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Three-Dimensional Aspect of the Surface Tension: An Approach Based on the Total Pressure Tensor

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Abstract—The conditions of mechanical equilibrium were considered, and the generalized notion of the surface tension at an arbitrarily curved surface layer was analyzed on the basis of the total nondiagonal pressure tensor including the external fields and anisotropic even in the bulk phases. It was shown that the transverse surface tension can be eliminated using the selection of a dividing surface; however, in the general case, this surface does not exhibit the properties of the tension surface. On the whole, three-dimensional and nondiagonal character of the tensors of excess surface stresses determined by the integration over the volume and the cross section of the surface layer is retained at any selection of the dividing surface.

1. INTRODUCTION

In the theory of capillarity, the surface tension is associated with the tension of two-dimensional membrane located at the boundary between two phases. In the absence of a field, the tensor of excess surface stresses (which is used to introduce the surface tension) is indeed two-dimensional for plane surfaces; however, for the spherical surface, the transverse surface tension (the normal component of the tensor of excess surface stresses) appears, which can be nullified by a simple selection of the position of the dividing surface as a tension surface [1]. In the presence of external (even such simple as gravitational) field, the transverse surface tension can hardly be eliminated by some conditional procedures. As a result of the permanent presence of three-dimensional aspect, the theory of interfacial phenomena begins to loose its inherent simplicity and attractiveness. How can this problem be solved? One of the possibilities is self-evident: if nothing happens in the absence of a field, the theory should be constructed using the total pressure tensor, which includes external fields and whose condition of mechanical equilibrium has exactly the same pattern as in the absence of a field. This possibility we would like to implement in this work; however, it is associated with one complication. As a rule, the common pressure tensor (where only the short-range interaction is taken into account) is diagonalized together with the metric tensor in a system of orthogonal curvilinear coordinates corresponding to the metrics of the surface layer. Therefore, in a theory of curved nonspherical surfaces (for example, see [1–8]), the pressure tensor is usually assumed to be diagonal and in the bulk phases, even isotropic. The case of the nondiagonal tensor of the surface tension (whose principal directions do not coincide with the curvature lines at the surface) has been considered only in [9], although the pressure tensor in the bulk phase was assumed to be isotropic. Meanwhile, already in an axially symmetric electric field, the total pressure tensor is nondiagonal [10] (the droplet in the field of the electric dipole of the condensation nucleus [11] or the droplet in the external homogeneous field [12] can serve as examples). In similar systems, during the determination of the tensor of excess surface stresses by the integration over the volume and cross section of the surface layer one has to deal with different three-dimensional nondiagonal tensors. It is necessary to study, using the tensors, how we can express the conditions of mechanical equilibrium at the surface, and is it possible to reduce these tensors to two-dimensional pattern by the selection of the dividing surface eliminating nondiagonal elements and transverse surface tension. This work is devoted precisely to the solution of these problems.

2. METRICS OF A SURFACE LAYER AND THE DIVIDING SURFACE

The dividing surface was determined [1] as the coordinate surface (u_1, u_2) of a system of orthogonal curvilinear coordinates u_1, u_2, and u_3 (u_3 is the coordinate normal to the surface), which diagonalizes the metric tensor of the surface layer considered as the Riemann surface with a curvature. Components of the metric tensor $\hat{g}$ have the form:

$$g_{ik} \equiv \mathbf{r}_{u_i} \cdot \mathbf{r}_{u_k} = \sum_{j=1}^{3} (\partial x_j/\partial u_i)(\partial x_j/\partial u_k) \quad (i, k = 1, 2, 3), \tag{2.1}$$

where $\mathbf{r}$ is the radius vector of the surface point; $\mathbf{r}_{u_i}$ is the partial derivative with respect to coordinate line u_i ($i = 1, 2, 3$; the vector $\mathbf{r}_{u_i}$ is tangential to the coordinate

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line u_i); $x_1 \equiv x$, $x_2 \equiv y$, $x_3 \equiv z$ are the Cartesian space coordinates; and the point denotes the scalar product of vectors. The tensor $\hat{g}$ is diagonalized in the orthogonal system of curvilinear coordinates, leaving only components g_{ii}. The variation in the length l_i of the coordinate line is connected with that of corresponding coordinate u_i by the relation:

$$dl_i = \sqrt{g_{ii}}du_i = h_i du_i, \tag{2.2}$$

where $h_i = \sqrt{g_{ii}}$ are the Lamé coefficients (i = 1, 2, 3). Correspondingly, we have

$$\mathbf{r}_{u_i} = h_i \mathbf{e}_i, \tag{2.3}$$

where $\mathbf{e}_i$ is the unit vector directed along the coordinate line u_i. The differential of the volume is set by the expression:

$$dV = h_1 h_2 h_3 du_1 du_2 du_3 = h_i du_i dA_i \quad (i = 1, 2, 3), \tag{2.4}$$

where A_i is the area of the coordinate surface normal to the coordinate line u_i.

The dividing surface satisfies the condition u_3 = const; however, its value remains arbitrary to some extent, i.e., any coordinate surface within the bounds of the surface layer or close to it can be selected as a dividing surface. In this case, the orthogonal coordinate system is characterized by the coincidence of its lines of curvature with the coordinate lines at the dividing surface. This implies that the radii of curvature R_1 and R_2 of the dividing surface directed along the unit vectors $\mathbf{e}_1$ and $\mathbf{e}_2$ corresponding to u_1 and u_2 are principal radii (maximal and minimal out of all radii of the surface curvature at a given point). As a result, the simple Rodrigues formula of differential geometry

$$\mathbf{n}_{u_i} = \mathbf{r}_{u_i}/R_i \quad (i = 1, 2), \tag{2.5}$$

where $\mathbf{n}$ is the unit vector of a normal to the dividing surface, is valid. The geometric relation

$$\partial \ln h_i / h_3 \partial u_3 = 1/R_i \quad (i = 1, 2) \tag{2.6}$$

is also fulfilled.

The mutual position of the coordinate surfaces is determined by the metrics of the surface layer; generally, one cannot state whether they are parallel or at least conform each other [1]. Gibbs [13] and then other authors took advantage of the approximation of conform surfaces where the passage from one position of nonspherical curved dividing surface to the other is performed by a simple displacement of each part of the surface along its normal. The meaning of this approximation can be explained as follows. Let in some position of the dividing surface $u_3 = u_{30}$, the value of the Lamé coefficient h_i (i = 1, 2) in a given surface point equals h_{i0}. After the displacement of the dividing surface by small value Δu_3, the selected point passes to the new position with the Lamé coefficient h_i. Expanding h_i near h_{i0} in powers of Δu_3 with allowance for Eq. (2.6), we have

$$\frac{h_i}{h_{i0}} = 1 + \frac{h_{30}\Delta u_3}{R_{i0}} + \frac{1}{2}\left[1 + \frac{R_{i0}}{h_{30}}\frac{\partial \ln h_3}{\partial u_3}\bigg|_0 - \frac{1}{h_{30}}\frac{\partial R_i}{\partial u_3}\bigg|_0\right]\left(\frac{h_{30}\Delta u_3}{R_{i0}}\right)^2 + \dots \tag{2.7}$$

It is seen from this expression that the expansion is actually performed with respect to the dimensionless parameter λ/R_{i0}, where $\lambda \equiv h_{30}\Delta u_3$.

If the coordinate line u_3 is the straight line ($h_3 = h_{30} = 1$, $\lambda = \Delta u_3$, $R_i = R_{i0} + \lambda$, $\partial R_i/\partial\lambda = 1$), the third term in the right-hand side of Eq. (2.7) and all subsequent terms of a series vanish; as a result, Eq. (2.7) transforms into the exact expression:

$$h_i/h_{i0} = R_i/R_{i0} = 1 + \lambda/R_{i0}, \tag{2.8}$$

where λ denotes the displacement of the dividing surface along the normal (i.e., the conformal transformation of the surface in its new position). In this case, we deal with the specific model of the surface layer with any (not definitely small) curvature. The Gibbs model is an example of the metrics of the surface layer; this model is rather general (the shapes of coordinate lines u_1 and u_2 and the dividing surface are arbitrary) and, at the same time, is rather simple (the coordinate line u_3 is the straight line) for analysis. This signifies the advance as compared with the spherical surface, where only one coordinate line is also the straight line but two other coordinate lines are characterized by the constant and equal curvatures.

On the other hand, addressing now to slightly curved surfaces and considering the displacements of the dividing surface within the bounds of the surface layer (whose thickness is much smaller than principal radii of the curvature of dividing surface), we can simply ignore the third term in the right-hand side of Eq. (2.7) and the subsequent terms of a series, because the expansion is performed precisely with respect to small parameter λ/R_{i0}. Then, we arrive again at expression (2.8), however, in this case, as an approximation for slightly curved surface layer with an arbitrary metrics. Hence, expression (2.8), largely simplifying the theory, retains its certain generality. It will be used below due to these considerations.

3. TOTAL PRESSURE TENSOR

Mechanical state of two-dimensional α–β system is characterized by setting the field of stress tensor $\hat{E}(\mathbf{r})$ or pressure tensor $\hat{p}(\mathbf{r})$ (they differ only in sign). The latter tensor is more widely applied to the fluid systems and we take advantage of its symbols. Generally, pressure tensor is nondiagonal; however, it is always symmetric and is characterized by not more than six different values out of nine components.

In the presence of the external field, acting on the unit volume of a system with force **f**, the condition of mechanical equilibrium is expressed as:

$$\nabla \cdot \hat{p} = \mathbf{f}, \tag{3.1}$$

where the point denotes the scalar product of a tensor by vector (it produces the vector). Condition (3.1) represents the balance between internal and external forces acting on the unit volume of a system (notation pattern using a Hamiltonian is convenient, because it is independent of the selection of the coordinate system). As is known for the gravitational field, $\mathbf{f} = \rho\mathbf{g}$, where ρ is the local density of a system, and **g** is the vector of the strength of gravitational field (gravitational acceleration); for the electromagnetic field, we have [14, pp. 346–347]

$$\mathbf{f} = (\rho_e + \mathbf{P} \cdot \nabla)\mathbf{E} + (\mathbf{M} \cdot \nabla)\mathbf{B} = \nabla \cdot \hat{T}_M, \tag{3.2}$$

where ρ_e is the local density of a space charge; **P** and **M** are the vectors of electric and magnetic polarizations, respectively; **E** is the vector of electric field strength; and **B** is the vector of the induction of the magnetic field. The value

$$\hat{T}_M \equiv \mathbf{D} \otimes \mathbf{E} + \mathbf{B} \otimes \mathbf{H} - (\mathbf{E}^2/2 + \mathbf{B}^2/2 - \mathbf{M} \cdot \mathbf{B})\hat{1} \tag{3.3}$$

characterizes the known Maxwell stress tensor (**D** is the vector of electric induction; **H** is the vector of the magnetic field strength; $\otimes$ symbolizes tensor product of the vectors; and $\hat{1}$ is the unit vector). Tensor products appearing in (3.3) include nondiagonal components (for example, the tensor $\mathbf{D} \otimes \mathbf{E}$ consists of components D_iE_k). Substitution of (3.2) and (3.3) into (3.1) yields the condition

$$\nabla \cdot \hat{p} = \nabla \cdot \hat{T}_M. \tag{3.4}$$

The external field is generated by the foreign bodies, i.e., by the bodies, which are not included into the system under consideration. However, the problem of which bodies should be included into a system is actually conventional. Interfacial phenomena can be considered the behavior of each of two contacting phases in the field of another phase. However, we already included both phases into the system considered. All other bodies (including the Earth) generating external fields can also be included in a system. With such an approach, the external field is always absent, and the condition of mechanical equilibrium (3.1) is written in the following form:

$$\nabla \cdot \hat{P} = 0, \tag{3.5}$$

where $\hat{P}$ is the total pressure tensor including the contributions of the fields, which we assumed to be the external fields prior to the inclusion of external bodies in a system. In other words, the total pressure tensor composed of the common pressure tensor and a certain tensor whose divergence is equal to –**f**. For example, comparing Eqs. (3.4) and (3.5), we conclude that, in the case of the electromagnetic field, the total pressure tensor is composed of the common pressure tensor and the Maxwell stress tensor taken with the minus sign (because the pressure differs from the stress in sign). The use of the total pressure tensor considerably simplifies the formulation of the conditions of mechanical equilibrium, because the pattern of principal Eq. (3.5) remains the same at the simultaneous action of any number of fields and coincides with the equilibrium condition in the absence of the field. At the same time, the structure of the pressure tensor per se becomes complicated during the passage to the total pressure tensor.

Vector equality (3.5) corresponds to three scalar equalities $e_i \cdot \nabla\hat{P} = 0$ ($i = 1, 2, 3$), which can be written as

$$\sum_{k=1}^{3}\left[\frac{1}{h_1h_2h_3}\frac{\partial}{\partial u_k}\left(\frac{h_1h_2h_3h_i}{h_k}P_{ik}\right) - P_{kk}\frac{\partial \ln h_k}{\partial u_i}\right] = 0 \quad (i = 1, 2, 3). \tag{3.6}$$

Equalities (3.6) are fulfilled in the surface layer as well as in both bulk phases; moreover, because the pressure tensor includes external fields, generally it cannot be considered an isotropic or at least a diagonal even in the fluid bulk phases in the selected system of curvilinear orthogonal coordinates connected with the metrics of a surface layer. However, if we digress from the existence of a surface layer, the system of curvilinear orthogonal coordinates (its selection depends on the external fields) diagonalizing the total pressure tensor can always be found in any bulk phase. In this coordinate system (connected with the metrics of the pressure tensor in the bulk phase and, generally speaking, is not coinciding with the coordinate system connected with the metrics of a surface layer), conditions (3.6) are simplified and written as

$$\frac{\partial P_{ii}}{\partial u_i} + \sum_{k=1}^{3}(P_{ii} - P_{kk})\frac{\partial \ln h_k}{\partial u_i} = 0 \quad (i = 1, 2, 3). \tag{3.7}$$

In the well-studied case of spherical symmetry ($P_{11} = P_{22} \equiv P_T$, $P_{33} \equiv P_N$, $h_1 = r$, $h_2 = r\sin\theta$, and $h_3 = 1$), equalities (3.7) at $i = 1, 2$ lead to the condition of the constancy of tangential pressure in the tangential direction, and the equality at $i = 3$ connects P_T and P_N by the relationship [15]:

$$dP_N/dr = 2(P_T - P_N)/r. \tag{3.8}$$

The latter expression is a good example of the relationship between the inhomogeneity and anisotropy of the equilibrium pressure tensor containing in Eq. (3.7) (this relationship vanishes only during the passage to the zero curvature). If the pressure tensor is isotropic ($P_N = P_T$), it is also spatially homogeneous ($dP_N/dr = dP_T/dr = 0$) in this and, hence, in any other coordinate system including that connected with the metrics of a surface layer. As we already know, the latter is always inhomogeneous and anisotropic; these considerations are of practical significance for the bulk phases.

In the other thoroughly studied case of cylindrical symmetry ($P_{11} = P_{\varphi\varphi}$, $P_{22} \equiv P_{zz}$, $P_{33} \equiv P_{rr}$, $h_1 = r$, and $h_2 = h_3 = 1$), equalities (3.7) at $i = 1, 2$ result in the condition of the constancy of the tangential pressure $P_{\varphi\varphi}$ in the direction of the variations in angle φ and pressure P_{zz} along the axis, and the equality at $i = 3$ connects $P_{\varphi\varphi}$ and P_{rr} by the relation

$$\partial(rP_{rr})/\partial r = P_{\varphi\varphi}. \tag{3.9}$$

4. TOTAL TENSOR OF EXCESS SURFACE STRESSES

The idea of passing to the total pressure tensor to introduce the surface tension [16] was exploited for a simple case of a spherical surface layer in the central electric field [17–22]. Now our task is the consideration of a more general case. Taking advantage of the common procedure for excess values [13] and method used in [1] for the common pressure tensor, let us introduce the total tensor of excess surface stresses $\bar{\bar{E}} \equiv \hat{\gamma}$ per unit area of an arbitrarily selected dividing surface between the α and β phases, which represents the coordinate surface (u_1, u_2). Let this surface be located at $u_3 = u_{30}$, and the surface layer extends from $u_3 = u_3^\alpha$ to $u_3 = u_3^\beta$. Let us single out the small part of a two-phase system (the narrow "flow tube" of the coordinate lines u_3) in preset intervals Δu_1 and Δu_2 of the variation of coordinates u_1 and u_2. Passing through any coordinate surface (u_1, u_2), this "flow tube" cuts-out the small area $\Delta l_1 \Delta l_2 = h_1 h_2 \Delta u_1 \Delta u_2$. Correspondingly, the area $\Delta l_{10} \Delta l_{20} = h_{10} h_{20} \Delta u_1 \Delta u_2$ is cut out at the dividing surface. Extrapolating Δu_1 and Δu_2 to zero, we establish the relation [1]

$$\hat{\gamma} = (1/h_{10}h_{20}) \times \left[\int_{u_3^\alpha}^{u_{30}} (\hat{P}^\alpha - \hat{P}) h_1 h_2 h_3 du_3 + \int_{u_{30}}^{u_3^\beta} (\hat{P}^\beta - \hat{P}) h_1 h_2 h_3 du_3\right], \tag{4.1}$$

which determines the tensor of excess surface stresses as an excess local value with respect to the pressure tensor. Considering the coordinate line u_3 to be the straight line ($h_3 = 1$, $u_3 = l_3$) and passing to the variable $\lambda \equiv u_3 - u_{30} = l_3 - l_{30}$, we can write Eq. (4.1) also as:

$$\hat{\gamma} = (1/R_{10}R_{20}) \times \left[\int_{\lambda^\alpha}^{0} (\hat{P}^\alpha - \hat{P}) R_1 R_2 d\lambda + \int_{0}^{\lambda^\beta} (\hat{P}^\beta - \hat{P}) R_1 R_2 d\lambda\right], \tag{4.2}$$

where Eq. (2.8) is taken into account. Note that, in this model, all values of R_1 in the integrand refer to the unique center of curvature located in the first principal cross section (we call it the first center of curvature); similarly, all values of R_2 refer to the unique second center of curvature; moreover, both centers are located at the same straight coordinate line u_3.

Like the pressure tensor, the tensor of excess surface stresses can be characterized by three vectors:

$$\boldsymbol{\gamma}_1 \equiv \hat{\gamma} \cdot \mathbf{e}_1, \quad \boldsymbol{\gamma}_2 \equiv \hat{\gamma} \cdot \mathbf{e}_2, \quad \boldsymbol{\gamma}_3 \equiv \hat{\gamma} \cdot \mathbf{n} \tag{4.3}$$

or by nine scalar terms (out of which no more than six terms are different). Among them, the diagonal elements γ_{11}, γ_{22}, and $\gamma_{33} \equiv \gamma_N$ are the largest. The first two vectors are responsible for the scalar surface tension, which, as is known, is expressed by the equation

$$\gamma = (\gamma_{11} + \gamma_{22})/2, \tag{4.4}$$

and the third vector is the transverse surface tension [1]. In accordance with Eq. (4.2), we can write

$$\gamma_{11} R_{10} R_{20} = \int_{\lambda^\alpha}^{0} (P_{11}^\alpha - P_{11}) R_1 R_2 d\lambda + \int_{0}^{\lambda^\beta} (P_{11}^\beta - P_{11}) R_1 R_2 d\lambda, \tag{4.5}$$

$$\gamma_{22} R_{10} R_{20} = \int_{\lambda^\alpha}^{0} (P_{22}^\alpha - P_{22}) R_1 R_2 d\lambda + \int_{0}^{\lambda^\beta} (P_{22}^\beta - P_{22}) R_1 R_2 d\lambda, \tag{4.6}$$

$$\gamma_N R_{10} R_{20} = \int_{\lambda^\alpha}^{0} (P_{33}^\alpha - P_{33}) R_1 R_2 d\lambda + \int_{0}^{\lambda^\beta} (P_{33}^\beta - P_{33}) R_1 R_2 d\lambda. \tag{4.7}$$

Multiplying the left- and right-hand sides of Eq. (4.5) by the unit angle $\delta\theta_2 = \delta l_2/R_2 = \delta l_{20}/R_{20}$, we obtain

$$\gamma_{11} R_{10} R_{20} \delta\theta_2 = \int_{\lambda^\alpha}^{0} R_1 (P_{11}^\alpha - P_{11}) R_2 \delta\theta_2 d\lambda + \int_{0}^{\lambda^\beta} R_1 (P_{11}^\beta - P_{11}) R_2 \delta\theta_2 d\lambda. \tag{4.8}$$

It is evident that $\gamma_{11} R_{20} \delta\theta_2 = \gamma_{11} \delta l_{20}$ is the excess force applied to the arc δl_{20} at the dividing surface and directed along the $\mathbf{e}_1$ vector. Since the $\gamma_{11} R_{20} \delta\theta_2$ force is directed perpendicular to the radius vector $\mathbf{R}_{10}$ (perpendicular to the vector of normal $\mathbf{n}$ to the dividing surface), the $\gamma_{11} R_{10} R_{20} \delta\theta_2$ product can be considered as an absolute value of the moment of this force with respect to the first center of curvature. The integrand $(P_{11}^\alpha - P_{11}) R_2 \delta\theta_2 d\lambda = (P_{11}^\alpha - P_{11}) \delta l_2 d\lambda$ is the excess force acting on the unit area $\delta l_2 d\lambda$ and directed perpendicular to radius vector $\mathbf{R}_1$. Consequently, the product of this force by R_1 is the absolute value of the moment of this local force with respect to the first center of curvature. The integration yields the torque for the whole surface layer, and hence, equality (4.5) determines the equivalence between the dividing surface and the real surface layer through the torque of the surface tension with respect to the first center of curvature. Similarly, multiplying the left- and right-hand sides of (4.6) by $\delta\theta_1 = \delta l_1/R_1 = \delta l_{10}/R_{10}$, we are ensured that the dividing surface allotted by the tension is equivalent to the real surface layer also through the torque of the surface tension with respect to the second center of curvature. As for the transverse surface tension γ_N, it is directed along the normal $\mathbf{n}$, and, hence, its torque with respect to both centers of curvature is equal to zero. Therefore, equality (4.7) for the transverse surface tension does not have the same meaning as equalities (4.5) and (4.6) have for the components γ_{11} and γ_{22} of the tensor of excess surface stresses.

Let us consider the dependence of $\hat{\gamma}$ on the position of the dividing surface at the fixed physical state of a system. Differentiation of (4.1) with respect to u_{30} gives

$$\begin{aligned}&\partial\hat{\gamma}/h_{30}\partial u_{30} + \hat{\gamma}\partial\ln(h_{10}h_{20})/h_{30}\partial u_{30}\\ &\quad = \hat{P}^{\alpha}(u_{30}) - \hat{P}^{\beta}(u_{30})\end{aligned} \tag{4.9}$$

or, with allowance made for (2.6),

$$\partial\hat{\gamma}/\partial l_{30} + \hat{\gamma}(1/R_{10} + 1/R_{20}) = \hat{P}^{\alpha}(l_{30}) - \hat{P}^{\beta}(l_{30}). \tag{4.10}$$

As is seen, the tensor of excess surface stresses depends on the position of the dividing surface. Let us assume that the α phase is located from the side of higher pressure (from the concave side of the surface, if both radii of surface curvature are of the same sign), and the distance l_{30} of the coordinate line to the dividing surface is counted from the boundary of the surface layer from the side of the α phase. Then, $R_{i0} = R_i^{\alpha} + l_{30}$, and (4.10) acquires the form of differential equation:

$$\begin{aligned}&\partial\hat{\gamma}/\partial l_{30} + \hat{\gamma}[(R_1^{\alpha} + l_{30})^{-1} + (R_2^{\alpha} + l_{30})^{-1}]\\ &\quad = \hat{P}^{\alpha}(l_{30}) - \hat{P}^{\beta}(l_{30}) \equiv \hat{P}_c(l_{30}),\end{aligned} \tag{4.11}$$

where, for brevity, the tensor of a capillary pressure is denoted as $\hat{P}_c$.

When total pressure tensor in the bulk phases is set as a function of spatial coordinates, Eq. (4.11) is solved as:

$$\begin{aligned}\hat{\gamma}(l_{30}) &= \hat{\gamma}(0)\frac{R_1^{\alpha}R_2^{\alpha}}{(R_1^{\alpha} + l_{30})(R_2^{\alpha} + l_{30})}\\ &+ \int_0^{l_{30}} dl\hat{P}_c(l)\frac{(R_1^{\alpha} + l)(R_2^{\alpha} + l)}{(R_1^{\alpha} + l_{30})(R_2^{\alpha} + l_{30})},\end{aligned} \tag{4.12}$$

where, according to (4.1), constant $\hat{\gamma}(0)$ is determined as:

$$\hat{\gamma}(0) = \frac{1}{h_1(u_3^{\alpha})h_2(u_3^{\alpha})}\int_{u_3^{\alpha}}^{u_3^{\beta}}(\hat{P}^{\beta} - \hat{P})h_1h_2h_3du_3. \tag{4.13}$$

In the simplest case of the constancy of the tensor of capillary pressure $\hat{P}_c$ (for example, as in the case of the gravitational field) relation (4.12) is reduced to:

$$\begin{aligned}\hat{\gamma}(l_{30}) &= \hat{\gamma}(0)\frac{R_1^{\alpha}R_2^{\alpha}}{(R_1^{\alpha} + l_{30})(R_2^{\alpha} + l_{30})}\\ &+ \hat{P}_c l_{30}\left[1 - \frac{(R_1^{\alpha} + R_2^{\alpha})l_{30}/2 + 2l_{30}^2/3}{(R_1^{\alpha} + l_{30})(R_2^{\alpha} + l_{30})}\right].\end{aligned} \tag{4.14}$$

Note that in the case of a slightly curved surface layer with an arbitrary metrics, the terms of the order of $(l_{30}/R_1^{\alpha})^2$ and $(l_{30}/R_2^{\alpha})^2$ and higher in relation (4.14) should be omitted.

Similar expressions can also be written for each (out of nine) component of the tensor of excess surface stresses. The most significant are the expressions for the diagonal components of the tensor of excess surface stresses:

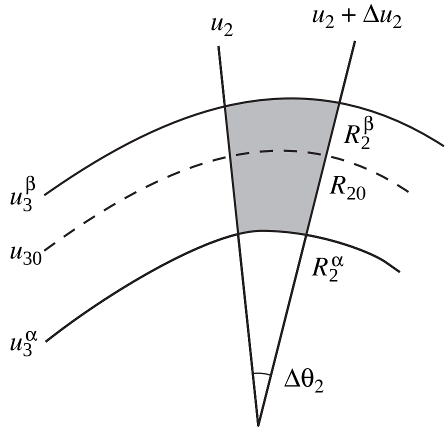
$$\begin{aligned}\gamma_{ii} &= \int_{\lambda^{\alpha}}^{0}(P_{ii}^{\alpha} - P_{ii})(1 + \lambda/R_{10})(1 + \lambda/R_{20})d\lambda\\ &+ \int_0^{\lambda^{\beta}}(P_{ii}^{\beta} - P_{ii})(1 + \lambda/R_{10})(1 + \lambda/R_{20})d\lambda;\end{aligned} \tag{4.15}$$

$$\begin{aligned}&\partial\gamma_{ii}/\partial l_{30} + \gamma_{ii}[(R_1^{\alpha} + l_{30})^{-1} + (R_2^{\alpha} + l_{30})^{-1}]\\ &\quad = P_{ii}^{\alpha}(l_{30}) - P_{ii}^{\beta}(l_{30});\end{aligned} \tag{4.16}$$

$$\begin{aligned}\gamma_{ii}(l_{30}) &= \frac{\gamma_{ii}(0)}{(1 + l_{30}/R_1^{\alpha})(1 + l_{30}/R_2^{\alpha})}\\ &+ (P_{ii}^{\alpha} - P_{ii}^{\beta})l_{30}\left[1 - \frac{(R_1^{\alpha} + R_2^{\alpha})l_{30}/2 + 2l_{30}^2/3}{(R_1^{\alpha} + l_{30})(R_2^{\alpha} + l_{30})}\right];\end{aligned} \tag{4.17}$$

$$\gamma_{ii}(0) = \frac{1}{h_1(u_3^{\alpha})h_2(u_3^{\alpha})}\int_{u_3^{\alpha}}^{u_3^{\beta}}(P_{ii}^{\beta} - P_{ii})h_1h_2h_3du_3. \tag{4.18}$$

Considering formula (4.17), let us attract our attention to the fundamental difference between the dependences $\gamma_{11}(l_{30})$ and $\gamma_{22}(l_{30})$, on the one hand, and $\gamma_{33}(l_{30}) \equiv \gamma_N(l_{30})$, on the other hand. We believe, as of today, that this difference is related to our understanding of the behavior of the tangential and normal pressures inside the surface layer. Tangential pressure (both P_{11} and P_{22}) changes its sign inside the surface layer and acquires quite large negative values (otherwise, we cannot explain the experimental values of the surface tension), whereas the normal component of the pressure tensor varies monotonically (by our assumption, it decreases)



Cross section of the surface layer.

while passing from the α to β phase. As a result, in accordance with Eq. (4.18), $\gamma_{11}(0) > 0$ and $\gamma_{22}(0) > 0$; however, $\gamma_N(0) < 0$. In the case of γ_N, the first terms in the right-hand sides of Eqs. (4.15) and (4.17) are negative, while the second terms are positive. As the dividing surface moves from the α to β phase, the γ_N tension passes from negative to positive values, so that we can always find the position of the dividing surface inside the surface layer for which $\gamma_N = 0$ (in this way, we can eliminate only one of non-two-dimensional components of nondiagonal tensor of excess surface stresses, which remains three-dimensional as a whole). In contrast, γ_{11} and γ_{22} are always positive and do not change their signs during the displacement of the dividing surface. Situation changes if we differentiate Eq. (4.17) with respect to l_{30}: then, on the contrary, there are always terms for γ_{11} and γ_{22} of opposite signs indicating the possibility of vanishing the derivatives of γ_{11} and γ_{22}, whereas derivative $\partial\gamma_N/\partial l_{30}$ does not change its sign during the displacement of the dividing surface. This means that γ_{11} and γ_{22} can pass the extremum (the minimum is especially evident at small values of R_1^α and R_2^α) although they remain positive, whereas the transverse surface tension does not exhibit extreme points.

5. EXCESS STRESSES IN CROSS SECTIONS OF A SURFACE LAYER

Above, we defined the tensor of excess surface stresses by the integration over the volume. However, excesses can also be taken by the integration over the cross section of the surface layer at a given position of the dividing surface. Selecting the cross section as a narrow band of the coordinate surface (u_2, u_3) within the u_2, $u_2 + \Delta u_2$ and u_3^α, u_3^β ranges (figure) and extrapolating Δu_2 to zero, we state, similarly to Eq. (4.1), that

$$\hat{\gamma}' = \frac{1}{h_{20}} \times \left[\int_{u_3^\alpha}^{u_{30}} (\hat{P}^\alpha - \hat{P}) h_2 h_3 du_3 + \int_{u_{30}}^{u_3^\beta} (\hat{P}^\beta - \hat{P}) h_2 h_3 du_3\right]. \tag{5.1}$$

Multiplying scalarly Eq. (5.1) by $\boldsymbol{e}_1$, we obtain:

$$\boldsymbol{\gamma}_1' = \frac{1}{h_{20}} \times \left[\int_{u_3^\alpha}^{u_{30}} (\hat{P}^\alpha - \hat{P}) \cdot \mathbf{e}_1 h_2 h_3 du_3 + \int_{u_{30}}^{u_3^\beta} (\hat{P}^\beta - \hat{P}) \cdot \mathbf{e}_1 h_2 h_3 du_3\right]. \tag{5.2}$$

Under the linearity of the coordinate line u_3 $h_3 = 1$ and $u_3 = l_3$ using variable $\lambda \equiv u_3 - u_{30} = l_3 - l_{30}$ with allowance for Eq. (2.8), we can express Eq. (5.2) also as

$$\gamma_1' R_{20} = \int_{\lambda^\alpha}^{0} (\hat{P}^\alpha - \hat{P}) \cdot \mathbf{e}_1 R_2 d\lambda + \int_{0}^{\lambda^\beta} (\hat{P}^\beta - \hat{P}) \cdot \mathbf{e}_1 R_2 d\lambda. \tag{5.3}$$

Multiplying both sides of Eq. (5.3) by the unit angle $d\theta_2$ (figure), in the left-hand side we obtain the excess force acting on the $R_{20}d\theta_2$ area of the cross section of the dividing surface. Integrands in the right-hand side are the excess forces acting on the unit area $R_2 d\theta_2 d\lambda$, and integrals give the total excess force acting on the cross section of the surface layer in the unit angle $d\theta_2$. Hence, expression (5.3) determines the excess force $\boldsymbol{\gamma}_1'$ per unit length of the cut-out of the dividing surface, which is equal exactly to the real excess force acting on the corresponding section of the surface layer.

All that has been said above refers to each component of force $\boldsymbol{\gamma}_1'$, of which the most interesting is the component of surface tension γ_{11}'. From Eq. (5.3), we have

$$\gamma_{11}' R_{20} = \int_{\lambda^\alpha}^{0} (P_{11}^\alpha - P_{11}) R_2 d\lambda + \int_{0}^{\lambda^\beta} (P_{11}^\beta - P_{11}) R_2 d\lambda. \tag{5.4}$$

This relation demonstrates that the surface tension in the u_1 direction is equivalent to the total excess force in the surface layer in this direction.

Differentiating Eq. (5.1) with respect to u_{30} and taking Eq. (2.6) into account, we arrive at a simple differential equation for the dependence of $\hat{\gamma}'$ on the position of the dividing surface

$$\frac{\partial \hat{\gamma}'}{\partial l_{30}} + \frac{\hat{\gamma}'}{R_{20}} = \hat{P}^{\alpha}(l_{30}) - \hat{P}^{\beta}(l_{30}), \tag{5.5}$$

that is similar to Eq. (4.10). Generally, the solution of Eq. (5.5) [written in the variables of expression (4.12)] can be represented as

$$\hat{\gamma}'(l_{30}) = \frac{\hat{\gamma}'(0)}{1 + l_{30}/R_2^{\alpha}} + \int_0^{l_{30}} dl \hat{P}_c(l) \frac{1 + l/R_2^{\alpha}}{1 + l_{30}/R_2^{\alpha}}, \tag{5.6}$$

where

$$\hat{\gamma}'(0) = \frac{1}{R_2^{\alpha}} \int_{u_3^{\alpha}}^{u_3^{\beta}} (\hat{P}^{\beta} - \hat{P}) R_2 du_3 \tag{5.7}$$

and, in the case of constant $\hat{P}_c \equiv \hat{P}^{\alpha} - \hat{P}^{\beta}$, as

$$\hat{\gamma}'(l_{30}) = \frac{\hat{\gamma}'(0)}{1 + l_{30}/R_2^{\alpha}} + (\hat{P}^{\alpha} - \hat{P}^{\beta}) l_{30} \frac{1 + l_{30}/2R_2^{\alpha}}{1 + l_{30}/R_2^{\alpha}}. \tag{5.8}$$

Similar speculations can be performed also for another principal section of the surface layer. The tensor of excess surface stresses is determined for this section by the relation

$$\hat{\gamma}'' = (1/h_{10}) \times \left[\int_{u_3^{\alpha}}^{u_{30}} (\hat{P}^{\alpha} - \hat{P}) h_1 h_3 du_3 + \int_{u_{30}}^{u_3^{\beta}} (\hat{P}^{\beta} - \hat{P}) h_1 h_3 du_3 \right], \tag{5.9}$$

and its vector component at the coordinate line u_1 is:

$$\boldsymbol{\gamma}_2'' = (1/h_{10}) \left[\int_{u_3^{\alpha}}^{u_{30}} (\hat{P}^{\alpha} - \hat{P}) \cdot \mathbf{e}_2 h_1 h_3 du_3 + \int_{u_{30}}^{u_3^{\beta}} (\hat{P}^{\beta} - \hat{P}) \cdot \mathbf{e}_2 h_1 h_3 du_3 \right], \tag{5.10}$$

that is equivalent to the condition

$$\boldsymbol{\gamma}_2'' R_{10} = \int_{\lambda^{\alpha}}^{0} (\hat{P}^{\alpha} - \hat{P}) \cdot \mathbf{e}_2 R_1 d\lambda + \int_0^{\lambda^{\beta}} (\hat{P}^{\beta} - \hat{P}) \cdot \mathbf{e}_2 R_1 d\lambda. \tag{5.11}$$

Correspondingly, condition

$$\gamma_{22}'' R_{10} = \int_{\lambda^{\alpha}}^{0} (P_{22}^{\alpha} - P_{22}) R_1 d\lambda + \int_0^{\lambda^{\beta}} (P_{22}^{\beta} - P_{22}) R_1 d\lambda \tag{5.12}$$

indicates that the surface tension in the direction of u_2 is equivalent to the total excess force in the surface layer in the same direction. From expression (5.9), we have the differential equation

$$\frac{\partial \hat{\gamma}''}{\partial l_{30}} + \frac{\hat{\gamma}''}{R_{10}} = \hat{P}^{\alpha}(l_{30}) - \hat{P}^{\beta}(l_{30}), \tag{5.13}$$

that describes the dependence of $\hat{\gamma}''$ on the position of the dividing surface. The solution of this equation at a constant $\hat{P}^{\alpha} - \hat{P}^{\beta}$ difference [written in the variables of expression (4.14)] has the form:

$$\hat{\gamma}''(l_{30}) = \frac{\hat{\gamma}''(0)}{1 + l_{30}/R_1^{\alpha}} + (\hat{P}^{\alpha} - \hat{P}^{\beta}) l_{30} \frac{1 + l_{30}/2R_1^{\alpha}}{1 + l_{30}/R_1^{\alpha}}. \tag{5.14}$$

Note that Eqs. (5.8) and (5.14) for the components γ_{11}' and γ_{22}'' of the surface tension are characterized by a single minimum.

6. CONSISTENCE BETWEEN THE DEFINITIONS OF THE TENSOR OF EXCESS SURFACE STRESSES DURING THE INTEGRATION OVER THE VOLUME AND CROSS SECTION OF THE SURFACE LAYER

As was shown in Sections 4 and 5, the integration of excess stresses in the surface layer over the volume or cross section allows us to determine the components of the tensor of excess surface stresses, so that the corresponding dividing surface is equivalent to the real surface layer through the torque of the surface tension with respect to corresponding center of curvature or through the force at the corresponding section of the surface layer. Let us consider now how these definitions agree with each other.

Let us compare expressions (4.17) and (5.8) for γ_{11} and γ_{11}'. In the limit of infinitely large R_1^{α} and R_2^{α} values, these expressions result in the same linear dependence; however, for finite R_1^{α} and R_2^{α}, the $\gamma_{11}(l_{30})$ and $\gamma_{11}'(l_{30})$ curves are characterized by the different slopes and can intersect each other, so that it becomes possible to select the position of the dividing surface from the condition

$$\gamma_{11} = \gamma_{11}', \tag{6.1}$$

when the dividing surface is equivalent to the surface layer both through the force and the torque acting in the u_1 direction (such a dividing surface is called the tension surface). Similarly, comparing expressions (4.17) and (5.14) for γ_{22} and γ_{22}'', we also arrive at the conclusion of the possibility of determining the position of the dividing surface (tension surface) from the condition

$$\gamma_{22} = \gamma_{22}''. \tag{6.2}$$

In the case of the surface layer with the spherical symmetry when the radii of curvature of principal normal sections coincide, conditions (6.1) and (6.2) are identical, and the position of the tension surface is determined uniquely from any of these conditions.

Let us consider now what conclusions follow from conditions (6.1) and (6.2) in the case of the surface layer with cylindrical symmetry. As at the end of Section 3, we assumed that $P_{11} = P_{\varphi\varphi}$, $P_{22} = P_{zz}$, $P_{33} = P_{rr}$, $h_1 = r$, and $h_2 = h_3 = 1$. Liquid cylinder possess the finite curvature only in one of the principal normal sections (along the variation of the φ coordinate). Let us select the cylindrical dividing surface in the surface layer at $r = R_{10} = R_\varphi$.

From Eq. (4.1), we find that the component of the tensor of surface tension $\gamma_{\varphi\varphi}$ defined as the excess torque acting in the surface layer along the variation of axial angle φ is equal to

$$\gamma_{\varphi\varphi}R_\varphi = \int_{R_\varphi^\alpha}^{R_\varphi}(P_{\varphi\varphi}^\alpha - P_{\varphi\varphi})r dr + \int_{R_\varphi}^{R_\varphi^\beta}(P_{\varphi\varphi}^\beta - P_{\varphi\varphi})r dr. \quad (6.3)$$

From Eq. (5.1), we find that the component of the tensor of surface tension $\gamma'_{\varphi\varphi}$ defined as the excess forces acting in the surface layer along the variation of axial angle φ is written as

$$\gamma'_{\varphi\varphi} = \int_{R_\varphi^\alpha}^{R_\varphi}(P_{\varphi\varphi}^\alpha - P_{\varphi\varphi})dr + \int_{R_\varphi}^{R_\varphi^\beta}(P_{\varphi\varphi}^\beta - P_{\varphi\varphi})dr. \quad (6.4)$$

In accordance with (6.1), we seek for the tension surface of a cylinder from the $\gamma_{\varphi\varphi} = \gamma'_{\varphi\varphi}$ condition. As follows from Eqs. (6.3) and (6.4), this condition uniquely determines the R_φ radius. Because the curvature in the second of principal normal sections (along the variation of coordinate z) is equal to zero in the cylindrical surface layer, then, as follows from Eqs. (4.6) and (5.12), the equality

$$\gamma_{zz} = \gamma''_{zz} = \frac{1}{R_\varphi}\left[\int_{R_\varphi^\alpha}^{R_\varphi}(P_{zz}^\alpha - P_{zz})r dr + \int_{R_\varphi}^{R_\varphi^\beta}(P_{zz}^\beta - P_{zz})r dr\right] \quad (6.5)$$

takes place at any value of R_φ. Correspondingly, condition (6.2) is fulfilled together with condition (6.1), and the tension surface is uniquely determined in this case. Note that formulas (6.3)–(6.5) already appeared in [23]; however, it was concluded in this work that it is impossible to determine the single tension surface for the cylindrical surface layer. This conclusion [23] was related to the use of determining tension surface as corresponding to the maximum at the dependence of γ_{zz} on the radius of the dividing surface. Such a dividing surface actually exists and its radius differs from R_φ but it is not equivalent to the real surface layer through the mechanical torque, because the arm of excess force at the dividing surface in the direction of the z axis is not equal to R_φ.

In the general case of arbitrarily curved surface layer, each of conditions (6.1) and (6.2) separately determines the position of the dividing surface as a tension surface. Simultaneous fulfillment of these conditions for a given dividing surface can result only from the occasional coincidence. As a result, the tension surfaces in different directions are generally different; however, for the large radii of curvature or small deviations from the sphericity of the surface layer, the difference in their positions inside the surface is negligible and it can be ignored.

7. CONDITION OF MECHANICAL EQUILIBRIUM AT THE SURFACE

Earlier we formulated the condition of mechanical equilibrium using local relations (3.6), which act both in the bulk phases and inside the surface layer. Passing now to the excess values, we express conditions of mechanical equilibrium in terms of surface tension. The most important out of these conditions is the condition of equilibrium across the surface layer (the Laplace formula), which can be derived using only the third of relations (3.6). The latter relation, with allowance for (2.6) and the linearity of coordinate line u_3 ($h_3 = 1$), has the following form:

$$\frac{1}{h_1 h_2}\left[\frac{\partial}{\partial u_1}(h_2 P_{31}) + \frac{\partial}{\partial u_2}(h_1 P_{32}) + \frac{\partial}{\partial u_3}(h_1 h_2 P_{33})\right] - \frac{P_{11}}{R_1} - \frac{P_{22}}{R_2} = 0. \quad (7.1)$$

Let us apply this equality to the narrow section of the surface layer within the range of coordinates $u'_1 \le u_1 \le u''_1$, $u'_2 \le u_2 \le u''_2$, $u_3^\alpha \le u_3 \le u_3^\beta$. Multiplying (7.1) by (2.4), integrating over this section, and using (2.8), we obtain

$$\int_{u = u''_1} P_{31}dA_1 - \int_{u = u'_1} P_{31}dA_1 + \int_{u = u''_2} P_{32}dA_2 - \int_{u = u'_2} P_{32}dA_2 + \int_{u_3 = u_3^\beta} P_{33}dA_3 - \int_{u_3 = u_3^\alpha} P_{33}dA_3 - \int_{A_0} dA_0\left[\frac{1}{R_{10}h_{20}}\int_{u_3^\alpha}^{u_3^\beta} P_{11}h_2 du_3 + \frac{1}{R_{20}h_{10}}\int_{u_3^\alpha}^{u_3^\beta} P_{22}h_1 du_3\right] = 0, \quad (7.2)$$

where A_0 is the area of the dividing surface within the bounds of selected section. Let us write the same expressions for the α and β bulk phases with respect to the regions of the selected section of the surface layer adjacent to these phases on both sides of the dividing surface and subtract these expressions from (7.2) using “force” definitions of the components of the surface tension in accordance with (5.1) and (5.9). As a result of these manipulations, we arrive at the condition

$$\int_{A_0}\left(P_{33}^{\alpha}-P_{33}^{\beta}-\frac{\gamma'_{11}}{R_{10}}-\frac{\gamma''_{22}}{R_{20}}\right)dA_0+\int_{u_1=u''_1}\gamma'_{31}dl_{20}$$
$$-\int_{u_1=u'_1}\gamma'_{31}dl_{20}+\int_{u_2=u''_2}\gamma''_{32}dl_{10}-\int_{u_2=u'_2}\gamma''_{32}dl_{10}=0. \quad (7.3)$$

Combining pairwise the latter four summands in (7.3), we can transform them into the form similar to that of the first summand

$$\int_{u_1=u''_1}\gamma'_{31}dl_{20}-\int_{u_1=u'_1}\gamma'_{31}dl_{20}$$
$$=\int_{u'_1}^{u''_1}\frac{\partial\gamma'_{31}}{\partial u_1}du_1dl_{20}=\int_{A_0}\frac{\partial\gamma'_{31}}{\partial l_{10}}dA_0, \quad (7.4)$$

$$\int_{u_2=u''_2}\gamma''_{32}dl_{10}-\int_{u_2=u'_2}\gamma''_{32}dl_{10}$$
$$=\int_{u'_2}^{u''_2}\frac{\partial\gamma''_{32}}{\partial u_2}du_2dl_{10}=\int_{A}\frac{\partial\gamma''_{32}}{\partial l_{20}}dA_0. \quad (7.5)$$

Substituting (7.4) and (7.5) into (7.3) and taking into account that the equality of the unique integral (which was obtained earlier) to zero should be fulfilled irrespective of the dimensions of the dividing surface, we obtain the condition of the mechanical equilibrium of the surface layer as

$$P_{33}^{\alpha}-P_{33}^{\beta}=\frac{\gamma'_{11}}{R_{10}}+\frac{\gamma''_{22}}{R_{20}}-\frac{\partial\gamma'_{31}}{\partial l_{10}}-\frac{\partial\gamma''_{32}}{\partial l_{20}}, \quad (7.6)$$

where all values refer to the dividing surface whose position can be selected arbitrarily. The equation similar to (7.6) and describing the mechanical equilibrium of the curved membrane was derived in [24].

In the case of the diagonal pressure tensor and, hence, the diagonal tensors of excess surface stresses, $\gamma'_{31}=\gamma''_{32}=0$, relation (7.6) transforms into common Laplace’s formula. Thus, relation (7.6) significantly generalizes Laplace’s formula for the case of nondiagonal tensor of excess surface stresses.

8. TRANSVERSE SURFACE TENSION

Let us consider now the transverse tension, which, according to (4.7) and (2.8), can be written as

$$\gamma_N\equiv\gamma_{33}=\frac{1}{R_{10}R_{20}}$$
$$\times\left[\int_{\lambda^{\alpha}}^{0}(P_{33}^{\alpha}-P_{33})R_1R_2d\lambda+\int_{0}^{\lambda^{\beta}}(P_{33}^{\beta}-P_{33})R_1R_2d\lambda\right] \quad (8.1)$$
$$=\frac{1}{h_{10}h_{20}}\left[\int_{\lambda^{\alpha}}^{0}(P_{33}^{\alpha}-P_{33})h_1h_2d\lambda+\int_{0}^{\lambda^{\beta}}(P_{33}^{\beta}-P_{33})h_1h_2d\lambda\right].$$

Integrating in parts (with allowance for the fact that the pressure difference is nullified within the limits of integration λ^{α} and λ^{β}) and using (7.1), we arrive at the expression:

$$\gamma_N=-\frac{1}{R_{10}R_{20}}$$
$$\times\left[\int_{\lambda^{\alpha}}^{0}(P_{11}^{\alpha}-P_{11})R_2\lambda d\lambda+\int_{0}^{\lambda^{\beta}}(P_{11}^{\beta}-P_{11})R_2\lambda d\lambda\right]$$
$$-\frac{1}{R_{10}R_{20}}\left[\int_{\lambda^{\alpha}}^{0}(P_{22}^{\alpha}-P_{22})R_1\lambda d\lambda+\int_{0}^{\lambda^{\beta}}(P_{22}^{\beta}-P_{22})R_1\lambda d\lambda\right]$$
$$+\frac{1}{h_{10}h_{20}}\left\{\int_{\lambda^{\alpha}}^{0}\frac{\partial[h_2(P_{31}^{\alpha}-P_{31})]}{\partial u_1}\lambda d\lambda\right. \quad (8.2)$$
$$\left.+\int_{0}^{\lambda^{\beta}}\frac{\partial[h_2(P_{31}^{\beta}-P_{31})]}{\partial u_1}\lambda d\lambda\right\}$$
$$+\frac{1}{h_{10}h_{20}}\left\{\int_{\lambda^{\alpha}}^{0}\frac{\partial[h_1(P_{32}^{\alpha}-P_{32})]}{\partial u_2}\lambda d\lambda\right.$$
$$\left.+\int_{0}^{\lambda^{\beta}}\frac{\partial[h_1(P_{32}^{\beta}-P_{32})]}{\partial u_2}\lambda d\lambda\right\}.$$

Let us use now relation (2.8) so that the substitution $\lambda=R_1-R_{10}$ is used in the first, $\lambda=R_2-R_{20}$ in the second, $\lambda=R_{10}(h_1-h_{10})/h_{10}$ in the third, and $\lambda=R_{20}(h_2-h_{20})/h_{20}$ in the fourth of four summands of expression (8.2). Remembering definitions γ_{11}, γ_{22}, γ_{31}, γ_{32}, γ'_{11}, γ''_{22}, γ'_{31}, and γ''_{32}, according to (4.1), (4.2), (5.1), and (5.9), we obtain rather remarkable relation:

$$\gamma_N = (\gamma'_{11} - \gamma_{11}) + (\gamma''_{22} - \gamma_{22})$$
$$- \frac{\partial}{\partial l_{10}}[R_{10}(\gamma'_{31} - \gamma_{31})] - \frac{\partial}{\partial l_{20}}[R_{20}(\gamma''_{32} - \gamma_{32})]. \quad (8.3)$$

As is seen from (8.3), even simultaneous fulfillment of conditions (6.1) and (6.2) does not lead to the elimination of the transverse tension in the general case of nondiagonal total pressure tensor, because for nullifying the right-hand side of (8.3) it is necessary to fulfill additional conditions of mechanical equivalence $\gamma'_{31} = \gamma_{31}$ and $\gamma''_{32} = \gamma_{32}$. Simultaneous fulfillment of all these conditions can result only from the occasional coincidence, because it is impossible to select the position of the dividing surface satisfying four independent conditions. Although, as was mentioned at the end of Section 4, the dividing surface, for which $\gamma_N = 0$, always exists. In the general case of nondiagonal pressure tensor, this surface is not the tension surface.

Let us consider the case of total nondiagonal pressure tensor in more detail. In this case, the third and fourth summands in (8.3) vanish, and the elimination of the transverse tension can result from only one condition:

$$\gamma'_{11} + \gamma''_{22} = \gamma_{11} + \gamma_{22}, \quad (8.4)$$

which is expressed as an equality of the sum of surface tension components determined by the force and the torque. Such a position of the dividing surface can always be found and it can be taken as a tension surface of a nonspherical curved surface in the case considered. Taking the definition of scalar surface tension (4.4) into account, condition (8.4) can be written as

$$\gamma^f = \gamma^m, \quad (8.5)$$

where

$$\gamma^f \equiv \frac{\gamma'_{11} + \gamma''_{22}}{2}, \quad \gamma^m \equiv \frac{\gamma_{11} + \gamma_{22}}{2} \quad (8.6)$$

represent the surface tension determined from the force and torque in the surface layer, respectively.

Let us illustrate all what have been said above by the examples of spherical and cylindrical surface layers. If we select the sphere with radius R as a dividing surface, the transverse surface tension γ_N for the spherical surface layer has, according to (8.1), the following form:

$$\gamma_N R^2 = \int_{R^\alpha}^{R} (P_N^\alpha - P_N) r^2 dr + \int_{R}^{R^\beta} (P_N^\beta - P_N) r^2 dr. \quad (8.7)$$

Similarly, using Eqs. (4.5), (4.6), (5.4), (5.12), and (8.6), for the selected dividing surface, we find:

$$\gamma^f R = \int_{R^\alpha}^{R} (P_T^\alpha - P_T) r dr + \int_{R}^{R^\beta} (P_T^\beta - P_T) r dr, \quad (8.8)$$

$$\gamma^m R^2 = \int_{R^\alpha}^{R} (P_T^\alpha - P_T) r^2 dr + \int_{R}^{R^\beta} (P_T^\beta - P_T) r^2 dr. \quad (8.9)$$

It can be easily seen with allowance for (3.8), (8.8), and (8.9) that, under the fulfillment of condition (8.5), the right-hand side of (8.7) can be reduced to zero. In the case in question, Laplace's formula (7.6) for the spherical tension surface can be rewritten in the form:

$$P_N^\alpha - P_N^\beta = \frac{2\gamma^m}{R}. \quad (8.10)$$

Hence, the right-hand side of the Kondo equation [resulted from (4.16) or readily derived by the differentiation of Eq. (8.9)]

$$\frac{\partial \gamma^m}{\partial R} = P_T^\alpha - P_T^\beta - \frac{2\gamma^m}{R} \quad (8.11)$$

for the tension surface, determined at the total pressure tensor, does not vanish, and, at $\gamma_N = 0$, the equality $\partial\gamma^m/\partial R = 0$ (which took place in the absence of the field) is not fulfilled.

According to (8.1), the transverse surface tension for the cylindrical surface layer acquires the form

$$\gamma_N R_\varphi = \int_{R_\varphi^\alpha}^{R_\varphi} (P_{rr}^\alpha - P_{rr}) r dr + \int_{R_\varphi}^{R_\varphi^\beta} (P_{rr}^\beta - P_{rr}) r dr. \quad (8.12)$$

Integrating in parts the right-hand side of (8.12) and using (3.9) and (6.3), we find

$$\gamma_N = R_\varphi \left\{ P_{rr}^\alpha - P_{rr}^\beta - \frac{\gamma_{\varphi\varphi}}{R_\varphi} \right\}. \quad (8.13)$$

Noting that, in the case considered, Laplace's formula (7.6) can be rewritten for the cylindrical surface in the following form:

$$P_{rr}^\alpha - P_{rr}^\beta = \frac{\gamma'_{\varphi\varphi}}{R_\varphi}, \quad (8.14)$$

we are ensured that $\gamma_N = 0$ under the condition (8.5) with allowance for (6.5) and (8.6). We can also see that the right-hand side of the Kondo equation [resulted from (4.16) or easily derived by the differentiation of (6.3)]

$$\frac{\partial \gamma_{\varphi\varphi}}{\partial R_\varphi} = P_{\varphi\varphi}^\alpha - P_{\varphi\varphi}^\beta - \frac{\gamma_{\varphi\varphi}}{R_\varphi} \quad (8.15)$$

for the cylindrical tension surface determined at the total pressure tensor does not vanish, and, at γ_N, the equality $\partial\gamma_{\varphi\varphi}/\partial R_\varphi = 0$ (taking place in the absence of field) is not fulfilled.

CONCLUSION

The analysis performed indicates that the three-dimensional aspect appears also in the total tensor of excess surface stresses. Selecting the position of the dividing surface, we can eliminate the transverse surface tension; however, we cannot avoid of the nondiagonal components of the three-dimensional tensor of excess surface stresses. Nondiagonal components of this tensor are present also in the condition of mechanical equilibrium across the surface layer generalizing Laplace's formula.

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