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CHAPTER 4

GENERAL CURVED INTERFACES AND BIOMEMBRANES

Mechanically, the stresses and moments acting in an interface or biomembrane can be taken into account by assigning tensors of the surface stresses and moments to the phase boundary. The three equations determining the interfacial/membrane shape and deformation represent the three projections of the vectorial local balance of the linear momentum. Its normal projection has the meaning of a generalized Laplace equation, which contains a contribution from the interfacial moments. Alternatively, variational calculus can be applied to derive the equations governing the interfacial/membrane shape by minimization of a functional – "the thermodynamic approach". The correct minimization procedure is considered, which takes into account the work of surface shearing.

Thus it turns out that the generalized Laplace equation can be derived following two alternative approaches: mechanical and thermodynamical. In fact, they are mutually complementary parts of the same formalism; they provide a useful tool to verify the selfconsistency of a given model. The connection between them has the form of relationships between the mechanical and thermodynamical surface tensions and moments. Different, but equivalent, forms of the generalized Laplace equation are considered and discussed.

The general theoretical equations can give quantitative predictions only if rheological constitutive relations are specified, which characterize a given interface (biomembrane) as an elastic, viscous or visco-elastic two-dimensional continuum. Thus the form of the generalized Laplace equation can be specified. Further, it is applied to determine the axisymmetric shapes of biological cells; a convenient computational procedure is proposed.

Finally, micromechanical expressions are derived for calculating the surface tensions and moments, the bending and torsion elastic moduli, k_c and \bar{k}_c , and the spontaneous curvature, H_0 , in terms of combinations from the components of the pressure tensor.

4.1. THEORETICAL APPROACHES FOR DESCRIPTION OF CURVED INTERFACES

A natural mathematical description of arbitrarily curved interfaces is provided by the differential geometry based on the apparatus of the tensor analysis. Our main purpose in this chapter is to demonstrate the application of this apparatus for generalization of the relationships described in Section 3.2 for spherical interface.

Firstly, the generalization of the theory includes presentation of the surface stresses and moments as tensorial quantities. Secondly, generalizations of the theoretical expressions, such as the Laplace equation and the micromechanical expressions (3.69)–(3.70), are considered. A special attention is paid to the connection between the two equivalent and complementary approaches: the thermodynamical and the mechanical one.

The thermodynamical approach to the theory of the curved interfaces, which is outlined in Sections 3.1 and 3.2 above, originates from the works of Gibbs [1] and has been further developed by Boruvka & Neumann [2]. In this approach a heterogeneous (multiphase) system is formally treated as a combination of bulk, surface and linear phases, each of them characterized by its own fundamental thermodynamic equation. The logical scheme of the Gibbs' approach consists of the following steps:

- (1) The extensive parameters (such as internal energy U , entropy S , number of molecules of the i -th component N_i , etc.) and their densities far from the phase boundaries are considered to be, in principle, known.
- (2) An imaginary *idealized* system is introduced, in which all phases (bulk, surface and linear) are uniform, the interfacial transition zones are replaced with sharp boundaries (geometrical surfaces and lines), and the excesses of the extensive parameters (in the idealized with respect to the real system) are ascribed to these boundaries; for example – see Figs 1.1 and 3.3.
- (3) The Gibbs fundamental equations are postulated for each bulk, surface and linear phase. Since the densities of the extensive parameters can vary along a curved interface, a local formulation of the fundamental equations should be used, see Eq. (3.13).
- (4) The last step is to impose the conditions for equilibrium in the multiphase system. These are (i) absence of hydrodynamic fluxes (mechanical equilibrium) (ii) absence of diffusion

fluxes (chemical equilibrium) and (iii) absence of heat transport (thermal equilibrium). As known [3], the conditions for thermal and chemical equilibrium imply uniformity of the temperature and the chemical potentials in the system. The conditions for mechanical equilibrium are multiform; examples are the Laplace and Young equations (Chapter 2). All conditions for equilibrium can be deduced by means of a variational principle, that is by minimization of the grand thermodynamic potential of the system, see Chapter 2 and Section 4.3.1.

The mechanical approach originates from the theory of elastic deformations of "plates" and "shells" developed by Kirchhoff [4] and Love [5]; a comprehensive review can be found in Ref. [6]. For the linear theory by Kirchhoff and Love it is typical that the stress depends linearly on the strain, and that the elastic energy is a quadratic function of the deformation. Similar form has Eq. (3.7), postulated by Helfrich [7,8], which expresses the work of flexural deformation as a quadratic function of the variations of the interfacial curvatures. Evans and Skalak [9] demonstrated that a relatively complex object, as a biomembrane, can be treated mechanically as a two-dimensional continuum, characterized by dilatational and shearing tensions, and elastic moduli of bending and torsion. The logical scheme of the mechanical approach consists of the following steps:

(1) Strain and stress tensors, as well as tensors of the moments (torques), are defined for the bulk phases and for the boundaries between them. A phase with a (nonzero) tensor of moments is termed *continuum of Cosserat* [10]; the liquid crystals represent an example [11]. Here we will restrict our considerations to bulk fluid phases without moments; action of moments will be considered only at the interfaces.

(2) Equations expressing the balances of mass, linear and angular momentum are postulated; they provide a set of differential equations and boundary conditions, which describe the dynamics of the processes in the system. In particular, the Laplace equation (2.17) can be deduced as a normal projection of the interfacial balance of the linear momentum; see Eq. (4.51) below and Refs. [12-14].

(3) The properties of a specific material continuum are taken into account by postulating appropriate rheological constitutive relations, which define connections between stresses (or

moments) and strains. In fact, the rheological constitutive relations represent mechanical models, say viscous fluid, elastic body, visco-elastic medium, etc. In Section 4.3.4 we demonstrate that the Helfrich equation (3.7) leads to a constitutive relation for the tensor of the interfacial moments.

In summary, the thermodynamical and the mechanical approaches are based on different concepts and postulates, but they are applied to the theoretical description of the same subject: the processes in multiphase systems. Then obligatorily these two approaches have to be equivalent, or at least complementary. One of our main goals below is to demonstrate the connections between them. The combination of the two approaches provides a deeper understanding of the meaning of quantities and equations in the theory of curved interfaces (membranes) and provides a powerful apparatus for solving problems in this field.

Below we first present the mechanical approach to the curved interfaces and membranes. Next we consider the connections between the thermodynamical and mechanical approaches. Further, we give a derivation of the generalized Laplace equation by minimization of the free energy of the system. A special form of this equation for axisymmetric interfaces is considered with application for determination of the shape of biological cells. Finally, some micro-mechanical expressions for the interfacial (membrane) properties are derived.

4.2. MECHANICAL APPROACH TO ARBITRARILY CURVED INTERFACES

4.2.1. ANALOGY WITH MECHANICS OF THREE-DIMENSIONAL CONTINUA

Balance of the linear momentum. First, it is useful to recall the “philosophy” and basic equations of the mechanics of three-dimensional continua. Consider a material volume V , which is bounded by a closed surface S with running outer unit normal \mathbf{n} . On the basis of the second Newton's law it is postulated (see e.g. Ref. 15)

$$\frac{d}{dt} \int_V \rho \mathbf{v} = \oint_S ds \mathbf{n} \cdot \mathbf{T} + \int_V \rho \mathbf{f} \quad (4.1)$$

Here t is time, \mathbf{v} is the velocity field; \mathbf{T} is the stress tensor; ds is a scalar surface element; ρ is

the mass density; \mathbf{f} is an acceleration due to body force (gravitational or centrifugal). Equation (4.1) expresses the *integral* balance of the linear momentum for the material volume V ; indeed, Eq. (4.1) states that the time-derivative of the linear momentum is equal to the sum of the surface and body forces exerted on the considered portion of the material continuum. Using the Gauss theorem and the fact that the volume V has been arbitrarily chosen, from Eq. (4.1) one can deduce the *local* balance of the linear momentum [15]:

$$\rho \frac{d\mathbf{v}}{dt} = \nabla \cdot \mathbf{T} + \rho \mathbf{f} \quad (4.2)$$

In the derivation of Eq. (4.2) the following known hydrodynamic relationships have been used:

$$\frac{d}{dt} \int_V dV \rho \mathbf{v} = \int_V dV \left[\frac{d(\rho \mathbf{v})}{dt} + \rho \mathbf{v} \nabla \cdot \mathbf{v} \right] \quad (4.3)$$

$$\frac{d\rho}{dt} + \rho \nabla \cdot \mathbf{v} = 0 \quad (4.4)$$

Equation (4.3) is a corollary from the known Euler formula, whereas Eq. (4.4) is the continuity equation expressing the local mass balance [15].

Rheological models. The continuum mechanics can give quantitative predictions only if a model expression for the stress tensor \mathbf{T} is specified. As a rule, such an expression has the form of relationship between stress and strain, which is termed rheological constitutive relation (defining, say, an elastic or a viscous body, see below). The vectors of displacement, \mathbf{u} , and velocity, \mathbf{v} , are simply related:

$$\mathbf{v} = \frac{d\mathbf{u}}{dt} \quad (4.5)$$

Further, the strain and rate-of-strain tensors are introduced:

$$\Phi = \frac{1}{2} [\nabla \mathbf{u} + (\nabla \mathbf{u})^T] \quad (\text{strain tensor}) \quad (4.6)$$

$$\Psi = \frac{1}{2} [\nabla \mathbf{v} + (\nabla \mathbf{v})^T] \quad (\text{rate-of-strain tensor}) \quad (4.7)$$

As usual, ∇ denotes the gradient operator in space and “T” denotes conjugation. The tensors Φ and Ψ are related as follows:

$$\Phi = \Psi \delta t \quad (4.8)$$

Here δt denotes an infinitesimal time interval.

An *elastic* body is defined by means of the following constitutive relation [16]

$$\mathbf{T} = \lambda \text{Tr}(\Phi) \mathbf{U} + 2\mu [\Phi - \frac{1}{3} \text{Tr}(\Phi) \mathbf{U}] \quad (\text{Hooke's law}) \quad (4.9)$$

where \mathbf{U} is the spatial unit tensor; λ and μ are the dilatational and shear bulk elastic moduli; as usual, “Tr” denotes trace of a tensor. Note that λ and μ multiply, respectively, the isotropic and the deviatoric part of the strain tensor Φ . (The trace of the deviatoric part is equal to zero, i.e. no dilatation, only shearing deformation). Similar consideration of the isotropic part (accounting for the dilatation) and deviatoric part (accounting for the shear deformation) is applied also to viscous bodies and two-dimensional continua (interfaces, biomembranes), see below. The substitution of Eq. (4.9) into the balance of linear momentum, Eq. (4.2), along with Eq. (4.6), yields the basic equation in the mechanics of elastic bodies [16]:

$$\rho \frac{d^2 \mathbf{u}}{dt^2} = \mu \nabla^2 \mathbf{u} + \left(\lambda + \frac{1}{3} \mu \right) \nabla \nabla \cdot \mathbf{u} + \rho \mathbf{f} \quad (\text{Navier equation}) \quad (4.10)$$

Likewise, a *viscous* body (fluid) is defined by means of the constitutive relation [17]

$$\mathbf{T} = -P \mathbf{U} + \zeta_v \text{Tr}(\Psi) \mathbf{U} + 2\eta_v [\Psi - \frac{1}{3} \text{Tr}(\Psi) \mathbf{U}] \quad (\text{Newton's law}) \quad (4.11)$$

where P is pressure, ζ_v and η_v are the dilatational and shear bulk viscosities; in fact η_v is the conventional viscosity of a liquid, whereas ζ_v is related to the decay of the intensity of sound in a liquid. The substitution of Eq. (4.11) into the balance of linear momentum, Eq. (4.2), along with Eq. (4.7), yields the basic equation of hydrodynamics [15, 17]:

$$\rho \frac{d\mathbf{v}}{dt} = -\nabla P + \eta_v \nabla^2 \mathbf{v} + \left(\zeta_v + \frac{1}{3} \eta_v \right) \nabla \nabla \cdot \mathbf{v} + \rho \mathbf{f} \quad (\text{Navier-Stokes equation}) \quad (4.12)$$

In Section 4.2.4 we will consider the two-dimensional analogues of Eqs. (4.1)-(4.12). Before that we need some relationships from differential geometry.

4.2.2. BASIC EQUATIONS FROM GEOMETRY AND KINEMATICS OF A CURVED SURFACE

The formalism of differential geometry, which is briefly outlined and used in this chapter, is described in details in Refs. [12, 18-20]. Let (u^1, u^2) be curvilinear coordinates on the dividing

surface between two phases, and let $\mathbf{R}(u^1, u^2, t)$ be the running position-vector of a material point on the interface, which depends also on the time, t . We introduce the vectors of the surface local basis and the surface gradient operator:

$$\mathbf{a}_\mu = \frac{\partial \mathbf{R}}{\partial u^\mu}, \quad \nabla_s = \mathbf{a}^\mu \frac{\partial}{\partial u^\mu} \quad (\mu=1, 2) \quad (4.13)$$

Here and hereafter the Greek indices take values 1 and 2; summation over the repeated indices is assumed. The curvature tensor \mathbf{b} is defined by Eq. (3.21); \mathbf{b} is a symmetric surface tensor, whose eigenvalues are the principal curvatures c_1 and c_2 . The surface unit tensor \mathbf{U}_s and curvature deviatoric tensor \mathbf{q} are defined as follows

$$\mathbf{U}_s \equiv \mathbf{a}^\mu \mathbf{a}_\mu, \quad \mathbf{q} \equiv \frac{1}{D} (\mathbf{b} - H \mathbf{U}_s) \quad (4.14)$$

where, as before, H and D denote the mean and deviatoric curvature, see Eq. (3.3). For every choice of the surface basis the eigenvalues of \mathbf{U}_s are both equal to 1; the tensor \mathbf{q} has diagonal form in the basis of the principal curvatures and has eigenvalues 1 and -1 . In particular, the covariant components of \mathbf{U}_s ,

$$a_{\mu\nu} \equiv \mathbf{a}_\mu \cdot \mathbf{a}_\nu \quad (4.15)$$

represent the components of the surface metric tensor; here “ \cdot ” is the standard symbol for scalar product of two vectors. The covariant derivative of $a_{\mu\nu}$ is identically zero, $a_{\lambda\mu,\nu} = 0$, whereas the covariant derivative $q_{\lambda\mu,\nu}$ of the components of the tensor \mathbf{q} is not zero, although its eigenvalues are constant at each point of the interface; in particular, the divergence of \mathbf{q} is [13]:

$$q_{\lambda\mu}{}^{,\mu} = \frac{1}{D} (a_{\lambda\mu} H^{,\mu} - q_{\lambda\mu} D^{,\mu}) \quad (4.16)$$

In view of Eq. (4.14), the curvature tensor can be expressed as a sum of an isotropic and a deviatoric part:

$$b_{\lambda\mu} = H a_{\lambda\mu} + D q_{\lambda\mu} \quad (4.17)$$

The velocity of a material point on the interface is defined as follows

$$\mathbf{v} = \left(\frac{\partial \mathbf{R}}{\partial t} \right)_{u^1, u^2} \quad (4.18)$$

According to Eliassen [21], the interfacial *rate-of-strain* tensor, which describes the two-dimensional dilatational and shear deformations, is defined by the expression:

$$d_{\mu\nu} = \frac{1}{2} \frac{\partial a_{\mu\nu}}{\partial t} = \frac{1}{2} (\mathbf{v}_{\mu,\nu} + \mathbf{v}_{\nu,\mu} - 2b_{\mu\nu} \mathbf{v}^{(n)}) \quad (4.19)$$

where

$$\mathbf{v}_{\mu} = \mathbf{a}_{\mu} \cdot \mathbf{v}; \quad \mathbf{v}^{(n)} = \mathbf{n} \cdot \mathbf{v} \quad (4.20)$$

are components of the velocity vector \mathbf{v} . Despite the fact that we will finally derive some quasistatic relationships, it is convenient to work initially with the rates (the time derivatives) of some quantities. For example, if δt is a small time interval and \dot{H} is the time derivative of the mean curvature then $\delta H = \dot{H} \delta t$ is the differential of H , which takes part in Eq. (3.1).

We will restrict our considerations to processes, for which the rate-of-strain tensor has always diagonal form in the basis of the principal curvatures. For example, such is the case of an axisymmetric surface subjected to an axisymmetric deformation [9]. A more general case is considered in Ref. [22]. In such cases the quantities $\dot{\alpha}$ and $\dot{\beta}$, defined by the relationships

$$\dot{\alpha} = a^{\mu\nu} d_{\mu\nu}, \quad \dot{\beta} = q^{\mu\nu} d_{\mu\nu}, \quad (4.21)$$

express the local surface rates of dilatation and shear [23]. Then, the infinitesimal deformations of dilatation and shearing, corresponding to a small time increment, δt , will be

$$\delta\alpha = \dot{\alpha} \delta t; \quad \delta\beta = \dot{\beta} \delta t \quad (4.22)$$

The latter two differentials also take part in Eq. (3.1). In view of Eq. (4.21) we can present $d_{\mu\nu}$ as a sum of an isotropic and a deviatoric part

$$d_{\mu\nu} = \frac{1}{2} \dot{\alpha} a_{\mu\nu} + \frac{1}{2} \dot{\beta} q_{\mu\nu} \quad (4.23)$$

4.2.3. TENSORS OF THE SURFACE STRESSES AND MOMENTS

Owing to the connections between stress and strain, an expression similar to Eq. (4.23) holds for the surface stress tensor [24]:

$$\sigma_{\mu\nu} = \sigma a_{\mu\nu} + \eta q_{\mu\nu} \tag{4.24}$$

(Each of Eqs. 4.23 and 4.24 represent the respective tensor as a sum of an isotropic and a deviatoric part.) Let σ_1 and σ_2 be the eigenvalues of the tensor $\sigma_{\mu\nu}$. The tensions σ_1 and σ_2 are directed along the lines of maximum and minimum curvature. From Eq. (4.24) it follows

$$\sigma = \frac{1}{2}(\sigma_1 + \sigma_2); \quad \eta = \frac{1}{2}(\sigma_1 - \sigma_2) \tag{4.25}$$

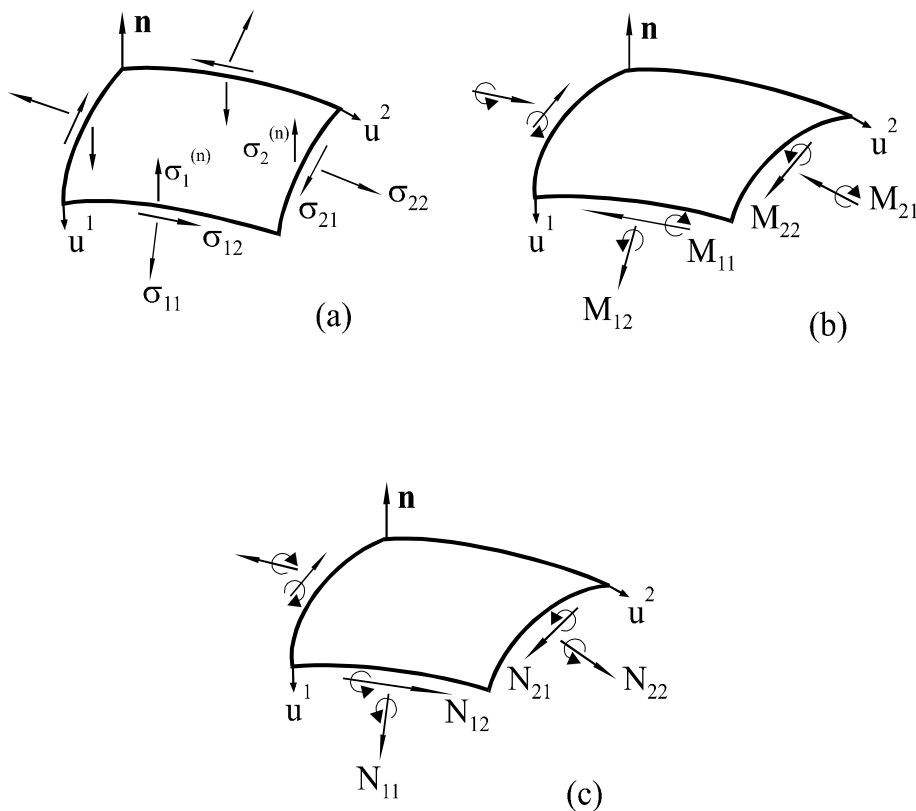


Fig. 4.1. Mechanical meaning of the components of (a) the surface stress tensor, $\sigma_{\mu\nu}$ and $\sigma_{\mu}^{(n)}$; (b) the tensor of surface moments $M_{\mu\nu}$; (c) the tensor of surface moments $N_{\mu\nu}$. The relationship between $M_{\mu\nu}$ and $N_{\mu\nu}$ is given by Eq. (4.29).

In fact, the quantity σ is the conventional mechanical surface tension, while η is the mechanical shearing tension [9, 24]. The physical meaning of the components $\sigma_{\mu\nu}$ ($\mu, \nu = 1, 2$) in an arbitrary basis is illustrated in Fig. 4.1. Note that in general the surface stress tensor $\underline{\sigma}$ is not purely tangential, but has also two normal components, $\sigma^{\mu(n)}$, $\mu = 1, 2$, see Refs. [6, 12]:

$$\underline{\sigma} = \mathbf{a}_\mu \mathbf{a}_\nu \sigma^{\mu\nu} + \mathbf{a}_\mu \mathbf{n} \sigma^{\mu(n)} \quad (4.26)$$

In other words, the matrix of the tensor $\underline{\sigma}$ is rectangular:

$$\underline{\sigma} = \begin{pmatrix} \sigma^{11} & \sigma^{12} & \sigma^{1(n)} \\ \sigma^{21} & \sigma^{22} & \sigma^{2(n)} \end{pmatrix} \quad (4.27)$$

Let us consider also the tensor of the surface moments (torques),

$$M_{\mu\nu} = \frac{1}{2}(M_1 + M_2) a_{\mu\nu} + \frac{1}{2}(M_1 - M_2) q_{\mu\nu}, \quad (4.28)$$

which is defined at each point of the interface; M_1 and M_2 are the eigenvalues of the tensor $M_{\mu\nu}$ supposedly it has a diagonal form in the basis of the principal curvatures. In the mechanics of the curved interfaces the following tensor is often used [6, 12]

$$N_{\mu\nu} = M_\mu^\lambda \varepsilon_{\nu\lambda} \quad (4.29)$$

where $\varepsilon_{\mu\nu}$ is the surface alternator [19]: $\varepsilon_{12} = \sqrt{a}$, $\varepsilon_{21} = -\sqrt{a}$, $\varepsilon_{11} = \varepsilon_{22} = 0$; a is the determinant of the surface metric tensor $a_{\mu\nu}$, see Eq. (4.15) The mechanical meaning of the components of the tensors $M_{\mu\nu}$ and $N_{\mu\nu}$ is illustrated in Fig. 4.1b,c. One sees that N_{11} and N_{22} are normal moments (they cause torsion of the surface element), while N_{12} and N_{21} are tangential moments producing bending. In this aspect there is an analogy between the interpretations of $N_{\mu\nu}$ and $\sigma_{\mu\nu}$ (Fig. 4.1a). Indeed, if \mathbf{v} is the running unit normal to a curve in the surface (\mathbf{v} is tangential to the surface), then the stress acting per unit length of that curve is $\mathbf{t} = \mathbf{v} \cdot \underline{\sigma}$ and the moment acting per unit length is $\mathbf{m} = \mathbf{v} \cdot \mathbf{N}$. On the other hand, as seen from Eqs. (4.28) and (4.29), the tensor $N_{\mu\nu}$ is not symmetric. For that reason the symmetric tensor $M_{\mu\nu}$ is often preferred in the mechanical description of surface moments [6, 9]. A necessary condition for mechanical equilibrium of an interface is

$$b^{\mu\nu} N_{\mu\nu} = \varepsilon^{\alpha\beta} \sigma_{\alpha\beta}, \tag{4.30}$$

which expresses the normal resultant of the surface balance of the angular momentum; see also Eq. (4.44) below. Substituting $\sigma_{\mu\nu}$ from Eq. (4.24) and $N_{\mu\nu}$ from Eqs. (4.28)–(4.29) into Eq. (4.30) one could directly verify that the latter condition for equilibrium (with respect to the acting moments) is satisfied by the above expressions for $\sigma_{\mu\nu}$ and $N_{\mu\nu}$.

4.2.4. SURFACE BALANCES OF THE LINEAR AND ANGULAR MOMENTUM

Balance of the linear momentum. First, let us identify the surface (two-dimensional) analogues of Eqs. (4.1)–(4.4). Following Podstrigach and Povstenko [12] we consider a material volume V , which contains a portion, A , from the boundary between phases I and II, together with the adjacent volumes, V_I and V_{II} , from these phases, see Fig. 4.2. In analogy with Eq. (4.1) one can postulate the *integral* balance of the linear momentum for the considered part of the system [12]:

$$\frac{d}{dt} \left(\sum_{Y=I,II} \int_{V_Y} dV \rho_Y \mathbf{v}_Y + \int_A ds \Gamma \mathbf{v}_s \right) = \sum_{Y=I,II} \left(\int_{S_Y} ds \mathbf{n} \cdot \mathbf{T}_Y + \int_{V_Y} dV \rho_Y \mathbf{f}_Y \right) + \int_A ds \Gamma \mathbf{f}_s + \oint_L dl \mathbf{v} \cdot \underline{\sigma} \tag{4.31}$$

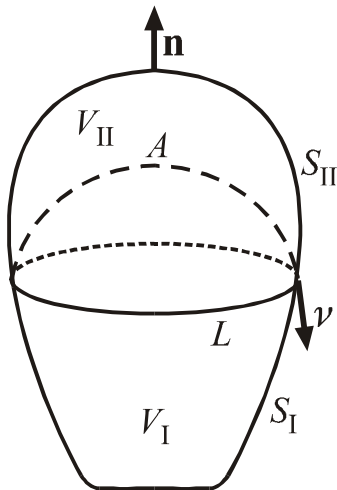


Fig. 4.2. Sketch of a material volume V , which contains a portion, A , of the boundary between phases I and II; V_I , V_{II} and S_I , S_{II} are parts of the volume V and its surfaces, which are located on the opposite sides of the interface A .

In Eq. (4.31) the subscript “s” denotes properties related to the interface; V_I , V_{II} and S_I , S_{II} are the two parts of the considered volume and its surface separated by the dividing surface A ; L is the contour which encircles A ; \mathbf{v} is an unit normal, which is simultaneously perpendicular to L

and tangential to A (Fig. 4.2); Γ is the surface excess of mass per unit area of the interface; as before, \mathbf{n} is running unit normal and $\underline{\sigma}$ is the surface stress tensor, see Eq. (4.26) and Fig. 4.1. For the sake of simplicity we will assume that the normal component of the velocity is continuous across the dividing surface:

$$(\mathbf{v}_I - \mathbf{v}_s) \cdot \mathbf{n} = (\mathbf{v}_{II} - \mathbf{v}_s) \cdot \mathbf{n} = 0 \quad (4.32)$$

Then the surface analogues of Eqs. (4.3) and (4.4) have the form [21]:

$$\frac{d}{dt} \int_A dV \Gamma \mathbf{v}_s = \int_A dV \left[\frac{d(\Gamma \mathbf{v}_s)}{dt} + \Gamma \mathbf{v}_s \nabla_s \cdot \mathbf{v}_s \right] \quad (4.33)$$

$$\frac{d\Gamma}{dt} + \Gamma \nabla_s \cdot \mathbf{v}_s = 0 \quad (4.34)$$

The latter equation is valid if there is no mass exchange between the bulk phases and the interface. Next, we will transform Eq. (4.31) with the help of the integral theorem of Green, which in a general vectorial form reads [12, 25]:

$$\int_A dA \nabla_s \cdot \mathbf{T} = \oint_L dl \nu \cdot \mathbf{T} - \int_A dA 2H \mathbf{n} \cdot \mathbf{T} \quad (\text{Green theorem}) \quad (4.35)$$

Here \mathbf{T} is an arbitrary vector or tensor; the meaning of ν is the same as in Fig. 4.2. If \mathbf{T} is a purely surface tensor, viz. $\mathbf{T} = \mathbf{a}^\mu \mathbf{a}^\nu T_{\mu\nu}$, or if \mathbf{T} has a rectangular matrix like that in Eqs. (4.26)–(4.27), then $\mathbf{n} \cdot \mathbf{T} = \mathbf{0}$ and the last integral in Eq. (4.35) is zero. In particular, the Green theorem (4.35), along with Eq. (4.26), yields

$$\oint_L dl \nu \cdot \underline{\sigma} = \int_A dA \nabla_s \cdot \underline{\sigma} \quad (4.36)$$

With the help of Eqs. (4.32)–(4.34), (4.36) and the versions of Eq. (4.1) for the material volumes V_I and V_{II} , from Eq. (4.31) one deduces the *local* surface balance of linear momentum [12]:

$$\Gamma \frac{d\mathbf{v}_s}{dt} = \nabla_s \cdot \underline{\sigma} + \Gamma \mathbf{f}_s + \mathbf{n} \cdot (\mathbf{T}_{II} - \mathbf{T}_I) \quad (4.37)$$

Here \mathbf{T}_I and \mathbf{T}_{II} are the subsurface values of the respective tensors. The last term in Eq. (4.37),

which accounts for the interaction of the interface with the two neighboring bulk phases, has no counterpart in Eq. (4.2). Differential geometry [18-21] yields the following expression for the surface divergence of the tensor $\underline{\sigma}$ defined by Eq. (4.26):

$$\nabla_s \cdot \underline{\sigma} = \left(\sigma_{,v}^{\nu\mu} - b_v^\mu \sigma^{\nu(n)} \right) \mathbf{a}_\mu + \left(b_{\mu\nu} \sigma^{\mu\nu} + \sigma_{, \mu}^{\mu(n)} \right) \mathbf{n} \quad (4.38)$$

Here $b_{\mu\nu}$ are components of the curvature tensor, see Eq. (4.17). In view of Eq. (4.38), the projections of Eq. (4.37) along the basis vectors \mathbf{a}_μ and \mathbf{n} have the form

$$\Gamma i^\mu = \sigma_{,v}^{\nu\mu} - b_v^\mu \sigma^{\nu(n)} + \Gamma f_s^\mu + \left(T_{\text{II}}^{(n)\mu} - T_{\text{I}}^{(n)\mu} \right) \quad \mu = 1, 2 \quad (4.39)$$

$$\Gamma i^{(n)} = \sigma_{, \mu}^{\mu(n)} + b_{\mu\nu} \sigma^{\mu\nu} + \Gamma f_s^{(n)} + \left(T_{\text{II}}^{(n)(n)} - T_{\text{I}}^{(n)(n)} \right) \quad (\text{normal balance}) \quad (4.40)$$

where i^μ and $i^{(n)}$ are components of the vector of acceleration, $d\mathbf{v}_s/dt$. Equations (4.39) and (4.40) coincide with the first three basic equations in the theory of elastic shells by Kirchhoff and Love, see e.g. Refs. [6, 12].

Balance of the angular momentum. In mechanics the rotational motion is treated similarly to the translational one. In particular, instead of velocity and force, angular velocity and force moment (torque) are considered. Three- and two-dimensional integral balances of the angular momentum, i.e. analogues of Eqs. (4.1) and (4.31), are postulated; see Refs. [6, 12] for details. From them the *local* form of the surface balance of the angular momentum can be deduced [12]:

$$\alpha \Gamma (d\boldsymbol{\omega}/dt) = \nabla_s \cdot \mathbf{N} + \Gamma \mathbf{m}_s + \mathbf{n} \cdot [(\underline{\boldsymbol{\sigma}} : \underline{\boldsymbol{\varepsilon}}) \mathbf{U}_s + \underline{\boldsymbol{\sigma}} \cdot \underline{\boldsymbol{\varepsilon}}] \quad (4.41)$$

The last equation is the analogue of Eq. (4.37) for rotational motion. Here α is a coefficient accounting for the interfacial moment of inertia; $\boldsymbol{\omega}$ is the vector of the angular velocity; \mathbf{m}_s is a counterpart of \mathbf{f}_s in Eq. (4.37);

$$\mathbf{N} = \mathbf{a}_\mu \mathbf{a}_\nu N^{\mu\nu} + \mathbf{a}_\mu \mathbf{n} N^{\mu(n)} \quad (4.42)$$

is the tensor of the surface moments (Fig. 4.1c); $\underline{\boldsymbol{\varepsilon}} = \mathbf{a}^\mu \mathbf{a}^\nu \varepsilon_{\mu\nu}$ is the surface alternator. Comparing Eqs. (4.37) with (4.41) one sees that for rotational motion \mathbf{N} plays the role of $\underline{\boldsymbol{\sigma}}$ for translational motion. Using Eq. (4.38) with \mathbf{N} instead of $\underline{\boldsymbol{\sigma}}$, along with Eqs. (4.26) and (4.42),

one can deduce equations, which represent the projections of the surface balance of the angular momentum, Eq. (4.41), along the basis vectors \mathbf{a}_μ and \mathbf{n} [12]:

$$\alpha \Gamma j^\mu = N_{,v}^{\nu\mu} - b_\nu^\mu N^{\nu(n)} + \Gamma m_s^\mu + \varepsilon^{\mu\nu} a_{\nu\lambda} \sigma^{\lambda(n)} \quad \mu = 1, 2. \quad (4.43)$$

$$\alpha \Gamma j^{(n)} = N_{,\mu}^{\mu(n)} + b_{\mu\nu} N^{\mu\nu} + \Gamma m_s^{(n)} - \varepsilon_{\mu\nu} \sigma^{\nu\mu} \quad (\text{normal balance}) \quad (4.44)$$

Here j^μ and $j^{(n)}$ are the respective projections of the angular acceleration vector $d\boldsymbol{\omega}/dt$. Equations (4.43) and (4.44) represent the second group of three basic equations in the theory of elastic shells by Kirchhoff and Love, see e.g. Refs. [6, 12].

Simplification of the equations. For fluid interfaces and biomembranes one can simplify the general surface balances of the linear and angular momentum, Eqs. (4.39)–(4.40) and (4.43)–(4.44), by using the following relevant assumptions:

- (i) Negligible contributions from the body forces ($\mathbf{f}_s \approx 0$) and couples ($\mathbf{m}_s \approx 0$).
- (ii) Quasistatic processes are considered ($i^\alpha = i^{(n)} = 0$, $j^\alpha = j^{(n)} = 0$).
- (iii) The stress tensors in the bulk phases are isotropic:

$$\mathbf{T}_I = -P_I \mathbf{U}, \quad \mathbf{T}_{II} = -P_{II} \mathbf{U} \quad (4.45)$$

- (iv) $\sigma_{\mu\nu}$ and $M_{\mu\nu}$ are symmetric surface tensors defined by Eqs. (4.24) and (4.28).

- (v) The transversal components of the tensor \mathbf{N} are equal to zero ($N^{\alpha(n)} = 0$); in such a case, with the help of Eq. (4.29), we can transform Eq. (4.42):

$$\mathbf{N} = \mathbf{a}_\alpha \mathbf{a}_\beta N^{\alpha\beta} = \mathbf{a}_\alpha \mathbf{a}_\beta M_\gamma^\alpha \varepsilon^{\gamma\beta} \quad (4.46)$$

If the above assumptions are fulfilled, then Eq. (4.44), representing the tangential resultant of the surface balance of the angular momentum, is identically satisfied; see Eq. (4.30) and the related discussion. The remaining balance equations, (4.39), (4.40) and (4.43), acquire the form:

$$\sigma_{,\mu} + (\eta q_\mu^v)_{,v} = b_{\mu\nu} \sigma^{\nu(n)}, \quad \mu = 1, 2. \quad (4.47)$$

$$2H\sigma + 2D\eta + \sigma_{,\mu}^{\mu(n)} = P_{II} - P_I \quad (\text{normal balance of linear momentum}) \quad (4.48)$$

$$\sigma^{\mu(n)} = -M_{,\nu}^{\mu\nu} \quad \mu = 1, 2. \quad (4.49)$$

To derive Eqs. (4.48) and (4.49) we have used Eqs. (4.17) and (4.29), respectively. Finally, substituting $\sigma^{\mu(n)}$ from Eq. (4.49) into Eqs. (4.47) and (4.48) we obtain

$$\sigma_{,\mu} + (\eta q_{\mu}^{\nu})_{,\nu} = -b_{\mu\nu} M_{,\lambda}^{\nu\lambda} \quad \mu = 1, 2. \quad (4.50)$$

$$2H\sigma + 2D\eta - M_{,\mu\nu}^{\mu\nu} = P_{\text{II}} - P_{\text{I}} \quad (\text{generalized Laplace equation}) \quad (4.51)$$

Eqs. (4.50) and (4.51) have the meaning of projections of the interfacial stress balance in tangential and normal direction with respect to the dividing surface. In fact, Eq. (4.51) represents a generalized form of the Laplace equation of capillarity. Indeed, if the effects of the shearing tension and surface moments are negligible ($\eta = 0$, $M^{\mu\nu} = 0$), then Eq. (4.51) reduces to the conventional Laplace equation, Eq. (2.17). In addition, a version of the generalized Laplace equation can be derived by using the thermodynamic approach, that is by minimization of the free energy of the system, see Eq (4.71) below. Of course, the two versions of that equation must be equivalent. Thus we approach the problem about the equivalence of the mechanical and thermodynamical approaches, which is considered in the next section.

4.3. CONNECTION BETWEEN MECHANICAL AND THERMODYNAMICAL APPROACHES

4.3.1. GENERALIZED LAPLACE EQUATION DERIVED BY MINIMIZATION OF THE FREE ENERGY

In this section we will follow the pure thermodynamic approach, described in Sections 3.1 and 3.2, to derive the generalized Laplace equation. Our goal is to compare the result with Eq. (4.51) which has been obtained in the framework of the mechanical approach. With this end in view we consider the two-phase system depicted in Fig. 4.2. The grand thermodynamic potential of the system can be expressed in the form

$$\Omega = \Omega_b + \Omega_s \quad (4.52)$$

where Ω_b and Ω_s account for the contributions from the bulk and the surface, respectively. For the bulk phases one has

$$\delta \Omega_b = -P_I \delta V_I - P_{II} \delta V_{II}, \quad V = V_I + V_{II} \quad (4.53)$$

The integral surface excess of the grand thermodynamic potential Ω_s , and its variation $\delta \Omega_s$, can be expressed in the form

$$\Omega_s = \int_A \omega_s dA, \quad (4.54)$$

$$\delta \Omega_s = \delta \int_A \omega_s dA = \int_A (\delta \omega_s + \omega_s \delta \alpha) dA, \quad (4.55)$$

where ω_s is the surface density of Ω_s , defined by Eq. (3.17); we have used the fact that $\delta \alpha = \delta(dA)/dA$, and the integration is carried out over the dividing surface between the two phases. A substitution of $\delta \omega_s$ from Eq. (3.18) into Eq. (4.55), along with the condition for constancy of the temperature and chemical potentials at equilibrium, yields

$$\delta \Omega_s = \int_A (\gamma \delta \alpha + \xi \delta \beta + B \delta H + \Theta \delta D) dA \quad (4.56)$$

The combination of Eqs. (4.52), (4.53) and (4.56) yields [23, 26]:

$$\delta \Omega = -(P_I - P_{II}) \delta V_I - P_{II} \delta V + \int_A (\gamma \delta \alpha + \xi \delta \beta + B \delta H + \Theta \delta D) dA \quad (4.57)$$

Let us consider a small deformation of the dividing surface at fixed volume of the system, $\delta V = 0$. The change in the shape of the interface is described by the variation of the position-vector of the points belonging to the dividing surface,

$$\delta \mathbf{R} = \zeta^\mu \mathbf{a}_\mu + \psi \mathbf{n}, \quad (4.58)$$

at fixed boundaries:

$$\zeta^1 = \zeta^2 = \psi = 0, \quad \psi_{,\mu} = 0 \quad \text{over the contour } L \quad (4.59)$$

Here $\zeta^\mu = v^\mu \delta t$ and $\psi = v^{(n)} \delta t$ are infinitesimal displacements; L is the contour encircling the surface A . With the help of Eqs. (4.19)–(4.22) we obtain [23, 26]

$$\delta \alpha = a^{\mu\sigma} \zeta_{\mu,\sigma} - 2H\psi, \quad \delta \beta = q^{\mu\sigma} \zeta_{\mu,\sigma} - 2D\psi. \quad (4.60)$$

Likewise, using the identities [12, 21]

$$\dot{H} = H_{,\sigma} v^\sigma + (H^2 + D^2) v^{(n)} + \frac{1}{2} a^{\mu\nu} v_{,\mu\nu}^{(n)} \quad (4.61)$$

$$\dot{D} = D_{,\sigma} v^\sigma + 2HD v^{(n)} + \frac{1}{2} q^{\mu\nu} v_{,\mu\nu}^{(n)} \quad (4.62)$$

we deduce

$$\delta H = H_{,\sigma} \zeta^\sigma + (H^2 + D^2) \psi + \frac{1}{2} a^{\mu\nu} \psi_{,\mu\nu}; \quad \delta D = D_{,\sigma} \zeta^\sigma + 2HD \psi + \frac{1}{2} q^{\mu\nu} \psi_{,\mu\nu} \quad (4.63)$$

The substitution of Eqs. (4.60) and (4.63) into Eq. (4.57), along with the condition for thermodynamic equilibrium, $\delta\Omega = 0$, leads to [23, 26]:

$$0 = \int_A \{ (BH_{,\mu} + \Theta D_{,\mu}) \zeta^\mu + [P_{II} - P_I - 2H\gamma - 2D\xi + (H^2 + D^2)B + 2HD\Theta] \psi \} dA \\ + \int_A \gamma^{\mu\sigma} \zeta_{\mu,\sigma} dA + \int_A \tilde{M}^{\mu\sigma} \psi_{,\mu\sigma} dA \quad (4.64)$$

where we have used the auxiliary notations

$$\tilde{M}^{\mu\sigma} \equiv \frac{1}{2} B a^{\mu\sigma} + \frac{1}{2} \Theta q^{\mu\sigma} \quad (4.65)$$

$$\gamma^{\mu\sigma} \equiv \gamma a^{\mu\sigma} + \xi q^{\mu\sigma} \quad (4.66)$$

$\gamma^{\mu\sigma}$ is called the “thermodynamic surface stress tensor” [22]. Next, we transform the integrands of the last two integrals in Eq. (4.64) using the identities:

$$\gamma^{\mu\sigma} \zeta_{\mu,\sigma} = (\gamma^{\mu\sigma} \zeta_\mu)_{,\sigma} - \gamma^{\mu\sigma}{}_{,\sigma} \zeta_\mu \quad (4.67)$$

$$\tilde{M}^{\mu\sigma} \psi_{,\mu\sigma} = (\tilde{M}^{\mu\sigma} \psi_{,\mu})_{,\sigma} - \tilde{M}^{\mu\sigma}{}_{,\sigma} \psi_{,\mu} \quad (4.68)$$

$$\tilde{M}^{\mu\sigma}{}_{,\sigma} \psi_{,\mu} = (\tilde{M}^{\mu\sigma}{}_{,\sigma} \psi)_{,\mu} - \tilde{M}^{\mu\sigma}{}_{,\mu\sigma} \psi \quad (4.69)$$

The first term in the right-hand side of Eqs. (4.67)–(4.69) represents a divergence of a surface vector. Integrating the latter, in accordance with the Green theorem, Eq. (4.35), we obtain an integral over the contour L , which is zero in view of Eq. (4.59). Thus the last two integrals in Eq. (4.64), which contain derivatives of ζ_μ and ψ , are reduced to integrals containing ζ_μ and ψ

themselves. Finally, we set equal to zero the coefficients multiplying the independent variations ζ_μ and ψ in the transformed Eq. (4.64); thus we obtain the following two condition for mechanical equilibrium of the interface [26,23,22,13]:

$$\gamma_{,\mu} + (\xi q_\mu^\sigma)_{,\sigma} = BH_{,\mu} + \Theta D_{,\mu}, \quad \mu = 1, 2; \quad (4.70)$$

$$-2H\gamma - 2D\xi + (H^2 + D^2)B + 2HD\Theta + \frac{1}{2}(Ba^{\mu\nu} + \Theta q^{\mu\nu})_{,\mu\nu} = P_I - P_{II} \quad (4.71)$$

Equation (4.71) represents a thermodynamic version of the generalized Laplace equation. From a physical viewpoint, Eqs. (4.70)–(4.71) should be equivalent to Eqs. (4.50)–(4.51). This is proven below, where relationships between the thermodynamical parameters γ , ξ , B , Θ , and the mechanical parameters σ , η , M_1 , M_2 are derived. For other equivalent forms of the generalized Laplace equation – see Section 4.3.3.

4.3.2. WORK OF DEFORMATION: THERMODYNAMICAL AND MECHANICAL EXPRESSIONS

Relationships between the mechanical and thermodynamical surface tensions and moments. In the thermodynamic approach the work of surface deformation (per unit area) is expressed as follows:

$$\delta w_s = \gamma \delta \alpha + \xi \delta \beta + B \delta H + \Theta \delta D, \quad (4.72)$$

see Eq. (3.1). On the other hand, the mechanics provides the following expression for the work of surface deformation (per unit area and per unit time):

$$\frac{\delta w_s}{\delta t} = \underline{\boldsymbol{\sigma}} : (\nabla_s \mathbf{v} + \mathbf{U}_s \times \boldsymbol{\omega}) + \mathbf{N} : (\nabla_s \boldsymbol{\omega}), \quad (4.73)$$

see e.g. Eq. (4.26) in the book by Podstrigach and Povstenko [12]. As in Eqs. (1.22)–(1.23), here the symbol “:” denotes a double scalar product of two tensors. The vector $\boldsymbol{\omega}$ expresses the angular velocity of rotation of the running unit normal to the surface, \mathbf{n} , which is caused by the change in the curvature of the interface [24]:

$$\boldsymbol{\omega} = \mathbf{n} \times \frac{d\mathbf{n}}{dt} \quad (4.74)$$

Here " \times " denotes vectorial product of two vectors. Hence, the vector $\boldsymbol{\omega}$ is perpendicular to the plane formed by the vectors \mathbf{n} and $d\mathbf{n}/dt$, which means that $\boldsymbol{\omega}$ is tangential to the surface. Equation (4.73) (multiplied by δt) should be equivalent to the thermodynamic relationship, Eq. (4.72).

Since $\underline{\boldsymbol{\sigma}}$ is a surface tensor ($\mathbf{n} \cdot \underline{\boldsymbol{\sigma}} = \mathbf{0}$), one can prove that $\underline{\boldsymbol{\sigma}} : (\mathbf{U}_s \times \boldsymbol{\omega}) = 0$. Next, with the help of Eqs. (4.23) and (4.24), one derives [24]

$$\underline{\boldsymbol{\sigma}} : (\nabla_s \mathbf{v}) = \sigma^{\mu\nu} d_{\mu\nu} = \sigma \dot{\alpha} + \eta \dot{\beta} \quad (4.75)$$

Further, after some mathematical transformations described in Ref. [24], one can bring the term with the moments in Eq. (4.73) to the form

$$\mathbf{N} : (\nabla_s \boldsymbol{\omega}) = (M_1 + M_2) (\dot{H} + \frac{1}{2} H \dot{\alpha} + \frac{1}{2} D \dot{\beta}) + (M_1 - M_2) (\dot{D} + \frac{1}{2} D \dot{\alpha} + \frac{1}{2} H \dot{\beta}) \quad (4.76)$$

Combining Eqs. (4.73), (4.75) and (4.76) one obtains

$$\begin{aligned} \frac{\delta w_s}{\delta t} = & \sigma \dot{\alpha} + \eta \dot{\beta} + (M_1 + M_2) (\dot{H} + \frac{1}{2} H \dot{\alpha} + \frac{1}{2} D \dot{\beta}) \\ & + (M_1 - M_2) (\dot{D} + \frac{1}{2} D \dot{\alpha} + \frac{1}{2} H \dot{\beta}) \end{aligned} \quad (4.77)$$

Further, taking into account that $\delta H = \dot{H} \delta t$, $\delta D = \dot{D} \delta t$ and using Eq. (4.22), we get

$$\begin{aligned} \delta w_s = & \left[\sigma + \frac{1}{2} (M_1 + M_2) H + \frac{1}{2} (M_1 - M_2) D \right] \delta \alpha + \\ & + \left[\eta + \frac{1}{2} (M_1 + M_2) D + \frac{1}{2} (M_1 - M_2) H \right] \delta \beta + \\ & + (M_1 + M_2) \delta H + (M_1 - M_2) \delta D \end{aligned} \quad (4.78)$$

which represents a corollary from Eq. (4.73). Comparing Eqs. (4.72) and (4.78) one can identify the coefficients multiplying the independent variations [24]:

$$B = M_1 + M_2 \quad (4.79)$$

$$\Theta = M_1 - M_2 \quad (4.80)$$

$$\gamma = \sigma + \frac{1}{2} B H + \frac{1}{2} \Theta D \quad (4.81)$$

$$\xi = \eta + \frac{1}{2} B D + \frac{1}{2} \Theta H \quad (4.82)$$

Discussion. Equations (4.79)–(4.80) show that the bending and torsion moments, B and Θ , represent isotropic and deviatoric scalar invariants of the tensor of the surface moments, \mathbf{M} . The substitution of Eqs. (4.79)–(4.80) into (4.28) yields

$$M_{\mu\nu} = \frac{1}{2}B a_{\mu\nu} + \frac{1}{2}\Theta q_{\mu\nu} \quad (4.83)$$

In addition, Eqs. (4.81) and (4.82) express the connection between the mechanical surface tensions, σ , η , and the thermodynamical surface tensions γ and ξ .

For a *spherical* interface $D = 0$ and $M_1 = M_2 = M$. Then Eqs. (4.79) and (4.81) are reduced to Eqs. (3.61) and (3.60), respectively, while Eqs. (4.80) and (4.82) yield $\Theta = 0$, $\xi = \eta = 0$; the latter relationship holds for an isotropic deformation of a spherical surface.

The concepts for the surface tension as (i) excess force per unit length and (ii) excess surface energy per unit area are usually considered as being equivalent for a fluid phase boundary [27–29]. Equation (4.81) shows that this is fulfilled only for a planar interface. In the general case, the difference between σ and γ is due to the existence of surface moments. This difference could be important for interfaces and membranes of high curvature and low tension, such as microemulsions, biomembranes, etc.

An interesting consequence from Eq. (4.82) is the existence of two possible definitions of *fluid* interface [13, 14]. From a *mechanical* viewpoint we could require the two-dimensional stress tensor, $\sigma_{\mu\nu}$, to be isotropic for a fluid interface (a two-dimensional analogue of the Pascal law). Thus from Eq. (4.25) we obtain as the mechanical definition of a fluid interface in the form $\eta \equiv 0$. The intriguing point is that for $\eta = 0$ Eq. (4.82) yields $\xi = \frac{1}{2}BD + \frac{1}{2}\Theta H$, and consequently the mechanical work of shearing, $\xi \delta\beta$, is not zero if surface moments are present.

On the other hand, from a *thermodynamical* viewpoint we may require the work of quasistatic shearing to be zero, that is $\xi \equiv 0$, for a *fluid* interface. However, it turns out that for such an interface the surface stress tensor $\sigma_{\mu\nu}$ is not isotropic; indeed, setting $\xi \equiv 0$ in Eq. (4.82) we obtain $\eta = -(\frac{1}{2}BD + \frac{1}{2}\Theta H)$. In our opinion, it is impossible to determine which is the "true" definition of a fluid interface ($\eta = 0$ or $\xi = 0$) by general considerations. Insofar as every

theoretical description represents a model of a real object, in principle it is possible to establish experimentally whether the behavior of a given real interface agrees with the first or the second definition ($\eta=0$ or $\xi\equiv 0$).

4.3.3. VERSIONS OF THE GENERALIZED LAPLACE EQUATION

First of all, using Eqs. (4.81)–(4.83), after some mathematical derivations one can transform Eqs. (4.70)–(4.71) into Eqs (4.50)–(4.51), and *vice versa* [14]. This is a manifestation of the equivalence between the mechanical and thermodynamical approaches, which are connected by Eqs. (4.81)–(4.83). In particular, Eqs. (4.51) and (4.71) represent two equivalent forms of the generalized Laplace equation. Another equivalent form of this equation is [14, 22]:

$$-2H\gamma - 2D\xi + (H^2 + D^2)B + 2HD\Theta + (\nabla_s \nabla_s) : \mathbf{M} = P_I - P_{II} \quad (4.84)$$

The most compact form of the latter equation is obviously Eq. (4.51). In terms of the coefficients C_1 and C_2 , see Eqs. (3.5) and (3.6), the generalized Laplace equation can be represented in another equivalent (but considerably longer) form [35]:

$$2H\gamma + 2D\xi - C_1(2H^2 - K) - 2C_2HK - \frac{1}{2}\nabla_s^2 C_1 - 2H\nabla_s^2 C_2 + \mathbf{b} : \nabla_s \nabla_s C_2 = P_{II} - P_I \quad (4.85)$$

Boruvka and Neumann [2] have derived an equation analogous to (4.85) without the shearing term $2D\xi$. These authors have used a definition of surface tension, which is different from the conventional definition given by Gibbs; the latter fact has been noticed in Refs. [26] and [30]. In an earlier work by Melrose [31] an incomplete form of the generalized Laplace equation has been obtained, which contains only the first, third and fourth term in the left-hand side of Eq. (4.85). Another incomplete form of the generalized Laplace equation was published in Refs. [32-34].

Further specification of the form of the surface tangential and normal stress balances, Eqs. (4.50)–(4.51), can be achieved if appropriate rheological constitutive relations are available, as discussed in the next section. For other forms of the generalized Laplace equation – see Eqs. (4.99), (4.103), (4.107) and (4.110) below.

4.3.4. INTERFACIAL RHEOLOGICAL CONSTITUTIVE RELATIONS

To solve whatever specific problem of the continuum mechanics, one needs explicit expressions for the tensors of stresses and moments. As already mentioned, such expressions typically have the form of relationships between stress and strain (or rate-of-strain), which characterize the rheological behavior of the specific continuum: elastic, viscous, plastic, etc.; see e.g. Refs. [6,20,35,36]. In fact, a constitutive relation represents a theoretical model of the respective continuum; its applicability for a given system is to be experimentally verified. Below in this section, following Ref. [14], we briefly consider constitutive relations, which are applicable to curved interfaces.

Surface stress tensor $\underline{\sigma}$ Boussinesq [37] and Scriven [38] have introduced a constitutive relation which models a phase boundary as a two-dimensional viscous fluid:

$$\sigma_{\mu\nu} = \sigma a_{\mu\nu} + \eta_d a_{\mu\nu} d_\lambda^\lambda + 2\eta_s \left(d_{\mu\nu} - \frac{1}{2} a_{\mu\nu} d_\lambda^\lambda \right) \quad (4.86)$$

where $d_{\mu\nu}$ is the surface rate-of-strain tensor defined by Eq. (4.19); d_λ^λ is the trace of this tensor; η_d and η_s are the coefficients of surface dilatational and shear viscosity, cf. Eq. (4.11). The elastic (non-viscous) term in Eq. (4.86), $\sigma a_{\mu\nu}$, is isotropic. Consequently, it is postulated that the shearing tension η is zero, see Eq. (4.25), i.e. there is no shear elasticity. In other words, in the model by Boussinesq-Scriven the deviatoric part of the tensor $\sigma_{\mu\nu}$ has entirely viscous origin. In Eq. (4.86) σ is to be identified with the mechanical surface tension, cf. Eq. (4.81). For emulsion phase boundaries of low interfacial tension the dependence of σ on the curvature should be taken into account. From Eqs. (3.39) and (4.81), in linear approximation with respect to the curvature, we obtain

$$\sigma = \gamma_0 + \frac{1}{2} B_0 H + O(H^2) \quad (4.87)$$

where γ_0 is the tension of a *flat* interface. For example, for an emulsion from oil drops in water we have $B_0 \approx 10^{-10}$ N and $H \approx 10^5 \text{ cm}^{-1}$; then we obtain that the contribution from the curvature effect to σ is $\frac{1}{2} B_0 H \approx 0.5$ mN/m. For such emulsions the latter value could be of the order of γ_0 , and even larger. Therefore, the curvature effect should be taken into account when

solving the hydrodynamic problem about flocculation and coalescence of the droplets in some emulsions.

Since the surface stress tensor $\underline{\sigma}$ has also transversal components, $\sigma^{\mu(n)}$, see Eq. (4.26), one needs also a constitutive relation for $\sigma^{\mu(n)}$ ($\mu=1, 2$). In analogy with Eq. (4.86) $\sigma^{\mu(n)}$ can be expressed as a sum of a viscous and a non-viscous term [14]:

$$\sigma^{\mu(n)} = \sigma_{(v)}^{\mu(n)} + \sigma_{(0)}^{\mu(n)} \tag{4.88}$$

The viscous term can be expressed in agreement with the Newton's law for the viscous friction [14]:

$$\sigma_{(v)}^{\mu(n)} = \chi_s v^{(n),\mu} \tag{4.89}$$

$v^{(n)}$ is defined by Eq. (4.20). As illustrated schematically in Fig. 4.3, equation (4.89) accounts for the lateral friction between the molecules in an interfacial adsorption layer; this effect could be essential for sufficiently dense adsorption layers, like those formed from proteins. χ_s is a coefficient of surface transversal viscosity, which is expected to be of the order of η_s by magnitude.

For quasistatic processes ($v \rightarrow 0$ and $\sigma_{(v)}^{\mu(n)} \rightarrow 0$), the transversal components of $\underline{\sigma}$ reduce to $\sigma_{(0)}^{\mu(n)}$. Then, in keeping with Eqs. (4.49), (4.83), (4.88) and (4.89), we can write [14]:

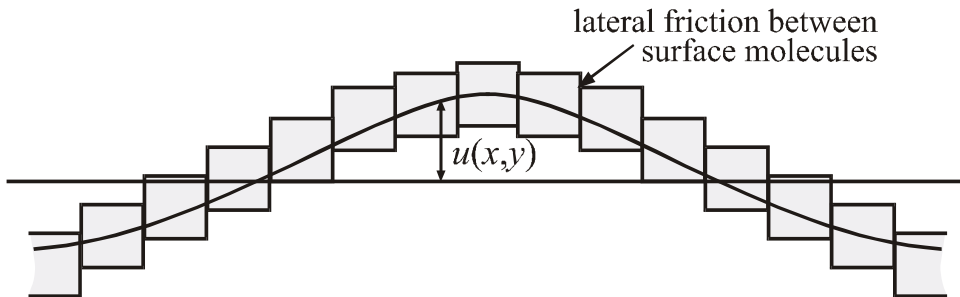


Fig. 4.3. An illustration of the relative displacement of the neighboring adsorbed molecules (the squares) in a process of interfacial wave motion; u is the local deviation from planarity.

$$\sigma^{\mu(n)} = \chi_s v^{(n),\mu} - \frac{1}{2}(Ba^{\mu\nu} + \Theta q^{\mu\nu})_{,\nu} \quad (4.90)$$

The surface rheological model, based on the constitutive relations (4.86) and (4.90), contains 3 coefficients of surface viscosity, viz. η_d , η_s and χ_s . Moreover, the surface bending and torsion elastic moduli do also enter the theoretical expressions through B and Θ , see Eqs. (3.9) and (4.90).

Tensor of the surface moments M. Equations (3.9) and (4.83) yield an expression for the non-viscous part of \mathbf{M} :

$$M_{(0)}^{\mu\nu} \equiv \frac{1}{2}(Ba^{\mu\nu} + \Theta q^{\mu\nu}) = \left[\frac{1}{2}B_0 + (2k_c + \bar{k}_c)H \right] a^{\mu\nu} - \bar{k}_c Dq^{\mu\nu} \quad (4.91)$$

In keeping with Eqs. (4.17), (4.49), (4.90) and (4.91) the total tensor of the surface moments (including a viscous contribution) can be expressed in the form [14]:

$$M^{\mu\nu} = \left[\frac{1}{2}B_0 + 2(k_c + \bar{k}_c)H \right] a^{\mu\nu} - \bar{k}_c b^{\mu\nu} - \chi_s v^{(n),\mu} a^{\mu\nu} \quad (4.92)$$

The latter equation can be interpreted as a rheological constitutive relation stemming from the Helfrich formula, Eq. (3.7). With the help of the Codazzi equation, $b^{\mu\nu,\lambda} = b^{v\lambda,\mu}$, see e.g. Ref. [19], we derive:

$$b_{,\nu}^{\mu\nu} = a_{\nu\lambda} b^{\mu\nu,\lambda} = a_{\nu\lambda} b^{v\lambda,\mu} = 2H^{,\mu} \quad (4.93)$$

The combination of Eqs. (4.92) and (4.93) yields

$$M_{,\nu}^{\mu\nu} = 2k_c H^{,\mu} - \chi_s v^{(n),\mu} \quad (4.94)$$

In the derivation of Eq. (4.94) we have treated B_0 as a constant. However, if the deformation is accompanied with a variation of the surface concentration Γ , then Eq. (4.94) should be written in the following more general form:

$$M_{,\nu}^{\mu\nu} = \frac{1}{2}B'_0 \Gamma^{,\mu} + 2k_c H^{,\mu} - \chi_s v^{(n),\mu}; \quad B'_0 \equiv \frac{\partial B_0}{\partial \Gamma} \quad (4.95)$$

The term with B'_0 has been taken into account by Dan et al. [39], as well as in Chapter 10 below, for describing the deformations in phospholipid bilayers caused by inclusions (like

membrane proteins). In the simpler case of a quasistatic process ($v^{(n)} = 0$) and uniform surface concentration ($\Gamma^{\mu} = 0$) Eq. (4.95) reduces to a quasistatic constitutive relation stemming from the Helfrich model:

$$M_{,v}^{\mu\nu} = 2k_c H_{,v}^{\mu} \quad (4.96)$$

It is worthwhile noting that the torsion (Gaussian) elasticity, \bar{k}_c , does not appear in Eqs. (4.94)–(4.96). Then, in view of Eq. (4.49) and (4.94), \bar{k}_c will not appear explicitly also in the tangential and normal balances of the linear momentum, Eqs. (4.39) and (4.40), which for small Reynolds numbers (inertial terms negligible) acquire the form

$$\sigma_{,v}^{\nu\mu} + b_{,v}^{\mu} (2k_c H_{,v}^{\nu} - \chi_s v^{(n),\nu}) = (T_I^{(n)\mu} - T_{II}^{(n)\mu}) \quad \mu = 1, 2. \quad (4.97)$$

$$b_{,\mu\nu} \sigma^{\mu\nu} - (2k_c H_{,v}^{\mu\nu} - \chi_s v^{(n),\mu\nu}) a_{\mu\nu} = (T_I^{(n)(n)} - T_{II}^{(n)(n)}) \quad (4.98)$$

$\sigma^{\mu\nu}$ is to be substituted from Eq. (4.86). It should be noted that Eq. (4.98) is another form of the generalized Laplace equation. In vectorial notation and for quasistatic processes ($v^{(n)} \rightarrow 0$) Eq. (4.98) reads

$$\mathbf{b} : \underline{\boldsymbol{\sigma}} - 2k_c \nabla_s^2 H = \mathbf{n} \cdot (\mathbf{T}_I - \mathbf{T}_{II}) \cdot \mathbf{n} \quad (4.99)$$

Application to capillary waves. As an example let us consider capillary waves on a flat (in average) interface. It is usually assumed that the amplitude of the waves u (see Fig. 4.3) is sufficiently small, and consequently Eqs. (4.97) and (4.98) can be linearized:

$$\sigma \nabla_s^2 u - k_c \nabla_s^2 \nabla_s^2 u + \chi_s \nabla_s^2 \frac{\partial u}{\partial t} = T_I^{(n)(n)} - T_{II}^{(n)(n)} \quad (4.100)$$

$$\nabla_s \sigma + \eta_d \nabla_s \nabla_s \cdot \mathbf{v}_{II} + \eta_s \nabla_s^2 \mathbf{v}_{II} = \mathbf{n} \cdot (\mathbf{T}_I - \mathbf{T}_{II}) \cdot \mathbf{U}_s \quad (4.101)$$

where we have used the constitutive relation, Eq. (4.86), and the relationships

$$2H \approx \nabla_s^2 u, \quad v^{(n)} = \frac{\partial u}{\partial t}, \quad \mathbf{v}_{II} \equiv \mathbf{a}^{\mu} v_{\mu} \quad (4.102)$$

One sees that in linear approximation the dependent variables u and \mathbf{v}_{II} are separated: the generalized Laplace equation, Eq. (4.100), contains the displacement u along the normal, whereas the two-dimensional Navier-Stokes equation (4.101) contains the tangential surface velocity, \mathbf{v}_{II} . In the linearized theory the curvature elasticities participate only through k_c in the normal stress balance, Eq. (4.100); \bar{k}_c does not appear.

4.4. AXISYMMETRIC SHAPES OF BIOLOGICAL CELLS

4.4.1. THE GENERALIZED LAPLACE EQUATION IN PARAMETRIC FORM

Equation (4.99) can be used to describe the shapes of biological membranes. For the sake of simplicity, let us assume that the phases on both sides of the membrane are fluid, i.e. Eq. (4.45) holds (the effect of cytoskeleton neglected). Then substituting Eqs. (4.17), (4.24) and (4.45) into Eq. (4.99) one derives [14]

$$2H\sigma + 2D\eta - 2k_c \nabla_s^2 H = P_{II} - P_I \quad (4.103)$$

Further, let us consider the special case of axisymmetric membrane and let the z -axis be the axis of revolution. In the plane xy we introduce polar coordinates (r, φ) ; $z = z(r)$ expresses the equation of the membrane shape. Then $\nabla_s^2 H$ can be presented in the form (see Ref. 37, Chapter XIV, Eq. 66):

$$\nabla_s^2 H = \frac{1}{r} (1 + z'^2)^{-1/2} \frac{d}{dr} \left[r (1 + z'^2)^{-1/2} \frac{dH}{dr} \right] \quad (4.104)$$

where

$$z' = \frac{dz}{dr} = \tan \theta \quad (4.105)$$

with θ being the running slope angle. The two principal curvatures of an axisymmetric surface are $c_1 = d(\sin \theta)/dr$ and $c_2 = \sin \theta/r$. In view of Eq. (3.3), we have

$$2H = \frac{d \sin \theta}{dr} + \frac{\sin \theta}{r}, \quad 2D = \frac{d \sin \theta}{dr} - \frac{\sin \theta}{r}, \quad (4.106)$$

Finally, with the help of Eqs. (4.104)–(4.106) we bring Eq. (4.103) into the form [14]

$$\sigma \left(\frac{d \sin \theta}{dr} + \frac{\sin \theta}{r} \right) + \eta \left(\frac{d \sin \theta}{dr} - \frac{\sin \theta}{r} \right) = \Delta P + \frac{k_c}{r} \cos \theta \frac{d}{dr} \left\{ r \cos \theta \frac{d}{dr} \left[\frac{1}{r} \frac{d}{dr} (r \sin \theta) \right] \right\} \quad (4.107)$$

where $\Delta P = P_{II} - P_I$. Equations (4.105) and (4.107) determine the generatrix of the membrane profile in a parametric form: $r = r(\theta)$, $z = z(\theta)$. In the special case, in which $\eta = 0$ and $k_c = 0$ (no shearing tension and bending elasticity), Eq. (4.107) reduces to the common Laplace equation of capillarity, Eq. (2.24). The approach based on Eq. (4.107) is equivalent to the approach based on the expression for the free energy, insofar as the generalized Laplace equation can be derived by minimization of the free energy, see Section 4.3.1.

The form of Eq. (4.107) calls for discussion. The possible shapes of biological and model membranes are usually determined by minimization of an appropriate expression for the free energy (or the grand thermodynamic potential) of the system, see e.g. Refs. [7,9,40-49]. For example, the integral bending elastic energy of a tension-free membrane is given by the expression [7]

$$W_B = \int [2k_c(H - H_0)^2 + \bar{k}_c K] dA \quad (4.108)$$

see Eq. (3.7). The above expression for W_B contains as parameters the spontaneous curvature H_0 and the Gaussian (torsion) elasticity \bar{k}_c , while the latter two parameters are missing in Eq. (4.107). As demonstrated in the previous section H_0 and \bar{k}_c must not enter the generalized Laplace equation, see Eq. (4.99); on the other hand, H_0 and \bar{k}_c can enter the solution through the boundary conditions [22]. For example, Deuling and Helfrich [43] described the myelin forms of an erythrocyte membrane assuming tension-free state of the membrane, that is $\sigma = \eta = 0$ and $\Delta P = 0$; then they calculated the shape of the membrane as a solution of the equation

$$\frac{1}{r} \frac{d}{dr} (r \sin \theta) = 2H_0 = \text{const.} \quad (4.109)$$

It is obvious that for $\sigma = \eta = 0$ and $\Delta P = 0$ every solution of Eq. (4.109) satisfies Eq. (4.107), and that the spontaneous curvature H_0 appears as a constant of integration.

In a more general case, e.g. swollen or adherent erythrocytes [50], one must *not* set $\sigma = 0$ and

$\Delta P = 0$, since the membrane is expected to have some tension, though a very low one. To simplify the mathematical treatment, one could set $\eta = 0$ in Eq. (4.107), i.e. one could neglect the effect of the shearing tension. Setting $\eta = 0$ means that the stresses in the membrane are assumed to be tangentially isotropic, that is the membrane behaves as a two-dimensional fluid. In fact, there are experimental indications that $\eta \ll \sigma$ for biomembranes at body temperature [9, 51]. Thus one could seek the membrane profile as a solution of the equation [50]

$$\sigma \left(\frac{d \sin \theta}{dr} + \frac{\sin \theta}{r} \right) = \Delta P + \frac{k_c}{r} \cos \theta \frac{d}{dr} \left\{ r \cos \theta \frac{d}{dr} \left[\frac{1}{r} \frac{d}{dr} (r \sin \theta) \right] \right\} \quad (4.110)$$

4.4.2. BOUNDARY CONDITIONS AND SHAPE COMPUTATION

To find the solution of Eq. (4.110), along with Eq. (4.105), one needs 4 boundary conditions. The following boundary conditions have been used in Ref. [50] to find the shape of erythrocytes attached to a glass substrate (Fig. 4.4):

- (i-ii) $z = 0$ and $\theta = 0$ at $r = 0$, i.e. at the apex of the membrane (the point where the membrane intersects the z -axis);
- (iii) the membrane curvature varies smoothly in a vicinity of the membrane apex;
- (iv) $\theta = \theta_h$ for $r = r_f$ (θ_h – contact angle; r_f – radius of the adhesive film);
- (v) the total area of the membrane, A_T , is known; this condition was used in Ref. [50] to determine the unknown material parameter

$$\lambda = \sigma / k_c \quad (4.111)$$

To solve Eq. (4.110) it is convenient to introduce the auxiliary function

$$F \equiv \frac{d \sin \theta}{dr} + \frac{\sin \theta}{r} - \frac{2}{b}, \quad b \equiv \frac{2\sigma}{\Delta P}, \quad (4.112)$$

where b is constant if the effect of gravity on the membrane shape is negligible. Then Eq. (4.110) acquires the form

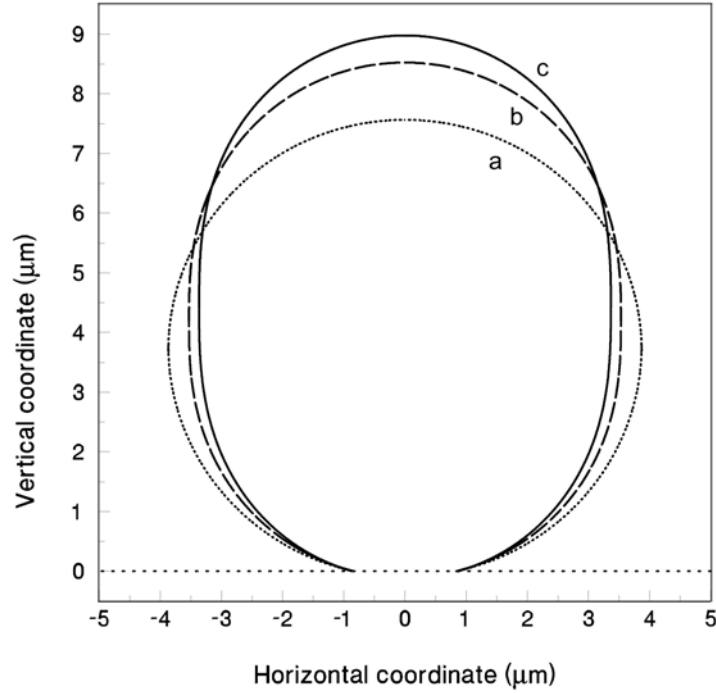


Fig. 4.4. Shape of an erythrocyte adherent to a glass substrate, determined in Ref. [50]; the zone of the flat adhesion film is in the lower part of the graph. (a) For osmolarity 143 mOsm of the hypotonic solution the non-adherent part of the membrane is spherical; the shape for (b) osmolarity 153 mOsm and (c) 156 mOsm is reconstructed from experimental data by solving Eq. (4.110) for $k_c = 1.8 \times 10^{-19}$ J and for fixed membrane area $A_T = 188 \mu\text{m}^2$.

$$\frac{\cos \theta}{r} \frac{d}{dr} \left(r \cos \theta \frac{dF}{dr} \right) = \lambda F \tag{4.113}$$

It is convenient to use as an independent variable the length of the generatrix of the membrane profile, s , whose differential is related to the differentials of the cylindrical coordinates (r, z) as follows:

$$dr = \cos \theta ds; \quad dz = \sin \theta ds \tag{4.114}$$

The introduction of s as a variable of integration helps to avoid divergence in the procedure of numerical integration at the "equator" of the erythrocyte, where $\cos \theta = 0$. The differential of the membrane area, A , is simply related to ds :

$$dA = 2\pi r ds \tag{4.115}$$

Combining Eqs. (4.112) and (4.114) one obtains

$$\frac{d\theta}{ds} = \frac{2}{b} - \frac{\sin\theta}{r} + F(s) \quad (4.116)$$

Likewise, from (4.113) and (4.114) one derives

$$\frac{d^2F}{ds^2} = \lambda F - \frac{|\cos\theta|}{r} \frac{dF}{ds} \quad (4.117)$$

Equations (4.114)–(4.117) form a set of 5 equations for determining the 5 unknown functions $r(s)$, $z(s)$, $\theta(s)$, $F(s)$ and $A(s)$. In particular, the functions $r(s)$ and $z(s)$ determine the profile of the axisymmetric membrane in a parametric form.

Following Ref. [50], to determine the profile of the adherent erythrocyte (Fig. 4.4) one starts the numerical integration of Eqs. (4.114)–(4.117) from the apex of the membrane surface, i.e. from the upper point of the profiles in Fig. 4.4, where the generatrix intersects the axis of revolution. The boundary conditions are:

$$r(s=0) = 0; \quad z(s=0) = 0; \quad \theta(s=0) = 0 \quad \text{and} \quad A(s=0) = 0 \quad (4.118)$$

b is assumed to be a known parameter; in Ref. [50] it has been determined from the experimental data. Finally, the two boundary conditions for Eq. (4.117) are:

$$F(s=0) = q \quad \text{and} \quad \frac{dF}{ds} = 0 \quad \text{for } s = 0 \quad (4.119)$$

The latter boundary condition removes a divergence in Eq. (4.117) for $s=0$ ($r=0$). On the other hand, q is a unknown parameter, which is to be determined, together with the other unknown parameter λ , from the area of the free (non-adherent) portion of the membrane:

$$A_F = A_T - \pi r_f^2 \quad (4.120)$$

where A_T is the total area of the membrane, assumed constant; r_f is assumed to be known from the experiment. The two unknown parameters, q and λ , are to be determined from the following two conditions:

$$r = r_f \quad \text{and} \quad \theta = \theta_h \quad \text{for} \quad A = A_F \quad (4.121)$$

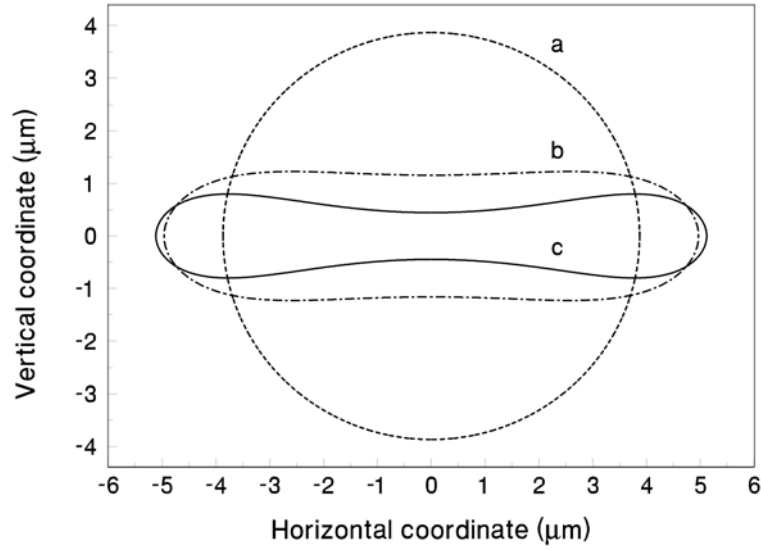


Fig. 4.5. Shape of a closed membrane calculated in Ref. [50] by means of Eq. (4.110): (a) spherocyte; (b) discocyte corresponding to $\sigma = 1.8 \times 10^{-4}$ mN/m and $\Delta P = 0.036$ Pa; (c) discocyte corresponding to $\sigma = 3.6 \times 10^{-4}$ mN/m and $\Delta P = 0.072$ Pa; k_c and A_T are the same as in Fig. 4.4.

To obtain the profiles of adherent cells shown in Fig. 4.4 one can start the integration from the membrane apex, $s=0$, with tentative values of the unknown parameters, q and λ . Further, the integration continues until the point with $A = A_F$ is reached. Then we check whether Eq. (4.121) is satisfied. If not, we assign new values of q and λ and start the integration again from the apex $s=0$. This continues until we find such values of q and λ , which lead to fulfillment of Eq. (4.121). These values can be automatically determined by numerical minimization of the function

$$\Phi(q, \lambda) = [r(A_F; q, \lambda) - r_f]^2 + [\theta(A_F; q, \lambda) - \theta_h]^2 \quad (4.122)$$

with respect of q and λ . Thus one determines the values of λ and q .

The curves in Fig. 4.5 illustrate what would be the shape of the same erythrocyte (of the same fixed area $A_T = 188 \mu\text{m}^2$ as in Fig. 4.4) if it were not attached to the substrate. In other words, Fig. 4.5 shows the shape of a free (non-attached) erythrocyte of area A_T at various values of the membrane tension σ and the transmembrane pressure difference ΔP , specified in the figure caption. The curves in Fig. 4.5 are obtained in Ref. [50] by numerical integration of Eqs. (4.114)–(4.117). As before, the integration starts from the apex of the profile, i.e. from the

intersection point of the generatrix with the axis of revolution, where we set $s = 0$. The numerical integration starts with a tentative value of q in Eq. (4.119). The value of q is determined from the condition that when the integration reaches the membrane "equator", where $\cos\theta = 0$, the membrane area must be $A = A_T/2$.

Since the membrane profile is symmetric with respect to the "equatorial" plane, in this case we carry out the numerical integration above the equator, and then we obtain the profile below the equator as a mirror image. Of course, one can continue the numerical integration after crossing the equator and the same profile will be obtained; however, due to accumulation of error from the numerical procedure this could decrease the accuracy of the calculated profile for the higher values of s (below the equator).

Such calculations indicate that the generalized Laplace equation, Eq. (4.110), or the equivalent set of equations (4.114)–(4.117), has at least two types of solutions for a free (non-adherent) erythrocyte of fixed area and given membrane tension σ . The first type is a "discocyte" like those in Fig. 4.5. The second type looks like an oblong ellipsoid of revolution, which resembles the shape of a red blood cell penetrating along a narrow capillary (blood vessel).

4.5. MICROMECHANICAL EXPRESSIONS FOR THE SURFACE PROPERTIES

In the Section 4.3.2 we derived the formula for the work of interfacial deformation, Eq. (4.72), starting from a purely phenomenological expression, Eq. (4.73); as a result we obtained relationships between the surface thermodynamical and mechanical properties, Eqs. (4.79)–(4.80). In the present section we will derive again Eq. (4.72), however this time by taking excesses with respect to the bulk phases; this alternative approach provides *micromechanical* expressions for the surface properties of an arbitrarily curved interface, such as generalizations of Eqs. (3.69) and (3.70).

4.5.1. SURFACE TENSIONS, MOMENTS AND CURVATURE ELASTIC MODULI

Basic relationships. Our purpose here is to extend the hydrostatic approach to the theory of a spherical phase boundary from Section 3.2.3 to the general case of an arbitrarily

curved interface. We follow Refs. [23, 26]. As discussed in Chapter 1, in a vicinity of a real fluid interface the pressure \mathbf{P} represents a tensorial quantity, which depends on the position in the transition zone between the two phases. After Gibbs [1], let us define an idealized (model) system, which is composed of two homogeneous and isotropic fluid phases, I and II, separated by a mathematical dividing surface. If $\mathbf{R}(u^1, u^2)$ is the running position vector of a point from the dividing surface, we can present the position-vector of a given point in space in the form:

$$\mathbf{r} = \mathbf{R}(u^1, u^2) + \lambda \mathbf{n}(u^1, u^2) \quad (4.123)$$

As before, \mathbf{n} is the running unit normal to the interface; λ is the distance from the given point in space to the dividing surface. The pressure in the idealized system can be expressed in the form

$$\bar{\mathbf{P}} = \bar{P}\mathbf{U}, \quad \bar{P} = P_I\theta(-\lambda) + P_{II}\theta(\lambda) \quad (4.124)$$

where

$$\theta(\lambda) = \begin{cases} 0 & \text{for } \lambda < 0; \\ 1 & \text{for } \lambda > 0, \end{cases} \quad (4.125)$$

is the step-wise function of Heaviside; P_I and P_{II} are the pressures in the bulk of the respective two neighboring phases, while \mathbf{U} is the unit tensor in space. Having in mind Eq. (1.22), one can express the work of interfacial deformation, produced during a time interval δt , [52]:

$$\int_A \delta w_s dA = - \int_V (\mathbf{P} - \bar{\mathbf{P}}) : (\boldsymbol{\Psi} \delta t) dV \quad (4.126)$$

As before, δw_s is the work of interfacial deformation per unit area, $dA = a^{1/2} du^1 du^2$ is a surface element, and $\boldsymbol{\Psi}$ is the spatial rate-of-strain tensor (the strain tensor is $\boldsymbol{\Phi} = \boldsymbol{\Psi} \delta t$):

$$\boldsymbol{\Psi} = \frac{1}{2} [\nabla \mathbf{w} + (\nabla \mathbf{w})^T] \quad (4.127)$$

Here \mathbf{w} is the velocity field in the bulk phases and the superscript ‘‘T’’ symbolizes conjugation. For slow quasistatic processes one can use the kinematic formula of Eliassen [21]:

$$\mathbf{w} = \mathbf{v} - \lambda (\nabla_s \mathbf{v}) \cdot \mathbf{n} \quad (4.128)$$

where the surface velocity \mathbf{v} is defined by Eq. (4.18). Equation (4.128) corresponds to such a deformation, for which every material point is fixed at a point of the curvilinear coordinate network (u^1, u^2, λ) , which moves together with the deforming dividing surface. In particular, every layer of material points, corresponding to $\lambda = \text{const.}$, remains parallel to the dividing surface in the course of deformation. The integration in the left-hand side of Eq. (4.126) is carried out over an arbitrarily chosen parcel A from the dividing surface, while the integration in the right-hand side – over the corresponding cylindrical volume depicted in Fig. 4.6. The lateral surface of this volume is perpendicular to the dividing surface. The vectorial surface element of the lateral surface can be expressed in the form [21]:

$$d\mathbf{s} = \mathbf{v} \cdot \mathbf{L} d\lambda dl \quad (4.129)$$

where dl is a linear element on the contour C , and \mathbf{v} is an outer unit normal to C , see Fig. 4.6;

$$\mathbf{L} = (1 - 2\lambda H)\mathbf{U}_s + \lambda \mathbf{b} \quad (4.130)$$

in Eq. (4.129) is a surface tensor, cf. Eqs. (4.14) and (4.17). The volume element dV can be expressed in the form [53]:

$$dV = \chi dA d\lambda, \quad \chi \equiv (1 - \lambda H)^2 - \lambda^2 D^2 = 1 - 2\lambda H + \lambda^2 K \quad (4.131)$$

A substitution of \mathbf{w} from Eq. (4.128) into Eq. (4.127) yields [23]

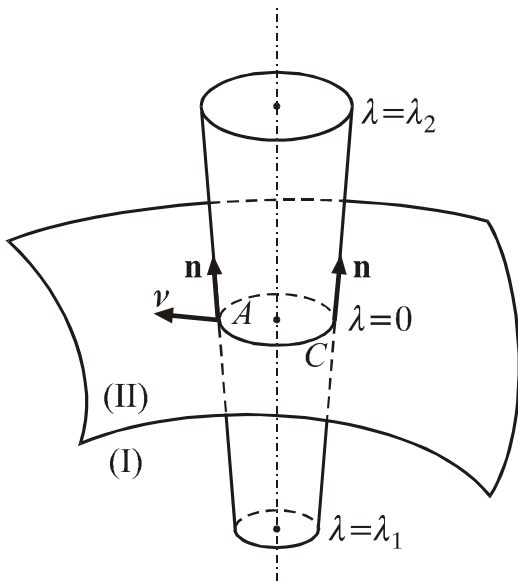


Fig. 4.6. An imaginary cylinder, whose lateral surface is perpendicular to the dividing surface between phases I and II, and whose bases are parallel to it; \mathbf{n} and \mathbf{v} ($\mathbf{n} \perp \mathbf{v}$) are running unit normals to the dividing surface and to the contour C , respectively; moreover, \mathbf{v} is tangential to the dividing surface.

$$\Psi = \mathbf{a}^\mu \mathbf{a}^\nu \left[(1 - 2\lambda H)(w_{\mu,\nu} + w_{\nu,\mu}) + \lambda(w_{\mu,\sigma} b_\nu^\sigma + w_{\nu,\sigma} b_\mu^\sigma) - 2(b_{\mu\nu} - \lambda K a_{\mu\nu}) \mathbf{v}^{(n)} \right] / 2\chi \quad (4.132)$$

Next, with the help of Eqs. (4.17), (4.19), (4.21), (4.128), (4.132) and the identities (4.61)–(4.62) one can prove that [23]

$$(\mathbf{U}_s : \Psi) \mathbf{U}_s + (\mathbf{q} : \Psi) \mathbf{q} = (\chi \mathbf{U}_s \dot{\alpha} + \chi \mathbf{q} \dot{\beta} - 2\lambda \mathbf{L} \dot{H} - 2\lambda \mathbf{q} \cdot \mathbf{L} \dot{D}) / \chi \quad (4.133)$$

Since the surface parcel A has been arbitrarily chosen, from Eqs. (4.126) and Eq. (4.131), we get:

$$\delta w_s = - \int_{\lambda_1}^{\lambda_2} (\mathbf{P}^s : \Psi) \delta t \chi d\lambda, \quad \mathbf{P}^s \equiv \mathbf{P} - \bar{\mathbf{P}} \quad (4.134)$$

A further simplification of Eq. (4.134) can be achieved if some specific information about the process of deformation is available. To specify the process one can assume that the surface rate-of-strain tensor can be expressed in the form [23]:

$$\Psi = \frac{1}{2} (\mathbf{U}_s : \Psi) \mathbf{U}_s + \frac{1}{2} (\mathbf{q} : \Psi) \mathbf{q} \quad (4.135)$$

The latter equation implies that the tensor Ψ has diagonal form in the basis of the principle curvatures. In other words, the deformation of the dividing surface is related to the deformation in the adjacent phases. Using Eq. (4.135) we obtain:

$$\mathbf{P}^s : \Psi = \frac{1}{2} \mathbf{P}^s : [\mathbf{U}_s (\mathbf{U}_s : \Psi) + \mathbf{q} (\mathbf{q} : \Psi)] \quad (4.136)$$

Equation (4.136) can be also obtained using the alternative assumption that the pressure tensor can be expressed in the form

$$\mathbf{P} = \frac{1}{2} (\mathbf{U}_s : \mathbf{P}) \mathbf{U}_s + \frac{1}{2} (\mathbf{q} : \mathbf{P}) \mathbf{q} + P_N \mathbf{nn} \quad (4.137)$$

From Eq. (4.137) one can deduce Eq. (4.136) without imposing any limitations on the form of the rate-of-strain tensor Ψ . The expression (4.137), which has been introduced by Buff [54, 55], means that at every point two of the eigenvectors of the tensor \mathbf{P} are directed along the lines of maximal and minimal curvature of the surface $\lambda = \text{const.}$, passing through this point, whereas the third eigenvector is always normal to the dividing surface. In other words, the

orientation of the eigenvectors of \mathbf{P} in a vicinity of the phase boundary is induced by the geometry of the interface, which is a reasonable presumption from a physical viewpoint.

Combining Eqs. (4.133), (4.134) and (4.136) one obtains again the known expression for the work of surface deformation, $\delta w_s = \gamma \delta \alpha + \xi \delta \beta + B \delta H + \Theta \delta D$, see Eq. (3.1), where [23, 26]:

$$\gamma = -\frac{1}{2} \int_{\lambda_1}^{\lambda_2} \mathbf{U}_s : \mathbf{P}^s \chi d\lambda \quad (4.138)$$

$$\xi = -\frac{1}{2} \int_{\lambda_1}^{\lambda_2} \mathbf{q} : \mathbf{P}^s \chi d\lambda \quad (4.139)$$

$$B = \int_{\lambda_1}^{\lambda_2} \mathbf{L} : \mathbf{P}^s \lambda d\lambda \quad (4.140)$$

$$\Theta = \int_{\lambda_1}^{\lambda_2} (\mathbf{q} \cdot \mathbf{L}) : \mathbf{P}^s \lambda d\lambda \quad (4.141)$$

Equations (4.138)–(4.141) provide general micromechanical expressions for the interfacial tensions and moments of an arbitrarily curved interface. In the special case of a spherical interface of radius a Eqs. (4.138) and (4.140) reduce to known expressions first derived by Tolman [56]: these are Eq. (3.59) and the equation

$$B = 2 \int_{\lambda_1}^{\lambda_2} (P_T - \bar{P})(1 + \lambda/a) \lambda d\lambda \quad (4.142)$$

The special form of Eqs. (4.138)–(4.141) for a cylindrical surface can be found in Refs. [14, 22].

Expressions for the spontaneous curvature and the elastic moduli k_c and \bar{k}_c . From Eqs. (4.140)–(4.141) one can deduce micromechanical expressions for the bending moment of a planar interface, B_0 , and for the bending and torsion elastic moduli, k_c and \bar{k}_c . We will use the simplifying assumption for “tangential isotropy”, which has been introduced by Buff [53]:

$$\mathbf{P}^s = P_T^s \mathbf{U}_s + P_N^s \mathbf{nn}; \quad P_T^s \equiv P_T - \bar{P}; \quad P_N^s \equiv P_N - \bar{P} \quad (4.143)$$

From Eqs. (4.17) and (4.130) we obtain

$$\mathbf{q} \cdot \mathbf{L} = (1 - \lambda H) \mathbf{q} + \lambda D \mathbf{U}_s \quad (4.144)$$

A substitution of Eqs. (4.143)–(4.144) into Eq. (4.141) yields

$$\Theta = 2D \int_{\lambda_1}^{\lambda_2} P_T^s \lambda^2 d\lambda \quad (4.145)$$

The comparison of the latter equation with Eq. (3.9) gives

$$\bar{k}_c = - \int_{\lambda_1}^{\lambda_2} P_T^s \lambda^2 d\lambda \quad (4.146)$$

Equation (4.146) has been first obtained by Helfrich [57]. Further, from Eqs. (4.17) and (4.130) one can derive

$$\mathbf{L} = (1 - \lambda H) \mathbf{U}_s + \lambda D \mathbf{q} \quad (4.147)$$

Substituting Eqs. (4.143) and (4.147) into Eq. (4.140) we get

$$B = 2 \int_{\lambda_1}^{\lambda_2} P_T^s (1 - \lambda H) \lambda d\lambda = 2 \int_{\lambda_1}^{\lambda_2} (P_T^s|_{H=0} + \frac{\partial P_T^s}{\partial H} H + \dots) (1 - \lambda H) \lambda d\lambda \quad (4.148)$$

From the latter equation, in view of Eqs. (3.9), (3.10) and (4.146), we obtain

$$B_0 = -4k_c H_0 = 2 \int_{\lambda_1}^{\lambda_2} P_T^s|_{H=0} \lambda d\lambda \quad (4.149)$$

$$k_c = \frac{1}{2} \int_{\lambda_1}^{\lambda_2} \left(\frac{\partial P_T^s}{\partial H} \right)_{H=0} \lambda d\lambda \quad (4.150)$$

As usual, H_0 is the spontaneous curvature. Equations (4.149) and (4.150) have been first obtained in a quite different way, respectively, by Helfrich [57] and Szleifer et al. [58]. Equations (4.146), (4.149) and (4.150) were utilized by Lekkerkerker [59] for calculating the electrostatic components of B_0 , k_c and \bar{k}_c , see Eqs. (3.91)–(3.93).

From the above equations we can deduce also expressions for the coefficients C_1 and C_2 , see Eqs. (3.5) and (3.6), in the framework of the simplifying assumption for tangential isotropy, Eq. (4.143). For example, combining Eqs. (4.145) and (4.148) with Eq. (3.6) one can derive

$$C_2 = \frac{-1}{2D} \Theta = - \int_{\lambda_1}^{\lambda_2} P_T^s \lambda^2 d\lambda; \quad C_1 = B - 2C_2 H = 2 \int_{\lambda_1}^{\lambda_2} P_T^s \lambda d\lambda \quad (4.151)$$

Likewise, a combination of Eqs. (4.131), (4.138) and (4.143) yields

$$\gamma = - \int_{\lambda_1}^{\lambda_2} (1 - 2H\lambda + K\lambda^2) P_T^s d\lambda \quad (4.152)$$

Equations (4.151) and (4.152) are equivalent to the results by Markin et al. [30] (the latter authors use the notation $J = -2H$ and $\tilde{C}_1 = -C_1/2$).

Expressions for the surface densities of extensive thermodynamic parameters. In Ref. [23] a micromechanical derivation of the fundamental thermodynamic equation, Eq. (3.16), was given, which provided expressions also for the adsorptions of the species, Γ_k , and the surface excesses of internal energy u_s and entropy s_s , as follows

$$\Gamma_k = \int_{\lambda_1}^{\lambda_2} (n_k - \bar{n}_k) \chi d\lambda, \quad u_s = \int_{\lambda_1}^{\lambda_2} (u - \bar{u}) \chi d\lambda, \quad s_s = \int_{\lambda_1}^{\lambda_2} (s - \bar{s}) \chi d\lambda \quad (4.153)$$

Here χ is defined by Eq. (4.131), n_k , u and s are bulk densities of the k -th species, internal energy and entropy in the real system; the respective densities in the idealized system are

$$\bar{n}_k \equiv n_k^I \theta(-\lambda) + n_k^{II} \theta(\lambda), \quad \bar{u} \equiv u^I \theta(-\lambda) + u^{II} \theta(\lambda), \quad \bar{s} \equiv s^I \theta(-\lambda) + s^{II} \theta(\lambda);$$

the superscripts ‘‘I’’ and ‘‘II’’ denote properties of phases I and II. Note that the expression for Γ_k in Eq. (4.153) represents a generalization of Eq. (1.36) for an arbitrarily curved interface.

4.5.2. TENSORS OF THE SURFACE STRESSES AND MOMENTS

General micromechanical expressions. Following Ref. [26] let us consider a sectorial strip ΔA_s , which is perpendicular to the interface and corresponds to a linear element dl from an arbitrarily chosen curve C on the dividing surface (Fig. 4.7). As usual, \mathbf{n} and \mathbf{v} ($\mathbf{n} \perp \mathbf{v}$) are, respectively, running unit normals to the dividing surface and the curve C . It is presumed that the ends of the sectorial strip ΔA_s , corresponding to $\lambda = \lambda_1$ and $\lambda = \lambda_2$, are located in the

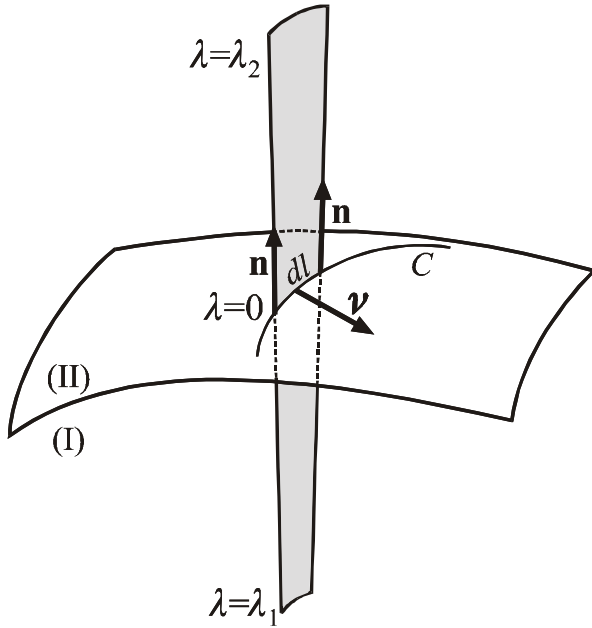


Fig. 4.7. Sketch of a sectorial strip, which is perpendicular to the dividing surface. The strip corresponds to an element dl from the curve C on the dividing surface; \mathbf{n} and \mathbf{v} are running unit normals to the surface and the curve C , respectively; in addition, $\mathbf{n} \perp \mathbf{v}$.

volume of the two adjacent phases, i.e. far enough from the interface to have isotropic pressure tensor \mathbf{P} . The force acting on the strip ΔA_s in the *real* system is

$$\int_{\Delta A_s} ds \mathbf{n} \cdot \mathbf{P} \tag{4.154}$$

In the idealized system the pressure tensor is assumed to be isotropic by definition, see Eq. (4.124); to compensate the difference with the real system, a surface stress tensor, $\underline{\sigma}$, is introduced. Hence, the force exerted on the strip ΔA_s in the *idealized* system is

$$\left(\int_{\Delta A_s} ds \mathbf{n} \cdot \bar{\mathbf{P}} \right) - \mathbf{v} \cdot \underline{\sigma} dl \tag{4.155}$$

Demanding the *force* acting on the strip ΔA_s to be the same in the real and idealized system, we obtain [14]:

$$\mathbf{v} \cdot \underline{\sigma} = - \mathbf{v} \cdot \int_{\lambda_1}^{\lambda_2} d\lambda \mathbf{L} \cdot \mathbf{P}^s, \quad \mathbf{P}^s \equiv \mathbf{P} - \bar{\mathbf{P}}, \tag{4.156}$$

where we have used Eq. (4.129). Likewise, demanding the *moment* acting on the strip ΔA_s to

be the same in the idealized and the real system, we obtain [14]:

$$\boldsymbol{\nu} \cdot \mathbf{N} - \boldsymbol{\nu} \cdot \underline{\boldsymbol{\sigma}} \times \mathbf{R} = -\boldsymbol{\nu} \cdot \int_{\lambda_1}^{\lambda_2} d\lambda \mathbf{L} \cdot \mathbf{P}^s \times \mathbf{r} \quad (4.157)$$

Using the arbitrariness of $\boldsymbol{\nu}$ and the identity $\mathbf{a}_\nu \times \mathbf{n} = \mathbf{a}^{\mu\nu} \varepsilon_{\mu\nu}$, from Eqs. (4.123), (4.156) and (4.157) one deduces [14]:

$$\underline{\boldsymbol{\sigma}} = - \int_{\lambda_1}^{\lambda_2} d\lambda \mathbf{L} \cdot \mathbf{P}^s \quad (4.158)$$

$$\mathbf{N} = - \int_{\lambda_1}^{\lambda_2} d\lambda \lambda \mathbf{L} \cdot \mathbf{P}^s \cdot \underline{\boldsymbol{\varepsilon}} \quad (4.159)$$

In addition, with the help of the identities $\mathbf{M} = \mathbf{N} \cdot \underline{\boldsymbol{\varepsilon}}$ and $\underline{\boldsymbol{\varepsilon}} \cdot \underline{\boldsymbol{\varepsilon}} = -\mathbf{U}_s$ from Eq. (4.159) one derives

$$\mathbf{M} = \int_{\lambda_1}^{\lambda_2} d\lambda \lambda \mathbf{L} \cdot \mathbf{P}^s \cdot \mathbf{U}_s \quad (4.160)$$

Equations (4.158)–(4.160) represent the sought for micromechanical expressions for the tensors of the surface stresses and moments, see Fig. 4.1. It is worthwhile noting that in contrast with the tensor $\underline{\boldsymbol{\sigma}}$, the tensors \mathbf{M} and \mathbf{N} , defined by Eqs. (4.159) and (4.160), have no transversal components (components directed along \mathbf{n}), which is consonant with Eqs. (4.28) and (4.46). In addition, Eq. (4.83) shows that the bending and torsion moments, B and Θ , are equal to the trace and the deviator of the tensor \mathbf{M} :

$$B = \mathbf{U}_s : \mathbf{M}, \quad \Theta = \mathbf{q} : \mathbf{M} \quad (4.161)$$

The substitution of \mathbf{M} from (4.160) into (4.161) gives exactly Eqs. (4.140) and (4.141), which is an additional evidence for the selfconsistency of the theory presented here. Likewise, from Eq. (4.24) we obtain

$$\sigma = \frac{1}{2} \mathbf{U}_s : \underline{\boldsymbol{\sigma}}, \quad \eta = \frac{1}{2} \mathbf{q} : \underline{\boldsymbol{\sigma}} \quad (4.162)$$

Combining Eqs. (4.158) and (4.162) one derives [14]:

$$\sigma = -\frac{1}{2} \int_{\lambda_1}^{\lambda_2} d\lambda \mathbf{L} : \mathbf{P}^s \quad (4.163)$$

$$\eta = -\frac{1}{2} \int_{\lambda_1}^{\lambda_2} d\lambda (\mathbf{q} \cdot \mathbf{L}) : \mathbf{P}^s \quad (4.164)$$

One can verify that if the micromechanical expressions for γ , ξ , B , Θ , σ and η , Eqs. (4.138)–(4.141) and (4.163)–(4.164), are substituted into Eqs. (4.81) and (4.82), the latter are identically satisfied; this is an additional test for selfconsistency of the theory.

Special case of tangentially isotropic tensor \mathbf{P} : From the definition $\mathbf{P}^s \equiv \mathbf{P} - \bar{\mathbf{P}}$ it follows that in such a case the tensor \mathbf{P}^s will be also tangentially isotropic, cf. Eq. (4.143), and γ will be given by Eq. (4.152). From Eqs. (4.139), (4.163) and (4.164) we obtain

$$\sigma = - \int_{\lambda_1}^{\lambda_2} d\lambda (1 - \lambda H) P_T^s \quad (4.165)$$

$$\xi = 0, \quad \eta = -D \int_{\lambda_1}^{\lambda_2} d\lambda \lambda P_T^s = -\frac{1}{2} (BD + \Theta H) \quad (4.166)$$

As mentioned at the end of Section 4.3.2, two alternative definitions of *fluid* interface are possible:

(i) *mechanical*: the surface stress tensor, $\underline{\sigma}$, is isotropic, that is $\eta = 0$.

(ii) *thermodynamical*: no work is produced upon a deformation of surface shearing, i.e. $\xi = 0$.

Equation (4.166) shows that the hypothesis for tangential isotropy, Eq. (4.143), is consistent with the *thermodynamic* definition for fluid interface, that is $\xi = 0$. On the other hand, from the tangential isotropy of the tensor \mathbf{P} (and \mathbf{P}^s) does not follow isotropy of its surface excess, the tensor $\underline{\sigma}$, cf. Eq. (4.158). In fact, the anisotropy of $\underline{\sigma}$ stems from the anisotropy of the curvature tensor \mathbf{b} of the arbitrarily curved interface, see Eqs. (4.130) and (4.158).

The fact that the hypothesis for tangential isotropy of the pressure tensor \mathbf{P} is consistent with the thermodynamic definition of surface fluidity should not be considered as an argument in

favor of the latter definition. One should have in mind that, in general, the statistical mechanics predicts a non-isotropic pressure tensor \mathbf{P} in a vicinity of an arbitrarily curved interface; see the review by Kuni and Rusanov [60].

4.6. SUMMARY

In mechanics the stresses and moments acting in an interface or biomembrane can be taken into account by assigning tensors of the surface stresses, $\underline{\sigma}$, and moments, \mathbf{M} , to the phase boundary, see Fig. 4.1. Three equations determine the shape and deformation of a curved interface or biomembrane: they correspond to the three projections of the vectorial local balance of the *linear* momentum, see Eqs. (4.37), (4.39) and (4.40). Additional useful information is provided by the vectorial local balance of the *angular* momentum, see Eqs. (4.43)–(4.44), which imply that the tensor \mathbf{M} is symmetric, and that its divergence is related to the transverse shear stress resultants of $\underline{\sigma}$, see Eqs. (4.28) and (4.49). The normal projection of the surface linear momentum balance has the meaning of a generalized Laplace equation, which contains a contribution from the interfacial moments, see Eq. (4.51).

Alternatively, variational calculus can be applied to derive the equations governing the interfacial/membrane shape by minimization of a functional – “the thermodynamic approach”. The surface/membrane tension depends on the local curvature of the surface and should not be treated as a constant Lagrange multiplier. The correct minimization procedure is considered in detail in Section 4.3.1. In the theoretical derivations one should take into account also the work of surface shearing, even in the case of *fluid* interface/membrane; see the discussions after Eqs. (4.83) and (4.166).

Thus it turns out that the generalized Laplace equation can be derived in two alternative ways: mechanical and thermodynamical, cf. Eqs. (4.50)–(4.51) and Eqs. (4.70)–(4.71). This fact provides a test for a given surface mechanical (rheological) model: if a model is selfconsistent, the two alternative approaches must give the same result. The connection between them has the form of relationships between the mechanical and thermodynamical surface tensions and moments, see Eqs. (4.79)–(4.82). Different, but equivalent, forms of the generalized Laplace equation are considered and discussed, see Section 4.3.3. In fact, the mechanical and

thermodynamical approaches are mutually complementary parts of the same formalism.

The general theoretical equations can give quantitative predictions if only rheological constitutive relations are specified, which characterize a given interface (biomembrane) as an elastic, viscous or visco-elastic two-dimensional continuum. The most popular constitutive relations for the tensors of the surface stresses $\underline{\sigma}$ and moments \mathbf{M} are Eqs. (4.86) and (4.96), which stem from the models of Boussinesq-Scriven and Helfrich. The latter leads to a specific form of the generalized Laplace equation, which is convenient to use in applications, such as determination of the axisymmetric shapes of biological cells, see Eq. (4.103) and the whole Section 4.4. In particular, the axial symmetry reduces the generalized Laplace equation to a system of ordinary differential equations, for which a convenient method of integration is proposed (Section 4.4.2).

Finally, micromechanical expressions for the surface tensions and moments are derived in terms of combinations from the components of the pressure tensor, see Eqs. (4.138)–(4.141) and (4.158)–(4.164). As corollaries from the latter general equations one can deduce theoretical expressions for calculation of the bending and torsion elastic moduli, k_c and \bar{k}_c , and the spontaneous curvature, H_0 , see Eqs. (4.146), (4.149) and (4.150).

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