

HYDROSTATICS OF SPHERICAL THIN FILMS

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The hydrostatic approach is applied to spherical films to define the film tension and the surface tensions of the two interfaces and to generalize the definition of the disjoining pressure to the case of systems with curved surfaces. Equations relating the thermodynamic parameters with the components of the pressure tensor are derived.

INTRODUCTION

An important step in the theory of the surface phenomena was taken by Bakker¹ who introduced the hydrostatic approach and derived an equation for the surface tension in terms of the components of the pressure tensor (for details see ^{2,3}). The same equation applies to a plane thin film separating two bulk phases^{4,5} when the film is considered as a membrane of zero thickness and the force acting per unit length along the film is the film tension γ . In contrast to an interface, the film can be considered also as a bulk phase of thickness h . Then two forces, acting per unit length along its surfaces must be introduced - the so called surface tensions of the film^{3,5,6,7}. A hydrostatic definition of the surface tension of the film was given in ref.5. A similar situation exists with curved films^{3,8} - the film can be considered from mechanical viewpoint either as a membrane with tension γ or as a bulk phase with two interfaces with surface tensions σ_1 and σ_2 .

The purpose of the present paper is to derive the hydrostatic equations of the film tension γ and the surface tensions σ_1 and σ_2 of a spherical film. When the film is considered as a membrane the hydrostatic equations for its tension γ are the same as for the surface tension of a spherical drop. However, new results are derived when the film is considered as a bulk phase. Moreover, in this case a hydrostatic definition of the dis-

joining pressure is also obtained in a natural way.

FILM TENSION

Imagine two bulk phases, α and β , separated by a spherical thin film, enveloping the phase α . Since this system is not homogeneous the force field in it is described by the pressure tensor. There can be no shear stresses in an equilibrium fluid system, so that the pressure tensor has only three non-zero components: P_{rr} and $P_{\theta\theta} = P_{\phi\phi}$ where r , θ and ϕ are polar coordinates (r is the distance to the center of the system). The force (per unit area), acting normally to any surface $r=\text{const}$ is P_{rr} and it is called the normal component of the pressure tensor $P_N(r)$; along the same surface acts $P_T(r) \equiv P_{\theta\theta} = P_{\phi\phi}$, which is called the tangential component of the pressure tensor. We will work with the total pressure tensor which encompasses all possible interactions in the system and can be defined in a unique way⁹. Note, however, that its decomposition into parts, accounting for the different kind of interactions (e.g. van der Waals¹, electrostatic etc.), is somewhat arbitrary and this can lead sometimes to difficulties (cf. ref.10). The condition for hydrostatic equilibrium can be expressed by any of the following three equivalent equations^{11,2}:

$$\frac{d(r^2 P_N)}{d(r^2)} = P_T, \quad (1)$$

$$\frac{dP_N}{dr} = \frac{2}{r} (P_T - P_N), \quad (2)$$

$$\frac{d(r^3 P_N)}{dr} = r^2 (P_N + 2P_T). \quad (3)$$

For convenience let us consider a portion of the system, enclosed between two spheres of radii r_α and r_β . The total force acting on the surface hatched in Fig.1a in a direction perpendicular to it will be

$$f \, d\theta = d\theta \int_{r_\alpha}^{r_\beta} P_T r \, dr. \quad (4)$$

The respective moment is defined by

$$M \, d\theta = d\theta \int_{r_\alpha}^{r_\beta} P_T r^2 \, dr. \quad (5)$$

Following Gibbs¹² we define an idealized system, by introducing two phases, α and β , homogeneous up to the dividing spherical surface of

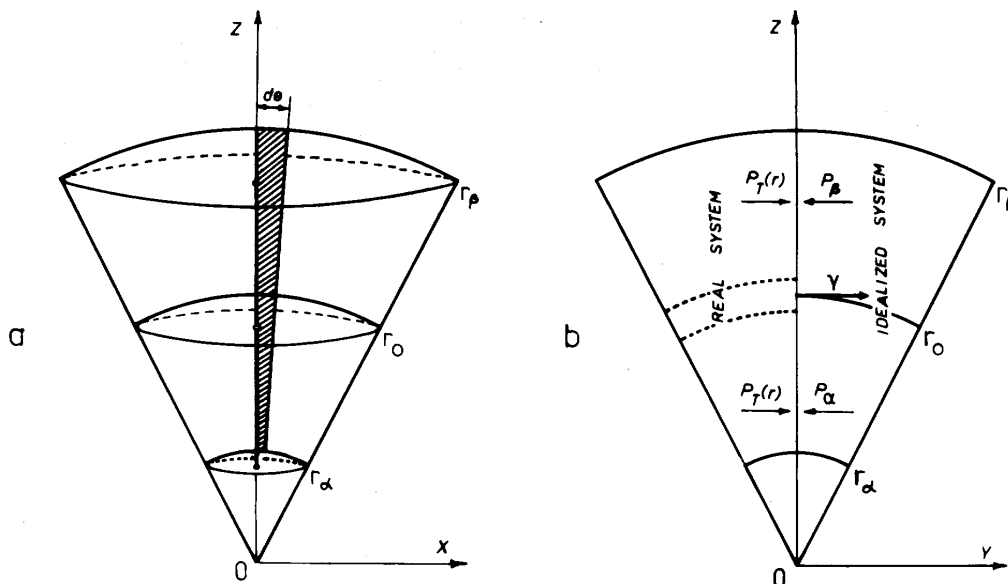


Figure 1. On the derivation of the conditions for mechanical equilibrium of a spherical film (see the text).

radius r_0 . We apply per unit length at r_0 a force γ (see Fig.1b) and require that the real and the idealized systems be mechanically equivalent (in terms of force and moment). If the pressures in the homogeneous phases are P_α and P_β respectively, from the conditions for mechanical equivalence of the two systems and Equations (4) and (5) it follows

$$\gamma = \frac{1}{r_0} \int_{r_\alpha}^{r_\beta} (P_{\alpha\beta} - P_T) r \, dr, \quad (6)$$

$$\gamma = \frac{1}{r_0^2} \int_{r_\alpha}^{r_\beta} (P_{\alpha\beta} - P_T) r^2 \, dr, \quad (7)$$

where

$$P_{\alpha\beta} = P_\alpha \theta(r_0 - r) + P_\beta \theta(r - r_0) \quad (8)$$

and

$$\theta(x) = \begin{cases} 1 & \text{for } x > 0, \\ 0 & \text{for } x < 0. \end{cases} \quad (9)$$

Equations (6) and (7) define the film tension γ and the radius of the dividing surface r_0 in terms of P_T , P_α and P_β . The dividing surface defined in this way is called "the surface of tension" ^{2,3}. Let us assume that the pressures P_α and P_β coincide with the values of P_N at $r = r_\alpha$ and $r = r_\beta$ respectively, i.e.

$$P_\alpha \equiv P_N(r_\alpha) \quad \text{and} \quad P_\beta \equiv P_N(r_\beta). \quad (10)$$

Then on integrating Equation (1) we obtain

$$\frac{1}{2}(P_{\beta}r_{\beta}^2 - P_{\alpha}r_{\alpha}^2) = \int_{r_{\alpha}}^{r_{\beta}} P_T r dr . \quad (11)$$

On performing the integration in Equation (6) and substituting the expression for the integral of P_T from (11) one easily obtains

$$P_{\alpha} - P_{\beta} = \frac{2\gamma}{r_0} , \quad (12)$$

which is the familiar Laplace's equation.

This result calls for some comments. It is well known that Laplace's equation holds only for the surface of tension. Therefore, γ in Equation (12) will have the meaning of surface tension only when r_0 is defined as in Equation (7), although we did not use the latter equation when deriving Equation (12) - cf. ref.2. When carrying out similar derivations for a spherical drop² one usually assumes that r_{α} and r_{β} lie in regions where there are homogeneous fluids, so that P_{α} and P_{β} are the respective isotropic pressures. This assumption substantially simplifies the thermodynamic treatment. However, as far as the mechanical equilibrium is concerned, this assumption is not necessary. Indeed, in our derivation r_{α} and r_{β} are arbitrary and P_{α} and P_{β} were defined by Equations (10): for example r_{α} can be zero and then P_{α} will be the pressure in the center of the inner phase α . This fact can be of importance in the treatment of very small drops, when the phase encircled by the film never becomes homogeneous. It is pertinent to derive expressions for γ only in terms of integrals of $(P_N - P_T)$. The integration of (2), along with (12) yields

$$\gamma = \int_{r_{\alpha}}^{r_{\beta}} (P_N - P_T) \frac{r_0}{r} dr . \quad (13)$$

An alternative expression is obtained by integrating Equation (3) and making use of Equations (7) and (12):

$$\gamma = \int_{r_{\alpha}}^{r_{\beta}} (P_N - P_T) \frac{r^2}{r_0} dr . \quad (14)$$

The analogs of these equations for the surface tension of a spherical drop were first derived by Goodrich¹³ and Buff¹⁴, respectively. Equations (13) and (14) lead to an explicit equation for r_0 :

$$r_0^3 = \frac{\int_{r_{\alpha}}^{r_{\beta}} (P_N - P_T) r^2 dr}{\int_{r_{\alpha}}^{r_{\beta}} (P_N - P_T) \frac{dr}{r}} . \quad (15)$$

SURFACE TENSIONS AND DISJOINING PRESSURE OF THE FILM

As already mentioned in the Introduction, the film, as opposite to the transition region between two phases, is a bulk (although non-homogeneous) phase. On the other hand, in the previous section the film was treated as a membrane of tension γ , radius r_0 and zero thickness, i.e. in the same way as the transition region between two bulk phases. This, of course, is permissible. Nevertheless, it is convenient to develop also a hydrostatic approach in which the finite thickness of the film is explicitly accounted for.

To do that, let us introduce an idealized system consisting of the bulk phase α with pressure P_α (lying within $r_\alpha < r < r_1$), bulk phase β with pressure P_β ($r_2 < r < r_\beta$) and a reference phase R (for details see below) with pressure P_R (note that $r_1 < r_0 < r_2$). The film is, therefore, represented as a spherical layer of thickness $h = r_2 - r_1$. We call the spheres of radii r_1 and r_2 "film surfaces" and by analogy with Equations (6) and (7) we define the respective surface tensions of the film σ_1 and σ_2 as:

$$\sigma_1 r_1 = \int_{r_\alpha}^{r_0} (P_{\alpha R} - P_T(r)) r dr, \quad (16)$$

$$\sigma_1 r_1^2 = \int_{r_\alpha}^{r_0} (P_{\alpha R} - P_T(r)) r^2 dr, \quad (17)$$

with

$$P_{\alpha R} = P_\alpha \theta(r_1 - r) + P_R \theta(r - r_1) \quad (18)$$

and

$$\sigma_2 r_2 = \int_{r_0}^{r_\beta} (P_{R\beta} - P_T(r)) r dr, \quad (19)$$

$$\sigma_2 r_2^2 = \int_{r_0}^{r_\beta} (P_{R\beta} - P_T(r)) r^2 dr, \quad (20)$$

with

$$P_{R\beta} = P_R \theta(r_2 - r) + P_\beta \theta(r - r_2). \quad (21)$$

To obtain an analog of Equation (12) (the normal force balance) we integrate Equations (1) and (18) (the latter multiplied by r) from r_α to r_0 and eliminate $P_\alpha r_\alpha^2$ from the result. Then keeping in mind Equation (16) we obtain

$$\frac{2\sigma_1}{r_1} = P_\alpha - P_R - \{P_N(r_0) - P_R\} \frac{r_0^2}{r_1^2}. \quad (22)$$

A similar result holds for the other surface. By analogy with the tensorial definition of the disjoining pressure Π in flat films^{5,15,16,17} let us call disjoining pressure of the spherical film the pressure difference

$$\Pi = P_N(r_0) - P_R . \quad (23)$$

Since the pressure tensor is connected with the intermolecular forces, the disjoining pressure so defined accounts for the alteration of the field of these forces in the film with respect to the reference phase.

Then

$$\frac{2\sigma_1}{r_1} = P_\alpha - P_R - \Pi \frac{r_0^2}{r_1^2} , \quad \frac{2\sigma_2}{r_2} = P_R - P_\beta + \Pi \frac{r_0^2}{r_2^2} . \quad (24)$$

In the limit $r_0 \rightarrow \infty$, one obtains from these equations

$$\Pi = P_\alpha - P_R = P_\beta - P_R , \quad (25)$$

which is a generalized form of the thermodynamic definition of the disjoining pressure for flat films.

The hydrostatical definitions of σ_i and r_i ($i = 1,2$) are the same as those of γ and r_0 , namely Equations (16), (17), (19) and (20) define the film surfaces by the conditions for full mechanical equivalence of the real and idealized systems. Therefore, following Gibbs¹², we again call the film surfaces defined by Equations (16), (17), (19) and (20) "surfaces of tension". For a liquid drop the "surface of tension" always coincides with the "surface of minimum surface tension" and this is the surface for which Laplace's equation holds^{2,12}. Equation (12) reveals that the same is true for a film as long as it is considered as a membrane of tension γ . The situation can be different when the film is represented as a phase of finite thickness h : beside the capillary pressure terms, Equations (24) contain disjoining pressure terms. The latter could be also eliminated by choosing in Equation (23) $P_R \equiv P_N(r_0)$. Then Equations (22) and (24) acquire the same form as the respective equations of Rusanov³, valid for the surface of minimum surface tension. However, as our derivation shows, for a film of finite thickness the surfaces of tension (as defined by Equations (16) - (21)) and the surfaces of minimum surface tensions (for which $2\sigma_i/r_i = P_{ci}$, $i=1,2$) do not necessarily coincide.

The choice of the pressure of the reference phase P_R can be arbitrary. That is why we kept it in our treatment as an undefined parameter. From the theoretical viewpoint it is convenient to choose as reference phase the bulk phase that would exist between the phases α and β in the limiting case $h \rightarrow \infty$ (thick film). It will be shown below that such an approach allows easy transition from curved to flat films.

By means of Equations (2) and (3) one can derive the following expressions analogous to Equations (13) and (14):

$$\frac{\sigma_1}{r_1} = \int_{r_\alpha}^{r_0} (P_N - P_T) \frac{dr}{r} - \frac{1}{2} \Pi (r_0^2/r_1^2 - 1) , \quad (26)$$

$$\frac{\sigma_2}{r_2} = \int_{r_0}^{r_\beta} (P_N - P_T) \frac{dr}{r} - \frac{1}{2} \Pi (1 - r_0^2/r_2^2) ; \quad (27)$$

$$\sigma_1 r_1^2 + \Pi h_1 r_0^2 = \int_{r_\alpha}^{r_0} (P_N - P_T) r^2 dr , \quad (28)$$

$$\sigma_2 r_2^2 + \Pi h_2 r_0^2 = \int_{r_0}^{r_\beta} (P_N - P_T) r^2 dr . \quad (29)$$

By summing up Equations (26) and (27) and keeping also in mind Equation (13), we obtain

$$\frac{\gamma}{r_0} = \frac{\sigma_1}{r_1} + \frac{\sigma_2}{r_2} + \frac{(r_1 + r_2)r_0^2}{2r_1^2 r_2^2} \Pi h , \quad (30)$$

where $h_1 = r_0 - r_1$, $h_2 = r_2 - r_0$ and $h = h_1 + h_2$. The limiting case of a flat film^{5,7} can be obtained by letting $r_0 \rightarrow \infty$ (but keeping h_1 and h_2 finite):

$$\gamma = \sigma_1 + \sigma_2 + \Pi h . \quad (31)$$

Another important relationship is obtained by summing up Equations (28) and (29) and taking into account Equation (14):

$$\gamma A_0 = \sigma_1 A_1 + \sigma_2 A_2 + \Pi h A_0 , \quad (32)$$

where A_0 , A_1 and A_2 are the areas of the surfaces of radii r_0 , r_1 and r_2 , respectively. In the limit $r_0 \rightarrow \infty$ Equation (32) also leads to Equation (31).

As already pointed out the definition of Π (Equation (23)) is a matter of convention. Since in a curved film P_N is not a constant (according to Equation (2) P_N is a function of r) one can define a local disjoining pressure $\Pi(r)$ for any surface of radius r . By making the normal force balance (along r) of a volume element confined between a conical surface and two spheres of radii r_0 and r , one can easily show that

$$\Pi(r) = \Pi(r_0) (r_0^2/r^2) . \quad (33)$$

Then Equations (24) yield

$$\frac{2\sigma_1}{r_1} = P_\alpha - P_R - \Pi(r_1) , \quad \frac{2\sigma_2}{r_2} = P_R - P_\beta + \Pi(r_2) . \quad (34)$$

These equations describe the normal force balances at the film surfaces. They show that in the pressure drops $P_\alpha - P_R$ and $P_R - P_\beta$ the interaction between the film surfaces is accounted for by two terms: the curvature term $2\sigma_i/r_i$, $i=1,2$ (in which the surface tensions σ_1 and σ_2 , due to the inter-

action, will be different from the surface tensions of drops of the same radii) and the disjoining pressure terms $\Pi(r_1)$ and $\Pi(r_2)$. In the limit $r_1, r_2 \rightarrow \infty$, both Equations (34) lead again to the known definition of Π in a flat film - see Equation (25).

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