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CHAPTER 3

SURFACE BENDING MOMENT AND CURVATURE ELASTIC MODULI

This chapter is devoted to a generalization of the theory of capillarity to cases, in which variations of the interfacial (membrane) curvature give an essential contribution to the total energy of the system. An interface (or membrane) possesses 4 modes of deformation: dilatation, shearing, bending and torsion. The first couple of modes represent two-dimensional analogues of respective deformations in the bulk phases. The bending and torsion modes are related to variations in the two principle curvatures of the interface, that is to the presence of two additional degrees of freedom. From a thermodynamic viewpoint, the curvature effects can be accounted for as contributions of the work of interfacial bending and torsion to the total energy of the system; the respective coefficients are the interfacial (surface) bending and torsion moments, B and Θ . The most popular model of the interfacial curvature effects provides an expression for the mechanical work of flexural deformation, which involves 3 parameters: bending and torsion elastic moduli, k_c and \bar{k}_c , and spontaneous curvature, H_0 .

Initially we consider the simpler case of spherical geometry. The dependence of the bending moment B on the choice of the dividing surface at fixed physical state of the system is investigated. The connection between the quantities bending moment, Tolman length and spontaneous curvature is demonstrated. Micromechanical expressions are derived, which allow one to calculate the surface tension and the bending moment if an expression for the pressure tensor is available.

From the viewpoint of the microscopic theory, various intermolecular forces may contribute to the interfacial moments B , Θ , and to the curvature elastic moduli, k_c and \bar{k}_c . Such are the van der Waals forces, the steric and electrostatic interactions.

The interfacial bending moment may give an essential contribution to the interaction between deformable droplets in emulsions. In general, the curvature effects are expected to be significant for interfaces of low tension and high curvature, including biomembranes.

3.1. BASIC THERMODYNAMIC EQUATIONS FOR CURVED INTERFACES

3.1.1. INTRODUCTION

The curvature dependence of the interfacial tension was first investigated by Gibbs in his theory of capillarity [1]. The approach of Gibbs has been further developed by Tolman [2], who established that such curvature dependence appears for sufficiently small liquid drops or gas bubbles, whose radii are comparable with the so called *Tolman length*, δ_0 . The latter represents the distance between the surface of tension and the equimolecular dividing surface, see Chapter 1. Further development in the thermodynamics of curved interfaces was given in the works of Koenig [3] and Buff [4-6]. Kondo [7] investigated how the choice of dividing surface affects the surface thermodynamic parameters; see also Refs. [8-11].

An additional interest in the curvature effects has been provoked by the studies on microemulsions [12-20]. The biomembranes, lipid bilayers and vesicles represent another class of systems, for which the curvature effects play an essential role on the background of a low interfacial tension. The predominant number of works on lipid membranes is based on the mechanics of *shells and plates*, originating from the studies by Kirchhoff [21], Love [22], see also Refs. [23-25], and on the related theory of *liquid crystals* [26-28], rather than on the Gibbs thermodynamics. The mechanics of biomembranes is a complex and rich in phenomena field, whose importance is determined by the fact that such membranes are basic structural and physiological element of the cells of all living organisms. In particular, in Chapter 10 below we apply the mechanics of curved interfaces to describe theoretically the membrane-mediated interaction between proteins incorporated in a lipid bilayer.

3.1.2. MECHANICAL WORK OF INTERFACIAL DEFORMATION

First we will make an overview of the most important equations in the thermodynamics of the curved interfaces. The work of deformation of an elementary parcel, ΔA , of a the boundary between two fluid phases, can be expressed in the form [29-31]

$$\delta w_s = \gamma \delta \alpha + \xi \delta \beta + B \delta H + \Theta \delta D, \quad \delta \alpha \equiv \delta(\Delta A) / \Delta A \quad (3.1)$$

Here δw_s is the mechanical work of deformation per unit area of the phase boundary; $\delta\alpha$ is the relative dilatation (increase of the area) of the surface element ΔA . If δu_{11} and δu_{22} are the two eigenvalues of the surface strain tensor, then $\delta\alpha$ and $\delta\beta$ can be expressed as follows:

$$\delta\alpha = \delta u_{11} + \delta u_{22}, \quad \delta\beta = \delta u_{11} - \delta u_{22} \tag{3.2}$$

see also Eq. (4.22) below. Consequently, $\delta\alpha$ and $\delta\beta$ characterize the isotropic and the deviatoric part of the surface strain tensor. In particular, $\delta\beta$ characterizes the interfacial deformation of shear, see Fig. 3.1. Likewise, the surface curvature tensor has two eigenvalues, c_1 and c_2 , representing the two principal curvatures; then

$$H = \frac{1}{2}(c_1 + c_2), \quad D = \frac{1}{2}(c_1 - c_2) \tag{3.3}$$

are the mean and deviatoric curvature; the latter is a measure for the local deviation from the spherical shape.

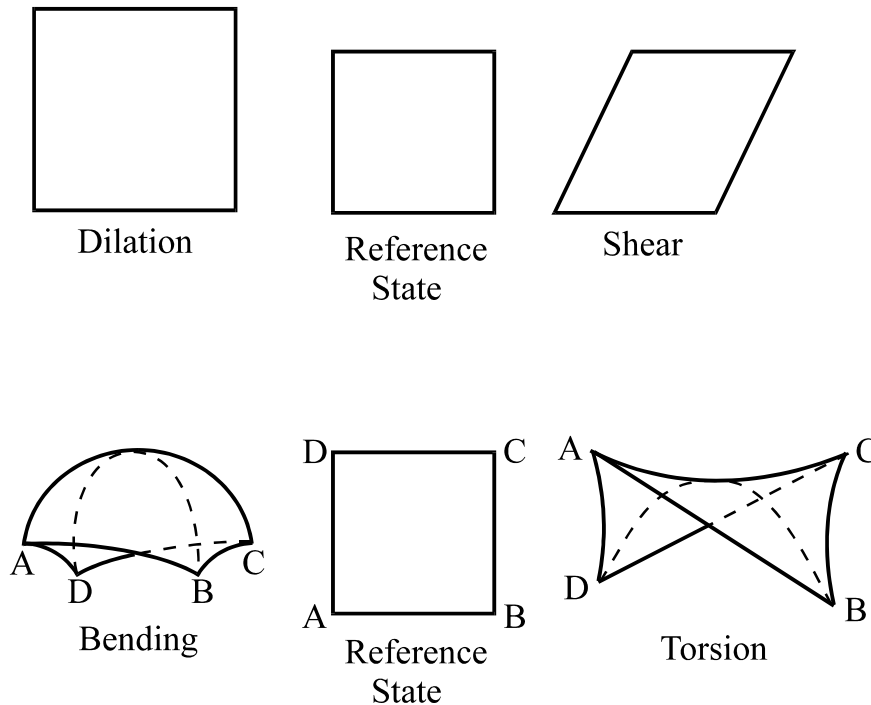


Fig. 3.1. Modes of deformation of a surface element: dilatation, shear, bending and torsion.

Equation (3.1), without the term $\xi\delta\beta$, was first formulated in the classical work by Gibbs [1], and without the curvature terms – in the study by Evans & Skalak [25]. In particular, $\gamma\delta\alpha$ is the work of pure *dilatation* ($\delta\beta = 0$; $\delta c_1 = \delta c_2 = 0$); $\xi\delta\beta$ is the work of pure *shearing* ($\delta\alpha = 0$; $\delta c_1 = \delta c_2 = 0$), $B\delta H$ is the work of pure *bending* ($\delta c_1 = \delta c_2$; $\delta\alpha = \delta\beta = 0$) and $\Theta\delta D$ is the work of pure *torsion* ($\delta c_1 = -\delta c_2$; $\delta\alpha = \delta\beta = 0$), termed also “work of saddle-shape deformation”, see Fig. 3.1. Correspondingly, B and Θ are called the interfacial bending and torsion moments [15]. Often in the literature the Gaussian curvature

$$K = c_1 c_2 = H^2 - D^2 \quad (3.4)$$

is being chosen as an independent thermodynamic parameter, instead of the deviatoric curvature D ; then Eq. (3.1) is transformed in the equivalent form

$$\delta w_s = \gamma\delta\alpha + \xi\delta\beta + C_1\delta H + C_2\delta K \quad (3.5)$$

Equation (3.5), without the term $\xi\delta\beta$, is used in the works by Boruvka & Neumann [32] and Markin et al. [33]. A comparison between Eqs. (3.1) and (3.5) yields [31,34]:

$$B = C_1 + 2C_2H, \quad \Theta = -2C_2D \quad (3.6)$$

Equation (3.1) is more convenient to use for spherical interfaces ($D = 0$), and Eq. (3.5) – for cylindrical interfaces ($K = 0$). Below we will follow the Gibbs approach, and will use H and D as thermodynamic variables; the latter have a simple geometric meaning (Fig. 3.1), and the respective moments B and Θ have the same physical dimension, in contrast with C_1 and C_2 .

In general, the surface moments B and Θ depend on the curvature. The latter dependence can be expressed in an explicit form by introducing some model of the interfacial flexural rheology. The following rheological constitutive relation, introduced by Helfrich [23,24], is frequently used in literature

$$w_f = 2k_c(H - H_0)^2 + \bar{k}_c K \quad (3.7)$$

Here w_f is the work of flexural deformation per unit area of the interface; H_0 , k_c and \bar{k}_c are constant parameters of the rheological model: H_0 is called the *spontaneous curvature*, k_c and \bar{k}_c are the *bending* and *torsion (Gaussian)* surface elastic moduli. From Eq. (3.1) it follows

$$\delta w_f = B\delta H + \Theta\delta D \quad (3.8)$$

Combining Eqs. (3.4), (3.7) and (3.8) one derives [34,35]

$$B = \left(\frac{\partial w_f}{\partial H} \right)_D = B_0 + 2(2k_c + \bar{k}_c)H, \quad \Theta = \left(\frac{\partial w_f}{\partial D} \right)_H = -2\bar{k}_c D \quad (3.9)$$

where

$$B_0 = -4k_c H_0 \quad (3.10)$$

is an expression for the bending moment of a planar interface in the framework of the Helfrich model.

In general, Eqs. (3.9) can be interpreted as truncated power expansions of B and Θ for small deviations from planar interface (small H and D ; quadratic and higher-order terms neglected). On the other hand, the original Helfrich formula, Eq. (3.7), has been postulated to give the leading term in the power expansion of w_f in the case when H is close to H_0 . If the values of B_0 and k_c are known for a planar interface ($H = 0$) and then H_0 is formally calculated from Eq. (3.10), there is no guarantee that the obtained result for H_0 could be physically interpreted as a spontaneous curvature, i.e. that for $H = H_0$ the free energy of flexural deformation w_f has a minimum. In other words, if Eq. (3.8) is integrated, along with Eq. (3.9), in general there is no guarantee that the integration constant will be equal to $2k_c H_0^2$, cf. Eq. (3.7).

3.1.3. FUNDAMENTAL THERMODYNAMIC EQUATION OF A CURVED INTERFACE

Let us consider an elementary interfacial parcel of area dA . The Gibbs excesses of internal energy, entropy and number of molecules from the i -the species, corresponding to this parcel, are

$$dU_s = u_s dA, \quad dS_s = s_s dA, \quad d\Omega_s = \omega_s dA, \quad dN_i^s = \Gamma_i dA, \quad (3.11)$$

where u_s , s_s , ω_s and Γ_i are surface densities of the respective quantities. Further, let the area dA of the elementary parcel increases with

$$\delta(dA) = \frac{\delta(dA)}{dA} dA = \delta\alpha dA \quad (3.12)$$

due to the occurrence of some thermodynamic process. The Gibbs approach to nonuniform interfaces consists in application of the fundamental equation of an uniform interface *locally*, i.e. to every element dA of the nonuniform interface [1]. (Of course, this approach is more general and applicable to any nonuniform phases, not necessarily curved interfaces.) Thus, in the course of a thermodynamic process the variations of the parameters in Eq. (3.11) obey the fundamental equation

$$\delta(dU_s) = T\delta(dS_s) + \sum_{i=1}^k \mu_i d(dN_i^s) + \delta W_s \quad (3.13)$$

where T and μ_i are the temperature and chemical potential, and δW_s is the mechanical work of deformation of the surface element dA . In keeping with Eq. (3.1) one can write [30, 31]:

$$\delta W_s = \delta w_s dA = (\gamma\delta\alpha + \xi\delta\beta + B\delta H + \Theta\delta D)dA \quad (3.14)$$

With the help of Eqs. (3.11) and (3.12) one obtains

$$\delta(dU_s) = (\delta u_s + u_s \delta\alpha) dA \quad (3.15)$$

Similar expressions can be deduced also for dS_s and dN_i^s . In this way the fundamental equation (3.13) can be transformed to read [29-31]

$$\delta u_s = T\delta s_s + \sum_{i=1}^k \mu_i \delta\Gamma_i + (\gamma - \omega_s)\delta\alpha + \xi\delta\beta + B\delta H + \Theta\delta D \quad (3.16)$$

where

$$\omega_s = u_s - T s_s - \sum_{i=1}^k \mu_i \Gamma_i \quad (3.17)$$

is the surface excess of the grand thermodynamic potential. Differentiation of Eq. (3.17) and substitution of the result for δu_s in Eq. (3.16) yields

$$\delta\omega_s = -s_s \delta T - \sum_{i=1}^k \Gamma_i \delta\mu_i + (\gamma - \omega_s) \delta\alpha + \xi \delta\beta + B \delta H + \Theta \delta D \quad (3.18)$$

If the interface can be treated as a *two-dimensional fluid*, then the interfacial tension equals the density of the surface excess grand thermodynamic potential [1]

$$\gamma = \omega_s \quad (3.19)$$

Equation (3.19) can be obtained in the following way. Imagine an elementary interfacial parcel of area dA , whose boundary is a contour permeable for the transport of all components. An imaginary process of expansion of this contour at constant intensive parameters ($\delta T = 0$, $\delta\mu_i = 0$, $\delta\beta = 0$, $\delta H = 0$, $\delta D = 0$) leads to enlargement of the parcel owing to the transfer of molecules across the permeable boundary line. In the course of this process matter with the same intensive properties, and especially with the same ω_s , is added to the considered parcel. Then, setting $\delta\omega_s = 0$ in Eq. (3.18) we arrive at Eq. (3.19).

If the interface represents such a two-dimensional fluid, then Eq. (3.19) is valid irrespective of whether components, which are insoluble in the bulk phases, are present at the interface. In this case, from Eqs. (3.18) and (3.19) we obtain a generalizes version of the Gibbs adsorption equation:

$$\delta\gamma = -s_s \delta T - \sum_{i=1}^k \Gamma_i \delta\mu_i + \xi \delta\beta + B \delta H + \Theta \delta D \quad (3.20)$$

cf. Eq. (1.35).

It is worthwhile noting that the sign of B and Θ is a matter of convention. It is determined by the choice of the direction of the running unit normal to the interface, \mathbf{n} . From the differential geometry it is known that the surface tensor of curvature, \mathbf{b} , can be defined as the surface gradient of \mathbf{n} [36]:

$$\mathbf{b} = -\nabla_s \mathbf{n} \quad (3.21)$$

The latter equation is known also as the Weingarten's formula [37]. Since the principal curvatures, c_1 and c_2 , are the eigenvalues of \mathbf{b} , then in view of Eqs. (3.3) and (3.21) an inversion of the direction of \mathbf{n} will lead to a change of the sign of H and D . Moreover, δw_f in

Eq. (3.8) must not depend on the choice of direction of \mathbf{n} ; consequently, the inversion of the direction of \mathbf{n} leads also to an inversion of the sign of B and Θ . From Eq. (3.8) it could be realized that a *positive* B tends to bend the interface around the *inner* phase, that is the phase for which \mathbf{n} is an *outer* normal. The latter rule is general, i.e. it is independent of the choice of the direction of \mathbf{n} .

3.2. THERMODYNAMICS OF SPHERICAL INTERFACES

3.2.1. DEPENDENCE OF THE BENDING MOMENT ON THE CHOICE OF DIVIDING SURFACE

Spherical fluid interfaces are often observed due to the fact that the spherical shape corresponds to minimal surface energy if the gravitational deformation is negligible. After Gibbs [1] an interface can be modeled as a mathematical dividing surface separating two bulk phases. As noticed in Chapter 1, in reality there is a narrow transitional zone between the two phases, whose thickness could be from few angstroms to dozens of angstroms. For that reason, a problem arises about the exact definition of the position of the dividing surface.

From symmetry considerations it follows that in the case of spherical interface the dividing surface must be a sphere. However, an additional condition must be imposed to uniquely define the radius of this sphere. It can be proven [7,8] that for an arbitrary definition of the spherical dividing surface the following two equations hold:

$$dw_s = \gamma d\alpha + \left[\frac{\partial \gamma}{\partial a} \right] da \quad (3.22)$$

$$\frac{2\gamma}{a} + \left[\frac{\partial \gamma}{\partial a} \right] = P_I - P_{II} \quad (3.23)$$

Here a is the radius of the dividing surface, P_I and P_{II} are the pressures, respectively, inside and outside the spherical drop (bubble, vesicle); $[\partial \gamma / \partial a]$ is a *formal* derivative of γ with respect to the radius a ; here and hereafter the brackets symbolize formal derivatives, which correspond to an imaginary variation of the choice of a at fixed physical state of the system. The comparison of Eqs. (3.22) and (3.1) (the latter for $\delta\beta = 0$, $\delta D = 0$ and $a = -1/H$) yields [29-31]:

$$B = a^2 \left[\frac{\partial \gamma}{\partial a} \right], \quad (3.24)$$

that is the formal derivative turns out to be proportional to the bending moment B . One way to uniquely define the dividing surface is to impose the additional condition the formal derivative of γ to be always equal to zero:

$$B|_{a=a_s} = a_s^2 \left[\frac{\partial \gamma}{\partial a} \right]_{a=a_s} = 0 \quad (3.25)$$

This special dividing surface, introduced by Gibbs [1], is called the *surface of tension*, cf. Eq. (1.13); here its radius is denoted by a_s . For this dividing surface Eq. (3.23) reduces to the common capillary equation of Laplace:

$$\frac{2\gamma_s}{a_s} = P_I - P_{II} \quad (3.26)$$

Eliminating $P_I - P_{II}$ between Eqs. (3.23) and (3.26) we obtain

$$\frac{dy}{dx} + \frac{2}{x}y - 2 = 0 \quad (3.27)$$

where we have introduced the notation

$$x = a/a_s, \quad y = \gamma/\gamma_s \quad (3.28)$$

The solution of Eq. (3.27), satisfying the boundary condition $y(1) = 1$, reads

$$y(x) = \frac{1}{3x^2} + \frac{2}{3}x \quad (3.29)$$

The latter equation, first derived by Kondo [7], describes the dependence of the interfacial tension γ on the choice of the dividing surface at fixed physical state of the system. From Eqs. (3.24), (3.28) and (3.29) one can deduce a similar dependence for the bending moment B [29]:

$$\bar{B} \equiv \frac{B}{2\gamma a} = \frac{x^3 - 1}{2x^3 + 1} \quad (3.30)$$

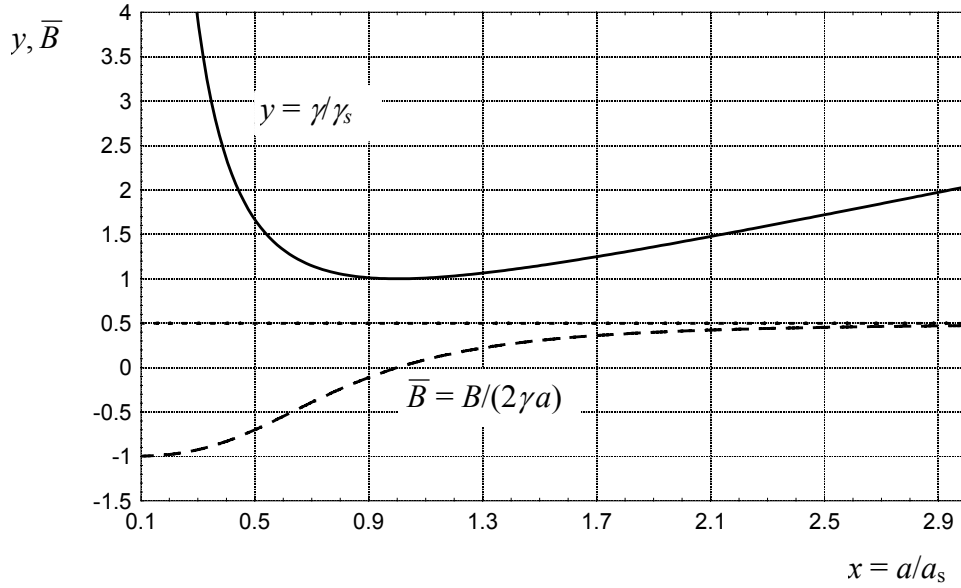


Fig. 3.2. Dependence of the thermodynamic interfacial tension, γ , and the dimensionless bending moment, \bar{B} , on the choice of the dividing surface (of radius a) for a fixed physical state of the system.

Equations (3.29) and (3.30) are illustrated graphically in Fig. 3.2. In accordance with Eq. (3.25), the surface of tension corresponds to the minimum of the curve γ vs. a . Moreover, the dimensionless bending moment, \bar{B} , which takes part in the Laplace equation,

$$\frac{2\gamma}{a}(1 + \bar{B}) = P_I - P_{II}, \quad (3.31)$$

cf. Eq. (3.23), (3.24) and (3.30), turns out to be a function of a with bounded variation (Fig. 3.2). In addition, one could verify that the dependence B vs a ,

$$B = \frac{2}{3}\gamma_s a_s \left(\frac{a^2}{a_s^2} - \frac{a_s}{a} \right), \quad (3.32)$$

which stems from Eqs. (3.28)–(3.30), satisfies the differential equation [31]

$$\left[\frac{\partial B}{\partial a} \right] = 2\gamma, \quad (3.33)$$

which is analogous to Eq. (3.24).

The surface of tension turns out to be convenient in many cases, because it simplifies the shape of the Laplace equation, which determines the shape of interfaces in the capillary hydrostatics,

see Chapter 2. On the other hand, as noticed by C. Miller [17], in the case of low interfacial tension (critical emulsions, microemulsions, lipid vesicles, biomembranes) the mathematical surface of tension is situated away from the physical transition zone between the two phases; see also eq. (3.62) below. In such a case, which is equivalent to the presence of essential contribution from the interfacial bending moment, it is appropriate to use the equimolecular dividing surface.

3.2.2. EQUIMOLECULAR DIVIDING SURFACE AND TOLMAN LENGTH

As mentioned above, an additional condition must be imposed to define uniquely the radius of the dividing surface. Instead of setting the formal derivative $[\partial\gamma/\partial a]$ equal to zero, as it is for the surface of tension, one could require the formal derivative to be equal to the physical derivative, viz.

$$\left[\frac{\partial\gamma}{\partial a} \right]_{a=a_v} = \frac{\partial\gamma_v}{\partial a_v} \quad \left(\gamma_v \equiv \gamma|_{a=a_v} \right) \quad (3.34)$$

where a_v is the radius of the dividing surface defined by Eq. (3.34), termed the *equimolecular* dividing surface [2,3,6,8]; see also Section 1.2.2 above. The partial derivative $\partial\gamma_v/\partial a_v$ is related to the physical dependence of γ_v on a_v for fixed values of the other thermodynamic parameters of state. Different possible choices of the latter parameters correspond to different definitions of a_v . The distance

$$\delta = a_v - a_s \quad (3.35)$$

between the surface of tension and the equimolecular dividing surface is called the Tolman length. Tolman [2] has derived the equation

$$\gamma_v = \gamma_0 \left(1 - \frac{2\delta_0}{a_v} + \dots \right), \quad (3.36)$$

$$\gamma_0 = \lim_{a_v \rightarrow \infty} \gamma_v, \quad \delta_0 = \lim_{a_v \rightarrow \infty} \delta \quad (3.37)$$

which expresses in first approximation the physical dependence of γ_v on the interfacial curvature. Setting $a = a_v$ in Eq. (3.32) and expanding in series for $\delta_0/a_v \ll 1$ we obtain [38]:

$$B_v = 2\gamma_0\delta_0 + \dots \quad \left(B_v \equiv B|_{a=a_v} \right) \quad (3.38)$$

The next terms in the expansion (3.38) can be found only if the dependence $\delta = \delta(a_v)$ is known. From Eqs. (3.36) and (3.38) we deduce

$$\gamma_v = \gamma_0 - \frac{B_0}{a_v} + \dots, \quad B_0 \equiv B_v|_{a \rightarrow \infty} = 2\gamma_0\delta_0 \quad (3.39)$$

The last equation allows estimates for the magnitude of B_0 to be made. For example, for the surface of liquid argon at temperature -188.85°C , we have $\gamma_0 = 13.45 \text{ mN/m}$, $\delta_0 = 3.6 \text{ \AA}$, see Ref. [39], and then from Eq. (3.39) we compute $B_0 = 9.7 \times 10^{-12} \text{ N}$. Equation (3.39) demonstrates the connection between the Tolman length, δ_0 , and the bending moment B_0 , which in its own turn is proportional to the Helfrich's spontaneous curvature H_0 , see Eq. (3.10); all these quantities are related to the curvature dependence of the surface tension.

Another relationship between the Tolman length and the parameters of the equimolecular dividing surface can be obtained in the following way. From Eqs. (3.28) and (3.29) one can deduce

$$\frac{\gamma_v}{a_v} = \frac{\gamma_s}{a_s} \left(\frac{2}{3} + \frac{1}{3} \frac{a_s^3}{a_v^3} \right) \quad (3.40)$$

Likewise, from Eqs. (3.26), (3.30) and (3.31) we obtain

$$\frac{2\gamma_v}{a_v} + \frac{B_v}{a_v^2} = \frac{2\gamma_s}{a_s} \quad (3.41)$$

The elimination of γ_s/a_s between Eqs. (3.40) and (3.41), along with Eq. (3.35), yields the sought for expression for δ [31]:

$$\delta = a_v \left[1 - \left(\frac{\gamma_v - B_v/a_v}{\gamma_v + \frac{1}{2} B_v/a_v} \right)^{1/3} \right] \quad (3.42)$$

Equation (3.42) shows that the sign of δ is connected with the sign of B_v : indeed, one could verify that Eq. (3.42) yields $\delta_v > 0$ for $B_v > 0$, and *vice versa*, $\delta_v < 0$ for $B_v < 0$.

3.2.3. MICROMECHANICAL APPROACH

Mechanical definitions of surface tension and bending moment. The hydrostatic approach to the theoretical description of curved interfaces has been developed by Buff [5], Ono & Kondo [8] and Rusanov [9]. Owing to the spherical symmetry, the pressure tensor can be expressed in the form [8]

$$\mathbf{P} = P_N \mathbf{e}_r \mathbf{e}_r + P_T (\mathbf{e}_\theta \mathbf{e}_\theta + \mathbf{e}_\varphi \mathbf{e}_\varphi) \quad (3.43)$$

where (r, θ, φ) are polar coordinates with center in the center of spherical symmetry; \mathbf{e}_r , \mathbf{e}_θ and \mathbf{e}_φ are the unit vectors of the curvilinear local basis; P_N and P_T represent the normal and tangential component of the tensor \mathbf{P} with respect to the spherical interface.

Let us consider a part of the system, which is confined between two concentric spheres of radii r_1 and r_2 , see Fig. 3.3. The total force acting on the shaded sectorial strip (Fig. 3.3) is [8]

$$d\theta \int_{r_1}^{r_2} P_T r dr \quad (3.44)$$

see Fig. 3.3 for the notation. The respective force moment is given by the expression

$$d\theta \int_{r_1}^{r_2} P_T r^2 dr \quad (3.45)$$

Following Gibbs [1] we define an idealized (model) system consisting of one spherical dividing surface of radius a and two bulk fluid phases, I and II, which are uniform and isotropic up to the very dividing surface. The pressure in the idealized system can be expressed in the form

$$\bar{P} = \begin{cases} P_I & \text{for } r < a \\ P_{II} & \text{for } r > a \end{cases} \quad (3.46)$$

As noted in Chapter 1 (Figs. 1.1 – 1.3) the pressure tensor \mathbf{P} is not isotropic in a vicinity of an interface. To compensate this difference between the real and the idealized system, the dividing

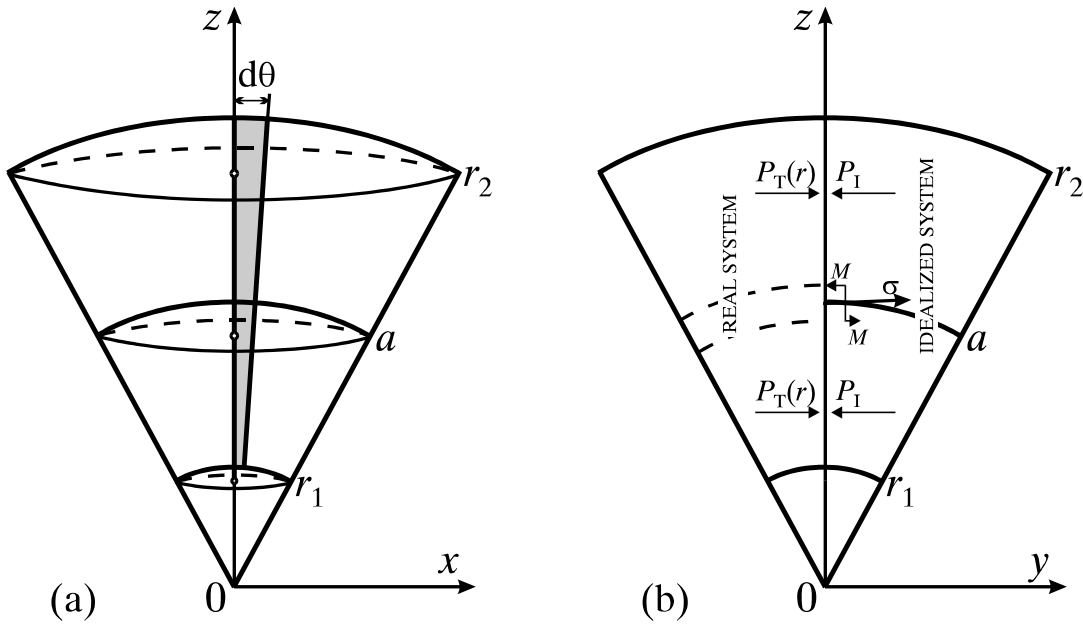


Fig. 3.3. Sketch of the real and idealized systems, and of the sectorial strip (shaded) used to give a mechanical definition of the surface tension, σ , and the bending moment, M .

surface is treated as a membrane with surface (membrane) tension σ and surface bending moment M , see Fig. 3.3b. Then the counterparts of Eqs. (3.44) and (3.45) for the *idealized* system are [31]:

$$d\theta \int_{r_1}^{r_2} \bar{P} r dr - \sigma d\theta \quad (3.47)$$

$$d\theta \int_{r_1}^{r_2} \bar{P} r^2 dr - \sigma a^2 d\theta + M a d\theta \quad (3.48)$$

To make the idealized system mechanically equivalent to the real one, we require that the force and the moment acting on the sectorial strip in the two systems (Fig. 3.3) to be equal. Thus setting equal the expressions in Eqs. (3.44) and (3.47) we obtain

$$\sigma a = \int_{r_1}^{r_2} (\bar{P} - P_T) r dr \quad (3.49)$$

Likewise, from Eqs. (3.45) and (3.48) we derive

$$\sigma a^2 - Ma = \int_{r_1}^{r_2} (\bar{P} - P_T) r^2 dr \quad (3.50)$$

In the above mechanical derivation we deliberately have used the notation σ and M for the *mechanical* surface tension and moment. Indeed, it is not obligatory the latter to coincide with their *thermodynamic* analogues, γ and B , defined by Eq. (3.1).

Relationship between the mechanical and thermodynamical surface tension. Under conditions of hydrostatic equilibrium the divergence of the pressure tensor is zero, that is $\nabla \cdot \mathbf{P} = 0$. In the considered case of spherical symmetry the latter equation yields [39]

$$\frac{d}{dr}(r^2 P_N) = 2r P_T \quad (3.51)$$

Integrating the latter equation we derive

$$\int_{r_1}^{r_2} P_T r dr = \frac{1}{2}(P_{II} r_2^2 - P_I r_1^2) \quad (3.52)$$

Substituting Eqs. (3.46) and (3.52) into (3.49) we obtain a version of the Laplace equation:

$$\frac{2\sigma}{a} = P_I - P_{II} \quad (3.53)$$

The comparison of Eqs. (3.53) and (3.31) yields

$$\gamma = \sigma - \frac{B}{2a} \quad (3.54)$$

To find a unique relationship between the couple of mechanical parameters (σ , M) and the couple of thermodynamical parameters (γ , B) we need a second relationship, in addition to Eq. (3.54). Such an equation can be obtained in the following way.

Let us consider a purely lateral displacement of the conical surface depicted in Fig. 3.3a. The work of this displacement, carried out by the outer forces, is [8]

$$dW = - \int_{r_1}^{r_2} (P_T 2\pi r \sin \theta dr) r d\theta = - d\omega \int_{r_1}^{r_2} P_T r^2 dr \quad (3.55)$$

where

$$d\omega = \sin\theta d\theta \int_0^{2\pi} d\varphi = 2\pi \sin\theta d\theta \quad (3.56)$$

is the increment of the spatial angle at the vertex of the cone corresponding to the considered infinitesimal displacement of the lateral surface. An alternative expression for dW is provided by thermodynamics [8]:

$$dW = -P_I dV_I - P_{II} dV_{II} + \gamma dA \quad (3.57)$$

where V_I and V_{II} represent the volumes of phases I and II, and A is the area of the spherical dividing surface. By means of geometrical considerations one obtains

$$dV_I = d\omega \int_{r_1}^a dr r^2; \quad dV_{II} = d\omega \int_a^{r_2} dr r^2; \quad dA = a^2 d\omega \quad (3.58)$$

Setting equal the two expressions for dW , Eqs. (3.55) and (3.57), and using Eqs. (3.46) and (3.58), one deduces [8]

$$\gamma a^2 = \int_{r_1}^{r_2} (\bar{P} - P_T) r^2 dr \quad (3.59)$$

Finally, by comparing Eqs. (3.50) and (3.59) we obtain the sought for second equation connecting the mechanical and thermodynamical parameters:

$$\gamma = \sigma - \frac{M}{a} \quad (3.60)$$

Equations (3.54) and (3.60) imply the following relationship between B and M :

$$B = 2M \quad (3.61)$$

Generalized versions of Eqs. (3.54) and (3.61) for an arbitrarily curved interface are derived below, see Eqs. (4.79) and (4.81).

Equation (3.54) shows that for a *curved* interface there is a difference between the mechanical and thermodynamical surface tension. This difference is zero only if the dividing surface is defined as surface of tensions, for which $B = 0$ by definition, cf. Eq. (3.25). However, from a physical viewpoint the surface of tension not always provides an adequate description of the real phase boundary or membrane. To demonstrate the latter fact we will use the equation [31]

$$\delta = a_v \left[1 - \left(\frac{\sigma_v - \frac{3}{2} B_v / a_v}{\sigma_v} \right)^{1/3} \right], \quad (3.62)$$

which follows from Eqs. (3.54) and (3.42). For interfaces of low interfacial tension, $\sigma_v \rightarrow 0$, e.g. microemulsions or lipid membranes, Eq. (3.62) gives $\delta \rightarrow \infty$, that is the surface of tension is situated far away from the real boundary between the two phases; see also Ref. [17].

Micromechanical expressions for σ , γ and B . The functions $P_N(r)$ and $P_T(r)$ provide a micromechanical description of the stresses acting in the transitional zone between the two neighboring phases [5]. Such a description takes an intermediate position between the *macroscopic* description in terms of quantities like σ , γ and B , and the *microscopic* description in terms of the correlation functions of the statistical mechanics, see e.g. Refs. [39-42]. Convenient for applications are expressions which represent the macroscopic parameters as integrals of the function

$$\Delta P(r) = P_N(r) - P_T(r), \quad (3.63)$$

$\Delta P(r)$ characterizes the anisotropy of the pressure tensor \mathbf{P} in a vicinity of the phase boundary, see Eqs. (1.8) and (1.12), as well as Figs. 1.2 and 1.3. For a spherical interface Buff [5] has derived the expression

$$\gamma_s = \int_{r_1}^{r_2} \Delta P(r) \frac{r^2}{a_s^2} dr, \quad (3.64)$$

which is valid only for the surface of tension. Below we describe the derivation of other micromechanical expressions obtained in Ref. [31], which are valid for an arbitrary choice of the spherical dividing surface.

Equation (3.51) can be represented in the form

$$\frac{dP_N}{dr} = \frac{2}{r} \Delta P \quad (3.65)$$

The integration of Eq. (3.65), along with Eq. (3.53), yields

$$\sigma = \int_{r_1}^{r_2} \Delta P \frac{a}{r} dr \quad (3.66)$$

The latter equation specifies that the analogous expression, derived by Goodrich [43], refers to the mechanical surface tension, σ , rather than to the thermodynamical one, γ . Further, from Eqs. (3.46) and (3.59) we obtain

$$\gamma a^2 = \frac{1}{3} a^3 (P_I - P_{II}) - \frac{1}{3} (P_I r_1^3 - P_{II} r_2^3) - \int_{r_1}^{r_2} P_T r^2 dr \quad (3.67)$$

On the other hand, the integration of Eq. (3.51) yields

$$2 \int_{r_1}^{r_2} P_T r^2 dr = P_{II} r_2^3 - P_I r_1^3 - \int_{r_1}^{r_2} P_N r^2 dr \quad (3.68)$$

With the help of Eqs. (3.53), (3.66) and (3.68) one can eliminate P_I and P_{II} from Eq. (3.67) [31]:

$$\gamma = \frac{1}{3} \int_{r_1}^{r_2} \Delta P(r) \left(\frac{2a}{r} + \frac{r^2}{a^2} \right) dr \quad (3.69)$$

In accordance with Eq. (3.24) we differentiate Eq. (3.69) to derive a micromechanical expression for the interfacial bending moment B [31]:

$$B = \frac{2}{3} \int_{r_1}^{r_2} \Delta P(r) \left(\frac{a^2}{r} - \frac{r^2}{a} \right) dr \quad (3.70)$$

The same expression for B can be obtained by substitution of the expressions for σ and γ , Eqs. (3.66) and (3.69), into Eq. (3.54). Moreover, the differentiation of Eq. (3.70), in accordance with Eq. (3.33), leads to Eq. (3.69). The latter facts demonstrate that the theory is selfconsistent.

Equations (3.66), (3.69) and (3.70), which are valid for an arbitrary choice of the spherical dividing surface, have been used in Refs. [44, 45] to calculate the contribution of the van der Waals forces to the interfacial bending moment B .

3.3. RELATIONS WITH THE MOLECULAR THEORY AND THE EXPERIMENT

3.3.1. CONTRIBUTIONS DUE TO VARIOUS KINDS OF INTERACTIONS

A typical example for an electrically charged fluid interface is shown in Fig. 3.4: the surface charge is due to the presence of an adsorption layer of ionic surfactant. Upon bending of the interface (decrease of the radius a of the equimolecular dividing surface) the distance between the charges of the surface-active ions increases. This is energetically favorable owing to the presence of repulsive forces between ions of the same electric charge. As a result, a surface bending moment appears, which tends to bend the interface around the non-aqueous phase.

In reality, not only the electrostatic interactions, but also other type of forces contribute to the interfacial bending and torsion moments; such are the van der Waals forces and the steric interactions between the hydrophilic headgroups and the hydrophobic tails of the surfactant molecules (Fig. 3.4). From Eq. (3.16) it follows

$$B = \left(\frac{\partial u_s}{\partial H} \right)_{s_s, \Gamma_i, \alpha, \beta, D}, \quad \Theta = \left(\frac{\partial u_s}{\partial D} \right)_{s_s, \Gamma_i, \alpha, \beta, H} \quad (3.71)$$

Insofar as the van der Waals, the electrostatic, and the steric interactions can be considered to be independent, they give additive contributions to the surface density of the internal energy u_s . Then, from Eq. (3.71) it follows that these interactions give also additive contributions to the interfacial bending and torsion moments,

$$B = B^{vw} + B^{el} + B^{st}, \quad \Theta = \Theta^{vw} + \Theta^{el} + \Theta^{st} \quad (3.72)$$

Here and hereafter the superscripts “vw”, “el” and “st” denote terms related to the corresponding interactions. In view of Eqs. (3.9) and (3.72) B_0 , k_c and \bar{k}_c can be expressed in the form

$$B_0 = B_0^{vw} + B_0^{el} + B_0^{st}, \quad k_c = k_c^{vw} + k_c^{el} + k_c^{st}, \quad \bar{k}_c = \bar{k}_c^{vw} + \bar{k}_c^{el} + \bar{k}_c^{st} \quad (3.73)$$

On the other hand, having in mind Eq. (3.10), one sees that the spontaneous curvature,

$$H_0 = - \frac{B_0^{vw} + B_0^{el} + B_0^{st}}{4(k_c^{vw} + k_c^{el} + k_c^{st})} \quad (3.74)$$

is not additive with respect to contributions from the various interactions; instead, H_0 represents a ratio of additive quantities.

In Ref. [45] an expression for the *van der Waals* contribution, B_0^{vw} , to the bending moment of the boundary between two fluid phases has been derived:

$$B_0^{vw} = \frac{8}{5} \pi^2 (\alpha_{11} \rho_1^2 - \alpha_{22} \rho_2^2) \left(\frac{\gamma_0}{5\pi A_H} \right)^{1/2} \quad (3.75)$$

$$A_H = \pi^2 (\alpha_{11} \rho_1^2 - 2\alpha_{12} \rho_1 \rho_2 + \alpha_{22} \rho_2^2) \quad (3.76)$$

Here γ_0 is the interfacial tension of the planar boundary between the two pure fluids (without surfactants) A_H is the Hamaker constant, ρ_1 and ρ_2 are the number densities of the two neighboring phases, α_{ik} are the constants in the van der Waals potential: $u_{ik} = -\alpha_{ik}/r^6$; the subscripts "1" and "2" refer to the phase inside and outside the fluid particle, respectively. In general, B_0^{vw} tends to bend around the phase, which has a larger Hamaker constant [45]. Equation (3.75) has been derived by means of Eq. (3.70) and an appropriate model expression for the anisotropy of the pressure tensor, ΔP . For an oil-water interface Eq. (3.75) predicts $B_0^{vw} \approx 5 \times 10^{-11}$ N. Theoretical expressions for k_c^{vw} and \bar{k}_c^{vw} are not available in the literature.

The contribution of the *steric* interaction can be related to the size and shape of the tails and headgroups of the surfactant molecules [46-53]. The following expression was proposed [52] for such amphiphiles as the n-alkyl-poly(glycol-ethers), $(C_2H_4)_n(OCH_2CH_2)_mOH$:

$$B_0^{st} = -\frac{\pi^2 v^2 b \tilde{\varepsilon} kT}{4a_M^4} \quad k_c^{st} = \frac{\pi^2 v^3 b kT}{64a_M^5} (1 + 12\tilde{\varepsilon}) \quad (3.77)$$

where $\tilde{\varepsilon} = (n - m) / (n + m)$ characterizes the asymmetry of the amphiphile, v is the volume of an amphiphile molecule, a_M is the interfacial area per molecule, k is the Boltzmann constant, b is a molecular length-scale in the used self-consistent field model [52].

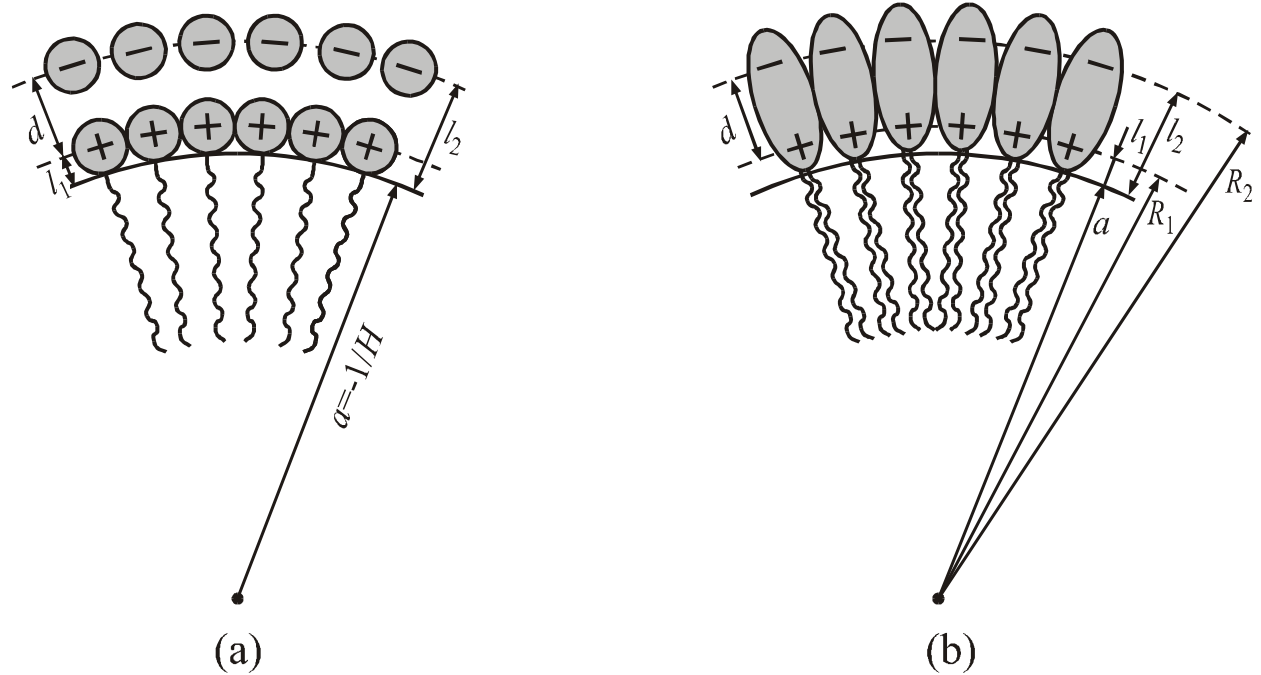


Fig. 3.4. Sketch of a "molecular condenser" of thickness d , which is formed (a) from adsorbed surfactant ions and their counterions and (b) from adsorbed zwitterionic surfactant. The dividing surface (of radius a) is chosen to be the boundary between the aqueous and the nonaqueous phase; l_1 and l_2 are the distances from the "charged" surfaces to the dividing surface.

Expressions for the *electrostatic* components of the bending moment, B_0^{el} , and the curvature elastic moduli, k_c^{el} and \bar{k}_c^{el} , have been also derived. For example, one can relate B_0^{el} , k_c^{el} and \bar{k}_c^{el} to the surface Volta potential, ΔV , which is a directly measurable parameter [54]:

$$B_0^{el} = \frac{\varepsilon}{8\pi} (\Delta V)^2 \left(1 + \frac{2l_1}{d} \right) \quad (3.78)$$

$$k_c^{el} = \frac{\varepsilon d}{12\pi} (\Delta V)^2 \left(1 + 3\frac{l_1}{d} + 3\frac{l_1^2}{d^2} \right) \quad (3.79)$$

$$\bar{k}_c^{el} = -\frac{\varepsilon d}{24\pi} (\Delta V)^2 \left(1 + 3\frac{l_1}{d} + 3\frac{l_1^2}{d^2} \right) \quad (3.80)$$

Here ε is the dielectric constant, d is the distance between the positive and negative charges; the other notation is explained in Fig. 3.4. In Eqs. (3.78) – (3.80) ΔV must be substituted in

CGSE-units, i.e. the value of ΔV in volts must be divided by 300. Note that ΔV expresses the change of the surface potential due to the presence of an adsorption monolayer. ΔV can be measured by means of the methods of the radio-active electrode or the vibrating electrode [55], which give the change in the electric potential across the interface.

Equations (3.78) – (3.80) could be used when the model of the “molecular condenser” is applicable, viz.: (i) when there is an adsorption layer of zwitterions or dipoles, such as non-ionic and zwitterionic surfactants or lipids, at the interface; (ii) when the electrolyte concentration is high enough and the counterions are located in a close vicinity of the charged interface to form a “molecular capacitor”; (iii) when the surface potential is low: then the Poisson-Boltzmann equation can be linearized and the diffuse layer behaves as a molecular capacitor of thickness equal to the Debye screening length [56]. For example, taking experimental value of the Volta potential for zwitterionic lipids [57], $\Delta V = 350$ mV, and assuming $\varepsilon = 78.2$, $d = 5$ Å, $l_1/d \ll 1$, from Eqs. (3.78) – (3.80) one calculates $B_0^{el} = 4.2 \times 10^{-11}$ N, $k_c^{el} = 1.4 \times 10^{-20}$ J and $\bar{k}_c^{el} = -0.7 \times 10^{-20}$ J.

Since, B_0^{el} , k_c^{el} and \bar{k}_c^{el} are proportional to $(\Delta V)^2$ their sign does not depend on the sign of the surface potential ΔV . For oil-water interface B_0^{el} and B_0^{vw} have the same sign: both of them tend to bend the interface around the oil phase. In contrast, for air-water interface B_0^{el} and B_0^{vw} have the opposite signs: B_0^{el} bends around the gas phase, while B_0^{vw} bends around the water phase (the phase of higher Hamaker constant).

Equations (3.78) – (3.80) show also that B_0^{el} , k_c^{el} and \bar{k}_c^{el} depend on the choice of the Gibbs dividing surface through the distances l_1 and l_2 . Moreover, if $d \equiv l_2 - l_1 > 0$, then k_c^{el} is positive, whereas \bar{k}_c^{el} is negative and $\bar{k}_c^{el} = -k_c^{el}/2$. It is interesting to note that the same relationship, $\bar{k}_c^{el} = -k_c^{el}/2$, has been obtained by Ennis [51] in the framework of a quite different model taking into account the steric interactions.

The surface charge density σ_s , i.e. the electric charge Q per unit area of the “plate” of the molecular condenser (Fig. 3.4), is simply related to ΔV :

$$\sigma_s = \frac{Q}{A} = \frac{\varepsilon \Delta V}{4\pi d} \quad (3.81)$$

Then a substitution of ΔV from (3.81) into Eqs. (3.78) – (3.80), in view of the identity $d \equiv l_2 - l_1$, leads to

$$B_0^{el} = \frac{2\pi}{\varepsilon} \sigma_s^2 (l_2^2 - l_1^2) \quad (3.82)$$

$$k_c^{el} = \frac{4\pi}{3\varepsilon} \sigma_s^2 (l_2^3 - l_1^3), \quad \bar{k}_c^{el} = -\frac{1}{2} k_c^{el} \quad (3.83)$$

As mentioned in Chapter 1, see Fig. 1.4, the double electric layer consists of a *Stern layer* and a *diffuse layer*, composed, respectively, of bound and free counterions. Correspondingly, the bending moment and the curvature elastic moduli are composed of contributions from these two layers [31,58]:

$$B_0^{el} = B_0^{Sm} + B_0^{dif}, \quad k_c^{el} = k_c^{Sm} + k_c^{dif}, \quad \bar{k}_c^{el} = \bar{k}_c^{Sm} + \bar{k}_c^{dif} \quad (3.84)$$

If the Stern layer is situated at a distance l_2 from the dividing surface, then it can be proven [31] that B_0^{Sm} , k_c^{Sm} and \bar{k}_c^{Sm} can be expressed by analogues of Eqs. (3.82) and (3.83):

$$B_0^{Sm} = \frac{2\pi}{\varepsilon} \sigma_s^2 (l_2^2 - l_1^2) \quad (3.85)$$

$$k_c^{Sm} = \frac{4\pi}{3\varepsilon} \sigma_s^2 (l_2^3 - l_1^3), \quad \bar{k}_c^{Sm} = -\frac{1}{2} k_c^{Sm} \quad (3.86)$$

where, as before, l_1 is the distance between the surface charges and the dividing surface, see Fig. 3.4a.

In the case of *low* surface electric potential, the Poisson-Boltzmann equation, describing the *diffuse* electric double layer (see Chapter 1) can be linearized. In such a case it turns out that the counterions can be treated as being situated at a distance $l_2 + \kappa^{-1}$ from the dividing surface, where κ^{-1} is the Debye length, see Eq. (1.56) and (1.64); the derived expressions for B_0^{el} , k_c^{el} and \bar{k}_c^{el} in this case are [31]

$$B_0^{el} = \frac{2\pi}{\varepsilon} \sigma_s^2 \left[(l_2 + \kappa^{-1})^2 - l_1^2 \right] \quad (3.87)$$

$$k_c^{el} = \frac{4\pi}{3\varepsilon} \sigma_s^2 \left[(l_2 + \kappa^{-1})^3 - l_1^3 \right], \quad \bar{k}_c^{el} = -\frac{1}{2} k_c^{el} \quad (3.88)$$

The latter equations look like Eqs. (3.82)–(3.83) in which l_2 is formally replaced by $(l_2 + \kappa^{-1})$. In accordance with Eq. (3.84) the respective contributions of the diffuse part of the electric double layer can be obtained by subtraction of Eqs. (3.85)–(3.86) from their counterparts among Eqs. (3.87)–(3.88):

$$B_0^{dif} = \frac{2\pi}{\varepsilon} \sigma_s^2 (2l_2 \kappa^{-1} + \kappa^{-2}) \quad (\text{low surface potential}) \quad (3.89)$$

$$k_c^{dif} = \frac{4\pi}{3\varepsilon} \sigma_s^2 (3l_2^2 \kappa^{-1} + 3l_2 \kappa^{-2} + \kappa^{-3}), \quad \bar{k}_c^{dif} = -\frac{1}{2} k_c^{dif} \quad (3.90)$$

In the case of *moderate and high* surface electric potentials the expressions related to the Stern layer, Eqs. (3.85)–(3.86) can be applied again, whereas Eqs. (3.89)–(3.90) are no longer valid. In this more complicated case expressions for B_0^{dif} , k_c^{dif} and \bar{k}_c^{dif} have been derived by means of a thermodynamic approach [31], and independently in Ref. [59] by using a hydrostatic approach based on Eqs. (4.146), (4.149) and (4.150) – see below. The results are [31,58]

$$B_0^{dif} = \mp \frac{16}{\kappa^2} c_0 kT \left[\ln \frac{1+y}{2} + \kappa l_2 (y-1) \right] \quad (3.91)$$

$$k_c^{dif} = \frac{4}{\kappa^3} c_0 kT \left[\frac{(y+2)(y-1)}{y(y+1)} + 4\kappa l_2 \left(\frac{2x^3}{y(y+1)} - \ln \frac{y+1}{2} \right) + 4\kappa^2 l_2^2 \left(\frac{2x^2}{y} - y + 1 \right) \right] \quad (3.92)$$

$$\bar{k}_c^{dif} = \frac{8}{\kappa^3} c_0 kT \left[\int_{\frac{2}{1+y}}^1 \frac{\ln z dz}{1-z} - 2\kappa l_2 \left(\frac{2x^3}{y(y+1)} - \ln \frac{y+1}{2} \right) - 3\kappa^2 l_2^2 \left(\frac{2x^2}{y} - y + 1 \right) \right] \quad (3.93)$$

Here c_0 is the bulk concentration of a $Z:Z$ electrolyte; x and y are quantities related to the surface potential as follows:

$$x = \pm \frac{2\pi Z e a^2}{\varepsilon \kappa kT R_2^2} \sigma_s, \quad y = \sqrt{1+x^2} \quad (3.94)$$

In the latter expression the signs “+” and “–” refer to an electric double layer, respectively, *inside* an aqueous drop and *outside* a non-aqueous drop (bubble). Setting $l_2 = 0$, that is neglecting the distance between the equimolecular dividing surface and the surface of location of the bound counterions, Eqs. (3.91)–(3.93) are reduced to the expressions derived by Lekkerkerker [59].

Numerical calculations based on Eqs. (3.84)–(3.86) and (3.91)–(3.93) show that B_0^{el} is dominated by B_0^{Stn} , i.e. by the contribution of the Stern layer, whereas k_c^{el} and \bar{k}_c^{el} contain a considerable contribution from the diffuse layer, that is from k_c^{dif} and \bar{k}_c^{dif} . The magnitude of B_0^{el} , k_c^{el} and \bar{k}_c^{el} is higher for lower electrolyte concentrations. For example, for $c_0 = 10^{-5}$ M one computes $B_0^{el} \approx 5 \times 10^{-11}$ N, $k_c^{el} \approx 1 \times 10^{-19}$ J and $\bar{k}_c^{el} \approx -3 \times 10^{-19}$ J [58].

3.3.2. BENDING MOMENT EFFECTS ON THE INTERACTION BETWEEN DROPS IN EMULSIONS

Interaction between deforming emulsion drops. The collisions between the drops in an emulsion are accompanied with a flattening in the zone of contact between such two drops, see Fig. 3.5. The conditions for the formation of a flat film between two similar droplets have been studied by Danov et. al. [60] and Denkov et al. [61]. A modeling of the shape of a deformed drop with portions of a sphere and a plane (Fig. 3.5) proved to be a very good approximation [62]. Despite the fact that area of the formed flat film is relatively small, its appearance leads to a strong enhancement (with dozens of kT) of the energy of interaction between the two drops.

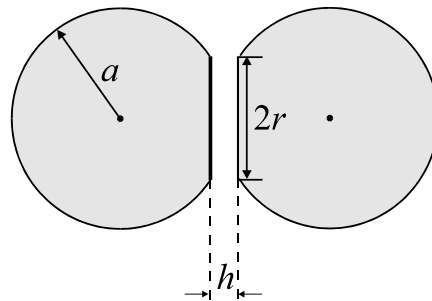


Fig. 3.5. Scheme of two emulsion drops deformed upon collision; the magnitude of the radius, r , of the formed flat film and its thickness, h , are exaggerated.

We have in mind interactions due to the various components of the disjoining pressure: electrostatic, van der Waals, steric, depletion, oscillatory-structural, etc., see Chapter 5 for details. It has been taken into account [61,63] that if an initially spherical droplet deforms at fixed volume, its surface area increases, which gives rise to an effective interdroplet repulsion. Moreover, work of flexural (bending) deformation is conducted when the initially spherical interface in the zone of contact is converted into the planar surface of the film (Fig. 3.5). To estimate this work one can use Eq. (3.7); viz. by expanding Eq. (3.7) in series, keeping linear terms with respect to the curvature one obtains [63]

$$W_f(H) \equiv 2\pi r^2 w_f = 2\pi r^2 (2k_c H_0^2 + B_0 H + \dots), \quad (r/a)^2 \ll 1. \quad (3.95)$$

cf. Eq. (3.10); here r is the radius of the flat film; the multiplier 2 accounts for the fact that the film has two surfaces. The increment of W_f , which is due to the formation of a flat film, is

$$\Delta W_f \equiv W_f(0) - W_f(H) = -2\pi r^2 B_0 H + O(H^2) = 2\pi r^2 B_0 / a + \dots \quad (3.96)$$

The bending moment can be estimated as follows: $|B_0| \approx |B_0^{vw} + B_0^{el}| \approx 5 \times 10^{-11} \text{ N}$, see the numerical values given above in this chapter. Using the latter value together with $kT = 4.1 \times 10^{-21} \text{ J}$ (room temperature) and a tentative value $r \approx a/20$, from Eq. (3.96) we estimate

$$|\Delta W_f| \approx (2 \times 10^6 \text{ cm}^{-1}) \times a kT \quad (3.97)$$

Consequently, for emulsion drops of radii $10^{-6} \text{ cm} < a < 10^{-4} \text{ cm}$ the contribution of the interfacial bending moment to the energy of interaction between two drops will be $2kT < |\Delta W_f| < 200kT$. In other words, we arrive at the conclusion that the interfacial bending moment B_0 could be important for the interactions between sub- μm , and even μm -sized, drops [63]. This conclusion is intriguing insofar as it is usually believed that the bending energy is essential only for objects of very high interfacial curvature, like the nuclei of a new fluid phase and the droplets in microemulsions.

It should be also noted that $B_0 > 0$ for emulsions type "oil-in-water", whereas $B_0 < 0$ for emulsions type "water-in-oil". Consequently, in view of Eq. (3.96) the energy of interfacial

bending deformation contributes to a *repulsion* between oil drops in water ($\Delta W_f > 0$), but to an *attraction* between water drops in oil ($\Delta W_f < 0$) [63]. For example, Koper et al. [64] have observed formation of doublets (with energy of bonding $\approx 10 kT$) from aqueous microemulsion drops dispersed in oil; this phenomenon could be attributed, at least in part, to the effect of $\Delta W_f < 0$.

Interactions between drops in double emulsions. As mentioned above, the effect of the interfacial bending moment B_0 can be important for emulsion systems of low interfacial tension. It has been demonstrated by Binks [65], that after intensive stirring in such systems one could observe a simultaneous formation of emulsion and microemulsion drops, see Fig. 3.6. Having in mind the above discussion, one expects that $\Delta W_f > 0$ helps for stabilization of the formed emulsion. Indeed, for $\Delta W_f > 0$ the bending moment opposes the flattening of the drops in the contact zone thus decreasing the probability for formation (and consecutive rupturing) of a thin liquid film between two colliding droplets; in other words, the bending moment counteracts the coalescence of emulsion drops. It is reasonable to assume that the condition $\Delta W_f > 0$ is fulfilled for the microemulsion drops, which do not increase their size with time, despite the intensive Brownian collisions between them. For the system depicted in Fig. 3.6a the microemulsion drops are in the *continuous* phase, i.e. the emulsion and microemulsion drops have the same sign of the curvature. Therefore, one could expect that

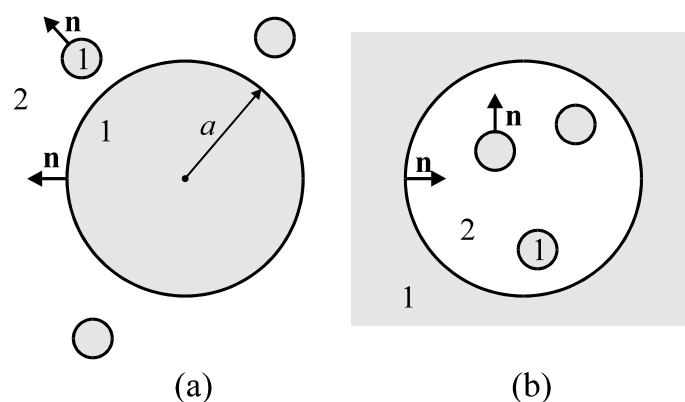


Fig. 3.6. Sketch of an emulsion drop coexisting with smaller microemulsion drops (a) in the continuous and (b) in the disperse phase. The running unit normal to the interface, \mathbf{n} , is directed from phase 1 toward phase 2.

$\Delta W_f > 0$ for the emulsion drops, as well. On the contrary, for the system depicted in Fig. 3.6b, that is the microemulsion drops are in the *disperse* phase, the emulsion and microemulsion drops have the opposite sign of the curvature, which is determined by the direction of the unit normal \mathbf{n} , see Eq. (3.21). Hence, if $\Delta W_f > 0$ for the *micro*-emulsion drops, then $\Delta W_f < 0$ for the emulsion drops. Consequently, for the system in Fig. 3.6b the bending moment contributes to an *attraction* between the emulsion drops and favors their coalescence.

According to Davies and Riedal [66] both types of emulsions, those from Fig. 3.6a,b and 3.6b, are formed upon stirring. That type of emulsion survives, for which the coalescence is slower. If the effect of the interfacial bending moment dominates the interactions between the emulsion droplets, one can expect that the emulsion in Fig. 3.6a will survive [63]. In fact, this is observed experimentally; viz. the emulsion which contains microemulsion drops in the continuous phase is more stable [65].

It is worthwhile noting that in emulsions the effect of the interfacial bending moment acts simultaneously with other type of interactions between the droplets, such as the surface forces of various origin: van der Waals interactions, electrostatic (double-layer), steric, depletion, oscillatory-structural, hydration and other forces. For that reason, the analysis of the stability of an emulsion needs a careful estimate of the relative contributions of various factors to the drop-drop interaction energy; see Ref. [67] for details.

It should be also noted that the bending effects may influence the stability of an emulsion when the rupturing of thin emulsion films happens through nucleation of pores, see e.g. Ref. [68].

3.4. SUMMARY

An interface (or membrane) possesses 4 modes of deformation: dilatation, shearing, bending and torsion (Fig. 3.1). The first couple of modes represent two-dimensional analogues of respective deformations in the bulk phases. The bending and torsion modes are related to variations in the two principle curvatures of the interface, that is to the presence of two additional degrees of freedom. From a *thermodynamic* viewpoint, the curvature effects can be accounted for as contributions of the work of interfacial bending and torsion to the total energy

of the system; the respective coefficients are the interfacial (surface) bending and torsion moments, B and Θ , see Eq. (3.1). The most popular model of the interfacial curvature effects provides an expression for the mechanical work of flexural deformation, Eq. (3.7), which involves 3 parameters: bending and torsion elastic moduli, k_c and \bar{k}_c , and spontaneous curvature, H_0 .

First we have considered the simpler case of spherical geometry. The dependence of the bending moment B on the choice of the dividing surface at fixed physical state of the system is investigated, see Eq. (3.32), (3.33) and Fig. 3.2. The connection between the quantities bending moment, Tolman length and spontaneous curvature has been demonstrated, see Eqs. (3.10) and (3.39). Micromechanical expressions, Eqs. (3.69) and (3.70), allow one to calculate the surface tension and the bending moment if an expression for the pressure tensor is available.

From the viewpoint of the microscopic theory, various intermolecular forces may contribute to the interfacial moments B , Θ , and to the curvature elastic moduli, k_c and \bar{k}_c , see Eqs. (3.72) and (3.73). Such are the *van der Waals* forces, Eq. (3.75), the *steric* interactions, Eq. (3.77) and the *electrostatic* interactions, Eqs. (3.78)–(3.80) and (3.82)–(3.93).

The interfacial bending moment may give an essential contribution to the interaction between deformable droplets in emulsions, see Eq. (3.96). In general, the curvature effects are expected to be significant for interfaces of low tension and high curvature. An example are the biomembranes, which usually have low tension. The present chapter is an introduction to the next Chapter 4, in which the general theory of curved interfaces and biomembranes is considered.

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