Molecular Physics, Vol. 103 No. 21-23 2005, pp 2911-2922

Taylor & Francis
Taylor & Francis Group

Local mechanical equilibrium conditions for interfaces and thin films of arbitrary shape*

ANATOLY I. RUSANOV and ALEKSANDR K. SHCHEKIN†
Mendeleev Centre, St. Petersburg State University, 199034 St. Petersburg, Russia

(*Received 21 March 2005; in final form 21 April 2005*)

A general approach to thermodynamics of arbitrarily and non-uniformly curved interfaces and films is formulated on the basis of the total non-diagonal pressure tensor including the case of external fields. The concept of a dividing surface is reformulated and generalized. The local mechanical equilibrium conditions are derived for interfaces and thin films containing not completely developed surface layers. A more general definition of the disjoining pressure is given for thin films non-uniform in thickness. The cases of flat, wedge-shaped, cylindrical and spherical films are analysed. The mechanical equilibrium condition including the disjoining and capillary pressures is derived for the surface of the transitional zone of a wetting film on a flat substrate. The results obtained are compared with the literature data.

1. Introduction

Among numerous relationships of interfacial mechanics and thermodynamics, the conditions of local mechanical equilibrium seem to be the most widely known, especially for a uniformly curved isotropic interface in a fluid system. In this simplest case, the condition of mechanical equilibrium along an interface is typically reduced to the constancy of surface tension and the condition of equilibrium across the interface is given by the classical Laplace (also named Young–Laplace) equation for the capillary pressure

$$P^{\alpha} - P^{\beta} = \gamma(c_1 + c_2) \tag{1}$$

where P is the pressure, γ is the surface tension, $c_1 \equiv 1/R_1$ and $c_2 \equiv 1/R_2$ are the principal surface curvatures (R_1 and R_2 are the principal curvature radii), and superscripts α and β are the symbols of adjacent bulk phases. As a real interface is a three-dimensional non-uniform region and curvature is a geometrical notion, Gibbs [1] specialized equation (1) by introducing a geometrical dividing surface and investigated the dependence of surface tension on the dividing surface location. Further development and generalization of the mechanical equilibrium condition proceeded (mainly during the second half of the 20th century) along the lines of accounting for the effects of high curvature of small objects and interfacial and bulk anisotropy, the non-uniformity of surface curvature, and the influence of external fields leading to a non-diagonal form of the pressure and surface tension tensors [2–21]. Here, we present general and simultaneously simple-in-form relationships describing the interfacial mechanical equilibrium condition.

The situation with thin films looks intricate. A thin film is a more complex object than an interface. Because of deficiency of space, the surface layers of a thin film are incompletely developed and overlap each other. This has two consequences. First, the tension of a thin film is not equal to the sum of surface tensions on the film sides (or to the double surface tension in the case of a symmetrical film). Thus, the surface tension of a thin film (we shall give a corresponding definition below) differs from ordinary interfacial tension. Second, an additional mechanical–thermodynamic quantity, the disjoining pressure, appears as a state parameter of a film. For a flat thin film between bulk phases β and γ (we use superscript α for the mother phase of the film), the film tension γ^f (not to be confused with the phase symbol γ used as a superscript only), the surface tensions of the film sides σ^{β} and σ^{γ}, and the disjoining pressure Π are related by the equation [22]

$$\gamma^f = \sigma^{\beta} + \sigma^{\gamma} + \Pi H \tag{2}$$

†Devoted to Professor Ben Widom in honour of his outstanding contribution to colloid and interface science.

*Corresponding author. Email: akshch@list.ru

Molecular Physics
ISSN 0026–8976 print/ISSN 1362–3028 online © 2005 Taylor & Francis Group Ltd
http://www.tandf.co.uk/journals
DOI: 10.1080/00268970500151510

where H is the film thickness. The thermodynamics of thin films [22] also yields the relationship

$$\frac{\partial(\sigma^\beta + \sigma^\gamma)}{\partial H} = -\Pi(H) \tag{3}$$

The disjoining pressure was first defined by Derjaguin [23] (see also [24]) as the difference between an external pressure P^β and the pressure P^α in the film mother phase provided it has the same values of temperature and chemical potentials as in the film:

$$\Pi \equiv P^\beta - P^\alpha \tag{4}$$

A modified definition was suggested by Rusanov and Kuni [25] as

$$\Pi \equiv P_N - P^\alpha \tag{5}$$

where P_N is the normal component of the pressure tensor inside a film. Although the definitions expressed in (4) and (5) are identical for flat films, the significance of equation (5) is in its local character. In principle, this allows one to extend the definition also to films of arbitrary shape (we shall give examples below).

Although the theory of thin films was formulated mainly for plane-parallel films, there were attempts to analyse films having a complicated shape. The most popular object was the transitional zone between a liquid bulk phase and a wetting thin film covering a horizontal flat solid surface. For the free surface of the transitional zone of variable thickness H, Derjaguin suggested the mechanical equilibrium condition [23, 24]

$$\gamma(c_1 + c_2) + \Pi(H) = P_c \tag{6}$$

where γ is the surface tension of the free surface, P_c is the capillary pressure (i.e. $P^\alpha - P^\beta$ or $P^\beta - P^\alpha$) of an equilibrium drop or a meniscus. This approach was used in a number of publications [26–30] (other references are given in review [31]) and was applied, in particular, for estimating the line tension at wetting. A modification of equation (6) was also suggested including the additional factor $\cos\varphi$ where φ is the local slope angle at the film/fluid interface [32, 33]. However, in all publications, the disjoining pressure was used locally as defined for a flat film, and the results are applicable only to slightly non-uniform (in thickness) films. Below, we describe a general and rigorous approach to characterize the mechanical equilibrium condition for a non-uniform thin film with arbitrary slopes of its surfaces and an arbitrary gradient of its thickness. To formulate the equilibrium condition, the concept of dividing surface is required both for interfaces and thin films. However, this important concept of surface thermodynamics itself needs a reformulation, and we begin with consideration of this problem.

2. Reformulation of the dividing surface concept

As already mentioned, the dividing surface concept was introduced by Gibbs. However, Gibbs did not give a mathematically exact definition and confined himself rather to an intuitive description from which a reader can understand the following. First, a dividing surface should reproduce a real shape of an interface. Second, the location of a dividing surface can be chosen arbitrarily. After Gibbs, the following procedure is typically used for shifting a dividing surface: if a particular dividing surface is given, other positions of the dividing surface can be found by consistently relocating all its points along a surface normal by a definite (the same for all points) distance. Mathematically, all surfaces obtained in this way are conformal to each other, so that surface relief reproduction is understood as conformity in this case. If we imagine orthogonal curvilinear coordinates u_1, u_2, u_3 whose coordinate surface $u_1 - u_2$ coincides with a dividing surface, we can say that the third coordinate line is restricted to be straight in the above approach.

An idea of a more general approach [17, 18] can be formulated as follows. The interfacial region is typically characterized at every point by the density (concentration) gradient. The family of gradient lines forms interfacial metrics, which, as is usual, is characterized by the metric tensor

$$g_{ik} \equiv \boldsymbol{r}_{u_i} \cdot \boldsymbol{r}_{u_k} = \sum_{j=1}^{3} (\partial x_j/\partial u_i)(\partial x_j/\partial u_k) \quad (i,k = 1,2,3) \tag{7}$$

where $\boldsymbol{r}$ is the radius vector of a space point, $\boldsymbol{r}_{u_i}$ is its partial derivative with respect to the curvilinear coordinate u_i (vector $\boldsymbol{r}_{u_i}$ is directed along the tangent to the coordinate line u_i); $x_1 \equiv x$, $x_2 \equiv y$, and $x_3 \equiv z$ are the Cartesian space coordinates, the dot symbolizes a scalar product of vectors. It is seen from equation (7) that an orthogonal coordinate system diagonalizes the metric tensor, so that only the components g_{ii} remain. The square roots of g_{ii} are also known as the Lame coefficients $h_i = r_{u_i} = \sqrt{g_{ii}}$ yielding the length elements $dl_i = h_i du_i$. We now define the coordinate surface $u_1 - u_2$ of such a coordinate system as a dividing surface. In other words, we define a dividing surface as the coordinate surface normal to the direction of gradients in an orthogonal curvilinear coordinate system that diagonalizes the metric tensor of an interfacial region.

The equation of a dividing surface is given by the condition

$$u_3 = u_{30} \tag{8}$$

where u_{30} is a constant that can be chosen arbitrarily. Passing from one to another position of a dividing surface now proceeds not along the normal straight line to the surface, but along the coordinate line u_3, which can be curved (e.g. because of the influence of external fields). In this complex case, positions of a dividing surface separated by a finite distance are not conformal any more. However, differentiation along the normal coincides with that along the u_3 coordinate since we deal with an orthogonal coordinate system.

A dividing surface possesses a network of coordinate lines and has its own two-dimensional metrics obeying the following rules. First, in accordance with the Dupin theorem of differential geometry, the coordinate lines coincide with the surface curvature lines in the coordinate system chosen. In other words, the curvatures c_1 and c_2 along the directions u_1 and u_2 are the principal curvatures (maximum and minimum among all the surface curvatures at a given point). Second, the simple Rodrigues formula is valid:

$$\boldsymbol{n}_{u_i} = \boldsymbol{r}_{u_i} c_i \quad (i = 1, 2) \tag{9}$$

where $\boldsymbol{n}$ is the unit vector normal to a dividing surface. Equation (9) shows that the variation of surface orientation at moving along a coordinate line is determined only by the curvature in a given direction. For the displacement of an elementary fragment of a dividing surface along the coordinate line u_3, we have the relation

$$\frac{\partial \ln l_i}{h_3 \partial u_3} = \frac{\partial \ln h_i}{h_3 \partial u_3} = c_i \quad (i = 1, 2) \tag{10}$$

where l_i is the length of the coordinate line u_i. We shall use these relationships below.

3. The mechanical equilibrium condition for an interfacial element

We select, with the coordinate surfaces, an element of the interfacial zone between bulk phases α and β (figure 1). Let the element be located in between the coordinates u_1, $u_1 + \Delta u_1$; u_2, $u_2 + \Delta u_2$; and u_3^α, u_3^β (superscripts α and β mark quantities on the corresponding phase side, but not necessarily related to the phases themselves; the element is arbitrary not only in width, but also in height and may not cover the whole thickness of the interface). The condition of mechanical

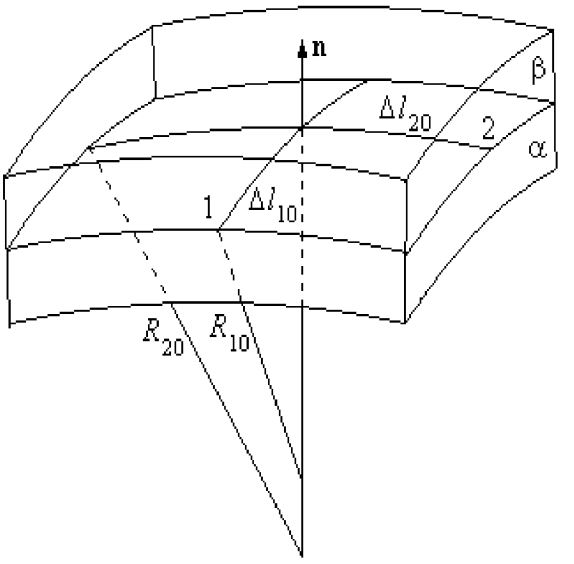


Figure 1. Element of a curved interface.

equilibrium for a given element states that the total force acting on the element is zero, that is

$$-\oint (\mathbf{P} \cdot \mathrm{d}A) = -\oint \boldsymbol{P}\, \mathrm{d}A = 0 \tag{11}$$

where $\mathbf{P}$ is the total pressure tensor (including the contribution of external fields if any [18]), $\mathrm{d}\boldsymbol{A} = \nu\, \mathrm{d}A$ is the vector of the element surface differential (ν is the unit vector of the outer normal to the element surface, A is the surface area), $-\boldsymbol{P} = -\mathbf{P} \cdot \nu$ is the vector of force applied to the unit element surface (the stress vector), the integration is carried out over the whole closed surface of the element. The element surface includes six facets. Correspondingly, the integral in equation (11) splits into six summands (we shall now supply each vector $\boldsymbol{P}$ with a subscript indicating the facet orientation). The integrals for the lower and upper facets are written as $\boldsymbol{P}_3(u_3^\alpha)\Delta l_1(u_3^\alpha)\Delta l_2(u_3^\alpha)$ and $\boldsymbol{P}_3(u_3^\beta)\Delta l_1(u_3^\beta)$ $\Delta l_2(u_3^\beta)$ where $\Delta l_1 = h_1 \Delta u_1$ and $\Delta l_2 = h_2 \Delta u_2$ are the portions of the coordinate lines u_1 and u_2 falling into the element chosen on the level of a corresponding facet. We have $\mathrm{d}A_1 = \Delta l_2\, \mathrm{d}l_3 = \Delta l_2 h_3\, \mathrm{d}u_3$ for the facet perpendicular to direction 1, and $\mathrm{d}A_2 = \Delta l_1\, \mathrm{d}l_3 = \Delta l_1 h_3\, \mathrm{d}u_3$ for the facet perpendicular to direction 2. We shall write the integrals pairwise as differences since the forces acting on subtending facets are directed oppositely. We now represent equation (11) as

$$\boldsymbol{P}_3(u_3^\alpha)\Delta l_1(u_3^\alpha)\Delta l_2(u_3^\alpha) - \boldsymbol{P}_3(u_3^\beta)\Delta l_1(u_3^\beta)\Delta l_2(u_3^\beta) - \Delta \int_{u_3^\alpha}^{u_3^\beta} \boldsymbol{P}_1 \Delta l_2 h_3\, \mathrm{d}u_3 - \Delta \int_{u_3^\alpha}^{u_3^\beta} \boldsymbol{P}_2 \Delta l_1 h_3\, \mathrm{d}u_3 = 0 \tag{12}$$

where the sign Δ before a quantity symbolizes its increment when passing from one opposite facet to the other along directions 1 and 2.

We now place, inside the element, a dividing surface with a certain coordinate u_{30} and the area $\Delta l_{10}\Delta l_{20}$. The dividing surface divides the element under consideration into the parts α and β (figure 1), each on the side of a corresponding phase. We now imagine part α to be filled with the matter of phase α, and part β with the matter of phase β under the condition of mechanical equilibrium. By analogy with equation (12), we may write separately for each part

$$\boldsymbol{P}_3^{\alpha}(u_3^{\alpha})\Delta l_1(u_3^{\alpha})\Delta l_2(u_3^{\alpha}) - \boldsymbol{P}_3^{\alpha}(u_{30}^{\alpha})\Delta l_{10}\Delta l_{20} - \Delta\int_{u_3^{\alpha}}^{u_{30}} \boldsymbol{P}_1^{\alpha}\Delta l_2 h_3\,\mathrm{d}u_3 - \Delta\int_{u_3^{\alpha}}^{u_{30}} \boldsymbol{P}_2^{\alpha}\Delta l_1 h_3\,\mathrm{d}u_3 = 0, \quad (13)$$

$$\boldsymbol{P}_3^{\beta}(u_{30})\Delta l_{10}\Delta l_{20} - \boldsymbol{P}_3^{\beta}(u_3^{\beta})\Delta l_1(u_3^{\beta})\Delta l_2(u_3^{\beta}) - \Delta\int_{u_{30}}^{u_3^{\beta}} \boldsymbol{P}_1^{\beta}\Delta l_2 h_3\,\mathrm{d}u_3 - \Delta\int_{u_{30}}^{u_3^{\beta}} \boldsymbol{P}_2^{\beta}\Delta l_1 h_3\,\mathrm{d}u_3 = 0 \quad (14)$$

Subtracting equations (13) and (14) from equation (12), we arrive at the expression

$$[\boldsymbol{P}_3^{\alpha}(u_{30}) - \boldsymbol{P}_3^{\beta}(u_{30})]\Delta l_{10}\Delta l_{20} + [\boldsymbol{P}_3(u_3^{\alpha}) - \boldsymbol{P}_3^{\alpha}(u_3^{\alpha})]\Delta l_1(u_3^{\alpha})\Delta l_2(u_3^{\alpha}) - [\boldsymbol{P}_3(u_3^{\beta}) - \boldsymbol{P}_3^{\beta}(u_3^{\beta})]\Delta l_1(u_3^{\beta})\Delta l_2(u_3^{\beta}) + \Delta\sigma_1\Delta l_{20} + \Delta\sigma_2\Delta l_{10} = 0 \quad (15)$$

where we have introduced the element tension vectors

$$\sigma_1 \equiv \frac{1}{\Delta l_{20}}\left[\int_{u_3^{\alpha}}^{u_{30}} (\boldsymbol{P}_1^{\alpha} - \boldsymbol{P}_1)\Delta l_2 h_3\,\mathrm{d}u_3 + \int_{u_{30}}^{u_3^{\beta}} (\boldsymbol{P}_1^{\beta} - \boldsymbol{P}_1)\Delta l_2 h_3\,\mathrm{d}u_3\right] \quad (16)$$

$$\sigma_2 \equiv \frac{1}{\Delta l_{10}}\left[\int_{u_3^{\alpha}}^{u_{30}} (\boldsymbol{P}_2^{\alpha} - \boldsymbol{P}_2)\Delta l_1 h_3\,\mathrm{d}u_3 + \int_{u_{30}}^{u_3^{\beta}} (\boldsymbol{P}_2^{\beta} - \boldsymbol{P}_2)\Delta l_1 h_3\,\mathrm{d}u_3\right] \quad (17)$$

Physically, σ_1 and σ_2 represent, for each of the cross-sections of the interfacial element, excess stresses at the lines Δl_{20} and Δl_{10}, respectively. A difference between the vectors σ_1 and σ_2 gives evidence of the two-dimensional anisotropy of an interface, while equality corresponds to isotropic states.

The last step remains. We divide equation (15) by $\Delta l_{10}\Delta l_{20}$ and let Δu_1 and Δu_2, as well as Δl_{10} and Δl_{20}, decrease to zero to proceed to a rigorous local relationship. Then the mechanical equilibrium condition finally takes the form

$$\boldsymbol{P}_3^{\alpha}(u_{30}) - \boldsymbol{P}_3^{\beta}(u_{30}) = -\frac{\partial\sigma_1}{\partial l_{10}} - \frac{\partial\sigma_2}{\partial l_{20}} - [\boldsymbol{P}_3(u_3^{\alpha}) - \boldsymbol{P}_3^{\alpha}(u_3^{\alpha})]\frac{h_1(u_3^{\alpha})h_2(u_3^{\alpha})}{h_{10}h_{20}} + [\boldsymbol{P}_3(u_3^{\beta}) - \boldsymbol{P}_3^{\beta}(u_3^{\beta})]\frac{h_1(u_3^{\beta})h_2(u_3^{\beta})}{h_{10}h_{20}} \quad (18)$$

with

$$\sigma_1 \equiv \frac{1}{h_{20}}\left[\int_{u_3^{\alpha}}^{u_{30}} (\boldsymbol{P}_1^{\alpha} - \boldsymbol{P}_1)h_2 h_3\,\mathrm{d}u_3 + \int_{u_{30}}^{u_3^{\beta}} (\boldsymbol{P}_1^{\beta} - \boldsymbol{P}_1)h_2 h_3\,\mathrm{d}u_3\right] \quad (19)$$

$$\sigma_2 \equiv \frac{1}{h_{10}}\left[\int_{u_3^{\alpha}}^{u_{30}} (\boldsymbol{P}_2^{\alpha} - \boldsymbol{P}_2)h_1 h_3\,\mathrm{d}u_3 + \int_{u_{30}}^{u_3^{\beta}} (\boldsymbol{P}_2^{\beta} - \boldsymbol{P}_2)h_1 h_3\,\mathrm{d}u_3\right] \quad (20)$$

Equation (18) is very general and applicable to an interface of any nature and aggregative state. As is seen from equations (19) and (20), the mechanical surface anisotropy (when $\sigma_1 \neq \sigma_2$) is not necessarily related to the anisotropy of bulk phases and can be realized even at the boundary of isotropic phases, for example, as a result of the surface shape anisotropy.

Passing to the analysis of equation (18), we first have to formulate three scalar relationships contained in this vector equation. Let us introduce the unit vectors $\boldsymbol{e}_1$, $\boldsymbol{e}_2$, and $\boldsymbol{e}_3$ along the coordinate lines of the above coordinate system and write the expressions

$$\boldsymbol{P}_3 = \sum_{i=1}^{3} P_{i3}\boldsymbol{e}_i \quad (21)$$

$$\sigma_k = \sum_{i=1}^{3} \sigma_{ik}\boldsymbol{e}_i \quad (k = 1, 2) \quad (22)$$

where the additional subscript i refers to the vector components along direction i. Putting equations (21)

and (22) in (18) yields

$$\sum_{i=1}^{3}[P_{i3}^{\alpha}(u_{30})-P_{i3}^{\beta}(u_{30})]\boldsymbol{e}_i = -\sum_{i=1}^{3}\frac{\partial\sigma_{i1}}{\partial l_{10}}\boldsymbol{e}_i-\sum_{i=1}^{3}\gamma_{i1}\frac{\partial\boldsymbol{e}_i}{\partial l_{10}}-\sum_{i=1}^{3}\frac{\partial\gamma_{i2}}{\partial l_{20}}\boldsymbol{e}_i-\sum_{i=1}^{3}\sigma_{i2}\frac{\partial\boldsymbol{e}_i}{\partial l_{20}} -\sum_{i=1}^{3}[P_{i3}(u_3^{\alpha})-P_{i3}^{\alpha}(u_3^{\alpha})]\frac{h_1(u_3^{\alpha})h_2(u_3^{\alpha})}{h_{10}h_{20}}\boldsymbol{e}_i+\sum_{i=1}^{3}[P_{i3}(u_3^{\beta}) -P_{i3}^{\beta}(u_3^{\beta})]\frac{h_1(u_3^{\beta})h_2(u_3^{\beta})}{h_{10}h_{20}}\boldsymbol{e}_i \tag{23}$$

To evaluate the derivatives of the unit vectors, we use the standard Serret–Frenet formulas of differential geometry

$$\mathrm{d}\boldsymbol{t}/\mathrm{d}l=c\boldsymbol{n},\quad \mathrm{d}\boldsymbol{n}/\mathrm{d}l=-c\boldsymbol{t}+T\boldsymbol{b},\quad \mathrm{d}\boldsymbol{b}/\mathrm{d}l=-T\boldsymbol{n} \tag{24}$$

where $\boldsymbol{t}$ is the unit vector of the tangent to a space line (a coordinate line in our case), $\boldsymbol{n}$ is the unit vector of the line principal normal, $\boldsymbol{b}$ is the unit vector of the binormal, c is the line curvature, T is the line torsion (to be zero for the above coordinate system), and l is the line length. For the coordinate lines on the dividing surface, we have $\boldsymbol{t}=\boldsymbol{e}_1$, $\boldsymbol{n}=-\boldsymbol{e}_3$, and $\boldsymbol{b}=-\boldsymbol{e}_2$ for $l\equiv l_{10}$ and $\boldsymbol{t}=\boldsymbol{e}_2$, $\boldsymbol{n}=-\boldsymbol{e}_3$, and $\boldsymbol{b}=-\boldsymbol{e}_1$ for $l\equiv l_{20}$. Applying now equation (10), we obtain the following expressions for the unit vector derivatives:

$$\frac{\partial\boldsymbol{e}_1}{\partial l_{10}}=-\frac{\boldsymbol{e}_3}{R_{10}},\quad \frac{\partial\boldsymbol{e}_2}{\partial l_{10}}=0,\quad \frac{\partial\boldsymbol{e}_3}{\partial l_{10}}=\frac{\boldsymbol{e}_1}{R_{10}} \tag{25}$$

$$\frac{\partial\boldsymbol{e}_2}{\partial l_{20}}=-\frac{\boldsymbol{e}_3}{R_{20}},\quad \frac{\partial\boldsymbol{e}_1}{\partial l_{20}}=0,\quad \frac{\partial\boldsymbol{e}_3}{\partial l_{20}}=\frac{\boldsymbol{e}_2}{R_{20}} \tag{26}$$

where R_{10} and R_{20} are the principal curvature radii of the dividing surface.

After putting equations (25) and (26) in equation (23) and subsequent scalar multiplying equation (23) by $\boldsymbol{e}_1$, $\boldsymbol{e}_2$, and $\boldsymbol{e}_3$, we obtain three scalar equations

$$P_{13}^{\alpha}(u_{30})-P_{13}^{\beta}(u_{30}) =-\frac{\sigma_{31}}{R_{10}}-\frac{\partial\sigma_{11}}{\partial l_{10}}-\frac{\partial\sigma_{12}}{\partial l_{20}}-[P_{13}(u_3^{\alpha})-P_{13}^{\alpha}(u_3^{\alpha})]\frac{h_1(u_3^{\alpha})h_2(u_3^{\alpha})}{h_{10}h_{20}} +[P_{13}(u_3^{\beta})-P_{13}^{\beta}(u_3^{\beta})]\frac{h_1(u_3^{\beta})h_2(u_3^{\beta})}{h_{10}h_{20}} \tag{27}$$

$$P_{23}^{\alpha}(u_{30})-P_{23}^{\beta}(u_{30}) =-\frac{\sigma_{32}}{R_{20}}-\frac{\partial\sigma_{21}}{\partial l_{10}}-\frac{\partial\sigma_{22}}{\partial l_{20}}-[P_{23}(u_3^{\alpha})-P_{23}^{\alpha}(u_3^{\alpha})]\frac{h_1(u_3^{\alpha})h_2(u_3^{\alpha})}{h_{10}h_{20}} +[P_{23}(u_3^{\beta})-P_{23}^{\beta}(u_3^{\beta})]\frac{h_1(u_3^{\beta})h_2(u_3^{\beta})}{h_{10}h_{20}} \tag{28}$$

$$P_{33}^{\alpha}(u_{30})-P_{33}^{\beta}(u_{30}) =\frac{\sigma_{11}}{R_{10}}+\frac{\sigma_{22}}{R_{20}}-\frac{\partial\sigma_{31}}{\partial l_{10}}-\frac{\partial\sigma_{32}}{\partial l_{20}} -[P_{33}(u_3^{\alpha})-P_{33}^{\alpha}(u_3^{\alpha})]\frac{h_1(u_3^{\alpha})h_2(u_3^{\alpha})}{h_{10}h_{20}} +[P_{33}(u_3^{\beta})-P_{33}^{\beta}(u_3^{\beta})]\frac{h_1(u_3^{\beta})h_2(u_3^{\beta})}{h_{10}h_{20}} \tag{29}$$

It is of note that the quantities σ_{12} and σ_{21} are not equal since the vectors σ_1 and σ_2 are determined by two different equations, (16) and (17). It also follows from equations (16) and (17) that all the quantities σ_{11}, σ_{12}, σ_{31}, σ_{32}, σ_{21}, and σ_{22} in equations (27)–(29) depend not only on the choice of the dividing surface location, but also on the choice of coordinates u_3^{α} and u_3^{β}. Below, we regard some particular cases of equations (27)–(29).

4. The mechanical equilibrium condition at an interface

In the case of an ordinary interface, an interfacial element considered in the preceding section (figure 1) can be chosen so that its upper and lower boundaries are located inside bulk phases α and β. Then both the differences in brackets in equation (18) vanish, whereas the element tension vectors σ_1 and σ_2 given by equations (19) and (20) are converted into the vector components γ_1 and γ_2 of the surface tension tensor. As a result, equation (18) is reduced to its simplest form [19, 20]

$$\boldsymbol{P}_3^{\alpha}(u_{30})-\boldsymbol{P}_3^{\beta}(u_{30})=-\frac{\partial\gamma_1}{\partial l_{10}}-\frac{\partial\gamma_2}{\partial l_{20}} \tag{30}$$

where the surface tension vectors γ_1 and γ_2 are defined as

$$\gamma_1\equiv\frac{1}{h_{20}}\left[\int_{-\infty}^{u_{30}}(\boldsymbol{P}_1^{\alpha}-\boldsymbol{P}_1)h_2h_3\,\mathrm{d}u_3+\int_{u_{30}}^{\infty}(\boldsymbol{P}_1^{\beta}-\boldsymbol{P}_1)h_2h_3\,\mathrm{d}u_3\right] \tag{31}$$

$$\gamma_2\equiv\frac{1}{h_{10}}\left[\int_{-\infty}^{u_{30}}(\boldsymbol{P}_2^{\alpha}-\boldsymbol{P}_2)h_1h_3\,\mathrm{d}u_3+\int_{u_{30}}^{\infty}(\boldsymbol{P}_2^{\beta}-\boldsymbol{P}_2)h_1h_3\,\mathrm{d}u_3\right] \tag{32}$$

One may understand the integral infinite limits in equations (31) and (32) as any coordinates beyond the interfacial region (where the integrands become zero). Note that the simplicity of the mechanical equilibrium condition was attained by using vector notations in equation (30). Earlier tensorial formulations for the general case [16, 21] looked much more complicated. As compared with all previous formulations, equation (30) also has an advantage in generality since it was derived

under the assumption that the normal-to-interface coordinate line was curved.

Correspondingly to equation (30), equations (27)–(29), after passing to an ordinary interface, take the forms

$$P_{13}^{\alpha}(u_{30}) - P_{13}^{\beta}(u_{30}) = -\frac{\gamma_{31}}{R_{10}} - \frac{\partial \gamma_{11}}{\partial l_{10}} - \frac{\partial \gamma_{12}}{\partial l_{20}} \tag{33}$$

$$P_{23}^{\alpha}(u_{30}) - P_{23}^{\beta}(u_{30}) = -\frac{\gamma_{32}}{R_{20}} - \frac{\partial \gamma_{21}}{\partial l_{10}} - \frac{\partial \gamma_{22}}{\partial l_{20}} \tag{34}$$

$$P_{33}^{\alpha}(u_{30}) - P_{33}^{\beta}(u_{30}) = \frac{\gamma_{11}}{R_{10}} + \frac{\gamma_{22}}{R_{20}} - \frac{\partial \gamma_{31}}{\partial l_{10}} - \frac{\partial \gamma_{32}}{\partial l_{20}} \tag{35}$$

As the pressure tensor is formed under the influence of the spatial distribution of matter, it is natural to suppose that, in the absence of external fields, the diagonalization of the metric tensor also leads to the diagonalization of the pressure tensor, which, in turn, causes the diagonalization of the surface tension tensor. Since we have chosen the coordinate system that diagonalizes the metric tensor, we can assume that, in the absence of external fields, all off-diagonal tensorial components are zeroes in equations (33)–(35). For this simple case, equations (33)–(35) become

$$\frac{\partial \gamma_{11}}{\partial l_{10}} = 0 \tag{36}$$

$$\frac{\partial \gamma_{22}}{\partial l_{20}} = 0 \tag{37}$$

$$P_{33}^{\alpha}(u_{30}) - P_{33}^{\beta}(u_{30}) = \frac{\gamma_{11}}{R_{10}} + \frac{\gamma_{22}}{R_{20}} \tag{38}$$

Equation (38) is the generalized Laplace equation derived first by Buff [2, 3] for anisotropic systems. Passing to mechanically isotropic phases, equation (38) changes to the classical Laplace equation.

For mechanically anisotropic interfaces, the scalar surface tension γ can be defined as

$$\gamma \equiv \frac{\gamma_{11} + \gamma_{22}}{2} \tag{39}$$

Introducing also the local mean curvature of the dividing surface

$$c \equiv \frac{1}{2}\left(\frac{1}{R_{10}} + \frac{1}{R_{20}}\right) \equiv \frac{c_1 + c_2}{2} \tag{40}$$

and using the identity

$$2\gamma c \equiv \gamma_{11} c_1 + \gamma_{22} c_2 - \frac{1}{2}(\gamma_{11} - \gamma_{22})(c_1 - c_2) \tag{41}$$

we can rewrite the mechanical equilibrium condition across an interface, equation (38), in the form

$$P_{33}^{\alpha}(u_{30}) - P_{33}^{\beta}(u_{30}) = 2\gamma c + \frac{1}{2}(\gamma_{11} - \gamma_{22})(c_1 - c_2) \tag{42}$$

It is seen from equation (41) that returning the local mechanical equilibrium condition to its classical Laplace form is possible both because of the isotropy of surface tension and surface curvature.

The surface tension vectors defined by equations (31) and (32) are dependent on the dividing surface location. To show this dependence explicitly, it is enough to differentiate equations (31) and (32) with respect to u_{30} or l_{30} at a given physical state with accounting for equation (10). In particular, for the principal components γ_{11} and γ_{22} and for the surface tension γ, we have

$$\frac{\partial \gamma_{11}}{\partial l_{30}} + \frac{\gamma_{11}}{R_{20}} = P_{11}^{\alpha}(l_{30}) - P_{11}^{\beta}(l_{30}) \tag{43}$$

$$\frac{\partial \gamma_{22}}{\partial l_{30}} + \frac{\gamma_{22}}{R_{10}} = P_{22}^{\alpha}(l_{30}) - P_{22}^{\beta}(l_{30}) \tag{44}$$

$$\frac{\partial \gamma}{\partial l_{30}} + \gamma c - \frac{1}{4}(\gamma_{11} - \gamma_{22})(c_1 - c_2) = \frac{P_{11}^{\alpha}(l_{30}) + P_{22}^{\alpha}(l_{30})}{2} - \frac{P_{11}^{\beta}(l_{30}) + P_{22}^{\beta}(l_{30})}{2} \tag{45}$$

For the case of isotropic and uniform bulk phases, equation (45) can be written as

$$\frac{\partial \gamma}{\partial l_{30}} + \gamma c - \frac{1}{4}(\gamma_{11} - \gamma_{22})(c_1 - c_2) = P^{\alpha} - P^{\beta} \tag{46}$$

The above surface tension components were defined as excess quantities by integrating over two principal cross-sections of an interface. Such a surface tension is equivalent to the real interface by force and is called force-defined surface tension. In the thermodynamics of curved interfaces, there is also moment-defined surface tension, which is equivalent to a real interface by the moment and derived as an excess quantity by integrating over the interfacial volume. The general definition of the

moment-defined surface tension tensor γ_{ik}^{m} is [18]

$$\gamma_{ik}^{m} = \frac{1}{h_{10}h_{20}}\left[\int_{-\infty}^{u_{30}} (P_{ik}^{\alpha} - P_{ik})h_1h_2h_3\,\mathrm{d}u_3 + \int_{u_{30}}^{\infty} (P_{ik}^{\beta} - P_{ik})h_1h_2h_3\,\mathrm{d}u_3\right] \quad (47)$$

The isotropic surface tension is again defined as

$$\gamma^{m} \equiv \frac{\gamma_{11}^{m} + \gamma_{22}^{m}}{2} \quad (48)$$

As follows from equations (31), (32), and (47), all the components of the force- and moment-defined surface tensions are identical for a flat interface (the consequence of the fact that all the Lame coefficients are unities in Cartesian coordinates) but generally different for curved interfaces. However, it is possible to find such a position of a dividing surface (Gibbs' surface of tension) for which the isotropic force- and moment-defined surface tensions, γ and γ^{m} are equal. This condition can be written as [18]

$$\gamma_{11} + \gamma_{22} = \gamma_{11}^{m} + \gamma_{22}^{m} \quad (49)$$

The components γ_{ik}^{m} are also dependent on the dividing surface location. Using equation (10) and differentiating equation (47) with respect to u_{30} or l_{30} at a given physical state, we obtain for the principal components of the surface tension tensor and the isotropic surface tension

$$\frac{\partial\gamma_{11}^{m}}{\partial l_{30}} + \gamma_{11}^{m}\left(\frac{1}{R_{10}} + \frac{1}{R_{20}}\right) = P_{11}^{\alpha} - P_{11}^{\beta} \quad (50)$$

$$\frac{\partial\gamma_{22}^{m}}{\partial l_{30}} + \gamma_{22}^{m}\left(\frac{1}{R_{10}} + \frac{1}{R_{20}}\right) = P_{22}^{\alpha} - P_{22}^{\beta} \quad (51)$$

$$\frac{\partial\gamma^{m}}{\partial l_{30}} + 2\gamma^{m}c = \frac{P_{11}^{\alpha}(l_{30}) + P_{22}^{\alpha}(l_{30})}{2} - \frac{P_{11}^{\beta}(l_{30}) + P_{22}^{\beta}(l_{30})}{2} \quad (52)$$

In the case of isotropic bulk phases, equation (52) becomes

$$\frac{\partial\gamma^{m}}{\partial l_{30}} + 2\gamma^{m}c = P^{\alpha} - P^{\beta} \quad (53)$$

and is a generalization of the known Kondo equation for a spherical interface [34]. In the completely isotropic case, it follows from equations (38) and (53) that the condition

$$\frac{\partial\gamma^{m}}{\partial l_{30}} = 0 \quad (54)$$

should be fulfilled for the surface of tension when $\gamma^{m} = \gamma$. Equation (54) was formulated by Kondo [34] as a minimum of γ^{m} and was understood for a long time as an indication of the surface of tension. In this capacity, however, equation (54) fails for anisotropic interfaces and should be replaced by equation (49) that is an actual attribute of the surface of tension. Indeed, it follows from (52), (49), and (42) for the surface of tension:

$$\frac{\partial\gamma^{m}}{\partial l_{30}} = \frac{1}{2}(\gamma_{11} - \gamma_{22})(c_1 - c_2) + \left[\frac{P_{11}^{\alpha} + P_{22}^{\alpha}}{2} - P_{33}^{\alpha}\right] - \left[\frac{P_{11}^{\beta} + P_{22}^{\beta}}{2} - P_{33}^{\beta}\right] \quad (55)$$

Equation (55) shows that the validity of equation (54) for the surface of tension is possible only a totally isotropic system (both in bulk phases and at an interface). For a simple cylindrical interface as an example, a minimum of surface tension does exist in the $\gamma^{m}(l_{30})$ curve, but the minimum location does not correspond to the position of surface of tension [18].

Returning to the general case, the right-hand sides of equations (45) and (52) are identical. This leads to the relationship

$$\frac{\partial\gamma}{\partial l_{30}} + \gamma c - \frac{1}{4}(\gamma_{11} - \gamma_{22})(c_1 - c_2) = \frac{\partial\gamma^{m}}{\partial l_{30}} + 2\gamma^{m}c \quad (56)$$

Equation (56) shows that, in spite of the equality of the force- and moment-defined surface tensions ($\gamma^{m} = \gamma$) for the surface of tension, their derivatives always remain different, including the case of total isotropy when equation (56) is reduced to

$$\frac{\partial\gamma}{\partial l_{30}} = \frac{\partial\gamma^{m}}{\partial l_{30}} + \gamma^{m}c \quad (57)$$

Since we derived the local mechanical equilibrium conditions at interface in terms of the force-defined surface tension, we need expressions relating the force- and moment-definitions to each other. To obtain such relationships, we first represent equations for γ_{11}^{m}, γ_{22}^{m}, γ_{11} and γ_{22} in a slightly different form. Let us take the dividing surface for the origin of a scale for l_3 and introduce a new variable $\lambda \equiv l_3 - l_{30}$. Expanding h_i in a power series of λ in the vicinity of h_{i0} yields

$$h_i = h_{i0}(1 + c_i\lambda) \quad (58)$$

which is a strict result for the case of a rectilinear coordinate u_3 (when all higher order terms are zeros) or, in general, an approximation for the case when the effective thickness of the interface is small as compared with the curvature radii R_{i0}. Using equation (58), we obtain from equations (47), (31), and (32)

$$\gamma_{ii}^{\mathrm{m}} = \int_{-\infty}^{\infty} (P_{ii}^{\alpha,\beta} - P_{ii})(1 + c_1\lambda)(1 + c_2\lambda)\,\mathrm{d}\lambda \tag{59}$$

$$\gamma_{11} = \int_{-\infty}^{\infty} (P_{11}^{\alpha,\beta} - P_{11})(1 + c_2\lambda)\,\mathrm{d}\lambda \tag{60}$$

$$\gamma_{22} = \int_{-\infty}^{\infty} (P_{22}^{\alpha,\beta} - P_{22})(1 + c_1\lambda)\,d\lambda \tag{61}$$

where $P_{ii}^{\alpha,\beta} \equiv P_{ii}^{\alpha}$ for $\lambda < 0$ and $P_{ii}^{\alpha,\beta} \equiv P_{ii}^{\beta}$ for $\lambda > 0$ ($i = 1, 2$). By differentiating equation (59) with respect to c_1 or c_2, we obtain the following expressions relating the principal values of surface tension and the isotropic surface tensions in the force and moment definitions:

$$\gamma_{11} = \gamma_{11}^{\mathrm{m}} - \frac{\partial \gamma_{11}^{\mathrm{m}}}{\partial \ln c_1} \tag{62}$$

$$\gamma_{22} = \gamma_{22}^{\mathrm{m}} - \frac{\partial \gamma_{22}^{\mathrm{m}}}{\partial \ln c_2} \tag{63}$$

$$\gamma = \gamma^{\mathrm{m}} - \frac{1}{2}\left(\frac{\partial \gamma_{11}^{\mathrm{m}}}{\partial \ln c_1} + \frac{\partial \gamma_{22}^{\mathrm{m}}}{\partial \ln c_2}\right) \tag{64}$$

Of course, equations (62)–(64) obeys the above restrictions related to equation (58).

5. The mechanical equilibrium condition at the surface of a thin film

We now return to equations (27)–(29) and apply them to one of the sides of a thin film. Let α be the film mother phase and β the surrounding medium adjacent to the film side under consideration. Obviously, the film surface layer on the outer side is developed completely, and this allows us to choose the u_3^{β} coordinate as located inside phase β. Then $\boldsymbol{P}_3(u_3^{\beta}) = \boldsymbol{P}_3^{\beta}(u_3^{\beta})$, and the last term in equation (18) disappears. As a consequence, equations (27)–(29) take the form

$$P_{13}^{\alpha}(u_{30}) - P_{13}^{\beta}(u_{30}) = -\frac{\sigma_{31}}{R_{10}} - \frac{\partial \sigma_{11}}{\partial l_{10}} - \frac{\partial \sigma_{12}}{\partial l_{20}} - [P_{13}(u_3^{\alpha}) - P_{13}^{\alpha}(u_3^{\alpha})]\frac{h_1(u_3^{\alpha})h_2(u_3^{\alpha})}{h_{10}h_{20}} \tag{65}$$

$$P_{23}^{\alpha}(u_{30}) - P_{23}^{\beta}(u_{30}) = -\frac{\sigma_{32}}{R_{20}} - \frac{\partial \sigma_{21}}{\partial l_{10}} - \frac{\partial \sigma_{22}}{\partial l_{20}} - [P_{23}(u_3^{\alpha}) - P_{23}^{\alpha}(u_3^{\alpha})]\frac{h_1(u_3^{\alpha})h_2(u_3^{\alpha})}{h_{10}h_{20}} \tag{66}$$

$$P_{33}^{\alpha}(u_{30}) - P_{33}^{\beta}(u_{30}) = \frac{\sigma_{11}}{R_{10}} + \frac{\sigma_{22}}{R_{20}} - \frac{\partial \sigma_{31}}{\partial l_{10}} - \frac{\partial \sigma_{32}}{\partial l_{20}} - [P_{33}(u_3^{\alpha}) - P_{33}^{\alpha}(u_3^{\alpha})]\frac{h_1(u_3^{\alpha})h_2(u_3^{\alpha})}{h_{10}h_{20}} \tag{67}$$

where the coordinate u_3^{α} demarcates two film parts relayed to the opposite sides of the film. Since a thin film is non-uniform everywhere inside, the choice of the coordinate u_3^{α} is pure conditional. If there are no external fields and bulk phases α and β are not only uniform, but also isotropic, all the off-diagonal elements of the bulk pressure tensors, as well as the corresponding components of vectors $\boldsymbol{P}_3^{\alpha}$ and $\boldsymbol{P}_3^{\beta}$, are zeroes. Then equations (65) and (66) become even simpler:

$$\frac{\sigma_{31}}{R_{10}} + \frac{\partial \sigma_{11}}{\partial l_{10}} + \frac{\partial \sigma_{12}}{\partial l_{20}} + P_{13}(u_3^{\alpha})\frac{h_1(u_3^{\alpha})h_2(u_3^{\alpha})}{h_{10}h_{20}} = 0 \tag{68}$$

$$\frac{\sigma_{32}}{R_{20}} + \frac{\partial \sigma_{21}}{\partial l_{10}} + \frac{\partial \sigma_{22}}{\partial l_{20}} + P_{23}(u_3^{\alpha})\frac{h_1(u_3^{\alpha})h_2(u_3^{\alpha})}{h_{10}h_{20}} = 0 \tag{69}$$

Accounting for the uniformity (the coordinates can be omitted) and isotropy of the bulk phases ($P_{11} = P_{22} = P_{33} = P$), equation (67) can be written as

$$P^{\alpha} - P^{\beta} = \frac{\sigma_{11}}{R_{10}} + \frac{\sigma_{22}}{R_{20}} - \frac{\partial \sigma_{31}}{\partial l_{10}} - \frac{\partial \sigma_{32}}{\partial l_{20}} - [P_{33}(u_3^{\alpha}) - P^{\alpha}]\frac{h_1(u_3^{\alpha})h_2(u_3^{\alpha})}{h_{10}h_{20}} \tag{70}$$

In the absence of external fields, the pressure tensor is formed under the influence of the space metrics. Since the metric tensor of a film has the diagonal form in the curvilinear orthogonal coordinate system chosen in this work (see section 2), the pressure tensor can be also considered as diagonal in all parts of the film. As a consequence, the surface tension vectors will contain only normal components. In this simple case,

equations (68)–(70) are replaced by relationships

$$\frac{\partial \sigma_{11}}{\partial l_{10}} = \frac{\partial \sigma_{22}}{\partial l_{20}} = 0 \tag{71}$$

$$P^{\alpha} - P^{\beta} = \frac{\sigma_{11}}{R_{10}} + \frac{\sigma_{22}}{R_{20}} - [P_{33}(u_3^{\alpha}) - P^{\alpha}] \frac{h_1(u_3^{\alpha}) h_2(u_3^{\alpha})}{h_{10} h_{20}} \tag{72}$$

For a flat film, the coordinate system chosen transforms into the Cartesian one (x, y, z), and the Lame coefficient ratio in equation (72) becomes unity. In addition, the terms related to curvature vanish. Denoting $P_{33}(u_3^{\alpha})$ as the normal component $P_{\mathrm{N}}(z^{\alpha})$ of the pressure tensor, we arrive at the relationship

$$P^{\alpha} - P^{\beta} = P^{\alpha} - P_{\mathrm{N}}(z^{\alpha}) \tag{73}$$

Equation (73) is reduced to the known equilibrium condition $P_{\mathrm{N}} = P^{\beta}$ and also yields the definition of the disjoining pressure of a thin film expressed in equation (5). Since the coordinate z^{α} is chosen arbitrarily, equation (73) shows P_{N} to be independent of z and, hence, of spatial coordinates at all.

The simplest case of a non-uniform (in thickness) film is a wedge-shaped film with plane sides. If the wedge sides are identical, it is natural to introduce the middle plane as a basement for the interfacial element considered in section 3 (figure 2). The dividing surfaces are plane in this case, and the coordinate system is the cylindrical one with the coordinates $u_1 = r$, $u_2 = z$, $u_3 = \varphi$ and with the Lame coefficients $h_1 = 1$, $h_2 = 1$, $h_3 = r$. Equation (72) now becomes

$$P^{\alpha} - P^{\beta} = P^{\alpha} - P_{33}(\varphi^{\alpha}) \tag{74}$$

from where P_{33} is seen to be again a constant (with respect to the coordinate φ this time). Denoting it as P_{N}, we can again define the disjoining pressure as was shown in equation (5). We see that introducing the disjoining pressure for a film of variable thickness bears no difficulties in this case. If phase β is a fluid phase of uniform pressure, equation (74) leads to the absurd conclusion of the independence of the disjoining pressure on the film thickness. This only means that the wedge shape is impossible for a free film. However, the wedge-shaped film is quite realizable if a liquid fills in a wedge-shaped slit in a rigid solid (figure 2). If one chooses a dividing surface as the natural solid boundary surface and, setting $u_{30} = u_3^{\beta}$, carries out the integration in equations (16) and (17) over the liquid region, then P^{β} in equation (74) should be interpreted as the surface local pressure created by internal stresses in the solid. At every surface point, these internal stresses counterbalance the disjoining pressure and, of course, are dependent on the location on the surface (on the coordinate r).

The cylindrical coordinates are also natural for a simple case when a film itself is of the shape of a circular cylindrical surface. The dividing surfaces are also cylindrical in this case (with radii $0 < R_{10} < \infty$, $R_{20} = \infty$).

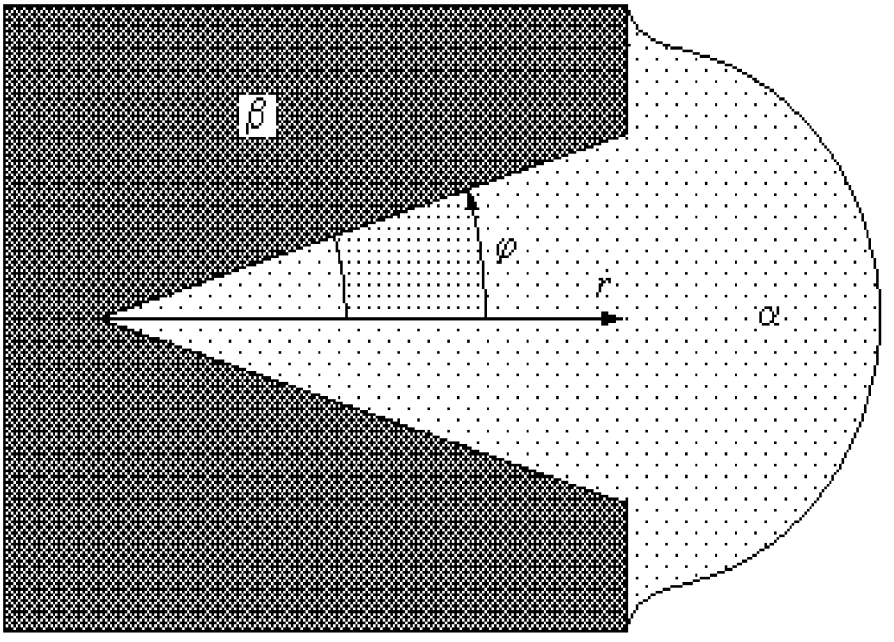


Figure 2. Element of a thin wedge-shaped film.

The coordinates are chosen as $u_1=\varphi$, $u_2=z$, $u_3=r$, and the Lame coefficients are $h_1=r$, $h_2=1$, $h_3=1$. Correspondingly, equation (72) takes the form

$$P^\alpha - P^\beta = \frac{\sigma_{11}}{R_{10}} - [P_{33}(r^\alpha) - P^\alpha]\frac{r^\alpha}{R_{10}} \tag{75}$$

If one chooses r^α in the middle of the film ($r^\alpha = R_{10} - H/2$), equation (75) can be written as

$$P^\alpha - P^\beta = \frac{\sigma_{11}^0}{R_{10}} - \left[P_N^0 - P^\alpha\right]\left(1 - \frac{H}{2R_{10}}\right) \tag{76}$$

where H is the distance between the dividing surfaces of the film (the film thickness), $P_N^0 \equiv P_{33}(R_{10} - H/2)$ is the normal component of the pressure tensor at the middle surface, and $\sigma_{11}^0 \equiv \sigma_{11}(R_{10} - H/2)$ is also related to the middle surface.

A similar formulation can be made for a spherical film when $R_{10}=R_{20}=R_0$ and $\sigma_{11}=\sigma_{22}=\sigma$. The spherical coordinates are $u_1=\theta$, $u_2=\varphi$, and $u_3=r$ and, correspondingly, $h_1=r$, $h_2=r\sin\theta$, and $h_3=1$. Then from equation (72) we have

$$P^\alpha - P^\beta = \frac{2\sigma}{R_0} - [P_{33}(r^\alpha) - P^\alpha]\frac{r^{\alpha 2}}{R_0^2} \tag{77}$$

or

$$P^\alpha - P^\beta = \frac{2\sigma^0}{R_0} - \left[P_N^0 - P^\alpha\right]\left(1 - \frac{H}{2R_0}\right)^2 \tag{78}$$

where $P_N^0 \equiv P_{33}(R_0 - H/2)$ and $\sigma^0 \equiv \sigma(R_0 - H/2)$, the superscript '0' refers to the middle spherical surface inside the film.

If a cylindrical or spherical film is a wetting film of uniform thickness between a cylindrical or spherical solid body and a vapour, we can choose coordinate u_3^α at the solid surface setting $r^\alpha = R_n$ where R_n is the radius of the solid body. As a result, we obtain from equations (75) and (77)

$$P^\alpha - P^\beta = \frac{\sigma_{11}}{R_{10}} - \left(P_N^s - P^\alpha\right)\frac{R_n}{R_{10}} \tag{79}$$

$$P^\alpha - P^\beta = \frac{2\sigma}{R_0} - \left(P_N^s - P^\alpha\right)\frac{R_n^2}{R_0^2} \tag{80}$$

where $P_N^s \equiv P_{33}(R_n)$ is the normal pressure on the solid surface. According to equation (5), the difference $P_N^s - P^\alpha$ in equations (79) and (80) has a meaning of the film disjoining pressure. Equations (79) and (80) are important in the thermodynamics of heterogeneous nucleation on cylindrical or spherical wettable solid particles [35].

6. The transitional zone of a wetting film

We now apply equation (72) to the transitional zone of a wetting film on a rigid flat solid surface. As the coordinate u_3^α is taken arbitrarily inside the film, we may bring it into coincidence with the solid surface (figure 3) to refer the whole film interior to the film surface layer at the boundary with an external fluid. Then $P_{33}(u_3^\alpha)$ acquires the meaning of the normal pressure P_N^s on the solid surface. In accordance with equation (72), we obtain

$$P^\alpha - P^\beta = \frac{\sigma_{11}}{R_{10}} + \frac{\sigma_{22}}{R_{20}} - [P_N^s - P^\alpha]\frac{h_1(u_3^\alpha)h_2(u_3^\alpha)}{h_{10}h_{20}} \tag{81}$$

The transitional zone metrics looks complex: the coordinate surface $u_1 - u_2$ is non-uniformly curved at the boundary with a fluid and is plane at the boundary with a solid. The contribution of the capillary pressure vanishes at the solid surface, so that the only cause of a difference between P_N^s and P^α is the interaction and overlapping of the opposite surface layers of the film. Therefore, the difference $P_N^s - P^\alpha$ may be termed a local disjoining pressure

$$\Pi(u_1^\alpha, u_2^\alpha) \equiv P_N^s - P^\alpha \tag{82}$$

In this definition, it is shown that the local disjoining pressure depends on the longitudinal coordinates, similarly to all other quantities on the right-hand side of equation (72). Using equation (82), equation (72) is written in the form

$$P^\alpha - P^\beta = \frac{\sigma_{11}}{R_{10}} + \frac{\sigma_{22}}{R_{20}} - \Pi\frac{h_1(u_3^\alpha)h_2(u_3^\alpha)}{h_{10}h_{20}} \tag{83}$$

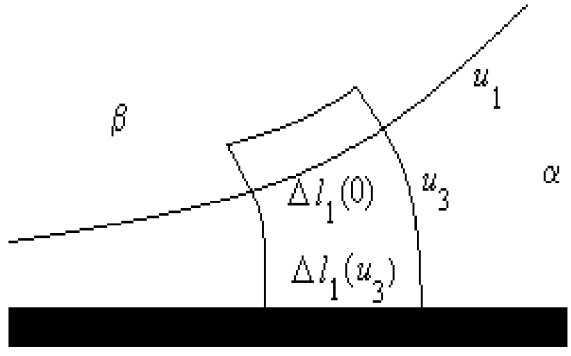


Figure 3. Element of the transitional zone of a wetting film.

In the particular case of a cylindrical dividing surface ($R_{20}=\infty$, $h_2=1$), the condition expressed in equation (83) is reduced to

$$P^\alpha - P^\beta = \frac{\sigma_{11}}{R_{10}} - \Pi\frac{h_1(u_3^\alpha)}{h_{10}} \tag{84}$$

Comparing figures 1 and 3, it is seen that the film surface curvature in figure 3 is negative. Taking this into account, it is convenient to write equations (83) and (84) in a general form as

$$P^\beta - P^\alpha = P_c + \Pi L \tag{85}$$

where P_c is the capillary pressure and L is the Lame coefficient ratio

$$L \equiv \frac{h_1(u_3^\alpha)h_2(u_3^\alpha)}{h_{10}h_{20}} \tag{86}$$

Above, we used explicit expressions for L corresponding to the simplest coordinate systems. In more complex cases, equation (10) can be used for the evaluation of L. Subsequently applying equation (10) to h_1 and h_2 with the integration from u_{30} to u_3^α and putting the results in equation (86), we obtain

$$L = \exp\left[2\int_{u_{30}}^{u_3^\alpha} du_3 h_3(u_3)c(u_3)\right] \tag{87}$$

where

$$c(u_3) \equiv \frac{1}{2}\left[\frac{1}{R_1(u_3)} + \frac{1}{R_2(u_3)}\right] \tag{88}$$

is the local mean curvature of the coordinate surface u_1–u_2. By applying the mean-value theorem and putting $h_3\,\mathrm{d}u_3 = \mathrm{d}l_3$, we can rewrite equation (87) as

$$L = \exp(2\bar{c}\Delta l_3) \tag{89}$$

where $\bar{c}$ is the averaged value of $c(u_3)$ and Δl_3 is the length of the segment of the coordinate line 3 between u_{30} and u_3^α (the curvilinear 'thickness' of the film). For a thin film whose real local thickness H is considerably smaller than any of the principal curvature radii of a dividing surface, we have $\bar{c}\Delta l_3 \ll 1$ and $\bar{c} \approx c(u_{30}) = c$ where c is as previously the mean curvature of the dividing surface, and, naturally, $\Delta l_3 \approx H$. As a consequence, equation (89) is represented in an approximate form

$$L \approx 1 + 2cH \tag{90}$$

It is valid $L \lesssim 1$ at the negative mean curvature of a film (as a reminder, we have $c<0$ since the curvature centre is located on the side of phase α).

In the approximation of an isotropic surface tension of a film (or rigorously for a cylindrical surface), equation (85) can be written in the form

$$P^\beta - P^\alpha = -2\sigma c + \Pi L \tag{91}$$

With $L=1$ equation (91) corresponds to Derjaguin's equation (6), except that Π in equation (6) was treated as the disjoining pressure of a flat film of an appropriate thickness. This assumption was maintained in all subsequent publications. As mentioned above, the cosine of the local slope angle was introduced, instead of L, in some versions of equation (6) [32, 33] for the case when the disjoining pressure was defined with respect to the normal to the horizontal plane, but not to the inclined film surface. Such inconsistency was avoided in our derivation by using curvilinear coordinates. As a result, the disjoining pressure acts along the normal to both the above film surfaces, so that equating the Lame coefficient ratio L to the above cosine looks problematic. It is also of note that using the Cartesian coordinates (as a unique case related to the use of the cosine) has one more undesirable consequence: the capillary part of equation (91) becomes inexact. This is related to the fact that the pressure tensor of the transitional zone becomes non-diagonal in the Cartesian coordinates, which requires returning to the more general case, equation (70). As was shown above, $L=1$ not only for a flat film, but also for a wedge-shaped film. Therefore, the condition $L \approx 1$ can happen to be not bad approximation for calculations according to equation (90) if the film profile is not very much different from the wedge shape and the profile curvature is sufficiently small.

We now have to discuss the well-known fact that the film surface tension σ in equation (91) does not coincide with the macroscopic surface tension (or with the sum of tensions on two sides of a thick film). A relation between these quantities does exist, but is known only for the case of a flat film up to the present, equation (3). In our case $\sigma^\beta + \sigma^\gamma$ has been replaced by σ that, in accordance with equation (16), is the integral estimated from the coordinate u_3^α. When integrating equation (3), it is convenient to count off u_3^α from the dividing surface. With this convention, u_3^α coincides with the curvilinear 'thickness' of the film at the beginning of integration. If this 'thickness' is considered as a constant in the process of integration (when the real film thickness increases without limit), the quantity σ changes to the macroscopic (tabular) surface tension σ_∞^β in the typical case when the film thickness is much greater that the

thickness of a completely developed surface layer at the $\alpha\beta$ boundary. The integration of equation (3) then yields

$$\sigma(H) = \sigma_\infty^\beta + \int_H^\infty \Pi(h)\,\mathrm{d}h \tag{92}$$

Naturally, equation (92) is applicable only to a thin film that is slightly non-uniform in thickness when equation (90) is valid. Putting equation (92) in equation (91) and accounting for equation (90), we arrive at the equation

$$P^\beta - P^\alpha = -2\left(\sigma_\infty^\beta + \int_H^\infty \Pi(h)\,\mathrm{d}h - \Pi H\right)c + \Pi \tag{93}$$

Equation (85) with $L=1$, with treating Π as the disjoining pressure of a flat-parallel film, and with taking tabular values of surface tension for estimating capillary pressure, was used many times for the calculation of a sufficiently gradual profile of the transitional zone. Our local equation (85) is valid for a profile of an arbitrary slope. It is important, however, for an arbitrary profile that the above local disjoining pressure of a film of varying thickness is not equivalent to the disjoining pressure of a flat film of a corresponding thickness and should be calculated separately, with the use of a given profile shape. Since the profile itself is to be calculated from the known dependence of the local disjoining pressure and the local film surface tension on the film thickness, the problem can be solved by the method of successive approximations. Herewith, the wedge-shaped profile can be taken for the zero approximation. However, the solution of this problem lies out of the scope of this paper.

Acknowledgement

This work was supported by RFBR (grant 04-03-32134) and the program 'Leading scientific schools of Russian Federation' (grant NS-789.2003.3).

References

[1] J.W. Gibbs. *Trans. Conn. Acad.*, **3**, 343 (1878).
[2] F.P. Buff. *J. chem. Phys.*, **23**, 419 (1955).
[3] F.P. Buff. The theory of capillarity. In *Handb d. Physik*, Vol. 10, S. Fluegge (Ed.), pp. 281–304, Springer, Berlin (1960).
[4] C.L. Murphy, Ph.D. Thermodynamics of low tension and highly curved interface. PhD thesis, University of Minnesota (1966).
[5] A.E. Evans, R. Skalak. *CRC Crit. Rev. Bioeng.*, **3**, 181 (1979).
[6] J.S. Rowlinson, B. Widom. *Molecular Theory of Capillarity*, Clarendon Press, Oxford (1982).
[7] V.V. Krotov, A.I. Rusanov, A. Blinowski. *Colloid J.*, **44**, 420 (1982).
[8] Y.S. Podstrigach, Y.Z. Povstenko. *Introduction into Mechanics of Surface Phenomena in Deformable Solids*, Naukova Dumka, Kiev; in Russian (1985).
[9] P.A. Kralchevsky. *J. colloid Interface Sci.*, **137**, 217 (1990).
[10] T.D. Gurkov, P.A. Kralchevsky. *Colloids Surf.*, **47**, 45 (1990).
[11] A.I. Rusanov. *Pure Appl. Chem.*, **64**, 111 (1992).
[12] J.C. Eriksson, S. Ljunggren. *J. colloid Interface Sci.*, **152**, 575 (1992).
[13] P.A. Kralchevsky, J.C. Eriksson, S. Ljunggren. *Adv. Colloid Interface Sci.*, **48**, 19 (1994).
[14] M. Pasandideh-Fard, P. Chen, J. Mostaghimi, A.W. Neumann. *Adv. Colloid Interface Sci.* **63**, 151 (1996).
[15] P. Chen, S.S. Susnar, M. Pasandideh-Fard, J. Mostaghimi, A.W. Neumann. *Adv. Colloid Interface Sci.*, **63**, 179 (1996).
[16] S. Ljunggren, J.C. Eriksson, P.A. Kralchevsky. *J. colloid Interface Sci.*, **191**, 424 (1997).
[17] A.I. Rusanov, A.K. Shchekin. *Colloid J.*, **61**, 403 (1999).
[18] A.I. Rusanov, A.K. Shchekin, V.B. Warshavsky. *Colloid J.*, **63**, 365 (2001).
[19] A.I. Rusanov, A.K. Shchekin. *Mendeleev Commun.*, **4**, 128 (2000).
[20] A.I. Rusanov, A.K. Shchekin. *Colloids Surf.*, **192**, 357 (2001).
[21] J.C. Eriksson, S. Ljunggren. In *Surface and Interfacial Tension. Measurement, Theory, and Applications*, Surfactant Science series, Vol. 119, S. Hartland (Ed.), pp. 547–614, Marcel Dekker, New York (2004).
[22] A.I. Rusanov. *Phase Equilibria and Surface Phenomena* (Khimiya, Leningrad: in Russian); Rusanov, A.I., 1978, *Phasengleichgewichte und Grenzflächenerscheinungen*, Akademie-Verlag, Berlin (1967).
[23] B.V. Derjaguin. *Kolloid Zh.*, **17**, 207 (1955).
[24] B.V. Derjaguin, N.V. Churaev, V.M. Muller. *Surface Forces*, Consultants Bureau, New York (1987).
[25] A.I. Rusanov, F.M. Kuni. *Research in Surface Forces*, Vol.3, B.V. Derjaguin (Ed.), pp. 111–122, Consultants Bureau, New York (1971).
[26] J.A. De Feijter, A. Vrij. *Electroanal. Chem. Interface Electrochem.*, **37**, 9 (1972).
[27] B.V. Derjaguin, V.M. Starov, N.V. Churaev. *Kolloid Zh.*, **38**, 875 (1976).
[28] B.V. Toshev. *Colloids Surf.*, **2**, 243 (1981).
[29] N.V. Churaev, V.M. Starov, B.V. Derjaguin. *J. Colloid Interface Sci.*, **89**, 16 (1982).
[30] J.C. Eriksson, B.V. Toshev. *Colloid Polym. Sci.*, **264**, 807 (1986).
[31] V.G. Babak. *Colloids Surf.*, **156**, 423 (1999).
[32] V.G. Babak. *Colloids Surf.*, **25**, 1 (1987).
[33] Yu. Solomentsev, L.R. White. *J. Colloid Interface Sci.*, **218**, 122 (1999).
[34] S. Kondo. *J. Chem. Phys.*, **25**, 662 (1956).
[35] F.M. Kuni, A.K. Shchekin, A.I. Rusanov, B. Widom. *Adv. Colloid Interface Sci.*, **65**, 71 (1996).