

On the mechanical equilibrium condition for incompletely developed interfaces

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The general mechanical equilibrium condition for an element of an arbitrarily curved incompletely developed interface is derived and applied to free and wetting films of distinct and variable local thickness with overlapping surface layers.

The interface is a transitional zone between two bulk phases with inhomogeneous local properties. A set of density (concentration) gradient lines determines the interface shape and creates the interface metrics whose knowledge is important for the choice of a dividing surface in Gibbs' interfacial thermodynamics. The most compact description is attained when using a (generally, curvilinear) co-ordinate system that diagonalises the metric tensor (which links the curvilinear and Cartesian co-ordinates), so that the normal co-ordinate corresponds to the gradient lines. Earlier,¹ we derived the local mechanical equilibrium condition for an interface between phases α and β in the vector form

$$\mathbf{P}_3^\alpha(u_{30}) - \mathbf{P}_3^\beta(u_{30}) = -\frac{\partial \boldsymbol{\gamma}_1}{\partial l_{10}} - \frac{\partial \boldsymbol{\gamma}_2}{\partial l_{20}} \quad (1)$$

from the condition that the total force acting on an elementary fragment of the interface is zero (we reproduce Figure 1 from the earlier publication¹). Here, \mathbf{P}_3^α and \mathbf{P}_3^β are the vector components of the pressure tensor in phases α and β , respectively, extrapolated to a dividing surface, and $\boldsymbol{\gamma}_1$ and $\boldsymbol{\gamma}_2$ are the vector components of the surface tension tensor (at its mechanical definition) for the principal directions on the interface, l_1 and l_2 are the lengths of the coordinate lines 1 and 2 (the additional subscript 0 refers to a dividing surface). Numbers 1, 2 and 3 correspond to 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 the interface can play the role of a Gibbs dividing surface, the u_3 co-ordinate corresponding to the direction perpendicular to the interface. If we now consider Figure 1 as an inner interface element (whose upper and lower boundaries do not attain the bulk phases) and repeat the derivation, equation (1) is replaced by the more general mechanical equilibrium condition

$$\begin{aligned} \mathbf{P}_3^\alpha(u_{30}) - \mathbf{P}_3^\beta(u_{30}) = & -\frac{\partial \boldsymbol{\sigma}_1}{\partial l_{10}} - \frac{\partial \boldsymbol{\sigma}_2}{\partial l_{20}} - \\ & - [\mathbf{P}_3(u_3^\alpha) - \mathbf{P}_3(u_3^\alpha)] \frac{h_1(u_3^\alpha)h_2(u_3^\alpha)}{h_{10}h_{20}} + \\ & + [\mathbf{P}_3(u_3^\beta) - \mathbf{P}_3(u_3^\beta)] \frac{h_1(u_3^\beta)h_2(u_3^\beta)}{h_{10}h_{20}}, \end{aligned} \quad (2)$$

where $\boldsymbol{\sigma}_1$ and $\boldsymbol{\sigma}_2$ are the element tension vectors, $h_i(u_3)$ are the Lamé coefficients [$h_{i0} \equiv h_i(u_{30})$], and the co-ordinates u_3^α and u_3^β correspond to the lower and upper boundaries of the element, respectively. Since all the quantities are written for a certain pair of co-ordinates u_1 and u_2 , only the dependence on u_3 is explicitly shown in equation (2). In the case when the element lower and upper boundaries approach the bulk phases, we have $\boldsymbol{\sigma}_i \rightarrow \boldsymbol{\gamma}_i$, $\mathbf{P}_3(u_3^\alpha) \rightarrow \mathbf{P}_3^\alpha(u_3^\alpha)$, $\mathbf{P}_3(u_3^\beta) \rightarrow \mathbf{P}_3^\beta(u_3^\beta)$, and equation (2) changes to equation (1).

Vector equation (2) comprises three scalar equations, which can be obtained by the subsequent scalar multiplying of equa-

tion (2) by the unit vectors e_1, e_2 , and n along the co-ordinate line directions. Using the standard Serret–Frenet formulas of differential geometry, as was demonstrated earlier,¹ the three resulting equations are

$$\begin{aligned} P_{13}^\alpha(u_{30}) - P_{13}^\beta(u_{30}) = & -\frac{\sigma_{31}}{R_{10}} - \frac{\partial \sigma_{11}}{\partial l_{10}} - \frac{\partial \sigma_{12}}{\partial l_{20}} - \\ & - [P_{13}(u_3^\alpha) - P_{13}(u_3^\alpha)] \frac{h_1(u_3^\alpha)h_2(u_3^\alpha)}{h_{10}h_{20}} + \\ & + [P_{13}(u_3^\beta) - P_{13}(u_3^\beta)] \frac{h_1(u_3^\beta)h_2(u_3^\beta)}{h_{10}h_{20}}, \end{aligned} \quad (3)$$

$$\begin{aligned} P_{23}^\alpha(u_{30}) - P_{23}^\beta(u_{30}) = & -\frac{\sigma_{32}}{R_{20}} - \frac{\partial \sigma_{21}}{\partial l_{10}} - \frac{\partial \sigma_{22}}{\partial l_{20}} - \\ & - [P_{23}(u_3^\alpha) - P_{23}(u_3^\alpha)] \frac{h_1(u_3^\alpha)h_2(u_3^\alpha)}{h_{10}h_{20}} + \\ & + [P_{23}(u_3^\beta) - P_{23}(u_3^\beta)] \frac{h_1(u_3^\beta)h_2(u_3^\beta)}{h_{10}h_{20}}, \end{aligned} \quad (4)$$

$$\begin{aligned} P_{33}^\alpha(u_{30}) - P_{33}^\beta(u_{30}) = & \frac{\sigma_{11}}{R_{10}} + \frac{\sigma_{22}}{R_{20}} - \frac{\partial \sigma_{31}}{\partial l_{10}} - \frac{\partial \sigma_{32}}{\partial l_{20}} - \\ & - [P_{33}(u_3^\alpha) - P_{33}(u_3^\alpha)] \frac{h_1(u_3^\alpha)h_2(u_3^\alpha)}{h_{10}h_{20}} + \\ & + [P_{33}(u_3^\beta) - P_{33}(u_3^\beta)] \frac{h_1(u_3^\beta)h_2(u_3^\beta)}{h_{10}h_{20}}, \end{aligned} \quad (5)$$

where R_{10} and R_{20} are the principal curvature radii at a given point on the dividing surface; σ_{11}, σ_{21} and σ_{31} are the components of vector $\boldsymbol{\sigma}_1$; and σ_{12}, σ_{22} and σ_{32} are the components of vector $\boldsymbol{\sigma}_2$. According to the curvature sign in a given co-ordinate system, the curvature radii can take both positive (as in Figure 1) and negative values.

Equations (2)–(5) are of practical importance for frequent cases with incompletely developed (truncated) surface layers as

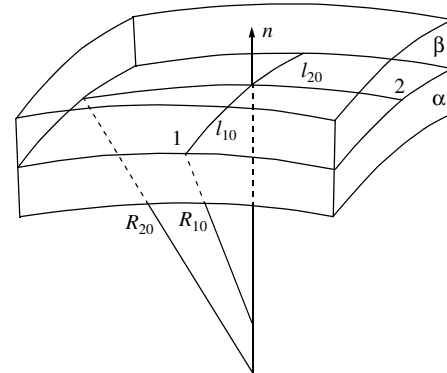


Figure 1 The element of a non-spherical interface.

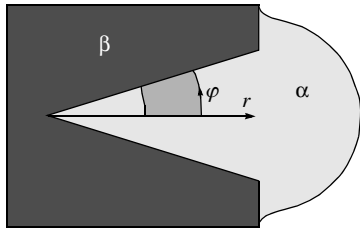


Figure 2 The element of a wedge-shaped thin film.

it happens in thin films, thin capillaries and many other one-, two-, or three-dimensionally small systems with interfaces. Let us consider a thin liquid film as an example and apply equations (3)–(5) to one of the sides of the film. Although a thin film contains no inside bulk phase because of overlapping its surface layers, there always exists a mother phase from which the film originates. Let it be phase α , and phase β be the surrounding medium adjacent to the film side under consideration. If β is a fluid phase, and the surface layer develops freely on the side of phase β , the last term disappears from equations (3)–(5). The same can be in the case of a solid phase β if considering only the liquid part of the interface as an element and the liquid contribution to the element tension. In the absence of external fields, the metrics of pressure and tension tensors is typically coherent with the film space metrics formed under the influence of the shapes of both of the film sides. Since the co-ordinate system chosen diagonalises the metric tensor, we assume the pressure and tension tensors also to be in a diagonal form. With all these simplifications, equations (3)–(5) are reduced to

$$\frac{\partial \sigma_{11}}{\partial l_{10}} = \frac{\partial \sigma_{22}}{\partial l_{20}} = 0, \tag{6}$$

$$P^\alpha - P^\beta = \frac{\sigma_{11}}{R_{10}} + \frac{\sigma_{22}}{R_{20}} - [P_{33}(u_3^\alpha) - P^\alpha] \frac{h_1(u_3^\alpha)h_2(u_3^\alpha)}{h_{10}h_{20}}. \tag{7}$$

For a flat film, the co-ordinate system chosen changes to the Cartesian one, so that the Lamé coefficient ratio becomes unity. In addition, the curvature terms disappear. Designating the pressure tensor component $P_{33}(u_3^\alpha)$ as the normal component P_N , equation (7) is transformed to

$$P^\alpha - P^\beta = P^\alpha - P_N = -\Pi, \tag{8}$$

where Π is the film disjoining pressure. Equation (8) expresses the well-known equilibrium condition that the normal pressure P_N is equal to the external pressure P^β and is independent of spatial co-ordinates.

A film in a wedge-shaped slit with flat walls is the simplest example of a film with a distinct local thickness. The film element between the middle plane and the slit wall can be taken in this case as shown in Figure 2. The cylindrical co-ordinates corresponding to this case are $u_1 = r$, $u_2 = z$ and $u_3 = \varphi$ with the Lamé coefficients $h_1 = 1$, $h_2 = 1$ and $h_3 = r$. Equation (7) then takes the form

$$P^\alpha - P^\beta = P^\alpha - P_{33}(\varphi), \tag{9}$$

from which it is seen that P_{33} again becomes a constant along the normal co-ordinate φ (but, certainly, P_{33} , as well as $P^\alpha - P^\beta$, is dependent on r and on the local wedge width corresponding to the degree of overlapping surface layers). Designating P_{33} again as P_N , we can introduce the local disjoining pressure Π in the film by using definition (8), as for a flat film. We see that introducing the disjoining pressure meets no difficulties in the case of a wedge-shaped film.

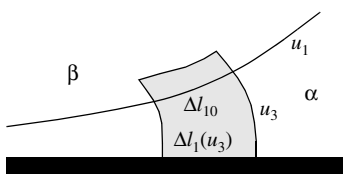


Figure 3 The element of the transitional zone of a wetting film.

The situation is different in another cylindrical configuration when a film itself is of the shape of a circular cylindrical surface. Then, $u_1 = \varphi$, $u_2 = z$, $u_3 = r$, $h_1 = r$, $h_2 = 1$, $h_3 = 1$, and equation (7) changes to the relationship

$$P^\alpha - P^\beta = \frac{\sigma_{11}}{R_{10}} - [P_{33}(r^\alpha) - P^\alpha] \frac{r^\alpha}{R_{10}}. \tag{10}$$

If one chooses r^α at the inner shell of the film ($r^\alpha = R_{10} - H$), equation (10) can be rewritten as

$$P^\alpha - P^\beta = \frac{\gamma_{11}}{R_{10}} - [P_N^i - P^\alpha] \left(1 - \frac{H}{R_{10}}\right), \tag{11}$$

where H is the distance between the dividing surfaces of the film (the film thickness) and $P_N^i \equiv P_{33}(R_{10} - H)$ is the normal component of the pressure tensor on the inner shell.

Similarly, for a spherical film ($u_1 = \theta$, $u_2 = \varphi$, $u_3 = r$, $h_1 = r$, $h_2 = r \sin \theta$ and $h_3 = 1$) we have

$$P^\alpha - P^\beta = \frac{2\sigma}{R_0} - [P_{33}(r^\alpha) - P^\alpha] \frac{r^{\alpha 2}}{R_0^2} \tag{12}$$

or taking r^α at the inner spherical shell

$$P^\alpha - P^\beta = \frac{2\sigma}{R_0} - [P_N^i - P^\alpha] \left(1 - \frac{H}{R_0}\right)^2 = \frac{2\sigma}{R_0} - \Pi \left(1 - \frac{H}{R_0}\right)^2. \tag{13}$$

Formulas (11) and (13) are important when one considers an initial stage of heterogeneous condensation on cylindrical or, correspondingly, spherical solid particles.

One more example is the transitional zone of a wetting film with non-uniform thickness on a flat (rigid) solid surface. Since the co-ordinate u_3^α is chosen arbitrarily, we can refer it to the solid surface and define the surface element under consideration as is shown in Figure 3. In this approach, the tension contribution of the whole film thickness is attributed to the surface tension of the liquid/fluid boundary of the film. Then, $P_{33}(u_3^\alpha)$ acquires the meaning of the normal pressure P_N^s on the solid surface. In accordance with (7), we have

$$P^\alpha - P^\beta = \frac{\sigma_{11}}{R_{10}} + \frac{\sigma_{22}}{R_{20}} - [P_N^s - P^\alpha] \frac{h_1(u_3^\alpha)h_2(u_3^\alpha)}{h_{10}h_{20}}. \tag{14}$$

The metrics of the transitional zone is characterised by the fact that the film/fluid interface is non-uniformly curved whereas the film/solid interface is flat. This means that the u_1 – u_2 co-ordinate surface becomes more and more curved when ascending along the u_3 co-ordinate line from the solid surface. Correspondingly, the capillary gradient of the normal pressure is effectively concentrated in the upper part of the film (Figure 3) and is practically absent in the vicinity of the solid surface. The only reason for the difference between P_N^s and P^α is the overlapping of the opposite film surface layers. We now can define the local disjoining pressure of the transitional zone as

$$\Pi(u_1^\alpha, u_2^\alpha) \equiv P_N^s - P^\alpha, \tag{15}$$

where the disjoining pressure is shown to be location dependent similarly to all other quantities on the right-hand side of equation (14).

Using (15), equation (14) becomes

$$P^\alpha - P^\beta = \frac{\sigma_{11}}{R_{10}} + \frac{\sigma_{22}}{R_{10}} - \Pi \frac{h_1(u_3^\alpha)h_2(u_3^\alpha)}{h_{10}h_{20}}. \tag{16}$$

For the particular case of an optional cylindrical surface ($R_{20} = \infty$, $h_2 = 1$), equation (16) is reduced to

$$P^\alpha - P^\beta = \frac{\sigma_{11}}{R_{10}} - \Pi \frac{h_1(u_3^\alpha)}{h_{10}}. \tag{17}$$

Comparing Figures 1 and 3, it can be seen that the surface curvature in Figure 3 is negative. It is then convenient to rewrite (16) or (17) in the general form

$$P^\beta - P^\alpha = P_c + \Pi L, \tag{18}$$

where P_c is the capillary pressure and L is the Lamé coefficient ratio. With $L = 1$, equation (18) was first introduced by Derjaguin as the condition of constancy of the chemical potential in a film of variable thickness (see ref. 2). The above derivation is

more general since we considered a pure mechanical equilibrium. Equations of a similar form, but with $\cos \varphi$ in place of L (φ is the local slope angle at the film/fluid interface, not to be confused with the above co-ordinate φ) were also suggested previously^{3,4} when dealing with Cartesian co-ordinates. In our derivation, however, such a quantity does not appear. We demonstrated above that $L = 1$ not only for a flat, but also for a wedge-shaped film. If the transitional zone profile differs not very much from the wedge shape, the condition $L \approx 1$ can be a not bad approximation for calculations. More rigorously, the coefficient L can be shown to be dependent exponentially on the integral along the normal coordinate with the local median curvature as an integrand.

Equation (18), with $L = 1$ and Π as the disjoining pressure of a flat film, was used for the calculation of the transitional zone profile under the condition that the profile slope is small.² Equation (18) is valid for an arbitrary profile slope. However, the local disjoining pressure introduced is not equivalent to the disjoining pressure of a corresponding flat film and should be calculated separately with the use of the profile shape. Since the

profile itself is to be found from the known local disjoining pressure, the problem can be solved by the method of successive approximations by using, for example, the wedge-shaped profile as a zero approximation. The solution of such a problem is beyond the scope of this communication.

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References

- [doi>](#) 1 A. I. Rusanov and A. K. Shchekin, *Mendeleev Commun.*, 2000, 128.
- 2 B. V. Derjaguin, N. V. Churaev and V. M. Muller, *Surface Forces, Consultants Bureau*, Plenum, New York, 1987.
- [doi>](#) 3 V. G. Babak, *Colloids Surf.*, 1987, **25**, 1.
- [doi>](#) 4 Yu. Solomentsev and L. R. White, *J. Colloid Interface Sci.*, 1999, **218**, 122.

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