

Generalization of the Laplace equation for non-spherical interfaces in external fields

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A general form of the Laplace equation has been derived using non-diagonal tensors for pressure and surface tension typical of non-spherical interfaces in external fields.

The Laplace equation, the principal relationship of colloid science, is well known for a non-spherical interface with the scalar surface tension γ as

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

where p is the pressure (α and β indicate the adjacent phases) and R_i ($i = 1, 2$) are the principal curvature radii of the interface. Since surface tension depends on curvature, the interfacial non-sphericity itself leads to the anisotropy of surface tension, so that equation (1) can be written in the form

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

where γ_1 and γ_2 are the surface tensions along the principal directions on the interface. There were many attempts to generalise the Laplace equation, but the results (see, e.g., refs. 1–9) mostly referred to the case when the pressure tensor and/or the tensor of surface tension (defined as excess surface stress) are of a diagonal form. The latter, however, not always exists and is scarcely attainable if an interface is subjected to an arbitrarily directed external field. Using the total pressure and surface-tension tensors (including the field), the only problem remains to formulate the Laplace equation in terms of the non-diagonal pressure and surface-tension tensors, and this is the goal of this paper.

First, we have to choose a co-ordinate system. Studying the interface shape, it is most convenient to use such curvilinear co-ordinates as reflecting the interface shape. In the mathematical language, this means that we use an orthogonal curvilinear co-ordinate system (u_1, u_2, u_3) diagonalising the metric tensor of the interface, so that any co-ordinate surface (u_1, u_2) inside or near the interface can play a role of the Gibbs dividing surface, the u_3 co-ordinate corresponding to the direction perpendicular to the interface.⁹ In contrast with the metric tensor, the pressure and surface-tension tensors are assumed to maintain (e.g., due to an external field) their non-diagonal form even in the above co-ordinate system.

As the Laplace equation is a condition of mechanical equilibrium, it may be derived from the condition that the total force acting on any part of the system is zero. This can be formulated as

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

where \hat{p} is the local pressure tensor, $d\mathbf{A}$ is the vector of a surface element (i.e., an elementary surface area multiplied by the vector \mathbf{n} of the unit normal to the surface), and $\mathbf{P} = \hat{p}\mathbf{n}$ is the vector of force applied to the elementary unit surface. The integration in (3) is carried out over the whole closed surface of a system part selected. Let us select an element at the interface between the phases α and β , the interphase thickness being so chosen as to attain bulk phases on both sides of the interface. Introducing a dividing surface inside the interphase divides the interface element into the α -layer (adjacent to the phase α and depicted as opaque in Figure 1) and the β -layer (adjacent to the phase β and depicted as transparent in Figure 1). Within the boundaries of the element, the dividing surface area is $A_0 = l_{10}l_{20}$, where l_{10} and l_{20} are the lengths of the dividing surface in directions 1 and 2 (Figure 1).

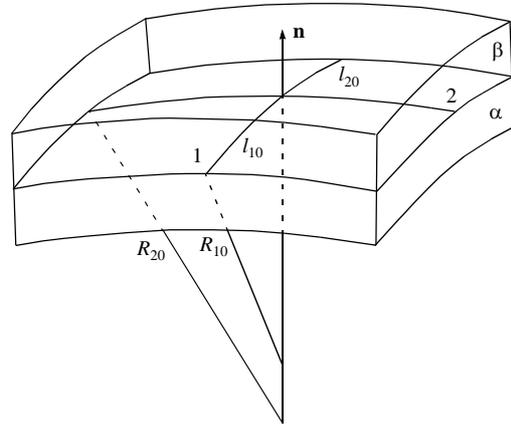


Figure 1 Element of a non-spherical interface.

Let us apply, as the first step, equation (3) to the α -layer filled (in mind) with the matter of the bulk phase α (extrapolated to the α -layer). As the second step, we similarly apply equation (3) to the β -layer filled with the matter of the bulk phase β . Then, we subtract both of the relationships obtained from equation (3) applied to the real interface element under consideration as a whole. In this way, we arrive at the mechanical equilibrium condition in the vector form

$$(\mathbf{P}_3^\alpha - \mathbf{P}_3^\beta)l_{10}l_{20} + \Delta\boldsymbol{\gamma}'_1 l_{20} + \Delta\boldsymbol{\gamma}'_2 l_{10} = 0, \quad (4)$$

where the first term represents the pressure-force difference at the dividing surface on its opposite sides, and the second and third terms represent the tension-force differences on the opposite edges of the dividing surface in directions 1 and 2, respectively. Note that, according to the above procedure, the vectors $\boldsymbol{\gamma}'_1$ and $\boldsymbol{\gamma}'_2$ correspond to the force definition of the surface-tension vector (which is equivalent to the definition by integration of the excess strain over the cross-sections for directions 1 and 2, respectively¹⁰). Equation (4) implies the vectors \mathbf{P}_3 , $\boldsymbol{\gamma}'_1$ and $\boldsymbol{\gamma}'_2$ not to be directed, by necessity, along the normal or the tangent to the dividing surface, respectively.

Dividing (4) by $l_{10}l_{20}$ with the subsequent transitions $l_{10} \rightarrow 0$ and $l_{20} \rightarrow 0$, we proceed to the rigorous local formulation of the mechanical equilibrium condition

$$\mathbf{P}_3^\alpha - \mathbf{P}_3^\beta = -\frac{\partial \boldsymbol{\gamma}'_1}{\partial l_{10}} - \frac{\partial \boldsymbol{\gamma}'_2}{\partial l_{20}}. \quad (5)$$

Equation (5), the main result of this work, is a generalization of the Laplace equation valid for any (diagonal or non-diagonal) forms of the pressure and surface-tension tensors. Surprisingly, the Laplace equation exhibits an extremely compact form even in the general and complicated case.

Vector equation (5) comprises three scalar equations, which can be deduced as described below. There are the identities [with \mathbf{e}_i ($i = 1, 2, 3$) as unit vectors along the co-ordinate line directions]

$$\mathbf{P}_3^\alpha - \mathbf{P}_3^\beta = \sum_{i=1}^3 (P_{i3}^\alpha - P_{i3}^\beta) \mathbf{e}_i, \quad \boldsymbol{\gamma}'_1 = \sum_{i=1}^3 \gamma'_{i1} \mathbf{e}_i, \quad \boldsymbol{\gamma}'_2 = \sum_{i=1}^3 \gamma'_{i2} \mathbf{e}_i. \quad (6)$$

where γ'_{i1} and γ'_{i2} are the components of the surface-tension tensors as excess stress tensors over the cross-sections for direc-

tions 1 and 2, respectively. Using (6), we can write equation (5) in the form

$$\sum_{i=1}^3 (P_{i3}^{\alpha} - P_{i3}^{\beta}) \mathbf{e}_i = - \sum_{i=1}^3 \frac{\partial \gamma'_{i1}}{\partial l_{10}} \mathbf{e}_i - \sum_{i=1}^3 \gamma'_{i1} \frac{\partial \mathbf{e}_i}{\partial l_{10}} - \sum_{i=1}^3 \frac{\partial \gamma''_{i2}}{\partial l_{20}} \mathbf{e}_i - \sum_{i=1}^3 \gamma''_{i2} \frac{\partial \mathbf{e}_i}{\partial l_{20}}. \quad (7)$$

Now, we have to account for the standard Serret-Frenet equations of differential geometry

$$d\mathbf{t}/dL = c\mathbf{n}, \quad d\mathbf{n}/dL = -c\mathbf{t} + T\mathbf{b}, \quad d\mathbf{b}/dL = -T\mathbf{n}, \quad (8)$$

where \mathbf{t} , \mathbf{n} and \mathbf{b} are the unit vectors of the line tangent, the line principal normal and the line binormal, respectively; c and T are the line curvature and the line torsion, respectively. According to the above choice of the co-ordinate system, $T = 0$ in our case. Then, applying (8) to the co-ordinate lines on the dividing surface (we have $\mathbf{t} = \mathbf{e}_1$, $\mathbf{n} = -\mathbf{e}_3$, $\mathbf{b} = -\mathbf{e}_2$ with $L = l_{10}$ and $\mathbf{t} = \mathbf{e}_2$, $\mathbf{n} = -\mathbf{e}_3$, $\mathbf{b} = -\mathbf{e}_1$ with $L = l_{20}$), we obtain

$$\begin{aligned} \frac{\partial \mathbf{e}_1}{\partial l_{10}} &= -\frac{\mathbf{e}_3}{R_{10}}, & \frac{\partial \mathbf{e}_2}{\partial l_{10}} &= 0, & \frac{\partial \mathbf{e}_3}{\partial l_{10}} &= \frac{\mathbf{e}_1}{R_{10}}, \\ \frac{\partial \mathbf{e}_2}{\partial l_{20}} &= -\frac{\mathbf{e}_3}{R_{20}}, & \frac{\partial \mathbf{e}_1}{\partial l_{20}} &= 0, & \frac{\partial \mathbf{e}_3}{\partial l_{20}} &= \frac{\mathbf{e}_2}{R_{20}}. \end{aligned} \quad (9)$$

Putting now (9) in (7), we can pass to separate scalar components of equation (7). In particular, multiplying (7) scalarly by \mathbf{e}_3 , we have

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

Equation (10) was derived by Evans and Skalak¹¹ for a curved membrane. In the case when the surface-tension tensor is diagonal ($\gamma_{31} = \gamma_{32} = 0$), equation (10) is identical to equation (2).

Multiplying now equation (7) by \mathbf{e}_1 and \mathbf{e}_2 , we obtain, respectively,

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

$$P_{23}^{\alpha} - P_{23}^{\beta} = -\frac{\partial \gamma'_{21}}{\partial l_{10}} - \frac{\partial \gamma'_{22}}{\partial l_{20}} - \frac{\gamma'_{32}}{R_{20}}. \quad (12)$$

Nobody seems to consider these equilibrium conditions so far. Passing to the diagonal form of the pressure and surface-tension tensors, equations (11) and (12) change to the known conditions

$$\frac{\partial \gamma'_{11}}{\partial l_{10}} = 0, \quad \frac{\partial \gamma'_{22}}{\partial l_{20}} = 0 \quad (13)$$

that means the conservation of the principal surface-tension components along the corresponding co-ordinate lines.

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