k = \underline{df_k\, m_{\mathrm{A}k} + d\bar{y}_{\mathrm{O}k}\, m_{\mathrm{O}k} + d\bar{y}_{\mathrm{W}k}\, m_{\mathrm{W}k}} + \underbrace{f_k\, dm_{\mathrm{A}k} + \bar{y}_{\mathrm{O}k}\, dm_{\mathrm{O}k} + \bar{y}_{\mathrm{W}k}\, dm_{\mathrm{W}k}} \tag{6.73}$$

However, the underlined expression is zero so that only the underbraced one remains. This follows from the fact that the free energy F_k is a minimum and hence $dF_k = 0$ must be valid, if the masses are kept constant but any other parameter varied. We further infer

$$\begin{aligned} d\left(\frac{F_k}{m_{\mathrm{A}k}}\right) &= \frac{dF_k}{m_{\mathrm{A}k}} - \frac{F_k\, dm_{\mathrm{A}k}}{m_{\mathrm{A}k}^2} \\ &= \bar{y}_{\mathrm{O}k}\, d\left(\frac{m_{\mathrm{O}k}}{m_{\mathrm{A}k}}\right) + \bar{y}_{\mathrm{W}k}\, d\left(\frac{m_{\mathrm{W}k}}{m_{\mathrm{A}k}}\right) = \bar{y}_{\mathrm{O}k}\, d\alpha_{\mathrm{O}k} + \bar{y}_{\mathrm{W}k}\, d\alpha_{\mathrm{W}k} \end{aligned} \tag{6.74}$$

Since the rating function is defined by

$$R_k = \frac{\mu_{\mathrm{b}}}{w_1}\left(\left.\frac{F}{m_{\mathrm{A}}}\right|_k - \left.\frac{F}{m_{\mathrm{A}}}\right|_{\mathrm{L}k}\right) \tag{6.75}$$

according to (6.29), we obtain

$$\frac{\partial R_k}{\partial \alpha_{\mathrm{O}k}} = \frac{\mu_{\mathrm{b}}}{w_1}\left(\bar{y}_{\mathrm{O}k} - \bar{y}_{\mathrm{OL}}\right) \tag{6.76}$$

So (6.70) leads to

$$\lambda_{\mathrm{O}} = \frac{\mu_{\mathrm{b}}}{w_1}\left(\bar{y}_{\mathrm{O}1} - \bar{y}_{\mathrm{OL}}\right) = \frac{\mu_{\mathrm{b}}}{w_1}\left(\bar{y}_{\mathrm{O}2} - \bar{y}_{\mathrm{OL}}\right) \tag{6.77}$$

and

$$\lambda_{\mathrm{W}} = \frac{\mu_{\mathrm{b}}}{w_1}\Big(\bar{y}_{\mathrm{W}1} - \bar{y}_{\mathrm{WL}}\Big) = \frac{\mu_{\mathrm{b}}}{w_1}\Big(\bar{y}_{\mathrm{W}2} - \bar{y}_{\mathrm{WL}}\Big) \tag{6.78}$$

and this implies the relations (6.67), which are known from chapter 2.

Introducing (6.59), (6.62) into (6.75), we arrive at the representation

$$R_k = \frac{\mu_{\mathrm{b}}}{w_1}\Big(f_k - f_{\mathrm{L}} + \big(\bar{y}_{\mathrm{O}k} - \bar{y}_{\mathrm{OL}}\big)\alpha_{\mathrm{O}k} + \big(\bar{y}_{\mathrm{W}k} - \bar{y}_{\mathrm{WL}}\big)\alpha_{\mathrm{W}k}\Big) \tag{6.79}$$

Noting (6.77),(6.78), the condition (6.71) is seen to be satisfied if $f_1 = f_2$ holds, in accordance with (6.66), as was also derived in chapter 2.

Now, let us define a new pair of orthogonal axes in the $\alpha_{\mathrm{O}}, \alpha_{\mathrm{W}}$-plane by

$$\alpha^{*} = \frac{1}{g}\Big(\lambda_{\mathrm{O}}\,\alpha_{\mathrm{O}} + \lambda_{\mathrm{W}}\,\alpha_{\mathrm{W}}\Big)\,, \qquad \alpha^{**} = \frac{1}{g}\Big(-\lambda_{\mathrm{W}}\,\alpha_{\mathrm{O}} + \lambda_{\mathrm{O}}\,\alpha_{\mathrm{W}}\Big) \tag{6.80}$$

This implies

$$\begin{aligned}
\frac{\partial R_j}{\partial \alpha_j^{*}} &= \frac{g}{\lambda_{\mathrm{O}}^2 + \lambda_{\mathrm{W}}^2}\left(\lambda_{\mathrm{O}}\frac{\partial R_j}{\partial \alpha_{\mathrm{O}j}} + \lambda_{\mathrm{W}}\frac{\partial R_j}{\partial \alpha_{\mathrm{W}j}}\right) \\
\frac{\partial R_j}{\partial \alpha_j^{**}} &= \frac{g}{\lambda_{\mathrm{O}}^2 + \lambda_{\mathrm{W}}^2}\left(-\lambda_{\mathrm{W}}\frac{\partial R_j}{\partial \alpha_{\mathrm{O}j}} + \lambda_{\mathrm{O}}\frac{\partial R_j}{\partial \alpha_{\mathrm{W}j}}\right)
\end{aligned} \tag{6.81}$$

and (6.70), (6.71) yield

$$\frac{\partial R_1}{\partial \alpha_1^{*}} = \frac{\partial R_2}{\partial \alpha_2^{*}} = \frac{R_2 - R_1}{\alpha_2^{*} - \alpha_1^{*}} = g \tag{6.82}$$

$$\frac{\partial R_1}{\partial \alpha_1^{**}} = \frac{\partial R_2}{\partial \alpha_2^{**}} = 0 \tag{6.83}$$

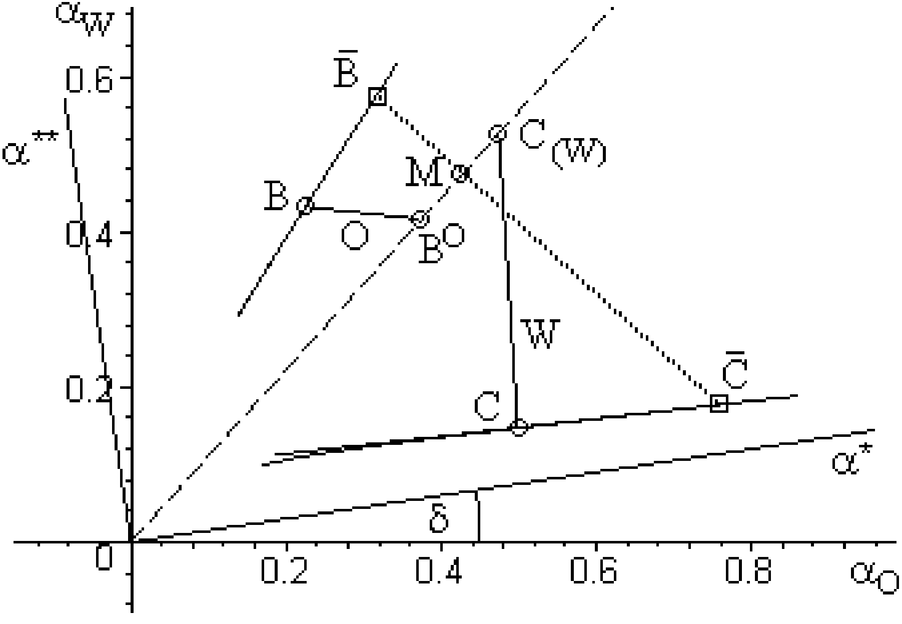
Now, λ_{O} and λ_{W} depend on the actual problem according to (6.77), (6.78). In our coarse approach, however, we decreed

$$\lambda_{\mathrm{O}} = \lambda_{\mathrm{W}} = g \quad \Longrightarrow \quad \alpha^{*} = \alpha \equiv \alpha_{\mathrm{O}} + \alpha_{\mathrm{W}} \tag{6.84}$$

Our construction satisfies (6.82) — g gives the value of the gradient of the straight line as well as of the derivatives of the two graphs at its ends — but (6.83) is surely not fulfilled.

Fig. 6.11 visualizes the situation in the $\alpha_{\mathrm{O}}, \alpha_{\mathrm{W}}$-plane. The point M characterizes the given mixture. The coarse approach represents it as a coexistence of a mixture of type B^{O} and a mixture of type $\mathrm{C}_{(\mathrm{W})}$. Each of these three mixtures has equal volumes of oil and water and hence the same value of the ratio $\alpha_{\mathrm{W}}/\alpha_{\mathrm{O}}$. The points B and C represent mixtures with the same structures but without the oil excess and the diluting excess water, respectively. The connecting line between B and B^{O} is a line of type O according to fig. 6.1 while the connecting line between C and $\mathrm{C}_{(\mathrm{W})}$ is a line of type W.

Fig. 6.11 Possibilities of coexistence



Now, if the two coexisting structures exchange all of their excess oil and water then each of them may reach a state of lower free energy. An example is given by the points $\bar{\mathrm{B}}$ and $\bar{\mathrm{C}}$. Since there is no excess, neither of the values of p_{O} or p_{W} must equal p_{e} any longer.

However, it is arduous to find the points $\bar{\mathrm{B}}$ and $\bar{\mathrm{C}}$ which minimize the rating function of a given point M. Therefore we adopt an inverse proceeding. First, we choose

$$g^2 = \lambda_{\mathrm{O}}^2 + \lambda_{\mathrm{W}}^2 \,, \qquad \lambda_{\mathrm{O}} = g\,\cos\delta \,, \qquad \lambda_{\mathrm{W}} = g\,\sin\delta \tag{6.85}$$

and obtain

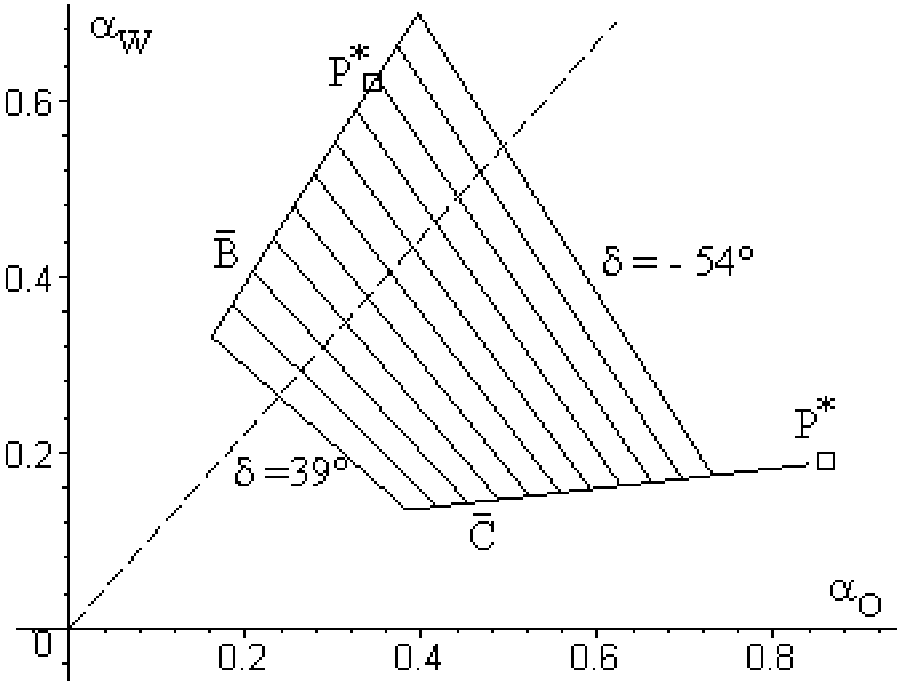
$$\alpha^* = \cos\delta\,\alpha_{\mathrm{O}} + \sin\delta\,\alpha_{\mathrm{W}} \,, \qquad \alpha^{**} = -\sin\delta\,\alpha_{\mathrm{O}} + \cos\delta\,\alpha_{\mathrm{W}} \tag{6.86}$$

Next, we select one special angle δ and hence one special orthogonal coordinate system α^*, α^{**}.

We might think of seeking all those points in the plane where the gradient vector of R_1 and R_2, respectively, is parallel to the α^* axis so that (6.83) is satisfied. These points then constitute trajectories $\mathrm{T_B}$ and $\mathrm{T_C}$ in the plane. Actually, it is not necessary to carry through this task. We see this if we consider the region N of fig. 6.1, which characterizes states without excesses. The representation of fig. 6.11 is even more realistic, showing that these regions are extremely narrow. Numerical studies reveal that the values of $\bar{y}_{\mathrm{O}k}$, $\bar{y}_{\mathrm{W}k}$, $p_{\mathrm{O}k}$, $p_{\mathrm{W}k}$, $k_{\mathrm{O}k}$, $k_{\mathrm{W}k}$ vary rapidly over the width of N. The same is true with the derivative of R in the direction of the normal to the trajectory, and hence also the derivative $\partial R/\partial\alpha^{**}$ will show a marked variation. (The pathological case where the chosen α^{**} axis is parallel to a local tangent of the trajectory may be excluded and does not cause problems.) So the aforementioned trajectory, characterized by $\partial R/\partial\alpha^{**}$=0, can be found within this region N or in its immediate neighbourhood. (When only one kind of structure was admitted, this neighbourhood indicated an excess, but now we treat two coexisting structures without excesses.)

In contrast to this, the variation of the rating function R and hence of the derivative of R in the direction of the trajectory over the width of N is negligible. So the mentioned trajectory need not really be constructed. It is sufficient to calculate R on a trajectory which has already been investigated, namely, one of the boundaries of the region N, characterized by the conditions $p_{\mathrm{O}} = p_{\mathrm{e}}$ or $p_{\mathrm{W}} = p_{\mathrm{e}}$. If the rating functions on these trajectories are plotted over the α^* axis, then (6.82) can be fulfilled by a construction like that of fig. 6.10. So the coordinates $\alpha_{\mathrm{O}1}$, $\alpha_{\mathrm{W}1}$ and $\alpha_{\mathrm{O}2}$, $\alpha_{\mathrm{W}2}$ of two special points $\bar{\mathrm{B}}$ and $\bar{\mathrm{C}}$ are gained. If we connect these points by a straight line then the minimal rating function of any point M on that line is obtained from (6.56), (6.57), (6.63). Finally, this procedure has to be performed with various angles δ in order to obtain information for a whole region in the $\alpha_{\mathrm{O}}, \alpha_{\mathrm{W}}$-plane. The straight lines corresponding to values of δ from the intervall $[-54°, 39°]$ can be seen in fig. 6.12.

Fig. 6.12 Corresponding points on B and C



We notice that it is necessary to regard also a part of the trajectory $\mathrm{T_B}$ beyond the point P*. (That point limited the region of two excesses, when only one kind of structure was admitted.) The evaluation for points with the constant ratio $\alpha_\mathrm{W}/\alpha_\mathrm{O}$ according to (6.34) (dashed line in fig. 6.12) can be found in fig. 6.13. We obtain the new graph BC, which is definitely below the old one based on the coarse approach.

If we connect the two graphs BC and C by a straight line BCC in the sense of the coarse approach, we identify states with even lower values of the rating function. This indicates that a refined treatment of this coexistence of one bi-continuous structure with two kinds of cylinders might reveal that, in this case, the minimum condition of the free energy even favours a coexistence of three different structures.

6.11.4 Coexistence with Lamellae

We come back to line LC of fig. 6.10, which was constructed on the basis of the coarse approach, and want to prove that this line also satisfies the requirements of the refined treatment. We numerate the mixtures with lamellae and cylinders by 1 and 2, respectively. If we would attribute some oil to the lamellae, then its pressure had to satisfy $p_\mathrm{O1} = p_\mathrm{e}$ which conflicts with the postulate (6.64). So only the choice $\alpha_\mathrm{O1} = 0$ is admissible, letting $\bar{y}_\mathrm{O1}$ undefined. Moreover, the rating function of lamellae is zero by definition, and hence $R_1 \equiv 0$. Thus (6.69) reduces to

$$\begin{aligned} &\psi\, R_2(\alpha_\mathrm{O2}, \alpha_\mathrm{W2}) + \lambda_\mathrm{O}\Big(\alpha_\mathrm{O} - \psi\,\alpha_\mathrm{O2}\Big) \\ &\qquad + \lambda_\mathrm{W}\Big(\alpha_\mathrm{W} - (1-\psi)\,\alpha_\mathrm{W1} - \psi\,\alpha_\mathrm{W2}\Big) \;=\; \min \end{aligned} \tag{6.87}$$

The derivatives of this expression with respect to α_O2, α_W1, α_W2, and ψ are zero, if

$$\lambda_\mathrm{O} = \frac{\partial R_2}{\partial \alpha_\mathrm{O2}} = \frac{R_2}{\alpha_\mathrm{O2}}\,, \qquad \lambda_\mathrm{W} = \frac{\partial R_2}{\partial \alpha_\mathrm{W2}} = 0 \tag{6.88}$$

hold. The second postulate is satisfied according to (6.76) (read W instead of O) by

$$\bar{y}_\mathrm{W2} = \bar{y}_\mathrm{WL} = \bar{y}_\mathrm{W1} \tag{6.89}$$

and the first one according to (6.76), (6.79), and (6.89) by $f_2 = f_\mathrm{L} = f_1$ and

$$\lambda_\mathrm{O} = \frac{\mu_\mathrm{b}}{w_1}\Big(\bar{y}_\mathrm{O2} - \bar{y}_\mathrm{OL}\Big) \tag{6.90}$$

But equal values of $\bar{y}_\mathrm{W}$ and f of the two coexisting mixtures imply equal values of p_W and k_W of the water excesses that are attributed to the lamellae and to the cylinders. Actually, a separation of these two excesses is impossible

Fig. 6.13 Coexistence, refined treatment

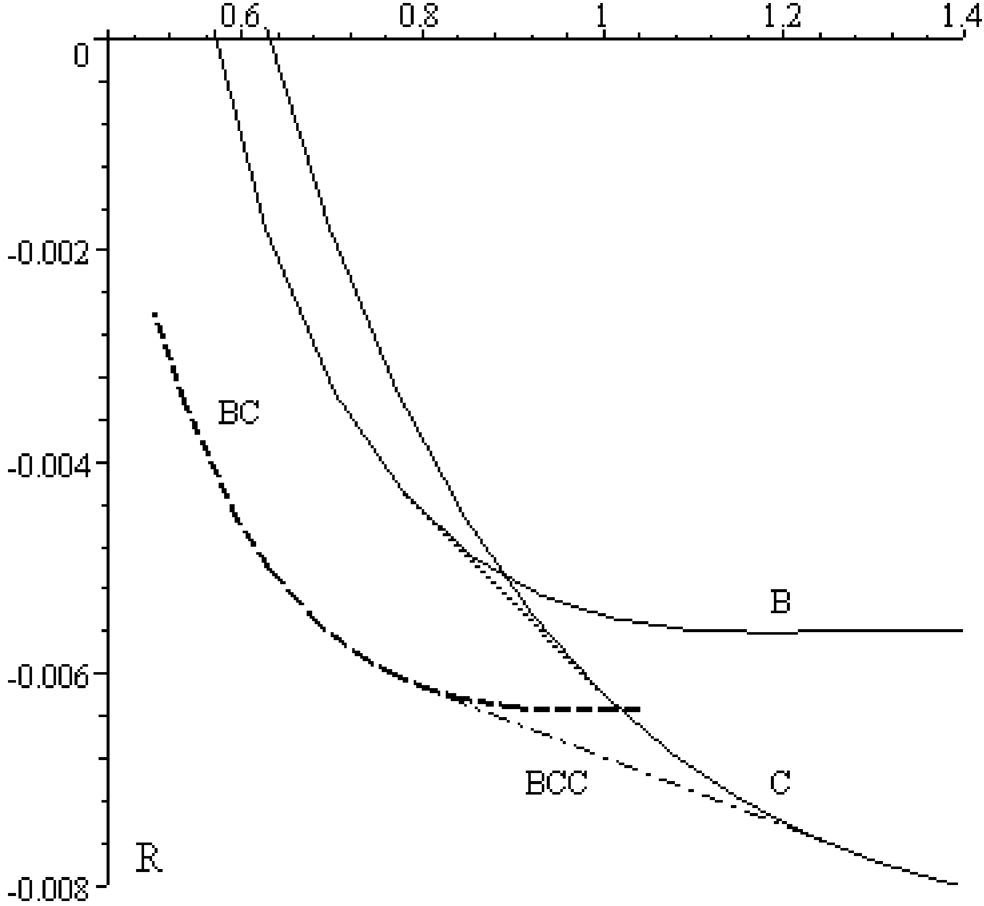


Fig. 6.14 Coexistence of cylinders and lamellae

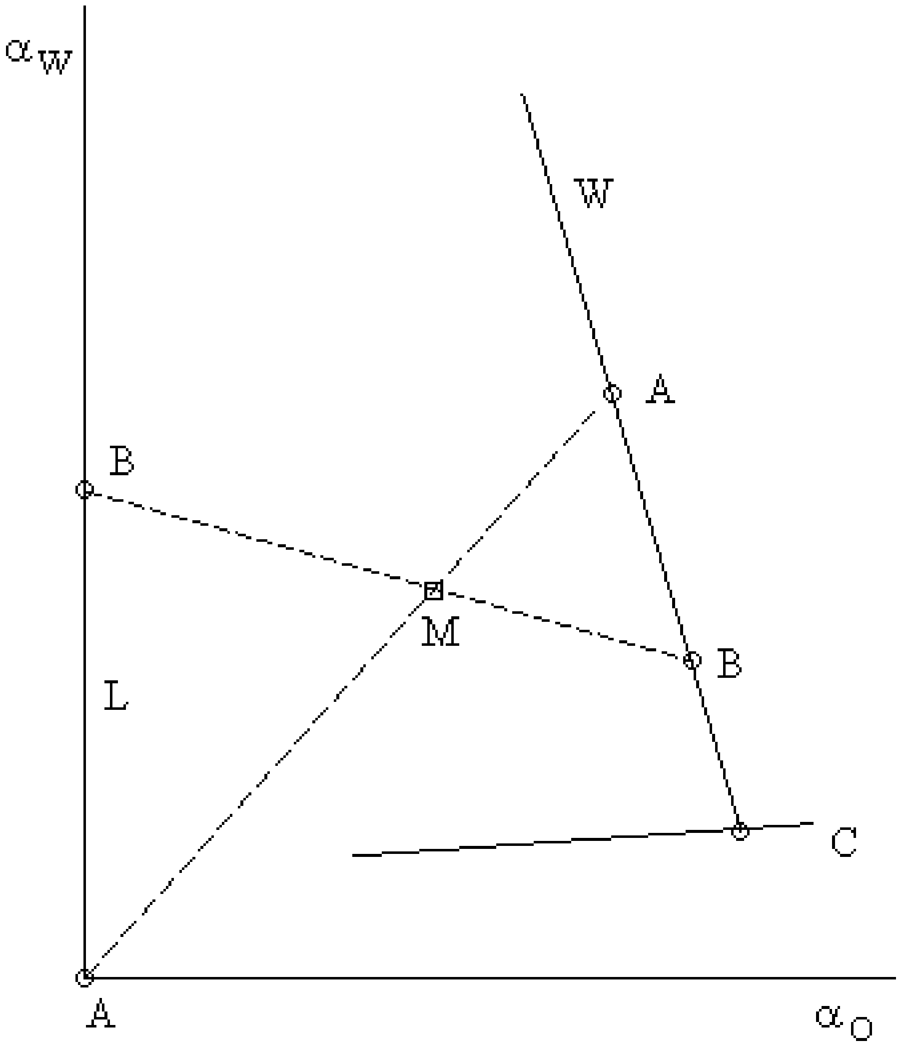
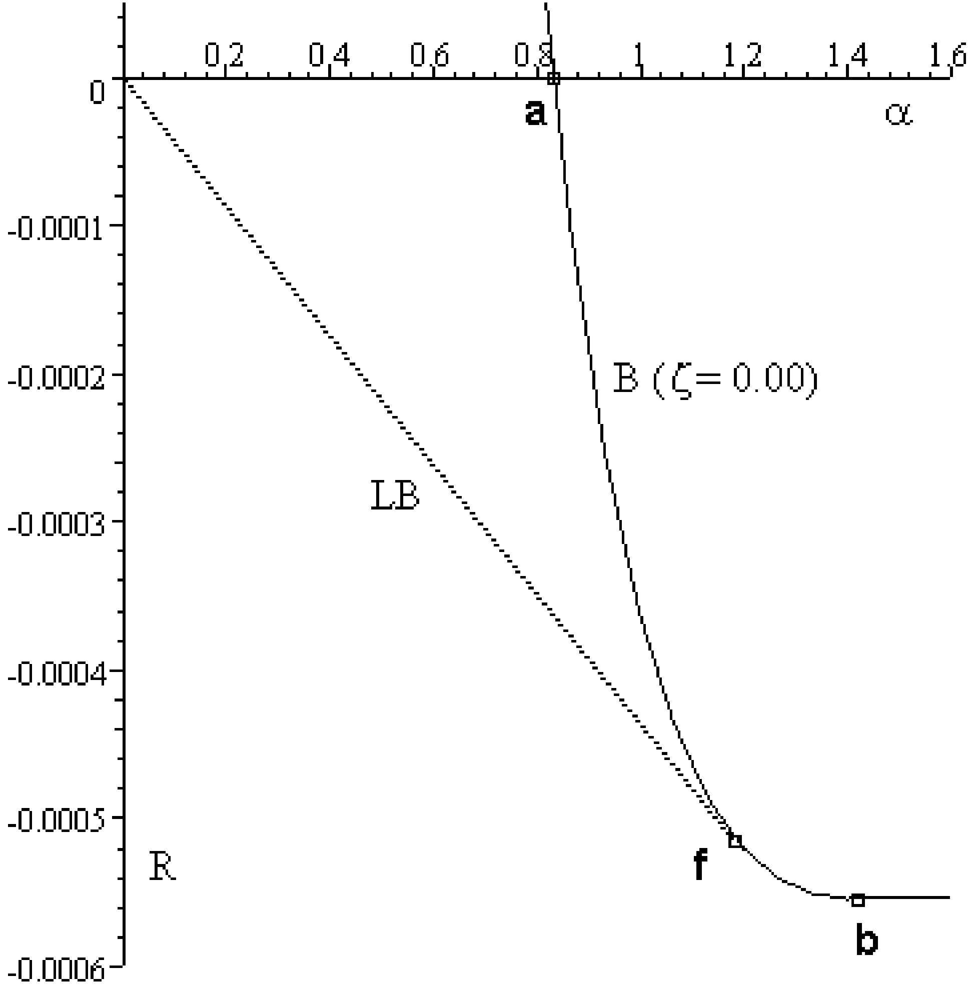


Fig. 6.15 Coexistence of bi-c. structure with lamellae



and physically meaningless. So different choices of α_{W1} and α_{W2} must yield the same result. Two possibilities A and B are singled out in the qualitative picture of fig. 6.14. As in fig. 6.1, the line W characterizes states with constant values of f_2, $\bar{y}_{O2}$, and hence λ_O. However, the values of α_{O2}, of $\psi = \alpha_O/\alpha_{O2}$ according to (6.56), and, with (6.77), (6.79), of $R_2 = \lambda_O \alpha_{O2}$ are not constant on that line. Nevertheless, the two possibilities A and B yield the same value of R at the point M, namely — note (6.63) —

$$R = \psi R_2 = \frac{\alpha_O}{\alpha_{O2}} R_2 = \lambda_O \alpha_O \tag{6.91}$$

In case A, we have chosen $\alpha_{W1} = 0$, thus attributing all of the water to the cylinders as was done in the construction of fig. 6.10. Our numerical computation was based on the assumption $\alpha_2/\alpha_{O2} = \mathit{const}\,(= 2.11)$. Therefore, (6.88) implies

$$\frac{\partial R_2}{\partial \alpha_2} = \frac{R_2}{\alpha_2} \tag{6.92}$$

and this was, indeed, the basis of the construction of fig. 6.10, which is, therefore, seen to satisfy the refined requirements of coexistence.

It is also interesting to study the coexistence of lamellae with the isometric bi-continuous structure in the case $h_0 = 0$. Since neither p_O nor p_W are equal to p_e, only the choice $\alpha_{O1} = \alpha_{W1} = 0$ is possible. The minimization of R leads to

$$R_2 = \alpha_{O2} \frac{\partial R_2}{\partial \alpha_{O2}} + \alpha_{W2} \frac{\partial R_2}{\partial \alpha_{W2}} = \alpha_2 \frac{\partial R_2}{\partial \alpha_2} \tag{6.93}$$

The result is illustrated in fig. 6.15. The point **b** represents the X point, *i.e.* the transition from one to three phases, point **a** would mark the phase boundary between the bi-continuous and the lamellar phase, but actually, a coexistence of both phases gives lower values of the free energy in a region which extends from $\alpha = 0$ to the new point **f**, characterized by the condition (6.93).

Appendices

A Tensor Notation

Symbolic vector and tensor notation is used. Bold face minuscules and majuscules $\mathbf{v}$, $\mathbf{T}$ denote vectors and second-order tensors, respectively. A second-order tensor is thought to be a linear mapping from one vector space to the same or to another vector space, both equipped with an inner product. 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 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 $\mathbf{a}\otimes\mathbf{b} : \mathbf{c}\otimes\mathbf{d} = (\mathbf{a}\cdot\mathbf{c})(\mathbf{b}\cdot\mathbf{d})$.

If vectors and tensors are referred to an orthonormal basis $\{\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3\}$, then these operations in three-dimensional space read

$$\mathbf{v} = \sum_{i=1}^{3} v_i \mathbf{e}_i \qquad \mathbf{T} = \sum_{k=1}^{3}\sum_{l=1}^{3} t_{kl}\,\mathbf{e}_k \otimes \mathbf{e}_l \qquad \mathbf{T}\cdot\mathbf{v} = \sum_{k=1}^{3}\Big(\sum_{l=1}^{3} t_{kl} v_l\Big)\mathbf{e}_k$$

$$\mathbf{T}\cdot\mathbf{W} = \sum_{k=1}^{3}\sum_{n=1}^{3}\Big(\sum_{l=1}^{3} t_{kl} w_{ln}\Big)\mathbf{e}_k \otimes \mathbf{e}_n \qquad \mathbf{T} : \mathbf{W} = \sum_{k=1}^{3}\sum_{l=1}^{3} t_{kl} w_{kl}$$

Accents are sometimes used to indicate fields which are to be differentiated. So $\nabla_T(\acute{\mathbf{a}}\cdot\mathbf{b})$ means that the differentiation ∇_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.

B Description of a Material Surface

B.1 Actual and Reference Placement

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. (This may be the placement at time $t = 0$ or some fictitious placement. An example would be the placement of a part of a sphere in a plane by means of Mercator's projection.) Vectors $d\mathbf{x}_0$ from $\mathbf{x}_0$ to the reference positions of infinitesimally neighbouring material points constitute the tangential plane T_0 at $\mathbf{x}_0$.

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 $\mathbf{x}$ (Eulerian description) or as a function of the vector $\mathbf{x}_0$ (Lagrangean description), *i.e.*,

$$\Phi = \bar{\Phi}(\mathbf{x}) = \tilde{\Phi}(\mathbf{x}_0) \tag{B.1}$$

It was Sommerfeld[14] 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

$$d\Phi = \bar{\Phi}(\mathbf{x}) \otimes \nabla_T \cdot d\mathbf{x} = \tilde{\Phi}(\mathbf{x}_0) \otimes \nabla_{T_0} \cdot d\mathbf{x}_0 \tag{B.2}$$

The operators ∇_T and ∇_{T_0} denote tangential differentiation with respect to the position vectors $\mathbf{x}$ and $\mathbf{x}_0$, respectively, and their algebraical behaviour is that of vectors in T and T_0, respectively. Component formulae of these operations will be given in chapters H and J.

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

$$d\mathbf{x} = \mathbf{x} \otimes \nabla_T \cdot d\mathbf{x} = \mathbf{x} \otimes \nabla_{T_0} \cdot d\mathbf{x}_0 \tag{B.3}$$

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

$$\mathbf{x} \otimes \nabla_T = \mathbf{1}_T \tag{B.4}$$

while the transplacement

$$\mathbf{F} = \mathbf{x} \otimes \nabla_{T_0} \tag{B.5}$$

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

$$d\mathbf{x} = \mathbf{F} \cdot d\mathbf{x}_0 \tag{B.6}$$

We note

$$\mathbf{F} \cdot \mathbf{F}^{-1} = \mathbf{1}_T\,, \qquad \mathbf{F}^{-1} \cdot \mathbf{F} = \mathbf{1}_{T_0}\ . \tag{B.7}$$

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

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

Introducing (B.6) into (B.2) we obtain

$$\Phi \otimes \nabla_T \cdot d\mathbf{x} = \Phi \otimes \nabla_T \cdot \mathbf{F} \cdot d\mathbf{x}_0 = \Phi \otimes \nabla_{T_0} \cdot d\mathbf{x}_0 \tag{B.9}$$

for any $d\mathbf{x}_0$ and hence the relation

$$\Phi \otimes \nabla_T \cdot \mathbf{F} = \Phi \otimes \nabla_{T_0} \tag{B.10}$$

or with (B.7)

$$\Phi \otimes \nabla_{T_0} \cdot \mathbf{F}^{-1} = \Phi \otimes \nabla_T \cdot \mathbf{1}_T = \Phi \otimes \nabla_T \tag{B.11}$$

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

$$\begin{aligned} d\mathbf{n} &= \mathbf{n} \otimes \nabla_T \cdot d\mathbf{x} = \mathbf{n} \otimes \nabla_{T_0} \cdot d\mathbf{x}_0 \\ &= -\mathbf{C} \cdot d\mathbf{x} = -\mathbf{C} \cdot \mathbf{F} \cdot d\mathbf{x}_0 \end{aligned} \tag{B.12}$$

with the definition of the curvature tensor $\mathbf{C}$ by

$$\mathbf{C} = -\mathbf{n} \otimes \nabla_T \tag{B.13}$$

and a comparison shows

$$\mathbf{C} \cdot \mathbf{F} = -\mathbf{n} \otimes \nabla_{T_0} \tag{B.14}$$

B.2 Motion of the Surface

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.*,

$$\mathbf{v} = \dot{\mathbf{x}} \tag{B.15}$$

and the rate of the transplacement $\mathbf{F}$ is obtained by differentiation of (B.5)

$$\dot{\mathbf{F}} = \dot{\mathbf{x}} \otimes \nabla_{T_0} = \mathbf{v} \otimes \nabla_{T_0} \tag{B.16}$$

(Note that the material time derivative $\dot{()}$, 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.)
We also need the rate of deformation tensor — note (B.11) —

$$\mathbf{L} \equiv \dot{\mathbf{F}} \cdot \mathbf{F}^{-1} = \mathbf{v} \otimes \nabla_{T_0} \cdot \mathbf{F}^{-1} = \mathbf{v} \otimes \nabla_T \tag{B.17}$$

which is seen to be the tangential velocity gradient on the actual surface.

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

$$0 = \mathbf{n} \cdot d\mathbf{x} = \mathbf{n} \cdot \mathbf{F} \cdot d\mathbf{x}_0 \tag{B.18}$$

for any $d\mathbf{x}_0$ and hence

$$0 = \mathbf{n} \cdot \mathbf{F} \tag{B.19}$$

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

$$\dot{\mathbf{n}} \cdot \mathbf{F} = -\mathbf{n} \cdot \dot{\mathbf{F}} \tag{B.20}$$

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

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

we infer from (B.20)

$$\dot{\mathbf{n}} \cdot \mathbf{F} \cdot \mathbf{F}^{-1} = \dot{\mathbf{n}} \cdot \mathbf{1}_T = \dot{\mathbf{n}} = -\mathbf{n} \cdot \dot{\mathbf{F}} \cdot \mathbf{F}^{-1} = -\mathbf{n} \cdot \mathbf{L} \tag{B.22}$$

and hence with (B.17)

$$\dot{\mathbf{n}} = -\mathbf{n} \cdot \big(\mathbf{v} \otimes \nabla_T\big) \tag{B.23}$$

Differentiating (B.14) we get information on the rate of the curvature tensor

$$\dot{\mathbf{C}} \cdot \mathbf{F} + \mathbf{C} \cdot \dot{\mathbf{F}} = -\dot{\mathbf{n}} \otimes \nabla_{T_0} \tag{B.24}$$

From this we infer

$$\dot{\mathbf{C}} \cdot \mathbf{F} \cdot \mathbf{F}^{-1} + \mathbf{C} \cdot \dot{\mathbf{F}} \cdot \mathbf{F}^{-1} = -\dot{\mathbf{n}} \otimes \nabla_{T_0} \cdot \mathbf{F}^{-1} \tag{B.25}$$

or — with (B.7) and (B.11) —

$$\dot{\mathbf{C}} \cdot \mathbf{1}_T + \mathbf{C} \cdot \mathbf{L} = -\dot{\mathbf{n}} \otimes \nabla_T \tag{B.26}$$

The rate of a material line element is obtained by differentiating (B.6)

$$\dot{\overline{d\mathbf{x}}} = \dot{\mathbf{F}} \cdot d\mathbf{x}_0 = \mathbf{L} \cdot d\mathbf{x} \tag{B.27}$$

Two orthogonal material line elements $d\mathbf{x}_1 = ds_1\mathbf{e}_1$ and $d\mathbf{x}_2 = ds_2\mathbf{e}_2$ determine a material surface element according to

$$d\mathbf{a} = d\mathbf{x}_1 \times d\mathbf{x}_2 = ds_1 ds_2\, \mathbf{e}_1 \times \mathbf{e}_2 = dA\, \mathbf{n} \tag{B.28}$$

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

$$\begin{aligned}
&\mathbf{n} \cdot \dot{\overline{d\mathbf{a}}} = \mathbf{n} \cdot \Big(\dot{\overline{dA}}\, \mathbf{n} + dA\, \dot{\mathbf{n}}\Big) = \dot{\overline{dA}} = \\
&\mathbf{n} \cdot \Big(\dot{\overline{d\mathbf{x}_1}} \times d\mathbf{x}_2 + d\mathbf{x}_1 \times \dot{\overline{d\mathbf{x}_2}}\Big) = \mathbf{n} \cdot \Big((\mathbf{L} \cdot d\mathbf{x}_1) \times d\mathbf{x}_2 + d\mathbf{x}_1 \times (\mathbf{L} \cdot d\mathbf{x}_2)\Big) = \\
&ds_1 ds_2 \Big((\mathbf{e}_2 \times \mathbf{n}) \cdot \mathbf{L} \cdot \mathbf{e}_1 + (\mathbf{n} \times \mathbf{e}_1) \cdot \mathbf{L} \cdot \mathbf{e}_2\Big) = \\
&dA\big(\mathbf{e}_1 \cdot \mathbf{L} \cdot \mathbf{e}_1 + \mathbf{e}_2 \cdot \mathbf{L} \cdot \mathbf{e}_2\big) = dA\big(\mathbf{e}_1 \otimes \mathbf{e}_1 + \mathbf{e}_2 \otimes \mathbf{e}_2\big) : \mathbf{L} = dA\, \mathbf{1}_T : \mathbf{L}
\end{aligned} \tag{B.29}$$

and hence

$$\frac{\dot{\overline{dA}}}{dA} = \mathbf{1}_T : \mathbf{L} = \mathbf{1}_T : \mathbf{v} \otimes \nabla_T = \mathbf{v} \cdot \nabla_T = \nabla_T \cdot \mathbf{v} \tag{B.30}$$

B.3 The Vicinity of the Surface

The position vector of a point in the vicinity of a given surface may be written

$$\mathbf{x}_z = \mathbf{x} + z\,\mathbf{n}(\mathbf{x}) \tag{B.31}$$

Here $\mathbf{x}$ is the position vector of a point on the surface, where the unit normal vector is $\mathbf{n}$, and $|z|$ is the shortest distance of the point under discussion from the surface, *i.e.* the distance measured in the direction of $\mathbf{n}$. We may extend $\mathbf{n}$ into the vicinity of the surface by defining the following three-dimensional vector field

$$\mathbf{n}(\mathbf{x}_z) = \mathbf{n}(\mathbf{x}) \tag{B.32}$$

C Properties of the Curvature Tensor

C.1 Symmetry of the Curvature Tensor

We may interpret $z(\mathbf{x}_z)$ as a three-dimensional scalar field in the vicinity of the surface and note that its spatial gradient is nothing but the vector field $\mathbf{n}(\mathbf{x}_z)$, defined in (B.32). The vector $\mathbf{n}$ does not change when z varies while $\mathbf{x}$ is fixed. Hence we have

$$\mathbf{n} = \nabla z \qquad \text{and} \qquad \frac{\partial \mathbf{n}}{\partial z} = 0 \tag{C.1}$$

On the surface, we have

$$\nabla = \nabla_T + \mathbf{n}\frac{\partial}{\partial z} \tag{C.2}$$

and therefore

$$\mathbf{C} = -\mathbf{n} \otimes \nabla_T = -\mathbf{n} \otimes \nabla + \frac{\partial \mathbf{n}}{\partial z} \otimes \mathbf{n} = -\nabla \otimes \nabla z \tag{C.3}$$

This reveals the symmetry of the curvature tensor $\mathbf{C}$.

C.2 Invariants of the Curvature Tensor

The tensor $\mathbf{C}$, connnecting $d\mathbf{x} \in T$ with $d\mathbf{n} \in T$ according to (B.12) — 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, it possesses a spectral representation

$$\mathbf{C} = c_1\,\mathbf{e}_1 \otimes \mathbf{e}_1 + c_2\,\mathbf{e}_2 \otimes \mathbf{e}_2 \tag{C.4}$$

with the principal curvatures c_1, c_2 and the principal axes given by the orthonormal vectors $\mathbf{e}_1$, $\mathbf{e}_2 \in T$. The tangential unity tensor may also be represented by means of these vectors in the form

$$\mathbf{1}_T = \mathbf{e}_1 \otimes \mathbf{e}_1 + \mathbf{e}_2 \otimes \mathbf{e}_2 \tag{C.5}$$

The classical invariants of the curvature tensor are the trace and the (two-dimensional) determinant

$$\operatorname{tr}\mathbf{C} = \mathbf{1}_T : \mathbf{C} = c_1 + c_2 \tag{C.6}$$

$$\det\mathbf{C} = c_1 c_2 \tag{C.7}$$

The two-dimensional tensor $\mathbf{C}$ satisfies the equation of Cayley-Hamilton

$$\mathbf{C}^2 - \operatorname{tr}\mathbf{C}\,\mathbf{C} + \det\mathbf{C}\,\mathbf{1}_T = 0 \tag{C.8}$$

which is easily verified if we write down the components of this tensor equation with respect to the principal axes

$$\begin{aligned} c_1^2 - (c_1 + c_2)\,c_1 + c_1 c_2 = 0\,, \\ c_2^2 - (c_1 + c_2)\,c_2 + c_1 c_2 = 0 \end{aligned} \tag{C.9}$$

The trace of (C.8), *i.e.* the sum of the last two equations yields

$$\mathbf{C} : \mathbf{C} - \big(\operatorname{tr}\mathbf{C}\big)^2 + 2\det\mathbf{C} = 0 \tag{C.10}$$

or

$$c_1^2 + c_2^2 - (c_1 + c_2)^2 + 2c_1 c_2 = 0 \tag{C.11}$$

Half of the trace and the determinant are also called mean curvature H and Gaussian curvature K, respectively.

$$H = \tfrac{1}{2}\operatorname{tr}\mathbf{C} = \tfrac{1}{2}(c_1 + c_2) \qquad K = \det\mathbf{C} = 2H^2 - \tfrac{1}{2}\mathbf{C} : \mathbf{C} = c_1 c_2 \tag{C.12}$$

Another useful invariant is

$$D^2 = H^2 - K = \left(\frac{c_1 - c_2}{2}\right)^2 \tag{C.13}$$

while $D = (c_1 - c_2)/2$ is not invariant since the numbering of the principal curvatures is arbitrary.

The rate of the curvature tensor can be derived from equation (C.4), giving

$$\dot{\mathbf{C}} = \dot{c}_1\,\mathbf{e}_1\otimes\mathbf{e}_1 + \dot{c}_2\,\mathbf{e}_2\otimes\mathbf{e}_2 + c_1\,\big(\dot{\mathbf{e}}_1\otimes\mathbf{e}_1 + \mathbf{e}_1\otimes\dot{\mathbf{e}}_1\big) + c_2\,\big(\dot{\mathbf{e}}_2\otimes\mathbf{e}_2 + \mathbf{e}_2\otimes\dot{\mathbf{e}}_2\big) \tag{C.14}$$

which allows to conclude

$$\mathbf{e}_1\cdot\dot{\mathbf{C}}\cdot\mathbf{e}_1 = \dot{c}_1\,, \qquad \mathbf{e}_2\cdot\dot{\mathbf{C}}\cdot\mathbf{e}_2 = \dot{c}_2 \tag{C.15}$$

From this we obtain the rate of the trace

$$\overset{\cdot}{\overline{\operatorname{tr}\mathbf{C}}} = \dot{c}_1 + \dot{c}_2 = \big(\mathbf{e}_1\otimes\mathbf{e}_1 + \mathbf{e}_2\otimes\mathbf{e}_2\big) : \dot{\mathbf{C}} = \mathbf{1}_T : \dot{\mathbf{C}} \tag{C.16}$$

The rate of the determinant is given by

$$\overset{\cdot}{\overline{\det\mathbf{C}}} = \frac{1}{2}\overset{\cdot}{\overline{\Big(\big(\operatorname{tr}\mathbf{C}\big)^2 - \mathbf{C} : \mathbf{C}\Big)}} = -\big(\mathbf{C} - \operatorname{tr}\mathbf{C}\,\mathbf{1}_T\big) : \dot{\mathbf{C}} \tag{C.17}$$

or, explicitly,

$$\overset{\cdot}{\overline{c_1 c_2}} = c_2\dot{c}_1 + c_1\dot{c}_2 \tag{C.18}$$

C.3 Functions of the Curvature

Let us consider a scalar field ϕ on the surface which is an isotropic function of the curvature tensor $\mathbf{C}$, *i.e.* it depends on the principal values c_1, c_2 of $\mathbf{C}$ only. We use the notation $\tilde{\phi}(\mathbf{C}) = \check{\phi}(c_1, c_2)$.
The rate of ϕ can be written

$$\begin{aligned}
\dot{\phi} = \frac{\partial\tilde{\phi}}{\partial\mathbf{C}} : \dot{\mathbf{C}} &= \frac{\partial\check{\phi}}{\partial c_1}\dot{c_1} + \frac{\partial\check{\phi}}{\partial c_2}\dot{c_2} = \frac{\partial\check{\phi}}{\partial c_1}\,\mathbf{e}_1 \cdot \dot{\mathbf{C}} \cdot \mathbf{e}_1 + \frac{\partial\check{\phi}}{\partial c_2}\,\mathbf{e}_2 \cdot \dot{\mathbf{C}} \cdot \mathbf{e}_2 \\
&= \left(\frac{\partial\check{\phi}}{\partial c_1}\,\mathbf{e}_1 \otimes \mathbf{e}_1 + \frac{\partial\check{\phi}}{\partial c_2}\,\mathbf{e}_2 \otimes \mathbf{e}_2\right) : \dot{\mathbf{C}} \qquad \text{(C.19)}
\end{aligned}$$

and a comparison shows

$$\frac{\partial\tilde{\phi}}{\partial\mathbf{C}} = \frac{\partial\check{\phi}}{\partial c_1}\,\mathbf{e}_1 \otimes \mathbf{e}_1 + \frac{\partial\check{\phi}}{\partial c_2}\,\mathbf{e}_2 \otimes \mathbf{e}_2 \qquad \text{(C.20)}$$

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

$$\mathbf{D} \equiv -\frac{\partial\phi}{\partial\mathbf{C}} \qquad \text{(C.21)}$$

is a mapping of T into itself. It has the same principal axes as $\mathbf{C}$ and hence commutes with $\mathbf{C}$, *i.e.*, $\mathbf{D} \cdot \mathbf{C} = \mathbf{C} \cdot \mathbf{D}$ is a symmetric tensor. So — with equations (B.26) and (B.17)—

$$\begin{aligned}
\frac{\partial\phi}{\partial\mathbf{C}} : \dot{\mathbf{C}} &= -\mathbf{D} : \dot{\mathbf{C}} = -\left(\mathbf{D} \cdot \mathbf{1}_T\right) : \dot{\mathbf{C}} = -\mathbf{D} : \left(\dot{\mathbf{C}} \cdot \mathbf{1}_T\right) \\
&= -\mathbf{D} : \left(-\mathbf{C} \cdot \mathbf{L} - \dot{\mathbf{n}} \otimes \nabla_T\right) \\
&= \left(\mathbf{C} \cdot \mathbf{D}\right) : \left(\mathbf{v} \otimes \nabla_T\right) + \mathbf{D} : \left(\dot{\mathbf{n}} \otimes \nabla_T\right) \qquad \text{(C.22)}
\end{aligned}$$

C.4 Some Differential Identities

We want to calculate the tangential derivatives of some tensors which are mappings of T into itself. Since these tensors act on different spaces T at neighbouring points, it is necessary, to consider them as (non-invertible) mappings of the three-dimensional observer space V into itself.

First we obtain the tangential divergence of the tangential unit tensor by

$$\acute{\mathbf{1}}_T \cdot \nabla_T = (\mathbf{1} - \mathbf{n} \otimes \mathbf{n}) \cdot \nabla_T = -\mathbf{n}\,(\acute{\mathbf{n}} \cdot \nabla_T) = -\mathbf{n}\,\mathrm{tr}\,(\acute{\mathbf{n}} \otimes \nabla_T) = \mathrm{tr}\,\mathbf{C}\;\mathbf{n} \qquad \text{(C.23)}$$

We infer from (C.2)

$$\nabla_T = \mathbf{1}_T \cdot \nabla \qquad \text{(C.24)}$$

(note that here $\mathbf{1}_T$ must not be differentiated !). The gradient of $\mathbf{C}$ along the surface is therefore given by

$$\mathbf{C} \otimes \nabla_T = -\nabla \otimes \nabla \acute{z} \otimes \mathbf{1}_T \cdot \nabla = -\nabla \otimes \nabla \otimes \mathbf{1}_T \cdot \nabla \acute{z} \tag{C.25}$$

and hence we get the important result that the third-order tensor

$$\mathbf{1}_T \cdot \acute{\mathbf{C}} \cdot \mathbf{1}_T \otimes \nabla_T = -\mathbf{1}_T \cdot \nabla \otimes \mathbf{1}_T \cdot \nabla \otimes \mathbf{1}_T \cdot \nabla \acute{z} \tag{C.26}$$

is obviously totally symmetric.

Another useful identity is obtained as follows. First we analyze

$$\frac{\partial}{\partial z} \nabla \otimes \nabla z = \frac{\partial}{\partial z} \nabla \otimes \mathbf{n} = (\mathbf{n} \cdot \nabla)\, \nabla \otimes \acute{\mathbf{n}} = \nabla \otimes (\mathbf{n} \cdot \nabla)\, \acute{\mathbf{n}}$$

$$= \quad \nabla \otimes \overline{(\mathbf{n} \cdot \acute{\nabla})\, \mathbf{n}} - (\nabla \otimes \acute{\mathbf{n}}) \cdot (\nabla \otimes \acute{\mathbf{n}}) = \nabla \otimes \frac{\partial \mathbf{n}}{\partial z} - \mathbf{C} \cdot \mathbf{C} = -\,\mathbf{C}^2 \tag{C.27}$$

the trace of which yields

$$\frac{\partial}{\partial z} \nabla \cdot \nabla z = -\,\mathbf{C} : \mathbf{C} \tag{C.28}$$

Now we are able to prove — note (C.2), (C.3), (C.10), (C.23) —

$$\big(\mathbf{C} - \operatorname{tr} \mathbf{C}\, \mathbf{1}_T\big) \cdot \nabla_T = \mathbf{C} \cdot \nabla_T - \big(\operatorname{tr} \mathbf{C}\big)\, \nabla_T - \operatorname{tr} \mathbf{C}\, \big(\acute{\mathbf{1}}_T \cdot \nabla_T\big)$$

$$= -(\nabla \otimes \nabla z) \cdot \left(\nabla - \mathbf{n} \frac{\partial}{\partial z}\right) + (\nabla \cdot \nabla z) \left(\nabla - \mathbf{n} \frac{\partial}{\partial z}\right) - \big(\operatorname{tr} \mathbf{C}\big)^2 \mathbf{n}$$

$$= \underline{-\nabla(\nabla \cdot \nabla z) + (\nabla \cdot \nabla z)\nabla + \frac{\partial}{\partial z}\big(\nabla \otimes \nabla z\big) \cdot \mathbf{n}} - \frac{\partial}{\partial z}\big(\nabla \cdot \nabla z\big)\mathbf{n} - \big(\operatorname{tr} \mathbf{C}\big)^2 \mathbf{n}$$

$$= \Big(\mathbf{C} : \mathbf{C} - \big(\operatorname{tr} \mathbf{C}\big)^2\Big)\mathbf{n} = -2 \ \det \mathbf{C}\ \mathbf{n} \tag{C.29}$$

The first two of the underlined terms cancel each other while the third vanishes due to (C.27).

D Description of a Thick Layer

If the region on both sides of a surface, characterized by $-h/2 \le z \le h/2$ is filled with matter, then we speak of a layer with thickness h and call the surface under discussion the middle surface of the layer.

For convenience we choose a plane reference placement of the middle surface and denote its unit normal by $\mathbf{n}_0$. A point with the actual position vector — *cf.* (B.31) —

$$\mathbf{x}_z = \mathbf{x} + z\, \mathbf{n}(\mathbf{x}) \tag{D.1}$$

is then given the reference placement

$$\mathbf{x}_{z\,0} = \mathbf{x}_0 + z\,\mathbf{n}_0 \tag{D.2}$$

A material line element connecting points with equal values of z satisfies — note the fact that $\mathbf{n}_0$ does not depend on $\mathbf{x}_0$ and (B.4), (B.6), (B.12) —

$$d\mathbf{x}_{z\,0} = d\mathbf{x}_0 \tag{D.3}$$

$$\begin{aligned} d\mathbf{x}_z &= d\mathbf{x} + z\,d\mathbf{n} = \big(\mathbf{1}_T - z\,\mathbf{C}\big)\cdot d\mathbf{x} = \big(\mathbf{1}_T - z\,\mathbf{C}\big)\cdot \mathbf{F}\cdot d\mathbf{x}_0 \\ &= \big(\mathbf{1}_T - z\,\mathbf{C}\big)\cdot \mathbf{F}\cdot d\mathbf{x}_{z\,0} \equiv \mathbf{F}_z\cdot d\mathbf{x}_{z\,0} \end{aligned} \tag{D.4}$$

Thus we obtain the relation between the transplacement $\mathbf{F}$ of line elements of the tangential plane of the middle surface and the transplacement of line elements in a parallel plane.

$$\mathbf{F}_z = \big(\mathbf{1}_T - z\,\mathbf{C}\big)\cdot \mathbf{F} \tag{D.5}$$

Now let $d\mathbf{x}_1 = ds_1\mathbf{e}_1$ and $d\mathbf{x}_2 = ds_2\mathbf{e}_2$ be two orthogonal line elements of the tangential plane of the middle surface, which span an area $dA = ds_1 ds_2$. If $\mathbf{e}_1$ and $\mathbf{e}_2$ are chosen as principal directions of the tensor $\mathbf{C}$, then the corresponding line elements in a parallel plane become

$$\big(\mathbf{1}_T - z\,\mathbf{C}\big)\cdot d\mathbf{x}_1 = ds_1(1-zc_1)\,\mathbf{e}_1\,, \quad \big(\mathbf{1}_T - z\,\mathbf{C}\big)\cdot d\mathbf{x}_2 = ds_2(1-zc_2)\,\mathbf{e}_2 \tag{D.6}$$

and they span the area

$$\begin{aligned} dA_z &= (1-zc_1)(1-zc_2)\,ds_1 ds_2 = (1-zc_1)(1-zc_2)\,dA \\ &= \big(1-(c_1+c_2)\,z + c_1c_2\,z^2\big)dA = \big(1 - \operatorname{tr}\mathbf{C}\,z + \det\mathbf{C}\,z^2\big)dA \end{aligned} \tag{D.7}$$

On the boundary surfaces we get

$$dA_+ = dA_z(z=h/2) = \left(1 - \operatorname{tr}\mathbf{C}\frac{h}{2} + \det\mathbf{C}\frac{h^2}{4}\right)dA \tag{D.8}$$

$$dA_- = dA_z(z=-h/2) = \left(1 + \operatorname{tr}\mathbf{C}\frac{h}{2} + \det\mathbf{C}\frac{h^2}{4}\right)dA \tag{D.9}$$

The volumes between the middle surface and each of the boundary surfaces amount to

$$dV_\pm = \pm\int_{z=0}^{\pm h/2} dA_z(z)\,dz = v_\pm dA \quad \text{with} \quad v_\pm = \frac{h}{2} \mp \operatorname{tr}\mathbf{C}\frac{h^2}{8} + \det\mathbf{C}\frac{h^3}{24} \tag{D.10}$$

and hence the volume between the two boundary surfaces to

$$dV = dV_+ + dV_- = \left(h + \det\mathbf{C}\frac{h^3}{12}\right)\,dA \tag{D.11}$$

E The Divergence Theorem of a Curved Surface

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

$$\int_A \mathbf{n} \cdot (\nabla \times \mathbf{w})\, dA = \oint d\mathbf{x} \cdot \mathbf{w} \tag{E.1}$$

It allows us to transform an integral over a curved surface into a line integral along the boundary curves of the surface. Noting equation (C.2) and the identity $\mathbf{n} \times \mathbf{n} = 0$ we find

$$\mathbf{n} \cdot (\nabla \times \mathbf{w}) = (\mathbf{n} \times \nabla) \cdot \acute{\mathbf{w}} = (\mathbf{n} \times \nabla_T) \cdot \acute{\mathbf{w}} = \mathbf{n} \cdot (\nabla_T \times \mathbf{w}) \tag{E.2}$$

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

$$\mathbf{w} = \mathbf{n} \times \mathbf{z}_T \tag{E.3}$$

With the identity

$$\nabla_T \times (\acute{\mathbf{n}} \times \acute{\mathbf{z}}_T) = (\nabla_T \cdot \acute{\mathbf{z}}_T)\, \acute{\mathbf{n}} - (\nabla_T \cdot \acute{\mathbf{n}})\, \acute{\mathbf{z}}_T \tag{E.4}$$

and the product rule, we find

$$\begin{aligned}
&\mathbf{n} \cdot (\nabla_T \times \mathbf{w}) = \mathbf{n} \cdot \big(\nabla_T \times (\mathbf{n} \times \mathbf{z}_T)\big) \\
&= \mathbf{n} \cdot \Big((\nabla_T \cdot \acute{\mathbf{z}}_T)\, \mathbf{n} + \mathbf{z}_T \cdot (\nabla_T \otimes \acute{\mathbf{n}}) - (\nabla_T \cdot \acute{\mathbf{n}})\, \mathbf{z}_T - \mathbf{n} \cdot (\nabla_T \otimes \acute{\mathbf{z}}_T)\Big) \\
&= \nabla_T \cdot \mathbf{z}_T
\end{aligned} \tag{E.5}$$

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

$$d\mathbf{x} = \mathbf{g}\, ds \quad \text{and} \quad \mathbf{e} = \mathbf{g} \times \mathbf{n} \tag{E.6}$$

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

$$\int_A \nabla_T \cdot \mathbf{z}_T\, dA = \oint \mathbf{e} \cdot \mathbf{z}_T\, ds \tag{E.7}$$

It has the same appearance as the corresponding theorem of the plane. This is caused by the fact, that $\mathbf{z}_T$ is a tangential vector field. If the vector field had also a component in the direction of $\mathbf{n}$, an additional term would be present.

F The Euler-Lagrangean Differential Equations of Our Variational Problem

That part of the extended energy which is related with the geometry of a single cell of a structure can be written — *cf.* (2.38) —

$$\Phi = \int_{A_{\mathrm{C}k}} \phi \; dA - \big(p_{\mathrm{O}k} - p_{\mathrm{e}}\big) V_{\mathrm{OC}k} - \big(p_{\mathrm{W}k} - p_{\mathrm{e}}\big) V_{\mathrm{WC}k} \tag{F.1}$$

with the abbreviation

$$\phi = w(c_1, c_2, \mu) + p_{\mathrm{e}} \left(h + \det \mathbf{C} \, \frac{h^3}{12} \right) - f \, \mu \tag{F.2}$$

Now let the amphiphilic film be deformed. During a time increment δt, the material points of the middle surface undergo displacements $\delta \mathbf{u} = \mathbf{v} \, \delta t$ and the area of a surface element dA increases — note (B.30) — by an increment $\delta(dA) = dA \, \mathbf{1}_T : (\delta \mathbf{u} \otimes \nabla_T)$. We use the abbreviation

$$\mathbf{D} = - \frac{\partial \phi}{\partial \mathbf{C}} \tag{F.3}$$

of (C.21) and further introduce

$$\mathbf{S} = \phi \, \mathbf{1}_T + \mathbf{C} \cdot \mathbf{D} \tag{F.4}$$

With the help of (C.22), we are able to determine the variation of the integral

$$\begin{aligned} \delta \int_{A_{\mathrm{C}k}} \phi \; dA &= \int_{A} \left(\frac{\partial \phi}{\partial \mathbf{C}} : \delta \mathbf{C} + \phi \, \frac{\delta(dA)}{dA} \right) dA \\ &= \int_{A_{\mathrm{C}k}} \Big((\mathbf{C} \cdot \mathbf{D}) : (\delta \mathbf{u} \otimes \nabla_T) + \mathbf{D} : (\delta \mathbf{n} \otimes \nabla_T) + \phi \mathbf{1}_T : (\delta \mathbf{u} \otimes \nabla_T) \Big) \, dA \\ &= \int_{A_{\mathrm{C}k}} \Big(\mathbf{S} : (\delta \mathbf{u} \otimes \nabla_T) + \mathbf{D} : (\delta \mathbf{n} \otimes \nabla_T) \Big) \, dA \end{aligned} \tag{F.5}$$

Application of the product rule gives

$$\begin{aligned} \delta \int_{A_{\mathrm{C}k}} \phi \; dA &= \int_{A_{\mathrm{C}k}} \Big(\mathbf{S} : (\delta \mathbf{u} \otimes \nabla_T) + \mathbf{D} : (\delta \mathbf{n} \otimes \nabla_T) \Big) \, dA \\ = \quad & \int_{A_{\mathrm{C}k}} \big(\delta \acute{\mathbf{u}} \cdot \mathbf{S} + \delta \acute{\mathbf{n}} \cdot \mathbf{D} \big) \cdot \nabla_T \, dA \\ = \quad & \int_{A_{\mathrm{C}k}} \overset{\prime}{\overline{\big(\delta \mathbf{u} \cdot \mathbf{S} + \delta \mathbf{n} \cdot \mathbf{D} \big)}} \cdot \nabla_T \, dA - \int_{A_{\mathrm{C}k}} \Big(\delta \mathbf{u} \cdot \acute{\mathbf{S}} \cdot \nabla_T + \delta \mathbf{n} \cdot \acute{\mathbf{D}} \cdot \nabla_T \Big) \, dA \end{aligned} \tag{F.6}$$

Now, the fields of the increments $\delta\mathbf{u}$ and $\delta\mathbf{n}$ are not independent but satisfy the equation — note (B.23) —

$$\mathbf{0} = \delta\mathbf{n} + \mathbf{n} \cdot (\delta\mathbf{u} \otimes \nabla_T) \tag{F.7}$$

We multiply this side condition with a Lagrangean parameter $\mathbf{q}_T$, which is a tangential vector field,

$$0 = \delta\mathbf{n} \cdot \mathbf{q}_T + \mathbf{n} \cdot \delta\acute{\mathbf{u}} \otimes \nabla_T \cdot \mathbf{q}_T = \delta\mathbf{n} \cdot \mathbf{q}_T + \delta\acute{\mathbf{u}} \cdot \mathbf{n} \otimes \mathbf{q}_T \cdot \nabla_T \tag{F.8}$$

and obtain, with integration by parts,

$$\begin{aligned} 0 &= \int_{A_{\mathrm{C}k}} \delta\mathbf{n} \cdot \mathbf{q}_T \, dA + \int_{A_{\mathrm{C}k}} \delta\acute{\mathbf{u}} \cdot \mathbf{n} \otimes \mathbf{q}_T \cdot \nabla_T \, dA \\ &= \int_{A_{\mathrm{C}k}} \delta\mathbf{n} \cdot \mathbf{q}_T \, dA + \int_{A_{\mathrm{C}k}} \overset{\acute{}}{\overline{\delta\mathbf{u} \cdot \mathbf{n} \otimes \mathbf{q}_T}} \cdot \nabla_T \, dA - \int_{A_{\mathrm{C}k}} \delta\mathbf{u} \cdot \overset{\acute{}}{\overline{\mathbf{n} \otimes \mathbf{q}_T}} \cdot \nabla_T \, dA \end{aligned} \tag{F.9}$$

Adding this identity to (F.6), we arrive at

$$\begin{aligned} \delta \int_{A_{\mathrm{C}k}} \phi \; dA &= \underline{\int_{A_{\mathrm{C}k}} \overset{\acute{}}{\overline{\Big(\delta\mathbf{u} \cdot \big(\mathbf{S} + \mathbf{n} \otimes \mathbf{q}_T\big) + \delta\mathbf{n} \cdot \mathbf{D}\Big)}} \cdot \nabla_T \, dA} \\ &- \int_{A_{\mathrm{C}k}} \Big(\delta\mathbf{u} \cdot \overset{\acute{}}{\overline{\big(\mathbf{S} + \mathbf{n} \otimes \mathbf{q}_T\big)}} \cdot \nabla_T + \delta\mathbf{n} \cdot \big(\acute{\mathbf{D}} \cdot \nabla_T - \mathbf{q}_T\big)\Big) \, dA \end{aligned} \tag{F.10}$$

Now, $\delta\mathbf{u}\cdot\mathbf{n}\otimes\mathbf{q}_T = (\delta\mathbf{u}\cdot\mathbf{n})\,\mathbf{q}_T \in T$ and also $\delta\mathbf{u}\cdot\mathbf{S} \in T$ and $\delta\mathbf{n}\cdot\mathbf{D} \in T$, because the (symmetric) tensors $\mathbf{D}$ and $\mathbf{S}$ are mappings of T into itself. Hence the divergence theorem (E.7) can be applied to the underlined integral in the last equation. We get the result

$$\begin{aligned} \delta \int_{A_{\mathrm{C}k}} \phi \; dA &= \oint \delta\mathbf{u} \cdot (\mathbf{S} + \mathbf{n} \otimes \mathbf{q}_T) \cdot \mathbf{e} \, ds + \oint \delta\mathbf{n} \cdot \mathbf{D} \cdot \mathbf{e} \, ds \\ &- \int_{A_{\mathrm{C}k}} \delta\mathbf{u} \cdot \overset{\acute{}}{\overline{(\mathbf{S} + \mathbf{n} \otimes \mathbf{q}_T)}} \cdot \nabla_T \, dA - \int_{A_{\mathrm{C}k}} \delta\mathbf{n} \cdot \big(\acute{\mathbf{D}} \cdot \nabla_T - \mathbf{q}_T\big) \, dA \end{aligned} \tag{F.11}$$

The variation of the oil and water volumes is determined as follows. If an element dA_+ of the oil-sided boundary surface of the film with unit normal vector $\mathbf{n}$ undergoes a displacement $\delta\mathbf{u}_+$ then it diminishes the oil volume by $dA_+\mathbf{n} \cdot \delta\mathbf{u}_+$. Now that displacement is obtained from

$$\delta\mathbf{u}_+ = \delta\mathbf{u} + \delta\boldsymbol{\psi} \times \mathbf{n} \, \frac{h}{2} \tag{F.12}$$

where $\delta\mathbf{u}$ is the displacement of the point on the middle surface and $\delta\boldsymbol{\psi}$ the vector of rotation of the tangential plane. Because of $\mathbf{n} \times \mathbf{n} = \mathbf{0}$, we find

$$\mathbf{n} \cdot \delta\mathbf{u}_+ = \mathbf{n} \cdot \left(\delta\mathbf{u} + \delta\boldsymbol{\psi} \times \mathbf{n}\,\frac{h}{2}\right) = \mathbf{n} \cdot \delta\mathbf{u} \tag{F.13}$$

Moreover, according to (D.8), we have

$$dA_+ = \left(1 - \operatorname{tr}\mathbf{C}\frac{h}{2} + \det\mathbf{C}\frac{h^2}{4}\right)dA \tag{F.14}$$

Thus we arrive at

$$\delta V_{\mathrm{OC}k} = -\int_{A_{\mathrm{C}k}} \mathbf{n} \cdot \delta\mathbf{u}\,\left(1 - \operatorname{tr}\mathbf{C}\frac{h}{2} + \det\mathbf{C}\frac{h^2}{4}\right)dA \tag{F.15}$$

and, analogously, to

$$\delta V_{\mathrm{WC}k} = \int_{A_{\mathrm{C}k}} \mathbf{n} \cdot \delta\mathbf{u}\,\left(1 + \operatorname{tr}\mathbf{C}\frac{h}{2} + \det\mathbf{C}\frac{h^2}{4}\right)dA \tag{F.16}$$

The variation of the last terms in (F.1) yields

$$\begin{aligned} &-\big(p_{\mathrm{O}k} - p_{\mathrm{e}}\big)\delta V_{\mathrm{OC}k} - \big(p_{\mathrm{W}k} - p_{\mathrm{e}}\big)\delta V_{\mathrm{WC}k} \\ &= \int_{A_{\mathrm{C}k}} \delta\mathbf{u} \cdot \mathbf{n}\, p_{\mathrm{e}}\, h \operatorname{tr}\mathbf{C}\, dA - \int_{A_{\mathrm{C}k}} \delta\mathbf{u} \cdot \mathbf{n}\, p_n\, dA \end{aligned} \tag{F.17}$$

with the abbreviation

$$p_n = p_{\mathrm{W}k}\left(1 + \operatorname{tr}\mathbf{C}\frac{h}{2} + \det\mathbf{C}\frac{h^2}{4}\right) - p_{\mathrm{O}k}\left(1 - \operatorname{tr}\mathbf{C}\frac{h}{2} + \det\mathbf{C}\frac{h^2}{4}\right) \tag{F.18}$$

Now we introduce the internal forces of the fluid film, which are detailed in appendix G, namely the tensor of moments

$$\mathbf{M} = -\frac{\partial w}{\partial \mathbf{C}} \tag{F.19}$$

and the tensor of membrane forces

$$\mathbf{T} = \Big(w - f\,\mu\Big)\mathbf{1}_T + \mathbf{C} \cdot \mathbf{M} \tag{F.20}$$

while the Lagrangean multiplier q_T may be called the operator of transverse forces. With (C.17), we find

$$\mathbf{D} = \mathbf{M} + p_{\mathrm{e}}\,\frac{h^3}{12}\big(\mathbf{C} - \operatorname{tr}\mathbf{C}\,\mathbf{1}_T\big) \tag{F.21}$$

while (C.8) allows $\mathbf{S}$ to be reduced to

$$\mathbf{S} = \mathbf{T} + p_{\mathrm{e}}h\,\mathbf{1}_T \tag{F.22}$$

So we have, with (C.29) and (C.23),

$$\mathbf{D}\cdot\nabla_T = \mathbf{M}\cdot\nabla_T - p_{\mathrm{e}}\,\frac{h^3}{6}\,\det\mathbf{C}\,\mathbf{n} \tag{F.23}$$

(the second term will not enter (F.11), since $\delta\mathbf{n}\cdot\mathbf{n}=0$) and

$$\mathbf{S}\cdot\nabla_T = \mathbf{T}\cdot\nabla_T + p_{\mathrm{e}}\,h\,\mathrm{tr}\,\mathbf{C}\,\mathbf{n} \tag{F.24}$$

Now we sum the expressions of the type Φ of (F.1) over the cells of all structures and postulate that their variation must vanish under any variation $\delta\mathbf{u}$ and $\delta\mathbf{n}$.

$$\begin{aligned} 0 \;=\;& \sum_k n_k\Big(\oint \delta\mathbf{u}\cdot(\mathbf{S}+\mathbf{n}\otimes\mathbf{q}_T)\cdot\mathbf{e}\,ds + \oint \delta\mathbf{n}\cdot\mathbf{D}\cdot\mathbf{e}\,ds\Big) \\ & -\sum_k n_k\int_{A_{\mathrm{C}k}} \delta\mathbf{u}\cdot\Big(\acute{\overline{(\mathbf{T}+\mathbf{n}\otimes\mathbf{q}_T)}}\cdot\nabla_T + p_n\mathbf{n}\Big)\,dA \\ & -\sum_k n_k\int_{A_{\mathrm{C}k}} \delta\mathbf{n}\cdot\Big(\acute{\mathbf{M}}\cdot\nabla_T - \mathbf{q}_T\Big)\,dA \end{aligned} \tag{F.25}$$

If the structures are closed and hence have no boundaries at all — an example is given by spheres — or if the boundaries are fixed at the wall of the test-tube so that $\delta\mathbf{u}=\mathbf{0}$ and $\delta\mathbf{n}=\mathbf{0}$ is valid, then the line integrals over the boundaries yield no contribution. If, however, there are free boundaries, then the natural boundary conditions

$$(\mathbf{S}+\mathbf{n}\otimes\mathbf{q}_T)\cdot\mathbf{e}=\mathbf{0} \qquad\Longleftrightarrow\qquad \mathbf{T}\cdot\mathbf{e}=-p_{\mathrm{e}}h\mathbf{e}\,,\quad \mathbf{q}_T\cdot\mathbf{e}=0 \tag{F.26}$$

$$\mathbf{M}\cdot\mathbf{e} = -p_{\mathrm{e}}\,\frac{h^3}{12}\big(\mathbf{C}\cdot\mathbf{e}-\mathrm{tr}\,\mathbf{C}\,\mathbf{e}\big) \tag{F.27}$$

must be satisfied. Moreover, the vector field $\delta\mathbf{u}$ on the surface is arbitrary while the vectors of the field $\delta\mathbf{n}$ lie in the local tangential plane, so that the following Euler-Lagrangean differential equations must be valid

$$\big(\mathbf{T}+\mathbf{n}\otimes\mathbf{q}_T\big)\cdot\nabla_T + p_n\mathbf{n} = \mathbf{0} \tag{F.28}$$

$$\mathbf{1}_T\cdot\big(\acute{\mathbf{M}}\cdot\nabla_T - \mathbf{q}_T\big) = \mathbf{0} \tag{F.29}$$

They are further discussed in appendix G.3.

G The Internal Forces of a Shell

G.1 General Considerations

Imagine that we cut out an arbitrary part of a material surface. If that surface is an amphiphilic film, then the free energy of that part with area A is

$$F = \int_A w(c_1,c_2,\mu)\,dA \tag{G.1}$$

and its variation is

$$\delta F = \int_A \left(\frac{\partial w}{\partial \mu} \delta\mu + \frac{\partial w}{\partial \mathbf{C}} : \delta\mathbf{C} + w \, \frac{\delta(dA)}{dA} \right) dA \tag{G.2}$$

We restrict our attention to a purely elastic deformation from the relaxed state (*i.e.* the state of minimal free energy) without any exchange of mass with the environment. This means $\delta(\mu \, dA) = 0$ or

$$-\frac{\delta\mu}{\mu} = \frac{\delta dA}{dA} = \mathbf{1}_T : (\delta\mathbf{u} \otimes \nabla_T) \tag{G.3}$$

(Note that the reached state will not be a relaxed state unless $\delta dA = 0$ holds.) We use the abbreviations

$$\mathbf{M} = -\frac{\partial w}{\partial \mathbf{C}} \tag{G.4}$$

and

$$\mathbf{T} = \left(w - \mu \, \frac{\partial w}{\partial \mu} \right) \mathbf{1}_T + \mathbf{C} \cdot \mathbf{M} \tag{G.5}$$

which coincide with (F.19), (F.20), since we have

$$\frac{\partial w}{\partial \mu} = f \tag{G.6}$$

according to (2.41) in the relaxed state. With the way of reasoning that led us from (F.5) to (F.11) we arrive at

$$\begin{aligned} \delta F &= \int_A \Big(\mathbf{T} : (\delta\mathbf{u} \otimes \nabla_T) + \mathbf{M} : (\delta\mathbf{n} \otimes \nabla_T) \Big) \, dA \\ &= \oint \delta\mathbf{u} \cdot (\mathbf{T} + \mathbf{n} \otimes \mathbf{q}_T) \cdot \mathbf{e} \, ds + \oint \delta\mathbf{n} \cdot \mathbf{M} \cdot \mathbf{e} \, ds \\ &\quad - \int_A \delta\mathbf{u} \cdot \overline{(\mathbf{T} + \acute{\mathbf{n}} \otimes \mathbf{q}_T)} \cdot \nabla_T \, dA - \int_A \delta\mathbf{n} \cdot \big(\acute{\mathbf{M}} \cdot \nabla_T - \mathbf{q}_T \big) \, dA \end{aligned} \tag{G.7}$$

The first of these two representations reveals the variation of the free energy to be equivalent to the virtual work of two kinds of internal forces: the first contribution is the virtual work of the membrane forces **T** and the second one is the virtual work of the moments **M**. The second representation, resulting from the application of the divergence theorem, shows that there exists an equivalence between the virtual work of internal and external forces. (This equivalence is called the work theorem of statics.) An inspection reveals that the external virtual work on the considered part of the material surface is exerted by four external agents. Two of them act on the boundary and two directly on the surface. That boundary is in general not a real boundary of the material surface but a virtual cut through the surface in the sense of Euler. 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.

These are the four external agents:
1) If a point on the boundary undergoes a virtual displacement $\delta\mathbf{u}$, then the work of the boundary force (per unit length of the boundary) is

$$\delta\mathbf{u}\cdot(\mathbf{T}+\mathbf{n}\otimes\mathbf{q}_T)\cdot\mathbf{e} \tag{G.8}$$

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

$$\mathbf{f}=(\mathbf{T}+\mathbf{n}\otimes\mathbf{q}_T)\cdot\mathbf{e}=\mathbf{T}\cdot\mathbf{e}+(\mathbf{q}_T\cdot\mathbf{e})\,\mathbf{n} \tag{G.9}$$

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 $\mathbf{n}$.

2) Defining the vector of virtual rotation $\delta\boldsymbol{\psi}\in T$ of the tangential plane T by

$$\delta\boldsymbol{\psi}=\mathbf{n}\times\delta\mathbf{n} \tag{G.10}$$

we find

$$\delta\mathbf{n}=\delta\boldsymbol{\psi}\times\mathbf{n} \tag{G.11}$$

If the tangential plane at a point of the boundary undergoes a virtual rotation $\delta\boldsymbol{\psi}$, then the work of the boundary torque (per unit length of the boundary) is

$$\delta\mathbf{n}\cdot\mathbf{M}\cdot\mathbf{e}=\big(\delta\boldsymbol{\psi}\times\mathbf{n}\big)\cdot\mathbf{M}\cdot\mathbf{e}=\delta\boldsymbol{\psi}\cdot\big(\mathbf{n}\times\mathbf{M}\cdot\mathbf{e}\big) \tag{G.12}$$

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

$$\mathbf{m}=\mathbf{n}\times\mathbf{M}\cdot\mathbf{e} \tag{G.13}$$

In general, it has components parallel and normal to the boundary, *i.e.* bending and torsional moments.

3) If a point within the cut out part of our material surface undergoes a virtual displacement $\delta\mathbf{u}$, then the work of the distributed surface force (per unit area of the surface) is

$$-\,\delta\mathbf{u}\cdot\acute{\overline{(\mathbf{T}+\mathbf{n}\otimes\mathbf{q}_T)}}\cdot\nabla_T \tag{G.14}$$

and hence the surface force (per unit area) is

$$\mathbf{p}=-\big(\mathbf{T}+\mathbf{n}\otimes\mathbf{q}_T\big)\cdot\nabla_T \tag{G.15}$$

Noting

$$\mathbf{n}\cdot\acute{\mathbf{T}}\cdot\nabla_T=\acute{\overline{\mathbf{n}\cdot\mathbf{T}}}\cdot\nabla_T-\mathbf{T}:\acute{\mathbf{n}}\otimes\nabla_T=\mathbf{T}:\mathbf{C} \tag{G.16}$$

and

$$\overset{\prime}{\overline{\mathbf{n}\otimes\mathbf{q}_T}}\cdot\nabla_T = \mathbf{n}\,(\nabla_T\cdot\acute{\mathbf{q}}_T) + \acute{\mathbf{n}}\otimes\nabla_T\cdot\mathbf{q}_T = \mathbf{n}\,(\nabla_T\cdot\acute{\mathbf{q}}_T) - \mathbf{C}\cdot\mathbf{q}_T \qquad \text{(G.17)}$$

we can decompose the surface force into components tangential and normal to the surface.

$$\mathbf{1}_T\cdot\mathbf{p} = \mathbf{p}_T = -\mathbf{1}_T\cdot\acute{\mathbf{T}}\cdot\nabla_T + \mathbf{C}\cdot\mathbf{q}_T \qquad \text{(G.18)}$$

$$\mathbf{n}\cdot\mathbf{p} = p_n = -\mathbf{T}:\mathbf{C} - \nabla_T\cdot\mathbf{q}_T \qquad \text{(G.19)}$$

4) If the tangential plane at a point within the cut out part of our material surface undergoes a virtual rotation $\delta\boldsymbol{\psi}$, then the work of the distributed surface torque (per unit area of the surface) is

$$-\,\delta\mathbf{n}\cdot\big(\acute{\mathbf{M}}\cdot\nabla_T-\mathbf{q}_T\big) = -\big(\delta\boldsymbol{\psi}\times\mathbf{n}\big)\cdot\big(\acute{\mathbf{M}}\cdot\nabla_T-\mathbf{q}_T\big) = -\,\delta\boldsymbol{\psi}\cdot\Big(\mathbf{n}\times\big(\acute{\mathbf{M}}\cdot\nabla_T-\mathbf{q}_T\big)\Big) \qquad \text{(G.20)}$$

and hence the surface torque (per unit area) is

$$\mathbf{t} = -\,\mathbf{n}\times\big(\acute{\mathbf{M}}\cdot\nabla_T-\mathbf{q}_T\big) \qquad \text{(G.21)}$$

which implies

$$\mathbf{1}_T\cdot\acute{\mathbf{M}}\cdot\nabla_T-\mathbf{q}_T = \mathbf{n}\times\mathbf{t} \qquad \text{(G.22)}$$

Using the abbreviations (G.9), (G.13), (G.15), (G.21), we can give the external virtual work the illuminating form

$$\delta F = \oint(\delta\mathbf{u}\cdot\mathbf{f}+\delta\boldsymbol{\psi}\cdot\mathbf{m})\,ds + \int_A(\delta\mathbf{u}\cdot\mathbf{p}+\delta\boldsymbol{\psi}\cdot\mathbf{t})\,dA \qquad \text{(G.23)}$$

The equations (G.18), (G.19), (G.22) 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 ([1], [10]). But the solid elastic shells of the engineering applications possess an energy density of the more general form $w(\mathbf{C},\mathbf{F})$ instead of $w(\mathbf{C},\mu)$ so that their membrane force $\mathbf{T}$ mainly depends on the surface strains.

G.2 Restrictions in the Case of a Fluid Film

In the case of a relaxed fluid film, the membrane force $\mathbf{T}$ has a special form according to (G.5), (G.6). 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

$$\mathbf{p}_T + \mathbf{C}\cdot(\mathbf{n}\times\mathbf{t}) \equiv 0 \qquad \text{(G.24)}$$

In order to see this, we use (G.18) and (G.22) and find

$$\mathbf{p}_T+\mathbf{C}\cdot(\mathbf{n}\times\mathbf{t})=-\mathbf{1}_T\cdot\acute{\overline{\big((w-f\mu)\,\mathbf{1}_T+\mathbf{C}\cdot\mathbf{M}\big)}}\cdot\nabla_T+\mathbf{C}\cdot\mathbf{1}_T\cdot\acute{\mathbf{M}}\cdot\nabla_T$$

$$=-\nabla_T(w-f\mu)-(w-f\mu)\,\underline{\mathbf{1}_T\cdot\acute{\mathbf{1}}_T\cdot\nabla_T}$$

$$-\mathbf{1}_T\cdot\acute{\mathbf{C}}\cdot\mathbf{M}\cdot\nabla_T\underline{-\mathbf{C}\cdot\acute{\mathbf{M}}\cdot\nabla_T+\mathbf{C}\cdot\acute{\mathbf{M}}\cdot\nabla_T} \tag{G.25}$$

The last two underlined terms obviously cancel each other. The first underlined term is equal to zero according to (C.23). Now

$$\nabla_T(w-f\mu)=\frac{\partial w}{\partial\mathbf{C}}:\big(\acute{\mathbf{C}}\otimes\nabla_T\big)+\underline{\left(\frac{\partial w}{\partial\mu}-f\right)}\nabla_T\mu \tag{G.26}$$

But the underlined term vanishes according to (G.6). So (G.25) with (G.4) reduces to

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

$$=\mathbf{M}:\mathbf{1}_T\cdot\acute{\mathbf{C}}\cdot\mathbf{1}_T\otimes\nabla_T-\mathbf{1}_T\cdot\acute{\mathbf{C}}\cdot\mathbf{1}_T\otimes\nabla_T:\mathbf{M} \tag{G.27}$$

The right-hand side expression is, indeed, equal to zero, since the third-order tensor $\mathbf{1}_T\cdot\acute{\mathbf{C}}\cdot\mathbf{1}_T\otimes\nabla_T$ is totally symmetric according to (C.26).

We notice: While it is possible to apply arbitrary surface forces and torques on solid elastic shells, this is by no means the case with relaxed fluid films.

G.3 Simplification of the Euler-Lagrange Equations

The condition (G.24) causes no problem in our case, since it is trivially satisfied. This is seen by a comparison of (G.15) with (F.28) — which implies $\mathbf{p}_T=\mathbf{0}$ — and (G.21) with (F.29) — which implies $\mathbf{t}=\mathbf{0}$. It shows that the water and the oil on the two sides of the thick amphiphilic layer apply neither a tangential surface force $\mathbf{p}_T$ nor a surface torque $\mathbf{t}$. There is only a surface force normal to the middle surface of the film, the magnitude of which is easily interpreted, since (F.18) with (D.8), (D.9) implies

$$p_n\,dA=p_{\mathrm{W}k}\,dA_- - p_{\mathrm{O}k}\,dA_+ \tag{G.28}$$

Equation (F.29) may be rearranged to read

$$\mathbf{q}_T=\mathbf{1}_T\cdot\acute{\mathbf{M}}\cdot\nabla_T \tag{G.29}$$

But this statement alone secures $\mathbf{t}=\mathbf{0}$ according to (G.22) and hence $\mathbf{p}_T=\mathbf{0}$ according to (G.24). Therefore the equilibrium condition of the tangential forces (G.18) is identically satisfied and need not be discussed separately in the case of a relaxed fluid film. Only the one scalar condition of the equilibrium of the normal forces (G.19)

$$p_n=-\mathbf{T}:\mathbf{C}-\nabla_T\cdot\mathbf{q}_T \tag{G.30}$$

with p_n according to (F.18) and $\mathbf{q}_T$ according to (G.29) must be solved.

H A Class of Bi-continuous Surfaces

H.1 A Substitute of Schwarz's P surface

We want to construct a model of the bi-continuous phase, consisting of two systems of intertwining tubes in the three directions of space. At the moment, we restrict our attention to the isometric case, *i.e.* the volumes inside the two systems of tubes, containing oil and water, respectively, are equal. Let us consider a typical cell of this triply periodic structure (*cf.* fig. H.1). We study the reference structure with characteristic length $L = 1$. (More general structures may then be obtained by affine magnification.) The periodicity of the (reference) structure in each of the three directions of space is $4L$. The side length of the cell is $2L$. The contours of the cell are characterized by a dashed line in the figure. The topology of the structure is best understood by assuming provisionally, that the surface consists of plane square patches. The cell contains six such patches. Two complementary systems of triply orthogonal tubes can now be imagined. We obtain a smooth surface, if we deform the square cross-sections of the tubes on the planes of symmetry into circles. The patch which is marked by a bold boundary is then deformed into a curved surface patch. It is this quadrilateral curved patch, from which the whole surface structure can be built up by means of reflexions. The following investigation is based on an analytic representation of this patch.

All vectors will be referred to the basis $\mathbf{e}_x$, $\mathbf{e}_y$, $\mathbf{e}_z$ of the Cartesian coordinate system so that we only write down the rows of their components. The position vector $\mathbf{x}$ of the patch can be represented as a function of two Gaussian parameters ξ and η.

$$\mathbf{x}(\xi,\eta) \hat{=} \begin{pmatrix} x(\xi,\eta) & y(\xi,\eta) & z(\xi,\eta) \end{pmatrix} \tag{H.1}$$

The tangent vectors are given by

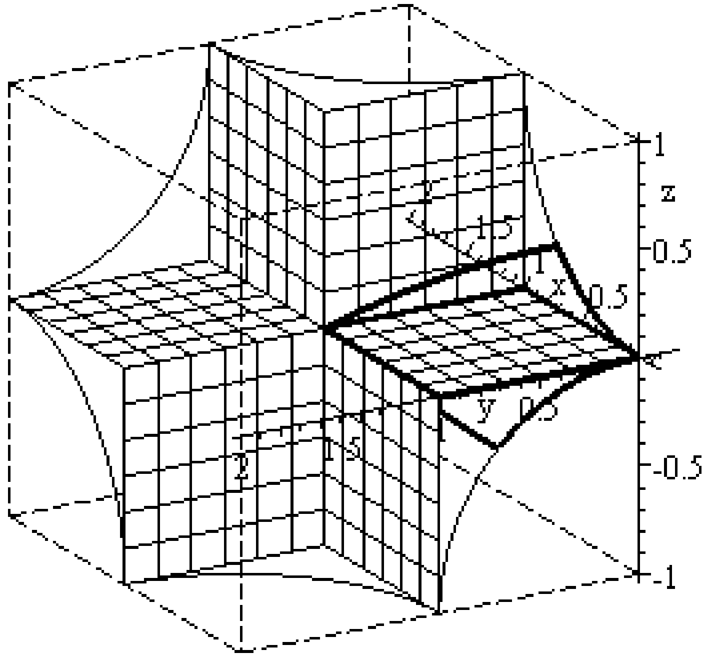
$$\mathbf{g}_\xi = \frac{\partial \mathbf{x}}{\partial \xi} \hat{=} \begin{pmatrix} \dfrac{\partial x}{\partial \xi} & \dfrac{\partial y}{\partial \xi} & \dfrac{\partial z}{\partial \xi} \end{pmatrix} \tag{H.2}$$

$$\mathbf{g}_\eta = \frac{\partial \mathbf{x}}{\partial \eta} \hat{=} \begin{pmatrix} \dfrac{\partial x}{\partial \eta} & \dfrac{\partial y}{\partial \eta} & \dfrac{\partial z}{\partial \eta} \end{pmatrix} \tag{H.3}$$

The parameter lines $\xi = const$ and $\eta = const$ form an oblique-angled pattern on the surface, and the tangent vectors are neither normalized nor mutually orthogonal. The cross product of the tangent vectors is normal to the surface and normalization yields the unit normal vector of the surface.

$$\mathbf{n} = \frac{\mathbf{g}_\xi \times \mathbf{g}_\eta}{|\mathbf{g}_\xi \times \mathbf{g}_\eta|} \tag{H.4}$$

Fig. H.1   A cell of the triply periodic structure



In order to study the curvatures, we first need the cotangent vectors, defined by

$$\mathbf{g}^{\xi} = \frac{\mathbf{g}_{\eta} \times \mathbf{n}}{|\mathbf{g}_{\xi} \times \mathbf{g}_{\eta}|} \tag{H.5}$$

$$\mathbf{g}^{\eta} = \frac{\mathbf{n} \times \mathbf{g}_{\xi}}{|\mathbf{g}_{\xi} \times \mathbf{g}_{\eta}|} \tag{H.6}$$

and satisfying

$$\mathbf{g}_{\xi} \cdot \mathbf{g}^{\xi} = 1\,, \quad \mathbf{g}_{\xi} \cdot \mathbf{g}^{\eta} = 0\,, \quad \mathbf{g}_{\eta} \cdot \mathbf{g}^{\xi} = 0\,, \quad \mathbf{g}_{\eta} \cdot \mathbf{g}^{\eta} = 1 \tag{H.7}$$

as well as the derivatives of $\mathbf{n}$ with respect to ξ and η:

$$\mathbf{n}_{,\xi} = \frac{\partial \mathbf{n}}{\partial \xi}\,, \qquad \mathbf{n}_{,\eta} = \frac{\partial \mathbf{n}}{\partial \eta}\,, \tag{H.8}$$

The operator of tangential differentiation may be represented as

$$\nabla_T = \mathbf{g}^{\xi} \frac{\partial}{\partial \xi} + \mathbf{g}^{\eta} \frac{\partial}{\partial \eta} \quad \Longrightarrow \quad \mathbf{g}_{\xi} \cdot \nabla_T = \frac{\partial}{\partial \xi}\,, \qquad \mathbf{g}_{\eta} \cdot \nabla_T = \frac{\partial}{\partial \eta} \tag{H.9}$$

The mixed components of the tensor of curvature $\mathbf{C}$ are then given by — note (B.13) —

$$c^{\alpha}_{\beta} = \mathbf{g}^{\alpha} \cdot \mathbf{C} \cdot \mathbf{g}_{\beta} = -\,\mathbf{g}^{\alpha} \cdot \mathbf{n} \otimes \nabla_T \cdot \mathbf{g}_{\beta} = -\,\mathbf{g}^{\alpha} \cdot \mathbf{n}_{,\beta} \qquad \alpha,\, \beta = \xi,\, \eta \tag{H.10}$$

The invariants of the curvature are

$$\operatorname{tr} \mathbf{C} = c^{\xi}_{\xi} + c^{\eta}_{\eta}\,, \qquad \det \mathbf{C} = c^{\xi}_{\xi}\, c^{\eta}_{\eta} - c^{\xi}_{\eta}\, c^{\eta}_{\xi} \tag{H.11}$$

i.e., they are simply computed as the trace and the determinant of the matrix of the mixed components (c^{α}_{β}).

This rule, which is not valid in the case of purely co-variant or contra-variant components, can be demonstrated as follows. According to (C.10) we have

$$2 \det \mathbf{C} = \big(\operatorname{tr} \mathbf{C}\big)^2 - \mathbf{C} : \mathbf{C} = \big(\operatorname{tr} \mathbf{C}\big)^2 - \operatorname{tr}\big(\mathbf{C}^2\big)$$

Now

$$\mathbf{C} = \sum_{\alpha=1}^{2} \sum_{\beta=1}^{2} c^{\alpha}_{\beta} \mathbf{g}_{\alpha} \otimes \mathbf{g}^{\beta}\,, \qquad \mathbf{C}^2 = \sum_{\alpha=1}^{2} \sum_{\beta=1}^{2} \Big(\sum_{\gamma=1}^{2} c^{\alpha}_{\gamma} c^{\gamma}_{\beta} \Big) \mathbf{g}_{\alpha} \otimes \mathbf{g}^{\beta}$$

and hence

$$\operatorname{tr} \mathbf{C} = \sum_{\alpha=1}^{2} \sum_{\beta=1}^{2} c^{\alpha}_{\beta} \mathbf{g}_{\alpha} \cdot \mathbf{g}^{\beta} = \sum_{\alpha=1}^{2} c^{\alpha}_{\alpha}\,, \qquad \operatorname{tr}\big(\mathbf{C}^2\big) = \sum_{\alpha=1}^{2} \sum_{\gamma=1}^{2} c^{\alpha}_{\gamma} c^{\gamma}_{\alpha}$$

If the Cartesian components of the position vector, *i.e.* the functions $\big(x(\xi,\eta),\, y(\xi,\eta), z(\xi,\eta)\big)$ are given, then all the algebraic or differential computations (H.2) to (H.6), (H.8) and (H.10) can be done with Cartesian components.

Now we need to specify our patch. To this purpose we choose four linearly independent cubic splines

$$\begin{aligned} h_0(u) &\equiv 1 - 3u^2 + 2u^3\,, \quad h_1(u) \equiv 3u^2 - 2u^3 \\ k_0(u) &\equiv u - 2u^2 + u^3\,, \quad k_1(u) \equiv -u^2 + u^3 \end{aligned} \tag{H.12}$$

defined on $u \in [0,1]$ and represent the components of the position vector as sums of products of these splines, valid on a domain defined by $\xi \in [0,1]$, $\eta \in [0,1]$. Thus we introduce $3 \times 4 \times 4 = 48$ degrees of freedom, which may be interpreted as the values of the components, of their two partial derivatives and of their mixed second derivative at the four corners of the patch. Let w denote any one of the components x, y or z. Then we put

$$\begin{aligned} & w(\xi,\eta) \equiv \\ & w_{00}\, h_0(\xi)\, h_0(\eta) + w_{10}\, h_1(\xi)\, h_0(\eta) + w_{01}\, h_0(\xi)\, h_1(\eta) + w_{11}\, h_1(\xi)\, h_1(\eta) \\ & + w_{\xi\,00}\, k_0(\xi)\, h_0(\eta) + w_{\xi\,10}\, k_1(\xi)\, h_0(\eta) + w_{\xi\,01}\, k_0(\xi)\, h_1(\eta) + w_{\xi\,11}\, k_1(\xi)\, h_1(\eta) \\ & + w_{\eta\,00}\, h_0(\xi)\, k_0(\eta) + w_{\eta\,10}\, h_1(\xi)\, k_0(\eta) + w_{\eta\,01}\, h_0(\xi)\, k_1(\eta) + w_{\eta\,11}\, h_1(\xi)\, k_1(\eta) \\ & + w_{\xi\eta\,00}\, k_0(\xi)\, k_0(\eta) + w_{\xi\eta\,10}\, k_1(\xi)\, k_0(\eta) + w_{\xi\eta\,01}\, k_0(\xi)\, k_1(\eta) + w_{\xi\eta\,11}\, k_1(\xi)\, k_1(\eta) \end{aligned} \tag{H.13}$$

Since we are considering the isometric case, our patch is antimetric with respect to the straight line which connects $\mathbf{x}\hat{=}(\,0\,0\,0\,)$ with $\mathbf{x}\hat{=}(\,1\,1\,0\,)$. Therefore we have to impose the restrictions

$$y(\xi,\eta) = x(\eta,\xi)\,, \qquad z(\xi,\eta) = -z(\eta,\xi) \tag{H.14}$$

which yield

$$y_{00} = x_{00}\,, \qquad y_{10} = x_{01}\,, \qquad y_{01} = x_{10}\,, \qquad y_{11} = x_{11} \tag{H.15}$$

$$y_{\xi\,00} = x_{\eta\,00}\,, \qquad y_{\eta\,00} = x_{\xi\,00}\,, \qquad y_{\xi\,01} = x_{\eta\,10}\,, \qquad y_{\eta\,01} = x_{\xi\,10} \tag{H.16}$$

$$y_{\xi\,10} = x_{\eta\,01}\,, \qquad y_{\eta\,10} = x_{\xi\,01}\,, \qquad y_{\xi\,11} = x_{\eta\,11}\,, \qquad y_{\eta\,11} = x_{\xi\,11} \tag{H.17}$$

$$y_{\xi\eta\,00} = x_{\xi\eta\,00}\,, \quad y_{\xi\eta\,01} = x_{\xi\eta\,10}\,, \quad y_{\xi\eta\,10} = x_{\xi\eta\,01}\,, \quad y_{\xi\eta\,11} = x_{\xi\eta\,11} \tag{H.18}$$

$$z_{00} = 0\,, \qquad z_{01} = -z_{10}\,, \qquad z_{11} = 0 \tag{H.19}$$

$$z_{\eta\,00} = -z_{\xi\,00}\,, \quad z_{\eta\,10} = -z_{\xi\,01}\,, \quad z_{\eta\,01} = -z_{\xi\,10}\,, \quad z_{\eta\,11} = -z_{\xi\,11} \tag{H.20}$$

$$z_{\xi\eta\,00} = 0\,, \qquad z_{\xi\eta\,01} = -z_{\xi\eta\,10}\,, \qquad z_{\xi\eta\,11} = 0 \tag{H.21}$$

and reduce the number of degrees of freedom to 22. This number may be further diminished due to the fact, that the quadrilateral patch under consideration is bounded by four planes of symmetry of the triply periodic structure. Since we take care that the normal of the patch at the boundaries lies within the corresponding plane of symmetry, the resulting periodic structure is C_2 continuous.

The points of the boundary $\xi = 0$ lie on the plane of symmetry $x = 0$. Moreover, we postulate that the tangent vector $\mathbf{g}_\xi$ be normal to that plane. We obtain

$$x(0,\eta) = 0 \quad : \quad x_{00} = 0\,, \quad x_{01} = 0\,, \quad x_{\eta\,00} = 0\,, \quad x_{\eta\,01} = 0 \tag{H.22}$$

$$\mathbf{e}_y \cdot \mathbf{g}_\xi(0,\eta) = 0 \quad : \quad y_{\xi\,00} = 0\,, \quad y_{\xi\,01} = 0\,, \quad y_{\xi\eta\,00} = 0\,, \quad y_{\xi\eta\,01} = 0 \tag{H.23}$$

$$\mathbf{e}_z \cdot \mathbf{g}_\xi(0,\eta) = 0 \quad : \quad z_{\xi\,00} = 0\,, \quad z_{\xi\,01} = 0\,, \quad z_{\xi\eta\,00} = 0\,, \quad z_{\xi\eta\,01} = 0 \tag{H.24}$$

A similar discussion of the boundary $\eta = 0$ yields no additional restrictions because of the identities (H.15) to (H.21).

The points of the boundary $\xi = 1$ lie on the plane of symmetry $x = 1 - z$.

$$x(1,\eta) = 1 - z(1,\eta) :$$

$$x_{10} = 1 - z_{10}\,,\ x_{11} = 1 - z_{11}\,,\ x_{\eta\,10} = -z_{\eta\,10}\,,\ x_{\eta\,11} = -z_{\eta\,11} \tag{H.25}$$

The points of the boundary $\eta = 1$ lie on the plane of symmetry $y = 1 + z$. This is automatically achieved by (H.15) to (H.21).

We have adopted the postulate that the tangent vectors $\mathbf{g}_\xi$ and $\mathbf{g}_\eta$ be mutually orthogonal on the lines $\xi = 0$ and $\eta = 0$. We cannot impose the same restriction to the lines $\xi = 1$ or $\eta = 1$, since this would imply also the orthogonality at the corner $\xi = 1$, $\eta = 1$. But there are six quadrilateral patches adjacent to this corner, so that the angle of each of them must amount to 60°.

What we can do, is observe that the vector $\mathbf{v}_\xi = \mathbf{e}_x + \mathbf{e}_z$, which is normal to the plane of symmetry $x = 1 - z$ at $\xi = 1$, must lie in the tangential plane of the surface, and, therefore, the following linear relation between this vector and the tangent vectors must hold.

$$\mathbf{g}_\xi(1,\eta) = \lambda(\eta)\mathbf{v}_\xi + \mu(\eta)\mathbf{g}_\eta(1,\eta) \tag{H.26}$$

The unknown function $\lambda(\eta)$ is eliminated if we multiply this vector equation with two vectors that are orthogonal to $\mathbf{v}_\xi$. We obtain

$$\mathbf{e}_y \cdot \big(\mathbf{g}_\xi(1,\eta) - \mu(\eta)\mathbf{g}_\eta(1,\eta)\big) = 0 \tag{H.27}$$

$$\big(\mathbf{e}_x - \mathbf{e}_z\big) \cdot \big(\mathbf{g}_\xi(1,\eta) - \mu(\eta)\mathbf{g}_\eta(1,\eta)\big) = 0 \tag{H.28}$$

First we consider the corner point with $\eta = 0$. The condition $y(\xi, 0) = 0$, which is already fulfilled, implies $\partial y(\xi, 0)/\partial\xi = 0$ and hence especially $\partial y/\partial\xi(1,0) = \mathbf{e}_y \cdot \mathbf{g}_\xi(1,0) = 0$. So the choice $\mu(0) = 0$ satisfies (H.27), while (H.28) then implies

$$z_{\xi\,10} = x_{\xi\,10} \tag{H.29}$$

In a similar manner, we observe that the vector $\mathbf{v}_\eta = \mathbf{e}_y - \mathbf{e}_z$, which is normal to the plane of symmetry $y = 1 + z$, must lie in the tangential plane of the surface at $\eta = 1$.

Now, the normal vector at the boundary $\xi = 1$ is orthogonal to $\mathbf{v}_\xi$ and the normal vector at the boundary $\eta = 1$ is orthogonal to $\mathbf{v}_\eta$. Hence, the normal vector at the corner $\xi = 1$, $\eta = 1$ has to be orthogonal to both of these vectors and must therefore point into the direction of

$$\mathbf{v_n} = \mathbf{v}_\xi \times \mathbf{v}_\eta = \big(\mathbf{e}_x + \mathbf{e}_z\big) \times \big(\mathbf{e}_y - \mathbf{e}_z\big) = -\mathbf{e}_x + \mathbf{e}_y + \mathbf{e}_z \tag{H.30}$$

Thus the condition

$$0 = \mathbf{v_n} \cdot \mathbf{g}_\xi(1,1) = \big(-\mathbf{e}_x + \mathbf{e}_y + \mathbf{e}_z\big) \cdot \mathbf{g}_\xi(1,1) = -x_{\xi\,11} + y_{\xi\,11} + z_{\xi\,11} \tag{H.31}$$

is valid at the corner. Together with (H.17), (H.25), (H.20), it implies

$$z_{\xi\,11} = \frac{1}{2} x_{\xi\,11} \tag{H.32}$$

Noting (H.17), (H.20), (H.25), (H.31), (H.32) we find that (H.27) and (H.28) are satisfied at the corner with $\eta = 1$ if we choose $\mu(1) = 1/2$. The simplest functional form which fits this condition and $\mu(0) = 0$ is

$$\mu(\eta) = \frac{1}{2}\eta \tag{H.33}$$

If we adopt it, we can satisfy (H.27) and (H.28) for each value of η by putting

$$z_{10} = \frac{1}{2} - \frac{1}{6} x_{\xi\,01} \tag{H.34}$$

$$x_{\xi\eta\,01} = \frac{1}{2} x_{\xi\,01} \tag{H.35}$$

$$x_{\xi\eta\,11} = \frac{5}{2} x_{\xi\,11} + x_{\xi\,01} - 3 \tag{H.36}$$

After all, only four of the original 48 degrees of freedom have remained over. The numerical values of them are chosen in such a way that the resulting variation of the mean curvature over the surface patch is as small as possible. After some trials we arrive at

$$x_{\xi\,00} = 0.867\,, \qquad x_{\xi\,11} = 0.857\,, \qquad x_{\xi\,10} = 0.5\,, \qquad x_{\xi\,01} = 1.2 \tag{H.37}$$

The curvature of the boundaries $\eta = 0$ and $\xi = 0$ is almost constant. Hence, the curves are almost circles with radius 1 as mentioned earlier. The principal curvatures at the corner $\xi = 1$, $\eta = 1$ are equal. This follows from the fact that 6 patches meet at that corner so that the curvature tensor must be isotropic. Their value is, of course, 0 in this isometric case. The maximum magnitude of the mean curvature H is about 0.012, *i.e.* 1.2% of the maximum magnitude of the principal curvatures. Thus, our surface is nearly a minimal surface, *i.e.* a surface with $H = 0$, and hence a useful numerical substitute of Schwarz's P surface ([13]).

H.2 Definition of a Class of Surfaces

By displacing each point $\mathbf{x}(\xi, \eta)$ of the surface of the preceding section by a distance ζ in the direction of the local unit normal vector $\mathbf{n}(\xi, \eta)$ into a new position

$$\mathbf{x}_\zeta(\xi, \eta, \zeta) = \mathbf{x}(\xi, \eta) + \zeta \mathbf{n}(\xi, \eta) \tag{H.38}$$

we generate another surface with the same local unit normal vector. Letting ζ be any value of, say, the interval (-0.8, 0.8) we obtain a class of surfaces, depending on the parameter ζ. The original surface is characterized by $\zeta = 0$ and describes the isometric case.

The following reasonings are similar to those of appendix D, but in a totally different context. We denote the curvature tensors of the surface with $\zeta = 0$ and of the surface with $\zeta \neq 0$ by $\bar{\mathbf{C}}$ and $\hat{\mathbf{C}}$, respectively. If ξ and η are varied by $d\xi$ and $d\eta$, then the resulting changes of the position vectors $\mathbf{x}$ and $\mathbf{x}_\zeta$ are connected by — note (B.12) —

$$d\mathbf{x}_\zeta = d\mathbf{x} + \zeta d\mathbf{n} = d\mathbf{x} - \zeta \bar{\mathbf{C}} \cdot d\mathbf{x} = \left(\mathbf{1}_T - \zeta \bar{\mathbf{C}}\right) \cdot d\mathbf{x} \tag{H.39}$$

The connexion of the curvature tensors can be inferred from

$$d\mathbf{n} = -\bar{\mathbf{C}} \cdot d\mathbf{x} = -\hat{\mathbf{C}} \cdot d\mathbf{x}_\zeta = -\hat{\mathbf{C}} \cdot \left(\mathbf{1}_T - \zeta \bar{\mathbf{C}}\right) \cdot d\mathbf{x} \tag{H.40}$$

whence follows

$$\hat{\mathbf{C}} = \bar{\mathbf{C}} \cdot \left(\mathbf{1}_T - \zeta \bar{\mathbf{C}}\right)^{-1} \tag{H.41}$$

The principal values are therefore connected by

$$\hat{c}_1 = \frac{\bar{c}_1}{1 - \zeta \bar{c}_1}, \qquad \hat{c}_2 = \frac{\bar{c}_2}{1 - \zeta \bar{c}_2} \tag{H.42}$$

and the invariants — *cf.* (C.12) — by

$$\hat{H} = \frac{1}{2}(\hat{c}_1 + \hat{c}_2) = \frac{\bar{H} - \zeta \bar{K}}{1 - 2\zeta \bar{H} + \zeta^2 \bar{K}}, \qquad \hat{K} = \hat{c}_1 \hat{c}_2 = \frac{\bar{K}}{1 - 2\zeta \bar{H} + \zeta^2 \bar{K}} \tag{H.43}$$

The surface elements are related by

$$d\hat{A} = \left(1 - 2\zeta \bar{H} + \zeta^2 \bar{K}\right) d\bar{A} \tag{H.44}$$

and the volume between these elements is

$$d\hat{V}_\zeta = \Big(\zeta - \zeta^2 \bar{H} + \frac{\zeta^3}{3}\bar{K}\Big)\, d\bar{A} \tag{H.45}$$

— *cf.* (D.7) and (D.9). If we make use of the fact, that the mean curvature of our original surface is nearly zero and hence put $\bar{H} = 0$, we find the simpler formulae

$$\hat{H} = \frac{-\zeta \bar{K}}{1 + \zeta^2 \bar{K}}\,, \qquad \hat{K} = \frac{\bar{K}}{1 + \zeta^2 \bar{K}} \tag{H.46}$$

$$d\hat{A} = \big(1 + \zeta^2 \bar{K}\big)\, d\bar{A} \tag{H.47}$$

$$\hat{V}_\zeta = \int_{\bar{A}} \Big(\zeta + \frac{\zeta^3}{3}\bar{K}\Big)\, d\bar{A} = \zeta \int_{\bar{A}} d\bar{A} + \frac{\zeta^3}{3}\int_{\bar{A}} \bar{K}\, d\bar{A} \tag{H.48}$$

The equations (H.46) have the interesting consequence

$$-\,\zeta = \frac{\hat{H}}{\hat{K}} = \frac{1}{2}\Big(\frac{1}{\hat{c}_1} + \frac{1}{\hat{c}_2}\Big) \tag{H.49}$$

The ratio of $\hat{H}$ and $\hat{K}$ possesses the constant value $-\zeta$ on the whole surface. While the arithmetic mean $\hat{H}$ of the principal curvatures is only constant in the special case $\zeta = 0$, the harmonic mean is constant for each ζ. Now, we remember our convention that the normal vector tends to the oil side of the surface. This indicates that the displacement of the points of our original surface in the direction of positive values of ζ diminishes the total oil-sided volume $\hat{V}_\mathrm{O}$ of the cell, which originally is half of the cell volume $\bar{V} = (2L)^3 = 8$. Since there are six deforming patches, we get

$$\frac{\hat{V}_\mathrm{O}}{\bar{V}} = \frac{4 - 6\,\hat{V}_\zeta}{8} = \frac{1}{2} - \frac{3}{4}\,\hat{V}_\zeta \tag{H.50}$$

and hence

$$\frac{\hat{V}_\mathrm{W}}{\bar{V}} = \frac{1}{2} + \frac{3}{4}\,\hat{V}_\zeta \tag{H.51}$$

Remark: A similar class of bi-continuous surfaces was studied in [7]. While the surface with $\zeta = 0$ was practically identical to the one defined above, the surfaces with $\zeta \neq 0$ were constructed on the basis of (H.13) instead of (H.38).

H.3 Numerical Integration on the Surfaces

The area element of the original surface can be written

$$d\bar{A} = \left|\frac{\partial \mathbf{x}}{\partial \xi}\, d\xi \times \frac{\partial \mathbf{x}}{\partial \eta}\, d\eta\right| = \big|\mathbf{g}_\xi \times \mathbf{g}_\eta\big| d\xi d\eta \tag{H.52}$$

and the integration of some function Φ over a surface patch is performed as follows

$$\begin{aligned}\int_{\hat{A}} \Phi \, d\hat{A} &= \int_{\bar{A}} \Phi \left(1+\zeta^2 \bar{K}\right) d\bar{A} \\ &= \int_{\xi=0}^{1} \int_{\eta=0}^{1} \Phi(\xi,\eta) \left(1+\zeta^2 \bar{K}(\xi,\eta)\right) \left|\mathbf{g}_\xi \times \mathbf{g}_\eta\right|(\xi,\eta) \, d\xi d\eta \qquad \text{(H.53)}\end{aligned}$$

This definite integral can easily be evaluated numerically.

Results for special cases are

$$\bar{A} = \int_{\bar{A}} d\bar{A} = 0.7816 \,, \qquad \int_{\bar{A}} \bar{K} \, d\bar{A} = -\frac{\pi}{6} = -0.5236 \qquad \text{(H.54)}$$

and hence

$$\hat{A} = \bar{A} - \frac{\pi}{6} \zeta^2 = 0.7816 - 0.5236 \, \zeta^2 \qquad \text{(H.55)}$$

and — with (H.50), (H.48) —

$$\frac{\hat{V}_{\mathrm{O}}}{\bar{V}} = \frac{1}{2} - \frac{3}{4} \bar{A} \, \zeta + \frac{\pi}{24} \zeta^3 = 0.5 - 0.5862 \, \zeta + 0.1309 \, \zeta^3 \qquad \text{(H.56)}$$

The last two formulae show the dependence of the patch area and the oil-sided volume on the parameter ζ. The value $-\pi/6$ in (H.54) can be obtained without integration from the Gauss-Bonnet theorem, since it represents the excess angle of the patch (sum of the four angles minus sum of the four angles of a quadrangle in a plane): $90^\circ + 90^\circ + 90^\circ + 60^\circ - 360^\circ = -30^\circ$.

I Inelastic Behaviour of a Thick Layer

I.1 Decomposition of the Transplacement

In chapter 3, the elastic and inelastic behaviour of a thick layer was discussed under the special assumption, that the principal axes of the stretching of the middle surface and of the bending of the layer coincide. In the following, we study the general case, but must use more advanced mathematical methods. It turns out that the co-axial case is the most interesting one if we restrict our attention to the relaxed state. But that is actually the state which we are in fact interested in.

The standard method of treating inelastic behavior is the multiplicative decomposition of the transplacement into an elastic and an inelastic part. (For a rigorous basis of this method *cf.* Krawietz [5]). We imagine the transplacement $\mathbf{F}$ of the line elements of the middle surface (which is a mapping from T_0 into T) as the succession of a transplacement $\mathbf{F}_{\mathrm{b}}$ (from T_0

into T_0) into the basic placement (often called intermediate placement) and an elastic transplacement $\mathbf{F}_\mathrm{e}$ (from T_0 into T).

$$\mathbf{F} = \mathbf{F}_\mathrm{e} \cdot \mathbf{F}_\mathrm{b} \tag{I.1}$$

The elastic transplacement is defined to be responsible for the stressing. That means: In the basic placement, before the elastic transplacement is performed, *i.e.* if $\mathbf{F}_\mathrm{e} = \mathbf{1}_{T_0}$ and $\mathbf{F} = \mathbf{F}_\mathrm{b}$, the middle surface is free of stress.
Another possible decomposition is the following one

$$\mathbf{F} = \mathbf{F}_\mathrm{e}^*(z) \cdot \mathbf{F}_{z\mathrm{b}}(z) \tag{I.2}$$

It is based on the definition that the layer at z is free of stress if $\mathbf{F}_\mathrm{e}^*(z) = \mathbf{1}_{T_0}$ and $\mathbf{F} = \mathbf{F}_{z\mathrm{b}}(z)$. Thus obviously

$$\mathbf{F}_\mathrm{e}^*(z=0) = \mathbf{F}_\mathrm{e}\,, \qquad \mathbf{F}_{z\mathrm{b}}(z=0) = \mathbf{F}_\mathrm{b}\,, \tag{I.3}$$

We set

$$\mathbf{F}_\mathrm{e}^*(z) = \mathbf{F}_\mathrm{e} \cdot \mathbf{F}_\mathrm{p}(z) \tag{I.4}$$

Then $\mathbf{F}_\mathrm{p}(z)$, called the predeformation, describes the elastic deformation of the layer at z which is present while the middle surface is not yet elastically stretched. These predeformations cause the prestress of the different layers. It seems reasonable to assume that the predeformation is isotropic, *i.e.* of the form

$$\mathbf{F}_\mathrm{p}(z) = \lambda_\mathrm{p}(z)\mathbf{1}_{T_0} \qquad \text{with} \qquad \lambda_\mathrm{p}(0) = 1 \tag{I.5}$$

We may additionally introduce the unloading deformation by

$$\mathbf{F}_\mathrm{u}(z) = \mathbf{F}_\mathrm{p}^{-1}(z) = \lambda_\mathrm{p}^{-1}(z)\mathbf{1}_{T_0} \tag{I.6}$$

Thus, from (I.1), (I.2), (I.4), we find

$$\mathbf{F}_{z\mathrm{b}}(z) = \mathbf{F}_\mathrm{u}(z) \cdot \mathbf{F}_\mathrm{b} \tag{I.7}$$

So the transplacement of the layer at z into its stress free placement is seen to be the basic transplacement $\mathbf{F}_\mathrm{b}$ of the middle layer (at $z = 0$) — which makes this layer free of stress —, followed by the unloading transplacement $\mathbf{F}_\mathrm{u}(z)$ — which stresses the middle layer and makes the layer at z free of stress.

After all, we need the multiplicative decomposition of the transplacement of the line elements of a layer at z in the form

$$\mathbf{F}_z(z) = \mathbf{F}_{z\mathrm{e}}(z) \cdot \mathbf{F}_{z\mathrm{b}}(z) \tag{I.8}$$

Noting (D.5), (I.2), (I.4), we get

$$\mathbf{F}_z(z) = \big(\mathbf{1}_T - z\,\mathbf{C}\big) \cdot \mathbf{F} = \big(\mathbf{1}_T - z\,\mathbf{C}\big) \cdot \mathbf{F}_\mathrm{e} \cdot \mathbf{F}_\mathrm{p}(z) \cdot \mathbf{F}_{z\mathrm{b}}(z) \tag{I.9}$$

and infer

$$\mathbf{F}_{z\mathrm{e}}(z) = \big(\mathbf{1}_T - z\,\mathbf{C}\big) \cdot \mathbf{F}_\mathrm{e} \cdot \mathbf{F}_\mathrm{p}(z) \tag{I.10}$$

We make use of the polar decomposition theorem

$$\mathbf{F}_\mathrm{e} = \mathbf{R}_\mathrm{e} \cdot \mathbf{U}_\mathrm{e} \tag{I.11}$$

saying that the elastic transplacement of the line elements of the middle surface may be regarded as the succession of a stretch tensor $\mathbf{U}_\mathrm{e}$, which is a symmetric and positive definite mapping of T_0 into T_0 and hence possesses a spectral representation

$$\mathbf{U}_\mathrm{e} = \lambda_{\mathrm{e}1}\,\mathbf{a}_1 \otimes \mathbf{a}_1 + \lambda_{\mathrm{e}2}\,\mathbf{a}_2 \otimes \mathbf{a}_2 \tag{I.12}$$

and a tensor of rotation $\mathbf{R}_\mathrm{e}$ which is a metric-preserving mapping of T_0 into T.

We denote the principal vectors of the tensor of curvature $\mathbf{C}$ by $\mathbf{e}_1, \mathbf{e}_2 \in T$ and define two orthogonal vectors $\mathbf{d}_1, \mathbf{d}_2 \in T_0$ by

$$\mathbf{d}_1 = \mathbf{R}_\mathrm{e}^T \cdot \mathbf{e}_1\,, \quad \mathbf{d}_2 = \mathbf{R}_\mathrm{e}^T \cdot \mathbf{e}_2 \tag{I.13}$$

whence follows the representation

$$\mathbf{R}_\mathrm{e} = \mathbf{e}_1 \otimes \mathbf{d}_1 + \mathbf{e}_2 \otimes \mathbf{d}_2 \tag{I.14}$$

We obtain with (C.4), (C.5)

$$\begin{aligned} \mathbf{1}_T - z\,\mathbf{C} &= (1 - c_1 z)\,\mathbf{e}_1 \otimes \mathbf{e}_1 + (1 - c_2 z)\,\mathbf{e}_2 \otimes \mathbf{e}_2 \\ &= \mathbf{R}_\mathrm{e} \cdot \Big((1 - c_1 z)\,\mathbf{d}_1 \otimes \mathbf{d}_1 + (1 - c_2 z)\,\mathbf{d}_2 \otimes \mathbf{d}_2\Big) \cdot \mathbf{R}_\mathrm{e}^T \equiv \mathbf{R}_\mathrm{e} \cdot \mathbf{U}_\mathrm{c}(z) \cdot \mathbf{R}_\mathrm{e}^T \end{aligned} \tag{I.15}$$

Finally we arrive at the decomposition — note (I.5), (I.10), (I.11), (I.15) —

$$\mathbf{F}_{z\mathrm{e}}(z) = \mathbf{R}_\mathrm{e} \cdot \mathbf{U}_\mathrm{c}(z) \cdot \mathbf{U}_\mathrm{e} \cdot \lambda_\mathrm{p}(z)\mathbf{1}_{T_0} \tag{I.16}$$

The elastic deformation of the layer at z is therefore seen to be the succession of an isotropic predeformation of this layer, the elastic stretching of the middle layer, a stretching due to the bending of the thick layer, and a rigid body rotation from the plane T_0 of the reference placement into the actual tangential plane T.

It will also be useful to introduce the polar decomposition of this elastic deformation

$$\mathbf{F}_{z\mathrm{e}}(z) = \mathbf{R}_{z\mathrm{e}}(z) \cdot \mathbf{U}_{z\mathrm{e}}(z) \tag{I.17}$$

where the stretch tensor $\mathbf{U}_{z\mathrm{e}}(z)$ is a symmetric and positive definite mapping of T_0 into T_0 and $\mathbf{R}_{z\mathrm{e}}(z)$ a rotation from T_0 into T.

With (I.6), (I.7), (I.8) and (I.17), we may represent the transplacement of the layer z as

$$\mathbf{F}_z(z) = \mathbf{R}_{z\mathrm{e}}(z) \cdot \mathbf{U}_{z\mathrm{e}}(z) \cdot \mathbf{F}_\mathrm{p}^{-1}(z) \cdot \mathbf{F}_\mathrm{b} \tag{I.18}$$

We further define, in analogy to (B.17) the rate of deformation tensor of the layer z and find — note that the predeformation $\mathbf{F}_\mathrm{p}$ does not change with time —

$$\begin{aligned}\mathbf{L}_z \quad &\equiv \quad \dot{\mathbf{F}}_z \cdot \mathbf{F}_z^{-1} = \dot{\mathbf{R}}_{z\mathrm{e}} \cdot \mathbf{R}_{z\mathrm{e}}^T + \mathbf{R}_{z\mathrm{e}} \cdot \dot{\mathbf{U}}_{z\mathrm{e}} \cdot \mathbf{U}_{z\mathrm{e}}^{-1} \cdot \mathbf{R}_{z\mathrm{e}}^T \\ &\quad + \mathbf{R}_{z\mathrm{e}} \cdot \mathbf{U}_{z\mathrm{e}} \cdot \mathbf{F}_\mathrm{p}^{-1} \cdot \dot{\mathbf{F}}_\mathrm{b} \cdot \mathbf{F}_\mathrm{b}^{-1} \cdot \mathbf{F}_\mathrm{p} \cdot \mathbf{U}_{z\mathrm{e}}^{-1} \cdot \mathbf{R}_{z\mathrm{e}}^T \end{aligned} \qquad (I.19)$$

I.2 Elastic Strains and Invariants

The rotation in (I.17) is eliminated by introducing the right Cauchy-Green tensor, which is the square of the stretch tensor and hence also symmetric and positive definite and of which we will also need the spectral representation

$$\begin{aligned}\mathbf{C}_{z\mathrm{e}}(z) \quad &\equiv \quad \mathbf{F}_{z\mathrm{e}}^T(z) \cdot \mathbf{F}_{z\mathrm{e}}(z) = \lambda_\mathrm{p}^2(z)\, \mathbf{U}_\mathrm{e} \cdot \mathbf{U}_\mathrm{c}^2(z) \cdot \mathbf{U}_\mathrm{e} \\ = \mathbf{U}_{z\mathrm{e}}^2(z) \quad &= \quad \lambda_{z\mathrm{e}1}^2(z)\, \mathbf{b}_1(z) \otimes \mathbf{b}_1(z) + \lambda_{z\mathrm{e}2}^2(z)\, \mathbf{b}_2(z) \otimes \mathbf{b}_2(z) \end{aligned} \qquad (I.20)$$

The logarithmic principal strains

$$\epsilon_1(z) = \ln \lambda_{z\mathrm{e}1}(z)\,, \quad \epsilon_2(z) = \ln \lambda_{z\mathrm{e}2}(z) \qquad (I.21)$$

are the proper numbers of the logarithmic elastic strain tensor of the layer at z

$$\mathbf{H}(z) \equiv \ln \mathbf{U}_{z\mathrm{e}}(z) = \frac{1}{2} \ln \mathbf{C}_{z\mathrm{e}}(z) = \epsilon_1(z)\, \mathbf{b}_1(z) \otimes \mathbf{b}_1(z) + \epsilon_2(z)\, \mathbf{b}_2(z) \otimes \mathbf{b}_2(z) \qquad (I.22)$$

We further introduce the logarithmic prestrain

$$\epsilon_\mathrm{p}(z) = \ln \lambda_\mathrm{p}(z) \qquad \text{with} \qquad \epsilon_\mathrm{p}(0) = 0 \qquad (I.23)$$

and the logarithmic elastic principal strains of the middle surface

$$\epsilon_{\mathrm{e}1} = \ln \lambda_{\mathrm{e}1}\,, \quad \epsilon_{\mathrm{e}2} = \ln \lambda_{\mathrm{e}2} \qquad (I.24)$$

as well as their sum and difference

$$\epsilon_\mathrm{es} = \epsilon_{\mathrm{e}1} + \epsilon_{\mathrm{e}2}\,, \quad \epsilon_\mathrm{ed} = \epsilon_{\mathrm{e}1} - \epsilon_{\mathrm{e}2} \qquad (I.25)$$

This allows the representation — *cf.* (I.12) —

$$\mathbf{U}_\mathrm{e} = \exp(\epsilon_\mathrm{es}/2)\Big(\exp(\epsilon_\mathrm{ed}/2)\, \mathbf{a}_1 \otimes \mathbf{a}_1 \, + \, \exp(-\epsilon_\mathrm{ed}/2)\, \mathbf{a}_2 \otimes \mathbf{a}_2 \Big) \qquad (I.26)$$

Next we want to determine some invariants of the tensor $\mathbf{H}$. To this purpose, we first introduce the angle α between the principal axes of $\mathbf{U}_\mathrm{e}$ and $\mathbf{U}_\mathrm{c}$ by putting

$$\mathbf{d}_1 = \cos\alpha\, \mathbf{a}_1 + \sin\alpha\, \mathbf{a}_2 \qquad \mathbf{d}_2 = -\sin\alpha\, \mathbf{a}_1 + \cos\alpha\, \mathbf{a}_2 \qquad (I.27)$$

Then we evaluate the tensor $\mathbf{C}_{ze}(z)$ by means of (I.15), (I.20), (I.21), (I.23), (I.26) and obtain

$$\begin{aligned}\mathbf{C}_{ze}(z) &= \exp\big(2\epsilon_1(z)\big)\,\mathbf{b}_1(z)\otimes\mathbf{b}_1(z)+\exp\big(2\epsilon_2(z)\big)\,\mathbf{b}_2(z)\otimes\mathbf{b}_2(z)\\ &= \exp\big(2\epsilon_{\rm p}(z)\big)\exp\big(\epsilon_{\rm es}\big)\big(1-c_1z\big)\big(1-c_2z\big)\,\mathbf{B}(z) \qquad \text{(I.28)}\end{aligned}$$

with

$$\begin{aligned}\mathbf{B}(z) \;&\equiv\; \beta_1(z)\,\mathbf{b}_1(z)\otimes\mathbf{b}_1(z)+\beta_2(z)\,\mathbf{b}_2(z)\otimes\mathbf{b}_2(z)\\ &= \frac{1-c_1z}{1-c_2z}\Big(\exp(\epsilon_{\rm ed})\cos^2\alpha\;\mathbf{a}_1\otimes\mathbf{a}_1\\ &\qquad +\cos\alpha\sin\alpha\,\big(\mathbf{a}_1\otimes\mathbf{a}_2+\mathbf{a}_2\otimes\mathbf{a}_1\big)+\exp(-\epsilon_{\rm ed})\sin^2\alpha\;\mathbf{a}_2\otimes\mathbf{a}_2\Big)\\ &\quad+\frac{1-c_2z}{1-c_1z}\Big(\exp(\epsilon_{\rm ed})\sin^2\alpha\;\mathbf{a}_1\otimes\mathbf{a}_1\\ &\qquad -\cos\alpha\sin\alpha\,\big(\mathbf{a}_1\otimes\mathbf{a}_2+\mathbf{a}_2\otimes\mathbf{a}_1\big)+\exp(-\epsilon_{\rm ed})\cos^2\alpha\;\mathbf{a}_2\otimes\mathbf{a}_2\Big)\end{aligned} \qquad \text{(I.29)}$$

The classical invariants of this auxiliary tensor are found to be

$$\det\mathbf{B}(z)=1 \qquad \text{(I.30)}$$

and

$$\begin{aligned}\operatorname{tr}\mathbf{B}(z) &= \frac{1-c_1z}{1-c_2z}\Big(\exp(\epsilon_{\rm ed})\cos^2\alpha+\exp(-\epsilon_{\rm ed})\sin^2\alpha\Big)\\ &\quad+\frac{1-c_2z}{1-c_1z}\Big(\exp(\epsilon_{\rm ed})\sin^2\alpha+\exp(-\epsilon_{\rm ed})\cos^2\alpha\Big)\\ &= \frac{1-c_1z}{1-c_2z}\exp(\epsilon_{\rm ed})+\frac{1-c_2z}{1-c_1z}\exp(-\epsilon_{\rm ed})\\ &\quad+\Big(\frac{1-c_2z}{1-c_1z}-\frac{1-c_1z}{1-c_2z}\Big)\Big(\exp(\epsilon_{\rm ed})-\exp(-\epsilon_{\rm ed})\Big)\sin^2\alpha\end{aligned} \qquad \text{(I.31)}$$

The proper numbers of (I.28) are

$$\exp\big(2\epsilon_j(z)\big)=\exp\big(2\epsilon_{\rm p}(z)\big)\exp\big(\epsilon_{\rm es}\big)\big(1-c_1z\big)\big(1-c_2z\big)\beta_j(z)\,,\qquad j=1,2 \qquad \text{(I.32)}$$

whence follows

$$\epsilon_j(z)=\epsilon_{\rm p}(z)+\frac{1}{2}\epsilon_{\rm es}+\frac{1}{2}\ln\big(1-c_1z\big)+\frac{1}{2}\ln\big(1-c_2z\big)+\frac{1}{2}\ln\beta_j(z)\,,\qquad j=1,2 \qquad \text{(I.33)}$$

We are now interested in the following invariants of the Tensor $\mathbf{H}$

$$I_1(z) = \epsilon_1(z) + \epsilon_2(z)\,, \qquad I_2(z) = \big(\epsilon_1(z) - \epsilon_2(z)\big)^2 \tag{I.34}$$

Because of

$$\frac{1}{2}\Big(\ln\beta_1(z) + \ln\beta_2(z)\Big) = \frac{1}{2}\ln\Big(\beta_1(z)\beta_2(z)\Big) = \frac{1}{2}\ln\det\mathbf{B}(z) = 0 \tag{I.35}$$

we easily get the first invariant

$$I_1(z) = 2\epsilon_{\rm p}(z) + \epsilon_{\rm es} + \ln(1 - c_1\, z) + \ln(1 - c_2\, z) \tag{I.36}$$

The ansatz

$$\beta_1(z) = \exp(q(z))\,, \qquad \beta_2(z) = \exp(-q(z)) \tag{I.37}$$

satisfies (I.35) and leads to

$$\operatorname{tr}\mathbf{B}(z) = \beta_1(z) + \beta_2(z) = 2\cosh q(z) \tag{I.38}$$

We assume

$$q(z) \geq 0 \quad \Longleftrightarrow \quad \beta_1(z) \geq \beta_2(z) \tag{I.39}$$

(This implies a special numbering of the principal values of $\mathbf{B}$.) So we obtain

$$q(z) = \operatorname{arccosh}\frac{\operatorname{tr}\mathbf{B}(z)}{2} \tag{I.40}$$

and arrive at the second invariant

$$I_2(z) = \left(\frac{1}{2}\big(\ln\beta_1(z) - \ln\beta_2(z)\big)\right)^2 = q(z)^2 = \left(\operatorname{arccosh}\frac{\operatorname{tr}\mathbf{B}(z)}{2}\right)^2 \tag{I.41}$$

with $\operatorname{tr}\mathbf{B}(z)$ according to (I.31).

The derivative of this invariant with respect to some parameter p is obtained as

$$\frac{\partial I_2(z)}{\partial p} = I_{\rm d}(z)\,\frac{\partial \operatorname{tr}\mathbf{B}(z)}{\partial p} \tag{I.42}$$

with the abbreviation

$$I_{\rm d}(z) = \frac{dI_2(z)}{d\operatorname{tr}\mathbf{B}(z)} = \frac{\sqrt{I_2(z)}}{\sinh\sqrt{I_2(z)}} \tag{I.43}$$

Finally we provide a representation of $\dot{\mathbf{U}}_{z\rm e}(z)\cdot\mathbf{U}_{z\rm e}^{-1}(z)$ for later use. We get from (I.20), (I.21)

$$\mathbf{U}_{z\rm e} = \exp\big(\epsilon_1\big)\;\mathbf{b}_1\otimes\mathbf{b}_1 + \exp\big(\epsilon_2\big)\;\mathbf{b}_2\otimes\mathbf{b}_2 \tag{I.44}$$

(The dependence on z will not be mentioned explicitly.) During an increase of elastic deformation, not only the principal strains ϵ_1, ϵ_2 change but also the principal directions may rotate according to

$$\dot{\mathbf{b}}_1 = \omega\,\mathbf{b}_2\,, \qquad \dot{\mathbf{b}}_2 = -\omega\,\mathbf{b}_1 \tag{I.45}$$

Therefore

$$\begin{aligned}
\dot{\mathbf{U}}_{z\mathrm{e}} \cdot \mathbf{U}_{z\mathrm{e}}^{-1} \;=\; & \Big(\dot{\epsilon_1}\,\exp\big(\epsilon_1\big)\,\mathbf{b}_1\otimes\mathbf{b}_1 + \dot{\epsilon_2}\,\exp\big(\epsilon_2\big)\,\mathbf{b}_2\otimes\mathbf{b}_2 \\
& + \exp\big(\epsilon_1\big)\,(\dot{\mathbf{b}}_1\otimes\mathbf{b}_1 + \mathbf{b}_1\otimes\dot{\mathbf{b}}_1) + \exp\big(\epsilon_2\big)\,(\dot{\mathbf{b}}_2\otimes\mathbf{b}_2 + \mathbf{b}_2\otimes\dot{\mathbf{b}}_2)\Big) \times \\
& \Big(\exp\big(-\epsilon_1\big)\,\mathbf{b}_1\otimes\mathbf{b}_1 + \exp\big(-\epsilon_2\big)\,\mathbf{b}_2\otimes\mathbf{b}_2\Big) \\
= \;& \dot{\epsilon_1}\,\mathbf{b}_1\otimes\mathbf{b}_1 + \dot{\epsilon_2}\,\mathbf{b}_2\otimes\mathbf{b}_2 \\
& + \omega\Big(\Big(\exp\big(\epsilon_1-\epsilon_2\big)-1\Big)\,\mathbf{b}_1\otimes\mathbf{b}_2 + \Big(1-\exp\big(\epsilon_2-\epsilon_1\big)\Big)\,\mathbf{b}_2\otimes\mathbf{b}_1\Big) \qquad \text{(I.46)}
\end{aligned}$$

An important consequence of this formula is — note (I.34) —

$$\mathbf{1}_{T_0} : \dot{\mathbf{U}}_{z\mathrm{e}}(z)\cdot\mathbf{U}_{z\mathrm{e}}^{-1}(z) = \dot{\epsilon_1}(z) + \dot{\epsilon_2}(z) = \dot{I}_1(z) \qquad \text{(I.47)}$$

I.3 Mass

Computing the determinant of (I.16), (I.17), we find

$$\det\mathbf{F}_{z\mathrm{e}}(z) = \det\mathbf{U}_{z\mathrm{e}}(z) = \det\mathbf{U}_{\mathrm{c}}(z)\;\det\mathbf{U}_{\mathrm{e}}\,\lambda_{\mathrm{p}}^2(z) \qquad \text{(I.48)}$$

While the elastic stretch of the layer at z from its stress free placement is built up from a prestretch, the stretch of the middle surface and the stretch of bending, the sequence of the corresponding area elements is $dA_{z\mathrm{b}}$, dA_{b}, dA, and dA_z. Their ratios are obtained from — note (I.23), (I.26), (I.15) (see also (D.7)), and (I.44) with (I.34) —

$$\frac{dA_{\mathrm{b}}}{dA_{z\mathrm{b}}} = \lambda_{\mathrm{p}}^2(z) = \exp\big(2\epsilon_{\mathrm{p}}(z)\big) \qquad \text{(I.49)}$$

$$\frac{dA}{dA_{\mathrm{b}}} = \det\mathbf{U}_{\mathrm{e}} = \exp\big(\epsilon_{\mathrm{es}}\big) \qquad \text{(I.50)}$$

$$\frac{dA_z}{dA} = \det\mathbf{U}_{\mathrm{c}}(z) = (1-c_1\,z)(1-c_2\,z) \qquad \text{(I.51)}$$

$$\frac{dA_z}{dA_{z\mathrm{b}}} = \det\mathbf{U}_{z\mathrm{e}}(z) = \exp\big(\epsilon_1(z)+\epsilon_2(z)\big) = \exp\big(I_1(z)\big) \qquad \text{(I.52)}$$

The last equation gives an interpretation of I_1 as a measure of the elastic change of area of the layer.

We assume for the sake of simplicity that neither the thickness dz of the layer at z nor the total thickness h of the thick layer undergo any change during a deformation process. Then equation (3.19)

$$\begin{aligned} dm &= \int_{z=-h/2}^{h/2} \varrho(z)\, dA_z(z)\, dz = \int_{z=-h/2}^{h/2} (1-c_1 z)(1-c_2 z)\, \varrho(z)\, dz\, dA \\ &\equiv \mu\, dA = \mu \exp\big(\epsilon_{\mathrm{es}}\big)\, dA_{\mathrm{b}} = \mu_{\mathrm{b}}\, dA_{\mathrm{b}} \end{aligned} \tag{I.53}$$

is seen to remain valid even if the axes of the stretch of the middle surface and of the curvature do not coincide. The same is true with its consequence

$$\frac{\dot\mu}{\mu} = -\,\dot\epsilon_{\mathrm{es}} \tag{I.54}$$

which results from the postulate that μ_{b} must be constant with time.

The trace of (I.19) yields — note (B.30) and (I.47)—

$$\frac{\dot{\overline{dA_z}}}{dA_z} = \mathrm{tr}\, \mathbf{L}_z = \mathrm{tr}\Big(\dot{\mathbf{U}}_{z\mathrm{e}} \cdot \mathbf{U}_{z\mathrm{e}}^{-1}\Big) + \mathrm{tr}\Big(\dot{\mathbf{F}}_{\mathrm{b}} \cdot \mathbf{F}_{\mathrm{b}}^{-1}\Big) = \dot I_1(z) + \mathrm{tr}\Big(\dot{\mathbf{F}}_{\mathrm{b}} \cdot \mathbf{F}_{\mathrm{b}}^{-1}\Big) \tag{I.55}$$

and restricting our attention to the middle surface $z = 0$, we find, with (I.36),

$$\frac{\dot{\overline{dA}}}{dA} - \mathrm{tr}\Big(\dot{\mathbf{F}}_{\mathrm{b}} \cdot \mathbf{F}_{\mathrm{b}}^{-1}\Big) = \dot I_1(z=0) = \dot\epsilon_{\mathrm{es}} = -\frac{\dot\mu}{\mu} \tag{I.56}$$

The mass which is supplied from the environment per unit time and unit area of the actual middle surface shall be denoted by $\tilde\mu$, and the rate of mass can be written

$$\begin{aligned} \dot{\overline{dm}} = \tilde\mu\, dA &= \big(\mu\, dA\big)^{\bullet} = \left(\frac{\dot\mu}{\mu} + \frac{\dot{\overline{dA}}}{dA}\right) \mu\, dA = \mathrm{tr}\Big(\dot{\mathbf{F}}_{\mathrm{b}} \cdot \mathbf{F}_{\mathrm{b}}^{-1}\Big)\, \mu\, dA \\ &= \big(\mu_{\mathrm{b}} dA_{\mathrm{b}}\big)^{\bullet} = \mu_{\mathrm{b}} \dot{\overline{dA_{\mathrm{b}}}} \end{aligned} \tag{I.57}$$

from which we infer

$$\frac{\tilde\mu}{\mu} = \frac{\dot{\overline{dA_{\mathrm{b}}}}}{dA_{\mathrm{b}}} = \mathrm{tr}\Big(\dot{\mathbf{F}}_{\mathrm{b}} \cdot \mathbf{F}_{\mathrm{b}}^{-1}\Big) \tag{I.58}$$

I.4 Power and Energy

We describe the state of plane stress in the layer at z by a tensor $\boldsymbol{\sigma}(z)$, which is a mapping of T into T. Now $\mathbf{b}_1(z),\ \mathbf{b}_2(z)$ form an orthonormal basis of T_0 and hence $\mathbf{R}_{z\mathrm{e}}(z) \cdot \mathbf{b}_1(z),\ \mathbf{R}_{z\mathrm{e}}(z) \cdot \mathbf{b}_2(z)$ an orthonormal basis of T. The stress tensor may hence be written — the dependence on z is not made explicit —

$$\boldsymbol{\sigma} = \mathbf{R}_{z\mathrm{e}} \cdot \big(\sigma_{11}\, \mathbf{b}_1 \otimes \mathbf{b}_1 + \sigma_{12} \mathbf{b}_1 \otimes \mathbf{b}_2 + \sigma_{21} \mathbf{b}_2 \otimes \mathbf{b}_1 + \sigma_{22}\, \mathbf{b}_2 \otimes \mathbf{b}_2\big) \cdot \mathbf{R}_{z\mathrm{e}}^T \tag{I.59}$$

With (I.19), the stress power in the layer at z referred to the actual unit volume can be represented as

$$\begin{aligned} P_z \;&=\; \boldsymbol{\sigma} : \mathbf{L}_z = \boldsymbol{\sigma} : \Big(\dot{\mathbf{R}}_{z\mathrm{e}} \cdot \mathbf{R}_{z\mathrm{e}}^T + \mathbf{R}_{z\mathrm{e}} \cdot \dot{\mathbf{U}}_{z\mathrm{e}} \cdot \mathbf{U}_{z\mathrm{e}}^{-1} \cdot \mathbf{R}_{z\mathrm{e}}^T \\ &\qquad + \mathbf{R}_{z\mathrm{e}} \cdot \mathbf{U}_{z\mathrm{e}} \cdot \mathbf{F}_{\mathrm{p}}^{-1} \cdot \dot{\mathbf{F}}_{\mathrm{b}} \cdot \mathbf{F}_{\mathrm{b}}^{-1} \cdot \mathbf{F}_{\mathrm{p}} \cdot \mathbf{U}_{z\mathrm{e}}^{-1} \cdot \mathbf{R}_{z\mathrm{e}}^T \Big) \end{aligned} \tag{I.60}$$

In case of a pure rigid body rotation, we have $\dot{\mathbf{U}}_{z\mathrm{e}} = 0$ and $\dot{\mathbf{F}}_{\mathrm{b}} = 0$ while $\dot{\mathbf{R}}_{z\mathrm{e}} \cdot \mathbf{R}_{z\mathrm{e}}^T$ is an arbitrary skew tensor which maps T into T. The condition that the internal forces of a body do no work during a rigid body motion is satisfied, if and only if the stress tensor $\boldsymbol{\sigma}$ is symmetric, *i.e.* $\sigma_{12} = \sigma_{21}$. In case of a sudden and hence purely elastic deformation, we have with (I.46)

$$\begin{aligned} P_z \;&=\; \mathbf{R}_{z\mathrm{e}}^T \cdot \boldsymbol{\sigma} \cdot \mathbf{R}_{z\mathrm{e}} : \dot{\mathbf{U}}_{z\mathrm{e}} \cdot \mathbf{U}_{z\mathrm{e}}^{-1} \\ &=\; \sigma_{11}\,\dot{\epsilon}_1 + \sigma_{22}\,\dot{\epsilon}_2 + \sigma_{12}\,\omega \Big(\exp(\epsilon_1 - \epsilon_2) - \exp(\epsilon_2 - \epsilon_1) \Big) \end{aligned} \tag{I.61}$$

Moreover, the value of dA_{z0} is not changed and (I.55) reduces to

$$\frac{\dot{\overline{dA_z}}}{dA_z} = \dot{I}_1 = \dot{\epsilon}_1 + \dot{\epsilon}_2 \tag{I.62}$$

Then all of the work of the stresses is fully stored and gives rise to an increase of the strain energy. This strain energy — referred to the actual unit volume — depends on the elastic deformation only through its invariants, because the elastic behaviour is assumed to be isotropic within the layer. Therefore we write $w_z(I_1, I_2)$ or $w_z(\epsilon_1, \epsilon_2)$ and find

$$P_z\, dA_z\, dz = (w_z\, dA_z\, dz)^{\bullet} = \left(\dot{w}_z + w_z \frac{\dot{\overline{dA_z}}}{dA_z} \right) dA_z\, dz \tag{I.63}$$

and hence

$$\begin{aligned} P_z \;&=\; \sigma_{11}\,\dot{\epsilon}_1 + \sigma_{22}\,\dot{\epsilon}_2 + \sigma_{12}\,\omega \Big(\exp(\epsilon_1 - \epsilon_2) - \exp(\epsilon_2 - \epsilon_1) \Big) \\ &=\; \frac{\partial w_z}{\partial \epsilon_1} \dot{\epsilon}_1 + \frac{\partial w_z}{\partial \epsilon_2} \dot{\epsilon}_2 + w_z \big(\dot{\epsilon}_1 + \dot{\epsilon}_2 \big) \end{aligned} \tag{I.64}$$

Since $\dot{\epsilon}_1$, $\dot{\epsilon}_2$ and ω are arbitrary, we infer the potential relations

$$\begin{aligned} \sigma_{11} = w_z + \frac{\partial w_z}{\partial \epsilon_1} = w_z + \frac{\partial w_z}{\partial I_1} + 2(\varepsilon_1 - \varepsilon_2) \frac{\partial w_z}{\partial I_2} = w_z + \frac{\partial w_z}{\partial I_1} + (4\varepsilon_1 - 2I_1) \frac{\partial w_z}{\partial I_2} \\ \sigma_{22} = w_z + \frac{\partial w_z}{\partial \epsilon_2} = w_z + \frac{\partial w_z}{\partial I_1} + 2(\varepsilon_2 - \varepsilon_1) \frac{\partial w_z}{\partial I_2} = w_z + \frac{\partial w_z}{\partial I_1} + (4\varepsilon_2 - 2I_1) \frac{\partial w_z}{\partial I_2} \end{aligned} \tag{I.65}$$

Moreover, we must have $\sigma_{12} = 0$ in the case $\epsilon_1 \neq \epsilon_2$. The back-rotated stress tensor $\mathbf{R}_{z\mathrm{e}}^T \cdot \boldsymbol{\sigma} \cdot \mathbf{R}_{z\mathrm{e}}$ is therefore co-axial to the strain tensor $\mathbf{H}_\mathrm{e}$. The case $\epsilon_1 = \epsilon_2$ yields $\sigma_{11} = \sigma_{22}$. Any direction in T_0 may then be chosen as $\mathbf{b}_1$ or $\mathbf{b}_2$, the normal stresses are equal in all directions and therefore $\sigma_{12} = 0$ must be valid in this case, too. The equations (I.65) turn out to be the principal components of the tensor equation

$$\mathbf{R}_{z\mathrm{e}}^T \cdot \boldsymbol{\sigma} \cdot \mathbf{R}_{z\mathrm{e}} = w_z \mathbf{1}_{T_0} + \frac{\partial w_z}{\partial \mathbf{H}} = \left(w_z + \frac{\partial w_z}{\partial I_1} \right) \mathbf{1}_{T_0} + 4 \, \frac{\partial w_z}{\partial I_2} \left(\mathbf{H} - \frac{I_1}{2} \mathbf{1}_{T_0} \right) \tag{I.66}$$

The tensor on the right-hand side appears decomposed into an isotropic and a deviatoric part (in two dimensions), since the tensor in the bracket is the deviator of $\mathbf{H}$.

A part of the thick layer corresponding to the area dA of the middle surface contains the energy

$$\begin{aligned} & \int_{z=-h/2}^{h/2} w_z\big(I_1(z), I_2(z)\big) \, dA_z(z) \, dz \\ = & \int_{z=-h/2}^{h/2} (1 - c_1 z)(1 - c_2 z) \, w_z\big(I_1(z), I_2(z)\big) \, dz \, dA \\ = & \; w\big(c_1, c_2, \epsilon_{\mathrm{es}}, \epsilon_{\mathrm{ed}}, \alpha\big) \, dA \, . \end{aligned} \tag{I.67}$$

While w_z denotes the energy per actual unit volume of the layer at z, w refers the energy of the thick layer to the actual unit area of the middle surface.

The rate of energy can be written with (I.56)

$$\begin{aligned} \big(w \, dA\big)^{\bullet} &= \left(\dot{w} + w \, \frac{\dot{\overline{dA}}}{dA} \right) dA \\ &= \left(\frac{\partial w}{\partial c_1} \dot{c}_1 + \frac{\partial w}{\partial c_2} \dot{c}_2 + \frac{\partial w}{\partial \epsilon_{\mathrm{es}}} \dot{\epsilon}_{\mathrm{es}} + \frac{\partial w}{\partial \epsilon_{\mathrm{ed}}} \dot{\epsilon}_{\mathrm{ed}} + \frac{\partial w}{\partial \alpha} \dot{\alpha} \right) dA \\ & \quad + w \left(\dot{\epsilon}_{\mathrm{es}} + \mathrm{tr} \left(\dot{\mathbf{F}}_\mathrm{b} \cdot \mathbf{F}_\mathrm{b}^{-1} \right) \right) dA \end{aligned} \tag{I.68}$$

with

$$\frac{\partial w}{\partial c_1} = -\int\limits_{z=-h/2}^{h/2} (1-c_1 z)(1-c_2 z)\left(w_z + \frac{\partial w_z}{\partial I_1} + I_{\mathrm{d}}(z)\, y_{\mathrm{c}}(z)\frac{\partial w_z}{\partial I_2}\right)\frac{z}{1-c_1 z}\, dz\,,$$

$$\frac{\partial w}{\partial c_2} = -\int\limits_{z=-h/2}^{h/2} (1-c_1 z)(1-c_2 z)\left(w_z + \frac{\partial w_z}{\partial I_1} - I_{\mathrm{d}}(z)\, y_{\mathrm{c}}(z)\frac{\partial w_z}{\partial I_2}\right)\frac{z}{1-c_2 z}\, dz\,,$$

$$\frac{\partial w}{\partial \epsilon_{\mathrm{es}}} = \int_{z=-h/2}^{h/2} (1-c_1 z)(1-c_2 z)\,\frac{\partial w_z}{\partial I_1}\, dz\,,$$

$$\frac{\partial w}{\partial \epsilon_{\mathrm{ed}}} = \int_{z=-h/2}^{h/2} (1-c_1 z)(1-c_2 z)\, I_{\mathrm{d}}(z)\, y_{\mathrm{d}}(z)\frac{\partial w_z}{\partial I_2}\, dz\,,$$

$$\frac{\partial w}{\partial \alpha} = \int_{z=-h/2}^{h/2} (1-c_1 z)(1-c_2 z)\, I_{\mathrm{d}}(z)\, y_{\alpha}(z)\frac{\partial w_z}{\partial I_2}\, dz \tag{I.69}$$

and the abbreviations

$$\begin{aligned} y_{\mathrm{c}}(z) &= -\frac{1-c_1\,z}{z}\,\frac{\partial\,\mathrm{tr}\,\mathbf{B}(z)}{\partial c_1} = \frac{1-c_2\,z}{z}\,\frac{\partial\,\mathrm{tr}\,\mathbf{B}(z)}{\partial c_2} \\ &= \frac{1-c_1\,z}{1-c_2\,z}\,\exp(\epsilon_{\mathrm{ed}}) - \frac{1-c_2\,z}{1-c_1\,z}\,\exp(-\epsilon_{\mathrm{ed}}) \\ &\quad -\left(\frac{1-c_2\,z}{1-c_1\,z} + \frac{1-c_1\,z}{1-c_2\,z}\right)\big(\exp(\epsilon_{\mathrm{ed}}) - \exp(-\epsilon_{\mathrm{ed}})\big)\sin^2\alpha \end{aligned} \tag{I.70}$$

$$\begin{aligned} y_{\mathrm{d}}(z) &= \frac{\partial \mathrm{tr}\,\mathbf{B}(z)}{\partial \epsilon_{\mathrm{ed}}} = \frac{1-c_1\,z}{1-c_2\,z}\,\exp(\epsilon_{\mathrm{ed}}) - \frac{1-c_2\,z}{1-c_1\,z}\,\exp(-\epsilon_{\mathrm{ed}}) \\ &\quad +\left(\frac{1-c_2\,z}{1-c_1\,z} - \frac{1-c_1\,z}{1-c_2\,z}\right)\big(\exp(\epsilon_{\mathrm{ed}}) + \exp(-\epsilon_{\mathrm{ed}})\big)\sin^2\alpha \end{aligned} \tag{I.71}$$

$$\begin{aligned} y_{\alpha}(z) &= \frac{\partial \mathrm{tr}\,\mathbf{B}(z)}{\partial \alpha} \\ &= \left(\frac{1-c_2\,z}{1-c_1\,z} - \frac{1-c_1\,z}{1-c_2\,z}\right)\big(\exp(\epsilon_{\mathrm{ed}}) - \exp(-\epsilon_{\mathrm{ed}})\big)2\,\sin\alpha\cos\alpha \end{aligned} \tag{I.72}$$

We go back to (I.59) and (I.60). Since we know meanwhile that $\sigma_{12} = \sigma_{21} = 0$, we obtain

$$\sigma_{11}\,\mathbf{b}_1\!\otimes\!\mathbf{b}_1\!+\!\sigma_{22}\,\mathbf{b}_2\!\otimes\!\mathbf{b}_2=\mathbf{R}^T_{z\mathrm{e}}\!\cdot\!\boldsymbol{\sigma}\!\cdot\!\mathbf{R}_{z\mathrm{e}}=\mathbf{F}_\mathrm{p}\!\cdot\!\mathbf{U}^{-1}_{z\mathrm{e}}\!\cdot\!\mathbf{R}^T_{z\mathrm{e}}\!\cdot\!\boldsymbol{\sigma}\!\cdot\!\mathbf{R}_{z\mathrm{e}}\!\cdot\!\mathbf{U}_{z\mathrm{e}}\!\cdot\!\mathbf{F}^{-1}_\mathrm{p} \quad \text{(I.73)}$$

The last equation is valid since $\mathbf{F}_\mathrm{p}$ and $\mathbf{U}_{z\mathrm{e}}$ commute with $\mathbf{R}^T_{z\mathrm{e}}\cdot\boldsymbol{\sigma}\cdot\mathbf{R}_{z\mathrm{e}}$ according to (I.5) and (I.44) because they have common principal axes. The power of the layer at z during an elastic and inelastic deformation can therefore be written

$$P_z=\big(\sigma_{11}\,\mathbf{b}_1\otimes\mathbf{b}_1+\sigma_{22}\,\mathbf{b}_2\otimes\mathbf{b}_2\big):\Big(\dot{\mathbf{U}}_{z\mathrm{e}}\cdot\mathbf{U}^{-1}_{z\mathrm{e}}+\dot{\mathbf{F}}_\mathrm{b}\cdot\mathbf{F}^{-1}_\mathrm{b}\Big) \quad \text{(I.74)}$$

The power of the thick layer is

$$\begin{aligned}
P\,dA \;&=\; \int_{z=-h/2}^{h/2} P_z(z)\,dA_z(z)\,dz\\
&= \int_{z=-h/2}^{h/2}\Big(\sigma_{11}\,\dot\epsilon_1+\sigma_{22}\,\dot\epsilon_2\\
&\qquad\qquad +\big(\sigma_{11}\,\mathbf{b}_1\otimes\mathbf{b}_1+\sigma_{22}\,\mathbf{b}_2\otimes\mathbf{b}_2\big):\dot{\mathbf{F}}_\mathrm{b}\cdot\mathbf{F}^{-1}_\mathrm{b}\Big)\,dA_z(z)\,dz\\
&= \Big(\int_{z=-h/2}^{h/2}\big(\sigma_{11}\,\dot\epsilon_1+\sigma_{22}\,\dot\epsilon_2\big)(1-c_1z)(1-c_2z)\,dz+\tilde{\mathbf{T}}:\dot{\mathbf{F}}_\mathrm{b}\cdot\mathbf{F}^{-1}_\mathrm{b}\Big)\,dA
\end{aligned} \quad \text{(I.75)}$$

with the abbreviation

$$\begin{aligned}
\tilde{\mathbf{T}} \;&=\; \int_{z=-h/2}^{h/2}(1-c_1z)(1-c_2z)\,\big(\sigma_{11}\,\mathbf{b}_1\otimes\mathbf{b}_1+\sigma_{22}\,\mathbf{b}_2\otimes\mathbf{b}_2\big)\,dz\\
&=\; \int_{z=-h/2}^{h/2}(1-c_1z)(1-c_2z)\;\mathbf{R}^T_{z\mathrm{e}}(z)\cdot\boldsymbol{\sigma}(z)\cdot\mathbf{R}_{z\mathrm{e}}(z)\,dz
\end{aligned} \quad \text{(I.76)}$$

Next we need the rates of the elastic principal strains. We obtain from (I.33), (I.37)

$$\dot\epsilon_{1,2}=\frac{1}{2}\left(\dot\epsilon_\mathrm{es}-\dot c_1\,\frac{z}{1-c_1\,z}-\dot c_2\,\frac{z}{1-c_2\,z}\pm\dot q\right) \quad \text{(I.77)}$$

The derivative of (I.38) is

$$\big(\mathrm{tr}\,\mathbf{B}\big)^\bullet=2\sinh q\;\dot q \quad \text{(I.78)}$$

Since $q=\sqrt{I_2}$ according to (I.41), we get

$$\begin{aligned}
\dot q &= \frac{1}{2\sinh\sqrt{I_2}}\big(\mathrm{tr}\,\mathbf{B}\big)^\bullet\\
&= \frac{1}{2\sinh\sqrt{I_2}}\left(-y_\mathrm{c}\,\frac{z}{1-c_1\,z}\,\dot c_1+y_\mathrm{c}\,\frac{z}{1-c_2\,z}\,\dot c_2+y_\mathrm{d}\,\dot\epsilon_\mathrm{ed}+y_\alpha\,\dot\alpha\right)
\end{aligned} \quad \text{(I.79)}$$

Now we are able to evaluate the integral

$$\int_{z=-h/2}^{h/2} \big(\sigma_{11}\,\dot{\epsilon_1}+\sigma_{22}\,\dot{\epsilon_2}\big)(1-c_1z)(1-c_2z)\,dz = -m_1\dot{c_1}-m_2\dot{c_2}+\tilde{t}_{\rm s}\dot{\epsilon}_{\rm es}+\tilde{t}_{\rm d}\dot{\epsilon}_{\rm ed}+\tilde{t}_\alpha\dot{\alpha} \tag{I.80}$$

and find the following coefficients

$$m_1 = \int\limits_{z=-h/2}^{h/2} (1-c_1z)(1-c_2z)\left(\frac{\sigma_{11}+\sigma_{22}}{2}+\frac{\sigma_{11}-\sigma_{22}}{2}\,\frac{y_{\rm c}}{2\sinh\sqrt{I_2}}\right)\frac{z}{1-c_1\,z}\,dz \tag{I.81}$$

$$m_2 = \int\limits_{z=-h/2}^{h/2} (1-c_1z)(1-c_2z)\left(\frac{\sigma_{11}+\sigma_{22}}{2}-\frac{\sigma_{11}-\sigma_{22}}{2}\,\frac{y_{\rm c}}{2\sinh\sqrt{I_2}}\right)\frac{z}{1-c_2\,z}\,dz \tag{I.82}$$

$$\tilde{t}_{\rm s} = \int_{z=-h/2}^{h/2} (1-c_1z)(1-c_2z)\,\frac{\sigma_{11}+\sigma_{22}}{2}\,dz \tag{I.83}$$

$$\tilde{t}_{\rm d} = \int_{z=-h/2}^{h/2} (1-c_1z)(1-c_2z)\,\frac{\sigma_{11}-\sigma_{22}}{2}\,\frac{y_{\rm d}}{2\sinh\sqrt{I_2}}\,dz \tag{I.84}$$

$$\tilde{t}_\alpha = \int_{z=-h/2}^{h/2} (1-c_1z)(1-c_2z)\,\frac{\sigma_{11}-\sigma_{22}}{2}\,\frac{y_\alpha}{2\sinh\sqrt{I_2}}\,dz \tag{I.85}$$

It can be demonstrated, that the last three quantities are related to the tensor $\tilde{\mathbf{T}}$. To this purpose, we first calculate the deviator of the tensor $\mathbf{B}$ taking into account (I.29), (I.71), and (I.72).

$$\begin{aligned}
\mathbf{B}(z)-\frac{\operatorname{tr}\mathbf{B}}{2}(z)\;\mathbf{1}_{T_0} &= \frac{\beta_1(z)-\beta_2(z)}{2}\Big(\mathbf{b}_1(z)\otimes\mathbf{b}_1(z)-\mathbf{b}_2(z)\otimes\mathbf{b}_2(z)\Big)\\
= \quad & \sinh\sqrt{I_2(z)}\Big(\mathbf{b}_1(z)\otimes\mathbf{b}_1(z)-\mathbf{b}_2(z)\otimes\mathbf{b}_2(z)\Big)\\
= \quad & \frac{1}{2}\Bigg(\frac{1-c_1z}{1-c_2z}\Big(\exp(\epsilon_{\rm ed})\cos^2\alpha-\exp(-\epsilon_{\rm ed})\sin^2\alpha\Big)\\
&+\frac{1-c_2z}{1-c_1z}\Big(\exp(\epsilon_{\rm ed})\sin^2\alpha-\exp(-\epsilon_{\rm ed})\cos^2\alpha\Big)\Bigg)\big(\mathbf{a}_1\otimes\mathbf{a}_1-\mathbf{a}_2\otimes\mathbf{a}_2\big)\\
&+\left(\frac{1-c_1z}{1-c_2z}-\frac{1-c_2z}{1-c_1z}\right)\sin\alpha\cos\alpha\,\big(\mathbf{a}_1\otimes\mathbf{a}_2+\mathbf{a}_2\otimes\mathbf{a}_1\big)
\end{aligned}$$

$$
\begin{aligned}
= \quad & \frac{y_{\mathrm{d}}(z)}{2}\big(\mathbf{a}_1 \otimes \mathbf{a}_1 - \mathbf{a}_2 \otimes \mathbf{a}_2\big) \\
& \qquad - \frac{y_\alpha(z)}{2}\Big(\exp(\epsilon_{\mathrm{ed}}) - \exp(-\epsilon_{\mathrm{ed}})\Big)^{-1}\big(\mathbf{a}_1 \otimes \mathbf{a}_2 + \mathbf{a}_2 \otimes \mathbf{a}_1\big) \qquad \text{(I.86)}
\end{aligned}
$$

Introducing this into (I.76) we get the deviator of $\tilde{\mathbf{T}}$

$$
\begin{aligned}
& \tilde{\mathbf{T}} - \frac{1}{2}\operatorname{tr}\tilde{\mathbf{T}}\,\mathbf{1}_{T_0} \\
= \quad & \int_{z=-h/2}^{h/2} (1 - c_1 z)(1 - c_2 z)\,\frac{\sigma_{11} - \sigma_{22}}{2}\,\big(\mathbf{b}_1 \otimes \mathbf{b}_1 - \mathbf{b}_2 \otimes \mathbf{b}_2\big)\,dz \\
= \quad & \big(\mathbf{a}_1 \otimes \mathbf{a}_1 - \mathbf{a}_2 \otimes \mathbf{a}_2\big) \times \\
& \qquad \int_{z=-h/2}^{h/2} (1 - c_1 z)(1 - c_2 z)\,\frac{\sigma_{11} - \sigma_{22}}{2}(z)\,\frac{y_{\mathrm{d}}(z)}{2\sinh\sqrt{I_2(z)}}\,dz \\
& - \big(\mathbf{a}_1 \otimes \mathbf{a}_2 + \mathbf{a}_2 \otimes \mathbf{a}_1\big)\Big(\exp(\epsilon_{\mathrm{ed}}) - \exp(-\epsilon_{\mathrm{ed}})\Big)^{-1} \times \\
& \qquad \int_{z=-h/2}^{h/2} (1 - c_1 z)(1 - c_2 z)\,\frac{\sigma_{11} - \sigma_{22}}{2}(z)\,\frac{y_\alpha(z)}{2\sinh\sqrt{I_2(z)}}\,dz \\
= \quad & \big(\mathbf{a}_1 \otimes \mathbf{a}_1 - \mathbf{a}_2 \otimes \mathbf{a}_2\big)\,\tilde{t}_{\mathrm{d}} - \big(\mathbf{a}_1 \otimes \mathbf{a}_2 + \mathbf{a}_2 \otimes \mathbf{a}_1\big)\Big(\exp(\epsilon_{\mathrm{ed}}) - \exp(-\epsilon_{\mathrm{ed}})\Big)^{-1}\tilde{t}_\alpha \\
& \qquad \text{(I.87)}
\end{aligned}
$$

Moreover, we easily see

$$
\tilde{t}_{\mathrm{s}} = \frac{1}{2}\operatorname{tr}\tilde{\mathbf{T}} \qquad \text{(I.88)}
$$

I.5 Relaxation

As in (3.33), we postulate that the sum of the external power and the energy supply of the absorbed mass together must be greater than or at least equal to the rate of the elastic strain energy.

$$
P\,dA + f\tilde{\mu}\,dA \geq \big(w\,dA\big)^{\bullet} \qquad \text{(I.89)}
$$

Introduction of (I.75) with (I.80), (I.58), and (I.68) yields

$$
\begin{aligned}
& -\underline{\left(m_1 + \frac{\partial w}{\partial c_1}\right)}\dot{c}_1 - \underline{\left(m_2 + \frac{\partial w}{\partial c_2}\right)}\dot{c}_2 \\
& + \underline{\left(\tilde{t}_{\mathrm{s}} - \frac{\partial w}{\partial \epsilon_{\mathrm{es}}} - w\right)}\dot{\epsilon}_{\mathrm{es}} + \underline{\left(\tilde{t}_{\mathrm{d}} - \frac{\partial w}{\partial \epsilon_{\mathrm{ed}}}\right)}\dot{\epsilon}_{\mathrm{ed}} + \underline{\left(\tilde{t}_\alpha - \frac{\partial w}{\partial \alpha}\right)}\dot{\alpha} \\
& + \Big(\tilde{\mathbf{T}} + \big(f\mu - w\big)\mathbf{1}_{T_0}\Big) : \dot{\mathbf{F}}_{\mathrm{b}} \cdot \mathbf{F}_{\mathrm{b}}^{-1} \geq 0 \qquad \text{(I.90)}
\end{aligned}
$$

If (I.65) is inserted into (I.81) to (I.85) and the result compared with (I.69), then it is seen that all the underlined terms vanish. Note (I.33) and the choice of the signs in (I.38) which implies

$$\sqrt{I_2} = \sqrt{(\epsilon_1 - \epsilon_2)^2} = |\epsilon_1 - \epsilon_2| = +(\epsilon_1 - \epsilon_2) \tag{I.91}$$

so that we have according to (I.43)

$$I_\mathrm{d} = \frac{\epsilon_1 - \epsilon_2}{\sinh\sqrt{I_2}} \tag{I.92}$$

We learn that the rate of the basic transplacement cannot be arbitrary but must obey the remaining inequality

$$\Big(\tilde{\mathbf{T}} + \big(f\mu - w\big)\mathbf{1}_{T_0}\Big) : \dot{\mathbf{F}}_\mathrm{b} \cdot \mathbf{F}_\mathrm{b}^{-1} \geq 0 \tag{I.93}$$

The simplest ansatz which guarantees the fulfilment of this inequality is the following one

$$\dot{\mathbf{F}}_\mathrm{b} \cdot \mathbf{F}_\mathrm{b}^{-1} = \frac{1}{\eta_1}\left(\frac{1}{2}\operatorname{tr}\tilde{\mathbf{T}} + f\mu - w\right)\mathbf{1}_{T_0} + \frac{1}{\eta_2}\left(\tilde{\mathbf{T}} - \frac{1}{2}\operatorname{tr}\tilde{\mathbf{T}}\;\mathbf{1}_{T_0}\right) \tag{I.94}$$

Here the positive material parameters η_1 and η_2 characterize the isotropic and deviatoric viscosity, respectively.

The relaxed state, which will asymptotically be reached, is characterized by $\dot{\mathbf{F}}_\mathrm{b} = 0$ and hence by

$$\frac{1}{2}\operatorname{tr}\tilde{\mathbf{T}} + f\mu - w = 0 \tag{I.95}$$

and

$$\tilde{\mathbf{T}} - \frac{1}{2}\operatorname{tr}\tilde{\mathbf{T}}\;\mathbf{1}_{T_0} = 0 \tag{I.96}$$

whence we may infer

$$\tilde{\mathbf{T}} = \big(w - f\mu\big)\mathbf{1}_{T_0} \tag{I.97}$$

This property of the relaxed state has some important consequences. Since the last three underlined terms in (I.90) vanish, we infer from (I.95) and (I.88) and from (I.96) and (I.87)

$$\frac{\partial w}{\partial \epsilon_\mathrm{es}} = \tilde{t}_\mathrm{s} - w = -f\mu \tag{I.98}$$

$$\frac{\partial w}{\partial \epsilon_\mathrm{ed}} = \tilde{t}_\mathrm{d} = 0 \tag{I.99}$$

$$\frac{\partial w}{\partial \alpha} = \tilde{t}_\alpha = 0 \tag{I.100}$$

I.6 Link to the Mesoscopic Approach

The last two equations, completely written as

$$\frac{\partial w}{\partial \epsilon_{\mathrm{ed}}}\big(c_1, c_2, \epsilon_{\mathrm{es}}, \epsilon_{\mathrm{ed}}, \alpha\big) = 0 \tag{I.101}$$

$$\frac{\partial w}{\partial \alpha}\big(c_1, c_2, \epsilon_{\mathrm{es}}, \epsilon_{\mathrm{ed}}, \alpha\big) = 0 \tag{I.102}$$

are assumed to determine unique solutions ϵ_{ed} and α. We write them

$$\epsilon_{\mathrm{ed}} = \bar{\epsilon}_{\mathrm{ed}}\big(c_1, c_2, \epsilon_{\mathrm{es}}\big)\,, \qquad \alpha = \bar{\alpha}\big(c_1, c_2, \epsilon_{\mathrm{es}}\big) \tag{I.103}$$

Now, according to (I.53), we have

$$\mu = \mu_{\mathrm{b}} \exp(-\epsilon_{\mathrm{es}}) \quad \Longrightarrow \quad \epsilon_{\mathrm{es}} = \ln \frac{\mu_{\mathrm{b}}}{\mu}\,, \qquad \frac{d\mu}{d\epsilon_{\mathrm{es}}} = -\mu \tag{I.104}$$

So the dependence of the energy density w on the variable ϵ_{es} may be substituted by a dependence on μ and the energy density of the relaxed state written as

$$w_{\mathrm{rel}}(c_1, c_2, \mu) \equiv w\Big(c_1, c_2, \ln(\mu_{\mathrm{b}}/\mu), \bar{\epsilon}_{\mathrm{ed}}\big(c_1, c_2, \ln(\mu_{\mathrm{b}}/\mu)\big), \bar{\alpha}\big(c_1, c_2, \ln(\mu_{\mathrm{b}}/\mu)\big)\Big) \tag{I.105}$$

This functional form of the energy density constitutes the basis of the mesoscopic approach, discussed in chapter 2.

The chain rule gives

$$\frac{\partial w_{\mathrm{rel}}}{\partial c_1} = \frac{\partial w}{\partial c_1} + \underline{\frac{\partial w}{\partial \epsilon_{\mathrm{ed}}}}\frac{\partial \bar{\epsilon}_{\mathrm{ed}}}{\partial c_1} + \underline{\frac{\partial w}{\partial \alpha}}\frac{\partial \bar{\alpha}}{\partial c_1} = \frac{\partial w}{\partial c_1} \tag{I.106}$$

— the underlined terms are zero because of (I.101), (I.102). Moreover, since the first two underlined terms in (I.90) vanish, we find in the relaxed state

$$m_1 = -\frac{\partial w}{\partial c_1} = -\frac{\partial w_{\mathrm{rel}}}{\partial c_1}\,, \qquad m_2 = -\frac{\partial w}{\partial c_2} = -\frac{\partial w_{\mathrm{rel}}}{\partial c_2} \tag{I.107}$$

A similar line of reasoning gives, with (I.98) and (I.104),

$$f = -\frac{1}{\mu}\frac{\partial w}{\partial \epsilon_{\mathrm{es}}} = \frac{\partial w}{\partial \mu} = \frac{\partial w_{\mathrm{rel}}}{\partial \mu} \tag{I.108}$$

The search for the minimum of the free energy in chapter 2 made use of the special form w_{rel} of the energy density of the fluid film — but w was simply written instead of w_{rel} —, and the relevant contribution to the extended energy was

$$\int_A \big(w_{\mathrm{rel}}(c_1, c_2, \mu) - f\mu\big)\, dA \tag{I.109}$$

according to (2.28). The variation of this expression with respect to μ

$$\int_A \left(\frac{\partial w_{\mathrm{rel}}(c_1, c_2, \mu)}{\partial \mu} - f \right) \delta\mu \, dA \tag{I.110}$$

vanishes for arbitrary fields $\delta\mu$, if (I.108) is valid. One could however have based the investigation on the more general representation

$$\int_A \Big(w\big(c_1, c_2, \epsilon_{\mathrm{es}}, \epsilon_{\mathrm{ed}}, \alpha\big) - f\mu \Big) \, dA \tag{I.111}$$

of the extended energy. Its variation with respect to ϵ_{es}, ϵ_{ed}, and α

$$\begin{aligned} \int_A \Bigg(\bigg(& \frac{\partial w\big(c_1, c_2, \epsilon_{\mathrm{es}}, \epsilon_{\mathrm{ed}}, \alpha\big)}{\partial \epsilon_{\mathrm{es}}} - f \frac{d\mu}{d\epsilon_{\mathrm{es}}} \bigg) \delta\epsilon_{\mathrm{es}} \\ & + \frac{\partial w\big(c_1, c_2, \epsilon_{\mathrm{es}}, \epsilon_{\mathrm{ed}}, \alpha\big)}{\partial \epsilon_{\mathrm{ed}}} \delta\epsilon_{\mathrm{ed}} + \frac{\partial w\big(c_1, c_2, \epsilon_{\mathrm{es}}, \epsilon_{\mathrm{ed}}, \alpha\big)}{\partial \alpha} \delta\alpha \Bigg) \, dA \end{aligned} \tag{I.112}$$

vanishes for arbitrary fields $\delta\epsilon_{\mathrm{es}}$, $\delta\epsilon_{\mathrm{ed}}$, and $\delta\alpha$, if the conditions (I.98) with (I.104), (I.99), (I.100) are valid.

So it is indeed possible and advantegous to eliminate ϵ_{ed} and α in advance by means of (I.101) and (I.102) and work with (I.109) instead of (I.111). Note, however, that one cannot proceed in the same manner and get rid of the variable ϵ_{es}, too, by means of equation (I.108). That equation introduces the additional variable f, which does not depend on the local properties of the film alone but — as is shown in chapter 2 — also on the whole system into which it is embedded.

I.7 The Angle α in the Relaxed State

We want to obtain information on the angle α from equation (I.102). We find with (I.69), (I.72), (I.43)

$$\begin{aligned} 0 = \frac{\partial w}{\partial \alpha} &= \int_{z=-h/2}^{h/2} \Big((1 - c_2 z)^2 - (1 - c_1 z)^2 \Big) \frac{\sqrt{I_2(z)}}{\sinh \sqrt{I_2(z)}} \frac{\partial w_z}{\partial I_2}(z) \, dz \times \\ & \Big(\exp(\epsilon_{\mathrm{ed}}) - \exp(-\epsilon_{\mathrm{ed}}) \Big) 2 \sin\alpha \cos\alpha \end{aligned} \tag{I.113}$$

There are four possibilities to satisfy this condition:

- We have $c_1 = c_2$ so that the integrand vanishes. The tensor $\mathbf{U}_{\mathrm{c}}$ is then isotropic and hence co-axial with $\mathbf{U}_{\mathrm{e}}$ so that $\alpha = 0$ may be chosen.

- We have $\epsilon_{\mathrm{ed}} = 0$. The tensor $\mathbf{U}_{\mathrm{e}}$ is then isotropic and hence co-axial with $\mathbf{U}_{\mathrm{c}}$ so that $\alpha = 0$ may be chosen.

- We have $\sin\alpha\cos\alpha = 0$, *i.e.* the principal axes of the tensors $\mathbf{U}_\mathrm{e}$ and $\mathbf{U}_\mathrm{c}$ coincide. Without loss of generality, the axes may be numbered in such a way that $\alpha = 0$ holds.

- The invariant I_2 depends on α according to (I.41), (I.31). Therefore, the integral may vanish for some $\alpha \neq 0$ even in the case $c_1 \neq c_2$.

It is by no means obvious whether the last mentioned possibility will or will not exist at all. If it did, then a unique solution in the sense of (I.103) would not exist, since we have seen, that a choice of α with $\sin\alpha\cos\alpha = 0$ always satisfies the equation (I.113). So we concentrate on the solution $\alpha = 0$ alone. Then the proper vectors $\mathbf{a}_j$ of $\mathbf{U}_\mathrm{e}$ according to (I.12), $\mathbf{d}_j$ of $\mathbf{U}_\mathrm{c}(z)$ according to (I.15), and $\mathbf{b}_j(z)$ of $\mathbf{U}_{z\mathrm{e}}(z)$ according to (I.20) coincide. Since $\mathbf{U}_\mathrm{c}(z)$ and $\mathbf{U}_\mathrm{e}$ now commute we infer from (I.20)

$$\mathbf{U}_{z\mathrm{e}}(z) = \lambda_\mathrm{p}(z)\ \mathbf{U}_\mathrm{e} \cdot \mathbf{U}_\mathrm{c}(z) \tag{I.114}$$

and also

$$\mathbf{H}(z) = \ln \mathbf{U}_{z\mathrm{e}}(z) = \ln \lambda_\mathrm{p}(z)\, \mathbf{1}_{T_0} + \ln \mathbf{U}_\mathrm{e} + \ln \mathbf{U}_\mathrm{c}(z) \tag{I.115}$$

(I.29) simplifies to

$$\beta_1(z) = \frac{1 - c_1 z}{1 - c_2 z} \exp(\epsilon_\mathrm{ed})\,, \quad \beta_2(z) = \frac{1 - c_2 z}{1 - c_1 z} \exp(-\epsilon_\mathrm{ed}) \tag{I.116}$$

and (I.33) yields

$$\begin{aligned} \epsilon_1(z) &= \epsilon_\mathrm{p}(z) + \frac{1}{2}\Big(\epsilon_\mathrm{es} + \epsilon_\mathrm{ed}\Big) + \ln(1 - c_1\, z) \\ \epsilon_2(z) &= \epsilon_\mathrm{p}(z) + \frac{1}{2}\Big(\epsilon_\mathrm{es} - \epsilon_\mathrm{ed}\Big) + \ln(1 - c_2\, z) \end{aligned} \tag{I.117}$$

These equations give the proper numbers of the tensor equation (I.115) — note (I.15) and (I.22) to (I.25). The invariants according to (I.34) become

$$I_1(z) = \epsilon_1(z) + \epsilon_2(z) = 2\epsilon_\mathrm{p}(z) + \epsilon_\mathrm{es} + \ln(1 - c_1\, z) + \ln(1 - c_2\, z) \tag{I.118}$$

$$I_2(z) = \big(\epsilon_1(z) - \epsilon_2(z)\big)^2 = \Big(\epsilon_\mathrm{ed} + \ln(1 - c_1\, z) - \ln(1 - c_2\, z)\Big)^2 \tag{I.119}$$

where (I.118) is identical to (I.36) but (I.119) is much simpler than (I.41) with (I.31).

The last four equations are those which were also found in case of the relaxed state on the basis of the much simpler approach in chapter 3, where co-axiality of $\mathbf{U}_\mathrm{c}(z)$ and $\mathbf{U}_\mathrm{e}$ was supposed from the beginning.

J The Spinning Drop Test

J.1 The Free Energy

Let us consider a tube, containing water and a spherical inclusion of oil surrounded by an amphiphilic film. If the tube rotates about its axis with an angular velocity ω, then the bubble will deform under the influence of the centrifugal force. Such a test is often performed in order to obtain information about the internal forces of the film.

In order to investigate the deformed shape of the bubble, we must modify our previous setting. Now we have only one kind of structure and only one cell. The equation (2.12) becomes

$$\upsilon_{\mathrm{O}} = \frac{1}{\varrho_{\mathrm{O}}(p_{\mathrm{O}})} + \frac{k_{\mathrm{O}}}{\varrho_{\mathrm{A}}(p_{\mathrm{O}})} \tag{J.1}$$

but now, k_{O}, p_{O} and υ_{O} are not constants but fields. The volume element of the oil-sided cavity is described by $dV_{\mathrm{O}} = \upsilon_{\mathrm{O}}\, dm_{\mathrm{O}}$, and the total mass in that volume element is

$$dm = dm_{\mathrm{O}} + dm_{\mathrm{A}} = \big(1 + k_{\mathrm{O}}\big) dm_{\mathrm{O}} = \big(1 + k_{\mathrm{O}}\big) \upsilon_{\mathrm{O}}^{-1}\, dV_{\mathrm{O}} \tag{J.2}$$

We define the effective density of the oil with solved monomeric amphiphile by

$$\varrho_{\mathrm{Oe}} = \frac{dm}{dV_{\mathrm{O}}} = \big(1 + k_{\mathrm{O}}\big) \upsilon_{\mathrm{O}}^{-1} = \big(1 + k_{\mathrm{O}}\big) \left(\frac{1}{\varrho_{\mathrm{O}}(p_{\mathrm{O}})} + \frac{k_{\mathrm{O}}}{\varrho_{\mathrm{A}}(p_{\mathrm{O}})} \right)^{-1} \tag{J.3}$$

The free energy of the system is given by

$$\begin{aligned} F = {} & p_{\mathrm{e}} V + \\ & \int_A w(c_1, c_2, \mu)\, dA + \int_{V_{\mathrm{O}}} f_{\mathrm{O}}(k_{\mathrm{O}}, p_{\mathrm{O}})\, \upsilon_{\mathrm{O}}^{-1}\, dV_{\mathrm{O}} + \int_{V_{\mathrm{W}}} f_{\mathrm{W}}(k_{\mathrm{W}}, p_{\mathrm{W}})\, \upsilon_{\mathrm{W}}^{-1}\, dV_{\mathrm{W}} \\ & - \frac{\omega^2}{2} \left(\int_A r^2 \mu\, dA + \int_{V_{\mathrm{O}}} r^2 \big(1 + k_{\mathrm{O}}\big)\, \upsilon_{\mathrm{O}}^{-1}\, dV_{\mathrm{O}} + \int_{V_{\mathrm{W}}} r^2 \big(1 + k_{\mathrm{W}}\big)\, \upsilon_{\mathrm{W}}^{-1}\, dV_{\mathrm{W}} \right) \end{aligned} \tag{J.4}$$

The terms with ω^2 represent the contribution of the field of centrifugal forces, since the potential of the centrifugal force acting on the mass dm in the distance r from the axis of rotation is $\omega^2 r^2 dm/2$.

The three constraints (2.5), (2.25), (2.26) have to be modified to read

$$g \equiv m_{\mathrm{A}} - \int_A \mu\, dA - \int_{V_{\mathrm{O}}} k_{\mathrm{O}} \upsilon_{\mathrm{O}}^{-1}\, dV_{\mathrm{O}} - \int_{V_{\mathrm{W}}} k_{\mathrm{W}} \upsilon_{\mathrm{W}}^{-1}\, dV_{\mathrm{W}} = 0 \tag{J.5}$$

$$h_{\mathrm{O}} \equiv m_{\mathrm{O}} - \int_{V_{\mathrm{O}}} \upsilon_{\mathrm{O}}^{-1}\, dV_{\mathrm{O}} = 0 \tag{J.6}$$

$$h_{\mathrm{W}} \equiv m_{\mathrm{W}} - \int_{V_{\mathrm{W}}} \upsilon_{\mathrm{W}}^{-1}\, dV_{\mathrm{W}} = 0 \tag{J.7}$$

The extended energy (2.27) becomes

$$\begin{aligned} E \;=\; & \int_A \Big(w(c_1, c_2, \mu) + p_{\mathrm{e}} \Big(h + c_1 c_2 \,\frac{h^3}{12} \Big) - \Big(f + \frac{\omega^2}{2} r^2 \Big) \mu \Big)\, dA \\ & + \int_{V_{\mathrm{O}}} \Big(f_{\mathrm{O}}(k_{\mathrm{O}}, p_{\mathrm{O}}) + p_{\mathrm{e}} \upsilon_{\mathrm{O}} - f\, k_{\mathrm{O}} - \frac{\omega^2}{2} r^2 \big(1 + k_{\mathrm{O}}\big) - y_{\mathrm{O}} \Big)\, \upsilon_{\mathrm{O}}^{-1}\, dV_{\mathrm{O}} \\ & + \int_{V_{\mathrm{W}}} \Big(f_{\mathrm{W}}(k_{\mathrm{W}}, p_{\mathrm{W}}) + p_{\mathrm{e}} \upsilon_{\mathrm{W}} - f\, k_{\mathrm{W}} - \frac{\omega^2}{2} r^2 \big(1 + k_{\mathrm{W}}\big) - y_{\mathrm{W}} \Big)\, \upsilon_{\mathrm{W}}^{-1}\, dV_{\mathrm{W}} \\ & + f\, m_{\mathrm{A}} + y_{\mathrm{O}}\, m_{\mathrm{O}} + y_{\mathrm{W}}\, m_{\mathrm{W}} \end{aligned} \tag{J.8}$$

In order to find the minimum of E, we can vary the degrees of freedom f, y_{O}, and y_{W}, the fields k_{O}, k_{W}, p_{O}, p_{W}, μ and the shape of the film, which determines the fields c_1, c_2 of the principal curvatures, the oil and water volumes V_{O}, V_{W} and the area A.

J.2 Necessary Conditions of a Minimum

If we compare (J.8) with (2.28), we see that the following substitutions have to be performed.

$$f \;\rightarrow\; f + \frac{\omega^2}{2} r^2\,, \qquad y_{\mathrm{O}} \;\rightarrow\; y_{\mathrm{O}} + \frac{\omega^2}{2} r^2\,, \qquad y_{\mathrm{W}} \;\rightarrow\; y_{\mathrm{W}} + \frac{\omega^2}{2} r^2 \tag{J.9}$$

Therefore, the equation (2.31) has to be replaced by

$$p_{\mathrm{O}} = -\Big(f_{\mathrm{O}}(k_{\mathrm{O}}, p_{\mathrm{O}}) - f\, k_{\mathrm{O}} - \frac{\omega^2}{2} r^2 \big(1 + k_{\mathrm{O}}\big) - y_{\mathrm{O}} \Big) \frac{1}{\upsilon_{\mathrm{O}}(k_{\mathrm{O}}, p_{\mathrm{O}})} \tag{J.10}$$

and the equations (2.32) and (2.41) by

$$f + \frac{\omega^2}{2} r^2 = \frac{\partial f_{\mathrm{O}}}{\partial k_{\mathrm{O}}}(k_{\mathrm{O}}, p_{\mathrm{O}}) + \frac{p_{\mathrm{O}}}{\varrho_{\mathrm{A}}(p_{\mathrm{O}})} = \frac{\partial f_{\mathrm{W}}}{\partial k_{\mathrm{W}}}(k_{\mathrm{W}}, p_{\mathrm{W}}) + \frac{p_{\mathrm{W}}}{\varrho_{\mathrm{A}}(p_{\mathrm{W}})} = \frac{\partial w(c_1, c_2, \mu)}{\partial \mu} \tag{J.11}$$

The extended energy (J.8) may considerably be simplified by means of (J.10) to read

$$\begin{aligned} E \;=\; & \int_A \Big(w(c_1, c_2, \mu) + p_{\mathrm{e}} \Big(h + c_1 c_2 \,\frac{h^3}{12} \Big) - \Big(f + \frac{\omega^2}{2} r^2 \Big) \mu \Big)\, dA \\ & - \int_{V_{\mathrm{O}}} \big(p_{\mathrm{O}} - p_{\mathrm{e}} \big)\, dV_{\mathrm{O}} - \int_{V_{\mathrm{W}}} \big(p_{\mathrm{W}} - p_{\mathrm{e}} \big)\, dV_{\mathrm{W}} \\ & + f\, m_{\mathrm{A}} + y_{\mathrm{O}}\, m_{\mathrm{O}} + y_{\mathrm{W}}\, m_{\mathrm{W}} \end{aligned} \tag{J.12}$$

Now, E must also be a minimum with respect to any change of the shape of the film. We modify the discussion of appendix F, replace the abbreviation (F.2) by

$$\phi = w(c_1, c_2, \mu) + p_\mathrm{e} \left(h + \det \mathbf{C}\, \frac{h^3}{12} \right) - \left(f + \frac{\omega^2}{2} r^2 \right) \mu \tag{J.13}$$

and arrive at the result (F.11) with an additional term, which is underlined in the following

$$\begin{aligned} \delta \int_A \phi \; dA &= \oint \delta\mathbf{u} \cdot (\mathbf{S} + \mathbf{n} \otimes \mathbf{q}_T) \cdot \mathbf{e}\, ds + \oint \delta\mathbf{n} \cdot \mathbf{D} \cdot \mathbf{e}\, ds \\ & - \int_A \delta\mathbf{u} \cdot \overline{(\mathbf{S} + \acute{\mathbf{n}} \otimes \mathbf{q}_T)} \cdot \nabla_T \, dA - \int_A \delta\mathbf{n} \cdot \big(\acute{\mathbf{D}} \cdot \nabla_T - \mathbf{q}_T \big)\, dA \\ & \underline{- \int_A \omega^2 r \, \delta r \, \mu \, dA} \end{aligned} \tag{J.14}$$

That term takes into account that the distance r of a surface element dA will vary by $\delta r = \delta\mathbf{u} \cdot \nabla r = \delta\mathbf{u} \cdot \mathbf{e}_r$, if the shape of the film changes.

The variation of the oil and water volumes is also determined along the line of reasoning of appendix F. However, since the pressures are now not constant within the two fluids, we obtain the result

$$\begin{aligned} & -\delta \int_{V_\mathrm{O}} \big(p_\mathrm{O} - p_\mathrm{e} \big)\, dV_\mathrm{O} - \delta \int_{V_\mathrm{W}} \big(p_\mathrm{W} - p_\mathrm{e} \big)\, dV_\mathrm{W} \\ & = \int_A \delta\mathbf{u} \cdot \mathbf{n}\, p_\mathrm{e}\, h \operatorname{tr} \mathbf{C}\, dA - \int_A \delta\mathbf{u} \cdot \mathbf{n}\, \bar{p}_n \, dA \end{aligned} \tag{J.15}$$

with the abbreviation

$$\bar{p}_n = p_\mathrm{W} \left(1 + \operatorname{tr} \mathbf{C} \frac{h}{2} + \det \mathbf{C} \frac{h^2}{4} \right) - p_\mathrm{O} \left(1 - \operatorname{tr} \mathbf{C} \frac{h}{2} + \det \mathbf{C} \frac{h^2}{4} \right) \tag{J.16}$$

in analogy to (F.18), but must keep in mind that now p_O and p_W denote the local pressures on the oil-sided and water-sided surface, respectively, of the film.

While (F.19) remains valid,

$$\mathbf{M} = -\frac{\partial w}{\partial \mathbf{C}} \tag{J.17}$$

(F.20) has to be replaced by

$$\mathbf{T} = \left(w - \left(f + \frac{\omega^2}{2} r^2 \right) \mu \right) \mathbf{1}_T + \mathbf{C} \cdot \mathbf{M} = \left(w - \mu \frac{\partial w}{\partial \mu} \right) \mathbf{1}_T + \mathbf{C} \cdot \mathbf{M} \tag{J.18}$$

The last representation results from (J.11) and is identical with (G.5). Since the structure is closed, the line integrals of (J.14) do not appear. After all, the postulate that the variation of E under any change of the shape vanishes, leads to

$$\begin{aligned} 0 \quad = \quad & -\int_A \delta\mathbf{u} \cdot \Big(\acute{\overline{(\mathbf{T} + \mathbf{n} \otimes \mathbf{q}_T)}} \cdot \nabla_T + \bar{p}_n \mathbf{n} + \mu\, \omega^2\, r\, \mathbf{e}_r \Big)\, dA \\ & -\int_A \delta\mathbf{n} \cdot \Big(\acute{\mathbf{M}} \cdot \nabla_T - \mathbf{q}_T \Big)\, dA \qquad \text{(J.19)} \end{aligned}$$

and yields the following Euler-Lagrangean differential equations

$$\big(\mathbf{T} + \mathbf{n} \otimes \mathbf{q}_T\big) \cdot \nabla_T + \bar{p}_n \mathbf{n} + \mu\, \omega^2\, r\, \mathbf{e}_r = \mathbf{0} \qquad \text{(J.20)}$$

$$\mathbf{1}_T \cdot \big(\acute{\mathbf{M}} \cdot \nabla_T - \mathbf{q}_T\big) = \mathbf{0} \qquad \text{(J.21)}$$

Wherever $\mathbf{n} \neq \mathbf{e}_r$, the third term of (J.20) possesses a component in the tangential direction. But we proved in G.2, that tangential surface forces are not admissible, if (J.21) is satisfied, and this seems to suggest that the equilibrium condition (J.20) cannot be fulfilled. However, our proof was based on the special representation (F.20) of the membrane forces, which is not applicable here. In our case, the tangential component of the first term of (J.20) reads — note (J.18), (J.11), (J.21) —

$$\begin{aligned} & \mathbf{1}_T \cdot \acute{\mathbf{T}} \cdot \nabla_T - \mathbf{C} \cdot \mathbf{q}_T \\ = \quad & \mathbf{1}_T \cdot \acute{\overline{\bigg(\Big(w - \Big(f + \frac{\omega^2}{2} r^2\Big)\mu \Big) \mathbf{1}_T + \mathbf{C} \cdot \mathbf{M} \bigg)}} \cdot \nabla_T - \mathbf{C} \cdot \acute{\mathbf{M}} \cdot \nabla_T \\ = \quad & \nabla_T \Big(w - \Big(f + \frac{\omega^2}{2} r^2\Big)\mu \Big) + \underline{\mathbf{1}_T \cdot \acute{\mathbf{C}} \cdot \mathbf{M} \cdot \nabla_T} \qquad \text{(J.22)} \end{aligned}$$

Now

$$\begin{aligned} & \nabla_T \Big(w - \Big(f + \frac{\omega^2}{2} r^2\Big)\mu \Big) \\ = \quad & \underline{\frac{\partial w}{\partial \mathbf{C}} : \big(\acute{\mathbf{C}} \otimes \nabla_T\big)} + \underbrace{\Big(\frac{\partial w}{\partial \mu} - f - \frac{\omega^2}{2} r^2 \Big)} \nabla_T \acute{\mu} - \mu\omega^2 r\, \nabla_T \acute{r} \quad \text{(J.23)} \end{aligned}$$

But the underbraced term vanishes according to (J.11), and the underlined terms in (J.22), (J.23) cancel each other (*cf.* the argument of (G.27)).

So we retain $-\mu\omega^2 r\, \nabla_T \acute{r} = -\mu\omega^2 r\, \mathbf{1}_T \cdot \nabla \acute{r} = -\mu\omega^2 r\, \mathbf{1}_T \cdot \mathbf{e}_r$, and introducing this into (J.20), we see that the tangential part of that equation is identically satisfied.

After all, we only have to consider the equilibrium of forces in the normal direction, which can be written

$$\mathbf{T} : \mathbf{C} + \nabla_T \cdot \mathbf{q}_T = -\bar{p}_n - \mu\, \omega^2\, r\, \mathbf{e}_r \cdot \mathbf{n} \qquad \text{(J.24)}$$

with $\bar{p}_n$ according to (J.16), and observe the equilibrium of moments

$$\mathbf{q}_T = \mathbf{1}_T \cdot \acute{\mathbf{M}} \cdot \nabla_T \tag{J.25}$$

The pressure field p_O of the oil is implicitly given by (J.10). We get better insight, if we use this equation to compute its gradient field.

$$\begin{aligned} \upsilon_\mathrm{O} \nabla p_\mathrm{O} &= -\frac{\partial f_\mathrm{O}}{\partial k_\mathrm{O}} \nabla k_\mathrm{O} - \frac{\partial f_\mathrm{O}}{\partial p_\mathrm{O}} \nabla p_\mathrm{O} + \Big(f + \frac{\omega^2}{2} r^2\Big) \nabla k_\mathrm{O} \\ &\quad + \omega^2 \big(1 + k_\mathrm{O}\big) r \nabla r - p_\mathrm{O} \left(\frac{\partial \upsilon_\mathrm{O}}{\partial k_\mathrm{O}} \nabla k_\mathrm{O} + \frac{\partial \upsilon_\mathrm{O}}{\partial p_\mathrm{O}} \nabla p_\mathrm{O} \right) \\ &= \underline{\left(-\frac{\partial f_\mathrm{O}}{\partial k_\mathrm{O}} + f + \frac{\omega^2}{2} r^2 - \frac{p_\mathrm{O}}{\varrho_\mathrm{A}(p_\mathrm{O})} \right)} \nabla k_\mathrm{O} - \underbrace{\left(\frac{\partial f_\mathrm{O}}{\partial p_\mathrm{O}} + p_\mathrm{O} \frac{\partial \upsilon_\mathrm{O}}{\partial p_\mathrm{O}} \right)} \nabla p_\mathrm{O} \\ &\quad + \omega^2 \big(1 + k_\mathrm{O}\big) r \nabla r \end{aligned} \tag{J.26}$$

The underlined expression vanishes because of (J.11) and the underbraced one because of (2.23). So the gradient of p_O points in the direction of the gradient of r, which means that the pressure is a function of the distance r alone. With the effective density according to (J.3), we arrive at the differential equation

$$\frac{dp_\mathrm{O}}{dr} = \varrho_\mathrm{Oe}(r)\, \omega^2\, r \tag{J.27}$$

J.3 Introduction of the Constitutive Assumption

We have to replace f by $f + \omega^2 r^2/2$ in the condition (4.16). The energy density (4.19) of the relaxed state

$$w(c_1, c_2, \mu) = \frac{\mu}{\mu_\mathrm{b}} \left(w_0 + w_1 \left(\Big(G_\mathrm{s}(c_1, c_2) - \ln \frac{\mu}{\mu_\mathrm{b}} \Big)^2 + G(c_1, c_2) \right) \right) \tag{J.28}$$

and the expression (4.24)

$$\tilde{t} \equiv w - \mu \frac{\partial w}{\partial \mu} = 2 w_1 \frac{\mu}{\mu_\mathrm{b}} \left(G_\mathrm{s} - \ln \frac{\mu}{\mu_\mathrm{b}} \right) \tag{J.29}$$

remain valid. Moreover, we introduce a reference state of the film. Its curvatures and the distance from the axis of rotation are zero, and its mass density μ_P is hence defined by — *cf.* (J.11) —

$$\frac{\partial w}{\partial \mu} \big(0, 0, \mu_\mathrm{P}\big) = f = \frac{\partial w}{\partial \mu} \big(c_1, c_2, \mu\big) - \frac{\omega^2}{2} r^2 \tag{J.30}$$

This leads to the following modification of (4.22)

$$\ln \frac{\mu}{\mu_\mathrm{b}} = G_\mathrm{s} - 1 + \sqrt{G_\mathrm{P} - G + S_\mathrm{P}^2 + \frac{\mu_\mathrm{b} \omega^2}{2 w_1} r^2} \tag{J.31}$$

with the abbreviations

$$S_{\mathrm{P}} = 1 - G_{\mathrm{sP}} + \ln\frac{\mu_{\mathrm{P}}}{\mu_{\mathrm{b}}} \tag{J.32}$$

and — note (4.37), (4.38) —

$$G_{\mathrm{sP}} = G_{\mathrm{s}}(0,0) = \frac{2}{3}q\,, \quad G_{\mathrm{P}} = G(0,0) = \frac{16}{45}q^2 + \frac{4}{3}\bar{h}_0^2 \tag{J.33}$$

Now, the radii of curvature of the amphiphilic bubble will be much larger than the thickness of the film. So the dimensionless quantities

$$\bar{h} = \frac{h}{2}\,H = \frac{h}{4}\,\bigl(c_s + c_\phi\bigr)\,, \qquad \bar{d} = \frac{h}{2}\,D = \frac{h}{4}\,\bigl(c_s - c_\phi\bigr) \tag{J.34}$$

according to (4.35) will be very small. Moreover, the expression $\mu_{\mathrm{b}}\omega^2\,r^2/(2w_1)$ will also be a small quantity. So it seems sufficient to express w and $\tilde{t}$ by second-order Taylor approximations in $\bar{h}$, $\bar{d}$, and r.

With the help of (4.37), (4.38), and with the abbreviation

$$w^* = 2w_1\frac{\mu_{\mathrm{P}}}{\mu_{\mathrm{b}}} \tag{J.35}$$

we arrive at

$$w = w_{\mathrm{P}} + w_h\bar{h} + w_{hh}\bar{h}^2 + w_{dd}\bar{d}^2 + w_{rr}\frac{\mu_{\mathrm{b}}\omega^2}{4w_1}r^2 \tag{J.36}$$

with

$$w_{\mathrm{P}} = \frac{1}{2}w^*\left(\frac{w_0}{w_1} + \bigl(1 - S_{\mathrm{P}}\bigr)^2 + G_{\mathrm{P}}\right) \tag{J.37}$$

$$w_h = \frac{4}{3}\bigl(w_{\mathrm{P}} - w^*\bigr)S_{\mathrm{P}}^{-1}\bar{h}_0 \tag{J.38}$$

$$\begin{aligned} w_{hh} \;\; = \;\; & \frac{8}{9}\Bigl(\bigl(1 - S_{\mathrm{P}}^{-1}\bigr)w_{\mathrm{P}} - \bigl(2 - S_{\mathrm{P}}^{-1}\bigr)w^*\Bigr)S_{\mathrm{P}}^{-2}\bar{h}_0^2 \\ & -\frac{1}{3}w_{\mathrm{P}} - \frac{2}{3}\bigl(w_{\mathrm{P}} - w^*\bigr)S_{\mathrm{P}}^{-1}\Bigl(1 - \frac{4}{15}q\Bigr) \end{aligned} \tag{J.39}$$

$$w_{dd} = -\frac{1}{3}w_{\mathrm{P}} - \frac{2}{3}\bigl(w_{\mathrm{P}} - w^*\bigr)S_{\mathrm{P}}^{-1}\Bigl(\kappa - \frac{4}{15}q\Bigr) \tag{J.40}$$

$$w_{rr} = S_{\mathrm{P}}^{-1}w_{\mathrm{P}} + \bigl(1 - S_{\mathrm{P}}^{-1}\bigr)w^* \tag{J.41}$$

and

$$\tilde{t} = \tilde{t}_{\mathrm{P}} + \tilde{t}_h\bar{h} + \tilde{t}_{hh}\bar{h}^2 + \tilde{t}_{dd}\bar{d}^2 + \tilde{t}_{rr}\frac{\mu_{\mathrm{b}}\omega^2}{4w_1}r^2 \tag{J.42}$$

with

$$\tilde{t}_{\mathrm{P}} = w^*\big(1 - S_{\mathrm{P}}\big) \tag{J.43}$$

$$\tilde{t}_h = -\frac{4}{3}w^*\bar{h}_0 \tag{J.44}$$

$$\tilde{t}_{hh} = -\frac{8}{9}w^* S_{\mathrm{P}}^{-1}\bar{h}_0^2 - \frac{1}{3}w^*\big(1 - S_{\mathrm{P}}\big) + \frac{2}{3}w^*\Big(1 - \frac{4}{15}q\Big) \tag{J.45}$$

$$\tilde{t}_{dd} = -\frac{1}{3}w^*\big(1 - S_{\mathrm{P}}\big) + \frac{2}{3}w^*\Big(\kappa - \frac{4}{15}q\Big) \tag{J.46}$$

$$\tilde{t}_{rr} = -w^* \tag{J.47}$$

J.4 Cylindrical Co-ordinates

An axi-symmetric surface under axi-symmetric loading is best described with cylindrical co-ordinates r, ϕ, z. The scalar components of all field quantities may be represented as functions of the arc length s on the meridian. The unit normal vector $\mathbf{n}$ of the surface, the unit tangent vector $\mathbf{e}$ of the meridian and the basis vectors of the co-ordinate system are related by (*cf.* fig. J.1)

$$\mathbf{n} = -\sin\alpha\,\mathbf{e}_r - \cos\alpha\,\mathbf{e}_z\,, \qquad \mathbf{e} = \cos\alpha\,\mathbf{e}_r - \sin\alpha\,\mathbf{e}_z\ . \tag{J.48}$$

The following formulae are valid

$$\frac{\partial\mathbf{e}_r}{\partial\phi} = \mathbf{e}_\phi\,, \qquad \frac{\partial\mathbf{e}_\phi}{\partial\phi} = -\mathbf{e}_r\,, \tag{J.49}$$

$$\frac{\partial\mathbf{e}}{\partial s} = \frac{\partial}{\partial s}\Big(\cos\alpha(s)\,\mathbf{e}_r(\phi) - \sin\alpha(s)\,\mathbf{e}_z\Big) = (-\sin\alpha\,\mathbf{e}_r - \cos\alpha\,\mathbf{e}_z)\frac{d\alpha}{ds} = \frac{d\alpha}{ds}\mathbf{n} \tag{J.50}$$

$$\frac{\partial\mathbf{e}}{\partial\phi} = \frac{\partial}{\partial\phi}\Big(\cos\alpha(s)\,\mathbf{e}_r(\phi) - \sin\alpha(s)\,\mathbf{e}_z\Big) = \cos\alpha\ \mathbf{e}_\phi \tag{J.51}$$

$$\frac{\partial\mathbf{n}}{\partial s} = -\frac{d\alpha}{ds}\,\mathbf{e}\,, \qquad \frac{\partial\mathbf{n}}{\partial\phi} = -\sin\alpha\ \mathbf{e}_\phi\ . \tag{J.52}$$

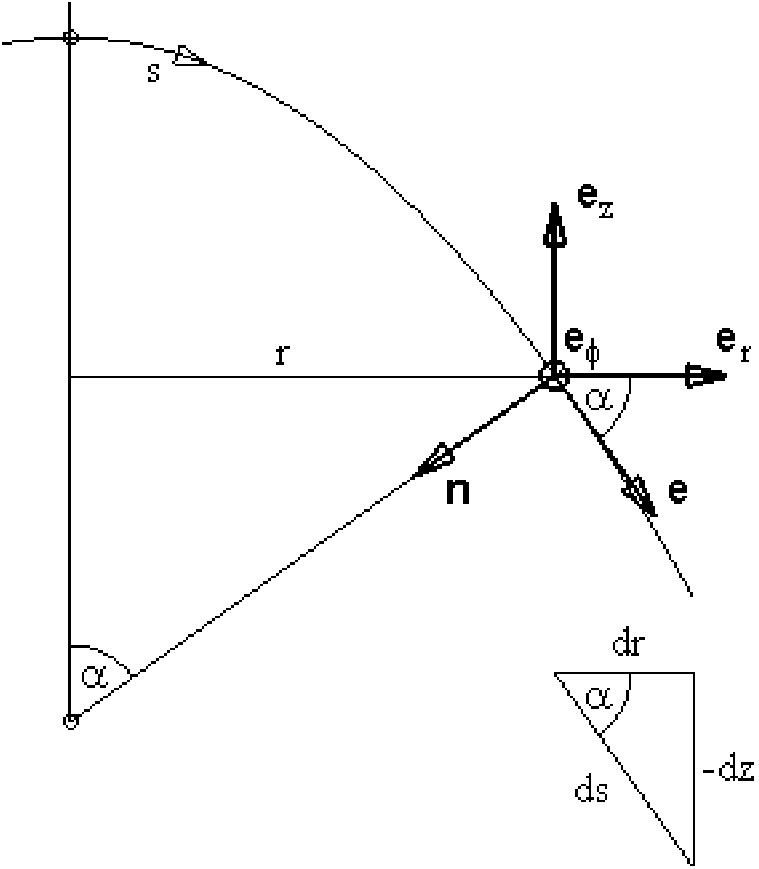
The curvature tensor becomes

$$\begin{aligned} \mathbf{C} \quad &= \quad -\mathbf{n}\otimes\nabla_T = -\acute{\mathbf{n}}\otimes\left(\mathbf{e}\frac{\partial}{\partial s} + \mathbf{e}_\phi\frac{\partial}{r\partial\phi}\right) = -\frac{\partial\mathbf{n}}{\partial s}\otimes\mathbf{e} - \frac{\partial\mathbf{n}}{r\partial\phi}\otimes\mathbf{e}_\phi \\ &= \quad \frac{d\alpha}{ds}\,\mathbf{e}\otimes\mathbf{e} + \frac{\sin\alpha}{r}\,\mathbf{e}_\phi\otimes\mathbf{e}_\phi = c_s\,\mathbf{e}\otimes\mathbf{e} + c_\phi\,\mathbf{e}_\phi\otimes\mathbf{e}_\phi\ . \end{aligned} \tag{J.53}$$

with the principal curvatures

$$c_s = \frac{d\alpha}{ds}\,, \qquad c_\phi = \frac{\sin\alpha}{r}\ . \tag{J.54}$$

Fig. J.1 Geometry of the bubble



Since the tensor of membrane forces and the tensor of moments are co-axial with the tensor of curvature, their spectral form is given by

$$\mathbf{T} = t_s\,\mathbf{e}\otimes\mathbf{e} + t_\phi\,\mathbf{e}_\phi\otimes\mathbf{e}_\phi\,, \qquad \mathbf{M} = m_s\,\mathbf{e}\otimes\mathbf{e} + m_\phi\,\mathbf{e}_\phi\otimes\mathbf{e}_\phi\;. \tag{J.55}$$

The divergence of the tensor of moments becomes

$$\begin{aligned} &\mathbf{M}\cdot\nabla_T \\ =\;& \big(\overset{\acute{}}{\overline{m_s(s)\,\mathbf{e}(s,\phi)\otimes\mathbf{e}(s,\phi) + m_\phi(s)\,\mathbf{e}_\phi(\phi)\otimes\mathbf{e}_\phi(\phi)}}\big)\cdot\left(\mathbf{e}\frac{\partial}{\partial s} + \mathbf{e}_\phi\frac{\partial}{r\partial\phi}\right) \\ =\;& \frac{dm_s}{ds}\,\mathbf{e} + m_s\frac{\partial\mathbf{e}}{\partial s} + m_s\mathbf{e}\left(\frac{\partial\mathbf{e}}{r\partial\phi}\cdot\mathbf{e}_\phi\right) + m_\phi\frac{\partial\mathbf{e}_\phi}{r\partial\phi} \\ =\;& \frac{dm_s}{ds}\,\mathbf{e} + m_s c_s\mathbf{n} + m_s\frac{\cos\alpha}{r}\mathbf{e} - \frac{m_\phi}{r}\mathbf{e}_r\,, \end{aligned} \tag{J.56}$$

According to (J.25), this implies

$$\mathbf{q}_T = \mathbf{1}_T\;\cdot\;\big(\acute{\mathbf{M}}\cdot\nabla_T\big) = (\mathbf{e}\otimes\mathbf{e} + \mathbf{e}_\phi\otimes\mathbf{e}_\phi)\cdot\big(\acute{\mathbf{M}}\cdot\nabla_T\big) = q\,\mathbf{e} \tag{J.57}$$

with the transverse force

$$q = \frac{dm_s}{ds} + \frac{m_s - m_\phi}{r}\cos\alpha \tag{J.58}$$

and we get

$$\nabla_T\cdot\mathbf{q}_T = \left(\mathbf{e}\frac{\partial}{\partial s} + \mathbf{e}_\phi\frac{\partial}{r\partial\phi}\right)\cdot\overset{\acute{}}{\overline{(q\,\mathbf{e})}} = \frac{dq}{ds} + q\left(\frac{\partial\mathbf{e}}{r\partial\phi}\cdot\mathbf{e}_\phi\right) = \frac{dq}{ds} + \frac{q}{r}\cos\alpha\;. \tag{J.59}$$

Thus (J.24) yields

$$-\,\bar{p}_n + \mu\omega^2\,r\sin\alpha = \mathbf{T}:\mathbf{C} + \nabla_T\cdot\mathbf{q}_T = t_s c_s + t_\phi c_\phi + \frac{dq}{ds} + \frac{q}{r}\cos\alpha\;. \tag{J.60}$$

Moreover, we know that the tangential part of (J.20) is identically satisfied, and its component in the direction $\mathbf{e}$ reads

$$\begin{aligned} 0 \;&=\; \mathbf{e}\cdot\big(\acute{\mathbf{T}}\cdot\nabla_T\big) - \mathbf{e}\cdot\mathbf{C}\cdot\mathbf{q}_T + \mu\omega^2\,r\,\mathbf{e}_r\cdot\mathbf{e} \\ &=\; \frac{dt_s}{ds} + \frac{t_s - t_\phi}{r}\cos\alpha - qc_s + \mu\omega^2\,r\cos\alpha \end{aligned} \tag{J.61}$$

We multiply (J.60) by $r\cos\alpha$ and (J.61) by $r\sin\alpha$, add these equations, note (J.54) and the identity

$$\frac{dr}{ds} = \cos\alpha \tag{J.62}$$

and find

$$\frac{d}{ds}\Big(r\big(t_s\sin\alpha + q\cos\alpha\big)\Big) = -r\,\bar{p}_n\cos\alpha \tag{J.63}$$

Now, $-2\pi r\,(t_s \sin\alpha + q\cos\alpha)$ is the resultant of the z-components of the internal forces on a cut at $z = const$, and $-2\pi r \bar{p}_n \cos\alpha$ is the z-component of the surface load on a unit ring. Therefore (J.63) is easily interpreted as the condition of global equilibrium of the forces in the z-direction.

(J.54) and (J.62) imply

$$\frac{d}{ds}\big(r\sin\alpha\big) = r\cos\alpha\frac{d\alpha}{ds} + r\frac{dr}{ds}\frac{\sin\alpha}{r} = r\cos\alpha\big(c_s + c_\phi\big) \tag{J.64}$$

Multiplying this with some constant t_0, which will be fixed later, and adding it to (J.63), we obtain

$$\frac{d}{ds}\Big(r\big((t_s + t_0)\sin\alpha + q\cos\alpha\big)\Big) = -r\,\Big(\bar{p}_n - t_0\big(c_s + c_\phi\big)\Big)\cos\alpha \tag{J.65}$$

Integrating this equation from the pole — where $s = 0$ and $r = 0$ hold — we arrive at a finite expression for the transverse force q.

$$q = -(t_s + t_0)\tan\alpha - \frac{1}{r\cos\alpha}\int_{\bar{s}=0}^{s} r(\bar{s})\ \Big(\bar{p}_n - t_0\big(c_s + c_\phi\big)\Big)(\bar{s})\cos\alpha(\bar{s})\,d\bar{s} \tag{J.66}$$

We recall (J.36), (J.34) and obtain the bending moments

$$m_s \;=\; -\frac{\partial w}{\partial c_s} = -\left(w_h\frac{h}{4} + w_{hh}\frac{h^2}{8}\big(c_s + c_\phi\big) + w_{dd}\frac{h^2}{8}\big(c_s - c_\phi\big)\right) \tag{J.67}$$

$$m_\phi \;=\; -\frac{\partial w}{\partial c_\phi} = -\left(w_h\frac{h}{4} + w_{hh}\frac{h^2}{8}\big(c_s + c_\phi\big) - w_{dd}\frac{h^2}{8}\big(c_s - c_\phi\big)\right) \tag{J.68}$$

Now, (J.54) and (J.62) also imply

$$\frac{dc_\phi}{ds} = \big(c_s - c_\phi\big)\frac{\cos\alpha}{r} \tag{J.69}$$

which is a special case of Codazzi's identity. Noting this and inserting (J.67), (J.68) into (J.58), we obtain

$$q = -\big(w_{hh} + w_{dd}\big)\frac{h^2}{4}\frac{dH}{ds} \tag{J.70}$$

If an element dA of the middle surface of the film possesses the distance r from the axis, then the distances of the corresponding elements dA_+ and dA_- on the boundary surfaces according to (D.8), (D.9) are — note (J.54) — $r \mp (h/2)\sin\alpha = r(1 \mp hc_\phi/2)$.

Now, we adopt the simplifying assumption that the effective density ϱ_{Oe} of the oil does not depend on r. Then (J.27) can be integrated to give the oil pressure field

$$p_{\mathrm{O}} = p_{\mathrm{O}0} + \varrho_{\mathrm{Oe}}\frac{\omega^2}{2}r^2 \tag{J.71}$$

and the expression (J.16) reads

$$\begin{aligned}
\bar{p}_n &= \left(p_{\mathrm{W}0} + \varrho_{\mathrm{We}}\frac{\omega^2}{2}r^2\left(1+\frac{h}{2}c_\phi\right)^2\right)\left(1+\frac{h}{2}(c_s+c_\phi)+\frac{h^2}{4}c_sc_\phi\right) \\
&\quad -\left(p_{\mathrm{O}0} + \varrho_{\mathrm{Oe}}\frac{\omega^2}{2}r^2\left(1-\frac{h}{2}c_\phi\right)^2\right)\left(1-\frac{h}{2}(c_s+c_\phi)+\frac{h^2}{4}c_sc_\phi\right) \\
&= \big(p_{\mathrm{W}0}-p_{\mathrm{O}0}\big)\left(1+\underline{\frac{h^2}{4}c_sc_\phi}\right)+\big(p_{\mathrm{O}0}+p_{\mathrm{W}0}\big)\frac{h}{2}(c_s+c_\phi) \\
&\quad +\big(\varrho_{\mathrm{We}}-\varrho_{\mathrm{Oe}}\big)\frac{\omega^2}{2}r^2\left(1+\underline{\frac{3h^2}{4}c_\phi(c_s+c_\phi)+\frac{h^4}{16}c_sc_\phi^3}\right) \\
&\quad \underline{+\big(\varrho_{\mathrm{We}}+\varrho_{\mathrm{Oe}}\big)\frac{\omega^2}{2}r^2\left(\frac{h}{2}c_s+3\frac{h}{2}c_\phi+\frac{3h^3}{8}c_sc_\phi^2+\frac{h^3}{8}c_\phi^3\right)}
\end{aligned} \tag{J.72}$$

The terms containing the curvatures are very small compared to 1. On the other hand, the pressure difference $p_{\mathrm{W}0} - p_{\mathrm{O}0}$ at the pole will be very small compared with the mean pressure $(p_{\mathrm{O}0}+p_{\mathrm{W}0})/2$. So we neglect the underlined terms and arrive at the simple representation

$$\bar{p}_n - t_0(c_s+c_\phi) = p_{\mathrm{W}0} - p_{\mathrm{O}0} + \big(\varrho_{\mathrm{We}}-\varrho_{\mathrm{Oe}}\big)\frac{\omega^2}{2}r^2 \tag{J.73}$$

if we give t_0 the following meaning

$$t_0 \equiv \big(p_{\mathrm{O}0}+p_{\mathrm{W}0}\big)\frac{h}{2} \tag{J.74}$$

The integral of (J.66) can then be evaluated with the help of (J.62), as long as r is monotonously increasing with s, to give

$$\begin{aligned}
&\int_{\bar{s}=0}^{s} r(\bar{s})\,\Big(\bar{p}_n - t_0\big(c_s+c_\phi\big)\Big)(\bar{s})\cos\alpha(\bar{s})\,d\bar{s} \\
&= \int_{\bar{r}=0}^{r} \bar{r}\,\Big(\bar{p}_n - t_0\big(c_s+c_\phi\big)\Big)(\bar{r})\,d\bar{r} \\
&= \big(p_{\mathrm{W}0}-p_{\mathrm{O}0}\big)\frac{r^2}{2}+\big(\varrho_{\mathrm{We}}-\varrho_{\mathrm{Oe}}\big)\frac{\omega^2}{2}\frac{r^4}{4}
\end{aligned} \tag{J.75}$$

The membrane force in the direction $\mathbf{e}$ may be read from (J.18) with (J.29)

$$t_s = w - \mu\frac{\partial w}{\partial \mu} + m_sc_s = \tilde{t} + m_sc_s \tag{J.76}$$

In addition to (J.34), we define

$$\bar{c}_\phi = \bar{h}-\bar{d} = \frac{h}{2}\,c_\phi\,, \qquad \bar{c}_s = \bar{h}+\bar{d} = \frac{h}{2}\,c_s \tag{J.77}$$

Introducing (J.42), (J.67) with (J.34), (J.47) into (J.76) we obtain

$$t_s(\bar h,\bar c_\phi,r)=t_{00}+t_{10}\bar h+t_{01}\bar c_\phi+t_{20}\bar h^{\,2}+t_{11}\bar h\,\bar c_\phi+t_{02}\bar c_\phi^2-w^*\frac{\mu_{\mathrm{b}}\omega^2}{4w_1}r^2 \qquad \text{(J.78)}$$

with

$$t_{00}=\tilde t_{\mathrm{P}}\,,\qquad t_{10}=\tilde t_h-w_h\,,\qquad t_{01}=\frac{1}{2}w_h \qquad \text{(J.79)}$$

$$t_{20}=\tilde t_{hh}+\tilde t_{dd}-2\big(w_{hh}+w_{dd}\big) \qquad \text{(J.80)}$$

$$t_{11}=-2\tilde t_{dd}+w_{hh}+3w_{dd}\,,\qquad t_{02}=\tilde t_{dd}-w_{dd} \qquad \text{(J.81)}$$

J.5 The Differential Equations of the Bubble

We choose

$$\bar r=\frac{2}{h}\,r \qquad \text{(J.82)}$$

as the dimensionless independent variable, note

$$\frac{2}{h}\frac{d}{d\bar r}=\frac{d}{dr}=\frac{1}{\cos\alpha}\frac{d}{ds} \qquad \text{(J.83)}$$

according to (J.62), and replace the trigonometric functions of α by means of $\sin\alpha=r\,c_\phi=\bar r\,\bar c_\phi$ according to (J.54). Then (J.69) and (J.70) with (J.66), (J.75) yield a system of one linear and one nonlinear differential equation for the computation of $\bar c_\phi(\bar r)$ and $\bar h(\bar r)$:

$$\frac{d\bar c_\phi}{d\bar r} \;=\; \frac{2}{\bar r}\big(\bar h-\bar c_\phi\big)\,, \qquad \text{(J.84)}$$

$$\frac{d\bar h}{d\bar r} \;=\; \frac{\bar r}{1-\bar r^{\,2}\bar c_\phi^2}\,\big(w_{hh}+w_{dd}\big)^{-1}\times$$

$$\Bigg(\big(t_s(\bar h,\bar c_\phi,\bar r)+t_0\big)\,\bar c_\phi+\frac{h}{4}\big(p_{\mathrm{W}0}-p_{\mathrm{O}0}\big)+\big(\varrho_{\mathrm{We}}-\varrho_{\mathrm{Oe}}\big)\frac{h^3}{64}\omega^2\bar r^{\,2}\Bigg) \qquad \text{(J.85)}$$

With (J.78), equation (J.85) may be rewritten as follows

$$\Big(t_{00}+t_0\underbrace{+t_{10}\bar h+t_{01}\bar c_\phi+t_{20}\bar h^{\,2}+t_{11}\bar h\bar c_\phi+t_{02}\bar c_\phi^2}\Big)\bar c_\phi$$

$$\underline{-\big(w_{hh}+w_{dd}\big)\frac{1-\bar r^{\,2}\bar c_\phi^2}{\bar r}\,\frac{d\bar h}{d\bar r}} \;=\; b_0-b_1\,\bar r^{\,2} \qquad \text{(J.86)}$$

with the abbreviations

$$b_0=\frac{h}{4}\big(p_{\mathrm{O}0}-p_{\mathrm{W}0}\big) \qquad \text{(J.87)}$$

and

$$b_1 = \Big(\big(\varrho_{\mathrm{We}} - \varrho_{\mathrm{Oe}} \big) h - 8\,\mu_{\mathrm{P}}\,\bar{c}_\phi \Big) \frac{h^2\omega^2}{64} \approx \big(\varrho_{\mathrm{We}} - \varrho_{\mathrm{Oe}} \big) \frac{h^3}{64}\,\omega^2 \tag{J.88}$$

The second term is negligible compared to the first one because of the very small factor $\bar{c}_\phi$. This reflects the fact that the effect of the centrifugal force acting on the thin film is much smaller than that of the centrifugal forces acting on the bulk oil and water.

J.6 The Membrane Solution

The equations (J.84) and (J.85) take into account the bending behaviour of the film, *i.e.* the existence of bending moments and transverse forces and the fact that the membrane forces are different in the meridional and latitudinal direction. Conventionally, the spinning drop test is interpreted on the basis of the theory of capillarity, which allows nothing but an isotropic membrane force t_{M}, that does not depend on the curvature. Therefore, we have to put $\mathbf{q}_T = \mathbf{0}$ and $\mathbf{T} = t_{\mathrm{M}} \mathbf{1}_T$ in equation (J.24). Moreover the second term on the right-hand side of (J.24) can be neglected with respect to the first one according to (J.88). So we retain the so-called membrane equation — note (J.73), (J.87), (J.88) —

$$t_{\mathrm{M}} \mathbf{1}_T : \mathbf{C} = 2\,t_{\mathrm{M}} H = -\bar{p}_n = -2\,t_0 H + b_0 \frac{4}{h} - b_1\,\frac{32}{h^3}\,r^2 \tag{J.89}$$

It seems useful to define the surface tension by

$$t_{\mathrm{S}} = t_{\mathrm{M}} + t_0 = t_{\mathrm{M}} + \big(p_{\mathrm{O}0} + p_{\mathrm{W}0} \big) \frac{h}{2} \tag{J.90}$$

so that we obtain

$$2\,t_{\mathrm{S}} H = b_0 \frac{4}{h} - b_1\,\frac{32}{h^3}\,r^2 \tag{J.91}$$

In order to extract the same result from (J.86), we must omit the underbraced terms, which represent a dependence of the membrane forces on the curvature, and the underlined term, which describes the contribution of the transverse force as can be seen from (J.70). This leads to

$$\bar{c}_\phi = \bar{c}_0 - \bar{c}_1 \bar{r}^{\,2} \tag{J.92}$$

with

$$\bar{c}_0 = \frac{b_0}{t_{\mathrm{S}}}\,, \qquad \bar{c}_1 = \frac{b_1}{t_{\mathrm{S}}} \tag{J.93}$$

and (J.84) yields

$$\bar{h} = \bar{c}_0 - 2\bar{c}_1 \bar{r}^{\,2} \tag{J.94}$$

But the last equation is, indeed, equivalent to (J.91).

We need some geometrical properties of the shape of the film according to this membrane solution. The function

$$\sin\alpha = \bar{r}\bar{c}_\phi = \bar{c}_0\bar{r} - \bar{c}_1\bar{r}^{\,3} \tag{J.95}$$

must reach the value 1 at the equator of the bubble, the radius of which shall be denoted by a . If we define $\bar{a} = (2a)/h$, then the dimensionless principal curvatures at the equator are given by

$$\bar{c}_{\phi\mathrm{E}} = \bar{c}_0 - \bar{c}_1\bar{a}^{\,2} = \frac{1}{\bar{a}}\,, \qquad \bar{c}_{s\mathrm{E}} = \bar{c}_0 - 3\bar{c}_1\bar{a}^{\,2} \tag{J.96}$$

and yield

$$\bar{c}_0 = \frac{1}{2}\left(\frac{3}{\bar{a}} - \bar{c}_{s\mathrm{E}}\right)\,, \qquad \bar{c}_1 = \frac{1}{2\bar{a}^2}\left(\frac{1}{\bar{a}} - \bar{c}_{s\mathrm{E}}\right) \tag{J.97}$$

We consider the ratio

$$\beta = \frac{\bar{c}_1}{\bar{c}_0^3} = \frac{4}{\bar{a}^2}\left(\frac{1}{\bar{a}} - \bar{c}_{s\mathrm{E}}\right)\left(\frac{3}{\bar{a}} - \bar{c}_{s\mathrm{E}}\right)^{-3} \approx \frac{4}{27} - \frac{4}{81}\bar{a}^{\,2}\bar{c}_{s\mathrm{E}}^2 \tag{J.98}$$

and find

$$\beta \leq \frac{4}{27} \quad\Longrightarrow\quad \bar{c}_1 \leq \frac{4}{27}\bar{c}_0^3 \tag{J.99}$$

Since the bubble is prolate, the curvature $\bar{c}_{s\mathrm{E}}$ of the meridian at the equator is small compared to the curvature $\bar{c}_{\phi\mathrm{E}} = 1/\bar{a}$ of the equator line. If it is neglected, as has been practised by Vonnegut, then (J.97) simplifies to

$$\bar{c}_0 = \frac{3}{2\bar{a}}\,, \qquad \bar{c}_1 = \frac{1}{2\bar{a}^3} \tag{J.100}$$

This implies, with (J.93), (J.87), (J.88),

$$t_\mathrm{S} = \frac{b_1}{\bar{c}_1} = \big(\varrho_\mathrm{We} - \varrho_\mathrm{Oe}\big)\frac{a^3}{4}\,\omega^2 \tag{J.101}$$

$$= \frac{b_0}{\bar{c}_0} = \frac{a}{3}\big(p_\mathrm{O0} - p_\mathrm{W0}\big) \tag{J.102}$$

The quantities on the right-hand-side of (J.101) can be measured so that t_S can be inferred. Then (J.102) yields the pressure difference at the pole.

Finally, the constraints (J.5), (J.6), (J.7) have to be discussed. The deformation of the bubble increases its surface. Therefore amphiphile which was solved within the oil or the water must be embedded into the film. The second term in (J.5) increases while the last two terms diminish. Nevertheless, this effect is so small that the oil-sided and water-sided volumes almost remain constant according to (J.6), (J.7). If we neglect the thickness h of the film with respect to the dimensions of the bubble and note $dz = -dr \tan\alpha$ and (J.95), (J.98), we obtain the volume of the oil-sided cavity in the form

$$V_{\mathrm{O}} = \int \pi r^2 \, dz = -2\pi \int_{r=a}^{0} \tan\alpha(r)\, r^2 \, dr = \frac{\pi}{6} \frac{h^3}{\bar{c}_0^3} \,\Theta(\beta) \tag{J.103}$$

with the abbreviations

$$\Theta(\beta) \equiv \frac{3}{2} \int_{u=0}^{u_a(\beta)} \frac{u - \beta u^3}{\sqrt{1 - (u - \beta u^3)^2}} \, u^2 \, du \tag{J.104}$$

$u = \bar{c}_0 \bar{r}$ and $u_a = \bar{c}_0 \bar{a}$. According to (J.96), the latter is the smallest positive solution of the cubic equation

$$u_a - \beta u_a^3 = 1 \tag{J.105}$$

which varies from $u_a(\beta = 0) = 1$ to $u_a(\beta = 4/27) = 3/2$. Now, $\Theta(\beta)$ increases from $\Theta(0) = 1$ to $\Theta(4/27) = \infty$. Therefore, if we assume the conservation of V_{O}, we see that the curvature $\bar{c}_0$ increases according to

$$\bar{c}_0(\beta) = \bar{c}_0(0) \sqrt[3]{\Theta(\beta)} \tag{J.106}$$

with increasing β, while the radius at the equator decreases according to

$$\bar{a}(\beta) = \frac{u_a(\beta)}{\bar{c}_0(\beta)} = \bar{a}(0) \frac{u_a(\beta)}{\sqrt[3]{\Theta(\beta)}} \tag{J.107}$$

After all, we see that the fulfilment of the constraints (J.5), (J.6), (J.7) is possible without difficulties. Since we will have $\bar{a}(\beta) \ll \bar{a}(0)$ in case of sufficiently high angular velocities, the value of β will be near to $4/27$ and hence $\bar{c}_{s\mathrm{E}} \approx 0$ according to (J.98). So the approximation (J.100) is accurate enough, and an evaluation of (J.104) to (J.107) is not necessary in order to obtain the membrane force t_{M}.

The knowledge of the surface tension yields information on the mass density and the energy density. (J.32), (J.33), (J.43), and (J.35) give

$$\delta \equiv G_{\mathrm{sP}} - \ln \frac{\mu_{\mathrm{P}}}{\mu_{\mathrm{b}}} = \frac{2}{3} q - \ln \frac{\mu_{\mathrm{P}}}{\mu_{\mathrm{b}}} = 1 - S_{\mathrm{P}} = \frac{t_{\mathrm{M}}}{w^*} = \frac{t_{\mathrm{M}}}{2 w_1} \frac{\mu_{\mathrm{b}}}{\mu_{\mathrm{P}}} \tag{J.108}$$

Hence

$$\frac{\mu_{\mathrm{P}}}{\mu_{\mathrm{b}}} = \exp\Big(\frac{2}{3} q\Big) \exp(-\delta) = \frac{t_{\mathrm{M}}}{2 w_1} \,\delta^{-1} \tag{J.109}$$

and, since $|\delta|$ is small,

$$\exp\Big(-\frac{2}{3} q\Big) \frac{t_{\mathrm{M}}}{2 w_1} = \delta \exp(-\delta) \approx \delta \tag{J.110}$$

and the mass density becomes

$$\frac{\mu_{\mathrm{P}}}{\mu_{\mathrm{b}}} = \exp\Big(\frac{2}{3} q\Big) \exp(-\delta) \approx \exp\Big(\frac{2}{3} q\Big) \big(1 - \delta\big) \approx \exp\Big(\frac{2}{3} q\Big) - \frac{t_{\mathrm{M}}}{2 w_1} \tag{J.111}$$

Introducing this together with (J.35), (J.33), (J.108) into (J.37) we obtain the energy density

$$w_{\mathrm{P}} = w_1 \frac{\mu_{\mathrm{P}}}{\mu_{\mathrm{b}}} \left(\frac{w_0}{w_1} + \frac{16}{45} q^2 + \frac{4}{3} \bar{h}_0^2 + \left(\frac{t_{\mathrm{M}}}{2 w_1} \frac{\mu_{\mathrm{b}}}{\mu_{\mathrm{P}}} \right)^2 \right) \tag{J.112}$$

Noting (J.11) and (J.74), assuming incompressibility of the fluids, and putting $r = 0$, we further get

$$f = \frac{1}{2} \left(\frac{df_{\mathrm{O}}}{dk_{\mathrm{O}}}(k_{\mathrm{O}}) + \frac{df_{\mathrm{W}}}{dk_{\mathrm{W}}}(k_{\mathrm{W}}) + \frac{p_{\mathrm{O}0} + p_{\mathrm{W}0}}{\varrho_{\mathrm{A}}} \right) = k + \frac{t_0}{h \varrho_{\mathrm{A}}} \tag{J.113}$$

with the abbreviation

$$k = \frac{1}{2} \left(\frac{df_{\mathrm{O}}}{dk_{\mathrm{O}}}(k_{\mathrm{O}}) + \frac{df_{\mathrm{W}}}{dk_{\mathrm{W}}}(k_{\mathrm{W}}) \right) \tag{J.114}$$

Now, if $r = 0$, (J.29) implies

$$\tilde{t} = w - \mu \frac{\partial w}{\partial \mu} = \tilde{t}_{\mathrm{P}} = w_{\mathrm{P}} - f \mu_{\mathrm{P}} = t_{\mathrm{M}} \tag{J.115}$$

and hence

$$\frac{t_{\mathrm{M}}}{w_1} \frac{\mu_{\mathrm{b}}}{\mu_{\mathrm{P}}} = \frac{w_0}{w_1} + \frac{16}{45} q^2 + \frac{4}{3} \bar{h}_0^2 + \left(\frac{t_{\mathrm{M}}}{2 w_1} \frac{\mu_{\mathrm{b}}}{\mu_{\mathrm{P}}} \right)^2 - \frac{\mu_{\mathrm{b}}}{w_1} k - \frac{t_0}{w_1} \frac{\mu_{\mathrm{b}}}{h \varrho_{\mathrm{A}}} \tag{J.116}$$

The introduction of (J.111) and (J.90) yields a quadratic equation in t_{S} with the solution

$$\frac{t_{\mathrm{S}}}{w_1} = \frac{t_0}{w_1} + 2 \exp\left(\frac{2}{3} q \right) \times$$

$$\left(1 - \left(2 - \sqrt{1 - \frac{w_0}{w_1} - \frac{16}{45} q^2 - \frac{4}{3} \bar{h}_0^2 + \frac{\mu_{\mathrm{b}}}{w_1} k + \frac{t_0}{w_1} \frac{\mu_{\mathrm{b}}}{h \varrho_{\mathrm{A}}}} \right)^{-1} \right) \tag{J.117}$$

If the expression under the square root is almost 1, then we may use a first order Taylor approximation and obtain

$$t_{\mathrm{S}} = t_{\mathrm{S}0} + t_{\mathrm{S}1} \bar{h}_0^2 \tag{J.118}$$

with

$$t_{\mathrm{S}0} = \exp\left(\frac{2}{3} q \right) \left(w_0 + w_1 \frac{16}{45} q^2 - \mu_{\mathrm{b}} k \right) + t_0 \left(1 - \exp\left(\frac{2}{3} q \right) \frac{\mu_{\mathrm{b}}}{h \varrho_{\mathrm{A}}} \right) \tag{J.119}$$

$$t_{\mathrm{S}1} = \frac{4}{3} w_1 \exp\left(\frac{2}{3} q \right) \tag{J.120}$$

It is to be expected that the dependence of the coefficients $t_{\mathrm{S}0}$ and $t_{\mathrm{S}1}$ on the temperature is negligible, while the dependence of the preferred curvature $\bar{h}_0$

is strong. If a linear relation between $\bar{h}_0$ and the temperature holds, then the surface tension is, in good approximation, a quadratic function of the temperature with a minimum at some temperature which characterizes $\bar{h}_0 = 0$. This is confirmed by experimental findings of Sottmann[15]. We see, that the minimum value $t_{\mathrm{S}0}$ of the surface tension depends on k and t_0 and hence on the mass fractions of the monomeric solutions of the amphiphile and on the mean pressure which will be nearly the environmental pressure. All the other symbols in (J.119) represent material constants of the film. The coefficient $t_{\mathrm{S}1}$ is a material constant, too, and can be inferred from measurements if the relation between $\bar{h}_0$ and the temperature is known.

J.7 The part of the bending moments

In the last section, we discussed the spinning drop test on the basis of the membrane theory, *i.e.* we totally disregarded bending effects. However, bending moments are actually present and we have to find out whether the membrane solution is of any use at all in the context of the more general bending theory. To this purpose, we introduce (J.92) and (J.94) with (J.93), (J.79), (J.80), (J.81) into (J.86) and obtain

$$\begin{aligned}
&\underline{\underline{\big(\tilde{t}_{\mathrm{P}} + t_0\big)\big(\bar{c}_0 - \bar{c}_1\bar{r}^{\,2}\big)}} \;+\; \underline{\big(\bar{c}_0 - \bar{c}_1\bar{r}^{\,2}\big)\Big(\tilde{t}_h\big(\bar{c}_0 - 2\bar{c}_1\bar{r}^{\,2}\big) - \frac{1}{2}w_h\big(\bar{c}_0 - 3\bar{c}_1\bar{r}^{\,2}\big)\Big)} \\
&+\big(\bar{c}_0 - \bar{c}_1\bar{r}^{\,2}\big)\Big(\tilde{t}_{hh}\big(\bar{c}_0 - 2\bar{c}_1\bar{r}^{\,2}\big)^2 + \tilde{t}_{dd}\big(\bar{c}_1\bar{r}^{\,2}\big)^2\Big) \\
&+w_{hh}\Big(4\bar{c}_1 - \big(\bar{c}_0 - \bar{c}_1\bar{r}^{\,2}\big)\big(\bar{c}_0^2 - \bar{c}_0\bar{c}_1\bar{r}^{\,2} + 2(\bar{c}_1\bar{r}^{\,2})^2\big)\Big) \\
&+w_{dd}\Big(4\bar{c}_1 - \big(\bar{c}_0 - \bar{c}_1\bar{r}^{\,2}\big)\big(3\bar{c}_0 - \bar{c}_1\bar{r}^{\,2}\big)\bar{c}_1\bar{r}^{\,2}\Big) \quad = \quad \underline{\underline{t_{\mathrm{S}}\big(\bar{c}_0 - \bar{c}_1\bar{r}^{\,2}\big)}} \qquad \text{(J.121)}
\end{aligned}$$

The dimensionless curvatures $\bar{c}_\phi$ and $\bar{h}$ are very small everywhere and so are $\bar{c}_0$ and $\bar{c}_1\bar{r}^{\,2}$ according to (J.92), (J.94). The terms that are not underlined in (J.121) are of the third order in these quantities. (Note, that (J.99) implies that $\bar{c}_1$ is of the third order, too.) The once underlined terms are of the second order and the twice underlined ones of the first order. Only the terms of the leading order need to be retained since all the others are negligible compared to them. So we arrive at the conclusion $\tilde{t}_{\mathrm{P}} = t_{\mathrm{S}} - t_0 = t_{\mathrm{M}}$, and the surface tension inferred from the membrane theory minus the contribution of the mean pressure is thus seen to describe the membrane force of the film accurately.

Actually, the situation is a little more complex. If we introduce (J.118) and (J.38), (J.44) into the left-hand side of (J.121) and consider only the pole of the bubble, *i.e.* the point with $\bar{r} = 0$, then the underlined terms become

$$\underline{\underline{\big(t_{\mathrm{S0}} + t_{\mathrm{S1}}\bar{h}_0^2\big)\bar{c}_0}} - \underline{\frac{2}{3}\left(2w^* + (w_{\mathrm{P}} - w^*)\,S_{\mathrm{P}}^{-1}\right)\bar{h}_0\bar{c}_0^2} \tag{J.122}$$

If $|\bar{h}_0| \gg \bar{c}_0$, then, indeed, the once underlined term is of the second order and the twice underlined one of the first order in $\bar{c}_0$. If, however, the order of magnitude of $|\bar{h}_0|$ is the same as that of $\bar{c}_0$, then we are near the minimum of the surface tension, the once underlined term is even of the third order and can be neglected all the more.

The situation would be totally different, however, if the minimum value t_{S0} of the surface tension were exactly equal to zero. In this pathological case, the twice underlined term is of the third order, too, no simplification of the bending differential equation is possible, and the membrane solution is not applicable in this range.

The bending moment at the pole can be inferred from (J.67), (J.68) with (J.38) to be

$$m = -\frac{h}{6}\Big(2\big(w_{\mathrm{P}} - w^*\big)S_{\mathrm{P}}^{-1}\bar{h}_0 + 3w_{hh}\bar{c}_0\Big) \tag{J.123}$$

We are confronted with a paradoxical situation. If $|\bar{h}_0|$ is large, then the bending moments of the film are large, too. But then the bending effects can totally be neglected and only membrane theory be applied. If, however, $|\bar{h}_0|$ is small, then the bending moments are small, too. In the mentioned pathological case, this is just the range where membrane theory must be discarded since bending effects become dominant.

The paradox can be resolved as follows. The surface tension in the middle surface and the bending moment together can be replaced by a force in a distance e from the middle surface such that $|m| = t_{\mathrm{S}}\,e$. We find

$$\frac{e}{h} = \frac{|m|}{h\,t_{\mathrm{S}}} = \frac{|2\big(w_{\mathrm{P}} - w^*\big)S_{\mathrm{P}}^{-1}\bar{h}_0 + 3w_{hh}\bar{c}_0|}{6\big(t_{\mathrm{S0}} + t_{\mathrm{S1}}\bar{h}_0^2\big)} \tag{J.124}$$

If $|\bar{h}_0| \gg \bar{c}_0$, then the offset e turns out to be of the order of magnitude of the film thickness h. Therefore, from the point of view of the film, the strain due to the bending moment is at least as large as the strain due to the surface tension and by no means negligible. But from the point of view of the bearing behaviour of the bubble, the tiny deviation of the force from the middle surface is of no account.

If $\bar{h}_0 \to 0$, then, in general, e/h will become very small. In the pathological case $t_{\mathrm{S0}} = 0$, however, this ratio tends to infinity. We can resume: Bending effects can be neglected, if the offset of the surface tension is small compared to the dimensions of the cell. This applies to the spinning drop test except in the pathological case. On the other hand, such a restriction to the membrane theory is surely not justified with the nanostructures of a microemulsion, where the dimension of the cell and the thickness of the film are of the same order of magnitude.

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