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# Theory of Curved Interfaces and Membranes: Mechanical and Thermodynamical Approaches

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## Abstract

The mechanical and thermodynamical approaches to the theory of the general curved interfaces are presented and compared. In the mechanical approach a curved interface or membrane is characterized by the tensors of surface stresses and moments. They are connected by the surface balances of the linear and angular momentum. On the other hand, in the thermodynamical approach the surface is characterized by the scalar dilation and shear tensions as well as by the bending and torsion moments. In this review we investigate the problem about the relationships connecting the mechanical and thermodynamical approaches. We find that these two approaches are in a good agreement, that they are complementary to each other and represent the two parts of a self-consistent theory. The latter can be applied to any system where curved interfaces, thin films or membranes are present: microemulsions, lamellar and sponge phases, lipid vesicles and cell membranes, capillary waves at interfaces, undulation and peristaltic surface forces, lateral capillary forces between particles in thin liquid films, etc.

## 1. Introduction

Various experimental studies in the fields of colloid science and biophysics show that the classical Young-Laplace theory [1] where a curved interface or membrane is described as a two-dimensional continuum in a state of position-independent, isotropic tension, is insufficient in several cases. The famous theory of a capillarity derived by Gibbs [2] is likewise founded on this Young-Laplace concept but, in addition, Gibbs introduced the notion of a surface of tension in order to be able to retain a simple formal scheme even when curvature effects are of importance. To account explicitly for the bending properties of monolayers, lipid bilayers and biomembranes with vanishing tension Helfrich [3] introduced additional mechanical parameters for a curved interface, *viz.*, bending and torsion moduli and spontaneous curvature. These parameters were soon recognized to be crucial also for understanding microemulsions [4-6].

Evans and Shalak [7] demonstrated that even such a complex entity as a biomembrane can be treated mechanically as a two-dimensional continuum characterized by dilational and shearing membrane tensions as well as by bending and torsion surface moments. For example, the special biconcave disk shape of erythrocytes was found to correspond to a minimum flexural interfacial energy of the system [7,8]. Other examples of systems where the interfacial flexural properties have been shown to play important roles are microemulsions [9,10] and surfactant micelles [11,12]. Moreover, the interfacial bending moment affects the amplitude of the fluctuation capillary waves on surfaces of low enough tension [13] and determines the magnitude of the repulsive "undulation" forces between two approaching fluid interfaces in solution [14,15].

In essence, there are two approaches to the theoretical description of a general curved interface which, however, at first sight may seem diametrically opposite. The first of them is the *mechanical approach* originating from the Kirchhoff-Love theory of plates and shells [16,17], which is standard in the mechanical sciences and which is sometimes applied to biomembranes and lipid bilayers. A main advantage of this approach is its powerful mathematical framework, which is basis of continuum mechanics in two dimensions, tensor analysis and differential geometry. Moreover it can be applied to both quasistatic and dynamic processes.

The second approach is founded on *thermodynamics* which is encompassed by the Gibbs theory of capillarity [2] and is frequently referred to in physical chemistry and surface science. The main advantage of this latter approach lies in its close relation with chemical thermodynamics. Hence, it provides a valid description of the variations of surface tensions, moments and deformations due to composition changes and, moreover, it establishes a link to the molecular theory which is based on statistical mechanics.

Considering these rather different approaches to the theory of curved surfaces which are taken in mechanics and surface thermodynamics, it is obvious that widely different notions and basic equations are being employed to account for the same phenomena. Ultimately, the two approaches have to be equivalent or at least complementary, since the same physical reality is actually being described.

Our aim with the present review article is, hence, to establish the connecting links between the mechanical and thermodynamical approaches to the theory of general, curved interfaces. We believe that the combined power of these two main routes will facilitate solving some pending theoretical problems in the field of interfaces and membranes.

## **2. The Mechanical Approach**

The mechanical theory of the extensional and flexural deformations of a two-dimensional continuum originates from the classical theory of shells and plates developed in 1850 by Kirchhoff [16] and extended in 1888 by Love [17]. A comprehensive review of this theory is given in the monograph by Naghdi [18].

Historically the derivation of the Kirchhoff-Love theory had the practical purpose to treat vibrations of plates and shells in order to predict the tones of vibrating bells [17,18]. However, the underlying mathematical formalism can be applied to describe the deformations of any two-dimensional continuum, including fluid interfaces and biomembranes. Since our ultimate aim is to compare the Kirchhoff-Love theory with the Gibbs theory of capillarity, we will first focus our attention on some general equations of the theory of shells and plates.

*(a) Surface balance of the linear momentum*

It is appropriate to start with a three-dimensional continuum and then to proceed with a two-dimensional continuum.

Let us consider a material volume  $V$  enclosed by a surface  $S$  with running outer unit normal  $\mathbf{n}$ . Then, in conformity with the Newton's second law it is postulated (see e.g. Ref. [19]):

$$\frac{d}{dt} \int_V dV \rho \mathbf{v} = \oint_S ds \mathbf{n} \cdot \mathbf{T} + \int_V dV \rho \mathbf{f} \quad (2.1)$$

Here  $t$  is time,  $\rho$  is mass density,  $\mathbf{v}$  is velocity field,  $\mathbf{T}$  is the stress tensor,  $ds$  is a scalar surface element and  $\mathbf{f}$  is the body force per unit mass (if the body force is due to gravity, then  $\mathbf{f}$  coincides with the gravitational acceleration  $\mathbf{g}$ ). Eqn (2.1) states that the rate of increase of the linear momentum of material volume  $V$  is equal to the sum of the surface and body forces exerted on the volume  $V$ . In other words, Eqn (2.1) expresses the integral balance of linear momentum for the volume  $V$ . Since volume  $V$  is arbitrarily chosen, one can obtain the known local form of the linear momentum balance, which is valid at each point of a three-dimensional continuum [19,20]

$$\rho \frac{d\mathbf{v}}{dt} = \nabla \cdot \mathbf{T} + \rho \mathbf{f} \quad (2.2)$$

Eqn (2.2) is derived from Eqn (2.1) by using the Gauss-Ostrogradsky theorem along with the following known hydrodynamic relations:

$$\frac{d}{dt} \int_V dV \rho \mathbf{v} = \int_V dV \left[ \frac{d(\rho \mathbf{v})}{dt} + \rho \mathbf{v} \nabla \cdot \mathbf{v} \right] \quad (2.3)$$

$$\frac{d\rho}{dt} + \rho \nabla \cdot \mathbf{v} = 0. \quad (2.4)$$

We next continue with the derivation of a two-dimensional analogue of Eqn (2.2). Following Podstrigach and Povstenko [21] we consider a material volume  $V$  confining a portion,  $A$ , of an interface (membrane) together with volumes  $V_I$  and  $V_{II}$  of the adjacent bulk phases I and II - see Fig. 1.

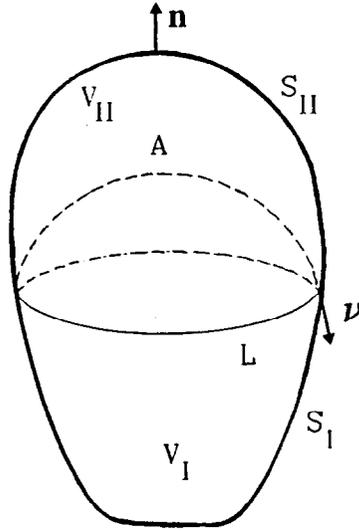


Fig. 1 Sketch of material volume  $V$  confining a portion  $A$  of an interface.  $V_I$ ,  $V_{II}$  and  $S_I$ ,  $S_{II}$  are the parts of volume  $V$  and its surface situated on the two sides of the interface  $A$ .

A counterpart of Eqn (2.1) is postulated [21]:

$$\begin{aligned} & \frac{d}{dt} \left( \sum_{Y=I,II} \int_{V_Y} dV \rho_Y v_Y + \int_A ds \Gamma v_s \right) = \\ & = \sum_{Y=I,II} \left( \int_{S_Y} ds n \cdot T_Y + \int_{V_Y} dV \rho_Y f_Y \right) + \int_A ds \Gamma f_s + \oint_L dl v \cdot \sigma \end{aligned} \quad (2.5)$$

Here the subscript  $s$  refers to the interface between the bulk phases I and II;  $S_I$  and  $S_{II}$  are the parts of the surface of volume  $V$ , which are situated on the two sides of the dividing surface  $A$ ;  $\Gamma$  is the mass density per unit area of this surface;  $\sigma$  is the surface stress tensor;  $L$  is the contour encompassing the interfacial portion  $A$ ;  $v$  is a unit vector which is simultaneously normal to contour  $L$  and tangential to surface  $A$  - see Fig. 1.

It should be noted that the surface stress tensor can be represented in the form [16,21]:

$$\sigma = a_\alpha a_\beta \sigma^{\alpha\beta} + a_\alpha n \sigma^{\alpha(n)} \quad (2.6)$$

where  $a_1$  and  $a_2$  are the vectors of a local basis in the surface  $A$  and  $n$  is the running unit

normal to this surface;  $\sigma^{\alpha\beta}$  and  $\sigma^{\alpha(n)}$  are tangential and transversal shear stress components, respectively. Here and hereafter the Greek indices take the values 1 and 2, and summation is assumed over the repeated indices.

For the sake of simplicity we assume continuity of the normal component of the velocity field at the interface:

$$(\mathbf{v}_I - \mathbf{v}_s) \cdot \mathbf{n} = (\mathbf{v}_{II} - \mathbf{v}_s) \cdot \mathbf{n} = 0 \quad (\text{at surface } A) \quad (2.7)$$

(The more general case, when Eqn (2.7) is not satisfied, is considered in Ref. [21]). Eqn (2.1) holds for each of the volumes  $V_Y$  ( $Y = I, II$ ):

$$\frac{d}{dt} \int_{V_Y} dV \rho \mathbf{v}_Y = \int_{s_Y \cup A} ds \mathbf{n} \cdot \mathbf{T}_Y + \int_{V_Y} dV \rho \mathbf{v}_Y \mathbf{f}_Y \quad (2.8)$$

In addition, from Eqn (2.6) and the Green-Gauss-Ostrogradsky theorem [22] one derives the relationship

$$\oint_L d\mathbf{l} \mathbf{v} \cdot \boldsymbol{\sigma} = \int_A ds \nabla_s \cdot \boldsymbol{\sigma} \quad (2.9)$$

where  $\nabla_s$  is two-dimensional gradient operator in the surface  $A$ :

$$\nabla_s = a_\alpha \frac{\partial}{\partial u^\alpha} \quad (2.10)$$

where  $u^\alpha$ ,  $\alpha = 1, 2$ , are curvilinear coordinates in the surface  $A$ . The surface counterparts of Eqns (2.3) and (2.4) read [23]:

$$\frac{d}{dt} \int_A ds \Gamma \mathbf{v}_s = \int_A ds \left[ \frac{d(\Gamma \mathbf{v}_s)}{dt} + \Gamma \mathbf{v}_s \nabla_s \cdot \mathbf{v}_s \right] \quad (2.11)$$

$$\frac{d\Gamma}{dt} + \Gamma \nabla_s \cdot \mathbf{v}_s = 0 \quad (2.12)$$

The last equation is valid when there is no exchange of mass between the bulk and the surface. Finally, by means of Eqns (2.8), (2.9), (2.11) and (2.12) the integral linear momentum balance, Eqn (2.5), can be transformed into a local form [21,23]

$$\Gamma \frac{d\mathbf{v}_s}{dt} = \nabla_s \cdot \boldsymbol{\sigma} + \Gamma \mathbf{f}_s + \mathbf{n} \cdot (\mathbf{T}_{II} - \mathbf{T}_I) \quad (2.13)$$

which is the sought-for two-dimensional analogue of Eqn (2.2). The last term in Eqn (2.13) accounts for the interaction between the surface and the two adjacent bulk phases; this term has no counterpart in Eqn (2.2). The components of the stress tensors  $T_I$  and  $T_{II}$  in Eqn (2.13) are to be evaluated at the surface  $A$ .

Differential geometry [23-25] provides the following expression for the surface divergence of the surface stress tensor  $\boldsymbol{\sigma}$  given by Eqn (2.6):

$$\nabla_s \cdot \boldsymbol{\sigma} = \left( \sigma_{,\beta}^{\beta\alpha} - b_{\beta}^{\alpha} \sigma^{\beta(n)} \right) \mathbf{a}_{\alpha} + \left( b_{\alpha\beta} \sigma^{\alpha\beta} + \sigma_{,\alpha}^{\alpha(n)} \right) \mathbf{n} \quad (2.14)$$

where  $b_{\alpha\beta}$  are the components of the surface curvature tensor and the commas denote covariant derivatives. Then the projections of Eqn (2.13) along vectors  $\mathbf{a}_{\alpha}$  and  $\mathbf{n}$  become [18,21]

$$\Gamma i^{\alpha} = \sigma^{\beta\alpha}_{,\beta} - b_{\beta}^{\alpha} \sigma^{\beta(n)} + \Gamma f_s^{\alpha} + \left( T_{II}^{(n)\alpha} - T_I^{(n)\alpha} \right), \quad \alpha = 1, 2 \quad (2.15)$$

$$\Gamma i^{(n)} = \sigma^{\alpha(n)}_{,\alpha} + b_{\alpha\beta} \sigma^{\alpha\beta} + \Gamma f_s^{(n)} + \left( T_{II}^{(n)(n)} - T_I^{(n)(n)} \right) \quad (2.16)$$

where  $i^{\alpha}$  and  $i^{(n)}$  are components of the acceleration vector  $d\mathbf{v}_s/dt$ . Equations (2.15) and (2.16) coincide with the first three basic equations of the theory of shells due to Kirchhoff and Love - see Refs. [18,21].

Eqns (2.15) and (2.16) are quite general; they can be specified when the rheological properties of the bulk phases and the surface are known, i.e. when *constitutive relations* connecting stress and strain are available (see Section 5 below).

As an example let us consider a quasistatic deformation ( $\mathbf{v}_s \approx 0$ ) of a fluid interface between two fluid bulk phases. In this case the bulk and surface stress tensors are isotropic:

$$\mathbf{T}_Y = -P_Y \mathbf{U}, \quad Y = I, II \quad (2.17)$$

$$\boldsymbol{\sigma} = \sigma \mathbf{U}_s \quad (2.18)$$

Here  $\sigma$  is the scalar surface tension,  $P_I$  and  $P_{II}$  are the pressures in the bulk phases,  $\mathbf{U}$  and  $\mathbf{U}_s$

are the bulk and surfaces unit tensors (idemfactors) respectively. By substituting Eqns (2.17) and (2.18) into Eqns (2.15) and (2.16) for the case of a quasistatic process one derives (assuming negligible surface weight  $\Gamma f_s$ ):

$$\sigma,^\alpha = 0 \quad (2.19)$$

$$2H\sigma = P_{II} - P_I \quad (2.20)$$

where

$$2H = a^{\alpha\beta} b_{\alpha\beta} \quad (2.21)$$

is the surface mean curvature with  $a^{\alpha\beta}$  being the surface metric tensor - see e.g. [23-25]. Eqns (2.19) and (2.20) represent the basis of the classical theory of capillarity developed by Young [26] and Laplace [1], which presumes the the surface tension,  $\sigma$ , is constant throughout the interface (membrane) and that the surface shape is determined by Eqn (2.20) frequently referred to as the Laplace equation. In particular, if the equation of the surface shape in Cartesian coordinates is

$$z = u(x, y), \quad (2.22)$$

the mean curvature can be expressed as a surface divergence [27]

$$2H = \nabla_s \cdot \left[ \frac{\nabla_s u}{(1 + |\nabla_s u|^2)^{\frac{1}{2}}} \right] \quad (2.23)$$

and Eqn (2.20) reduces to a second order nonlinear differential equation for determining the function  $u$ .

In the case of strongly curved surfaces (microemulsions, biomembranes) the role of surface bending moments becomes significant and the surface (membrane) tension is generally neither isotropic nor constant. Then Eqns (2.18) and (2.19) are no longer valid. The contribution of the surface moments is discussed below.

*(b) Surface balance of angular momentum*

In mechanics, rotational motion can be treated analogously to translational motion. In

particular, angular velocity and force moments (torques) are considered instead of linear velocity and forces. Three- and two-dimensional balances of the angular momentum, i.e. counterparts of Eqns (2.1) and (2.5), can be postulated - for details see Refs. [18,21]. A local form of the surface angular momentum balance

$$\alpha \Gamma \frac{d\mathbf{w}}{dt} = \nabla_s \cdot \mathbf{N} + \Gamma \mathbf{m} + \mathbf{n} \cdot [(\boldsymbol{\sigma} : \boldsymbol{\varepsilon}) \mathbf{U}_s + \boldsymbol{\sigma} \cdot \boldsymbol{\varepsilon}] \quad (2.24)$$

can be deduced, which constitutes a counterpart of Eqn (2.13). Here  $\alpha$  is a coefficient accounting for the moment of inertia;  $\mathbf{w}$  is the vector of angular velocity;

$$\mathbf{N} = \mathbf{a}_\alpha \mathbf{a}_\beta N^{\alpha\beta} + \mathbf{a}_\alpha n N^{\alpha(n)} \quad (2.25)$$

is the tensor of surface moments, which is an analogue of the surface stress tensor,  $\boldsymbol{\sigma}$ ;  $\mathbf{m}$  is a surface director couple per unit mass due to external body force;  $\mathbf{n}$  is a counterpart of  $\mathbf{f}_s$  in Eqn (2.13);

$$\boldsymbol{\varepsilon} = \mathbf{a}^\alpha \mathbf{a}^\beta \boldsymbol{\varepsilon}_{\alpha\beta} = \mathbf{a}^\alpha \mathbf{a}^\beta \sqrt{\alpha} \boldsymbol{\varepsilon}_{\alpha\beta} \quad (2.26)$$

is surface alternator;  $\alpha$  is the determinant of the surface metric tensor and

$$\boldsymbol{\varepsilon}_{12} = -\boldsymbol{\varepsilon}_{21} = \mathbf{1}, \quad \boldsymbol{\varepsilon}_{11} = \boldsymbol{\varepsilon}_{22} = \mathbf{0} \quad (2.27)$$

- cf. e.g. Ref. [24]; the symbol ":" denotes double scalar product of two dyadics see e.g. Refs. [23,28]. When deriving Eqn (2.24) it is assumed that there are no bulk torques (bulk counterpart of the surface tensorial field  $\mathbf{N}$ ); such bulk couples would appear if the bulk phase is a liquid crystal.

The last term in Eqn (2.24) expresses the force moments due to the interaction of the surface with the adjacent bulk phases.

Sometimes (cf. Refs. [7,18,21,28]) the surface moments are characterized by another tensor, viz.,

$$\mathbf{M}_{\alpha\beta} = N_\alpha^\gamma \boldsymbol{\varepsilon}_{\gamma\beta} \quad (2.28)$$

The meaning of the components of the tensors  $N_{\alpha\beta}$  and  $M_{\alpha\beta}$  is illustrated in Figs. 2b and 2c. One realizes that  $N_{11}$  and  $N_{22}$  represent normal moments (they cause torsion of the surface

element), whereas  $N_{12}$  and  $N_{21}$  represent tangential moments causing bending of the surface element. Hence, the mechanical interpretation of  $N_{\alpha\beta}$  is similar to that of  $\sigma_{\alpha\beta}$  (cf. Figs. 2a and 2b). On the other hand, the diagonal components of  $M_{\alpha\beta}$  represent bending moments and the nondiagonal ones - torsion moments - Fig. 2c.

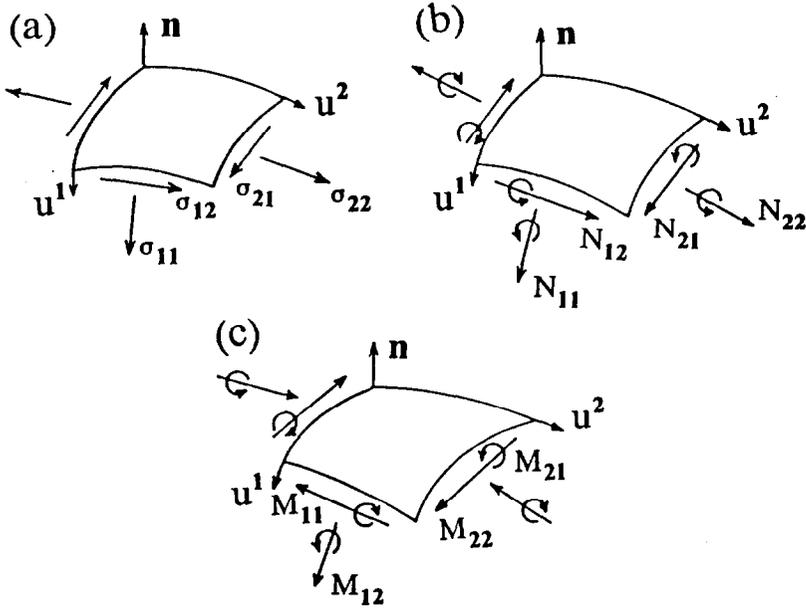


Fig. 2 Components of the surface stress tensor  $\sigma$  (a); of the surface moment tensor  $N$  (b); and of the surface moment tensor  $M$  (c).

By using Eqn (2.14) (with  $N$  instead of  $\sigma$ ), along with Eqns (2.6), (2.25) and (2.26), one can find the projections of the surface angular momentum balance, Eqn (2.27), along vectors  $a_\alpha$  and  $\mathbf{n}$  [21]:

$$\alpha \Gamma j^\alpha = N^{\beta\alpha}{}_{,\beta} - b_\beta^\alpha N^{\beta(n)} + \Gamma m^\alpha + \varepsilon^{\alpha\beta} a_{\beta\gamma} \sigma^{\gamma(n)} \tag{2.29}$$

$$\alpha \Gamma j^{\alpha(n)} = N^{\alpha(n)}{}_{,\alpha} + b_{\alpha\beta} N^{\alpha\beta} + \Gamma m^{\alpha(n)} - \varepsilon_{\alpha\beta} \sigma^{\beta\alpha} \tag{2.30}$$

where  $j^\alpha$  and  $j^{\alpha(n)}$  are components of angular acceleration vector  $d\mathbf{w}/dt$ . Eqns (2.29) and (2.30)

represent the second group of three basic equations in the theory of Kirchhoff and Love - see e.g. Refs. [18,21]

As an example for application of Eqns (2.29) and (2.30) let us consider the case of quasistatic process ( $j^\alpha \approx j^{(n)} \approx 0$ ) with a negligible effect of surface director couples,  $\Gamma m$ . In addition, let us assume that (i)  $\sigma_{\alpha\beta}$  and  $M_{\alpha\beta}$  are symmetric surface tensors:

$$\sigma_{\alpha\beta} = \sigma_{\beta\alpha}, \quad M_{\alpha\beta} = M_{\beta\alpha} \quad (2.31)$$

(ii)  $M_{\alpha\beta}$  diagonalizes in the basis of the principle curvatures, which is equivalent to commutativity of the tensorial product

$$b_{\alpha\beta} M_\gamma^\alpha = b_{\beta\gamma} M_\beta^\alpha \quad (2.32)$$

and that (iii) the transverse components of  $N$  are zero, i.e.

$$N = a_\alpha a_\beta N^{\alpha\beta} = a_\alpha a_\beta M_\gamma^\alpha e^{\gamma\beta} \quad (2.33)$$

- cf. Eqns (2.25) and (2.28). Then in view of Eqns (2.31) - (2.33) one can verify that the normal projection of the angular momentum balance, Eqn (2.30), is identically satisfied. In addition, the tangential projection, Eqn (2.29), can be transformed to read [7,18]:

$$\sigma^{\alpha(n)} = -M^{\alpha\beta}_{,\beta} \quad (2.34)$$

Eqn (2.34) shows that in the case of quasistatic processes the very existence of surface moments,  $M^{\alpha\beta}$ , gives rise to the transverse shear stress resultants  $\sigma^{\alpha(n)}$ . (When the process is not quasistatic, e.g. capillary waves, there is also a viscous contribution to  $\sigma^{\alpha(n)}$  - cf. Eqn (5.3) below.)

Substitution of Eqns (2.17) and (2.34) into Eqn (2.16) results in a generalization of the Laplace equation, Eqn (2.20), for the case, when surface moments are present [7,18]

$$b_{\alpha\beta} \sigma^{\alpha\beta} - M^{\alpha\beta}_{,\alpha\beta} = P_{II} - P_I \quad (2.35)$$

Under the same assumption Eqn (2.15) reduces to

$$\sigma^{\alpha\beta}{}_{,\beta} + b_{\beta}^{\alpha} M^{\beta\gamma}{}_{,\gamma} = 0 \quad (2.36)$$

Eqns (2.35) and (2.36) were utilized in the mechanics of biomembranes developed by Evans and Skalak [7]. In Section 3 below we compare Eqns (2.35) and (2.36) with the corresponding results from the Gibbs theory of capillarity.

(c) *Micromechanical expressions for  $\sigma$ ,  $N$  and  $M$*

So far we have been dealing with an *idealized* system, composed of two bulk phases separated with a mathematical (infinitely thin) surface. This is obviously an idealization since the real transition region between two bulk phases has always some finite physical thickness. This transition region is characterized by a nonuniform density and nonisotropic pressure even at equilibrium conditions [29,30]. There is a micromechanical approach originating from the work of Bakker [31] which identifies the surface tension with an integral of the excess pressure (difference between the pressure tensors in the real and idealized systems) across the transition region. In the original work of Bakker this approach was applied to planar interfaces. Later on it was extended to spherical interfaces in Refs. [29,32] and to arbitrary curved interfaces in Refs. [33-36]. Below, following Ref. [34], we derive micromechanical expressions for the surface stress tensor  $\sigma$  and the surface moment tensors  $N$  and  $M$ . The micromechanical expressions elucidate the physical meaning of these tensors and make possible their calculation by means of statistical mechanics.

Consider an interface separating two bulk phases I and II. Following the tradition [31-33] we will make use of the *pressure* tensor, which is in fact the stress tensor with opposite sign:

$$P = -T \quad (2.37)$$

As mentioned above, even under equilibrium conditions the pressure tensor  $P$  is non-isotropic in the interfacial zone; its components can be calculated by using some statistical mechanical model like that of Irving and Kirkwood [37] or the model of Kirkwood and Buff [38], later on extended by Harasima [39]. These models are not equivalent [29,40]. However, their adequacy has not yet been fully checked against experimental data, because of the difficulties connected with a realistic estimate of the molecular pair correlation function in the interfacial transition zone.

The tensor  $P$  represents the actual pressure in the *real* system. On the other hand, the

*idealized* system consists of two homogeneous phases, which preserve their bulk properties right up to a mathematical dividing surface. The pressure tensors  $P_I$  and  $P_{II}$  are ascribed to these two phases. In addition, tensors of surface tension,  $\sigma$ , and surface moments,  $N$ , are attributed to the dividing surface. At equilibrium conditions the pressure in the idealized system is isotropic everywhere, i.e.

$$P_I = P_I U \quad \text{and} \quad P_{II} = P_{II} U \quad (2.38)$$

However, it is worthwhile noting that the considerations below are valid even for non-equilibrium conditions in the system.

Let  $(u^1, u^2)$  be curvilinear coordinates in the dividing surface and  $\lambda$  be the distance from a point in the space to the dividing surface. Then  $(u^1, u^2, \lambda)$  represent curvilinear coordinates in space and

$$r = R(u^1, u^2) + \lambda n(u^1, u^2) \quad (2.39)$$

is the position vector of a point in space with  $R$  being the position vector of a point on the dividing surface whose running unit normal is  $n$ . Obviously, the surface with  $\lambda = 0$  is the dividing surface, and any surface with  $\lambda = \text{const} \neq 0$  is parallel to it [23,33]. The pressure tensor in the idealized system can be represented in the form

$$\bar{P} = P_I \theta(-\lambda) + P_{II} \theta(\lambda) \quad (2.40)$$

where  $\theta$  is the Heaviside step-wise function:

$$\theta = 0 \quad \text{for} \quad \lambda < 0 \quad \text{and} \quad \theta = 1 \quad \text{for} \quad \lambda > 0 \quad (2.41)$$

Next, following Ref. [34] we consider a perpendicular sectorial strip  $\Delta A_s$  for each element  $dl$  of a curve  $C$  lying on the dividing surface - see the hatched area in Fig. 3, where  $\nu$  is unit normal to curve  $C$  and the surfaces  $\lambda = \lambda_1$  and  $\lambda = \lambda_2$  are supposed to be located inside the bulk of the two adjacent phases.

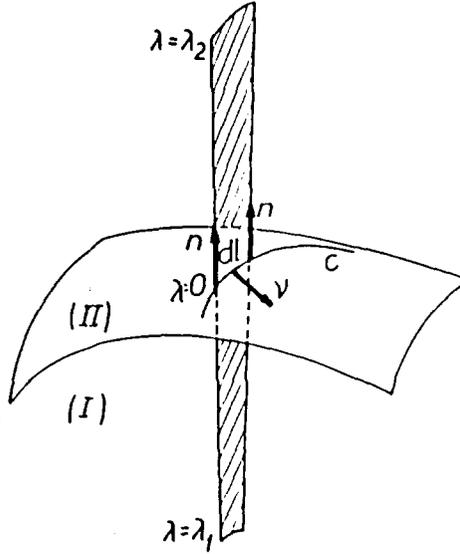


Fig. 3 A sectorial strip (hatched) associated with an element  $dl$  of curve  $C$  lying in the surface;  $n$  is the running unit normal to the surface.

The force exerted on the strip  $\Delta A_s$  in the *real* system is

$$\int_{\Delta A_s} ds n \cdot P$$

The corresponding force in the *idealized* system is

$$\left[ \int_{\Delta A_s} ds n \cdot \bar{P} \right] - v \cdot \sigma dl$$

Setting the forces in the real and idealized systems equal one can derive [34]

$$v \cdot \sigma = -v \cdot \int_{\lambda_1}^{\lambda_2} d\lambda L \cdot P^s \quad (2.42)$$

where

$$P^s = P - \bar{P} \quad (2.43)$$

is the excess pressure tensor and Eliassen's [23] finding

$$nds = \mathbf{v} \cdot L d\lambda dl, \quad L \equiv (1 - 2\lambda H) U_s + \lambda b \quad (2.44)$$

is being used, where

$$b = a_\alpha a_\beta b^{\alpha\beta} \quad (2.45)$$

is the surface curvature tensor.

Similarly, the condition for equivalence of the real and idealized systems with respect to the force moments yields

$$\mathbf{v} \cdot N - \mathbf{v} \cdot \sigma \times R = \mathbf{v} \cdot \int_{\lambda_1}^{\lambda_2} d\lambda L \cdot P^s \times r \quad (2.46)$$

Because of the arbitrariness of  $\mathbf{v}$ , from Eqns (2.39), (2.42) and (2.46) one finds:

$$\sigma = - \int_{\lambda_1}^{\lambda_2} d\lambda L \cdot P^s \quad (2.47)$$

$$N = \int_{\lambda_1}^{\lambda_2} d\lambda \lambda L \cdot P^s \times n \quad (2.48)$$

Eqns (2.47) and (2.48) are the sought-for micromechanical expressions for  $\sigma$  and  $N$ . By making use of the identity [23]

$$a_\gamma \times n = a^\delta \varepsilon_{\delta\gamma}$$

one can derive an alternative expression for  $N$ :

$$N = - \int_{\lambda_1}^{\lambda_2} d\lambda \lambda L \cdot P^s \cdot \varepsilon \quad (2.49)$$

In addition, having in mind that

$$M = N \cdot e, \quad e \cdot e = -U_z \quad (2.50)$$

(cf. Eqn (2.28)) from Eqn (2.49) one obtains

$$M = \int_{\lambda_1}^{\lambda_2} d\lambda \lambda L \cdot P^s \cdot U_z \quad (2.51)$$

It is worth noting that unlike the tensor  $\sigma$ , given by Eqn (2.47), the surface moment tensors  $M$  and  $N$ , as given by Eqns (2.49) and (2.51), do not have transverse components (resultants along  $n$ ) is agreement with Eqn (2.33).

As an illustrative example let us consider a cylindrical interface (membrane) between phases I and II. (We are aware of the fact that a cylindrical surface is not ever stable, nevertheless we choose it as the simplest example for a geometrically non-isotropic surface.) It is natural to introduce cylindrical coordinates  $(r, \varphi, z)$  with  $z$ -axis directed along the cylinder axis. At static conditions the excess pressure tensor can be represented in the form

$$P^s = P_{rr}^s e_r e_r + P_{\varphi\varphi}^s e_\varphi e_\varphi + P_{zz}^s e_z e_z \quad (2.52)$$

where  $e_r$ ,  $e_\varphi$  and  $e_z$  are unit vectors along the respective axes of the local basis. In addition,

$$b = 2H e_\varphi e_\varphi \quad (2.53)$$

Then from Eqns (2.44), (2.47) and (2.51) - (2.53) one obtains expressions for the components of  $\sigma$  and  $M$ :

$$\sigma_{\varphi\varphi} = - \int_{\lambda_1}^{\lambda_2} d\lambda P_{\varphi\varphi}^s \quad \sigma_{zz} = - \int_{\lambda_1}^{\lambda_2} d\lambda (1 - 2\lambda H) P_{zz}^s \quad (2.54)$$

$$M_{\varphi\varphi} = \int_{\lambda_1}^{\lambda_2} d\lambda \lambda P_{\varphi\varphi}^s \quad M_{zz} = \int_{\lambda_1}^{\lambda_2} d\lambda \lambda (1 - 2\lambda H) P_{zz}^s \quad (2.55)$$

Here the boundaries  $\lambda_1$  and  $\lambda_2$  are to be specified in an appropriate way. Alternatively the radial coordinate  $r$  and cylinder radius  $R$  can be used instead of distance  $\lambda$  and mean curvature  $H$ :

$$r = \lambda + R, \quad H = -\frac{1}{2R} \quad (2.56)$$

Then Eqns (2.54) and (2.55) can be represented in the form:

$$\sigma_{\varphi\varphi} = -\int_0^{\infty} dr P_{\varphi\varphi}^s \quad \sigma_{zz} = -\int_0^{\infty} dr \frac{r}{R} P_{zz}^s \quad (2.57)$$

$$M_{\varphi\varphi} = \int_0^{\infty} dr (r - R) P_{\varphi\varphi}^s \quad M_{zz} = \int_0^{\infty} dr \frac{r}{R} (r - R) P_{zz}^s \quad (2.58)$$

Eqns (2.57) - (2.58) will be compared below with micromechanical expressions resulting from the thermodynamical approach to the theory of curved interfaces and membranes.

### 3. The Thermodynamical Approach

#### a) Basic equations

In the thermodynamical approach of Gibbs [2], which was later on extended by Boruvka and Neumann [41], a multiphase system is treated as a set of bulk, surface and linear phases, each of them characterized by a fundamental equation.

The logical scheme of the Gibbs approach is the following:

(1) The extensive parameters (internal energy  $U$ , entropy  $S$ , number of molecules  $N_i$  of the  $i$ -th component, etc.) and their densities in all phases far away from the phase boundaries are in principle regarded as known.

(2) An idealized hypothetical system is introduced in which all the phases (bulk, interface or linear) are considered as being homogeneous, the interfacial regions are replaced by sharp boundaries (geometrical surfaces or lines), and the resulting excesses of the extensive parameters in the idealized system with respect to the real one are ascribed to these boundaries. A detailed description of this procedure can be found in the following references: Hill [42] Ono and Kondo [29], Boruvka and Neumann [41], Rusanov [43], Rowlinson and Widom [30], Ivanov and Kralchevsky [34].

(3) Next, fundamental equations of the various phases in the idealized system are formulated. In so far as our attention in the present review is focused on surfaces, it is appropriate to consider in detail the fundamental equation of a curved surface (membrane). Since the curvature of such a surface varies from point to point, a local formulation is

required. In accordance with Refs. [28,35] the local form of the surface fundamental equation is

$$\delta f_s = -s_s \delta T + \sum_{k=1}^N \mu_k \delta \Gamma_k - \omega_s \delta \alpha + \delta w_s \quad (3.1)$$

where  $f_s$ ,  $s_s$ ,  $\omega_s$ , and  $\Gamma_k$  are the surface densities of excess free energy, entropy, grand thermodynamic potential and number of molecules of components  $k$ , respectively;  $T$  is temperature,  $\mu_k$  is chemical potential. Further,

$$\delta \alpha = \delta(\Delta A)/\Delta A \quad (3.2)$$

is the local relative dilation of a surface element  $\Delta A$  and

$$\delta w_s = \gamma \delta \alpha + \zeta \delta \beta + B \delta H + \Theta \delta D \quad (3.3)$$

is the work of surface deformation per unit area;  $\delta \alpha$ ,  $\delta \beta$ ,  $\delta H$  and  $\delta D$  characterize the four independent modes of elementary surface deformation; dilation, shear, bending and torsion - see Fig. 4.

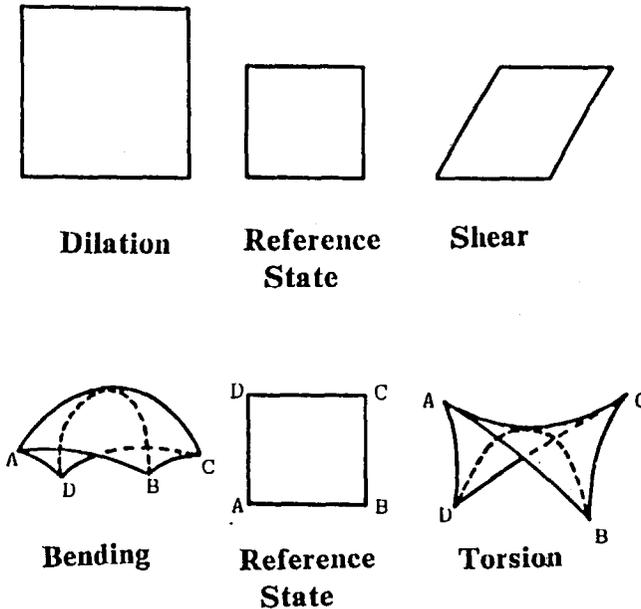


Fig. 4 Independent modes of surface deformation.

In particular,  $H$  and  $D$  are the mean and deviatoric curvatures:

$$H = \frac{1}{2}(c_1 + c_2), \quad D = \frac{1}{2}(c_1 - c_2) \quad (3.4)$$

with  $c_1$  and  $c_2$  being the two principle curvatures at a certain point in the surface. The shear parameter  $\beta$  is discussed in more detail in Ref. [35]. The coefficients  $\gamma$  and  $\zeta$  in Eqn (3.3) have the meaning of thermodynamic surface tension and shearing tension, respectively whereas  $B$  and  $\Theta$  are interfacial bending and torsion moments [44]. Note that the thermodynamical surface tension  $\gamma$  is a *scalar* quantity, whereas the mechanical surface tension,  $\sigma$  (see Eqn (2.6)), is a *tensorial* quantity.

By combining Eqns (3.1) and (3.3) and making use of the thermodynamic definition relation

$$\omega_s = f_s - \sum_{k=1}^N \mu_k \Gamma_k$$

we obtain the expression

$$\delta \omega_s = -s_s \delta T - \sum_{k=1}^N \Gamma_k \delta \mu_k + (\gamma - \omega_s) \delta \alpha + \zeta \delta \beta + B \delta H + \Theta \delta D \quad (3.5)$$

For *fluid* interface such that all of its constituents are soluble in (and equilibrated with) the adjacent bulk phases we have that a quasistatic stretching made in an arbitrary manner, is equivalent to forming more of the interface already present, see e.g. Refs. [28,35,45,46]. If so is actually the case, one realizes that the work of formation per unit area is independent of both of the strain variables  $\alpha$  and  $\beta$ , i.e.  $\delta \omega_s / \delta \alpha = \delta \omega_s / \delta \beta \equiv \zeta = 0$ , implying that the thermodynamic interfacial tension  $\gamma$  can be identified with  $\omega_s$ . Accordingly, for this common case we can easily recover the Gibbs surface tension equation in the form

$$\delta \gamma = -s_s \delta T - \sum_{k=1}^N \Gamma_k \delta \mu_k + B \delta H + \Theta \delta D \quad (3.6)$$

which is implicit in a general version of the Gibbs theory of interfaces where an arbitrary dividing surface is being employed. As a matter of fact, by comparing with Eqn (494) in the original text of Gibbs [2], one finds that  $B = C_1^G + C_2^G$  and  $\Theta = C_1^G - C_2^G$  where the coefficients  $C_1^G$  and  $C_2^G$  used by Gibbs are defined by  $\delta \gamma / \delta c_1$  and  $\delta \gamma / \delta c_2$ , respectively,  $c_1$  and  $c_2$  denoting the principal curvatures. In Section 4 below we will show that  $C_1^G$  and  $C_2^G$  correspond mechanically to the eigen-values of the surface moment tensor  $M$ .

What concerns the work of flexural deformation,  $\delta w_f$ , it can be represented in two alternative forms [36,47]:

$$\delta w_f = B \delta H + \Theta \delta D = C_1 \delta H + C_2 \delta K \quad (3.7)$$

is the Gaussian curvature. Since  $K = H^2 - D^2$ , from Eqn (3.7) it follows [48]

$$B = C_1 + 2C_2H, \quad \Theta = -2C_2D \quad (3.8)$$

The values of  $B$  and  $\Theta$  for an interface depend on the choice of the Gibbsian dividing surface. In particular, a special *surface of tension* exists for which  $B = \Theta = 0$  by definition [34]. However, there is no guarantee that this surface of tension will be located close to the real phase boundary, especially in the case of highly curved interfaces [4,11,28,47,49]. This is the main reason why different kind of *equimolecular* dividing surfaces or midsurfaces are used instead of the surface of tension [47,50].

Model calculation of the contribution of the van der Waals [51,52] and electrostatic [53,54] interactions to the surface bending moment  $B$  have been carried out for spherical interfaces (microemulsion type of systems). It should be noted also that in the limiting case of planar interface [32,54]

$$B \rightarrow 2\gamma_0 \delta_0 \quad \text{for} \quad H \rightarrow 0 \quad (3.9)$$

where  $\delta_0$  is the Tolman parameter, which by definition is equal to the distance between the equimolecular dividing surface and the surface of tension [29,30,55]; the subscript "0" in Eqn (3.9) symbolizes limiting value for  $H \rightarrow 0$ .

The final step of the Gibbs [2] thermodynamic approach is to impose conditions for equilibrium. The system is in complete thermodynamic equilibrium when there are no macroscopic convective fluxes (mechanical equilibrium), no diffusion fluxes (chemical equilibrium) and no heat transfer (thermal equilibrium). As it is well known, the conditions for *thermal* and *chemical* equilibrium imply uniformity of temperature and chemical potentials throughout the thermodynamic system.

The condition for *mechanical* equilibrium at each point of the dividing surface between two bulk phases, I and II, is the Laplace equation of capillarity. It can be derived by means of a variational method, i.e. by setting the first variation of the overall free energy of the system equal to zero [35]

$$0 = \delta F = -P_I \delta V_I - P_{II} \delta V_{II} + \delta F_s \quad (3.10)$$

where

$$\delta F_s = \delta \int_A f_s dA = \int_A (\delta f_s + f_s \delta \alpha) dA \quad (3.11)$$

and constancy of temperature and chemical potentials is assumed. Then by using the thermodynamic identity

$$f_s = \omega_s + \sum_{k=1}^N \mu_k \Gamma_k$$

along with Eqns (3.1), (3.3) and (3.10) we can derive the following conditions for surface mechanical equilibrium [35]

$$(\gamma a^{\alpha\beta} + \zeta q^{\alpha\beta})_{,\beta} = BH^{,\alpha} + \Theta D^{,\alpha}, \quad \alpha = 1, 2 \quad (3.12)$$

$$2H\gamma + 2D\zeta - (H^2 + D^2)B - 2HD\Theta - \frac{1}{2}(a^{\alpha\beta}B + q^{\alpha\beta}\Theta)_{,\alpha\beta} = P_{II} - P_I \quad (3.13)$$

where

$$q^{\alpha\beta} = \frac{1}{D}(b^{\alpha\beta} - Ha^{\alpha\beta}) \quad (3.14)$$

is the definition of the deviatoric curvature tensor. (A slight difference between Eqns (3.12) and (3.13) and the respective equations in Ref. [35] is due to the fact that  $q^{\alpha\beta}$  is incorrectly treated there as a constant surface tensor, i.e. the terms  $q^{\alpha\beta}\Theta_{,\alpha\beta}$  and  $\zeta_{,\beta}q^{\alpha\beta}$  should read  $(q^{\alpha\beta}\Theta)_{,\alpha\beta}$  and  $(\zeta q^{\alpha\beta})_{,\beta}$ ; the remaining equations in Ref. [35] are not affected by this change.) Eqns (3.12) - (3.13) in fact represent the three equations resulting from the three independent translational variations of the position of a point on the dividing surface (two tangential and one normal with respect to the surface). The physical meaning of Eqns (3.12) and (3.13) suggests that they should be equivalent to Eqns (2.35) and (2.36). This point is discussed in Section 4 below.

Finally, we note that by means of Eqns (3.7) and (3.8) Eqns (3.12) and (3.13) can be transformed in the following equivalent form [48]

$$\nabla_s \gamma - C_1 \nabla_s H - C_2 \nabla_s K + \nabla \cdot (\zeta \mathbf{q}) = 0 \quad (3.15a)$$

$$2H\gamma + 2D\zeta - C_1(2H^2 - K) + 2C_2HK - \frac{1}{2}\nabla_s^2 C_1 - \quad (3.15b)$$

$$- 2H\nabla_s^2 C_2 + \mathbf{b} : \nabla_s \nabla_s C_1 = P_{II} - P_I .$$

Eqns (3.15a) and (3.15b) are equivalent to the corresponding expressions derived by Boruvka and Neumann [41] for the case when the shearing tension  $\zeta = 0$ .

*b) Bending moment due to steric interactions*

As mentioned earlier, the *electrostatic* and *van der Waals* contributions to the interfacial bending moment,  $B$ , are studied in Refs. [51-54]. Here we will briefly consider the contribution due to the *steric* interactions as an illustration of the applicability of the basic equations in the previous section to phospholipid monolayers and bilayers. We will make use of the Helfrich [3] expression for the energy of flexural deformation,  $w_f$ , per unit area of the curved surface:

$$w_f = 2k_c(H - H_0)^2 \quad (3.16)$$

where  $H_0$  is the spontaneous curvature and  $k_c$  is coefficient of bending elasticity. The contribution due to the torsion (Gaussian) elasticity is neglected in the present context. Typically  $k_c = 10^{-19}$  J for bilayers of phospholipids [56,57]. Unlike  $k_c$ , the spontaneous curvature  $H_0$  depends strongly on the composition of the monolayer. For a two-component monolayer an expression due to Markin [8] may be used:

$$H_0 = e_1 \Gamma_1 + e_2 \Gamma_2 \quad (3.17)$$

Here  $\Gamma_1$  and  $\Gamma_2$  express the number of molecules per unit area of the monolayer (in half of a lipid bilayer);  $e_1$  and  $e_2$  are coefficients. Depending on their shape the molecules in the bilayer can be characterized as "boys" or "girls" - see Fig. 5. The coefficients  $e_k$  ( $k = 1,2$ ) in Eqn (3.17) are positive for "girls" and negative for "boys". (Sometimes  $e_k$  are called in jest "erotic coefficients".) If  $l$  is the length of a molecule and  $a_k$  and  $v_k$  are the molecular area and volume, then [58,59]:

$$\frac{v_k}{a_k l} = 1 - \frac{l}{R_{ok}} + \frac{1}{3} \frac{l^2}{R_{ok}^2}, \quad (k = 1, 2) \quad (3.18)$$

where  $R_{ok}$  is the curvature radius. Usually  $l \ll R_{ok}$  and thus

$$H_{ok} \equiv -\frac{1}{R_{ok}} \approx \frac{\left(\frac{v_k}{a_k l} - 1\right)}{l} \quad (3.19)$$

see also Ref. [60].  $H_{ok}$  is the spontaneous curvature per molecule. The coefficients  $e_k$  can be expressed in the form

$$e_k = a_k H_{ok}, \quad k = 1, 2 \quad (3.20)$$

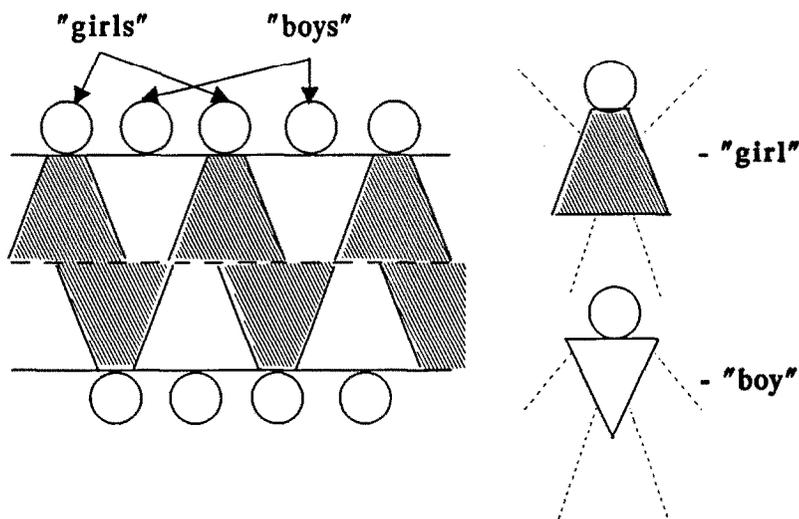


Fig. 5 Schematic presentation of a lipid bilayer composed of two components of different molecular shape: "boys" and "girls".

For numerical estimates one can use the following data for lipids from egg yolk [58]:  
(1 = phosphatidyl choline; 2 = phosphatidyl ethanolamine):

$$a_1 = 72 \text{ \AA}^2, \quad v_1 = 1060 \text{ \AA}^3, \quad l = 17 \text{ \AA}, \quad H_{o1}^{-1} = -850 \text{ \AA}, \quad e_1 = -8,5 \times 10^{-10} \text{ cm}$$

$$a_2 = 42 \text{ \AA}^2, \quad v_2 = 700 \text{ \AA}^3, \quad l = 17 \text{ \AA}, \quad H_{02}^{-1} = -130.8 \text{ \AA}, \quad e_2 = -32 \times 10^{-10} \text{ cm}$$

We note that both these lipids behave like "boys". On the contrary, the cholesterol in a membrane behaves like a "girl".

From Eqn (3.16) one derives

$$B = \left( \frac{\partial w_f}{\partial H} \right)_{\Gamma_1, \Gamma_2} = 4k_c(H - H_0) \quad (3.21)$$

By integrating the thermodynamic relation (cf. Eqns (3.1) and (3.3))

$$\left( \frac{\partial \mu_k}{\partial H} \right)_{\Gamma_1, \Gamma_2} = \left( \frac{\partial B}{\partial \Gamma_k} \right)_{H, \Gamma_1}, \quad (k = 1, 2) \quad (3.22)$$

along with Eqns (3.17) and (3.21) one obtains [61]

$$\mu_k = \mu_k^0 + kT \ln x_k - 4k_c e_k H, \quad (k = 1, 2) \quad (3.23)$$

where  $x_k$  is the area fraction; the difference in the molecular interactions between the adsorbed species is neglected. At chemical equilibrium ( $\mu_k = \text{const}$ ) Eqn (3.23) yields Boltzmann distribution of the species:

$$\Gamma_k \propto \exp \frac{4k_c e_k H}{kT}, \quad (k = 1, 2) \quad (3.24)$$

Accordingly, the concentration of "girls" ( $e_k > 0$ ) will be larger in the concave ( $H > 0$ ) parts of the surface, whereas the "boys" ( $e_k < 0$ ) will prefer the convex parts ( $H < 0$ ). Such an effect can be observed for curvatures of the order of  $H = kT/(4k_c e_k)$  and greater; for phosphatidyl choline this estimate yields  $H^{-1} \leq 2 \text{ nm}$ . Hence, curvature induced variations in the concentration of the adsorbed species can appear only on interfaces of high and nonuniform curvature.

Usually  $e_k H \ll 1$  and the exponent in Eqn (3.24) can be linearized, whereby Eqn (3.17) takes the form

$$H_0 = H_0^{(0)} + \kappa^2 H + \dots \quad (3.25)$$

where

$$\kappa^2 = \frac{4k_c}{kT} [e_1^2 \Gamma_1^{(0)} + e_2^2 \Gamma_2^{(0)}] \quad (3.26)$$

$$H_0^{(0)} = e_1 \Gamma_1^{(0)} + e_2 \Gamma_2^{(0)} \quad (3.27)$$

Substitution of Eqn (3.25) into Eqn (3.21) yields [61]

$$B = -4k_c H_0^{(0)} + 4k_c (1 - \kappa^2) H + O(H^2) \quad (3.28)$$

An estimate of  $B$  may be based on the first term in Eqn (3.28), because usually  $H_0^{(0)} \gg H$ :

$$B \approx -4k_c H_0^{(0)} = \text{const} \quad (3.29)$$

For example, by using the data given after Eqn (3.20) for phosphatidyl ethanolamine above we obtain  $B = 3 \times 10^{-11}$  N.

### c) Micromechanical expressions

Similarly to the surface stress and moment tensors,  $\sigma$  and  $M$ , the coefficients in Eqn

(3.3) ( $\gamma$ ,  $\zeta$ ,  $B$  and  $\Theta$ ) are surface excess quantities and can be expressed as integrals over the excess pressure tensor  $P^s$  - of Eqn (2.43). As shown in Refs. [34,35] the respective expressions read:

$$\gamma = -\frac{1}{2} \int_{\lambda_1}^{\lambda_2} U_s : P^s \chi \, d\lambda ; \quad \zeta = -\frac{1}{2} \int_{\lambda_1}^{\lambda_2} q : P^s \chi \, d\lambda \quad (3.30)$$

$$B = \int_{\lambda_1}^{\lambda_2} L : P^s \lambda \, d\lambda ; \quad \Theta = \int_{\lambda_1}^{\lambda_2} (q \cdot L) : P^s \lambda \, d\lambda \quad (3.31)$$

where

$$q = a_\alpha a_\beta q^{\alpha\beta} , \quad \chi = (1 - \lambda H)^2 - \lambda^2 D^2 \quad (3.32)$$

$L$  is given by Eqn (2.44) and  $q^{\alpha\beta}$  - by Eqn [3.14]. Just like in Eqns (2.47) and (2.48), the integration is carried along the normal to the surface at the respective point. The symbol ":"

denotes the double scalar product of two dyadics - see e.g. [23,28].

For illustration let us apply Eqns (3.30) and (3.31) to a cylindrical interface, when  $P^s$  is given by Eqn (2.52). In this special case one obtains

$$U_s : P^s = P_{\varphi\varphi}^s + P_{zz}^s, \quad q : P^s = P_{\varphi\varphi}^s - P_{zz}^s \quad (3.33)$$

$$L = (1 - \lambda H) U_s + \lambda H q, \quad q \cdot L = (1 - \lambda H) q + \lambda H U_s \quad (3.34)$$

$$\chi = 1 - 2\lambda H \quad (3.35)$$

Substitution of Eqns (3.33) - (3.34) into Eqns (3.30) and (3.31), and using Eqn (2.56), yields

$$\gamma = -\frac{1}{2} \int_0^{\infty} (P_{\varphi\varphi}^s + P_{zz}^s) \frac{r}{R} dr, \quad \zeta = -\frac{1}{2} \int_0^{\infty} (P_{\varphi\varphi}^s - P_{zz}^s) \frac{r}{R} dr \quad (3.36)$$

$$B = \int_0^{\infty} \left( P_{\varphi\varphi}^s + \frac{r}{R} P_{zz}^s \right) (r - R) dr, \quad \Theta = \int_0^{\infty} \left( P_{\varphi\varphi}^s - \frac{r}{R} P_{zz}^s \right) (r - R) dr \quad (3.37)$$

Coming back to the case of a general curved interface we note, that the interfacial bending and torsion moments,  $B$  and  $\Theta$ , as determined by Eqn (3.31), represent the trace and the deviator of the tensor of the interfacial moments,  $M$ , given by Eqn (2.51):

$$B = U_s : M, \quad \Theta = q : M \quad (3.38)$$

As demonstrated in Ref. [28], the halved trace and deviator of the interfacial stress tensor,

$$\sigma = \frac{1}{2} U_s : \sigma \quad \text{and} \quad \eta = \frac{1}{2} q : \sigma, \quad (3.39)$$

are the mechanical dilation and shear tensions. By substituting  $\sigma$  from Eqn (2.47) into Eqn

(3.29) one derives micromechanical expressions for  $\sigma$  and  $\eta$ :

$$\sigma = -\frac{1}{2} \int_{\lambda_1}^{\lambda_2} L : P^s d\lambda, \quad \eta = -\frac{1}{2} \int_{\lambda_1}^{\lambda_2} (q : L) : P^s d\lambda \quad (3.40)$$

The relationships between the *thermodynamical* dilation and shear tensions,  $\gamma$  and  $\zeta$ , and their *mechanical* counterparts,  $\sigma$  and  $\eta$ , read [28]:

$$\gamma = \sigma + \frac{1}{2}BH + \frac{1}{2}\Theta D \quad (3.41)$$

$$\zeta = \eta + \frac{1}{2}BD + \frac{1}{2}\Theta H \quad (3.42)$$

One can directly verify the validity of Eqns (3.41) and (3.42) by substituting the *micromechanical* expressions for  $\gamma$ ,  $\zeta$ ,  $B$ ,  $\Theta$ ,  $\sigma$  and  $\eta$  given by Eqns (3.30), (3.31) and (3.40). It will be shown in the next Section that Eqns (3.41) and (3.42) can be derived in an alternative way by using purely *macroscopic* considerations.

The fact that the mechanical and thermodynamical tensions of a curved interface are different ( $\gamma \neq \sigma$ ,  $\zeta \neq \eta$ ) makes possible two alternative definitions of *fluid* interface to be given [48]. Indeed, from a thermodynamical viewpoint one can state that the work of local interfacial shear deformation of a *fluid* interface must be zero. i.e.  $\zeta = 0$ . Eqn (3.42) shows that even if  $\zeta = 0$ , the mechanical shearing tension  $\eta$  is not zero, i.e. the surface stress tensor is not isotropic for such a fluid interface at quasistatic conditions.

Alternatively, one can define *fluid* interface by means of a two-dimensional version of the Pascal law, that is the surface stress tensor to be isotropic at quasistatic conditions, i.e.  $\eta = 0$ . However, in such a case the work of shear is not zero and it is determined by the bending and torsion moments:  $\zeta = (BD + \Theta H)/2$ (cf. Eqn (3.42)). One realizes that the two alternative definitions of *fluid* interface are not equivalent for a general curved interface. The above complications originate from the fact that a *flexural* deformation of a surface is usually coupled with a *shear* deformation and *vice versa*. Of course, it is a matter of convention what is called "fluid" interface. What makes physical since it is whether the real curved boundaries between fluid phases comply with  $\zeta = 0$  or with  $\eta = 0$ . This is a problem for a future study based on comparison between experimental data and theoretical predictions.

#### 4. Relating between the Mechanical and Thermodynamical Approaches

In order to establish connection between the mechanical and thermodynamical approaches we note, that mechanics provides an expression for the work of surface deformation per unit area and unit time [21,28];

$$\frac{\delta w_s}{\delta t} = \sigma : (\nabla_s \mathbf{v} + \mathbf{U}_s \times \mathbf{w}) + \mathbf{N} : \nabla_s \mathbf{w} \quad (4.1)$$

where  $\mathbf{v}$  and  $\mathbf{w}$  are linear and angular velocities and  $t$  is time. Eqn (4.1), multiplied by  $\delta t$ , should reduce to Eqn (3.3) for a quasistatic process. Comparing the coefficients at the

independent differential in Eqn (3.3) with those resulting from Eqn (4.1) we can obtain the desired connections between the mechanical and thermodynamical surface tensions and moments.

The velocity of a surface point can be represented in the form

$$\mathbf{v} = \mathbf{a}_\alpha \mathbf{v}^\alpha + \mathbf{n} v^{(n)} \quad (4.2)$$

According to Eliassen [23], the rate-of-strain tensor of the interface is defined by the expression

$$d_{\alpha\beta} = \frac{1}{2} \frac{\partial a_{\alpha\beta}}{\partial t} = \frac{1}{2} (v_{\alpha,\beta} + v_{\beta,\alpha} - 2b_{\alpha\beta} v^{(n)}) \quad (4.3)$$

In spite of the fact that we will eventually arrive at some quasistatic relationships, it is convenient to the begin with considering the rates of change. It is easy to obtain the corresponding infinitesimal increments during an elementary quasistatic process. For example with  $\delta t$  as the time increment,  $d_{\mu\nu} \delta t$  are the components of the surface strain tensor. Similarly, if  $\dot{H}$  is the time derivative of the mean curvature, then  $\delta H = \dot{H} \delta t$  is the differential of  $H$ , which enters into Eqn (3.3).

As shown in Ref. [35] the scalar quantities

$$\dot{\alpha} = a^{\mu\nu} d_{\mu\nu} \quad \text{and} \quad \dot{\beta} = q^{\mu\nu} d_{\mu\nu} \quad (4.5)$$

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

$$\delta \alpha = \dot{\alpha} \delta t \quad \text{and} \quad \delta \beta = \dot{\beta} \delta t \quad (4.6)$$

which take place in Eqn (3.3).

As mentioned above, we restrict our considerations to quasistatic processes for which the motion of a surface material point is caused by the deformation of the surface (zero fluxes of surface convection or diffusion are assumed). In this case, having in mind Eqn (4.5), one can write [28]

$$d_{\mu\nu} = \frac{1}{2} \dot{\alpha} a_{\mu\nu} + \frac{1}{2} \dot{\beta} q_{\mu\nu} \quad (4.7)$$

Similarly we can represent the surface stress tensor in the form [28]:

$$\sigma_{\mu\nu} = \sigma a_{\mu\nu} + \eta q_{\mu\nu} \quad (4.8)$$

If  $\sigma_1$  and  $\sigma_2$  are the eigenvalues of the tensor  $\sigma_{\mu\nu}$  (in our case they are the tensions acting along the lines of curvature), then it follows from Eqns (3.39) and (4.8)

$$\sigma = \frac{1}{2}(\sigma_1 + \sigma_2) \quad \text{and} \quad \eta = \frac{1}{2}(\sigma_1 - \sigma_2) \quad (4.9)$$

Similarly, the tensorial field of the surface moments can be represented in the form:

$$M_{\alpha\beta} = \frac{1}{2}(M_1 + M_2)a_{\alpha\beta} + \frac{1}{2}(M_1 - M_2)q_{\alpha\beta} \quad (4.10)$$

where  $M_1$  and  $M_2$  are the eigenvalues of tensor  $M$ . We recall that the connection between tensors  $M$  and  $N$  is given by Eqn (1.28). Moreover, the angular velocity of a surface point is related to the running unit normal,  $n$ , by means of the expression [28]:

$$\mathbf{w} = \mathbf{n} \times \frac{d\mathbf{n}}{dt} \quad (4.11)$$

It is shown in Ref. [28] that by substituting Eqns (4.8), (4.10) and (4.11) into Eqn (4.1) one can derive Eqn (3.3) with  $\gamma$  and  $\zeta$  being determined by Eqns (3.41) and (3.42), and with

$$B = M_1 + M_2, \quad \Theta = M_1 - M_2 \quad (4.12)$$

(In fact, Eqn (4.12) is a special case of Eqn (3.38);  $M_1$  and  $M_2$  can be identified with the Gibbs coefficients  $C_1^G$  and  $C_2^G$  as discussed after Eqn (3.6) above.) In this way the general validity of Eqns (3.41) - (3.42) is established. These equations form a bridge between the mechanical and thermodynamical approaches to the theory of curved interfaces. Indeed, by substituting Eqns (4.8) and (4.10) into the *mechanical* version of Laplace equation, Eqn (2.35), and by using Eqns (3.14), (3.41), (3.42) and (4.12), one arrives at the *thermodynamical* version of Laplace equation, Eqn (3.13). In particular, substitution of  $\gamma$  and  $\eta$  from Eqns (3.41) and (3.42) into Eqn (3.13) results in a more elegant and compact form of the generalized Laplace equation, viz.,

$$2H\sigma + 2D\eta - \frac{1}{2}(a^{\alpha\beta}B + q^{\alpha\beta}\Theta)_{,\alpha\beta} = P_{II} - P_I \quad (4.13)$$

In addition, by means of Eqns (3.14), (3.41), (3.42), (4.10) and (4.12) one can transform Eqn (4.8) to obtain

$$\sigma^{\alpha\beta} = \gamma a^{\alpha\beta} + \zeta q^{\alpha\beta} - b_{\gamma}^{\alpha} M^{\gamma\beta} \quad (4.14)$$

Then by using Eqns (4.10), (4.12), (4.14) and the mathematical identities

$$a^{\gamma\beta} b_{\gamma,\beta}^{\alpha} = 2H_{,\alpha} \quad \text{and} \quad q^{\gamma\beta} b_{\gamma,\beta}^{\alpha} = 2D_{,\alpha} \quad (4.15)$$

it is possible to transform the *mechanical* expression for the lateral surface balance of momentum, Eqn (2.36), into its *thermodynamical* counterpart, Eqn (3.12).

In summary, in this section we have demonstrated the general agreement between the mechanical and thermodynamical approaches. It should be noted, however, that the mechanical approach is somewhat more general, because Eqns (2.35) and (2.36) can be employed with constitutive equations for  $\sigma$  and  $M$ , other than Eqns (4.8) and (4.10), which are appropriate for quasistatic processes only. Such constitutive equations, which take into account also viscous effects, are considered in the next section.

At the end of this section we consider some special forms of Eqn (4.13) useful for application. If Eqn (3.16) holds, then  $\Theta = 0$  and  $B$  is determined by means of Eqn (3.21). In this case, assuming constant spontaneous curvature,  $H_0$ , we transform Eqn (4.13) to obtain

$$2H\sigma + 2D\eta - 2k_c \nabla_s^2 H = P_{II} - P_I \quad (4.16)$$

Let us now consider the special case of an axisymmetric interface. Such a symmetry is often observed in the experiment, e.g. when the so called *micropipet technique* [7] is used. We choose  $z$ -axis be the axis of revolution and we introduce polar coordinates  $(r, \varphi)$  in the plane  $xy$ . Let  $z(r)$  be the equation of the surface generatrix. Then one has (see Ref. 24, Chapter XIV, Eqn 66)

$$\nabla_s^2 H = \frac{1}{r} (1 + z'^2)^{-\frac{1}{2}} \frac{d}{dr} \left[ r (1 + z'^2)^{-\frac{1}{2}} \frac{dH}{dr} \right] \quad (4.17)$$

where

$$z' = \frac{dz}{dr} = \tan \theta \quad (4.18)$$

with  $\theta$  being the running slope angle. Besides, for an axisymmetric surface (see e.g. Ref. 62)

$$2H = \frac{d \sin \theta}{dr} + \frac{\sin \theta}{r}, \quad 2D = \frac{d \sin \theta}{dr} - \frac{\sin \theta}{r} \quad (4.19)$$

Then by means of Eqns (4.17) - (4.19) one can transform Eqn (4.16) to read

$$\begin{aligned} & \sigma \left( \frac{d \sin \theta}{dr} + \frac{\sin \theta}{r} \right) + \eta \left( \frac{d \sin \theta}{dr} - \frac{\sin \theta}{r} \right) = \\ & = P_{II} - P_I + \frac{k_c}{r} \cos \theta \frac{d}{dr} \left\{ r \cos \theta \frac{d}{dr} \left[ \frac{1}{r} \frac{d}{dr} (r \sin \theta) \right] \right\} \end{aligned} \quad (4.20)$$

The last term in Eqn (4.20) represents the contribution of the interfacial bending moment in the Laplace equation of capillarity for an axisymmetric surface.

### 5. Constitutive Relations

To solve any mechanical problem we need explicit expressions for the stress and moment tensors. These expressions usually have the form of constitutive relations between stress and strain characterizing the *rheological behavior* of the continuous medium: elastic, viscous, plastic [18,63]. It is important to note that a constitutive relation represents a *theoretical model* of the rheological properties of the medium, whose applicability to a given system is tested by experiment. Below we consider briefly some simple constitutive relations for curved interfaces.

#### a) Surface stress tensor $\sigma$

According to Scriven a liquid interface can be treated as a two-dimensional viscous fluid [23,64,65]:

$$\sigma_{\alpha\beta} = \sigma a_{\alpha\beta} + \xi_2 a_{\alpha\beta} d_{\gamma}^{\gamma} + 2\eta_2 \left( d_{\alpha\beta} - \frac{1}{2} a_{\alpha\beta} d_{\gamma}^{\gamma} \right) \quad (5.1)$$

where  $d_{\alpha\beta}$  is the surface rate-of-strain tensor defined by Eqn (4.3)  $d_{\gamma}^{\gamma}$  represents the trace of this tensor;  $\xi_2$  and  $\eta_2$  are the coefficients of surface dilational and shear viscosity. Note that in Eqn (5.1)  $\xi_2$  and  $\eta_2$  multiply the isotropic and deviatoric parts of the tensor  $d_{\alpha\beta}$ .

The elastic (nonviscous) part in Eqn (5.1),  $\sigma a_{\alpha\beta}$ , is isotropic. Hence, it is postulated that there are no *shear elastic* effects in a two-dimensional viscous *fluid*, i.e.  $\eta = 0$  - cf. Eqn (4.9). In other words, the surface *shear* stresses in the Scriven's rheological model have only a viscous origin.

Since the surface stress tensor  $\sigma$  has also transverse components, cf. Eqn (2.6), a constitutive equation is needed for  $\sigma^{\alpha(n)}$  too. In analogy with Eqn (5.1) one can represent  $\sigma^{\alpha(n)}$  as a superposition of a viscous and a nonviscous term:

$$\sigma^{\alpha(n)} = \sigma_{(v)}^{\alpha(n)} + \sigma_{(0)}^{\alpha(n)} \tag{5.2}$$

The viscous term,  $\sigma_{(v)}^{\alpha(n)}$ , can be expressed in accordance with Newton's law of viscosity [66]:

$$\sigma_{(v)}^{\alpha(n)} = \chi_2 v^{(n),\alpha} \tag{5.3}$$

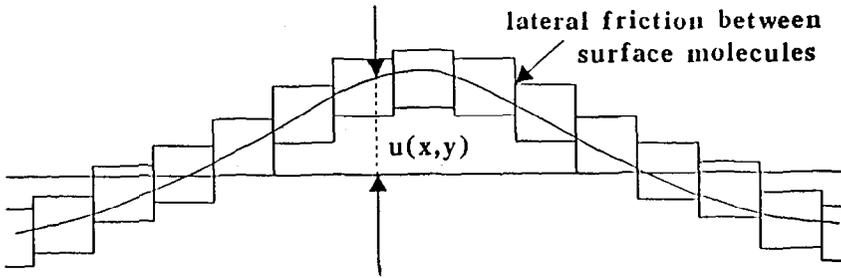


Fig. 6 Sketch of the relative displacement between the surface molecules (the rectangles) during the capillary wave motion;  $u$  is the local deviation from planarity.

As illustrated in Fig. 6, Eqn (5.3) accounts for the lateral friction between the molecules in the interfacial zone.  $\chi_2$  is the coefficient of transverse shear viscosity. For quasistatic processes, when  $v \rightarrow 0$  and  $\sigma_{(v)}^{\alpha(n)} \rightarrow 0$ , the transversal stress resultants reduce to  $\sigma_{(0)}^{\alpha(n)}$ . Then in accordance with Eqns (2.34), (4.10), (4.12), (5.2) and (5.3) one obtains

$$\sigma^{\alpha(n)} = \chi_2 v^{(n),\alpha} - \frac{1}{2} (B a^{\alpha\beta} + \Theta q^{\alpha\beta})_{,\beta} \tag{5.4}$$

The surface rheological model based on Eqns (5.1) and (5.4) contains 3 coefficients of surface viscosity:  $\xi_2$ ,  $\eta_2$  and  $\chi_2$ . In addition, two coefficients of flexural elasticity enter the theory through  $B$  and  $\Theta$  as discussed below.

b) *The Tensor of surface moments, M*

According to Helfrich [2] the energy of flexural deformation,  $w_f$ , can be written in the form:

$$w_f = 2k_c(H - H_0)^2 + \bar{k}_c K \quad (5.5)$$

Here  $k_c$  and  $\bar{k}_c$  are coefficients of bending and torsion elasticity,  $H_0$  is the spontaneous curvature, and  $K$  is the Gaussian curvature of the surface. Since  $K = H^2 - D^2$  from Eqns (3.7) and (5.5) one obtains

$$B = \left( \frac{\partial w_f}{\partial H} \right)_D = 4k_c(H - H_0) + 2\bar{k}_c H \quad (5.6)$$

$$\Theta = \left( \frac{\partial w_f}{\partial D} \right)_H = -2\bar{k}_c D \quad (5.7)$$

For the case of a small mean curvature from Eqn (5.6) we obtain

$$B \rightarrow -4k_c H_0 \quad \text{for } H \rightarrow 0 \quad (5.8)$$

A comparison between Eqns (3.9) and (5.8) yields a relationship between the Tolman length,  $\delta_0$ , and the spontaneous curvature  $H_0$ :

$$H_0^{-1} = -\frac{2k_c}{(\gamma_0 \delta_0)} \quad (5.9)$$

With  $k_c \approx 5 \times 10^{-21}$  J,  $\delta_0 \approx 3 \times 10^{-10}$  m,  $\gamma_0 \approx 70$  mN/m from Eqn (5.9) one estimates  $H_0^{-1} \approx 5$  Å as the order of magnitude of the spontaneous curvature of an aqueous drop.

By means of Eqns (4.10), (4.12), (5.6) and (5.7) one obtains an expression for the *non-viscous* part of the tensor of surface moments:

$$M_{(0)}^{\alpha\beta} = \frac{1}{2}(B a^{\alpha\beta} + \Theta q^{\alpha\beta}) = [(2k_c + \bar{k}_c)H - 2k_c H_0] a^{\alpha\beta} - \bar{k}_c D q^{\alpha\beta} \quad (5.10)$$

Thus in accordance with Eqns (2.34), (3.14), (5.4) and (5.10) for the total tensor of the surface moments we can write:

$$M^{\alpha\beta} = 2[(k_c + \bar{k}_c)H - k_c H_0]a^{\alpha\beta} - \bar{k}_c b^{\alpha\beta} - \chi_2 v^{(n)} a^{\alpha\beta} \quad (5.11)$$

In fact, Eqn (5.11) represents a constitutive equation for the tensor  $M$  stemming from the Helfrich's formula, Eqn (5.5). By using the Codazzi equation,  $b^{\alpha\beta\gamma} = b^{\beta\gamma\alpha}$ , see Ref. [24], we get

$$b^{\alpha\beta}{}_{,\beta} = a_{\beta\gamma} b^{\alpha\beta\gamma} = a_{\beta\gamma} b^{\beta\gamma\alpha} = 2H^{\cdot\alpha} \quad (5.12)$$

The above Eqns (5.11) and (5.12) yield

$$M^{\alpha\beta}{}_{,\beta} = 2k_c H^{\cdot\alpha} - \chi_2 v^{(n),\alpha} \quad (5.13)$$

Here we treated the spontaneous curvature  $H_0$  as a constant; this assumption can be violated when the distribution of the species is not uniform throughout the surface - cf. Eqns (3.17) and (3.24) above. Besides, it's worthwhile noting that the torsion elasticity,  $\bar{k}_c$ , is not involved in the right-hand side of Eqn (5.13). Hence,  $\bar{k}_c$ , does not enter into the transversal

and tangential surface balances of the linear momentum, Eqns (2.15) and (2.16), which (at negligible surface inertial and body-force terms) take the form

$$b_{\alpha\beta} \sigma^{\alpha\beta} - (2k_c H^{\cdot\alpha\beta} - \chi_2 v^{(n),\alpha\beta}) a_{\alpha\beta} = T_I^{(n)(n)} - T_{II}^{(n)(n)} \quad (5.14)$$

$$\sigma^{\alpha\beta}{}_{,\beta} + b_{\beta}^{\alpha} (2k_c H^{\cdot\beta} - \chi_2 v^{(n),\beta}) = T_I^{(n)\alpha} - T_{II}^{(n)\alpha} \quad (5.15)$$

Here  $\sigma^{\alpha\beta}$  is to be substituted from Eqn (5.1). It should be noted that Eqn (5.14) represents a generalized version of the Laplace equation of capillarity for dynamic processes.

### *c) Application to fluctuation capillary waves*

We consider capillary waves of amplitude  $u$  on a horizontal fluid interface - cf. Eqn (1.22). Usually it is supposed that the amplitude  $u$  is small enough [20] and that Eqns (5.14) and (5.15) can be linearized:

$$\sigma \nabla_s^2 u - k_c \nabla_s^2 \nabla_s^2 u + \chi_2 \nabla_s^2 \frac{\partial u}{\partial t} = T_1^{(n)(n)} \quad (5.16)$$

$$\nabla_s \sigma + \xi_2 \nabla_s \nabla_s \cdot \mathbf{v}_{II} + \eta_2 \nabla_s^2 \mathbf{v}_{II} = \mathbf{n} \cdot (T_I - T_{II}) \cdot \mathbf{U}_s \quad (5.17)$$

where we have used the relationships

$$2H \approx \nabla_s^2 u, \quad \mathbf{v}^{(n)} = \frac{\partial u}{\partial t} \quad \text{and} \quad \mathbf{v}_{II} \equiv \alpha_\alpha \mathbf{v}^\alpha \quad (5.18)$$

We note that the dependent variables,  $u$  and  $\mathbf{v}_{II}$ , are separated in *linear approximation*: the generalized Laplace equation (5.16) contains the normal displacement  $u$ , whereas the two-dimensional Navier-Stokes equation (5.17) contains the lateral surface velocity  $\mathbf{v}_{II}$ .

Eqn (5.16) can be utilized to analyze interfacial fluctuation - dissipation processes. Since the fluctuation capillary waves originate from the Brownian motion of the surface molecules, a Brownian force term it to be introduced in Eqn (5.16):

$$\sigma \nabla_s^2 u - k_c \nabla_s^2 \nabla_s^2 u + \chi_2 \nabla_s^2 \frac{\partial u}{\partial t} + s^{\alpha(n)}, \alpha = P_{II} - P_I \quad (5.19)$$

where  $s^{\alpha(n)}$  are the *random* transverse shear stress resultants ( $s^{\alpha(n)}$  are the random counterparts of  $\sigma^{\alpha(n)}$ ). The correlations of  $s^{\alpha(n)}$ , determined by means of the general theory of hydrodynamic fluctuations [20], read [66]:

$$\langle s^{\alpha(n)}(\mathbf{r}, t) s^{\beta(n)}(\mathbf{r}', t') \rangle = 2k_B T \chi_2 a^{\alpha\beta} \delta(\mathbf{r} - \mathbf{r}') \delta(t - t') \quad (5.20)$$

where  $k_B$  is Boltzmann constant,  $T$  is temperature and  $\delta$  is the Dirac function.

By using Fourier transformation, from Eqns (5.19) and (5.20) one derives the mean-square amplitude of the thermal corrugations with wave number  $q$ :

$$\langle u_q^2 \rangle = \frac{k_B T}{A} (\Delta \rho g + \sigma q^2 + k_c q^4)^{-1} \quad (5.21)$$

where  $A$  is surface area,  $g$  is gravity acceleration,  $\Delta \rho = \rho_I - \rho_{II}$  is the difference in density between the two neighboring phases. Eqn (5.21) is widely used to interpret data for light scattering from fluid interfaces [5,12].

Similarly, we can determine the averaged mean-square amplitude of the fluctuation capillary waves [30,66-68]:

$$\langle u^2 \rangle = \frac{k_B T}{4\pi\sigma} \ln(1+p) \quad (5.22)$$

(the contribution of  $k_c$  - neglected) as well as the relative dilation of the surface area,  $\alpha = \Delta A/A$ , due to the thermal corrugations [66]:

$$\alpha = \frac{1}{2} \langle |\nabla_s \mu|^2 \rangle = \frac{\pi}{8} \frac{k_B T}{\sigma a^2} \left[ 1 - \frac{1}{p} \ln(1+p) \right] \quad (5.23)$$

Here

$$p = \frac{\pi^2 \sigma}{(\Delta \rho g a^2)}; \quad (5.24)$$

$a$  is a cutoff parameter, accounting for the fact, that the wavelength can not be shorter than one molecular diameter. One can expect that

$$a \approx \sqrt{A_1} \quad (5.25)$$

where  $A_1$  is the area per one surface molecule. For instance, the experiment [69] yields  $A_1 = 52 \text{ \AA}^2$ . Then by using typical values,  $k_B T = 4.1 \times 10^{-21} \text{ J}$ ,  $\sigma = 32 \text{ mN/m}$ , and  $\Delta \rho = 1 \text{ g/cm}^3$ , from Eqns (5.22) - (5.25) one estimates  $\langle u^2 \rangle^{1/2} = 5.7 \text{ \AA}$  and  $\alpha = 0.10$ . The latter Figure means that the surface area is increased with 10 % due to the fluctuation surface corrugations. For surfaces of low surface tension ( $\sigma \rightarrow 0$ ), like lipid bilayers, biomembranes, microemulsion droplets, the bending elasticity,  $k_c$ , determines the magnitude of the fluctuation capillary waves - cf. Eqn (5.21). When two such surfaces approach each other at a mean distance  $h$ , the overlap of the surface corrugations gives rise to a repulsive force known as the "undulation" surface force, first introduced by Helfrich and coworkers [14,70]. The theoretical considerations [14,15,70] show that this force (per unit area of the surfaces) must be proportional to  $h^{-3}$ :

$$\Pi_{\text{und}}(h) = \frac{3\pi^2(k_B T)}{64k_c h^3} \quad (5.26)$$

The undulation component of the disjoining pressure,  $\Pi_{\text{und}}$  has been measured [66-68] and the inverse third power dependence of the film thickness  $h$  has been confirmed experimentally.

It should be noted that, in general, the shapes of two approaching fluid interfaces are affected by the surface forces, which can be due to van der Waals, electrostatic, steric, etc. interactions [74,75]. An implication of this fact is that a disjoining pressure term enters the

interfacial balances of the linear and angular momenta - see Refs. [34,76].

## 6. Conclusions

Our aim in this review was to compare the mechanical and thermodynamical approaches to the theory of an arbitrarily curved interface, to find the connections between them and to demonstrate their self-consistency.

Basic quantities of the *mechanical* approach are the tensors of surface stress and moments,  $\sigma$  and  $M$ . From a micromechanical viewpoint these are surface excesses with respect to the bulk stress (pressure) tensor - see Eqns (2.47) and (2.51). The basic equations of the mechanical approach, represent the vectorial balances of *linear* and *angular* momenta, Eqns (2.15) - (2.16) and (2.29) - (2.30). These equations are known from the theory of shells and plates by Kirchhoff and Love. Their implications for a fluid-liquid interface or membrane are discussed in Section 2 above - see Eqns (2.19) - (2.20) and (2.34) - (2.36). In particular, the known Laplace equation of capillarity is a special case of the interfacial balance of linear momentum.

The *thermodynamic* approach originates from the Gibbs theory of capillarity. The Gibbs fundamental equation of an interface includes a term accounting for the mechanical work of surface deformation. The latter consists of the works of interfacial dilation, shear, bending and torsion, characterized by the dilation and shear tensions,  $\gamma$  and  $\zeta$ , and by the bending and torsion moments,  $B$  and  $\Theta$  - see Eqn (3.3). These quantities are interrelated by the conditions for thermodynamic equilibrium corresponding to minimum free energy of the system. The thermodynamics provides expressions enabling one to calculate the dependencies of the surface tensions and moments on temperature and composition; an illustrative example for a mixed lipid monolayer is given in Section 3b.

To find the connection between the mechanical and thermodynamical approaches one should answer the following two questions:

(i) How the scalar *thermodynamical* quantities  $\gamma$ ,  $\zeta$ ,  $B$  and  $\Theta$  are related to the *mechanical* stress and moment tensors,  $\sigma$  and  $M$ ?

(ii) What is the relation between the *thermodynamical* equilibrium conditions, and the *mechanical* balances of linear and angular momentum?

The replies to these questions are given in Section 4 above. In particular, the thermodynamic bending and torsion moments,  $B$  and  $\Theta$ , turn out to be equal to the trace and the deviator of the tensor of surface moments,  $M$  - cf. Eqn (3.38). Similarly, the trace and the deviator of the surface stress tensor,  $\sigma$ , determine the *mechanical* dilational and shear

tensions,  $\sigma$  and  $\eta$ , respectively - see Eqn (3.39).  $\sigma$  and  $\eta$  are related to their *thermodynamical* counterparts,  $\gamma$  and  $\zeta$ , by means of Eqns (3.41) and (3.42).

By using the aforementioned relationships between the thermodynamical and mechanical tensions and moments, in Section 4 demonstrate that the thermodynamical conditions for equilibrium, Eqns (3.12) and (3.13), are corollaries from the mechanical balances of linear and angular momentum in the special case of quasistatic processes. The mechanical approach can be applied also for dynamic processes, when viscous effects have to be taken into account - see Section 5.

To solve any mechanical problem, one needs constitutive relations between stress and strain. Such a relation represents a *theoretical model* of the rheological properties of an interface. In Section 5 we discuss a rheological model based on the constitutive relations due to Scriven [64] and Helfrich [3]. This model contains 6 surface rheological parameters: the *viscous* behavior is characterized by the surface dilational viscosity,  $\xi_2$ , and by the surface lateral and transversal shear viscosities,  $\eta_2$  and  $\chi_2$ ; the surface *flexural elastic* behavior is characterized by the bending and torsion moduli,  $k_c$  and  $\bar{K}_c$ , and by the spontaneous curvature,  $H_0$ . This rheological model represents the basis of the theory of fluctuation capillary waves and undulation surface forces.

In conclusion, we found out that the mechanical and thermodynamical approaches are in a good agreement. Moreover, they are complementary to each other and represent the two parts of a self-consistent theory of the general curved interfaces. We hope that the interconnecting between these two approaches, considered in the present review, will be helpful for a further advance in this field.

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