I. TRANSITION REGIONS, LINE TENSIONS AND CONTACT ANGLES IN SOAP FILMS*

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INTRODUCTION

Thin liquid films, especially soap films, are considered useful model systems for the study of long range interaction forces¹⁻³. In a plane-parallel equilibrium film a disjoining pressure $\Pi(h)$, which is a result of these forces, must balance with the excess hydrostatic pressure P in the film^{3,4}:

$$\Pi(h_e) + P = 0 \quad (1)$$

where h_e is the equilibrium thickness of the film. Usually $\Pi(h)$ is assumed to consist of two components^{3,4}:

$$\Pi(h) = \Pi_{el}(h) + \Pi_w(h) \quad (2)$$

where $\Pi_{el}(h)$ is a repulsive force due to overlap of electrical double layers in the film and $\Pi_w(h)$ is a van der Waals attractive force, both per unit of surface area.

A well-known technique for studying these forces is to measure the variation of h_e on changing the concentration of electrolyte in the bulk solution from which the film is drawn^{4,5}. The usual procedure is to assume that Π_{el} as a function of the electrolyte concentration and film thickness is known from theory, an assumption which is necessary as both Π_{el} and Π_w vary simultaneously. $\Pi_w(h)$ is then calculated with the help of eqns. (1) and (2) and compared with theory. An implicit assumption is that Π_w depends only on h and not on the composition of the bulk solution. The agreement between theory and experiment is usually rather poor, especially at high electrolyte concentrations^{4,6}. However, these experiments alone do not justify a rejection of the theories on these forces at high concentrations. Other parameters besides h_e are needed to draw more definite conclusions. Such an extra parameter is the contact angle between film and bulk liquid. It gives the interaction free energy due to the long range interaction forces at equilibrium film thickness h_e ^{7,8}:

$$\Delta F(h_e) = 2\sigma_0(\cos \theta - 1) \quad (3)$$

where σ_0 is the surface tension of the bulk solution and θ the contact angle. Nevertheless, the limitation of the procedure remains that a change in h_e and θ can only be achieved by changing the composition of the bulk solution. For the interpretation of

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experimental results we still have to assume that $\Pi_w(h)$ does not vary with composition.

In this paper an analysis is given of the thickness profile of a soap film in contact and equilibrium with its Plateau border. It will show the possibilities there are of deriving the entire interaction free energy curve, $\Delta F(h)$, from a single soap film.

DEFINITION OF THE SYSTEM

Consider a horizontal liquid sheet in contact and equilibrium with the bulk liquid at a level z below the sheet (Fig. 1). It is assumed that everywhere in the sheet $h \ll z$, i.e. the hydrostatic pressure P in the sheet is constant. At equilibrium the following pressure balance at the liquid surface must hold in the whole sheet:

$$P + \Pi(h) + P_c = 0 \quad (4)$$

where P_c is capillary pressure as given by Laplace's law and hydrostatic pressure $P = -dgz$; d = difference in density between liquid and vapour phase and g = acceleration of gravity.

The liquid sheet is now subdivided into three regions:

(a) A plane parallel, very thin central part, i.e. the film, where P_c can be neglected with respect to $\Pi(h)$ and P .

(b) A thick part at the periphery, the Plateau border, where $\Pi(h)$ can be neglected.

(c) A region connecting both parts, the transition region, where none of the terms of eqn. (4) can be neglected.

Fig. 1. Circular liquid sheet with radius R in contact with bulk soln. Vertical distance between liquid sheet and surface of bulk soln. is z .

Fig. 2. Part of liquid sheet with $R = \infty$ between x and $x + dx$.

The circular cuvette that holds the sheet is totally wetted by the liquid; its inner radius is R (Fig. 1).

Although the shape of the liquid sheet can be derived from the pressure balance eqn. (4), we will follow an alternative procedure which can be called the "film tension approach". Here the starting point is the equilibrium condition according to which the forces that act on a certain part of the liquid sheet must cancel. This has the advantage that it makes the mathematics simpler and the physical meaning of the equations clearer.

LARGE FILMS

We will first discuss the situation where the radius R of the film cuvette is infinitely large. In this case the liquid surface has only one radius of curvature. Consider the part of the liquid sheet between x and $x + dx$ (Fig. 2), where x is the distance from the cuvette wall. The X-components of the forces that act on a length unit of the sheet element cancel at equilibrium:

$$[2\sigma(h) \cos \Phi(x) - hP] - [2\sigma(h + dh) \cos \Phi(x + dx) - (h + dh)P] = 0 \quad (5)$$

$\sigma(h)$ is the thickness dependent surface tension of the sheet and $\Phi(x)$ is the slope angle of the liquid surface with the horizontal at x . Integration of eqn. (5) using the boundary condition $h = h_c$ and $\cos \Phi(x) = 1$ when $x = \infty$, gives:

$$2\sigma(h) \cos \Phi(x) - hP = \text{const.} = 2\sigma(h_c) - h_c P \quad (6)$$

According to (6) the net force that acts perpendicularly on a vertical plane through the sheet at x is independent of x . This net force per length unit is the film tension $\gamma(h)$. Therefore⁸:

$$\gamma(h) = 2\sigma(h) \cos \Phi(x) - hP = \gamma(h_c) = 2\sigma(h_c) - h_c P \quad (7)$$

From eqn. (6) the profile $h(x)$ of the sheet can be calculated when the thickness dependence of $\sigma(h)$ is known. For a plane parallel film it is given by⁷⁻⁸:

$$2\sigma(h) = 2\sigma_0 + \Delta F(h) \quad (8)$$

where σ_0 is the surface tension of the bulk solution and $\Delta F(h)$ the interaction free energy which is related to the disjoining pressure $\Pi(h)$ by^{4,7}:

$$\Delta F(h) = - \int_{\infty}^h \Pi(h) dh \quad \text{or} \quad \Pi(h) = - \frac{\delta \Delta F(h)}{\delta h} \quad (9)$$

Both $\Delta F(h)$ and $\Pi(h)$ approach zero for large h .

When the surfaces are no longer plane parallel the surface tension is expected to be a function of both h and Φ . Although it is not entirely consistent we shall neglect terms dependent on Φ . As in our derivations Φ will always be small when $\Delta F(h) \neq 0$, the approximation will not significantly affect the results.

Combination of (6) and (8) leads to:

$$\cos \Phi(h) = \frac{2\sigma_0 + \Delta F(h_c) + (h - h_c)P}{2\sigma_0 + \Delta F(h)} \quad (10)$$

When $\Delta F(h)$ is known, the profile $h(x)$ of the whole sheet can be calculated by a numerical integration, remembering that $-\frac{1}{2} \cot \Phi = dx/dh$. On the other hand, $\Delta F(h)$ might be obtained from the *measured* profile $h(x)$. It is obvious that the transition region is the part of the sheet that contains most information on $\Delta F(h)$.

Before we consider to what extent such a measurement is feasible, we will investigate the relation between eqn. (10) and the macroscopic description of the transition between film and border which presupposes a "contact angle" (see eqn. (3)).

CONTACT ANGLE IN LARGE FILMS

From eqn. (10) it follows that Φ changes continuously with x at the transition

between film and border. In the derivation of eqn. (3) however, it is assumed that film and border meet each other at a sharp and unique angle θ without a transition region. It will be clear from the outset that such a rough description is only of practical value if Φ changes sufficiently abruptly in the transition region.

Equation (3) is obtained from eqn. (10) when in the actual sheet the Plateau border and the film with thickness h_e are extrapolated until they meet at a line of contact. Extrapolation of the Plateau border means that we neglect $\Delta F(h)$. If we denote this profile by $h'(x)$, eqn. (10) gives:

$$\cos \Phi'(h') = [2\sigma(h_e) + (h' - h_e)P]/2\sigma_0 \quad (11)$$

Extrapolation to $h' = h_e$ gives:

$$\cos \Phi'(h_e) = 2\sigma(h_e)/2\sigma_0 = [2\sigma_0 + \Delta F(h_e)]/2\sigma_0 \quad (12)$$

When we compare this with eqn. (3) we see that contact angle θ is the angle $\Phi'(h_e)$ between the extrapolated Plateau border and film at the contact line. This is in accordance with the definition of θ as proposed by Sheludko *et al.*⁹

The actual sheet can be replaced by a simplified model, the profile of which is exactly equal to the profile of the extrapolated Plateau border and film in the actual sheet. Then contact angle θ is the angle between the Plateau border and film at their line of contact. Equation (3) follows directly from the force balance at the line of contact in the simplified model (see Fig. 3):

$$2\sigma_0 \cos \theta - Ph_e = 2\sigma(h_e) - Ph_e = 2\sigma_0 + \Delta F(h_e) - Ph_e \quad (13)$$

In order to find out if it is feasible to measure $h(x)$ in the transition region and in what cases the transition region will influence the experimental determination of θ , we will calculate the profile $h(x)$ with a simple model in the next paragraph.

Fig. 3. Force balance at contact line between Plateau border and film in simplified model of liquid sheet.

Fig. 4. Interaction free energy curve $\Delta F(h)$, (—), composed of repulsive double layer interaction component F_{el} (----) and attractive London-van der Waals component F_w (— · — · —). Note the steep repulsion at $h = 40 \text{ \AA}$.

CALCULATIONS OF TRANSITION REGIONS

For the $\Delta F(h)$ -function, to be used in our further calculations, we have chosen the function thought to be valid in soap films. It consists of two terms: the potential energy of London dispersion forces F_w and the potential energy of double layer interaction F_{el} ; $\Delta F(h)$ being the sum of both terms^{1,3,4,7}.

For F_w we use the relation^{1,3,4,10}:

$$F_w = -A/12\pi h^2 \quad (14)$$

where A = Hamaker's constant.

A good approximation for F_{el} with a solution of a 1:1 electrolyte in water at 23°C is^{7,10}:

$$F_{el} = 48.4 \times 10^{-3} c^{\frac{1}{2}} \beta e^{-\kappa h} \text{ Jm}^{-2} \quad (15)$$

when $\kappa h > 2$. The reciprocal of the Debye length κ is given by^{7,10}.

$$\kappa = 3.28 \times 10^9 c^{\frac{1}{2}} \text{ m}^{-1} \quad (16)$$

where c is the concentration of the 1:1 electrolyte in mol l^{-1} , β a function of the diffuse double layer potential ψ_d and β is assumed to be 1, i.e. ψ_d is large. Furthermore we assume a very steep repulsion at $h < 40\text{\AA}$ (Fig. 4).

In our calculations we use different values of Hamaker's constant A , electrolyte concentration c and hydrostatic pressure P in order to show how these parameters affect the profile. The surface tension σ_0 of the bulk solution was assumed to be 30 mN m^{-1} . The sheets for which the calculations were made are summarized in Table 1.

The film thickness h_c and $\Delta F(h_c)$ were found from eqns. (1), (2) and (9). The value of contact angle θ was calculated with eqn. (3). The profile of the transition region

TABLE 1

CALCULATED VALUES OF FILM THICKNESS h_c , CONTACT ANGLE θ , EXTENSION Δ OF THE TRANSITION REGION AND LINE TENSION τ FOR LIQUID SHEETS WITH DIFFERENT VALUES OF HAMAKER'S CONSTANT A , ELECTROLYTE CONCENTRATION c AND HYDROSTATIC PRESSURE P

Surface tension $\sigma_0 = 30 \text{ m Nm}^{-1}$

	$A \times 10^{19}/\text{J}$	$c/\text{mol l}^{-1}$	P/Nm^{-2}	$h_c/\text{\AA}$	θ/min	$\Delta/\mu\text{m}$	$-\tau \times 10^{12}/\text{Jm}^{-1}$
1a	1	0.001	- 25	810	5	18.5	2.1
1b	1	0.002	- 25	600	13	14.4	3.1
1c	1	0.01	- 25	260	34	7.6	4.8
1d	1	0.05	- 25	100	87	2.0	5.6
1e	1	∞	- 25	40	248	< 1	5.2
2a	0.2	0.01	- 25	310	12	11.5	1.5
2b	1	0.01	- 25	260	34	7.6	4.8
2c	4	0.01	- 25	190	89	3.8	11.3
3a	1	0.01	- 25	260	34	7.6	4.8
3b	1	0.01	- 50	255	34	6.0	4.6
3c	1	0.01	- 100	250	34	4.7	4.2

could then be calculated with eqn. (10) by a simple numerical integration of $\frac{1}{2} \cot \Phi(h)$. A typical example of the profile $h(x)$ of a transition region is given in Fig. 5A for a sheet with $h_c = 260 \text{ \AA}$ and $\theta = 34'$ (case 1c of Table 1). It shows the profile of the actual sheet (drawn line) and the profile $h'(x)$ of the idealized model (broken line). The angle at which the profile of the Plateau border and film of the idealized model meet at the line of contact is 2θ .

Figure 5B gives $\tan \Phi(x)$ and $\tan \Phi'(x)$ for the same sheet. In the idealized model the value of $\tan \Phi'$ jumps from zero to $\tan \theta$ at the contact line. Figure 5 shows that the transition region, where $h(x)$ and $h'(x)$, or $\tan \Phi(x)$ and $\tan \Phi'(x)$, differ appreciably, extends over a distance of several micrometers. The exact value of the extension Δ of the transition region depends on the definition of its beginning and end. When we compare Fig. 5A with 5B we see that the transition region appears to be more extended in 5B than in 5A. This means that the slope $\tan \Phi(x)$ is more sensitive to $\Delta F(h)$ than the profile $h(x)$.

For the definition of the extension Δ of the transition region we used the functions $\tan \Phi(x)$ and $\tan \Phi'(x)$ (Fig. 5B). It was assumed that the transition region meets the Plateau border at some point $x=a$ where $\tan \Phi'(a) - \tan \Phi(a) = 1\%$ of

Fig. 5. (A) Profile $h(x)$, in transition region of liquid sheet with $h_c = 260 \text{ \AA}$ and $\theta = 34'$ (sheet 1c of Table 1). Broken line represents extrapolated Plateau border and film. (B) slope $\tan \Phi(x) = -\frac{1}{2}(dh/dx)$ in transition region of same sheet as in (A)

$\tan \Phi(a)$. The value of $\tan \Phi(a)$ was then used to define the point $x=b$ where the transition region meets the film; we assumed that $x=b$ when $\tan \Phi(b)=1\%$ of $\tan \Phi(a)$.

As the general form of $h(x)$ and $\tan \Phi(x)$ is the same for all sheets considered, we will not show more detailed profiles, but give only the values of h_c , θ and Δ (see Table 1).

The influence of the form of the $\Delta F(h)$ -curve on Δ is largely determined by the sharpness of the minimum in the curve. We can state that a sharper minimum tends to give a smaller Δ . This can be seen from the series of sheets 1a-1e and 2a-2c in Table 1. In series 1a-1e the electrolyte concentration c is increased from 0.001 mol l^{-1} to ∞ . This makes the ascending branch of the $\Delta F(h)$ -curve steeper and the minimum sharper. The value of Δ diminishes from about $20 \mu\text{m}$ to less than $1 \mu\text{m}$. In series 2 the descending branch of $\Delta F(h)$ is made steeper by increasing the value of Hamaker's constant A from $2 \times 10^{-20} \text{ J}$ to $4 \times 10^{-19} \text{ J}$. Here the value of Δ decreases from 11.5 to $3.8 \mu\text{m}$. These series also show that a change in the repulsive component $F_{el}(h)$ has a stronger influence on Δ than a change in the attractive component $F_w(h)$. This is because the second derivative of $\Delta F(h)$ at the minimum, which is a measure of its sharpness, is almost entirely determined by $F_{el}(h)$. This can be seen by comparing sheets 1b-1d with sheets 2a-2c. In the two series the change of contact angle θ , and therefore of the depth of the minimum $\Delta F(h_c)$, is almost the same, but the variation of Δ is appreciably greater in the first series. Hydrostatic pressure P influences the profile through the $(h-h_c)P$ -term in eqns. (10) and (11). Series 3 of Table 1 shows that Δ becomes smaller when the absolute value of P increases*.

To what extent the value of contact angle θ , found from experiment, is affected by the transition region depends on the principles of the method. When θ is found by extrapolation of a measured profile the value of θ will be correct (see preceding paragraph). Sheludko's topographical method^{9,11} is based on this principle. The accuracy of the method will, however, be poor at small θ 's as the distance over which the extrapolation must be performed may be quite large.

When the method is based on the assumption that a sharp angle exists at the transition between Plateau border and film, as for instance in Mysels' bubble method^{7,12} and Princen's diffraction method^{13,14}, the transition region will introduce a systematic error. This will in general lead to values of θ which are too small. However, not all methods are equally sensitive to the rounding off of the "angle". The smallest contact angle which can be measured by a particular method will therefore depend on the principles of the method.

We would prefer to measure the detailed profile of the transition region instead of contact angle θ , as this would yield the $\Delta F(h)$ -curve for $h \geq h_c$. An optical method is probably most suitable because of the fragility of the sheet. This means, however, that when $\Delta < \text{wavelength of the light}$ we cannot expect to find the details of the profile. It will be possible only for sheets with small θ where Δ is large.

We have already seen that $\tan \Phi(x)$ is more sensitive to $\Delta F(h)$ than $h(x)$. The best results can therefore be expected from a technique which gives the slope $\tan \Phi$ directly as a function of x . A Schlieren method might for instance be suitable¹⁵.

* An estimate of the extension Δ of the transition region was made by Prins¹⁶. He notes that Δ will be about $1 \mu\text{m}$, but gives no further details.

It might be possible to derive the profile of the transition region from the detailed structure of the diffraction fringes as found in Princen's diffraction method¹⁴. An analysis of this method should answer the question as to what extent the transition region affects the fringes and how we may reconstruct its profile from the details of the fringes.

In the following paragraphs we shall show that for a complete macroscopic description of the liquid sheet a line tension τ must be attributed to the contact line in the simplified model of the sheet. When the contact line is curved this line tension will affect the force balance eqn. (13) at the contact line. In this case it will be given by:

$$2\sigma_0 \cos \theta - Ph_c = 2\sigma_0 + \Delta F(h_c) + \tau/r_c - Ph_c \quad (18)$$

where r_c is the radius of curvature of the contact line. This force balance will be derived and an expression for τ will be given which will make it possible to calculate the value of τ .

LINE TENSIONS

Mention is made of a line tension by several authors. However, the term does not always cover the same concept. Harkins¹⁷ states that the interactions between the molecules close to a three phase contact line can give rise to an excess free energy term. The excess free energy per unit length of the contact line is the line free energy. Line free energy and line tension are related in the same way as surface free energy and surface tension. For a liquid lens of ether with a very sharp edge he gives an estimated value of the line tension of $+2 \times 10^{-11} \text{ J m}^{-1}$ ($= 2 \times 10^{-6} \text{ erg cm}^{-1}$).

A general expression for the line tension of a three phase contact line in terms of hydrostatic force parameters is given by Buff and Saltsburg¹⁸. However, as they lacked a model of the microscopic distribution of matter close to the contact line they could not calculate it. They considered that the estimated value as given by Harkins was correct.

A different conception of a line tension was introduced by Langmuir¹⁹. He related the force balance at the edge of a liquid lens, floating on another liquid, to the spreading coefficient. As he used a cylindrical model of the lens the force balance had to be supplemented by, what he called, a line tension term; this in order to correct for the fact that the *macroscopic* shape of the actual lens differed from that of the cylindrical model.

His value of $6.54 \times 10^{-5} \text{ J m}^{-1}$ for the line tension of a lens of paraffin oil on water cannot therefore be compared with the value as given by Harkins. In our opinion it may be better not to use the word line tension for Langmuir's macroscopic corrective factor.

The occurrence of a line tension is not restricted to a three phase contact line. Mysels *et al.*²⁰ for instance, say that a positive line tension at the boundary of a so-called "black spot" in a thicker coloured soap film can account for the fact that these "black spots" tend to reduce their perimeter. Although the value of a line tension is presumably small in general, this does not mean that its influence will always be small. It might for instance affect markedly the properties of finely dispersed systems¹⁷. In a recent paper Torza and Mason²¹ showed that a line tension will influence the

interaction between two different drops in a third medium. Boys²² remarks that a line tension can have a great influence on critical phenomena in soap films. However, definite conclusions can be drawn only when reliable quantitative values of line tensions are available.

In the next paragraph we will derive eqn. (18) using the microscopic theory for the profile of the whole liquid sheet used before. This derivation will make it possible to comprehend the nature of τ in microscopic terms and to assess its magnitude.

CURVED CONTACT LINE: MICROSCOPIC THEORY OF LINE TENSION

Consider segment ABCD-EFGH of a circular liquid sheet between r and $r+dr$ and bounded by two vertical intersecting planes AEHD and BFGC which meet in the centre of the sheet at a small angle $d\alpha$ (Fig. 6): r is the distance from the centre of the film. At equilibrium the horizontal radial components of the forces that act on this segment must cancel. Taking into account the surface tension contributions of the lines AB, CD, EF, GH and AE, BF, CG, DH and the contributions of hydrostatic pressure on the planes ABCD, EFGH, AEHD and BFGC, we find:

$$(r+dr) 2\sigma(h+dh) \cos \Phi(r+dr) d\alpha - r 2\sigma(h) \cos \Phi(r) d\alpha \\ - 2\sigma(h) [dr/\cos \Phi(r)] d\alpha - (r+dr)(h+dh)P d\alpha \\ + rPh d\alpha + (h+\frac{1}{2}dh)P dr d\alpha = 0$$

This can be written in the more concise form:

$$\frac{d}{dr} [2\sigma(h)r \cos \Phi - Phr] - \left[\frac{2\sigma(h)}{\cos \Phi} - Ph \right] = 0 \quad (19)$$

Integration of (19) from $r=0$ to r leads to:

$$[2\sigma(h)r \cos \Phi - Phr] - \int_0^r \left[\frac{2\sigma(h)}{\cos \Phi} - Ph \right] dr = 0 \quad (20)$$

Fig. 6 Segment of horizontal circular liquid sheet between r and $r+dr$. Two vertical radial intersecting planes meet in the centre of the liquid sheet at a small angle $d\alpha$.

Equation (20) forms the mathematical basis for the calculation of the profile of a circular sheet. It can be compared with eqn. (10) which is valid when the cuvette radius $R = \infty$. Equation (20) shows that the value of slope angle Φ for a certain h can be found only when the detailed profile between the centre of the sheet and the point r with thickness h is known. This means that in a circular sheet the profile has to be "built up" from the centre of the sheet, using the proper boundary conditions. As we want to derive the force balance at the contact line between the extrapolated Plateau border and the film so as to compare it with eqn. (18), we rewrite eqn. (20) as:

$$[2\sigma(h)r \cos \Phi - Phr] + \int_r^R \left[\frac{2\sigma(h)}{\cos \Phi} - Ph \right] dr - \int_0^R \left[\frac{2\sigma(h)}{\cos \Phi} - Ph \right] dr = 0 \quad (21)$$

The third term in this equation is independent of r .

For the Plateau border profile $h'(r)$, where $\sigma(h) = \sigma_0$, eqn. (21) gives:

$$[2\sigma_0 r \cos \Phi' - Ph'r] + \int_r^R \left[\frac{2\sigma_0}{\cos \Phi'} - Ph' \right] dr - \int_0^R \left[\frac{2\sigma(h)}{\cos \Phi} - Ph \right] dr = 0 \quad (22)$$

Notice that the third terms in eqns. (21) and (22) are equal! When the profile of the Plateau border is now extrapolated until $h' = h_c$ where the extrapolated Plateau border and film meet, we find for the force balance at the contact line:

$$[2\sigma_0 r_c \cos \theta - Ph_c r_c] + \int_{r_c}^R \left[\frac{2\sigma_0}{\cos \Phi'} - Ph' \right] dr - \int_0^R \left[\frac{2\sigma(h)}{\cos \Phi} - Ph \right] dr = 0 \quad (23)$$

r_c is the radius of the contact line. Equation (23) can be rewritten as:

$$2\sigma_0 \cos \theta - Ph_c = 2\sigma(h_c) - Ph_c + \frac{1}{r_c} \left\{ \int_0^R \left[\frac{2\sigma(h)}{\cos \Phi} - Ph \right] dr - \int_{r_c}^R \left[\frac{2\sigma_0}{\cos \Phi'} - Ph' \right] dr - [2\sigma(h_c) - Ph_c] r_c \right\} \quad (24)$$

When in eqn. (24) we substitute:

$$\tau = \left\{ \int_0^R \left[\frac{2\sigma(h)}{\cos \Phi} - Ph \right] dr - \int_{r_c}^R \left[\frac{2\sigma_0}{\cos \Phi'} - Ph' \right] dr - [2\sigma(h_c) - Ph_c] r_c \right\} \quad (25)$$

it can be written as:

$$2\sigma_0 \cos \theta - Ph_c = 2\sigma(h_c) - Ph_c + \tau/r_c = 2\sigma_0 + \Delta F(h_c) - Ph_c + \tau/r_c \quad (26)$$

or:

$$2\sigma_0 \cos \theta = 2\sigma_0 + \Delta F(h_c) + \tau/r_c$$

By definition the profile of the simplified model of the sheet is equal to the profile of the extrapolated Plateau border and film in the actual sheet. This implies that in the simplified model there will only be mechanical equilibrium at the line of contact when a line tension τ , as given by eqn. (25), is attributed to it. The force balance at the contact line is then given by eqn. (18). A line tension can be considered a two dimensional analogue of surface tension and the term τ/r_c can be seen as the two dimensional form of Laplace's law:

The physical meaning of line tension τ , as given by eqn. (25), can be seen as follows: the first integral in eqn. (25) is the net tangential force (sum of surface tension and hydrostatic pressure terms) acting perpendicularly on the profile of the actual sheet. The second integral is the net force on the profile of the extrapolated Plateau border, and the last term is the net force on the extrapolated plane parallel film. Therefore τ is the *excess tangential force* acting on the transition region. As this transition region is neglected in the simplified model a line tension τ , numerically equal to this excess force, must be attributed to the line of contact in this model.

In the limiting case where $r_c \rightarrow \infty$ (straight contact line) eqn. (25) becomes:

$$\tau = \int_0^\infty \left[\frac{2\sigma(h)}{\cos \Phi} - Ph \right] dx - \int_0^{x_c} \left[\frac{2\sigma_0}{\cos \Phi'} - Ph' \right] dx - \int_{x_c}^\infty [2\sigma(h_c) - Ph_c] dx \quad (27)$$

It will be clear that only the transition region will contribute to τ . When the contact line is straight, the line tension does not appear in the force balance eqn. (13) as the term τ/r_c approaches to zero when $r_c \rightarrow \infty$. In the next paragraph we will show that τ is related to the interaction free energy $\Delta F(h)$ of the long range interaction forces. This means that τ could provide information about these forces if it could be measured.

RELATION BETWEEN LINE TENSION τ AND $\Delta F(h)$

To avoid complicating the derivation unnecessarily, we shall consider only the case where $r_c \gg \Delta$. Now we can use eqn. (27) as a good approximation of τ . From eqns. (10) and (11) it follows that: $Ph = 2\sigma(h) \cos \Phi - 2\sigma(h_c) + Ph_c$ and $Ph' = 2\sigma_0 \cos \Phi' - 2\sigma(h_c) + Ph_c$.

When we substitute this into eqn. (27) we find:

$$\tau = \int_0^\infty \left[\frac{2\sigma(h)}{\cos \Phi} - 2\sigma(h) \cos \Phi \right] dx - \int_0^{x_c} \left[\frac{2\sigma_0}{\cos \Phi'} - 2\sigma_0 \cos \Phi' \right] dx$$

Changing variables by substitution of: $-dx = \frac{1}{2} \cot \Phi dh = \frac{1}{2} \cot \Phi' dh'$ gives:

$$\tau = - \left\{ \int_{h_c}^\infty \sigma(h) \sin \Phi dh - \int_{h_c}^\infty \sigma_0 \sin \Phi' dh' \right\} \quad (28)$$

At this point we can already see that in our system the line tension is negative: In eqn. (28) both $\sin \Phi$ and $\sin \Phi'$ are negative and for every value of the sheet thickness the absolute value of $\sin \Phi$ is smaller than the absolute value of $\sin \Phi'$ (see Fig. 5A). Consequently both integrals in eqn. (28) are negative and the absolute value of the first integral is smaller than that of the second one. Therefore the line tension is negative. Free interaction energy $\Delta F(h)$ can now be introduced as follows: from eqns. (10), (11) and (7) we can derive for $\Delta F(h) \ll \sigma_0$:

$$-\sigma(h) \sin \Phi = \frac{1}{2} \{ [2\sigma(h)]^2 - [2\sigma(h_c) + P(h - h_c)]^2 \}^{\frac{1}{2}} \simeq \sigma_0^{\frac{1}{2}} \{ [\Delta F(h) - \Delta F(h_c) - P(h - h_c)] \}^{\frac{1}{2}}$$

$$-\sigma_0 \sin \Phi' = \frac{1}{2} \{ (2\sigma_0)^2 - [2\sigma(h_c) + (h' - h_c)P]^2 \}^{\frac{1}{2}} \simeq \sigma_0^{\frac{1}{2}} \{ -\Delta F(h_c) - (h' - h_c)P \}^{\frac{1}{2}}$$

When we substitute this into eqn. (28) we find:

$$\tau = \sigma_0^{\frac{1}{2}} \left\{ \int_{h_c}^{\infty} [\Delta F(h) - \Delta F(h_c) - (h - h_c)P]^{\frac{1}{2}} dh - \int_{h_c}^{\infty} [-\Delta F(h_c) - (h' - h_c)P]^{\frac{1}{2}} dh' \right\} \quad (29)$$

When contact angle θ is not too small we can neglect the hydrostatic pressure terms and a good approximation will be:

$$\tau = \sigma_0^{\frac{1}{2}} \int_{h_c}^{\infty} \{ [\Delta F(h) - \Delta F(h_c)]^{\frac{1}{2}} - [-\Delta F(h_c)]^{\frac{1}{2}} \} dh \quad (30)$$

Equations (29) and (30) show that there is a rather simple relation between line tension τ and interaction free energy $\Delta F(h)$. This means that in principle line tension τ could give information about $\Delta F(h)$ if it could be measured. It is important to know the order of magnitude of τ because this will tell us whether we may expect τ to be measurable or not.

In the following paragraph we shall calculate the value of τ for the sheets mentioned before.

CALCULATIONS OF LINE TENSIONS

The value of τ was calculated for the case of a straight contact line. We used eqn. (28) instead of (27) because in this way the line tension and the profiles of the actual sheet and the idealized model could be calculated at the same time. The results are tabulated in Table 1. We see that τ is negative and that it ranges from -10^{-12} to $-10^{-11} \text{ J m}^{-1}$. The absolute value is therefore close to the value given by Harkins for a liquid lens in air, but the sign is different. The series of sheets 1a–1e shows that τ is not very sensitive to a large variation of electrolyte concentration c . In this series the line tension varies by a factor of 2.5 only, while Δ changes by a factor of 20, and θ by a factor of 50. Therefore τ depends only slightly on the repulsive component F_{el} of the $\Delta F(h)$ -function. This in contrast to Δ which depends heavily on F_{el} .

Series 2a–2c shows that τ is much more sensitive to the attractive component F_w . Here the line tension changes by a factor of 8 while θ also changes by a factor of 8. From these results we can conclude that the line tension is sensitive to the form of the *tail* of the $\Delta F(h)$ -curve; in our case the London–van der Waals part F_w of $\Delta F(h)$. The line tensions of sheets with the same contact angle but different Hamaker's constant A are approximately proportional to $\sqrt{A}$ (compare sheet 1b with 2a and 1d with 2c). This leads to the interesting conclusion that if both the contact angle and the line tension of one sheet could be found from experiment they would not only give the value of $\Delta F(h_c)$ but would also allow $\Delta F(h_c)$ to be split up into its two components, $F_{el}(h_c)$ and $F_w(h_c)$. Series 3a–3c shows that the influence of hydrostatic pressure p on τ is small.

Qualitatively these results can be deduced from eqns. (29) and (30). These equations show that the value of $\Delta F(h_c)$, and therefore of θ , is not in the first place

decisive for the value of τ , but the range of h for which the two square root terms are different is. This explains the influence of the tail of the $\Delta F(h)$ -curve.

Conclusions about line tensions in other types of liquid films can also be drawn from eqns. (29) and (30). An oil film between two water phases will also have a negative line tension, but its absolute value will be smaller than in a soap film as both the interfacial tension and Hamaker's constant are smaller²³. The absolute value of the line tension of a so-called "second black"- or Perrin-film⁶ will presumably not be larger than the line tension of a "first black" soap film (the sheets given in Table 1 can be seen as models of "first black" soap films), despite the fact that their contact angles may be much larger⁷. This is so because most probably the $\Delta F(h)$ -curve is steeper. This is shown in series 1a-1e of Table 1; sheet 1e with the largest contact angle, which is most similar to a "second black" film, does not have the largest τ of the series.

Depending on the system, a line tension may be positive or negative. The line tension of the contact line between a "second black"- and a "first black" film, which can coexist in one soap film^{6,24} will for instance be *positive*. A rough estimate of this τ is: $\tau = \Delta h \sigma_f$ where Δh is the thickness jump at the transition and σ_f is the surface tension of the films. The exact value of τ can be found from eqns. (25) and (27) using the proper boundary conditions.

Our method can also be used to derive the line tension at a three phase contact line. For a first approximation it is not necessary to know the exact microscopic profile at the contact line. It can be assumed that the microscopic profile is equal to the profile of the extrapolated macroscopic interfaces. In the simplified model the interfacial tensions remain constant up to the contact line, while in the "actual" system the interfacial tensions close to the contact line are affected by molecular interaction forces. Whether τ will be positive or negative depends on whether the interfacial tensions close to the contact line are increased or decreased by the molecular interaction forces. Consequently, the line tension at a very sharp edge of a liquid lens in air (the system considered by Harkins¹⁷) will be *negative* as the London-v.d. Waals forces will *lower* the surface tension of the liquid surface close to the edge. When Harkins states that the line tension is positive because the potential energy of the molecules at the sharp edge is higher than that of the molecules at the liquid surface far from the edge, he is obviously mistaken. Following his line of reasoning the surface tension of a thin liquid film should be higher than the surface tension of the macroscopic bulk liquid, which evidently is not the case.

As the value of τ is small it will be difficult to measure it. In the paper of Torza and Mason²¹ mention is made of measured line tensions of a three phase contact line which were derived from the shape of two different drops in contact with each other in a third phase. For the system silicone oil/water/aniline they give positive values of τ up to 6×10^{-8} N ($= 6 \times 10^{-2}$ dyn) which is rather large. As their method is not very accurate these values are not reliable.

The above eqn. (18) suggests that τ can be found when contact angle θ is measured as a function of film radius r_c . However, for large contact angles the film will become unstable at a critical film radius—the smallest stable radius of the film^{9,11}—which is so large that the influence of τ on θ is still negligible. This will be shown in paper II. Consequently the method can only be used when θ is small, which in practice will be difficult because of the transition region.

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SUMMARY

An analysis is given of the thickness profile of a circular soap film and its Plateau border. It shows that in principle the thickness as a function of the radial distance, $h(r)$, for a single film, can provide details of the interaction free energy $\Delta F(h)$ over a large range of h . The transition region between film and Plateau border where $h(r)$ rapidly changes from microscopic to macroscopic values contains most information. With a simple model of $\Delta F(h)$, the profile and extension of the transition region is calculated for some "first black" soap films.

It is shown that to complete the macroscopic description of a liquid sheet, a line tension must be introduced. A theoretical expression for this line tension is given and its physical meaning is discussed. Some values are calculated using the same $\Delta F(h)$ as before.

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