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The Complete Condition of Mechanical Equilibrium at a Curved Nonspherical Surface

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Abstract—A simple procedure for deriving the complete condition of mechanical equilibrium at a curved nonspherical surface, valid both in the absence and in the presence of external fields, is described. The condition is written in the vector form, no less compact than the Laplace formula, and one of its components generalizes this formula.

INTRODUCTION

It may be said without exaggeration that Laplace's classic formula

$$p^\alpha - p^\beta = \gamma\left(\frac{1}{R_1} + \frac{1}{R_2}\right) \quad (1)$$

(where p^α and p^β are the pressures in the contacting phases, γ is the scalar surface tension, and R_1 and R_2 are the principal radii of the surface curvature) is the most important and the most well-known relationship in the theory of capillarity. For a nonspherical surface, it is natural to assume that the surface tension will be of an anisotropic (tensor) nature, and then formula (1) is written in the form [1, 2]

$$p^\alpha - p^\beta = \frac{\gamma_1}{R_1} + \frac{\gamma_2}{R_2}, \quad (2)$$

where γ_1 and γ_2 are the components of the surface tension along directions 1 and 2. Moreover, the form of Eq. (2) is preserved both for the principal directions of the surface and for the principal directions of the tensor of surface tension (where R_1 and R_2 are no longer principal radii but just radii of surface curvature in cross sections along directions 1 and 2, respectively) [3].

There have been many attempts to generalize the Laplace formula in thermodynamics of surface layers of an arbitrary curvature (in addition to [1–3], one can also mention, for example, [4–8]), but, as a rule, the pressure tensor was taken in the diagonal form. In other words, it was assumed (as is clear from our earlier publications [9, 10]) that the metric tensor of the surface layer and the pressure tensor are diagonalized concordantly. There was no such assumption only in [3, 11]. At the same time, the analysis in [3] was limited to the case of mechanically isotropic bulk phases. This restriction was removed (in the absence of external fields) in [11], where the concept of bending moments was used and the equilibrium condition for the surface layer was written with allowance for the pressure and tension anisotropies. Similar results have earlier been obtained in the theory of shells [12, 13]. The problem of deriving the complete condition of mechanical equilibrium for an arbitrarily curved nonspherical surface layer still remains to be solved in the general case in the presence of external fields (which may be the reason for anisotropy in the bulk phases). In analysis of this general case in [10], the Laplace formula was generalized [10, Eq. (7.6)]. However, the relationship provided in that work represents only one component of the complete condition of mechanical equilibrium at a curved surface, and now we will present this complete condition.

DERIVATION OF THE CONDITION OF INTERFACIAL MECHANICAL EQUILIBRIUM

To characterize the shape of the interface most completely, the metric tensor must be specified as a function of coordinates in the whole space of the surface layer. If we select an orthogonal coordinate system (u_1, u_2, u_3) diagonalizing the metric tensor so that the u_3-axis would be directed along the normal to the surface, then any coordinate surface (u_1, u_2) may be chosen as the dividing surface (this approach was substantiated in detail in [9, 10]). In accordance with the above statements, this coordinate system does not necessarily diagonalize the pressure tensor, and we will use it in the most general form.

Let us cut out an element of the surface layer by coordinate surfaces in such a way that it would also include some regions of the bulk phases α and β between which the surface layer is situated (see figure). Let this element be situated between the coordinates u_1, $u_1 + \Delta u_1$; u_2, $u_2 + \Delta u_2$; and u_3^α, u_3^β (hereafter, the superscripts α and β denote the quantities pertaining to the corresponding bulk phases). The condition of mechanical equilibrium for this element is expressed by the fact that the total force acting on it is zero, that is,

$$-\oint(\hat{p}d\mathbf{A}) = -\oint\mathbf{P}dA = 0. \quad (3)$$

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Here, $\hat{p}$ is the complete pressure tensor (including the contributions of external fields if they are present [10]); $\hat{E} \equiv -\hat{p}$ is the corresponding stress tensor; $d\mathbf{A} = \boldsymbol{\nu} dA$ is the vector of the differential of the element surface ($\boldsymbol{\nu}$ is the unit vector of the outer normal to the surface of the element); $-\mathbf{P} = -\hat{p}\,\boldsymbol{\nu}$ is the vector of the force applied to a unit surface area of the element (the stress vector); and integration is performed over the whole closed surface of the element. This surface includes six faces, and, accordingly, the integral in Eq. (3) may be represented by six summands (now we will supplement each vector $\mathbf{P}$ with a subscript showing the orientation of the face). The integrals for the lower and upper faces may be written in the form $(\mathbf{P}_3 \Delta l_1 \Delta l_2)^\alpha$ and $(\mathbf{P}_3 \Delta l_1 \Delta l_2)^\beta$, where $\Delta l_1 = h_1 \Delta u_1$ and $\Delta l_2 = h_2 \Delta u_2$ are the segments of the coordinate lines (corresponding to the coordinates u_1 and u_2) falling into the selected element at the level of the corresponding face; h_i are the Lamé coefficients, which are, just as these segments, the functions of spatial coordinates. For the faces perpendicular to directions 1 and 2, we obtain $dA_1 = \Delta l_2 dl_3 = \Delta l_2 h_3 du_3$ and $dA_2 = \Delta l_1 dl_3 = \Delta l_1 h_3 du_3$, respectively. In addition, let us write pairwise differences of the integrals in Eq. (3) for the element faces, because the forces acting on opposite faces are oppositely directed. Now we can represent Eq. (3) as

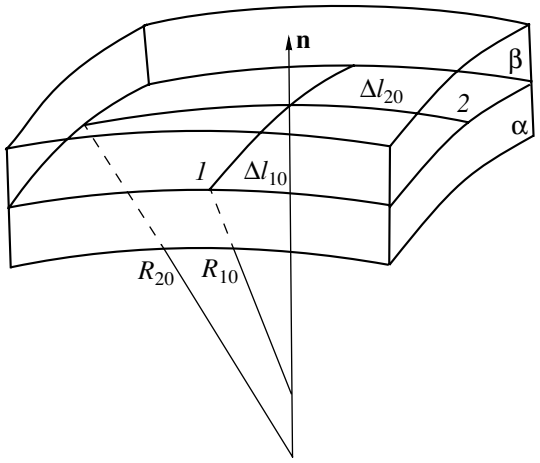
$$(\mathbf{P}_3 \Delta l_1 \Delta l_2)^\alpha - (\mathbf{P}_3 \Delta l_1 \Delta l_2)^\beta - \Delta \int_{u_3^\alpha}^{u_3^\beta} \mathbf{P}_1 \Delta l_2 h_3 du_3 - \Delta \int_{u_3^\alpha}^{u_3^\beta} \mathbf{P}_2 \Delta l_1 h_3 du_3 = 0, \tag{4}$$

where Δ in front of the integrals denote their increments due to passage from one of the opposite faces to the other one along directions 1 and 2.

Now let us place the dividing surface with the coordinate u_{30} and area $\Delta l_{10} \Delta l_{20}$ inside the element (in all other respects, its position may be arbitrary). The dividing surface separates this element into parts α and β (see figure) adjacent to the corresponding bulk phases. Now, if we assume that parts α and β are filled with the substances of phases α and β, respectively, and both parts are in the state of mechanical equilibrium, then we can write a condition similar to (4) for each of these parts separately:

$$(\mathbf{P}_3 \Delta l_1 \Delta l_2)^\alpha - \mathbf{P}_{30}^\alpha(u_{30}) \Delta l_{10} \Delta l_{20} - \Delta \int_{u_3^\alpha}^{u_{30}} \mathbf{P}_1^\alpha \Delta l_2 h_3 du_3 - \Delta \int_{u_3^\alpha}^{u_{30}} \mathbf{P}_2^\alpha \Delta l_1 h_3 du_3 = 0, \tag{5}$$

$$\mathbf{P}_3^\beta(u_{30}) \Delta l_{10} \Delta l_{20} - (\mathbf{P}_3 \Delta l_1 \Delta l_2)^\beta - \Delta \int_{u_{30}}^{u_3^\beta} \mathbf{P}_1^\beta \Delta l_2 h_3 du_3 - \Delta \int_{u_{30}}^{u_3^\beta} \mathbf{P}_2^\beta \Delta l_1 h_3 du_3 = 0. \tag{6}$$



Element of a curved surface layer.

Now, subtracting Eqs. (5) and (6) from Eq. (4), we arrive at the expression

$$[\mathbf{P}_3^\alpha(u_{30}) - \mathbf{P}_3^\beta(u_{30})] \Delta l_{10} \Delta l_{20} + \Delta \boldsymbol{\gamma}_1 \Delta l_{20} + \Delta \boldsymbol{\gamma}_2 \Delta l_{10} = 0, \tag{7}$$

where the vector designations

$$\boldsymbol{\gamma}_1 \equiv \frac{1}{\Delta l_{20}} \left[\int_{u_3^\alpha}^{u_{30}} (\mathbf{P}_1^\alpha - \mathbf{P}_1) \Delta l_2 h_3 du_3 + \int_{u_{30}}^{u_3^\beta} (\mathbf{P}_1^\beta - \mathbf{P}_1) \Delta l_2 h_3 du_3 \right], \tag{8}$$

$$\boldsymbol{\gamma}_2 \equiv \frac{1}{\Delta l_{10}} \left[\int_{u_3^\alpha}^{u_{30}} (\mathbf{P}_2^\alpha - \mathbf{P}_2) \Delta l_1 h_3 du_3 + \int_{u_{30}}^{u_3^\beta} (\mathbf{P}_2^\beta - \mathbf{P}_2) \Delta l_1 h_3 du_3 \right] \tag{9}$$

are introduced. These designations correspond to the force definition of the vector of surface tension in the cross-cuts of the surface layer perpendicular to directions 1 and 2—see formulas (5.2) and (5.10) in [10] with $\boldsymbol{\gamma}_1 \equiv \boldsymbol{\gamma}_1'$ and $\boldsymbol{\gamma}_2 \equiv \boldsymbol{\gamma}_2'$. The physical meaning of $\boldsymbol{\gamma}_1$ and $\boldsymbol{\gamma}_2$ is that they represent the excess stresses at the lines Δl_{20} and Δl_{10}, respectively, for each of the cross-cuts of the surface layer.

Now the last step remains. Let us divide Eq. (7) by $\Delta l_{10} \Delta l_{20}$ and, rigorously passing to a local relationship, let us consider Δu_1 and Δu_2 (and, accordingly, Δl_{10} and Δl_{20}) tending to zero. In this case, the condition of interfacial mechanical equilibrium assumes the form

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

which is the main result of this study. Note that now we have omitted the argument at $\mathbf{P}_3^\alpha$ and $\mathbf{P}_3^\beta$, because all quantities in Eq. (10) refer to the same point at the dividing surface. The actual $\mathbf{P}_3^\alpha$ and $\mathbf{P}_3^\beta$ values at the dividing surface are found by extrapolation of their bulk (not necessarily uniform) values.

Condition (10) is universal and applicable to systems in any aggregation state; however, the stress tensor $\hat{E} = -\hat{p}$ is generally used for solid bodies instead of the pressure tensor. Passing from the pressure vector $\mathbf{P}$ to the stress vector $\mathbf{E}$ ($\mathbf{P}_3^\alpha \equiv \mathbf{P}_3^\alpha(u_{30}) = -\mathbf{E}_3^\alpha(u_{30}) \equiv -\mathbf{E}_3^\alpha$, $\mathbf{P}_3^\beta \equiv \mathbf{P}_3^\beta(u_{30}) = -\mathbf{E}_3^\beta(u_{30}) \equiv -\mathbf{E}_3^\beta$), we can write condition (10) as

$$\mathbf{E}_3^\alpha - \mathbf{E}_3^\beta = \frac{\partial \boldsymbol{\gamma}_1}{\partial l_{10}} + \frac{\partial \boldsymbol{\gamma}_2}{\partial l_{20}}. \quad (11)$$

Relationship (10)–(11) is no less compact than the Laplace formula but much more universal than this formula or any of its known generalizations. The form and the (vector) nature of Eqs. (10)–(11) are very different from those of the Laplace formula, and this relationship cannot be called the generalized Laplace formula. It is another matter that such a generalized formula may be derived as one of the corollaries of this relationship (the dependence on the surface curvature is apparent, if only from the fact that the derivative of the vector depends on its turn due to a change in the orientation of the area element in the cross-cut of the surface layer). Below, we will show how to derive this formula.

MORE DETAILED FORMULATION OF THE CONDITION OF INTERFACIAL MECHANICAL EQUILIBRIUM

To distinguish between the changes in the modules and directions of all vectors in Eq. (10), let us introduce the unit vectors $\mathbf{e}_1$, $\mathbf{e}_2$, and $\mathbf{e}_3$ along the coordinate lines of our coordinate frame and write the relationships

$$\mathbf{P}_3^\alpha - \mathbf{P}_3^\beta = \sum_{i=1}^{3} (P_{i3}^\alpha - P_{i3}^\beta)\mathbf{e}_i, \quad (12)$$

$$\boldsymbol{\gamma}_1 = \sum_{i=1}^{3} \gamma_{i1}\mathbf{e}_i, \quad (13)$$

$$\boldsymbol{\gamma}_2 = \sum_{i=1}^{3} \gamma_{i2}\mathbf{e}_i, \quad (14)$$

where the additional subscript i refers to the components of the vectors along direction i [note that, according to definitions (8) and (9), the γ_{21} and γ_{12} components in Eqs. (13) and (14) are not equal]. Substituting Eqs. (12)–(14) into Eq. (10), we obtain

$$\sum_{i=1}^{3} (P_{i3}^\alpha - P_{i3}^\beta)\mathbf{e}_i = -\sum_{i=1}^{3} \frac{\partial \gamma_{i1}}{\partial l_{10}}\mathbf{e}_i - \sum_{i=1}^{3} \gamma_{i1}\frac{\partial \mathbf{e}_i}{\partial l_{10}} - \sum_{i=1}^{3} \frac{\partial \gamma_{i2}}{\partial l_{20}}\mathbf{e}_i - \sum_{i=1}^{3} \gamma_{i2}\frac{\partial \mathbf{e}_i}{\partial l_{20}}. \quad (15)$$

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

$$d\mathbf{t}/dL = c\mathbf{n}, \quad d\mathbf{n}/dL = -c\mathbf{t} + T\mathbf{b}, \quad d\mathbf{b}/dL = -T\mathbf{n}, \quad (16)$$

where $\mathbf{t}$ is the unit vector of the tangent to the spatial line (in our case, the coordinate line); $\mathbf{n}$ is the unit vector of its principal normal; $\mathbf{b}$ is the unit vector of the binormal; c is the curvature of the line; T is its torsion (in our coordinate system, the torsion is zero); and L is the length of the line. Considering the coordinate lines at the dividing surface, we obtain $\mathbf{t} = \mathbf{e}_1$, $\mathbf{n} = -\mathbf{e}_3$, $\mathbf{b} = \mathbf{e}_2$ for $L \equiv l_{10}$ and $\mathbf{t} = \mathbf{e}_2$, $\mathbf{n} = -\mathbf{e}_3$, $\mathbf{b} = -\mathbf{e}_1$ for $L \equiv l_{20}$. Now, using Eq. (16), we can find the following expressions for the derivatives of the unit vectors:

$$\frac{\partial \mathbf{e}_1}{\partial l_{10}} = -\frac{\mathbf{e}_3}{R_{10}}, \quad \frac{\partial \mathbf{e}_2}{\partial l_{10}} = 0, \quad \frac{\partial \mathbf{e}_3}{\partial l_{10}} = \frac{\mathbf{e}_1}{R_{10}}, \quad (17)$$

$$\frac{\partial \mathbf{e}_2}{\partial l_{20}} = -\frac{\mathbf{e}_3}{R_{20}}, \quad \frac{\partial \mathbf{e}_1}{\partial l_{20}} = 0, \quad \frac{\partial \mathbf{e}_3}{\partial l_{20}} = \frac{\mathbf{e}_2}{R_{20}}, \quad (18)$$

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

Substituting Eqs. (17) and (18) into Eq. (15) and successively multiplying expression (15) by $\mathbf{e}_1$, $\mathbf{e}_2$, and $\mathbf{e}_3$, we obtain three scalar equalities equivalent to the vector equality (10):

$$P_{13}^\alpha - P_{13}^\beta = -\frac{\gamma_{31}}{R_{10}} - \frac{\partial \gamma_{11}}{\partial l_{10}} - \frac{\partial \gamma_{12}}{\partial l_{20}}, \quad (19)$$

$$P_{23}^\alpha - P_{23}^\beta = -\frac{\gamma_{32}}{R_{20}} - \frac{\partial \gamma_{21}}{\partial l_{10}} - \frac{\partial \gamma_{22}}{\partial l_{20}}, \quad (20)$$

$$P_{33}^\alpha - P_{33}^\beta = \frac{\gamma_{11}}{R_{10}} + \frac{\gamma_{22}}{R_{20}} - \frac{\partial \gamma_{31}}{\partial l_{10}} - \frac{\partial \gamma_{32}}{\partial l_{20}}. \quad (21)$$

Equality (21) is just the generalization of the Laplace formula that was earlier obtained in [10]. In the absence of external fields, Eqs. (19)–(21) have the same form as the Kirchhoff–Love equations of mechanical equilibrium of thin shells [12, 13] and, in this sense, are equivalent to the equations of equilibrium derived by Eriksson, Ljunggren, and Kralchevsky [11, Eq. (192)]. An important new feature of formulas (19)–(21) compared to the Kirchhoff–Love formulas is that they assume a self-consistent force definition of the components of the vectors $\boldsymbol{\gamma}_1$ and $\boldsymbol{\gamma}_2$ according to Eqs. (8) and (9).

A self-consistent definition means that components of the vectors $\boldsymbol{\gamma}_1$ and $\boldsymbol{\gamma}_2$ must satisfy the generalized adsorption equation in a given external field.

In [9, 10], attention was paid to the three-dimensional aspect of surface tension, which is illustrated by the γ_{31} and γ_{32} quantities in Eqs. (19)–(21). If the surface tension were a purely two-dimensional tensor, these components would be absent, and Eq. (21) would pass into the Laplace formula (2) written for an arbitrary dividing surface. On the other hand, it also passes into the same formula in the case where the three-dimensional aspect of surface tension is present but the γ_{31} and γ_{32} values are constant along their coordinate lines, and their derivatives are zero. It is interesting that equalities (19) and (20) are preserved even in the absence of a three-dimensional aspect of surface tension; only the terms with the radii of curvature disappear. In the simple case where the selected coordinate system diagonalizes the pressure tensor, the γ_{31} and γ_{32} values are automatically nullified. Then, Eq. (21) passes into the Laplace formula (2) again, and Eqs. (19) and (20) are transformed into the constancy condition of the γ_{11} and γ_{22} values along their coordinate lines:

$$\frac{\partial \gamma_{11}}{\partial l_{10}} = \frac{\partial \gamma_{22}}{\partial l_{20}} = 0. \qquad (22)$$

This condition is far from trivial for the curved surfaces, since the surface tension is always regarded as dependent on the surface curvature, which may change as we move along the coordinate lines.

In the simple derivation procedure described here for the condition of interfacial mechanical equilibrium, we used only vectors of surface tension but did not introduce the complete tensors of surface tension (in the variant of the force definition) for both cross sections, as was done in [10]. If we use such tensors, then, to avoid confusion due to similar designations of their components, we should use primes to distinguish the cross sections: one prime for the cross section perpendicular to direction 1, and two for the cross section perpendicular to direction 2. In this notation, Eqs. (10), (11), and (19)–(21) assume the form [14]

$$\mathbf{E}_3^\beta - \mathbf{E}_3^\alpha = \mathbf{P}_3^\alpha - \mathbf{P}_3^\beta = -\frac{\partial \boldsymbol{\gamma}_1'}{\partial l_{10}} - \frac{\partial \boldsymbol{\gamma}_2''}{\partial l_{20}}, \qquad (23)$$

$$P_{13}^\alpha - P_{13}^\beta = -\frac{\partial \gamma_{11}'}{\partial l_{10}} - \frac{\partial \gamma_{31}'}{R_{10}} - \frac{\gamma_{12}''}{\partial l_{20}}, \qquad (24)$$

$$P_{23}^\alpha - P_{23}^\beta = -\frac{\partial \gamma_{21}'}{\partial l_{10}} - \frac{\partial \gamma_{22}''}{\partial l_{20}} - \frac{\gamma_{32}''}{R_{20}}, \qquad (25)$$

$$P_{33}^\alpha - P_{33}^\beta = -\frac{\partial \gamma_{31}'}{\partial l_{10}} + \frac{\gamma_{11}'}{R_{10}} - \frac{\partial \gamma_{32}''}{\partial l_{20}} + \frac{\gamma_{22}''}{R_{20}}. \qquad (26)$$

Condition (26) has just the same form as the one obtained (in a more complicated way) in [10].

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