The condition of mechanical equilibrium for a non-spherical interface between phases with a non-diagonal stress tensor

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Abstract

A compact form for the condition of mechanical equilibrium for arbitrary curved interfaces has been formulated in the case when the bulk pressures are non-diagonal local tensors. This form of the condition is applicable to a non-spherical interface between fluid or solid phases, without or with arbitrary number of any external fields. The equilibrium condition has been transformed into a set of differential equations for the tangential and transverse components of the mechanical surface tension and bulk pressure tensors at a dividing surface. One condition simplifies to the usual Laplace equation of capillarity for the transverse direction across the interface, while the other conditions relate to the tangential equilibrium state of the fluid. The amendment of the definition of a dividing surface has been given. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The condition of mechanical equilibrium for a spherical interface between two fluids with scalar bulk pressure and surface tension is expressed by the famous Laplace equation of capillarity. Gibbs [1] was first to make the Laplace equation a rigorous relationship of the theory of capillarity by introducing a dividing surface and defining surface tension as an excess surface stress related to the dividing surface. He also found, for a certain position of a dividing surface, the surface of tension, that the mechanical equilibrium condition for the dividing surface looks the same as that for a curved membrane in continuum mechanics. In the case of a non-spherical interface, since surface tension is dependent on curvature, the interfacial non-sphericity itself leads to anisotropy of surface tension even though the bulk pressures in adjacent phases remain as scalars. Additional difficulties arise when the bulk pressures are tensors with components depending on location within the phases and the interface layer. Previous attempts at a generalization of the condition for mechanical equilibrium for non-spherical interfaces [2–11] have concentrated primarily on the situation where the pressure and/or surface tension tensors were of diagonal form, although the general situation was also considered [4,10]. Most general solutions were also formulated within model approaches, which simulated surface

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layers as membranes or, more generally, shells of continuum mechanics with a similar treatment of linear interfaces [12,13]. This is a kind of approximation (with no dividing surface and with replacing excess surface stress by the stress of a shell), so that results obtained in such way should be compared with rigorous results of the theory of capillarity.

Formulation of the condition of mechanical equilibrium also requires taking into account the action of external forces. Beginning from Gibbs [1], many authors confined themselves by considering gravity. Apparently, adding every new field creates an additional term to the equilibrium condition. So the only way to account for all possible external forces at once is introducing a total stress tensor [14], which automatically includes external forces (if, for example, a system is in electric field, the total stress tensor includes the Maxwell stress tensor, etc.). The equilibrium condition for the total stress tensor is written as in the case of the usual sense as vectors $\mathbf{r}_1$ and $\mathbf{r}_2$, in the $u_1$ and $u_2$ directions (directions 1 and 2 below), respectively, and the normal direction to the surface may be oriented by the cross-product of these tangent vectors; that is, $\mathbf{r}_1 \times \mathbf{r}_2$. In contrast to this formulation for the metric, where the metric tensor is diagonal, we assume that the total pressure and the surface tension tensors are non-diagonal (say, due to an external electric field).

As a condition of mechanical equilibrium, one may state that the total force acting on any part of the system is zero. The local form of this condition for the case of total stress tensor $\mathbf{T}$ can be written as

$$\nabla T = 0$$  \hspace{1cm} (1.1)

where $\nabla$ is the nabla operator. But for our purposes it is more convenient to use this condition in the form for a part of the system.

Let us select a part of the surface layer between phases $\alpha$ and $\beta$, the interfacial thickness being so chosen as to attain bulk phases on both the sides of the layer, located between co-ordinates $u_1$, $u_1 + \Delta u_1$; $u_2$, $u_2 + \Delta u_2$; $u_3^\alpha$, $u_3^\beta$ (the superscripts $\alpha$ and $\beta$}

2. Orientation of and forces acting on a non-spherical, curved interface

We must select a coordinate system that will be suitable and convenient to use when we define orientation of and related forces, etc. at the interface. The most obvious candidate is an orthogonal, curvilinear coordinate system with the parameters $(u_1, u_2, u_3)$ denoting the space for the interfacial zone. Such a coordinate system corresponds to the natural metric of the interface with the $u_3$-line directed along the gradients of local properties. A related surface region, playing the role of a Gibbs dividing surface [11,14], may be defined by specifying the condition $u_3 = a$ constant and letting the parameters $(u_1, u_2)$ vary over the restricted surface region. In contrast with Gibbs’ treatment, we assume the $u_3$-line not to be necessary straight, so that various positions of the dividing surface are determined by moving along the $u_3$-line, but not along the normal to the surface for a finite distance (this is an amendment to Gibbs’ definition of a dividing surface [11,14]).

Tangent vectors to the surface may be defined in the usual sense as vectors $\mathbf{r}_1$ and $\mathbf{r}_2$ in the $u_1$ and $u_2$ directions (directions 1 and 2 below), respectively, and the normal direction to the surface may be oriented by the cross-product of these tangent vectors; that is, $\mathbf{r}_1 \times \mathbf{r}_2$. In contrast to this formulation for the metric, where the metric tensor is diagonal, we assume that the total pressure and the surface tension tensors are non-diagonal (say, due to an external electric field).
and let us assume that the increments indicating the orientation of the corresponding side the vector \( \mathbf{P} = \hat{\mathbf{n}} \times \mathbf{n} \) is the stress vector or traction force applied per unit area. The integration indicated in Eq. (1.2) must be carried out over the entire closed area of the system. In our situation, the system is a cube-like element with six sides and the integral splits into six terms. Let us provide the vector \( \mathbf{P} \) in these terms with a subscript indicating the orientation of the corresponding side and let us assume that the increments \( \Delta u_1 \) and \( \Delta u_2 \) are very small. For the lower and upper side of the interfacial element we can write the integration results in the form \((\mathbf{P}_2 \Delta l_1 \Delta I_2)^x\) and \((\mathbf{P}_3 \Delta l_1 \Delta I_2)^y\) where \( \Delta l_1 = h_1 \Delta u_1 \) and \( \Delta l_2 = h_2 \Delta u_2 \) are the segments of the co-ordinate lines which correspond to the increments \( \Delta u_1 \) and \( \Delta u_2 \) of the co-ordinates (see the cross-section of the surface layer in Fig. 1), \( h_i \) are the Lame coefficients which are, as well as the segments themselves, the functions of co-ordinates \( u_1, u_2, u_3 \). We have \( dA_1 = \Delta l_1 \Delta I_2 = \Delta l_2 h_3 du_3 \) perpendicular to the positive direction of \( u_1 \) and \( dA_2 = \Delta l_1 \Delta I_3 = \Delta l_1 h_3 du_3 \) perpendicular to the positive direction of \( u_2 \). Recognizing that the forces applied to the opposite sides of the element selected are directed oppositely, we can now rewrite Eq. (1.2) in the form

\[
(\mathbf{P}_2 \Delta l_1 \Delta I_2)^x - (\mathbf{P}_3 \Delta l_1 \Delta I_2)^y - \Delta \int_{u_3}^{u_3} \mathbf{P}_1 \Delta l_3 h_3 du_3
\]

where symbol \( \Delta \) before the integrals means increment of these integrals at opposite sides of the element selected along the directions 1 and 2.

Let us introduce a dividing surface inside the interfacial element that divides the element into an \( \alpha \)-layer (adjacent to phase \( \alpha \) and depicted as opaque in Fig. 2) and the \( \beta \)-layer (adjacent to phase \( \beta \) and depicted as transparent in Fig. 2). Within the boundaries of the element under consideration, the area of the dividing surface is \( A_0 = \Delta l_{10} \Delta l_{20} \) where \( \Delta l_{10} \) and \( \Delta l_{20} \) are the lengths of the dividing surface in directions 1 and 2 (Fig. 2). Applying Eq. (1.3) to the \( \alpha \)-layer (shaded in Fig. 2) filled (in mind) with the matter of bulk phase \( \alpha \) (extrapolated to the \( \alpha \)-layer) and to the \( \beta \)-layer filled with the matter of bulk phase \( \beta \) gives

\[
(\mathbf{P}_2 \Delta l_1 \Delta I_2)^x - \mathbf{P}_3^\alpha (u_{30}) \Delta l_{10} \Delta l_{20} - \Delta \int_{u_{30}}^{u_{30}} \mathbf{P}_1^\alpha \Delta l_3 h_3 du_3 = 0,
\]

\[
- \Delta \int_{u_{30}}^{u_{30}} \mathbf{P}_2^\alpha \Delta l_3 h_3 du_3 = 0,
\]

\[
(\mathbf{P}_3 \Delta l_1 \Delta I_2)^y - \mathbf{P}_2^\beta (u_{30}) \Delta l_{10} \Delta l_{20} - \Delta \int_{u_{30}}^{u_{30}} \mathbf{P}_1^\beta \Delta l_3 h_3 du_3 = 0,
\]

\[
- \Delta \int_{u_{30}}^{u_{30}} \mathbf{P}_3^\beta \Delta l_3 h_3 du_3 = 0.
\]
3. Local equilibrium condition at the dividing surface in the vector form

Subtracting both Eqs. (1.4) and (1.5) from Eq. (1.3) applied to the real interface element under consideration as a whole, we arrive at the mechanical equilibrium condition in the vector form

\[
[P_3(u_{30}) - P_0(u_{30})] \Delta l_{20} + \Delta \tau_1 \Delta l_{20} + \Delta \tau_2 \Delta l_{10} = 0
\]

(2.1)

where the first term represents the pressure–force difference at the dividing surface on its opposite sides, while the second and third terms represent the surface tension force differences on the opposite edges of the dividing surface in directions 1 and 2, respectively. Here

\[
\gamma_1 \equiv \frac{1}{\Delta l_{20}} \left[ \int_{w_{30}}^{w_{30}} (P_1 - P_2) \Delta l_{20} \, dt_3 \right]
+ \int_{w_{30}}^{w_{30}} (P_1^0 - P_2) \Delta l_{20} \, dt_3,
\]

\[
\gamma_2 \equiv \frac{1}{\Delta l_{10}} \left[ \int_{w_{30}}^{w_{30}} (P_2 - P_3) \Delta l_{10} \, dt_3 \right]
+ \int_{w_{30}}^{w_{30}} (P_2^0 - P_3) \Delta l_{10} \, dt_3.
\]

(2.2)

(2.3)

It follows from Eqs. (2.2) and (2.3) that the vectors \( \gamma_1 \) and \( \gamma_2 \) correspond to the mechanical force-definition of the surface tension vector through integration of the excess stress over the cross-sections for directions 1 and 2, respectively [11] (the cross-section for direction 1 is shown in Fig. 1). Eqs. (2.1), (2.2) and (2.3) also imply that the vectors \( P_3 \), \( \gamma_1 \) and \( \gamma_2 \) are not necessarily along either the normal or the tangent directions to the dividing surface.

After dividing Eq. (2.1) by the dividing surface area \( A_0 = \Delta l_{10} \Delta l_{20} \) and permitting the lengths \( \Delta l_{10} \) and \( \Delta l_{20} \) to go to zero, we proceed to the rigorous local formulation of the mechanical equilibrium condition at the dividing surface in the arbitrarily curved interface

\[
P_3(u_{30}) - P_3^0(u_{30}) = -\frac{\partial \gamma_1}{\partial l_{10}} - \frac{\partial \gamma_2}{\partial l_{20}}.
\]

(2.4)

The vector relation above is the main result of this note and it is valid for any (diagonal or non-diagonal) forms of the pressure and surface tension local tensors in absence and in presence of external fields. Surprisingly, the mechanical equilibrium condition at curved interface exhibits its extremely compact form even in the most general and complicated cases.

4. Local equilibrium conditions for components of the pressure and surface tension tensors

The vector Eq. (2.4) comprises three scalar equations, which can be deduced as follows. Introducing unit vectors \( e_i \) \((i = 1, 2, 3)\) along the co-ordinate line directions, one can represent vectors \( P_i \) \((i = 1, 2, 3)\) along the coordinate lines on the surface. For a curve or line in space the Serret–Frenet formulas of differential geometry and recast the coordinate system \((u_1, u_2, u_3)\) in terms of the local tangent \(t\), normal \(n\), and bi-normal \(b\) of the coordinate lines on the surface. For a curve or line in space the Serret–Frenet formulas are usually written in the form

\[
P_i = \sum_{k=1}^{3} P_{ki} e_k,
\]

\[
P_3(u_{30}) - P_3^0(u_{30}) = \sum_{i=1}^{3} (P_{3i}(u_{30}) - P_{3i}^0(u_{30})) e_i,
\]

\[
\gamma_1 = \sum_{i=1}^{3} \gamma_{1i} e_i, \quad \gamma_2 = \sum_{i=1}^{3} \gamma_{2i} e_i,
\]

where \( P_{ki} \) are the components of the pressure tensor, \( \gamma_{1i}, \gamma_{2i}, \gamma_{12}, \gamma_{21} \) are the tangential components of the surface tension tensor, while \( \gamma_{13}, \gamma_{23} \) are the corresponding transverse components. To obtain explicit micro-mechanical formulas for the components of the surface tensor, in view of Eq. (3.1), we need only multiply Eq. (2.4) by the appropriate unit vector \( e_i \) \((i = 1, 2, 3)\) to obtain a concatenation of the tensor relation to the direction \( e_i \). Using Eqs. (3.2) and (3.3), we can rewrite Eq. (2.4) in the form

\[
\sum_{i=1}^{3} (P_{3i}(u_{30}) - P_{3i}^0(u_{30})) e_i = -\sum_{j=1}^{3} \frac{\partial \gamma_{1j}}{\partial l_{10}} e_j
- \sum_{j=1}^{3} \frac{\partial \gamma_{2j}}{\partial l_{20}} e_j
- \sum_{i=1}^{3} \gamma_{1i} \frac{\partial e_i}{\partial l_{10}}
- \sum_{i=1}^{3} \gamma_{2i} \frac{\partial e_i}{\partial l_{20}}.
\]

(3.4)

In order to evaluate the terms in Eq. (3.4) in terms of local curvatures we introduce the Serret–Frenet formulas of differential geometry and recast the coordinate system \((u_1, u_2, u_3)\) in terms of the local tangent \(t\), normal \(n\), and bi-normal \(b\) of the coordinate lines on the surface. For a curve or line in space the Serret–Frenet formulas are usually written in the form
\[ \frac{dt}{dL} = -\mathbf{e}_n, \quad \frac{dn}{dL} = -\mathbf{t} + TB, \quad \frac{db}{dL} = -\mathbf{t}n \quad (3.5) \]

where \( \mathbf{t} \) and \( T \) are the line curvature and the line torsion, respectively. For our choice of coordinate system the torsion is zero. Eq. (3.5) may be used to write the derivative factors involving \( \mathbf{e}_i \) \((i = 1, 2, 3)\) that appear in Eq. (3.4) in terms of the local radii of curvature. Two cases of interest exist: when \( t = \mathbf{e}_1 \) with \( L = l_{10} \) and when \( t = \mathbf{e}_2 \) with \( L = l_{20} \). In the first case, the related normal and bi-normal vectors are, \( \mathbf{n} = -\mathbf{e}_3 \) and \( \mathbf{b} = \mathbf{e}_2 \) and the corresponding derivatives are

\[ \frac{\partial \mathbf{e}_1}{\partial l_{10}} = -\frac{\mathbf{e}_3}{R_{10}}, \quad \frac{\partial \mathbf{e}_2}{\partial l_{10}} = 0, \quad \frac{\partial \mathbf{e}_3}{\partial l_{10}} = \frac{\mathbf{e}_1}{R_{10}}. \quad (3.6) \]

In the second case, for \( t = \mathbf{e}_2 \) the related normal and bi-normal vectors are, \( \mathbf{n} = -\mathbf{e}_3 \) and \( \mathbf{b} = -\mathbf{e}_1 \). The derivatives are

\[ \frac{\partial \mathbf{e}_2}{\partial l_{20}} = -\frac{\mathbf{e}_3}{R_{20}} \quad \frac{\partial \mathbf{e}_1}{\partial l_{20}} = 0, \quad \frac{\partial \mathbf{e}_3}{\partial l_{20}} = \frac{\mathbf{e}_2}{R_{20}}. \quad (3.7) \]

Here \( R_{i0} \) \((i = 1, 2)\) are the local principal curvature radii of the dividing surface. Upon substituting Eqs. (3.6) and (3.7) into Eq. (3.4) it is possible to simplify Eq. (3.4) into three separate scalar relations. In particular, if we post-multiply Eq. (3.4) by the unit vector \( \mathbf{e}_i \), then we obtain a scalar relation in a direction perpendicular to the surface that is given by

\[ P_{ij}(u_{30}) - P_{ij}(u_{30}) = \gamma_{11} \frac{\gamma_{11}}{R_{10}} + \gamma_{22} \frac{\gamma_{22}}{R_{20}} - \frac{\gamma_{12}}{R_{10}} \frac{\gamma_{12}}{R_{20}}. \quad (3.8) \]

Multiplying Eq. (3.4) by \( \mathbf{e}_1 \) and \( \mathbf{e}_2 \), we obtain, respectively,

\[ P_{13} - P_{13} = \frac{\gamma_{13}}{R_{10}} \frac{\gamma_{13}}{R_{10}} + \frac{\gamma_{23}}{R_{20}} \frac{\gamma_{23}}{R_{20}} - \frac{\gamma_{12}}{R_{10}} \frac{\gamma_{12}}{R_{20}}. \quad (3.9) \]
\[ P_{23} - P_{23} = \frac{\gamma_{31}}{R_{10}} \frac{\gamma_{31}}{R_{10}} + \frac{\gamma_{32}}{R_{20}} \frac{\gamma_{32}}{R_{20}}. \quad (3.10) \]

When the surface tension tensor is diagonal; that is, \( \gamma_{ik} = 0 \) if \( i \neq k \), Eq. (3.8) simplifies to the classical Laplace equation of capillarity \[3]\). The transverse relations, Eqs. (3.9) and (3.10), reduce to the known conditions

\[ \frac{\partial \gamma_{11}}{\partial l_{10}} = 0, \quad \frac{\partial \gamma_{22}}{\partial l_{20}} = 0. \quad (3.11) \]

which imply that the in-plane, diagonal surface tension components \( \gamma_{11} \) and \( \gamma_{22} \) do not change value along the corresponding coordinate lines.

### 5. Discussion

The above derivation was carried out with no use of tensors, so we now have to compare the results with known tensorial formulations. First of all, it is interesting to verify whether or not the detailed known results of the model shell approach \[12,13\] corresponds to the above rigorous derivation. After passing to equilibrium and to the total stress tensor, Eq. (3.38) in \[13\] becomes

\[ \mathbf{n}_1 \hat{\sigma}_1 + \mathbf{n}_2 \hat{\sigma}_2 = \nabla_s \hat{\sigma}_s \quad (4.1) \]

where \( \mathbf{n} \) is the unit surface normal, \( \hat{\sigma} \) and \( \hat{\sigma}_s \) are the bulk and surface stress tensors, respectively, subscripts 1 and 2 refer to adjacent bulk phases and subscript \( s \) to the surface. Putting \( \hat{\sigma} = \hat{\rho}^\omega, \hat{\sigma}_s = \hat{\rho}^b \), and \( \mathbf{n} \equiv \mathbf{n}_1 = -\mathbf{n}_2 \), Eq. (4.1) may be rewritten

\[ \mathbf{n}(\hat{\rho}^\omega - \hat{\rho}^b) = -\nabla_s \hat{\sigma}_s \quad (4.2) \]

or

\[ \mathbf{P}_3^s - \mathbf{P}_3^b = -\nabla_s \hat{\sigma}_s \quad (4.3) \]

To transform also the right-hand side to the vector form, we represent the surface stress tensor as a diadic

\[ \hat{\sigma}_s \equiv \mathbf{e}_1 \gamma_{11} + \mathbf{e}_2 \gamma_{12} \quad (4.4) \]

Substituting Eq. (4.4) in Eq. (4.3) yields

\[ \mathbf{P}_3^s - \mathbf{P}_3^b = -\nabla_s (\mathbf{e}_1 \gamma_{11} + \mathbf{e}_2 \gamma_{12}) \]
\[ = -\nabla_s (\mathbf{e}_1 \gamma_{11} - \nabla_s \mathbf{e}_2 \gamma_{12}) = -\frac{\partial \gamma_{11}}{\partial l_{10}} - \frac{\partial \gamma_{12}}{\partial l_{20}}. \quad (4.5) \]

Comparing now Eqs. (2.4) and (4.5), we see that they coincide in form. Naturally, the three scalar components of Eqs. (2.4), (3.8), (3.9) and (3.10), coincide in form with the scalar components of Eq. (4.1), as well as with the first set of three basic equations of Kirchhoff and Love in the theory of elastic shells. So we may conclude that a dividing surface with excess surface stress behaves like a shell with real stress. This result is not surprising since we used the force definition

\[ \mathbf{A}_1 \mathbf{n}_1 + \mathbf{A}_2 \mathbf{n}_2 = \nabla_s \mathbf{n}_3 \]
for surface tension when the form of the mechanical equilibrium condition is known to be independent of the dividing surface location [5,14]. It is of interest, however, that, in this definition, excess surface stress tensors are defined separately for the two cross-sections (1 and 2) in Eq. (2.4), so that vectors $\gamma_1$ and $\gamma_2$ in Eq. (2.4) belong to two different excess surface stress tensors, while they belong to the unique surface stress tensor in Eq. (4.5).

The role and contribution of the bending and torsion moments associated with the transverse shear stress resultants in equilibrium of an arbitrary curved membrane or interface were considered by Kralchevsky, Eriksson and Ljunggren [7,10]. They used a complex thermodynamic and mechanical approach to this problem and obtained the local equilibrium conditions at the interface in a form, which differs from Eqs. (3.8), (3.9) and (3.10). However, bearing in mind the meaning of components $\gamma_{31}$ and $\gamma_{32}$ and their relation to the bending and torsion moments, one can prove that Eq. (3.8) may be rewritten in the form of Eq. (2.35) from [7], and Eqs. (3.9) and (3.10) transform into Eq. (2.36) from [7]. Equations (2.35) and (2.36) from [7] express the conditions of mechanical equilibrium at interface and serve as a mechanical basis for subsequent thermodynamic and geometrical analysis in [7,10]. Thus the resulting form of equilibrium conditions in [7,10] is in fact equivalent to Eqs. (3.8), (3.9) and (3.10). Vector Eq. (2.4) along with Eqs. (2.2) and (2.3) seems to be most compact and straightforward form of the condition of mechanical equilibrium for interface in general case.

Concluding the discussion, we may estimate the novelty of this presentation as giving a more precise definition for a dividing surface, introducing the total stress tensor and its surface excess in the mechanical equilibrium condition, exhibiting a simple way for the derivation of this condition, and representing the known equilibrium condition itself in the form understandable for every colloid scientist.

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