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The Condition of Mechanical Equilibrium on the Surface of a Nonuniform Thin Film

A. I. Rusanov and A. K. Shchekin

Mendeleev Center, St. Petersburg State University, Universitetskaya nab. 7, St. Petersburg, 199034 Russia

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Abstract—The condition of internal mechanical equilibrium of a curved surface layer is derived, and its application to practically important cases of incomplete formation of the surface layer (as is sometimes the case, for example, in thin films) is considered. The notion of a local disjoining pressure is introduced, and the equilibrium condition for a variable-thickness thin film is obtained; this condition is valid both in the absence and in the presence of external fields. The cases of a wedge-shaped film, cylindrical film, spherical film, and transition zone of a wetting film are analyzed.

DIVIDING SURFACE AND SURFACE TENSION

As is known, a thin film is wholly nonuniform, because its surface layers overlap. Therefore, the very notion of the surface of a thin film needs some explanation. The surface is a geometrical notion, inevitably related to the concept of a dividing surface (which was introduced into science by Gibbs) as a geometrical surface that repeats the shape of the physical surface but with an arbitrarily chosen position. In [1], it was generalized and raised to the rank of a rigorous definition as a coordinate surface u_1–u_2 of the orthogonal curvilinear coordinate system (u_1, u_2, u_3) that diagonalizes the metric tensor of the surface layer. The metric of this layer is formed by lines of the density gradient (under the effect of phase and external fields), which are perpendicular to the aforementioned coordinate surface in each of their points. According to Gibbs, the dividing surface can change its position by moving along the normal; accordingly, it remains conformal to itself even at long distances. In our approach, each element of the dividing surface moves along the gradient line (curved in the general case), which plays the role of curvilinear coordinate u_3 (the conformity is necessarily preserved only for infinitely small displacements of the dividing surface). As is shown below, these new concepts are important for nonplanar, irregular, and asymmetric variable-thickness films.

Always representing a nonuniform transition zone between two bulk phases, a thin film does not differ from a surface layer from the general theoretical standpoint, and approaches and relationships of the theory of surface phenomena can be extended to it. In particular, one can introduce a dividing surface to which surface tension is attributed. In the general case, surface tension is a tensor quantity, which is determined at each of the two principal cross sections of the surface layer by local excess stress tensors $\hat{\gamma}'$ and $\hat{\gamma}''$ as [2]

$$\hat{\gamma}' = \frac{1}{h_{20}}\left[\int_{u_3^\gamma}^{u_{30}} (\hat{P}^\gamma - \hat{P}) h_1 h_3 du_3 + \int_{u_{30}}^{u_3^\beta} (\hat{P}^\beta - \hat{P}) h_2 h_3 du_3\right], \quad (1)$$

$$\hat{\gamma}'' = \frac{1}{h_{10}}\left[\int_{u_3^\gamma}^{u_{30}} (\hat{P}^\gamma - \hat{P}) h_2 h_3 du_3 + \int_{u_{30}}^{u_3^\beta} (\hat{P}^\beta - \hat{P}) h_1 h_3 du_3\right], \quad (2)$$

where $\hat{P}$ is the local pressure tensor; h_i is the Lamé coefficient for curvilinear coordinate u_i; $i = 1, 2, 3$ ($h_i du_i$ yields the differential of the length of coordinate line i); superscripts β and γ (do not confuse the latter symbol with the designation of surface tension) are the symbols of bulk phases between which the film exists (phase symbol α will remain reserved for the time being); and subscript 0 refers to the dividing surface. An important prerogative of the tensor of surface tension is its participation in the condition of interfacial mechanical equilibrium. Just as any other tensor, the pressure tensor $\hat{P}$ and tension tensors $\hat{\gamma}'$, and $\hat{\gamma}''$ can be represented by the sets of their vector components $\mathbf{P}_i$ ($i = 1, 2, 3$) and $\boldsymbol{\gamma}_1'$, $\boldsymbol{\gamma}_2''$; as it turned out, it is for them that the condition of equilibrium has the simplest formulation [3]:

$$\mathbf{P}_3^\gamma - \mathbf{P}_3^\beta = -\frac{\partial \boldsymbol{\gamma}_1'}{\partial l_{10}} - \frac{\partial \boldsymbol{\gamma}_2''}{\partial l_{20}}, \quad (3)$$

where l_{10} and l_{20} are the lengths of the coordinate lines in the principal cross sections on the dividing surface. Evidently, the presence of a thin film at the interface does not cause any fundamental changes (although the surface tension is often called the film tension in this case), and this situation does not require any special theory.

The situation is completely different in the approach that is based on the introduction of two dividing sur-

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faces of a film [4, 5]. Although the introduction of two dividing surfaces is also used in the theory of surface phenomena (for substantiating the method of the finite-thickness layer [6]), the case of a thin film at the interface has a fundamental difference: the appearance of an image of the third (mother) phase α, from which the film was formed and with which it can even be in equilibrium through a contact at its edge surface. If now only phase α in the space between the dividing surfaces is used as the reference for introducing the surface tension (phases β and γ will be external in this case), the sum of the surface tension tensors $\hat{\sigma}'^{\beta}$, $\hat{\sigma}'^{\gamma}$ and $\hat{\sigma}''^{\beta}$, $\hat{\sigma}''^{\gamma}$, which pertain to the sides of the thin film, is determined for the principal cross sections by the relationships

$$\hat{\sigma}'^{\beta} + \hat{\sigma}'^{\gamma} = \frac{1}{h_{20}}\left[\int_{u_3^{\beta}}^{u_{30}^{\beta}} (\hat{P}^{\beta} - \hat{P}) h_2 h_3 du_3 + \int_{u_{30}^{\beta}}^{u_{30}^{\gamma}} (\hat{P}^{\alpha} - \hat{P}) h_2 h_3 du_3 + \int_{u_{30}^{\gamma}}^{u_3^{\gamma}} (\hat{P}^{\gamma} - \hat{P}) h_2 h_3 du_3\right], \quad (4)$$

$$\hat{\sigma}''^{\beta} + \hat{\sigma}''^{\gamma} = \frac{1}{h_{10}}\left[\int_{u_3^{\beta}}^{u_{30}^{\beta}} (\hat{P}^{\beta} - \hat{P}) h_1 h_3 du_3 + \int_{u_{30}^{\beta}}^{u_{30}^{\gamma}} (\hat{P}^{\alpha} - \hat{P}) h_1 h_3 du_3 + \int_{u_{30}^{\gamma}}^{u_3^{\gamma}} (\hat{P}^{\gamma} - \hat{P}) h_1 h_3 du_3\right], \quad (5)$$

where u_{30}^{β} and u_{30}^{γ} are the coordinates of the two dividing surfaces that face phases β and γ, respectively. Note that these expressions determine only the sum of the tensions, whereas their partition between the sides of the film is performed according to agreement. The difference between the pressure tensor $\hat{P}^{\alpha}$ and tensors $\hat{P}^{\beta}$ and $\hat{P}^{\gamma}$ is the reason for the appearance of disjoining pressure and for the discrepancy between the sum of surface tensions of film sides and the tension of the film as a whole. For the case of isotropic phases and a plane thin film, this fact is fixed by the known relationships [4]

$$\Pi = P^{\beta} - P^{\alpha}, \quad (6)$$

$$\gamma = \sigma^{\beta} + \sigma^{\gamma} + \Pi H, \quad (7)$$

where Π is the disjoining pressure of the film and H is the distance between the dividing surfaces (the thickness of the film).

After the introduction of two dividing surfaces and reference phase α, the surfaces of a thin film are naturally regarded as phase boundaries (αβ or αγ) with certain surface tensions. Any of such surfaces (for definiteness, let it be αβ) will be the subject of this study.

DERIVATION OF THE MECHANICAL EQUILIBRIUM CONDITION FOR AN ARBITRARY ELEMENT OF THE SURFACE LAYER

The shape of the interface is most completely characterized by specifying the metric tensor as a function of coordinates in the entire space of the transition zone. If we choose an orthogonal coordinate system (u_1, u_2, u_3) diagonalizing the metric tensor so that coordinate line u_3 is directed along the normal to the surface, then any coordinate surface u_1–u_2 can be selected as the dividing surface. Using coordinate surfaces, let us isolate an element of the surface layer situated between bulk phases α and β (Fig. 1). Let the element be located between coordinates u_1, $u_1 + \Delta u_1$; u_2, $u_2 + \Delta u_2$; u_3^{α}, u_3^{β} (superscripts α and β denote the quantities at the sides of the corresponding phases but not necessarily pertaining to the phases themselves: an element of the surface layer is not only of arbitrary thickness but also of arbitrary height, possibly not extending over the entire thickness of the surface layer). The condition of mechanical equilibrium for this element is expressed by the fact that the total force acting on the element is zero, i.e.,

$$-\oint(\hat{P} \cdot d\mathbf{A}) = -\oint \mathbf{P} dA = 0. \quad (8)$$

Here, $\hat{P}$ is the total pressure tensor (including also the contributions of external fields if they are present [2]); $d\mathbf{A} = \boldsymbol{\nu} dA$ is the vector of the differential of the element surface ($\boldsymbol{\nu}$ is the unit vector of the outer normal to the element surface); $-\mathbf{P} = -\hat{P} \cdot \boldsymbol{\nu}$ is the vector of the force applied to a unit area of the element surface (the stress vector); the integration is performed over the entire closed surface of the element. This surface includes six faces; accordingly, the integral in Eq. (8) can be partitioned into six components (each vector $\mathbf{P}$ is hereafter supplied with a subscript showing the orientation of the face). The integrals for the lower and upper faces can be written in the form $\mathbf{P}_3(u_3^{\alpha})\Delta l_1(u_3^{\alpha})\Delta l_2(u_3^{\alpha})$ and $\mathbf{P}_3(u_3^{\beta})\Delta l_1(u_3^{\beta})\Delta l_2(u_3^{\beta})$, where $\Delta l_1 = h_1 \Delta u_1$ and $\Delta l_2 = h_2 \Delta u_2$ are the segments of the coordinate lines (corresponding to coordinates u_1 and u_2) falling within the selected element at the level of the corresponding face. For the face perpendicular to direction 1, we have $dA_1 = \Delta l_2 dl_3 = \Delta l_2 h_3 du_3$; for the face perpendicular to direction 2, $dA_2 = \Delta l_1 dl_3 = \Delta l_1 h_3 du_3$. In addition, let us write the integrals in Eq. (3) for the element faces in pairs, as differences, because forces acting on opposite faces have opposite directions. Now we can represent Eq. (8) as

$$\mathbf{P}_3(u_3^{\alpha})\Delta l_1(u_3^{\alpha})\Delta l_2(u_3^{\alpha}) - \mathbf{P}_3(u_3^{\beta})\Delta l_1(u_3^{\beta})\Delta l_2(u_3^{\beta}) - \Delta\int_{u_3^{\alpha}}^{u_3^{\beta}} \mathbf{P}_1 \Delta l_2 h_3 du_3 - \Delta\int_{u_3^{\alpha}}^{u_3^{\beta}} \mathbf{P}_2 \Delta l_1 h_3 du_3 = 0, \quad (9)$$

where the Δ sign in front of the integrals denotes their increment corresponding to the transition from one opposite face to the other along directions 1 and 2.

Now let us place a dividing surface with the coordinate u_{30} and area $\Delta l_{10}\Delta l_{20}$ inside the element. The dividing surface separates this element into parts α and β (Fig. 1) facing the corresponding phases. Now, if we assume that part α is filled with the substance of phase α, part β is filled with the substance of phase β, and both parts are in the state of mechanical equilibrium, we can write a condition similar to Eq. (9) for each of the phases separately:

$$\begin{aligned}&\mathbf{P}_3^{\alpha}(u_3^{\alpha})\Delta l_1(u_3^{\alpha})\Delta l_2(u_3^{\alpha}) - \mathbf{P}_3^{\alpha}(u_{30}^{\alpha})\Delta l_{10}\Delta l_{20}\\ &-\Delta\int_{u_3^{\alpha}}^{u_{30}}\mathbf{P}_1^{\alpha}\Delta l_2 h_3 du_3 - \Delta\int_{u_3^{\alpha}}^{u_{30}}\mathbf{P}_2^{\alpha}\Delta l_1 h_3 du_3 = 0,\end{aligned} \tag{10}$$

$$\begin{aligned}&\mathbf{P}_3^{\beta}(u_{30})\Delta l_{10}\Delta l_{20} - \mathbf{P}_3^{\beta}(u_3^{\beta})\Delta l_1(u_3^{\beta})\Delta l_2(u_3^{\beta})\\ &-\Delta\int_{u_{30}}^{u_3^{\beta}}\mathbf{P}_1^{\beta}\Delta l_2 h_3 du_3 - \Delta\int_{u_{30}}^{u_3^{\beta}}\mathbf{P}_2^{\beta}\Delta l_1 h_3 du_3 = 0.\end{aligned} \tag{11}$$

Now, subtracting Eqs. (10) and (11) from Eq. (9), we arrive at the expression

$$\begin{aligned}&[\mathbf{P}_3^{\alpha}(u_{30}) - \mathbf{P}_3^{\beta}(u_{30})]\Delta l_{10}\Delta l_{20}\\ &+[\mathbf{P}_3(u_3^{\alpha}) - \mathbf{P}_3^{\alpha}(u_3^{\alpha})]\Delta l_1(u_3^{\alpha})\Delta l_2(u_3^{\alpha})\\ &-[\mathbf{P}_3(u_3^{\beta}) - \mathbf{P}_3^{\beta}(u_3^{\beta})]\Delta l_1(u_3^{\beta})\Delta l_2(u_3^{\beta})\\ &+\Delta\boldsymbol{\sigma}_1\Delta l_{20} + \Delta\boldsymbol{\sigma}_2\Delta l_{10} = 0,\end{aligned} \tag{12}$$

where the following vector notations are introduced:

$$\begin{aligned}\boldsymbol{\sigma}_1 \equiv \frac{1}{\Delta l_{20}}\Bigg[&\int_{u_3^{\alpha}}^{u_{30}}(\mathbf{P}_1^{\alpha} - \mathbf{P}_1)\Delta l_2 h_3 du_3\\ &+\int_{u_{30}}^{u_3^{\beta}}(\mathbf{P}_1^{\beta} - \mathbf{P}_1)\Delta l_2 h_3 du_3\Bigg],\end{aligned} \tag{13}$$

$$\begin{aligned}\boldsymbol{\sigma}_2 \equiv \frac{1}{\Delta l_{10}}\Bigg[&\int_{u_3^{\alpha}}^{u_{30}}(\mathbf{P}_2^{\alpha} - \mathbf{P}_2)\Delta l_1 h_3 du_3\\ &+\int_{u_{30}}^{u_3^{\beta}}(\mathbf{P}_2^{\beta} - \mathbf{P}_2)\Delta l_1 h_3 du_3\Bigg].\end{aligned} \tag{14}$$

According to comparison with Eqs. (4) and (5), we should have denoted $\boldsymbol{\sigma}_1$ by $\boldsymbol{\sigma}_1'$, and $\boldsymbol{\sigma}_2$ by $\boldsymbol{\sigma}_2''$, but we skip the primes for brevity. The physical meaning of $\boldsymbol{\sigma}_1$ and $\boldsymbol{\sigma}_2$ consists in the fact that they represent excess stresses on lines Δl_{20} and Δl_{10}, respectively, for each cross section of the surface layer element.

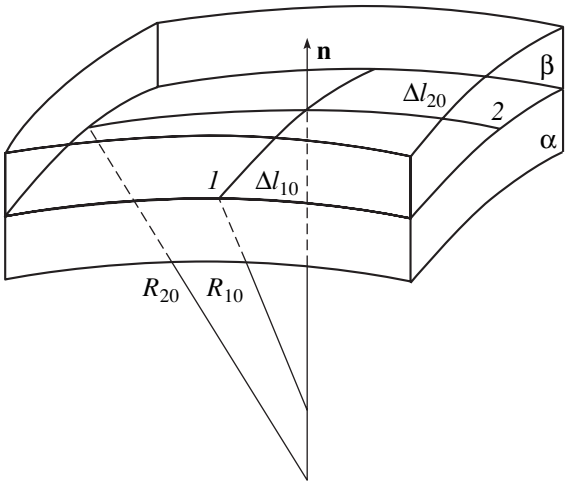

Fig. 1. Element of a curved surface layer.

The last step remains to be done. Let us divide Eq. (12) by $\Delta l_{10}\Delta l_{20}$ and, rigorously proceeding to the local relationship, consider Δu_1 and Δu_2 (and, accordingly, Δl_{10} and Δl_{20}) tending to zero. Then, the condition of mechanical equilibrium assumes the form

$$\begin{aligned}\mathbf{P}_3^{\alpha}(u_{30}) - \mathbf{P}_3^{\beta}(u_{30}) &= -\frac{\partial\boldsymbol{\sigma}_1}{\partial l_{10}} - \frac{\partial\boldsymbol{\sigma}_2}{\partial l_{20}}\\ &-[\mathbf{P}_3(u_3^{\alpha}) - \mathbf{P}_3^{\alpha}(u_3^{\alpha})]\frac{h_1(u_3^{\alpha})h_2(u_3^{\alpha})}{h_{10}h_{20}}\\ &+[\mathbf{P}_3(u_3^{\beta}) - \mathbf{P}_3^{\beta}(u_3^{\beta})]\frac{h_1(u_3^{\beta})h_2(u_3^{\beta})}{h_{10}h_{20}}.\end{aligned} \tag{15}$$

If the lower and upper boundaries of the surface layer element in question fall within the region of bulk phases α and β (in this case, the element is just a segment of the surface layer), the last two terms in Eq. (15) are nullified, vectors $\boldsymbol{\sigma}_1$ and $\boldsymbol{\sigma}_2$ pass into $\boldsymbol{\gamma}_1'$ and $\boldsymbol{\gamma}_2''$, and condition (15) is reduced to formula (3) with subscript γ replaced by α. This is possible when the surface layer is free and fully implemented. If there is overlapping or compression of the surface layer by other bodies (as it happens in thin films), it is condition (15) that is valid.

Condition (15) is universal and applicable to systems in any physical state; however, the stress tensor $\hat{E} = -\hat{p}$ rather than the pressure tensor is generally used for solids. Passing from the pressure vector $\mathbf{P}$ to the stress vector $\mathbf{E}$, one can write equilibrium condition (15) in the form

$$\mathbf{E}_3^{\alpha}(u_{30}) - \mathbf{E}_3^{\beta}(u_{30}) = \frac{\partial \boldsymbol{\sigma}_1}{\partial l_{10}} + \frac{\partial \boldsymbol{\sigma}_2}{\partial l_{20}}$$
$$- [\mathbf{E}_3(u_3^{\alpha}) - \mathbf{E}_3^{\alpha}(u_3^{\alpha})]\frac{h_1(u_3^{\alpha})h_2(u_3^{\alpha})}{h_{10}h_{20}} \quad (16)$$
$$+ [\mathbf{E}_3(u_3^{\beta}) - \mathbf{E}_3^{\beta}(u_3^{\beta})]\frac{h_1(u_3^{\beta})h_2(u_3^{\beta})}{h_{10}h_{20}}.$$

DETAILED FORMULATION OF THE MECHANICAL EQUILIBRIUM CONDITION

To separate the changes in the magnitudes and directions of all vectors present in Eq. (15), let us introduce unit vectors $\mathbf{e}_1$, $\mathbf{e}_2$, and $\mathbf{e}_3$ along the coordinate lines of our coordinate system and write the following relationships:

$$\mathbf{P}_3 = \sum_{i=1}^{3} P_{i3}\mathbf{e}_i, \quad (17)$$

$$\boldsymbol{\sigma}_k = \sum_{i=1}^{3} \sigma_{ik}\mathbf{e}_i \quad (k = 1, 2), \quad (18)$$

where the additional subscript i refers to components of vectors along direction i. Substitution of Eqs. (17) and (18) into Eq. (15) yields

$$\sum_{i=1}^{3} [P_{i3}^{\alpha}(u_{30}) - P_{i3}^{\beta}(u_{30})]\mathbf{e}_i$$
$$= -\sum_{i=1}^{3}\frac{\partial \sigma_{i1}}{\partial l_{10}}\mathbf{e}_i - \sum_{i=1}^{3}\sigma_{i1}\frac{\partial \mathbf{e}_i}{\partial l_{10}} - \sum_{i=1}^{3}\frac{\partial \gamma_{i2}}{\partial l_{20}}\mathbf{e}_i - \sum_{i=1}^{3}\sigma_{i2}\frac{\partial \mathbf{e}_i}{\partial l_{20}}$$
$$- \sum_{i=1}^{3}[P_{i3}(u_3^{\alpha}) - P_{i3}^{\alpha}(u_3^{\alpha})]\frac{h_1(u_3^{\alpha})h_2(u_3^{\alpha})}{h_{10}h_{20}}\mathbf{e}_i \quad (19)$$
$$+ \sum_{i=1}^{3}[P_{i3}(u_3^{\beta}) - P_{i3}^{\beta}(u_3^{\beta})]\frac{h_1(u_3^{\beta})h_2(u_3^{\beta})}{h_{10}h_{20}}\mathbf{e}_i.$$

To calculate the derivatives of unit vectors, let us use the standard Serret–Frenet formulas of differential geometry:

$$d\mathbf{t}/dL = c\mathbf{n}, \quad d\mathbf{n}/dL = -c\mathbf{t} + T\mathbf{b}, \quad d\mathbf{b}/dL = -T\mathbf{n}, \quad (20)$$

where $\mathbf{t}$ is the unit vector of the tangent to the spatial line (the coordinate line in our case); $\mathbf{n}$ is the unit vector of its principal normal; $\mathbf{b}$ is the unit vector of the binormal; c is the curvature of the line; T is its torsion (in our coordinate system, the torsion is zero); and L is the length of the line. For coordinate lines on the dividing surface, we have $\mathbf{t} = \mathbf{e}_1$, $\mathbf{n} = -\mathbf{e}_3$, $\mathbf{b} = -\mathbf{e}_2$ for $L \equiv l_{10}$ and $\mathbf{t} = \mathbf{e}_2$, $\mathbf{n} = -\mathbf{e}_3$, $\mathbf{b} = -\mathbf{e}_1$ for $L \equiv l_{20}$. Now, using Eq. (13), we arrive at the following expressions for the derivatives of the unit vectors:

$$\frac{\partial \mathbf{e}_1}{\partial l_{10}} = -\frac{\mathbf{e}_3}{R_{10}}, \quad \frac{\partial \mathbf{e}_2}{\partial l_{10}} = 0, \quad \frac{\partial \mathbf{e}_3}{\partial l_{10}} = \frac{\mathbf{e}_1}{R_{10}}, \quad (21)$$

$$\frac{\partial \mathbf{e}_2}{\partial l_{20}} = -\frac{\mathbf{e}_3}{R_{20}}, \quad \frac{\partial \mathbf{e}_1}{\partial l_{20}} = 0, \quad \frac{\partial \mathbf{e}_3}{\partial l_{20}} = \frac{\mathbf{e}_2}{R_{20}}, \quad (22)$$

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

Substituting Eqs. (21) and (22) into Eq. (19) and performing scalar multiplication of Eq. (19) by $\mathbf{e}_1$, $\mathbf{e}_2$, and $\mathbf{e}_3$ in turn, we arrive at three scalar equalities that are equivalent to vector equality (15):

$$P_{13}^{\alpha}(u_{30}) - P_{13}^{\beta}(u_{30}) = -\frac{\sigma_{31}}{R_{10}} - \frac{\partial \sigma_{11}}{\partial l_{10}} - \frac{\partial \sigma_{12}}{\partial l_{20}}$$
$$- [P_{13}(u_3^{\alpha}) - P_{13}^{\alpha}(u_3^{\alpha})]\frac{h_1(u_3^{\alpha})h_2(u_3^{\alpha})}{h_{10}h_{20}} \quad (23)$$
$$+ [P_{13}(u_3^{\beta}) - P_{13}^{\beta}(u_3^{\beta})]\frac{h_1(u_3^{\beta})h_2(u_3^{\beta})}{h_{10}h_{20}},$$

$$P_{23}^{\alpha}(u_{30}) - P_{23}^{\beta}(u_{30}) = -\frac{\sigma_{32}}{R_{20}} - \frac{\partial \sigma_{21}}{\partial l_{10}} - \frac{\partial \sigma_{22}}{\partial l_{20}}$$
$$- [P_{23}(u_3^{\alpha}) - P_{23}^{\alpha}(u_3^{\alpha})]\frac{h_1(u_3^{\alpha})h_2(u_3^{\alpha})}{h_{10}h_{20}} \quad (24)$$
$$+ [P_{23}(u_3^{\beta}) - P_{23}^{\beta}(u_3^{\beta})]\frac{h_1(u_3^{\beta})h_2(u_3^{\beta})}{h_{10}h_{20}},$$

$$P_{33}^{\alpha}(u_{30}) - P_{33}^{\beta}(u_{30}) = \frac{\sigma_{11}}{R_{10}} + \frac{\sigma_{22}}{R_{20}} - \frac{\partial \sigma_{31}}{\partial l_{10}} - \frac{\partial \sigma_{32}}{\partial l_{20}}$$
$$- [P_{33}(u_3^{\alpha}) - P_{33}^{\alpha}(u_3^{\alpha})]\frac{h_1(u_3^{\alpha})h_2(u_3^{\alpha})}{h_{10}h_{20}} \quad (25)$$
$$+ [P_{33}(u_3^{\beta}) - P_{33}^{\beta}(u_3^{\beta})]\frac{h_1(u_3^{\beta})h_2(u_3^{\beta})}{h_{10}h_{20}}.$$

These relationships are applicable to any capillary objects, no matter how nonuniform or small they are, both in the absence and in the presence of external fields. Note that, since vectors $\boldsymbol{\sigma}_1$ and $\boldsymbol{\sigma}_2$ are determined by different relationships (13) and (14), the σ_{12} and σ_{21} values are not equal. As also follows from Eqs. (13) and (14), all the quantities σ_{11}, σ_{12}, σ_{31}, σ_{32}, σ_{21}, and σ_{22} present in Eqs. (23)–(25) depend not only on the selected position of the dividing surface but also on the choice of coordinates u_3^{α} and u_3^{β}.

SURFACE OF A THIN FILM

Let us apply conditions (23)–(25) to one side of a thin film. Let α be the mother phase of the film and β be the external medium adjacent to the film side in question. Evidently, the surface layer of the film is completely formed at the side facing phase β, and coordinate u_3^β can be selected so as to be located inside phase β. Then, $\mathbf{P}_3(u_3^\beta) = \mathbf{P}_3^\beta(u_3^\beta)$; the last term in Eqs. (15), (16), and (19) disappears; and Eqs. (23)–(25) assume the form

$$P_{13}^\alpha(u_{30}) - P_{13}^\beta(u_{30}) = -\frac{\sigma_{31}}{R_{10}} - \frac{\partial\sigma_{11}}{\partial l_{10}} - \frac{\partial\sigma_{12}}{\partial l_{20}} - [P_{13}(u_3^\alpha) - P_{13}^\alpha(u_3^\alpha)]\frac{h_1(u_3^\alpha)h_2(u_3^\alpha)}{h_{10}h_{20}}, \quad (26)$$

$$P_{23}^\alpha(u_{30}) - P_{23}^\beta(u_{30}) = -\frac{\sigma_{32}}{R_{20}} - \frac{\partial\sigma_{21}}{\partial l_{10}} - \frac{\partial\sigma_{22}}{\partial l_{20}} - [P_{23}(u_3^\alpha) - P_{23}^\alpha(u_3^\alpha)]\frac{h_1(u_3^\alpha)h_2(u_3^\alpha)}{h_{10}h_{20}}, \quad (27)$$

$$P_{33}^\alpha(u_{30}) - P_{33}^\beta(u_{30}) = \frac{\sigma_{11}}{R_{10}} + \frac{\sigma_{22}}{R_{20}} - \frac{\partial\sigma_{31}}{\partial l_{10}} - \frac{\partial\sigma_{32}}{\partial l_{20}} - [P_{33}(u_3^\alpha) - P_{33}^\alpha(u_3^\alpha)]\frac{h_1(u_3^\alpha)h_2(u_3^\alpha)}{h_{10}h_{20}}, \quad (28)$$

where coordinate u_3^α is taken at the boundary of the inner part of the film that is regarded as referring to its side under consideration. If external fields are absent and bulk phases α and β are not only homogeneous but also isotropic, all nondiagonal components of their tensors and the corresponding components of vectors $\mathbf{P}_3^\alpha$ and $\mathbf{P}_3^\beta$ are zero. In this case, Eqs. (26) and (27) are simplified to an even greater extent:

$$\frac{\sigma_{31}}{R_{10}} + \frac{\partial\sigma_{11}}{\partial l_{10}} + \frac{\partial\sigma_{12}}{\partial l_{20}} + P_{13}(u_3^\alpha)\frac{h_1(u_3^\alpha)h_2(u_3^\alpha)}{h_{10}h_{20}} = 0, \quad (29)$$

$$\frac{\sigma_{32}}{R_{20}} + \frac{\partial\sigma_{21}}{\partial l_{10}} + \frac{\partial\sigma_{22}}{\partial l_{20}} + P_{23}(u_3^\alpha)\frac{h_1(u_3^\alpha)h_2(u_3^\alpha)}{h_{10}h_{20}} = 0, \quad (30)$$

whereas Eq. (28), with allowance for the conditions of homogeneity (the designations of coordinates can be omitted) and isotropy ($P_{11} = P_{22} = P_{33} = P$) of the bulk phases, can be written as

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

In the absence of external fields, the structure of the pressure tensor is formed under the influence of the space metric. Since the metric tensor of the film is diagonal in our selected system of orthogonal curvilinear coordinates, the pressure tensor can also be regarded as diagonal throughout the film. Consequently, the tension tensor will also be diagonal. In this simple case, instead of Eqs. (29)–(31), we have

$$\frac{\partial\sigma_{11}}{\partial l_{10}} = \frac{\partial\sigma_{22}}{\partial l_{20}} = 0, \quad (32)$$

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

For a plane film, our selected coordinate system passes into a Cartesian (x, y, z) system, and the ratio of the Lamé coefficients in Eq. (33) becomes equal to unity. In addition, terms related to the curvature disappear. Denoting $P_{33}(u_3^\alpha)$ as the normal component of the pressure tensor $P_N(z^\alpha)$, we transform Eq. (33) into the relationship

$$P^\alpha - P^\beta = P^\alpha - P_N(z^\alpha), \quad (34)$$

which is reduced to the known equilibrium condition $P_N = P^\beta$ and, by virtue of Eq. (6), to equality $P_N(z^\alpha) - P^\alpha = \Pi$ for the disjoining pressure of the film. Since coordinate z^α is chosen arbitrarily, condition (34) implies that P_N is independent of z and, consequently, of spatial coordinates in general.

The simplest case of a film with a nonuniform thickness is a film with planar sides in the form of a wedge. If the sides of the wedge are identical, it seems natural to introduce the median plane and consider the element in question with reference to it (Fig. 2). The case of a wedge corresponds to planar dividing surfaces with $R_{10} = R_{20} = \infty$ and cylindrical coordinates $u_1 = r$, $u_2 = z$, $u_3 = \varphi$ with Lamé coefficients $h_1 = 1$, $h_2 = 1$, $h_3 = r$. Now Eq. (33) assumes the form

$$P^\alpha - P^\beta = P^\alpha - P_{33}(\varphi^\alpha), \quad (35)$$

which shows that P_{33} again becomes a constant quantity (this time with respect to the φ coordinate). Denoting it by P_N, one can define the disjoining pressure as $\Pi \equiv P_N - P^\alpha$ for this case as well. We see that the introduction of the disjoining pressure for a film of nonuniform thickness does not cause any difficulties in this case. If β is a fluid phase with a uniform pressure, then formula (35) leads to the absurd conclusion that the disjoining pressure does not depend on the film thickness. This result means only that an equilibrium wedgelike shape is impossible for a free film. However, it is quite possible to implement this shape if the liquid fills a wedge-shaped slit in an (absolutely) solid body (Fig. 2).

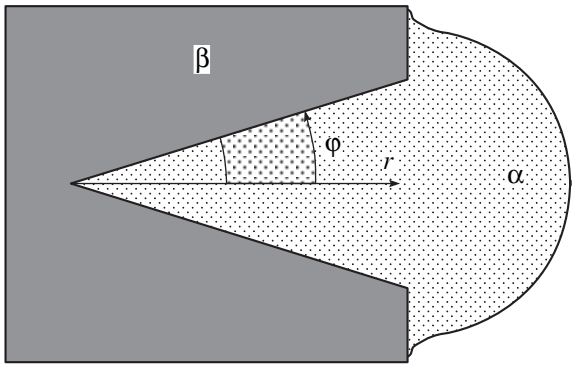

Fig. 2. Element of a thin wedge-shaped film.

If we select the dividing surface as the boundary surface of the solid and, putting $u_{30} = u_3^\beta$, perform integration in Eqs. (13) and (14) only over the region of the liquid film (thus introducing the surface tension that refers just to the liquid film), then P^β in formula (35) should be understood as the local pressure on the surface of the solid created by its internal stresses. In each point of the surface, these internal stresses balance the disjoining pressure and, naturally, depend on the position on the surface (on the r coordinate).

Naturally, the simple case where the film itself has the shape of a circular cylindrical surface is also considered in cylindrical coordinates. Now the dividing surfaces are also cylindrical ($0 < R_{10} < \infty$, $R_{20} = \infty$); the coordinate system is selected as $u_1 = \varphi$, $u_2 = z$, $u_3 = r$; and the values of the Lamé coefficients are $h_1 = r$, $h_2 = 1$, $h_3 = 1$. Accordingly, Eq. (33) assumes the form

$$P^\alpha - P^\beta = \frac{\sigma_{11}}{R_{10}} - [P_{33}(r^\alpha) - P^\alpha]\frac{r^\alpha}{R_{10}}. \quad (36)$$

If we choose r^α in the middle of the film ($r^\alpha = R_{10} - H/2$), then Eq. (36) can be rewritten as

$$P^\alpha - P^\beta = \frac{\sigma_{11}^m}{R_{10}} - [P_N^m - P^\alpha]\left(1 - \frac{H}{2R_{10}}\right), \quad (37)$$

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

Similarly, for a spherical film with $R_{10} = R_{20} = R_0$, $\sigma_{11} = \sigma_{22} = \sigma$, we choose $u_1 = \theta$, $u_2 = \varphi$, $u_3 = r$ and, accordingly, $h_1 = r$, $h_2 = r\sin\theta$, $h_3 = 1$. In this case, Eq. (33) yields

$$P^\alpha - P^\beta = \frac{2\sigma}{R_0} - [P_{33}(r^\alpha) - P^\alpha]\frac{r^{\alpha 2}}{R_0^2} \quad (38)$$

or

$$P^\alpha - P^\beta = \frac{2\sigma^m}{R_0} - [P_N^m - P^\alpha]\left(1 - \frac{H}{2R_0}\right)^2, \quad (39)$$

where $P_N^m \equiv P_{33}(R_0 - H/2)$ and $\sigma^m \equiv \sigma(R_0 - H/2)$.

TRANSITION ZONE OF A WETTING FILM

Now let us consider the application of formula (33) to the transition zone of a wetting film on an absolutely rigid planar surface. Since coordinate u_3^α is arbitrarily chosen within the film, one can select it as coinciding with the surface of the solid (Fig. 3), thus attributing the interior of the film to its surface layer at the boundary with the external fluid. Then $P_{33}(u_3^\alpha)$ assumes the meaning of the normal pressure acting on the solid surface (let us denote it by P_N^s). In accordance with Eq. (33), we obtain

$$P^\alpha - P^\beta = \frac{\sigma_{11}}{R_{10}} + \frac{\sigma_{22}}{R_{20}} - [P_N^s - P^\alpha]\frac{h_1(u_3^\alpha)h_2(u_3^\alpha)}{h_{10}h_{20}}. \quad (40)$$

The metric of the transition zone is characterized by the fact that coordinate surface u_1–u_2 is irregularly curved at the boundary with a gas (or another liquid) but is transformed into a plane at the boundary with a solid. The contribution of the capillary pressure disappears here, and the only reason for the difference between P_N^s and P^α is the interaction (overlapping) between opposite surface layers of the film. Therefore, the $P_N^s - P^\alpha$ difference can be termed the local disjoining pressure:

$$\Pi(u_1^\alpha, u_2^\alpha) \equiv P_N^s - P^\alpha. \quad (41)$$

Definition (41) shows that the local disjoining pressure, just as all other quantities in the right-hand side of Eq. (33), depends on the longitudinal coordinates. Using Eq. (41), one can write Eq. (33) in the form

$$P^\alpha - P^\beta = \frac{\sigma_{11}}{R_{10}} + \frac{\sigma_{22}}{R_{20}} - \Pi\frac{h_1(u_3^\alpha)h_2(u_3^\alpha)}{h_{10}h_{20}}. \quad (42)$$

In the specific case of a cylindrical dividing surface ($R_{20} = \infty$, $h_2 = 1$), this condition is reduced to

$$P^\alpha - P^\beta = \frac{\sigma_{11}}{R_{10}} - \Pi\frac{h_1(u_3^\alpha)}{h_{10}}. \quad (43)$$

Comparison of Figs. 1 and 3 shows that the curvature of the film surface in Fig. 3 is negative. Considering this, it is convenient to write Eqs. (42) and (43) in the general form

$$P^\beta - P^\alpha = P_c + \Pi L, \quad (44)$$

where P_c is the capillary pressure and L is the ratio of the Lamé coefficients:

$$L \equiv \frac{h_1(u_3^\alpha)h_2(u_3^\alpha)}{h_{10}h_{20}}. \quad (45)$$

The above explicit expressions for L corresponded to the simplest coordinate systems. In more complicated cases, one can calculate L using the formula [2]

$$\frac{1}{h_3}\frac{\partial \ln h_i}{\partial u_3} = \frac{1}{R_i} \quad (i = 1, 2). \quad (46)$$

Applying Eq. (46) to h_1 and h_2 in turn, integrating from u_{30} to u_3^α, and substituting the result into Eq. (45), we find

$$L = \exp\left[2\int_{u_{30}}^{u_3^\alpha} du_3 h_3(u_3)k(u_3)\right], \quad (47)$$

where

$$k(u_3) \equiv \frac{1}{2}\left(\frac{1}{R_1(u_3)} + \frac{1}{R_2(u_3)}\right) \quad (48)$$

is the local average curvature of coordinate surface u_1–u_2. Applying the mean value theorem and recalling that $h_3 du_3 = dl_3$, we can write Eq. (47) as

$$L = \exp(2\bar{k}\Delta l_3), \quad (49)$$

where $\bar{k}$ is the averaged value of $k(u_3)$ and Δl_3 is the length of the segment of coordinate line 3 between u_{30} and u_3^α (the curvilinear "thickness" of the film). For a thin film, whose actual local thickness H is much smaller than any of the curvature radii of the dividing surface, we have $\bar{k}\,\Delta l_3 \ll 1$, $\bar{k} \approx k_0$, where k_0 is the average curvature of the dividing surface, and $\Delta l_3 \approx H$. Consequently, formula (49) can be represented in the approximate form:

$$L \approx 1 + 2k_0 H. \quad (50)$$

For a negative average curvature of the film (remember that $k_0 < 0$ in our case, because the center of curvature is located at the side of phase α), $L \leqslant 1$ is true.

In the approximation of isotropic surface tension of the film (or rigorously for a cylindrical surface), formula (44) can be written in the form

$$P^\beta - P^\alpha = -2\sigma k_0 + \Pi L. \quad (51)$$

Equation (51) with $L = 1$ was introduced into science by Derjaguin [7] as the condition of the constancy of the chemical potential in a variable-thickness film; at the same time, the disjoining pressure of a uniform plane film of the corresponding thickness was used as Π. This assumption was also preserved in subsequent studies [8–12] (see reviews [13, 14] for other references). In [15, 16], the cosine of the local slope angle of the surface was introduced instead of L for the case where the disjoining pressure was determined along the normal to the horizontal plane rather than to the oblique plane of the film. In our derivation procedure, this inconsistency is removed at once through the use of curvilinear coordinates, so that the disjoining pressure acts along the normal to both aforementioned surfaces and equating the ratio L of Lamé coefficients to this cosine appears problematic. Note that another danger related to the use of Cartesian coordinates (it is within their framework that this cosine can be discussed) is that the capillary part of Eq. (51) becomes inexact. This is due to the fact that the pressure tensor of the transition zone of a wetting film becomes nondiagonal in Cartesian coordinates, and then one should return to the more general relation (31). As is shown above, $L = 1$ not only for a plane film but also for a wedge-shaped one. Therefore, if the profile of the transition zone does not differ from the wedgelike shape too much and its curvature is sufficiently low, then, according to formula (50), the condition $L \approx 1$ can turn out to be a fairly good approximation for calculations.

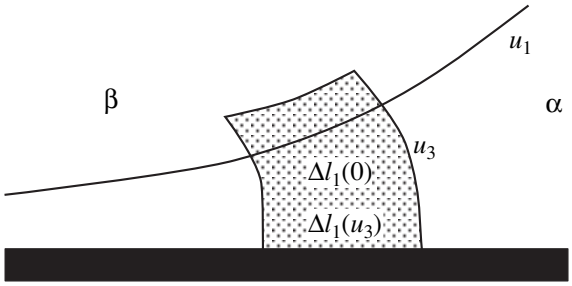

Fig. 3. Element of the transition zone of a wetting film.

Let us mention the known fact that the σ value in formula (51) does not coincide with the macroscopic surface tension (or with the sum of tensions at two sides of a thick film). A relationship between these values undoubtedly exists, although presently it is known only for the case of a plane thin film [4, Eq. (XIII.27)]:

$$\frac{\partial(\sigma^\beta + \sigma^\gamma)}{\partial H} = -\Pi(H) \quad (52)$$

[the designations are the same as in formula (7)]. In our case, $\sigma^\beta + \sigma^\gamma$ is replaced by the σ value, which, in accordance with Eq. (13), is an integral calculated with reference to the u_3^α coordinate. In the integration of Eq. (52), it is convenient to calculate this value with reference to the dividing surface; therefore, at the initial moment of integration, the chosen u_3^α value coincides with the curvilinear "thickness" of the film. However, if we regard it as constant in the process of integration (when the thickness of the film infinitely increases), then the σ value will pass into the macroscopic (tabulated) surface tension value αβ in the typical case, where the thickness of the thin film exceeds the thick-

ness of the fully developed surface layer at the σ_∞^β interface. In this case, integration of Eq. (52) yields

$$\sigma(H) = \sigma_\infty^\beta + \int_H^\infty \Pi(h)dh. \quad (53)$$

Naturally, formula (53) can be used only for a thin film with a slightly nonuniform thickness, when formula (50) is valid. Substituting Eq. (53) into Eq. (51) and considering Eq. (50), we arrive at the following equation:

$$P^\beta - P^\alpha = -2\left(\sigma_\infty^\beta + \int_H^\infty \Pi(h)dh - \Pi H\right)k_0 + \Pi. \quad (54)$$

Condition (44) at $L = 1$, interpretation of Π as the disjoining pressure of a plane-parallel film, and calculation of the capillary pressure with the use of tabulated surface tension values for a planar interface between the coexisting phases has repeatedly been used to calculate a sufficiently gentle sloping profile of the transition zone. Our local relationship (44) is true for the profile of arbitrary slope. However, if the profile has an arbitrary slope, the local disjoining pressure of a variable-thickness film, which is introduced above, is nonequivalent to the disjoining pressure of a plane-parallel film of corresponding thickness and should be calculated separately, with allowance for a given profile shape. Since the profile itself should be calculated for the already known dependence of the local disjoining pressure and local surface tension of the film on the film thickness, the problem can be solved by the method of successive approximations. In this case, a wedge-shaped profile can be used as the zero approximation. However, the solution of such a problem lies beyond the scope of this study.

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