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► **To cite this version:**

M. M. Kozlov, V.S. Markin. Mechanics of interfaces: the stability of a spherical shape. Journal de Physique, 1990, 51 (6), pp.559-574. 10.1051/jphys:01990005106055900 . jpa-00212390

**HAL Id: jpa-00212390**

**<https://hal.science/jpa-00212390>**

Submitted on 4 Feb 2008

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Classification  
 Physics Abstracts  
 82.65D — 87.20C

## Mechanics of interfaces : the stability of a spherical shape

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(Reçu le 20 février 1989, révisé le 17 novembre 1989, accepté le 23 novembre 1989)

**Résumé.** — On considère les conditions de perte de stabilité d'une interface sphérique. Une interface arbitraire est caractérisé par des facteurs tels que tension de surface, le premier et le deuxième moments, les modules d'élasticité. Dans un état déformé, on suppose que les conditions d'équilibre à l'interface interne sont respectées. On obtient des expressions générales pour les critères de stabilité qui mettent en rapport les paramètres du système et la différence de pression entre phases homogènes séparées par l'interface. On considère les cas particuliers de membranes qui ne se dilatent pas et d'une interface ayant un petit module de dilatation.

**Abstract.** — Conditions are considered for the loss of stability of a spherical interface. An arbitrary interface is characterized by the force factors, such as surface tension, first and second moments, moduli of elasticity and cutting forces. In a deformed state the conditions of internal interface equilibrium are assumed to be satisfied. General expressions are obtained for the stability criterion which relate the system parameters and the pressure drop between homogeneous phases separated by the interface. Particular cases are considered of a non-expansible membrane and an interface with a small expansion modulus of elasticity.

### Introduction.

In recent years researchers have become quite active in a traditionally explored field of chemistry, thermodynamics of interfaces. This concerns the study of systems such as microemulsions, water solutions of amphiphilic substances, and biological membranes. The classical approach to the description of interfaces developed by Gibbs [1] and followed by others [2-8] involves the concept of force factors, namely the Gibbs surface tension and two moments,  $C_1$  and  $C_2$ . The interface shape is described in terms of the Gibbs dividing surface, a normal to which in every point coincides with the density gradients of the system components (as well as other thermodynamics quantities). According to this approach, the variations of the Helmholtz free energy of a piece of an interface may be described as

$$\delta F = -S^s dT + \sum_i \mu_i \delta n_i^s + \gamma_G \delta A + C_1 A \delta J + C_2 A \delta K \quad (1)$$

where  $T$  is the absolute temperature ;  $\mu_i$  is the chemical potential of the  $i$ -th component ;  $S^s$  and  $n_i^s$  are the excesses of entropy and the amount of the  $i$ -th component, determined with

respect to the Gibbs dividing surface ;  $A$  is the area of the considered piece of interface ;  $J$  is the sum of principal curvatures hereafter referred to as the mean curvature ;  $K$  is the product of principal curvatures to be referred to as the Gaussian curvature. Let us emphasize that extensive quantities in expression (1) have the meaning of differential quantities describing a piece of interface.

The force factors were postulated by Gibbs. However, within an approach involving assumptions of local thermodynamics, the force factors may be expressed in terms of the components of a microscopic pressure tensor [2, 3, 6-11]. In this case the interface is regarded as a continuous layer, with the pressure tensor being specified in every point.

In describing classical capillary systems in which the surface tension  $\gamma_G$  is high, the dependence of the force factors on deformation may be neglected. The systems belonging to another class (interfaces with the surfactant-containing microemulsions ; films of amphiphilic substances making up such structures as e.g. lipid mesophases and biological membranes) have a very low surface tension [12]. For the description of such systems in terms of thermodynamics the dependence of the force factors of an interface on its geometrical characteristics is significant. This means that an interface should be regarded as an elastic system characterized by the moduli of elasticity [10] :

extension-compression modulus of elasticity :

$$E_{AA} \equiv A \left( \frac{\partial^2 F}{\partial A^2} \right)$$

first modulus of bending elasticity :

$$E_{JJ} \equiv \frac{1}{A} \left( \frac{\partial^2 F}{\partial J^2} \right)$$

second modulus of bending elasticity :

$$E_{KK} \equiv \frac{1}{A} \left( \frac{\partial^2 F}{\partial K^2} \right)$$

moduli of elasticity for the mixed deformations :

$$E_{AJ} = E_{JA} = \left( \frac{\partial^2 F}{\partial J \partial A} \right)_K ; E_{AK} = E_{KA} = \left( \frac{\partial^2 F}{\partial K \partial A} \right)_J ; E_{JK} = E_{KJ} = \frac{1}{A} \left( \frac{\partial^2 F}{\partial K \partial J} \right)_A .$$

Moduli of elasticity may be expressed through the force factors as

$$\begin{aligned} E_{AA} &= \frac{\partial \gamma_G}{\partial \ln(A)} ; E_{JJ} = \frac{\partial C_1}{\partial J} ; E_{KK} = \frac{\partial C_2}{\partial K} \\ E_{AJ} &= C_1 + \frac{\partial C_1}{\partial \ln A} ; E_{AK} = C_2 + \frac{\partial C_2}{\partial \ln A} ; \\ E_{JK} &= \frac{\partial C_1}{\partial K} = \frac{\partial C_2}{\partial J} . \end{aligned} \quad (2)$$

On the basis of the relationships between the force factors and geometrical characteristics the spontaneous geometrical characteristics of an interface may be determined, viz. the spontaneous area  $A_s$ , the spontaneous mean curvature  $J_s$ , and the spontaneous Gaussian curvature  $K_s$ , all for the zero values of the force factors [10].

The description in terms of thermodynamics and mechanics presented in the above-mentioned references makes it possible to study the shape and stability of structures produced within the multi-phase systems. Experimental findings revealed a variety of such structures and confirmed the feasibility of their transformations into each other. The most illustrative examples are lipid-water mixtures and biological membranes. Lipids form bilayers in water, with the bilayer surfaces being formed by polar heads of lipid molecules, and the inner volume occupied by hydrocarbon tails. Unilamellar spherical vesicles, multi-lamellar spherical liposomes, and flat lamellar systems are the most wide-spread structures formed by the lipid bilayers. In systems with a low water content, lipids also form normal and inverted micelles, and normal and inverted cylinders within a hexagonal lattice ( $H_{II}$ -phase). When temperature, water content, or other external factors change, a phase transition occurs, followed by changes in the shape of lipid structures [13]. A biological membrane whose bulk is the lipid bilayer forms the cell envelope and largely dictates the cell shape [14]. An erythrocyte is mechanically the most interesting cell. Depending on the conditions, an erythrocyte is capable of assuming the shape of a biconcave disc (dyscoocyte), a sphere (spherocyte), a cup (stomatocyte), a sphere with spicules (echinocyte), etc. [14].

Characteristic shapes of the structures formed by interfaces correspond to the system's equilibrium state. When equilibrium is no longer stable, the shape changes. There are reports [15, 16] of the studies of interface stability. One paper [15] discusses the stability of an interface with force factors and no elasticity, i.e. the moduli of elasticity are equal to zero. Reference [16] is concerned with an opposite case where variations in free energy are wholly associated with the bending elasticity  $E_{JJ}$  which responds to the variations of the total curvature.

This paper considers the stability of a spherical interface shape. The contributions of all the force factors and moduli of elasticity to the stability criteria are taken into account.

**Statement of the problem.**

Let the interface be spherical with the radius  $r_0$ . There is a drop of hydrostatic pressure at the interface between the bulk phase and the interior volume of the vesicle. The thermodynamic properties of the interface are determined by the force factors, namely the surface tension  $\gamma_G$  and the first and the second moments  $C_1$  and  $C_2$ .

Variations of the free energy of a piece of interface of an area  $A$  in the process of isothermal deformation with a constant amount of components may be described as

$$\delta F = \gamma_G \delta A + C_1 \cdot A \cdot \delta J + C_2 \cdot A \cdot \delta K$$

where the functions  $\gamma_G(A, J, K)$ ,  $C_1(A, J, K)$  and  $C_2(A, J, K)$  allow for a potential redistribution of the components ; all the geometrical characteristics describe the dividing surface. Variations of the force factors during deformation are, by definition, expressed in terms of the interface moduli of elasticity [10].

$$\gamma_G = \gamma_G^0 + E_{AA} \frac{\delta A}{A} + E_{AJ} \cdot \delta J + E_{AK} \cdot \delta K \tag{3}$$

$$C_1 = C_1^0 + (E_{AJ} - C_1^0) \frac{\delta A}{A} + E_{JJ} \cdot \delta J + E_{JK} \cdot \delta K \tag{4}$$

$$C_2 = C_2^0 + (E_{AK} - C_2^0) \frac{\delta A}{A} + E_{JK} \delta J + E_{KK} \delta K \tag{5}$$

where  $\gamma_G^0$ ,  $C_1^0$  and  $C_2^0$  are the initial values of the force factors.

Let us consider the interface in the state of internal mechanical equilibrium. The condition of equilibrium force a piece of interface with respect to lateral displacements [9] is expressed as

$$\frac{\partial \gamma_G}{\partial x} - c_x Q_x = 0 \quad (6)$$

$$\frac{\partial \gamma_G}{\partial y} - c_y Q_y = 0. \quad (7)$$

In equations (6) and (7) the operators  $\partial/\partial x$  and  $\partial/\partial y$  denote differentiation in a system of coordinates whose axes  $(x, y)$  are in a plane which is tangential to the considered interface and coincide with the direction of the principal curvatures;  $c_x$  and  $c_y$  are the principal curvatures,  $Q_x$  and  $Q_y$  are the values of the cutting forces which are applied to the edges of the surface element and are perpendicular to the axes  $x$  and  $y$ . Equilibrium equations describing rotation may be written as

$$\frac{\partial C_1}{\partial x} + c_y \frac{\partial C_2}{\partial x} = Q_x \quad (8)$$

$$\frac{\partial C_1}{\partial y} + c_x \frac{\partial C_2}{\partial y} = Q_y. \quad (9)$$

The equilibrium equations (6)-(9) were obtained on the basis of [9] assuming the membrane thickness  $h$  to be much less than the radius of curvature  $r_0$ . In equations (6)-(9) the terms of a higher order than  $(h/r_0)^2$  were disregarded.

Let us consider a minor deformation of a spherical interface. This deformation may be assumed to be axially symmetrical, and the interface shape may be described by the function (Fig. 1) as

$$r(\varphi) = r_0(1 + \lambda \xi) \quad (10)$$

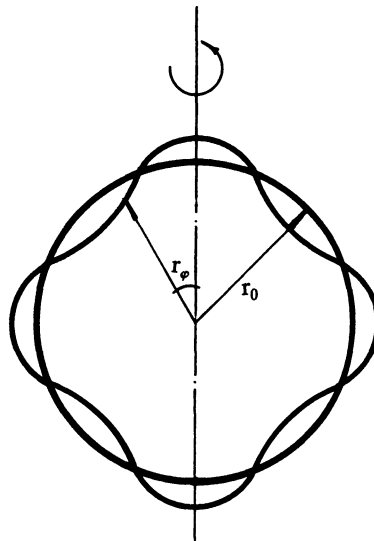


Fig. 1. — Axial symmetrical deformation of a spherical interface.

where  $r$  is the length of the radius vector drawn from the center of the sphere to a point on the dividing surface in the deformed state ;  $\varphi$  is the meridional angle ;  $\xi$  is the arbitrary angle function and  $\lambda$  is the deformation amplitude.

The curvatures and the element of the area of the dividing surface in the state of deformation may be presented, to an accuracy of the second-order terms with respect to  $\lambda$ , as

$$A = 2 \pi r_0^2 \sin \varphi \left[ 1 + 2 \lambda \xi + \lambda^2 \left( \xi^2 + \frac{1}{2} (\xi')^2 \right) \right] d\varphi \tag{11}$$

$$J = \frac{2}{r_0} \left\{ 1 - \lambda \left[ \xi + \frac{1}{2} \frac{(\xi' \sin \varphi)'}{\sin \varphi} \right] + \lambda^2 \xi \left[ \xi + \frac{(\xi' \sin \varphi)'}{\sin \varphi} \right] \right\} \tag{12}$$

$$K = \frac{1}{r_0^2} \left\{ 1 - 2 \lambda \left[ \xi + \frac{1}{2} \frac{(\xi' \sin \varphi)'}{\sin \varphi} \right] + 3 \lambda^2 \xi \left[ \xi + \frac{(\xi' \sin \varphi)'}{\sin \varphi} \right] + \lambda^2 \xi' \xi'' \operatorname{ctg} \varphi \right\} . \tag{13}$$

Let us assume that the deformed interface maintains an equilibrium and, in particular, the equation of lateral equilibrium (6) is satisfied. The objective of the investigation includes the study of the stability of a spherical interface to such deformations.

**Stability criteria.**

The thermodynamic stability of a spherically shaped interface is determined by the amount of work to be applied to the interface and its environment at a minor deformation. Zero work estimated in the first order of magnitude of deformation yields the condition of equilibrium between the interface and the bulk phases. The contribution made by the deformation of the second order of magnitude determines the stability of the equilibrium state. If the second order contribution is negative, equilibrium is unstable.

To determine the stability criterion, work must be calculated to an accuracy of the second order terms of deformation magnitude. By virtue of equations (1), (3)-(5) an elementary work applied to the deformed part of an interface and required for its further deformation is equal to

$$\begin{aligned} \delta W = & \left[ \gamma_G^0 + E_{AA} \frac{dA}{A} + E_{AJ} dJ + E_{AK} dK \right] \delta A + \\ & + \left[ C_1^0 + (E_{AJ} - C_1^0) \frac{dA}{A} + E_{JJ} dJ + E_{JK} dK \right] A \cdot \delta J \\ & + \left[ C_2^0 + (E_{AK} - C_2^0) \frac{dA}{A} + E_{JK} dJ + E_{KK} dK \right] A \cdot \delta K - \Delta P \cdot A \cdot \delta r . \tag{14} \end{aligned}$$

The last term in equation (14) is the work applied to the bulk phases, whereas  $\Delta P$  is equal to the difference between pressure values for the sphere interior and environment.

On the basis of the equation of lateral equilibrium (6) as well as equations (7)-(9), (3)-(5), (11)-(13), the relative expansion of an interface may be found (Appendix A) with an adequate accuracy yielding the solution

$$\frac{dA}{A} = \lambda V \int \xi \sin \varphi \, d\varphi + 2 \frac{\lambda}{r_0} \frac{m}{E_{AA}} \left[ \xi + \frac{1}{2} \frac{(\xi' \sin \varphi)'}{\sin \varphi} \right] \quad (15)$$

$$V = \frac{1 - \frac{1}{r_0} \frac{1}{E_{AA}} \left[ 2 E_{AJ} + 2 \frac{E_{AK}}{r_0} - \frac{E_{JJ}}{r_0} - 2 \frac{E_{JK}}{r_0^2} - \frac{E_{KK}}{r_0^3} - C_1^0 - \frac{C_2^0}{r_0} \right]}{1 - \frac{1}{r_0} \frac{1}{E_{AA}} \left[ E_{AJ} + \frac{E_{AK}}{r_0} - C_1^0 - \frac{C_2^0}{r_0} \right]}$$

$$m = \frac{E_{AJ} + \frac{E_{AK}}{r_0} - \frac{E_{JJ}}{r_0} - 2 \frac{E_{JK}}{r_0^2} - \frac{E_{KK}}{r_0^3}}{1 - \frac{1}{r_0} \frac{1}{E_{AA}} \left[ E_{AJ} + \frac{E_{AK}}{r_0} - C_1^0 - \frac{C_2^0}{r_0} \right]}$$

The expression for the deformation work obtained by integrating (14) over the deformation value and interface area may be presented, with an account for (11)-(13), (15), in the first order with respect to  $\lambda$  as

$$W_1 = 4 \pi r_0^2 \lambda \left( \gamma_G^0 - \frac{C_1^0}{r_0} - \frac{C_2^0}{r_0^2} - \frac{\Delta P r_0}{2} \right) \int d\varphi \cdot \sin \varphi \cdot \xi. \quad (16)$$

When  $W_1$  is zero at an arbitrary  $\xi$  an equilibrium equation may be written :

$$\gamma_G^0 - \frac{C_1^0}{r_0} - \frac{C_2^0}{r_0^2} = \frac{\Delta P r_0}{2} \quad (17)$$

which is a generalized Laplace equation for a spherical surface [9].

The second order work with respect to  $\lambda$  determines the stability of the spherical interface equilibrium and may be described (Appendix B) as

$$\begin{aligned} W_{II} = & 2 \pi r_0^2 \lambda^2 \left\{ \left[ \gamma_G^0 + \frac{C_2^0}{r_0^2} + \frac{2}{r_0} \left( m - E_{AJ} - \frac{E_{AK}}{r_0} \right) \right] \int \xi^2 \sin \varphi \, d\varphi + \right. \\ & + \frac{1}{2} \left[ \gamma_G^0 - \frac{2}{r_0} \left( m - E_{AJ} - \frac{E_{AK}}{r_0} \right) - \frac{2 C_1^0}{r_0} - \frac{3 C_2^0}{r_0^2} \right] \int \xi'^2 \sin \varphi \, d\varphi \\ & - \frac{2}{r_0^2} \left[ \frac{m}{E_{AA}} \left( E_{AJ} + \frac{E_{AK}}{r_0} - C_1^0 - \frac{C_2^0}{r_0} \right) - E_{JJ} - 2 \frac{E_{JK}}{r_0} - \frac{E_{KK}}{r_0^2} \right] \times \\ & \times \int \left[ \xi + \frac{1}{2} \frac{(\xi' \sin \varphi)'}{\sin \varphi} \right]^2 \sin \varphi \, d\varphi \\ & \left. + V \left[ E_{AA} - \frac{E_{AJ}}{r_0} - \frac{E_{AK}}{r_0^2} + \frac{C_1^0}{r_0} + \frac{C_2^0}{r_0^2} \right] \left( \int d\varphi \cdot \xi \cdot \sin \varphi \right)^2 \right\}. \quad (18) \end{aligned}$$

The work  $W_{II}$  to be applied to the environment and the spherical interface to deform the latter is determined by the type of the deformation  $\xi(\varphi)$  and by the interface parameters, such as the force factors associated with the initial state  $\gamma_G^0$ ,  $C_1^0$  and  $C_2^0$ , the moduli of elasticity  $E_{JJ}$ ,  $E_{AA}$ ,  $E_{KK}$ ,  $E_{AJ}$ ,  $E_{AK}$  and  $E_{JK}$ , and the pressure drop between the internal and external bulk phases.

It is convenient, and in most cases possible, to estimate the deformation  $\xi^*(\varphi)$  at which the system loses stability « for the first time ». Estimation of  $\xi^*$  is based on an assumption that there are values of the interface parameters for which the amount of work  $W_{II}$  required to implement the deformation  $\xi^*$  may be negative. For any other type of deformation  $\xi \neq \xi^*$ , however, the same values of the interface parameters result in a positive  $W_{II}$ ; in effect, the system is unstable only with respect to  $\xi^*$ .

The criterion for a loss of stability introduces a link between the force factors, the moduli of elasticity, and the pressure drop  $\Delta P$ , at which the spherical interface loses stability with respect to  $\xi^*$ .

Equation (18) appears to be too cumbersome for analysis ; let us consider extreme cases.

**NON-EXPANSIBLE INTERFACE.** — Let us consider an interface with a large extension-compression modulus of elasticity ( $E_{AA} \rightarrow \infty$ ). Such systems are represented by e.g. thin insoluble films and bilayer lipid membranes which do not exchange material with any reservoir during deformation. In this case the last term in equation (18) substantially exceeds all the other terms for an arbitrary form of deformation  $\xi$  and is positive. Therefore the deformation  $\xi^*$  at which stability is lost « for the first time » should comply with the zero value of this term

$$\int d\varphi \cdot \sin \varphi \cdot \xi^* = 0 . \tag{19}$$

This class of deformations will be analysed in this section. In this case equation (18) may be reduced to a simplified form where the surface tension  $\gamma_G^0$  is eliminated by using a generalized Laplace equation (17)

$$\begin{aligned} W_{II} = 2 \pi r_0^2 \lambda^2 \left\{ \left[ \frac{C_1^0}{r_0} + 2 \frac{C_2^0}{r_0^2} - \frac{\Delta P \cdot r_0}{2} \right] \int \xi^2 \sin \varphi \, d\varphi + \right. \\ \left. + \frac{1}{2} \left[ \frac{\Delta P r_0}{2} - \frac{C_1^0}{r_0} - 2 \frac{C_2^0}{r_0^2} - \frac{2}{r_0^2} \left( E_{JJ} + 2 \frac{E_{JK}}{r_0} + \frac{E_{KK}}{r_0^2} \right) \right] \int \xi'^2 \sin \varphi \, d\varphi \right. \\ \left. + \frac{1}{2 r_0^2} \left( E_{JJ} + 2 \frac{E_{JK}}{r_0} + \frac{E_{KK}}{r_0^2} \right) \int \frac{(\xi' \sin \varphi)^2}{\sin \varphi} \, d\varphi \right\} . \tag{20} \end{aligned}$$

The analysis of equation (20) reveals a relationship between the force factors and the interface moduli of elasticity for which the spherical shape becomes unstable. The deformation at which stability is lost « for the first time » is associated with a maximum characteristic wavelength of the perturbation imposed on the spherical interface. The longest-wave perturbation which satisfies equation (19) may be written as

$$\xi^* \sim \frac{1}{3} + \cos 2 \varphi . \tag{21}$$

The criterion of stability loss to deformation (21) can be expressed in terms of a pressure drop  $\Delta P$  equal to the difference between the pressure values for the bulk phase inside the sphere  $P_{in}$  and for the exterior bulk phase  $P_{out}$ ,  $\Delta P = P_{in} - P_{out}$ . The spherical shape loses stability if the pressure drop is less than the critical value

$$\Delta P < \Delta P_{cr}$$



where

$$\Delta P_{cr} \cdot r_0 = 2 \frac{C_1^0}{r_0} + 4 \frac{C_2^0}{r_0^2} - \frac{12}{r_0^2} \left( E_{JJ} + 2 \frac{E_{JK}}{r_0} + \frac{E_{KK}}{r_0^2} \right). \quad (22)$$

The value of the critical pressure drop  $\Delta P_{cr}$  which designates the boundary between the states of stable and unstable equilibrium of a spherical interface depends, in compliance with equation (22), on the moments  $C_1^0$  and  $C_2^0$ . As defined in references [8, 9], a positive value of the first moment  $C_1^0$  is related to a tendency of a part of the interface to reduce the total curvature or to cave in the sphere. Similarly, at a positive value of the second moment  $C_2^0$  that part of the interface tends to reduce the Gaussian curvature. The relationship between the critical value of the pressure drop  $\Delta P_{cr}$  and the moments is shown in figure 2. The unshaded area above the straight line represents a stable equilibrium of the spherical interface, whereas the shaded area below represents an unstable equilibrium of the system. Stability is lost in the points on the straight line.

Qualitatively, figure 2 suggests that for the fixed moments  $C_1^0$  and  $C_2^0$ , an increase in pressure inside the interface-formed sphere can bring the system to a stable equilibrium. Conversely, a decrease in the ambient pressure results in the destabilization of the spherical shape. With the value of  $\Delta P$  specified, at a greater  $C_1^0$  (the interface tends to cave in) and a greater  $C_2^0$  (a tendency to reduce the Gaussian curvature) the spherical shape may lose stability. The lesser and negative values of the moments stabilize the system.

Let us comment on the interceptions of the straight line and the axes (Fig. 2). If a sphere with radius  $r_0$  yields a spontaneous interface shape at  $C_1^0 = 0$  and  $C_2^0 = 0$ , the shape becomes unstable when there is a negative pressure drop equal to

$$\Delta P_{cr} = -\frac{12}{r_0^3} \left[ E_{JJ} + 2 \frac{E_{JK}}{r_0} + \frac{E_{KK}}{r_0^2} \right]. \quad (23)$$

If there is no pressure drop between two homogeneous phases,  $\Delta P = 0$ , the spherical interface is found to be unstable when the moments are large enough

$$C_1^0 + 2 \frac{C_2^0}{r_0} > \frac{6}{r_0} \left[ E_{JJ} + 2 \frac{E_{JK}}{r_0} + \frac{E_{KK}}{r_0^2} \right]. \quad (24)$$

Let us consider an even more specific case where the moments of a spherical interface may be linearly related to spontaneous curvatures [10]

$$\begin{aligned} C_1^0 &= E_{JJ}(J - J_s) + E_{JK}(K - K_s) \\ C_2^0 &= E_{JK}(J - J_s) + E_{KK}(K - K_s). \end{aligned} \quad (25)$$

In this case the criterion of the loss of stability relates the pressure drop, moduli of elasticity, and spontaneous curvatures as

$$\Delta P_{cr} \cdot r_0 = -\frac{8}{r_0^2} E_{JJ} - \frac{14}{r_0^3} E_{JK} - \frac{8}{r_0^4} E_{KK} - \frac{2}{r_0} \left( E_{JJ} + \frac{2}{r_0} E_{JK} \right) J_s - \frac{2}{r_0} \left( E_{JK} + \frac{2}{r_0} E_{KK} \right) K_s. \quad (26)$$

The relationship between the critical pressure drop  $\Delta P_{cr}$  and the spontaneous curvatures  $J_s$  and  $K_s$  is shown in figure 3. The unshaded area stands for a stable state, and the shaded area, for an unstable state of the spherical interface. At a specified value of  $\Delta P_{cr}$  a reduction

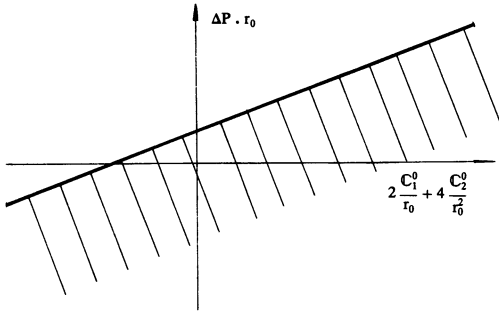


Fig. 2.

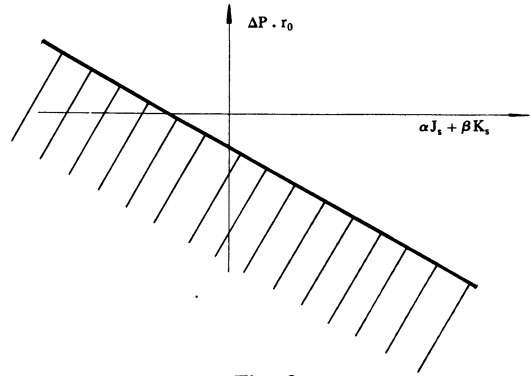


Fig. 3.

Fig. 2. — Stability criterion for a spherical non-expansible interface expressed in terms of the pressure drop and moments:  $\Delta P$  is the pressure drop between the bulk phase inside the sphere and environment;  $C_1^0$  and  $C_2^0$  are the first and second moments respectively; the shaded area designates the absence of a spherical shape.

Fig. 3. — Stability criterion for a spherical non-expansible interface: relationship between the pressure drop  $\Delta P$ , spontaneous total curvature  $J_s$ , and spontaneous Gaussian curvature  $K_s$ . The factors  $\alpha$  and  $\beta$  are expressed on the basis of the interface moduli of elasticity, as  $\alpha \equiv \frac{2}{r_0} \left( E_{JJ} + 2 \frac{E_{JK}}{r_0} \right)$ ;  $\beta \equiv \frac{2}{r_0} \left( E_{JK} + 2 \frac{E_{KK}}{r_0} \right)$ .

of spontaneous curvatures destabilizes the system. If the spontaneous state of the interface is flat,  $J_s = 0$ ,  $K_s = 0$ , the critical pressure value below which stability is lost is

$$\Delta P_{cr} = -\frac{8}{r_0^3} E_{JJ} - \frac{14}{r_0^4} E_{JK} - \frac{8}{r_0^5} E_{KK}. \tag{27}$$

According to equation (27), for a spherical interface with a zero spontaneous curvature of a sufficiently large radius (when the last two terms in the right-hand side may be neglected) the critical pressure drop is positive, i.e. the spherical shape may lose stability despite the pressure being higher inside than outside the sphere.

The stability criterion for a spherical interface may be expressed in terms of the Gibbs surface tension and the moments. A spherical shape corresponds to an equilibrium state of the system, thus the generalized Laplace equation (17) holds. Using this equation as a relationship between  $\Delta P$  and  $\gamma_G$ , we obtain a spherical shape which loses stability if the Gibbs surface tension is less than the critical value

$$\gamma_G < \gamma_{Gcr}$$

found as

$$\gamma_{cr} = 2 \frac{C_1^0}{r_0} + 3 \frac{C_2^0}{r_0^2} - \frac{6}{r_0^2} \left( E_{JJ} + 2 \frac{E_{JK}}{r_0} + \frac{E_{KK}}{r_0^2} \right).$$

The criterion of the loss of stability of a spherical shape of a non-expansible interface, expressed in terms of the Gibbs surface tension, is shown in figure 4. The shaded area stands for the absence of a stable equilibrium. Figure 4 shows, in particular, that at low and negative values of the moments

$$2 \frac{C_1^0}{r_0} + 3 \frac{C_2^0}{r_0^2} < \frac{6}{r_0^2} \left( E_{JJ} + 2 \frac{E_{JK}}{r_0} + \frac{E_{KK}}{r_0^2} \right)$$

the spherical shape is unstable even at some negative values of the surface tension  $\gamma_G$ . The spherical interface for which the moments are fairly large,

$$2 \frac{C_1^0}{r_0} + 3 \frac{C_2^0}{r_0^2} > \frac{6}{r_0^2} \left( E_{JJ} + 2 \frac{E_{JK}}{r_0} + \frac{E_{KK}}{r_0^2} \right)$$

loses stability even for positive values of the surface tension.

One case of an interface with a large elongation modulus of elasticity is a bilayer lipid membrane, which consists of two monolayers of lipid molecules. A spherical vesicle is a most often met membrane structure. A membrane is selectively permeable for water. Due to this the transmembrane pressure drop in the vesicles is osmotic. The force factors in the vesicle membrane, in particular the moments  $C_1^0$  and  $C_2^0$ , are related to both the structure of the lipid molecules forming monolayers and the interactions of monolayers (for more details, see [11]). The most frequent cause of the occurrence of moments in a bilayer lipid membrane is a non-optimum ratio of the numbers of molecules in the external and internal monolayers. For the moments to be absent in the membrane of a spherical vesicle, there must be fewer molecules in the internal monolayer than in the external one [11]. In this case, according to equation (23), a spherical vesicle remains stable even if the osmotic pressure inside is lower than outside (however, still being within the limits defined by Eq. (23)). If the number of molecules in the internal monolayer is equal to or greater than the respective number in the external monolayer, the positive values of  $C_1^0$  and  $C_2^0$  occur in the vesicle membrane [11]. In this case, as shown above, the spherical shape loses stability even for positive values of the transmembrane osmotic pressure drop. The loss of stability should obviously result in the membrane caving in and, possibly, in the phenomena resembling the endocytosis of live cells. To maintain a stable spherical shape in this situation, the concentration of an osmotically active substance inside the vesicle must be high enough to enable the pressure drop to exceed the critical value (27).

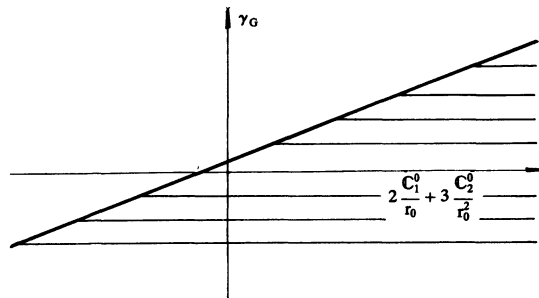


Fig. 4. — Stability criterion for a spherical non-expansible interface expressed in terms of the Gibbs surface tension  $\gamma_G^0$  and the moments  $C_1^0$  and  $C_2^0$ . Shaded area designates the absence of stability.

**An interface with a small extension-compression modulus of elasticity.**

Let us consider an interface whose extension-compression modulus of elasticity is small ( $E_{AA} \rightarrow 0$ ). This is the case of interfaces which are capable of exchanging components with the environment in the process of deformation (an extreme case of such a system is an interface of two pure liquids). In this case there is a weak dependence of the values of all force factors on the area  $A$  of a part of the interface. Using equation (2) which relates the moduli of elasticity with the force factors and neglecting the area derivatives of  $\gamma_G$ ,  $C_1$  and  $C_2$ , equation (18) may be rewritten as

$$\begin{aligned}
 W_{II} = & 2 \pi r_0^2 \lambda^2 \left\{ \left[ \frac{C_1^0}{r_0} + 2 \frac{C_2^0}{r_0^2} - \frac{\Delta P r_0}{2} \right] \int \xi^2 \sin \varphi \, d\varphi + \right. \\
 & + \frac{1}{2} \left[ \frac{\Delta P r_0}{2} - \frac{C_1^0}{r_0} - 2 \frac{C_2^0}{r_0^2} - \frac{2}{r_0} \left( E_{AJ} + \frac{E_{AK}}{r_0} \right) \right] \int \xi'^2 \sin \varphi \, d\varphi + \\
 & + \frac{1}{2 r_0} \left( E_{AJ} + \frac{E_{AK}}{r_0} \right) \int \frac{(\xi' \sin \varphi)^2}{\sin \varphi} \, d\varphi \\
 & \left. + \frac{1}{r_0} \left[ \frac{1}{r_0} E_{JJ} + \frac{2}{r_0^2} E_{JK} + \frac{1}{r_0^3} E_{KK} - 2 E_{AJ} - 2 \frac{E_{AK}}{r_0} + C_1^0 + \frac{C_2^0}{r_0} \right] \left( \int d\varphi \cdot \xi \cdot \sin \varphi \right)^2 \right\}. \quad (28)
 \end{aligned}$$

As in the case of a non-expansible interface, the stability of a spherical shape is « for the first time » lost to a deformation which has a maximum wavelength. In the case of the deformation specified as  $\xi = \mu + (1/3 + \cos 2 \varphi)$  the constant term determines the variation of the interface area ; the contribution of  $1/3 + \cos 2 \varphi$  is for the bending deformation at a constant area. In the case under consideration the work of an exterior source applied to a spherical interface in equilibrium and to the environment during deformation is equal to

$$\begin{aligned}
 W_{II} = & 2 \pi r_0^2 \lambda^2 \left\{ \frac{32}{45} \left[ \Delta P \cdot r_0 - 2 \frac{C_1^0}{r_0} - 4 \frac{C_2^0}{r_0^2} + \frac{12}{r_0} \left( E_{AJ} + \frac{E_{AK}}{r_0^2} \right) \right] - \right. \\
 & \left. - \mu^2 \left[ \Delta P \cdot r_0 - 3 \frac{C_1^0}{r_0} - 5 \frac{C_2^0}{r_0^2} - \frac{1}{r_0^2} \left( E_{JJ} + 2 \frac{E_{JK}}{r_0} + \frac{E_{KK}}{r_0^2} \right) + \frac{2}{r_0} \left( E_{AJ} + \frac{E_{AK}}{r_0} \right) \right] \right\}. \quad (29)
 \end{aligned}$$

Equation (29) shows that there are more chances for the loss of stability of a spherical shape of an expansible interface ( $E_{AA} \rightarrow 0$ ) than in the above case of a non-expansible interface ( $E_{AA} \rightarrow \infty$ ).

An expansible interface may lose stability in two ways. The first is similar to the above case of a non-expansible interface. In the case of deformation at  $\mu = 0$  for the pressure drop  $\Delta P$  (between the bulk phase inside the sphere and its environment) whose value is less than the critical one  $\Delta P_{cr}^{(1)}$

$$\Delta P_{cr}^{(1)} = 2 \frac{C_1^0}{r_0} + 4 \frac{C_2^0}{r_0^2} - \frac{12}{r_0} \left( E_{AJ} + \frac{E_{AK}}{r_0} \right)$$

the spherical shape of an expansible interface loses stability. The deformation for which stability is lost in this case amounts, as in the case of a non-expansible interface, to a flexure with the maintenance of the area (to an accuracy of the terms of the second-order infinitesimal for the deformation amplitude  $\lambda$ ).

For an expansible interface there is another way to lose stability, by virtue of the last term in the right-hand side of equation (29). If the coefficient by  $\mu^2$  is positive, then deformation, with the constant  $\mu$  being large enough, requires negative work to be done ; thus the system proves to be unstable to this deformation. Consequently, in the case of an expansible interface the system is characterized by one more critical pressure value  $\Delta P_{cr}^{(2)}$  equal to

$$\Delta P_{cr}^{(2)} \cdot r_0 = 3 \frac{C_1^0}{r_0} + 5 \frac{C_2^0}{r_0^2} + \frac{1}{r_0^2} \left( E_{JJ} + 2 \frac{E_{JK}}{r_0} + \frac{E_{KK}}{r_0^2} \right) - \frac{2}{r_0} \left( E_{AJ} + \frac{E_{AK}}{r_0} \right) .$$

If the pressure inside the sphere is high enough,

$$\Delta P > \Delta P_{cr}^{(2)} \tag{30}$$

the sphere loses stability for a deformation whose constant component  $\mu$  satisfies the inequality

$$\mu^2 > \frac{\frac{32}{45} \left[ \Delta P \cdot r_0 - 2 \frac{C_1^0}{r_0} - 4 \frac{C_2^0}{r_0^2} + \frac{12}{r_0} \left( E_{AJ} + \frac{E_{AK}}{r_0} \right) \right]}{\Delta P r_0 - 3 \frac{C_1^0}{r_0} - 5 \frac{C_2^0}{r_0^2} - \frac{1}{r_0^2} \left( E_{JJ} + 2 \frac{E_{JK}}{r_0} + \frac{E_{KK}}{r_0^2} \right) + \frac{2}{r_0} \left( E_{AJ} + \frac{E_{AK}}{r_0} \right)} \tag{31}$$

provided that the numerator in (31) is greater than zero. If the numerator is negative, stability is lost for deformations with any values of  $\mu$ .

The deformation for which the system loses stability entails an increase in the interface area, which actually amounts to a sphere bulging.

The criterion (30) of the loss of stability of an expansible spherical interface is illustrated in figure 5. The shaded area stands for the absence of a stable equilibrium of a spherical shape.

Both ways in which the stability of an expansible spherical interface may be lost are illustrated in figure 6. The unstable equilibrium of the system is represented by the unshaded area. The bulging-destabilized states are shown by vertically shaded area. The instability to a

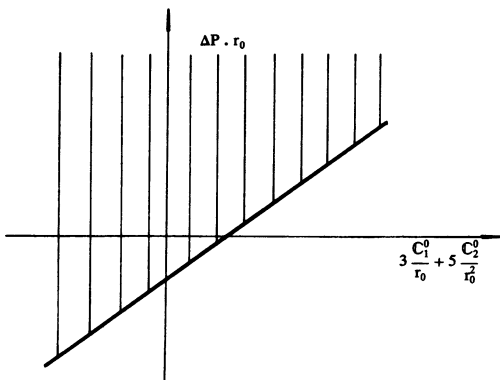


Fig. 5.

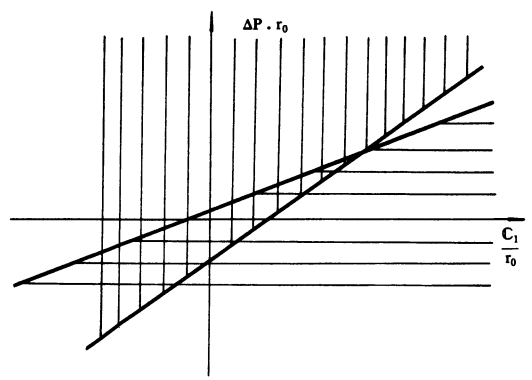


Fig. 6.

Fig. 5. — Stability criterion for a bulging deformation of a spherical interface. For notation, see figure 2. Shaded area designates the absence of a stable equilibrium.

Fig. 6. — Complete stability criterion for a spherical expansible interface. For notation, see figure 2. Unshaded area designates stable equilibrium. Shading designates the absence of stability : vertical, to expansion ; horizontal, to flexure ; crossed, to both types of deformation.

flexural deformation with no changes in the area is represented by horizontal shading. Finally, the area shaded both vertically and horizontally denotes the states in which the expansible spherical interface is unstable to both types of deformation.

An example of the systems discussed in this section is a drop of oil (or another liquid which does not mix with water) in water. For all the above effects to be possible, the internal volume of the drop must be able to exchange substances with the reservoir maintaining a constant pressure within the drop.

**Discussion.**

The paper discusses the conditions of thermodynamic stability of a spherical interface. The problem is solved by using the Gibbs approach to thermodynamics of interfaces extended to the case of elastic interfaces. Stability was studied for deformations that do not disturb the conditions of the internal interface equilibrium.

Equilibrium and stability criteria are defined with respect to axially symmetric perturbations. Such a loss of generality is compensated by the opportunity of analytical solution of the problem.

The investigation generalizes the available approaches to the study of the stability of structures formed by interfaces [15, 16]. In reference [15] the problem was solved within the Gibbs theory of capillarity for an elasticity-free interface of an arbitrary shape. Analysis reveals that for an interface whose moduli of elasticity and cutting components of the microscopic pressure tensor are zero, the equilibrium equation for the lateral direction holds only for the deformations involving a shift of every interface piece without an additional flexure. For this reason, the stability criteria were found only for that class of deformations [15].

The results of the present investigation include an analogue of the stability criterion for a spherical interface [15], viz. an inequality obtained for a membrane with a small elongation modulus ( $E_{AA} \rightarrow 0$ ) at which the spherical shape is unstable if  $\Delta P > \Delta P_{cr}^{(2)}$  (30).

Reference [16] discussed another extreme case, that of a non-expansible interface whose mechanical properties are described by using only the first-bending modulus of elasticity  $E_{JJ}$ . The authors [16] did not use the Gibbs approach ; they proceeded from a phenomenological formula for elastic bending energy which was originally derived and discussed by Helfrich [17]. The interface was assumed [16] to be completely non-expansible and the conditions of a lateral equilibrium during deformation was not discussed. Besides, the authors [16] did not study the response of the equilibrium condition to the elasticity-related factors for the deformations including changes in the Gaussian curvature, and to the factors related to the cutting components of a microscopic pressure tensor. The findings of the present investigation suggest that the spherical shape of a non-expansible interface ( $E_{AA} \rightarrow \infty$ ) may lose stability if the pressure drop between the homogeneous phases is less than the critical value  $\Delta P_{cr}$  obtained by equation (22). A particular case of expression (22) is

$$\Delta P_{cr} = - \frac{2}{r_0^2} E_{JJ} \left( \frac{4}{r_0} + 2 \cdot J_s \right) \tag{32}$$

where  $C_1$  was assumed to be related by equation (25) to the spontaneous total curvature  $J_s$  ; besides, all the factors in the Gaussian curvature and cutting components of a microscopic pressure tensor were neglected.

In the present investigation we took into account the full set of elasticity moduli and spontaneous geometrical characteristics of the membrane. The results of such a consideration give additional information about the dependence of instability criteria on the vesicle radius. It can be important for experimental investigations of the problem.

## Appendix A.

### Calculation of a relative expansion of a part of interface.

An equilibrium equation for the lateral interface displacement may be presented in the form of equation (6). Substituting in equation (6) an expression for the force factors where only the first order terms of the magnitude of deformation remain, it is possible, with an account for equations (3)-(5), (8)-(9) and (11)-(13), to integrate this expression, resulting in

$$\frac{dA}{A} \left[ E_{AA} - \frac{1}{r_0} E_{AJ} - \frac{1}{r_0^2} E_{AK} + \frac{1}{r_0} C_1^0 + \frac{1}{r_0^2} C_2^0 \right] - \frac{2}{r_0} \lambda \left[ E_{AJ} + \frac{E_{AK}}{r_0} - \frac{1}{r_0} \left( E_{JJ} + 2 \frac{E_{JK}}{r_0} + \frac{E_{KK}}{r_0^2} \right) \right] \left[ \xi + \frac{1}{2} \frac{(\xi' \sin \varphi)'}{\sin \varphi} \right] = \text{const.} \quad (\text{A1})$$

To find the constant in the right-hand side of equation (A1), let us integrate (A1) over the area of a non-deformed sphere, which yields

$$\text{const.} = \lambda \left[ E_{AA} - \frac{2}{r_0} \left( E_{AJ} + \frac{E_{AK}}{r_0} \right) + \frac{1}{r_0} \left( E_{JJ} + 2 \frac{E_{JK}}{r_0} + \frac{E_{KK}}{r_0^2} \right) + \frac{1}{r_0} \left( C_1^0 + \frac{C_2^0}{r_0} \right) \right] \times \int \xi \sin \varphi \, d\varphi. \quad (\text{A2})$$

The substitution of (A2) into (A1) and solution of the resulting equation for  $\frac{dA}{A}$  yields equation (15).

## Appendix B.

### Calculation of the work of interface deformation.

The work of interface deformation found by integrating equation (14) can be conveniently calculated by parts.

The elongation deformation work is

$$\delta W_1 = \left[ \gamma_G^0 + E_{AA} \cdot \frac{dA}{A} + E_{AJ} dJ + E_{AK} dK \right] \delta A.$$

The use of equations (11)-(13), (15) results in

$$\delta W_1 = 2 \pi r_0^2 \sin \varphi \left\{ \gamma_G^0 + \lambda V E_{AA} \int \xi \sin \varphi \, d\varphi + \frac{2}{r_0} \lambda \left[ m - E_{AJ} - \frac{E_{AK}}{r_0} \right] \cdot \left[ \xi + \frac{1}{2} \frac{(\xi' \sin \varphi)'}{\sin \varphi} \right] \right\} \cdot \left\{ 2 \xi + 2 \lambda \left( \xi^2 + \frac{1}{2} \xi'^2 \right) \right\} \delta \lambda \, d\varphi \quad (\text{B1})$$

where  $V$  and  $m$  are defined in the text.

The integration of equation (B1) over the angle  $d\varphi$  from 0 to  $\pi$  and over the deformation  $\delta \lambda$  from 0 to  $\lambda$  yields the following expression for the elongation deformation work

$$W_1 = 4 \pi r_0^2 \left\{ \lambda \gamma_G^0 \int \xi \sin \varphi \, d\varphi + \frac{\lambda^2}{2} \left[ \gamma_G^0 + \frac{2}{r_0} \left( m - E_{AJ} - \frac{E_{AK}}{r_0} \right) \right] \int \xi^2 \sin \varphi \, d\varphi + \frac{1}{2} \left[ \gamma_G^0 - \frac{2}{r_0} \left( m - E_{AJ} - \frac{E_{AK}}{r_0} \right) \right] \int \xi'^2 \sin \varphi \, d\varphi + V E_{AA} \left( \int d\xi \sin \varphi \, d\varphi \right)^2 \right\}. \quad (B2)$$

The work of the first-bending deformation is calculated in a similar way as

$$\begin{aligned} \delta W_2 = & -4 \pi r_0 \left\{ C_1^0 + (E_{AJ} - C_1^0) \lambda V \int \xi \sin \varphi \, d\varphi + \right. \\ & \left. + \frac{2}{r_0} \lambda \left[ \frac{(E_{AJ} - C_1^0)}{E_{AA}} m - E_{JJ} - \frac{E_{JK}}{r_0} \right] \left[ \xi + \frac{1}{2} \frac{(\xi' \sin \varphi)'}{\sin \varphi} \right] \right\} \\ & \times [1 + 2 \lambda \xi] \left\{ \left[ \xi + \frac{1}{2} \frac{(\xi' \sin \varphi)'}{\sin \varphi} \right] - 2 \lambda \xi \left[ \xi + \frac{(\xi' \sin \varphi)'}{\sin \varphi} \right] \right\} \delta \lambda \sin \varphi \, d\varphi. \end{aligned} \quad (B3)$$

Integration of (B3) results in the expression

$$\begin{aligned} W_2 = & - (4 \pi r_0) \left\{ \lambda C_1^0 \int \xi \sin \varphi \, d\varphi + \right. \\ & \left. + \frac{1}{2} \lambda^2 \left\{ C_1^0 \int \xi'^2 \sin \varphi \, d\varphi + V (E_{AJ} - C_1^0) \left( \int \xi \sin \varphi \, d\varphi \right)^2 \right. \right. \\ & \left. \left. + \frac{2}{r_0} \left[ \frac{(E_{AJ} - C_1^0)}{E_{AA}} m - E_{JJ} - \frac{E_{JK}}{r_0} \int \xi + \frac{1}{2} \frac{(\xi' \sin \varphi)'}{\sin \varphi} \right]^2 \sin \varphi \, d\varphi \right\} \right\}. \end{aligned} \quad (B4)$$

And finally the work of the second flexure is

$$\begin{aligned} \delta W_3 = & -4 \pi \left\{ C_2^0 + (E_{AK} - C_2^0) \lambda V \int \xi \sin \varphi \, d\varphi + \right. \\ & \left. + \frac{2}{r_0} \lambda \left[ \frac{(E_{AK} - C_2^0)}{E_{AA}} m - E_{JK} - \frac{E_{KK}}{r_0} \right] \left[ \xi + \frac{1}{2} \frac{(\xi' \sin \varphi)'}{\sin \varphi} \right] \right\} (1 + 2 \lambda \xi) \\ & \times \left\{ \left[ \xi + \frac{1}{2} \frac{(\xi' \sin \varphi)'}{\sin \varphi} \right] - 3 \lambda \xi \left[ \xi + \frac{(\xi' \sin \varphi)'}{\sin \varphi} \right] - \lambda \xi' \xi'' \operatorname{ctg} \varphi \right\} \delta \lambda \sin \varphi \, d\varphi. \end{aligned} \quad (B5)$$

Integration yields

$$\begin{aligned} W_3 = & -4 \pi \left\{ \lambda C_2^0 \int \xi \sin \varphi \, d\varphi + \right. \\ & \left. + \frac{\lambda^2}{2} \left[ -C_2^0 \int \xi^2 \sin \varphi \, d\varphi + \frac{3}{2} C_2^0 \int \xi'^2 \sin \varphi \, d\varphi + (E_{AK} - C_2^0) V \left( \int \xi \sin \varphi \, d\varphi \right)^2 \right. \right. \\ & \left. \left. + \frac{2}{r_0} \left[ \frac{(E_{AK} - C_2^0)}{E_{AA}} m - E_{JK} - \frac{E_{KK}}{r_0} \int \left[ \xi + \frac{1}{2} \frac{(\xi' \sin \varphi)'}{\sin \varphi} \right]^2 \sin \varphi \, d\varphi \right] \right\} \right\}. \end{aligned} \quad (B6)$$

The total of equations (B2), (B4) and (B6) presents a complete expression for the work of interface deformation.



## References

- [1] GIBBS G. W., The collected works (Longmans-Green, New York) 1928, Vol. 2.
- [2] RUSANOV A. I., Phasengleichgewichte und Grenzflächener Scheinungen (Academia Verlag, Berlin) 1978.
- [3] BUFF F. P., *J. Chem. Phys.* **25** (1956) 146.
- [4] MELROSE J. C., *Ind. Eng. Chem.* **60** (1968) 53.
- [5] BORUVKA L., NEUMANN A. W., *J. Chem. Phys.* **66** (1977) 5464.
- [6] ROTENBERG V., BORUVKA L., NEUMANN A. W., *Langmuir* **2** (1986) 533.
- [7] BORUVKA L., ROTENBERG V., NEUMANN A. W., *Langmuir* **1** (1985) 10.
- [8] MARKIN V. S., KOZLOV M. M., LEIKIN S. L., *J. Chem. Soc. Faraday Trans. 2* **84** (1988) 1149.
- [9] KOZLOV M. M., MARKIN V. S., *J. Chem. Soc. Faraday Trans. 2* **85** (1989) 261.
- [10] KOZLOV M. M., LEIKIN S. L., MARKIN V. S., *J. Chem. Soc. Faraday Trans.* **85**, 277.
- [11] KOZLOV M. M., MARKIN V. S., *Biologicheskije Membrany* **5** (1988) 1013 (in Russ.).
- [12] DE GENNES P. G., TAUPIN C., *J. Phys. Chem.* **86** (1982) 2294.
- [13] GRUEN D. W. R., MARCELJA S., PARSEGAN V., Cell Surface Dynamics, Eds. A. S. Perelson, C. Delisi, F. W. Wiegel (Marcel Dekker, New York-Basel) 1984, p. 54.
- [14] BESSIS M., Living blood cells and their ultrastructure (Springer-Verlag, Berlin) 1973.
- [15] NEOGI P., MYUNGSOO KIM, FRIBERG S. E., *J. Phys. Chem.* **91** (1987) 605.
- [16] ZHONG-CAN O.-Y., HELFRICH W., *Phys. Rev. Lett.* **59** (1987) 2486.
- [17] HELFRICH W., *Z. Naturforsch.* **28** (1973) 693.