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Three-Dimensional Aspect of Surface and Linear Tensions

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Abstract—The exact concepts of the dividing surface related to the metrics of an arbitrarily curved surface layer and the transverse surface tension as the excess surface value with respect to the normal component of stress tensor were introduced. It was shown that, in the absence of external fields, there will be a dividing surface in a slightly curved surface layer. This dividing surface satisfies the zero value of transverse surface tension and coincides with the tension surface. When external fields are present, the tensors of excess surface and linear stresses are three-dimensional parameters, whose dimensions generally cannot be diminished by the selection of the positions of dividing surfaces and lines. At the same time, the conditions of mechanical equilibrium for curved surfaces can be formulated without using the transverse surface tension. The conditions of mechanical equilibrium at the contact line include the transverse tension of a line and the normal components of linear tension.

1. INTRODUCTION

The key point of a theory of plane and curved interfaces is the concept of a stressed surface (tension surface) substituting for the real surface layer. Undoubtedly, the introduction of such an image for the plane surface layer should present no problems, but it becomes sensitive when passing to curved surface layers. As is known [1], Gibbs proceeded from the fundamental equation

$$d\bar{U} = Td\bar{S} + \gamma dA + \sum_i \mu_i d\bar{N}_i + AC_1 dc_1 + AC_2 dc_2, \quad (1.1)$$

where $\bar{U}$, $\bar{S}$, and $\bar{N}_i$ are the excess energy, entropy, and mass of component i related to a certain dividing surface with tension γ and area A; T is the temperature; μ_i is the chemical potential of ith component; c_1 and c_2 are the principal curvatures of the dividing surface; and C_1 and C_2 are the corresponding bending moments (per unit surface area). In equation (1.1), Gibbs employed the identity transformation

$$C_1 dc_1 + C_2 dc_2 = BdH + \Theta dD, \quad (1.2)$$

where $H \equiv (c_1 + c_2)/2$ is the mean curvature, $D \equiv (c_1 - c_2)/2$ is the deviation curvature, $B \equiv C_1 + C_2$ is the bending moment, and $\Theta = C_1 - C_2$ is the torque of a surface [2]. Assuming also that $D \approx 0$, Gibbs demonstrated that there is a position of the dividing surface (tension surface) where $B = 0$. Note that, for slightly curved surfaces, breaking the condition $D \approx 0$ means simply that one of the curvatures (for example, c_2) may be taken as equal to zero. The tension surface may then be found from the condition $C_1 = 0$.

If we digress from the case of a spherical surface (where $D = 0$ is strictly fulfilled), we may state that Gibbs created the theory of slightly curved surfaces. This event is of profound importance. The Gibbs method per se, when the substance excess (in fact, "smeared" over the entire surface layer) is related to the dividing surface, suggests that the surface is studied at distances that are much larger than the thickness of the surface layer. The smaller the radius of curvature, the larger will be, for example, the error when the real moment of excess mass of the surface layer is replaced by the moment related to the dividing surface.

The following circumstance is also of importance. Bodies with a nonspherical shape have a surface with a variable curvature. If the curvature is small, its change is also small; it may then be assumed that the surface energy is determined locally by the curvature of the surface, as suggested by equation (1.1). If the gradients of curvature are large, the applicability of equation (1.1) as the local relation becomes questionable because, strictly speaking, the surface energy should depend both on the curvature and its gradients of all orders of magnitude, similar to the dependence of the local free energy of heterogeneous systems on the density gradients of all orders of magnitude (although in theory one is usually restricted by the second gradient). In general, in a highly curved surface of variable curvature, the surface energy becomes a functional of the surface shape, and a local formulation of the fundamental equation becomes difficult. Hence, both the condition $D \approx 0$ and the pattern of fundamental equation (1.1) correspond to the case of a slightly curved surface.

Also note that, since the surface tension is dependent on the surface curvature, the curvature anisotropy inevitably causes anisotropy of the surface tension.

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Only the condition of small curvature makes it possible to assume that the surface tension is isotropic, as was done by Gibbs. Therefore, the passage to highly curved surfaces should be combined with taking into account the anisotropy of surface tension (it was Buff [3, 4] who did so first); the dependence of the surface tension on the curvature results in a change in the surface tension along the surface of variable curvature [5].

Attempts to modify the Gibbs theory have concerned mainly the conditions of mechanical equilibrium involving the surface tension (especially, the Laplace equations) [2–9]. The first attempt to derive the conditions of equilibrium taking into account the linear and pointwise phenomena based on the fundamental equations and the variation method was only made in [10]. However, the fundamental equations and the concepts of surface and linear tensions were determined in the wrong manner (the inadequate treatment of surface tension in [10] was discussed in detail in [7]). The thermodynamics of linear phenomena in the absence of fields was considered in [11], and in this work we would like to proceed further, focusing our attention on the conditions of mechanical equilibrium.

Note that it is not necessary to derive these conditions from the fundamental equations (in addition to encountering some difficulties at large curvatures, as was mentioned above for the surfaces). The conditions of mechanical equilibrium are simple, in such a way that they always correspond to a zero net force acting on an isolated object or its part. However, dealing with vectors, we should know where they are directed. Hence, the first question that must be answered before starting to study, for example, linear interfacial phenomena, is the following: does the direction of a force of linear tension coincides with that of a line itself, or not? Naturally, the same question arises also for the surface tension. The exact answer is known only for a plane surface [12] and the problem of the three-dimensional pattern of a tensor of surface tension are essentially undiscussed in the available reviews [13–15]. Therefore, in order to pass to the contact line, we should consider the general problem of a curved interface.

2. METRICS OF A SURFACE LAYER AND THE DIVIDING SURFACE

A surface is a geometrical concept, and it is physically set only in the case when a phase (for example, nonvolatile and insoluble solid) has a boundary surface. When the passage from one phase to the other proceeds continuously, the dividing surface is introduced in an artificial manner. Gibbs [1] defined the dividing surface as the geometrical surface that passes inside the surface layer (or near this layer) through the points arranged in a similar manner with respect to the adjacent substance. Let us refine this definition using the methods of differential geometry. The surface layer is a real three-dimensional body, which is formed under the influence of intermolecular interactions and external fields. As a result, the molecules are arranged and oriented in space and are characterized by a certain curvature and very large gradients of the local properties of the substance. At each point, the direction of the gradients may be related to the curvilinear coordinate (u_3), and we may introduce the normal (to this coordinate) coordinate surface of two other curvilinear coordinates (u_1, u_2). Treating the surface layer as the Riemann space, we may characterize it by the metric tensor $\hat{g}$ with components

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

where $\mathbf{r}$ is the radius vector of the point in space; $\mathbf{r}_{u_i}$ is its partial derivative with respect to curvilinear coordinate u_i (vector $\mathbf{r}_{u_i}$ is directed along the tangent to coordinate line u_i); $x_1 \equiv x$, $x_2 \equiv y$, $x_3 \equiv z$ are the Cartesian coordinates of the space; and the scalar product of vectors is shown by the dot. As is seen from (2.1), the orthogonal system of curvilinear coordinates diagonalizes the metric tensor: only the components g_{ii} remain in this tensor (their square roots are also known as the Lamé coefficients $h_i = r_{u_i} = \sqrt{g_{ii}}$; they result in elements of the length of coordinate lines $dl_i = h_i du_i$). The coordinate surface u_1, u_2 of such a coordinate system will be called the dividing surface. In other words, we define the dividing surface as the coordinate surface of a system of orthogonal curvilinear coordinates (which diagonalizes the metric tensor of a surface layer) normal to the direction of gradients.

The equation of the dividing surface is set by the condition

$$u_3 = u_{30} = \text{const}. \tag{2.2}$$

However, the value of constant u_{30} remains to some extent arbitrary in magnitude; i.e., any coordinate surface within the surface layer or near this layer may be chosen as the dividing surface. In a symmetric spherical system, such surfaces may be represented by spheres of various radii; this is a typical case where the coordinate surfaces are conformal to each other. In the general case, the coordinate surfaces should not always be conformal, because the dependence of their shapes on curvilinear coordinate u_3 is governed by the metrics of the surface layer. In other words, the passage from one position of the dividing surface to the other is not always possible by the simple displacement of each part of the surface along the normal, as was done by Gibbs, Buff, and other authors. As applied to finite changes, this procedure is approximate and may be substantiated by the small curvature and thickness of the surface layer when the section of coordinate line u_3 within the surface layer is so small that it may be

assumed to be linear. As will be seen from further discussion, such a procedure is unnecessary. For differential operations, when we are dealing with an orthogonal coordinate system, the differentiation with respect to the length of the coordinate line u_3 may be exactly replaced by differentiation with respect to normal N to the dividing surface

$$dN = dl_3 = h_3 du_3. \quad (2.3)$$

The dividing surface has a network of coordinate lines and its own metrics, which is characterized by two important positions. First, according to the Dupin theorem from differential geometry, the coordinate lines in a chosen system of orthogonal curvilinear coordinates coincide with the curvature lines of the dividing surface. This implies that the curvatures c_1 and c_2 of the dividing surface in the directions of unit vectors $\mathbf{e}_1$ and $\mathbf{e}_2$ corresponding to u_1 and u_2 are the principal curvatures (maximal and minimal of all surface curvatures at a given point). Secondly, as a result, the simple Rodrigues formula

$$\mathbf{n}_{u_i} = \mathbf{r}_{u_i} c_i \quad (i = 1, 2) \quad (2.4)$$

is valid. Here, $\mathbf{n}$ is the unit vector of a normal to the dividing surface. This formula indicates that the change in the surface orientation during its movement along the coordinate line is determined exclusively by the curvature in this direction. Taking into account (2.3), the following geometrical relations for the displacement of a unit part of the dividing surface along the coordinate line u_3 are also valid:

$$\partial \ln l_i / h_3 \partial u_3 = \partial \ln h_i / h_3 \partial u_3 = c_i \quad (i = 1, 2). \quad (2.5)$$

These relationships will be needed in further discussions.

3. PRESSURE TENSOR

The mechanical state of a two-phase system that includes the surface layer, is characterized by setting the field of stress tensor $\hat{E}(\mathbf{r})$ or pressure tensor $\hat{p}(\mathbf{r})$ (they differ only in the sign). The latter is more widely applied to fluid systems, and we will use its symbols.

The force acting on the unit volume of a system is composed of the contact force $-\nabla \hat{p}$ (here, the divergence of the pressure tensor is represented by its scalar product multiplied by the vector of the Hamiltonian nabla operator) and the volume force $\mathbf{f}$ of the external field. Under mechanical equilibrium, these force components balance each other, so that the condition

$$\nabla \hat{p} = \mathbf{f} \quad (3.1)$$

is fulfilled. Because the pressure tensor includes only the short-range contact forces (albeit affected by the external field), we may believe that its metrics correspond to that of the surface layer; hence, the pressure tensor is typically diagonalized in the same system of curvilinear orthogonal coordinates that diagonalizes the metric tensor. Restricting ourselves to this case and denoting the principal values by p_1, p_2, and p_3, we represent vector equality (3.1) in the form of three scalar relations:

$$\begin{aligned} &\frac{\partial p_1}{h_1 \partial u_1} + (p_1 - p_2)\frac{\partial \ln h_2}{h_1 \partial u_1} + (p_1 - p_3)\frac{\partial \ln h_3}{h_1 \partial u_1} = f_1, \\ &\frac{\partial p_2}{h_2 \partial u_2} + (p_2 - p_1)\frac{\partial \ln h_1}{h_2 \partial u_2} \\ &+ (p_2 - p_3)\frac{\partial \ln h_3}{h_2 \partial u_2} = f_2, \\ &\frac{\partial p_3}{h_3 \partial u_3} + (p_3 - p_1)\frac{\partial \ln h_1}{h_3 \partial u_3} + (p_3 - p_2)\frac{\partial \ln h_2}{h_3 \partial u_3} = f_3, \end{aligned} \quad (3.2)$$

where h_i and f_i $(i = 1, 2, 3)$ are the Lamé coefficients and vector components $\mathbf{f}$ in the coordinate directions, respectively. In the particular case of a flat surface layer, the chosen coordinate system is transformed into the Cartesian coordinate system ($h_1 = h_2 = h_3 = 1$), and only the first summand remains in each line of the left-hand part of (3.2). Conditions (3.2) then indicate explicitly the variations of pressure tensor components $p_1 \equiv p_{T1}$, $p_2 \equiv p_{T2}$, and $p_3 \equiv p_N$ along their coordinates in the external field:

$$\partial p_{T1}/\partial x = f_1, \quad \partial p_{T2}/\partial y = f_2, \quad \partial p_N/\partial z = f_3. \quad (3.3)$$

For example, for the gravitational field ($f_1 = 0$, $f_2 = 0$, $f_3 = \rho g$, where ρ is the local density of a substance and g is the acceleration of free fall), equation (3.3) acquires the form of the barometric formula:

$$\partial p_{T1}/\partial x = 0, \quad \partial p_{T2}/\partial y = 0, \quad \partial p_N/\partial z = -\rho g, \quad (3.4)$$

provided that the z-axis is directed upward. In the absence of an external field ($\mathbf{f} = 0$), all three pressures p_{T1}, p_{T2}, and p_N remain constant along their coordinates, the equality of pressures in the contacting phases resulting from the constancy of p_N.

In the case of spherical symmetry (that is not disturbed by the external field), the chosen coordinate system is transformed into the spherical system ($u_1 = \theta$, $u_2 = \varphi$, $u_3 = r$, $p_1 = p_2 \equiv p_T$, $p_3 \equiv p_N$, $h_1 = r$, $h_2 = r\sin\theta$, $h_3 = 1$, $f_1 = f_2 = 0$, $f_3 = f$), and conditions (3.2) acquire the following form:

$$\begin{aligned} &\partial p_T/\partial \theta = \partial p_T/\partial \varphi = 0, \\ &\partial p_N/\partial r + 2(p_N - p_T)/r = f, \end{aligned} \quad (3.5)$$

where the first two equalities provide the condition of constancy of tangential pressure in the tangential direction, while the third interrelates the normal and tangential pressures. Although spherical symmetry is possible also in rare cases in the presence of a field (for example, in the presence of a central electric charge in a droplet), it is more typical of capillary bodies in the absence of a

filed. At $f = 0$, the relation between p_T and p_N provided by equation (3.5) is represented also in the form [16]:

$$d(p_N r^2)/d(r^2) = p_T. \quad (3.6)$$

We return to these relations later.

4. TENSOR OF EXCESS SURFACE STRESSES

Taking advantage of the common procedure for excess values [1], let us introduce the tensor of excess surface stresses $\bar{\hat{E}}(u_1, u_2, u_3)$ for an arbitrary position of the dividing surface. To this end, let us single out (by circular rotation of the normal coordinate line u_3) the extremely narrow "flow tube" of the coordinate lines u_3 passing through many coordinate surfaces (u_1, u_2), each of which may be chosen, according to equation (2.2), as the dividing surface. Upon passing through each surface, the tube cuts the small area

$$A = l_1 l_2 = h_1 h_2 \Delta u_1 \Delta u_2 \quad (4.1)$$

varying from surface to surface and dividing the volume of a tube into volume V^α form the side of the α phase and volume V^β from the side of the β phase. For definiteness, let us chose the notation so that α corresponds to the phase with the larger pressure (if both principal curvatures are of the same sign, this phase represent the phase on the concave side of the surface layer).

If the surface layer inside a given flow tube extends between the coordinates u_3^α and u_3^β, the tensor of excess surface stresses is determined by the relation

$$\bar{\hat{E}} = (1/A_0) \times \left[\int_{u_3^\alpha}^{u_{30}} (\hat{p}^\alpha - \hat{p}) A h_3 du_3 + \int_{u_{30}}^{u_3^\beta} (\hat{p}^\beta - \hat{p}) A h_3 du_3\right], \quad (4.2)$$

where $A_0 \equiv A(u_{30})$ is the cut-out unit area related to the dividing surface with coordinate u_{30}, and $\hat{p}^\alpha$ and $\hat{p}^\beta$ are the values of the pressure tensor in bulk phases extrapolated to the region of the surface layer. Note that the values of u_3^α and u_3^β may readily be taken already during the passage to the bulk phases, because in this case the integrands vanish and nevertheless the integration is actually performed with respect to the parts of the surface layer adjacent to the α and β phases. Relation (4.2) determines the value of the tensor of excess surface stresses averaged over the small area of the dividing surface. Using expression (4.1) for A and A_0, composing the A/A_0 ratio, and passing to the limit $\Delta u_1 \longrightarrow 0$, $\Delta u_2 \longrightarrow 0$ in this expression, we obtain the exact local definition of the tensor of excess surface stresses at any point of the dividing surface

$$\bar{\hat{E}} = (1/h_{10}h_{20})\left[\int_{u_3^\alpha}^{u_{30}} (\hat{p}^\alpha - \hat{p}) h_1 h_2 h_3 du_3 + \int_{u_{30}}^{u_3^\beta} (\hat{p}^\beta - \hat{p}) h_1 h_2 h_3 du_3\right]. \quad (4.3)$$

Differentiating (4.3) with respect to the position of the dividing surface (i.e., with respect to coordinate u_{30}) at a fixed physical state of a system, assuming that even in the presence of a field the values of $\hat{p}^\alpha$ and $\hat{p}^\beta$ do not depend on the position of the dividing surface, and using (2.5), we arrive at the following equation:

$$\partial \bar{\hat{E}}/h_3 \partial u_{30} + \bar{\hat{E}}(c_1 + c_2) = \hat{p}^\alpha(u_{30}) - \hat{p}^\beta(u_{30}), \quad (4.4)$$

where the values of the pressure tensor in the bulk phases extrapolated to the coordinate u_{30} of the dividing surface are present. As is seen from (4.4), the tensor of excess surface stresses is dependent on the position of the dividing surface.

In general, the tensor of excess surface stresses is a three-dimensional tensor, so that expressions (4.3) and (4.4) may be written for each of its three components. Two tangential components form the tensor of the surface tension $\hat{\gamma}$ with components

$$\gamma_1 \equiv \bar{E}_{T1} = \frac{1}{h_{10}h_{20}}\left[\int_{u_3^\alpha}^{u_{30}} (p_{T1}^\alpha - p_{T1}) h_1 h_2 h_3 du_3 + \int_{u_{30}}^{u_3^\beta} (p_{T1}^\beta - p_{T1}) h_1 h_2 h_3 du_3\right], \quad (4.5)$$

$$\gamma_2 \equiv \bar{E}_{T2} = \frac{1}{h_{10}h_{20}}\left[\int_{u_3^\alpha}^{u_{30}} (p_{T2}^\alpha - p_{T2}) h_1 h_2 h_3 du_3 + \int_{u_{30}}^{u_3^\beta} (p_{T2}^\beta - p_{T2}) h_1 h_2 h_3 du_3\right], \quad (4.6)$$

and the normal component may be called the transverse surface tension γ_N:

$$\gamma_N \equiv \bar{E}_N = \frac{1}{h_{10}h_{20}}\left[\int_{u_3^\alpha}^{u_{30}}(p_N^\alpha - p_N)h_1h_2h_3du_3 + \int_{u_{30}}^{u_3^\beta}(p_N^\beta - p_N)h_1h_2h_3du_3\right]. \quad (4.7)$$

Correspondingly, from (4.4) we have

$$\partial\gamma_1/h_3\partial u_{30} + \gamma_1(c_1 + c_2) = p_{T1}^\alpha(u_{30}) - p_{T1}^\beta(u_{30}), \quad (4.8)$$

$$\partial\gamma_2/h_3\partial u_{30} + \gamma_2(c_1 + c_2) = p_{T2}^\alpha(u_{30}) - p_{T2}^\beta(u_{30}), \quad (4.9)$$

$$\partial\gamma_N/h_3\partial u_{30} + \gamma_N(c_1 + c_2) = p_N^\alpha(u_{30}) - p_N^\beta(u_{30}). \quad (4.10)$$

In the absence of a field, the values in the right-hand sides of these equations are constant, whereas in the presence of a field these values are the functions set by the equilibrium conditions (3.2) as applied to the bulk phases.The dependence of $(c_1 + c_2)$ on u_3 is set by the metrics of the surface layer. Thus, in each particular case, differential equations (4.8)–(4.10) may be solved, and the dependence of each component of the pressure tensor on the position of the dividing surface may be obtained in explicit form. If the bulk phases are isotropic, the same value is present in the right-hand sides of equations (4.8)–(4.10). However, as these equations demonstrate, the change in each component of the surface tension during the imaginary displacement of the dividing surface depends on the value of the component; because the values of γ_1, γ_2, and γ_N are different, their changes will also differ, although they are described by the same differential equation.

Among the relationships mentioned above, we are most interested in the relations concerning the transverse surface tension, because it is this tension that represents the three-dimensional aspect of the surface tension, and because it is scarcely investigated. However, for comparison, it is reasonable also to involve the other components of the surface tension and to continue our discussion with the most studied cases, the planar and spherical surface layers.

5. TRANSVERSE SURFACE TENSION OF THE PLANAR SURFACE LAYER

For the planar surface layer, the relationships (4.5)–(4.10) acquire the following form:

$$\gamma_1 = \int_{z^\alpha}^{z_0}(p_{T1}^\alpha - p_{T1})dz + \int_{z_0}^{z^\beta}(p_{T1}^\beta - p_{T1})dz, \quad (5.1)$$

$$\gamma_2 = \int_{z^\alpha}^{z_0}(p_{T2}^\alpha - p_{T2})dz + \int_{z_0}^{z^\beta}(p_{T2}^\beta - p_{T2})dz, \quad (5.2)$$

$$\gamma_N = \int_{z^\alpha}^{z_0}(p_N^\alpha - p_N)dz + \int_{z_0}^{z^\beta}(p_N^\beta - p_N)dz, \quad (5.3)$$

$$d\gamma_1/dz_0 = p_{T1}^\alpha(z_0) - p_{T1}^\beta(z_0), \quad (5.4)$$

$$d\gamma_2/dz_0 = p_{T2}^\alpha(z_0) - p_{T2}^\beta(z_0), \quad (5.5)$$

$$d\gamma_N/dz_0 = p_N^\alpha(z_0) - p_N^\beta(z_0) \quad (5.6)$$

(partial derivatives are transformed into the total derivatives, because all local values now depend only on z). In accordance with (3.3), in the absence of an external field, the normal component of the pressure tensor is independent of the position inside the surface layer $[p_N(z) = p_N^\alpha = p_N^\beta]$, and hence $\gamma_N = 0$, irrespective of the chosen position of the dividing surface. In this case, the tensor of excess surface stresses is a two-dimensional tensor even for solids [12]; hence, it implies that the forces of surface tension are directed along the surface. In other words, in this case, any dividing surface is nothing other than the tension surface.

The situation is changed in the presence of a field. In this case, the transverse surface tension is not equal to zero even for the planar surface, and it may be illustrated by the direct calculation of the transverse surface tension in a gravitational field using formula (5.3). Let the α phase be heavier and placed below, while the β phase is located above so that the z-axis is directed from the α phase toward the β phase. Using barometric formula (3.4) for both the bulk α phase and the surface layer, we have

$$p_N^\alpha(z) - p_N(z) = g\int_{z^\alpha}^{z}(\rho - \rho^\alpha)dz \equiv g\Gamma^\alpha(z), \quad (5.7)$$

where

$$\Gamma^\alpha(z) \equiv \int_{z^\alpha}^{z}(\rho - \rho^\alpha)dz \quad (5.8)$$

is the current value of mass adsorption from the side of the α phase (the boundary condition $\rho = \rho^\alpha$ at $z = z^\alpha$ was taken into account). Similarly,

$$p_N^\beta(z) - p_N(z) = g\int_{z^\beta}^{z}(\rho - \rho^\beta)dz \equiv -g\Gamma^\beta(z), \quad (5.9)$$

where

$$\Gamma^\beta(z) \equiv \int_{z}^{z^\beta}(\rho - \rho^\beta)dz \quad (5.10)$$

is the current value of mass adsorption from the side of the β phase. Substitution of (5.7) and (5.9) into (5.3) yields

$$\gamma_N = g\left[\int_{z^\alpha}^{z_0}\Gamma^\alpha(z)dz - \int_{z_0}^{z^\beta}\Gamma^\beta(z)dz\right]. \quad (5.11)$$

Assuming that the local density of the matter in the surface layer decreases monotonically while moving upward from the α phase to the β phase, we have $\Gamma^\alpha(z) < 0$, $\Gamma^\beta(z) > 0$, and consequently $\gamma_N < 0$. In this case, the transverse surface tension is negative; i.e., in essence, it is transformed into the transverse pressure created by the field.

Differentiating (5.11) with respect to z_0, we obtain

$$d\gamma_N/dz_0 = g[\Gamma^\alpha(z_0) + \Gamma^\beta(z_0)] \equiv g\Gamma(z_0), \quad (5.12)$$

where $\Gamma(z_0)$ is the total mass adsorption (mass excess per unit surface area) of a substance related to the dividing surface by coordinate z_0. Substituting now (5.12) into (5.6), we arrive at the condition of mechanical equilibrium [3]

$$p_N^\alpha(z_0) - p_N^\beta(z_0) = g\Gamma(z_0). \quad (5.13)$$

While treating the dividing surface as a two-dimensional stressed membrane, formula (5.13) represents the trivial fact that the a membrane in a gravitational field may affect the interfacial pressure drop only by its own mass. It is known [and is seen from the combination of (5.8) and (5.10)] that the value of the total adsorption depends on the position of the dividing surface. Because Γ^α and Γ^β, as we saw, are characterized by different signs, it is always possible to find a position of the dividing surface within the boundaries of the surface layer such that the total adsorption is nullified. Condition (5.13) then acquires the same form as in the absence of a field (the equality of pressures in contacting phases). However, the transverse surface tension does not vanish and it is still negative, thus continuing to be the specific indicator of an external field.

6. TRANSVERSE SURFACE TENSION OF THE SPHERICAL SURFACE LAYER

As applied to the spherical surface, relationships (4.5)–(4.10) acquire the following forms:

$$\gamma_1 = \gamma_2 \equiv \gamma$$

$$= \frac{1}{r_0^2}\left[\int_0^{r_0}(p^\alpha - p_T)r^2dr + \int_{r_0}^{r^\beta}(p^\beta - p_T)r^2dr\right], \quad (6.1)$$

$$\gamma_N = \frac{1}{r_0^2}\left[\int_0^{r_0}(p^\alpha - p_N)r^2dr + \int_{r_0}^{r^\beta}(p^\beta - p_N)r^2dr\right], \quad (6.2)$$

$$d\gamma/dr_0 + 2\gamma/r_0 = p^\alpha(r_0) - p^\beta(r_0), \quad (6.3)$$

$$d\gamma_N/dr_0 + 2\gamma_N/r_0 = p^\alpha(r_0) - p^\beta(r_0). \quad (6.4)$$

Formulas (6.1) and (6.3) are well-known for the case of the absence of external field. Formula (6.1) demonstrates that the surface tension of an arbitrarily chosen dividing surface is always equivalent to the real surface layer with respect to the force moment. Formula (6.3) is the Kondo equation for the dependence of the surface tension on the position of the dividing surface (simultaneously, this equation is the generalized Laplace equation). Two other relationships, (6.2) and (6.4), have received less recognition, although they are no less important. It should be emphasized that, irrespective of the identical forms of equations (6.3) and (6.4), the dependences for the normal and transverse surface tensions are different in principle. From a purely mathematical viewpoint, this is explained by the different signs of the integration constants in these equations. As is known, integration of the Kondo equation yields

$$\gamma = r_0[p^\alpha(r_0) - p^\beta(r_0)]/3 + K/r_0^2, \quad (6.5)$$

where constant K is positive (according to Buff, $4\pi K$ is the work of formation of a droplet of the α phase from the β phase), because the surface tension should always be larger than zero in accordance with the condition of stability. Hence, the $\gamma(r_0)$ function lies completely in the region of positive values and is characterized by the only minimum corresponding to the tension surface [where $d\gamma/dr_0 = 0$ and (6.3) is transformed into the Laplace equation]. The integration of (6.4) results in a similar expression

$$\gamma_N = r_0[p^\alpha(r_0) - p^\beta(r_0)]/3 + C/r_0^2, \quad (6.6)$$

where, however, $C < 0$. Indeed, because p_N decreases in the radial direction, it follows from (6.2) that γ_N should have a negative value at $r_0 \longrightarrow 0$. On the other hand, γ_N is positive at $r_0 \longrightarrow r^\beta$, so that inside the surface layer there will always be a position of the dividing surface for which $\gamma_N = 0$.

Let us check whether this position coincides with the tension surface or not. The latter is determined by the condition of equivalence both with respect to the force moment [as shown in (6.1)] and to the force itself, which is expressed by the condition [16]

$$\gamma = \frac{1}{r_0}\left[\int_0^{r_0}(p^\alpha - p_T)rdr + \int_{r_0}^{r^\beta}(p^\beta - p_T)rdr\right]. \quad (6.7)$$

Relationships (6.1) and (6.7) are two equations for finding the values of $\gamma = \gamma_s$ and $r_0 = r_s$ corresponding to the tension surface. Excluding γ from these relations, we obtain the following equation [16]

$$\int_0^{r_s}(p^\alpha - p_T)(r - r_s)rdr + \int_{r_s}^{r^\beta}(p^\beta - p_T)(r - r_s)rdr = 0. \quad (6.8)$$

The unknown values are separated, and now we have only one equation, which unambiguously determines the position of the dividing surface that satisfies both equations (6.1) and (6.7). Using (3.6), it is easy to reduce (6.8) to a simpler form:

$$\int_0^{r_s}(p^\alpha - p_N)r^2dr + \int_{r_s}^{r^\beta}(p^\beta - p_N)r^2dr = 0. \quad (6.9)$$

Comparing now (6.2) and (6.9), we note that, upon substitution of the value $r_0 = r_s$ into (6.2), the transverse surface tension γ_N inevitably vanishes. Thereby, we prove condition

$$\gamma_N = 0, \quad (6.10)$$

which means that the tensor of excess surface stresses is a two-dimensional parameter, and is simultaneously the equation that determines the position of the tension surface in the absence of an external field.

It would be unreasonable to extend this conclusion automatically to the case of the presence of a field. As is seen from (3.5), in the presence of a field the pattern of the normal component of the pressure tensor becomes complicated; and if we could not reach a zero value of the transverse surface tension for the plane surface in the gravitational field, moreover, this would hardly be possible for the spherical surface. Since spherical symmetry is typical of bodies in the absence of a field, we consider the case of the curved surface in a field for the more common nonspherical case.

7. THE SURFACE OF AN ARBITRARY SHAPE IN AN EXTERNAL FIELD

Addressing the general definition of transverse surface tension (4.7), we may state the following. Under equilibrium and in the absence of a external field, the values of p_N^α and p_N^β are constant, and the values of integrals are determined by the pattern of the $p_N(u_3)$ function. This value is known exactly for the case of a planar surface layer when p_N is constant, which is a particular form of monotonic dependence. It should then be reasonable to suggest that this dependence remains monotonic also for the curved (or, at least, slightly curved) surface, and under our choice of $p_N^\alpha > p_N^\beta$, p_N decreases while passing from the α phase to the β phase through the surface layer. Indeed, if the extrema of p_N had existed, it would be difficult to understand why they vanish during the leveling of the values of p_N^α and p_N^β (the extrema disclosed in numerical experiments [17] with small clusters, which do not obey the Laplace equation, should not be taken into account during the consideration of equilibrium systems). If $p_N^\alpha > p_N > p_N^\beta$, the integrals in (4.7) will acquire different signs. Placing the dividing surface alternately into the extreme positions $u_{30} = u_3^\alpha$ and $u_{30} = u_3^\beta$, we obtain $\gamma_N < 0$ and $\gamma_N > 0$, respectively; consequently, we may find inside the surface layer the position where $\gamma_N = 0$, i.e., where the condition (6.10), which we introduced for the tension surface, is fulfilled.

Problems arise only in the case of such a large curvature that the surface layer is not realized to a full extent, and the bulk phase is absent from the inner side of the layer. If the position of the tension surface is touched by the shift of the dividing surface, the space should be sufficiently large to maneuver. The smaller the radii of surface curvature, the smaller this space, and eventually it will not be large enough, to say nothing of the fact that representation of a curved surface layer by a dividing surface with an accuracy of the radius of curvature (when the thickness of the latter is on the order of the surface layer) is already meaningless. The other problem is related to the nonuniformity of the curvature. We may imagine the case of a rather complex shape of a solid surface or generally that of a nonequilibrium liquid (under local equilibrium at the surface), when condition (6.10) is achieved during the displacement of the coordinate surface only for its small areas. In other words, there is a chance that areas of the tension surface with strongly different curvatures cannot form a continuous surface. Therefore, it should be assumed that equation (6.10) is a local condition.

In the presence of a field, the values of p_N^α and p_N^β for the bulk phases become variables per se, and in general it is impossible even to estimate the signs of the integrals in (4.7). This means that in the general theory we should rely on the fact that the transverse surface tension is not equal to zero and take this into account in all the relationships. Among these relationships, the main equation is the Laplace equation, which (as is known) does not include the transverse surface tension even taking into account the gravitational field (the Gibbs formula). It is natural that the question arises whether this results from the simple neglect of this tension, which is based on the hypothesis (which, as we saw, is not always true) of a two-dimensional pattern of the tensor of excess surface stresses.

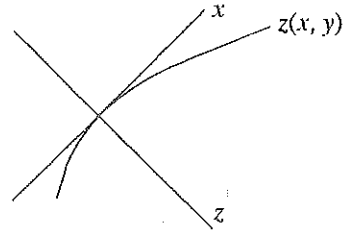
To answer this question, let us turn now to the conditions of equilibrium at the surface. Let us write down each of the equalities (3.2), first for the surface layer and then for the bulk phase, and obtain the difference of these expressions; further, we integrate this difference, respectively, for α phase over the volume V^α and for β phase over the volume V^β. Then, using definitions (4.5)–(4.7), let us pass to the excess surface values. Let us consider first the conditions of equilibrium along the surface. In general, rather cumbersome expressions are

obtained; therefore, we report the results only for the slightly curved surface, when [in view of the small thickness of the surface layer and the condition (2.5)] it may be assumed that $h_i \approx h_{i0}$ ($i = 1, 2$). Then, after performing the manipulations mentioned above, from the first two equations of (3.2) we obtain:

$$\frac{\partial\gamma_1}{h_{10}\partial u_1} + (\gamma_1 - \gamma_2)\frac{\partial \ln h_{20}}{h_{10}\partial u_1} + (\gamma_1 - \gamma_N)\frac{\partial \ln h_{30}}{h_{10}\partial u_1} = \bar{f}_1,$$
$$\frac{\partial\gamma_2}{h_{20}\partial u_2} + (\gamma_2 - \gamma_1)\frac{\partial \ln h_{10}}{h_{20}\partial u_2} + (\gamma_2 - \gamma_N)\frac{\partial \ln h_{30}}{h_{20}\partial u_2} = \bar{f}_2, \quad (7.1)$$

where $\bar{f}_i$ are the components of excess surface force created by the external field.

The detailed conditions of equilibrium (7.1) are determined by the shape of the dividing surface, which may be set, for example, by the function $z = z(x, y)$.



The choice of Cartesian coordinates at the point on the curved surface.

Let us take a certain point as the origin of the Cartesian coordinates, the tangent plane as the coordinate plane (x, y) (with the axes x and y in the main directions), and the external normal as the z-axis (figure). Let us expand function $z = z(x, y)$ in powers of x and y in the vicinity of the chosen point:

$$z = \frac{1}{2}c_1x^2 + \frac{1}{2}c_2y^2 + \ldots, \quad (7.2)$$

where c_1 and c_2 are the principal curvatures of the dividing surface (the zeroth and first terms of the expansion are absent because at the point considered, $z = 0$ and $\partial z/\partial x = \partial z/\partial y = 0$, Fig. 1). According to (2.1) and (7.2), in these local coordinates we have

$$h_1^2 = g_{11} = 1 + c_1^2x^2 + \ldots,$$
$$h_2^2 = g_{22} = 1 + c_2^2y^2 + \ldots, \quad h_3^2 = g_{33} = 1. \quad (7.3)$$

Confining ourselves to the main term of the expansion and substituting (7.3) into (7.1), we obtain the conditions of transverse mechanical equilibrium for the slightly curved surface

$$\partial\gamma_1/h_1\partial u_1 = \bar{f}_1, \quad \partial\gamma_2/h_2\partial u_2 = \bar{f}_2, \quad (7.4)$$

where the fact that $\partial\gamma_1/h_1\partial u_1 = \partial\gamma_1/\partial x$ and $\partial\gamma_2/h_2\partial u_2 = \partial\gamma_2/\partial y$ is taken into account. Conditions (7.4) indicate that the variation along the coordinate line is caused only by the variation in the external field and is equal to zero in the absence of a field. In the specific case of a gravitational field ($f_i = \Gamma g\partial h/h_i\partial u_i$, where h is the height), equation (7.4) acquires the following form:

$$d\gamma_1/dh = d\gamma_2/dh = \Gamma g. \quad (7.5)$$

The corresponding equation for the isotropic surface was obtained by Gibbs [1].

Let us consider now the condition of transverse equilibrium at the surface. Once the aforementioned pressure differences are obtained, the integration of the third equation of (3.2) yields

$$\int_{u_3 = u_3^\alpha}^{u_3 = u_{30}} A d(p_N - p_N^\alpha) + \int_{u_3 = u_{30}}^{u_3 = u_3^\beta} A d(p_N - p_N^\beta)$$
$$+ \int_{u_3 = u_3^\alpha}^{u_3 = u_{30}} (p_N - p_N^\alpha) A d\ln(h_1h_2) +$$
$$+ \int_{u_3 = u_{30}}^{u_3 = u_3^\beta} (p_N - p_N^\beta) A d\ln(h_1h_2)$$
$$- \int_{u_3^\alpha}^{u_{30}} (p_{T1} - p_{T1}^\alpha)\frac{\partial \ln h_1}{h_3\partial u_3} A h_3 du_3$$
$$- \int_{u_{30}}^{u_3^\beta} (p_{T1} - p_{T1}^\beta)\frac{\partial \ln h_1}{h_3\partial u_3} A h_3 du_3$$
$$- \int_{u_3^\alpha}^{u_{30}} (p_{T2} - p_{T2}^\alpha)\frac{\partial \ln h_2}{h_3\partial u_3} A h_3 du_3$$
$$- \int_{u_{30}}^{u_3^\beta} (p_{T2} - p_{T2}^\beta)\frac{\partial \ln h_2}{h_3\partial u_3} A h_3 du_3$$
$$= \int_{u_3^\alpha}^{u_{30}} (f_3 - f_3^\alpha) A h_3 du_3 + \int_{u_{30}}^{u_3^\beta} (f_3 - f_3^\beta) A h_3 du_3. \quad (7.6)$$

Two integrals appear after the integration by parts of the two first summands in (7.6), which are mutually removed with the third and forth summands in (7.6), provided that (2.5) is taken into account. Equation (2.5) is used in the remaining summands of the left-hand side of (7.6). Then, dividing this expression by A_0 and denoting the left-hand side of (7.6) by $\bar{f}_3$, we arrive at the relationship

$$p_N^{\alpha}(u_{30}) - p_N^{\beta}(u_{30}) = \frac{1}{A_0}\left[\int_{u_3^{\alpha}}^{u_{30}} (p_{T1}^{\alpha} - p_{T1})c_1 A h_3 du_3 + \int_{u_{30}}^{u_3^{\beta}} (p_{T1}^{\beta} - p_{T1})c_1 A h_3 du_3\right] + \frac{1}{A_0}\left[\int_{u_3^{\alpha}}^{u_{30}} (p_{T2}^{\alpha} - p_{T2})c_2 A h_3 du_3 - \int_{u_{30}}^{u_3^{\beta}} (p_{T2}^{\beta} - p_{T2})c_2 A h_3 du_3\right] + \bar{f}_3. \quad (7.7)$$

Comparing the expressions in square brackets with definitions (4.4) and (4.5), we note that only the curvatures c_1 and c_2, which in the integrands denote the functions of coordinate u_3, interfere with the passage to γ_1 and γ_2. However, these values may be taken out of the integral using the averaging theorem. The latter does not require the continuity of integrand functions (here, the pressure difference breaks at $u_3 = u_{30}$), but needs to have definite signs of pressure difference, which is, strictly speaking, fulfilled only for zeroth or negative pressures in the bulk phases. However, under normal conditions, the atmospheric pressure is low as compared to tangential pressures in the surface layer; hence, zero pressure in the bulk phase is a good approximation. Thus, we may represent (7.7) as

$$p_N^{\alpha}(u_{30}) - p_N^{\beta}(u_{30}) = \gamma_1 \tilde{c}_1 + \gamma_2 \tilde{c}_2 + \bar{f}_3, \quad (7.8)$$

where $\tilde{c}_1$ and $\tilde{c}_2$ are some average curvatures. Because $c_1(u_3)$ and $c_2(u_3)$ are continuous functions, then, according to the same averaging theorem, $\tilde{c}_1$ and $\tilde{c}_2$ may be interpreted as the values of curvature of some particular coordinate surfaces inside the surface layer. However, the point is that, in general, these surfaces do not coincide with the dividing surface to which the other surfaces represented in (7.8) are referred to. Only for a slightly curved surface layer, when the differences in the positions of these surfaces become insignificant, does formula (7.8) acquire the form of the Laplace equation, provided that the external field is present:

$$p_N^{\alpha} - p_N^{\beta} = \gamma_1 c_1 + \gamma_2 c_2 + \bar{f}_3. \quad (7.9)$$

In the particular case of the gravitational field, (7.9) is transformed into

$$p_N^{\alpha} - p_N^{\beta} = \gamma_1 c_1 + \gamma_2 c_2 + \Gamma g \cos\phi, \quad (7.10)$$

where $\cos\phi = \partial h / h_3 \partial u_3$, and ϕ is the angle between the normal to the surface and the vertical. A similar formula was derived by Gibbs for the isotropic case [in view of the smallness of the curvature in formula (7.10), we actually may assume that $\gamma_1 = \gamma_2$]. The relationship (5.13) discussed above is the specific case of (7.10) (and the Gibbs formula) for the plane surface.

As was demonstrated above, the conditions of transverse mechanical equilibrium (7.1) are formulated involving the transverse surface tension. Taking advantage of (4.10), we may represent the condition of transverse mechanical equilibrium (7.8) in terms of transverse surface tension, although it is not required at all. We have found that the absence of transverse surface tension under the condition of transverse mechanical equilibrium and in the Laplace equation for an arbitrary position of the dividing surface depends on the form of representation and is possible when the nonzero transverse surface tension is strictly taken into account.

8. MECHANICAL EQUILIBRIUM AT THE LINE

Hence, we have established that, at least in the absence of an external field and for a slightly curved surface, we may come to the situation where the forces of the surface tension are directed along the surface by choosing the dividing surface as the tension surface. Is this situation possible for a line? If the dividing surfaces of various surface phases meet at the same line, the tensor of excess linear stresses $\bar{\bar{\hat{E}}}$ may be determined in full analogy with the tensor of excess surface stresses in (4.3) as

$$\bar{\bar{\hat{E}}} \equiv (1/L)\sum_j \int \Delta \bar{\hat{E}}_j dA_j, \quad (8.1)$$

where $\bar{\hat{E}}_j$ is the tensor of excess surface stresses for the jth surface and $\Delta\bar{\hat{E}}_j$ is the difference between its local value near the line and the value extrapolated from the depth of the surface phase; the integration is carried out over the narrow region between the coordinate lines, which ends with the part of line with length L. In this case, the angle between the coordinate line at each surface and the contact line may be arbitrary; this implies that the structure of tensor $\bar{\bar{\hat{E}}}$ should be considered in the most general form (the presence or the absence of the transverse surface tension is already of no significance).

Tensor $\bar{\bar{\hat{E}}}$ may be characterized by two vectors, namely, by the vector of force (tension) $\boldsymbol{\gamma}^{L}$ applied to the unit length of a line and by the vector of linear tension $\boldsymbol{\tau}$ (using this notation, we distinguish between the force linear tension and thermodynamic linear tension κ) acting on the cross-section of a line. Vector $\boldsymbol{\gamma}^{L}$ may be called the transverse tension of a line (Kralchevsky and

Ivanov [18] were the first to introduce this term for the transition zone of a free film). The transverse tension of a line has the dimension of surface tension and in general is not always directed along the normal to the contact line. In accordance with (8.1), this tension is added from the similar values for each of the surfaces:

$$\gamma^{L} = \sum_{j} \gamma_{j}^{L}, \tag{8.2}$$

where γ_j^L is the excess force acting per unit length of the contact line from the jth surface. The transverse tension of a line is clearly demonstrated by the stresses in a solid along the three-phase contact line during wetting: when the excess values as compared to the bulk phase of a solid are introduced into consideration, this tension is transformed into the tensor of excess surface stresses, and after subsequent introduction of excess values with respect to the surface phases this tension is transformed into the tensor of excess linear stresses as the transverse tension. Can we avoid the transverse tension of a line by the choice of the position of the contact line? Unfortunately, there is no room to maneuver, because the line considered is the line where the dividing surfaces meet and its position is determined by the positions of these surfaces. If, in addition, we would like to avoid the transverse surface tension and choose the positions of the dividing surfaces as those of tension surfaces, the position of contact line is strictly fixed. Therefore, the absence of transverse tension of a line may result only from the simplicity of the physical state of the system (as, for example, in the case of straight line in a fluid system).

Something similar may be stated about the linear tension. Obviously, it can be directed along the contact line only in the case when the contact line itself is the coordinate line for all the surfaces simultaneously. Such a situation is simply improbable for nonuniformly curved surfaces with an independently formed relief and metrics. However, this situation is possible in a system with isotropic bulk and surface phases (without any definite directions) when the metrics of the entire region of multiphase contact is determined only by the direction of the contact line. If we are dealing with nonspherical surfaces, the main condition of their isotropic properties is, naturally, small curvature.

Let us determine the force of linear tension acting on the unit length dL of the contact line. If the force τ acts on one end of this unit length, the force $\tau + (d\tau/dL)dL$ is applied to the other end (the difference in signs reflects the opposite directions of these forces) so that the total force is equal to $(d\tau/dL)dL$. In the general case, vector $\boldsymbol{\tau}$ may always be expanded into three components:

$$\boldsymbol{\tau} = \tau_t \mathbf{t} + \tau_n \mathbf{n} + \tau_b \mathbf{b}, \tag{8.3}$$

where $\mathbf{t}$, $\mathbf{n}$, and $\mathbf{b}$ are the unit vectors of the tangent, the principal normal, and the binormal of the contact line. Their dependences on the line length is given by the Serret–Frenet equation from differential geometry:

$$d\mathbf{t}/dL = c\mathbf{n}, \quad d\mathbf{n}/dL = -c\mathbf{t} + T\mathbf{b}, \quad d\mathbf{b}/dL = -T\mathbf{n}, \tag{8.4}$$

where c and T are the curvature and the torque of the curve, respectively. Using (8.3) and (8.4), we obtain

$$\begin{aligned} d\boldsymbol{\tau}/dL &= (d\tau_t/dL - \tau_n c)\mathbf{t} \\ &+ (d\tau_n/dL + \tau_t c - \tau_b T)\mathbf{n} + (d\tau_b/dL + \tau_n T)\mathbf{b}, \end{aligned} \tag{8.5}$$

which is a relation additional to (8.3).

Taking into account the external field, the total balance of the forces acting on the unit line element is written as some vector equality

$$\sum_{j} \gamma_j + \gamma^{L} + d\boldsymbol{\tau}/dL + \mathbf{f} = 0, \tag{8.6}$$

where γ_j are the vectors of surface tension in the surface phases extrapolated to the line, and $\mathbf{f}$ is the force exerted by the external field on the unit length of contact line. The substitution of (8.5) into (8.6) yields

$$\begin{aligned} &\sum_{j} \gamma_j + \gamma^{L} + (d\tau_t/dL - \tau_n c)\mathbf{t} \\ &+ (d\tau_n/dL + \tau_t c - \tau_b T)\mathbf{n} + (d\tau_b/dL + \tau_n T)\mathbf{b} + \mathbf{f} = 0. \end{aligned} \tag{8.7}$$

Equality (8.7) represents precisely the condition of mechanical equilibrium at the contact line in the external field. This equation is simplified considerably if the surfaces are isotropic, so that the surface tensions are directed along the normal and the linear tension is directed along the line ($\tau = \tau_t$, $\tau_n = \tau_b = 0$):

$$\sum_{j} \gamma_j + \gamma^{L} + (d\tau/dL)\mathbf{t} + \tau c\mathbf{n} + \mathbf{f} = 0. \tag{8.8}$$

Taking scalar products of both sides of equation (8.8) by the unit vector $\mathbf{t}$, we find

$$d\tau/dL = -\mathbf{f} \cdot \mathbf{t}. \tag{8.9}$$

In the specific case of the gravitational field, we have

$$\mathbf{f} = \lambda \mathbf{g}, \tag{8.10}$$

where λ is the mass excess per unit length of the contact line and $\mathbf{g}$ is the vector of the strength of the gravitational field; equation (8.9) then acquires the following form:

$$d\tau/dL = \lambda g \cos\phi, \tag{8.11}$$

where ϕ is the angle of the slope to the vertical. Because $dh = dL\cos\phi$, where h is the height, condition (8.11) may be written in yet simpler form as

$$d\tau/dh = \lambda g. \tag{8.12}$$

Let us indicate the most important truncated forms of the equilibrium condition (8.8). In the absence of a field, $d\tau/dL = 0$, and (8.8) is reduced to condition [11]

$$\sum_j \gamma_j + \gamma^L + \tau c\mathbf{n} = 0. \quad (8.13)$$

If the line is free (a filament in an open space), we have $\gamma_j = 0$ and $\gamma^L = 0$, so that (8.8) is transformed into relationship

$$(d\tau/dL)\mathbf{t} + \tau c\mathbf{n} + \mathbf{f} = 0. \quad (8.14)$$

This case has been analyzed for the gravitational field [19].

9. CONCLUSION

In the presence of external fields, the tensors of excess surface and linear stresses are three-dimensional parameters, and, in general, their dimensions cannot be lowered by the choice of the positions of the dividing surfaces and lines. At the same time, the condition of transverse mechanical equilibrium for the curved surfaces and, in particular, the Laplace equation, may be formulated without the use of the transverse surface tension, as has been done heretofore.

In the absence of external fields, the dividing surface may always be found in a slightly curved surface layer that satisfies the zeroth value of the transverse surface tension. In the spherical case, this dividing surface coincides with the tension surface. The tension surface is determined by this criterion in a simpler manner than by the procedures applied earlier. The conditions of mechanical equilibrium at the contact line and in the absence of external fields include the transverse tension of a line and the normal components of linear tension.

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