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Thermodynamics of thin liquid films

II. Film thickness and its relation to the surface tension and the contact angle

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With 4 figures

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The problem of the thermodynamic definition of the film thickness and its influence on the other thermodynamic quantities is one of the most difficult and obscure. As far as we know, *Rusanov* (2) is the only one who has analysed some aspects of this problem. He has obtained an equation analogous to our eq. [II.8], and on that ground he has concluded that the film surface tension σ^f (1) is a linear function of the thermodynamic thickness b .

The soap films represent a three-layer system (fig. 1) – a liquid core and two surfactant monolayers where the surfactant molecules are perpendicular to the film surface (3). The distance between the two surfaces, separating the surfactant molecules from the gas phase, is relatively well defined. We shall call it real thickness b_r . The real thickness b_r , which depends on the physical state of the system, should not be confounded with the thermodynamic thickness b which is to some extent arbitrary and can have different values for a given physical state. By analogy with the usual way of defining *Gibbs' dividing surface*, the thermodynamic thickness b can be defined by

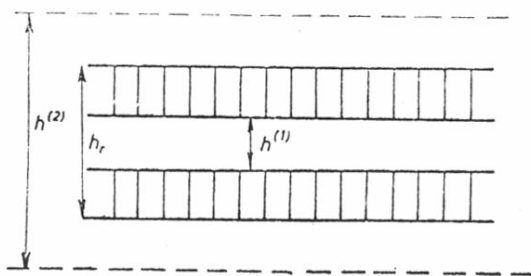


Fig. 1. Three-layer model of a soap film

ascribing a suitable chosen value to a given thermodynamic quantity (depending on b), e.g. $\Gamma_1 = 0$ or $\sum \Gamma_i = 0$ or $\sum \mu_i \Gamma_i = 0$ etc., where Γ_i is the *Gibbs' excess* in the film for the i -th component (Γ_i is defined by eq. [II.22] below) and μ_i is the respective chemical potential. Thus the thickness b will obviously depend on the manner it has been defined. We shall prove later on that the definitions $\Gamma_1 = 0$ and $\Gamma_2 = 0$ (1 – solvent, 2 – surfactant) correspond respectively to thickness $b^{(1)}$, approximately equal to the thickness of the liquid core and $b^{(2)}$, which is larger than b_r (see fig. 1). It must be emphasized, however, that once b is chosen, the change of the physical state of the system will lead to a corresponding change of the thickness b .

We shall assume now that the change of b at a constant physical state¹⁾ occurs continuously and we shall investigate the ensuing alterations of the values of the thermodynamic quantities. The corresponding derivatives which do not describe any physical process are denoted by an asterisk.

Let us consider as in ref. (1) a liquid film (f) at equilibrium with a gas phase (g) and a meniscus (l). In fig. 2 a part of the film (of area A) and the gas phase enclosed in a box of volume V are shown. The dotted lines denote the approximate positions of the transition regions between the film and the gas phase (the distance between them equals the real thickness b_r) and the full lines represent the *Gibbs' dividing*

¹⁾ This change corresponds to different ways of choosing b .

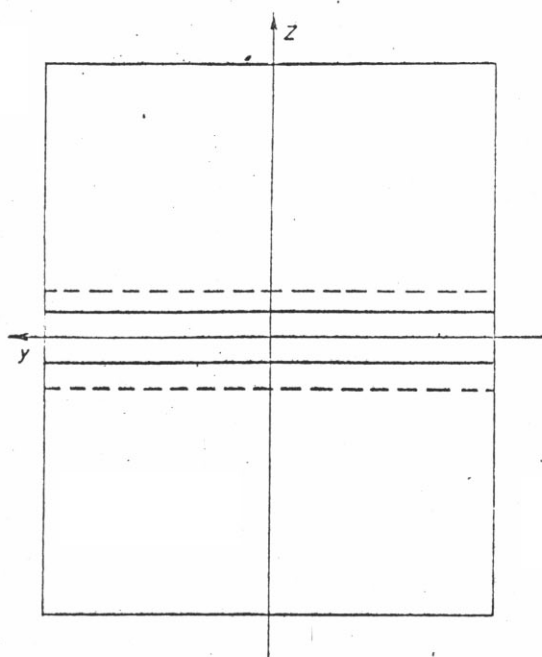


Fig. 2. Thin film and a part of the gas phase enclosed in a box of volume V

surfaces (the distance between them is the thermodynamic thickness b). It is shown in ref. (1), that the excess of any extensive thermodynamical property E is

$$\begin{aligned} \tilde{E} &= E - E^g - E^l = E - e^g V \\ &- (e^l - e^g)Ab. \end{aligned} \quad [\text{II.1}]$$

(e is the quantity of E per unit volume). The film tension Δ is defined (1,2) by the expression

$$\Delta = \int_{-h/2}^{h/2} (P_N - P_T) dz, \quad [\text{II.2}]$$

where P_N and P_T are respectively the normal and the tangential components of the pressure tensor (the co-ordinate system is shown in fig. 2).

We shall prove now that despite the apparent relation between Δ and b (see eq. [II.2]) these quantities are independent. Let us take the variation with respect to b of the Gibbs-Duhem's equation for the film (see ref. (1), eq. [I.24]):

$$\begin{aligned} \delta(d\Delta) &= \left[- \left(\frac{\partial \bar{s}}{\partial b} \right)^* dT + d\Pi \right. \\ &\quad \left. - \sum \left(\frac{\partial \Gamma_i}{\partial b} \right)^* d\mu_i \right] \delta b, \end{aligned} \quad [\text{II.3}]$$

where T denotes temperature, $\Pi = P^g - P^l = P^f - P^l$ - disjoining pressure (1) (P is pressure) and \bar{s} - the specific excess entropy defined by eq. [II.29]. On the other hand, from the definition of Π and Gibbs-Duhem's equations for the gas and for the liquid phase we have

$$\begin{aligned} d\Pi &= dP^g = dP^f - dP^l \\ &= (s^g - s^l)dT + \sum (n_i^g - n_i^l)d\mu_i, \end{aligned} \quad [\text{II.4}]$$

where P^g is capillary pressure and s and n_i respectively the entropy and the number of moles of the i -th component per unit volume. Substituting in [II.3] this expression for $d\Pi$ and the values of $\left(\frac{\partial \bar{s}}{\partial b} \right)^*$ and $\left(\frac{\partial \Gamma_i}{\partial b} \right)^*$, calculated from (II.1), we obtain $\delta(d\Delta) = 0$, i.e. Δ does not depend on b indeed.

In order to ensure the independence of Δ on b proved above, the limits of the integral in [II.2] must be taken in the homogeneous gas phase where $P_N = P_T$. This means that b must be greater than b_r . Since, however, some ways of choosing b correspond to b smaller than b_r (see further on), it is convenient to put (as in ref. (4)) the limits of integration in [II.2] equal to $\pm \infty$.

Thus we obtain

$$\Delta = \int_{-\infty}^{\infty} (P_N - P_T) dz, \quad [\text{II.5}]$$

which is similar to the known hydrostatic definition of the surface tension σ^l (5).

Bearing in mind that Δ is a constant (with respect to b) we can regard the equation

$$\Delta = 2\sigma^f + \Pi b, \quad [\text{II.6}]$$

obtained in ref. (1) (eq. [I.36]) as a relation describing the dependence of the film surface tension σ^f on b . This function is shown in fig. 3. The lines 1, 2 and 3 correspond to three different physical states of the system with disjoining pressure respectively $\Pi_1 > \Pi_2 > \Pi_3 = 0$. In the limiting case $\Pi_3 = 0$ ($b_r = \infty$) $\frac{\Delta}{2}$ and σ^f coincide for any choice of b and both are equal to σ^l . At $b = 0$ [II.6] yields

$$\Delta = 2\sigma_0^f, \quad [\text{II.7}]$$

where $\sigma_0^f = \sigma^f(b = 0)$.

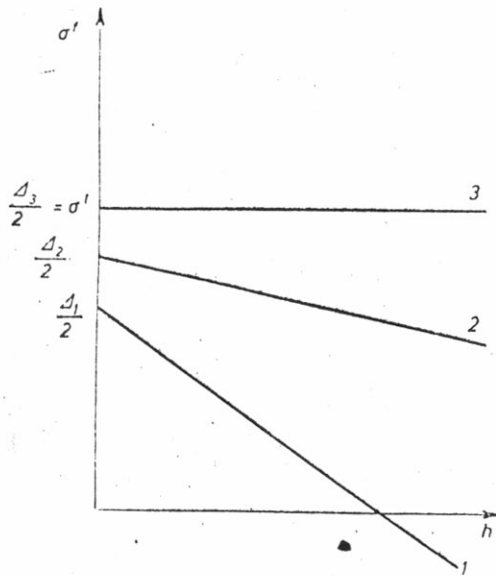


Fig. 3. Dependence of the film surface tension σ' on the thickness b for three values of the disjoining pressure ($\Pi_1 > \Pi_2 > \Pi_3 = 0$)

The differentiation of [II.6] with respect to b (Π is a function of the physical state of the system) yields

$$\left(\frac{\partial \Delta}{\partial b}\right)^* = 2 \left(\frac{\partial \sigma'}{\partial b}\right)^* + \Pi = 0.$$

Hence

$$2 \left(\frac{\partial \sigma'}{\partial b}\right)^* = -\Pi \quad [\text{II.8}]$$

The latter equation is analogous to eq. [XIII.27] of Rusanov (2).

The above considerations allow a more definite interpretation of the contact angle measurements. The condition for the contact angle θ , obtained in ref. (1), eq. [I.43], can be written in the form

$$\cos \theta = \frac{\Delta}{2\sigma'} - \frac{\Pi}{2\sigma'} b \quad [\text{II.9}]$$

This equation means that beside on the physical state of the system, θ depends on the location (to some extent arbitrary) of the dividing surfaces as well. The contact angle θ_0 , corresponding to $b = 0$, however, is a measure for Δ and is, therefore, a thermodynamic characteristic of the system. Indeed, with $b = 0$ eqs. [II.9] and [II.7] yields

$$\Delta = 2 \sigma' \cos \theta_0 \quad [\text{II.10}]$$

$$\sigma'_0 = \sigma' \cos \theta_0 \quad [\text{II.11}]$$

From [II.9] and [II.10] the relation between the values of θ and θ_0 is readily obtained:

$$\frac{\cos \theta}{\cos \theta_0} = 1 - \frac{\Pi}{\Delta} b \quad [\text{II.12}]$$

Let us apply the above results to the topographical method of Scheludko et al. (6) for measurement of contact angles. The profile of the meniscus surface in proximity to the film perimeter is approximately parabolic (6, 7)²⁾:

$$\begin{aligned} \text{a) } z &= ay^2 - c \\ \text{b) } z' &= 2ay \end{aligned} \quad [\text{II.13}]$$

(a and c are constants) (fig. 4). Putting here $z = 0$ and $y = r_0$ we obtain

$$r_0 = \sqrt{\frac{c}{a}} \quad [\text{II.14}]$$

$$\text{tg } \theta_0 = 2\sqrt{ac} \quad [\text{II.15}]$$

²⁾ Unlike refs. (6, 7) we have chosen the parabola to be symmetrical with respect to the z -axis.

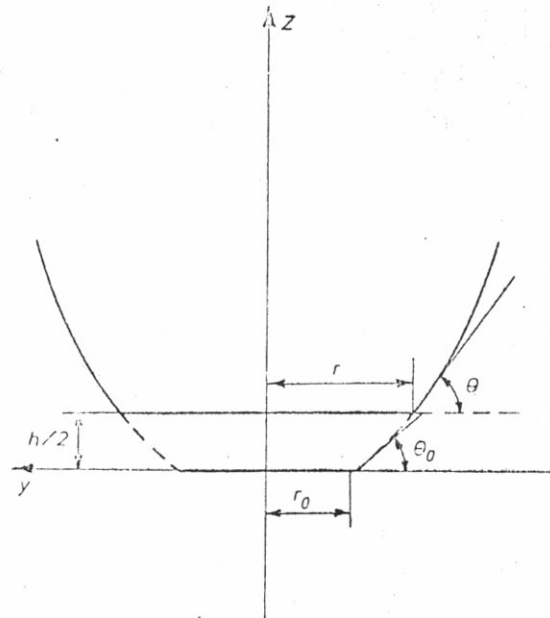


Fig. 4. The upper half of the system meniscus-film. θ and θ_0 are the contact angles corresponding to the thermodynamic thickness b and zero respectively

Thus if we chose $b = 0$ a and c are simply related to the contact angle θ_0 and the radius r_0 of the film. If $b > 0$ the contact angle θ is calculated from the equation

$$tg\theta = 2ar, \quad [\text{II.16}]$$

where r is determined from [II.13a] with $z = \frac{b}{2}$. Thus for small contact angles we obtain

$$\cos\theta \approx 1 - \frac{\theta^2}{2} \approx 1 - 2ac - ab \quad [\text{II.17}]$$

The comparison of [II.9] and [II.17] gives

$$\begin{aligned} \text{a) } \frac{\Delta}{2\sigma^l} &= 1 - 2ac \\ \text{b) } \frac{\Pi}{2\sigma^l} &= a \end{aligned} \quad [\text{II.18}]$$

From eq. [II.18] we see, therefore, that the topographical method allows the measurement not only of the contact angle but of Δ and the capillary pressure P_σ as well (we remind that $\Pi = P_\sigma$). The contact angle φ between the meniscus and the wall of the tube, in which it is formed, can also be determined by means of the formula (8)

$$\frac{P_\sigma}{\sigma^l} = \frac{2(R\cos\varphi - r_0\sin\theta_0)}{R^2 - r_0^2} \quad [\text{II.19}]$$

We shall note that the film radius r (and its area A) also depends on b (put $z = \frac{b}{2}$ and $y = r$ in [II.13a]). If the dependence were strong, it would lead to enormous difficulties in the thermodynamics of the thin films. Fortunately, this effect can be disregarded at least for the films usually investigated. Indeed, from [II.13a] with $z = \frac{b}{2}$ and $y = r$ we have

$$\left(\frac{\partial r}{\partial b}\right)^* = \frac{1}{4ar} \quad [\text{II.20}]$$

and

$$\frac{dA}{A} = \frac{\pi b\sigma^l}{AP_\sigma} \frac{db}{b} \quad [\text{II.21}]$$

(when deriving [II.21], eq. [II.18b] has been used). Taking for microscopic films the

typical values $b = 10^{-6}$ cm, $\sigma^l = 50$ dyne/cm, $P_\sigma = 10^3$ dyne/cm², $A = 10^{-4}$ cm², we obtain $1,5 \cdot 10^{-3}$ for the coefficient before $\frac{db}{b}$.

Hence the relative change of A is very small. This effect will be even smaller for macroscopic films.

The simplest way to define the thickness b is to set one of the Gibbs' excesses Γ_i (e.g. Γ_1) equal to zero. The excess Γ_i is defined (1) by the equation (see eq. [II.1])

$$\Gamma_i = \frac{\tilde{N}_i}{A} = \frac{N_i - n_i^q V}{A} - \Delta n_i b, \quad [\text{II.22}]$$

where N_i is the total amount of the i -th component in the system, shown in fig. 2, and

$$\Delta n_i = n_i^l - n_i^q \quad [\text{II.23}]$$

From [II.22] with $\Gamma_1 = 0$ we obtain³⁾

$$b = \frac{N_1 - n_1^q V}{A \Delta n_1} \quad [\text{II.24}]$$

This choice of b implies that in all equations in § 2 of ref. (1), valid for a k -component system, the terms, containing Γ_1 or \tilde{N}_1 , are zero. For example, eqs. [I.16], [I.22], [I.24] and [I.33] now read

$$dF^l = -SdT - \Pi dV^l + \Delta dA + \sum_{i=2}^k \mu_i d\tilde{N}_i \quad [\text{II.25}]$$

$$df^l = -sdT - \Pi db + \sum_{i=2}^k \mu_i d\Gamma_i \quad [\text{II.26}]$$

$$dA = -sdT + bd\Pi - \sum_{i=2}^k \Gamma_i d\mu_i \quad [\text{II.27}]$$

$$2d\sigma^l = -sdT - \Pi db - \sum_{i=2}^k \Gamma_i d\mu_i, \quad [\text{II.28}]$$

where (see [II.1], [II.22] and [II.24])

$$\begin{aligned} S &= A\bar{s} = S - s^q V \\ &- \frac{\Delta s}{\Delta n_1} (N_1 - n_1^q V); \quad \Delta s = s^l - s^q \end{aligned} \quad [\text{II.29}]$$

$$\begin{aligned} \tilde{N}_i &= A\Gamma_i = N_i - n_i^q V \\ &- \frac{\Delta n_i}{\Delta n_1} (N_1 - n_1^q V) \end{aligned} \quad [\text{II.30}]$$

³⁾ Component 1 can be any component in the system.

In the above equations \bar{F} , f ($=\frac{\bar{F}}{A}$) and \bar{N}_i are the excess functions; respectively for the free energy, the specific free energy and the number of moles of the i -th component (see [II.1], too ref. (1)). From [II.27] we obtain *Frumkin's* equation (9)

$$\left(\frac{\partial \Delta}{\partial \Pi}\right)_{T, \mu_2, \dots} = b \quad (1) \quad \text{[II.31]}$$

Derjaguin et al. (10) have used only one dividing surface. We shall show now that their approach is equivalent to ours and that their basic equations follow from our equations if b is put equal to zero and the summation on i is carried out from 1 to k . We shall do it only for *Gibbs-Duhem's* equation. Putting $b = 0$ in [II.27], we obtain

$$d\Delta = -\bar{s}^0 dT - \sum_{i=1}^k \Gamma_i^0 d\mu_i, \quad \text{[II.32]}$$

where (put $b = 0$ in [II.29] and [II.30])

$$\bar{s}^0 = \frac{S - s^0 V}{A} \quad \text{[II.33]}$$

and

$$\Gamma_i^0 = \frac{N_i - n_i^0 V}{A} \quad \text{[II.34]}$$

Eq. [II.32] coincides with eq. (8) from ref. (10)⁴. In order to prove the equivalency of [II.32] and [II.27], we shall introduce in [II.32] the disjoining pressure Π , expressing $d\mu_1$ from [II.4]:

$$d\Delta = -\left(\bar{s}^0 - \frac{\Gamma_1^0}{\Delta n_1} \Delta s\right) dT + \frac{\Gamma_1^0}{\Delta n_1} d\Pi - \sum_{i=2}^k \left(\Gamma_i^0 - \Gamma_1^0 \frac{\Delta n_i}{\Delta n_1}\right) d\mu_i \quad \text{[II.35]}$$

Eq. [II.35] together with [II.34] and [II.24] yields

$$\left(\frac{\partial \Delta}{\partial \Pi}\right)_{T, \mu_2, \dots} = \frac{\Gamma_1^0}{\Delta n_1} = \frac{N_1 - n_1^0 V}{A \Delta n_1} = b, \quad \text{[II.36]}$$

⁴ *Derjaguin et al.* (10) have considered the particular case of a three-component system: surfactant, water and gas.

which coincides with [II.31]. It is similarly shown that the coefficients before dT and $d\mu_i$ in [II.35] are identical with \bar{s} and Γ_i as defined by [II.29] and [II.30]. The quantity defined by [II.36] was called in ref. (11) virtual thickness.

We shall prove now that *Rusanov's* theory (2) is valid with $b > b_r$, i.e. in the case where the dividing surfaces (see fig. 2) are situated in the homogeneous gas phase. The value E of a given extensive property for the system, shown in fig. 2, as a whole, can be represented for $b > b_r$ as a sum of its values for the film (E^f) and for the gas phase (E^g):

$$E = E^f + E^g \quad \text{[II.37]}$$

On the other hand we have defined the excess function \bar{E} by eq. [II.1] (see ref. (1)), so that in this case

$$\bar{E} = E^f - E^g \quad \text{[II.38]}$$

From *Gibbs-Duhem's* equation (ref. (1), eq. [I.24]) (multiplied by A) we have

$$A d\Delta = -\bar{S} dT + V d\Pi - \sum \bar{N}_i d\mu_i, \quad \text{[II.39]}$$

where V is the volume of the film. Substituting here \bar{S} and \bar{N}_i from [II.38] and using the *Gibbs-Duhem's* equation for the liquid phase and the definition of Π ($= P^g - P^l$), we get the equation

$$A d\Delta = -\bar{S}^l dT + V dP^g - \sum N_i^l d\mu_i, \quad \text{[II.40]}$$

used by *Rusanov* (2).

In order to visualize the expressions [II.22] (or [II.30]) and [II.24] for Γ_i and b respectively, we consider now the case of a foam film containing three components: solvent-1, surfactant-2 and electrolyte-3. If the solvent is slightly volatile, the concentration of all the three components in the gas phase is negligible. Then the total quantity N_i^l ($i = 1, 2, 3$) of each component in the system, shown in fig. 2, will be equal to its content in the film N_i^f . Putting $n_i^g = 0$ and $N_i = N_i^f$ in [II.22], [II.23] and [II.24] we thus obtain the approximate expressions

$$\begin{aligned} \Gamma_{2,3} &= \frac{N_{2,3}^f}{A} - n_{2,3} b \\ &= \frac{1}{A} \left(N_{2,3}^f - \frac{n_{2,3}^l}{n_1^l} N_1^f \right) \end{aligned} \quad \text{[II.41]}$$

and

$$b^{(1)} = \frac{N_1^f}{An_1^f} \quad [\text{II.42}]$$

Eq. [II.42] shows that b is equal to the thickness of an imaginary layer of area A in the bulk liquid, containing N_1^f solvent molecules. In most cases b approximately equals the thickness of the liquid core (see fig. 1). If, however, the surfactant has a long polyoxyethylene chain (as in (12)) the mean solvent concentration in the second black film can be considerably smaller than n_1^f and hence, b can also be smaller than the thickness of the liquid core. If we define the thickness b through the condition $\Gamma_2 = 0$, instead of [II.42] the equation $b^{(2)} = \frac{N_2^f}{An_2^f}$ is obtained.

Because of the low bulk concentration of the surfactant n_2^f , the thickness in this case will be significantly higher than the real thickness b_r .

Useful relations are obtained by employing Gibbs' adsorption isotherm:

$$d\sigma^l = -\bar{s}^l dT - \sum_{i=2}^k \Gamma_i^l d\mu_i, \quad [\text{II.43}]$$

where \bar{s}^l and Γ_i^l are the respective excess quantities defined for the surface of the bulk liquid. Eqs. [II.27] and [II.43] yield

$$d(\Delta - 2\sigma^l) = -(\bar{s} - 2\bar{s}^l) dT + b d\Pi - \sum_{i=2}^k (\Gamma_i - 2\Gamma_i^l) d\mu_i \quad [\text{II.44}]$$

Similar equation have been used in refs. (13, 14). If we eliminate $d\mu_2$ from eqs. [II.44] and [II.43], we can obtain another equation relating Δ and σ^l :

$$d\left(\Delta - \frac{\Gamma_2}{\Gamma_2^l} \sigma^l\right) = -\left(\bar{s} - \frac{\Gamma_2}{\Gamma_2^l} \bar{s}^l\right) dT + b d\Pi - \sum_{i=3}^k \left(\Gamma_i - \frac{\Gamma_2}{\Gamma_2^l} \Gamma_i^l\right) d\mu_i \quad [\text{II.45}]$$

If component 2 is the surfactant and it is adsorbed to the same extent on the film as well as on the bulk surface (15), $\Gamma_2 = 2\Gamma_2^l$. In this case eq. [II.45] gives

$$d(\Delta - 2\sigma^l) = -(\bar{s} - 2\bar{s}^l) dT + b d\Pi - \sum_{i=3}^k (\Gamma_i - 2\Gamma_i^l) d\mu_i \quad [\text{II.46}]$$

Thus the difference $\Delta - 2\sigma^l$ in this case will be independent of μ_2 . This does not apply, however, to Δ and the contact angle θ .

Frumkin's equation [II.31] is usually employed to relate to the disjoining pressure isotherm $\Pi(b)$ (see e.g. ref. (6)):

$$\Delta = 2\sigma^l + \int_h^\infty \Pi db + \Pi b. \quad [\text{II.47}]$$

In deriving [II.47] the condition $\Pi b \rightarrow 0$ and $\Delta \rightarrow 2\sigma^l$ at $b \rightarrow \infty$ have been used. An analogous expression for σ^f can be obtained by integrating the equation

$$\Pi = -2 \left(\frac{\partial \sigma^f}{\partial b} \right)_{T, \mu_2, \dots}, \quad [\text{II.48}]$$

following from [II.28]. Thus we have

$$\sigma^f = \sigma^l + \frac{1}{2} \int_h^\infty \Pi db \quad [\text{II.49}]$$

The same result follows, of course, from [II.6] and [II.47]. Since according to [II.10], $\Delta \leq 2\sigma^l$ eq. [II.47] requires that the disjoining pressure isotherm $\Pi(b)$ at constant T, μ_2, \dots for any equilibrium film has a negative part, sufficiently great to ensure

$$\Pi b + \int_h^\infty \Pi db < 0 \quad [\text{II.50}]$$

If, however, T, μ_2, \dots are not held constant, the latter condition can be violated, because then Frumkin's equation [II.31] is no longer valid⁵⁾.

An equation similar to [II.31], but valid at constant T, Γ_2, \dots can be obtained on the basis of the equation

$$-\left(\frac{\partial \Pi}{\partial A} \right)_{T, V^f, \bar{N}_2, \dots} = \left(\frac{\partial \Delta}{\partial V^f} \right)_{T, A, \bar{N}_2, \dots} \quad [\text{II.51}]$$

⁵⁾ The inequality [II.50] refers only to the cases where it is possible to define a contact angle θ_0 corresponding to $b=0$. Read and Kitchener (16) have arrived to the condition $\int_h^\infty \Pi db < 0$, which is similar to [II.50].

which immediately follows from [II.25]. The left-hand side of [II.51] is transformed as follows:

$$\begin{aligned} \left(\frac{\partial \Pi}{\partial A} \right)_{T, V, \tilde{N}_2, \dots} &= \frac{\partial(\Pi, V)}{\partial(A, V)} \\ &= \frac{\partial(\Pi, V)}{\partial(\Pi, A)} \frac{\partial(\Pi, A)}{\partial(A, V)} \\ &= - \left(\frac{\partial V}{\partial A} \right)_{T, \Pi, \tilde{N}_2, \dots} \left(\frac{\partial \Pi}{\partial V} \right)_{T, A, \tilde{N}_2, \dots} \end{aligned} \quad \text{[II.52]}$$

where

$$\frac{\partial(u, v)}{\partial(x, y)} = \begin{vmatrix} \frac{\partial u}{\partial x} & \frac{\partial u}{\partial y} \\ \frac{\partial v}{\partial x} & \frac{\partial v}{\partial y} \end{vmatrix}$$

Using $dV = Adh + hdA$ we thus obtain

$$\left(\frac{\partial A}{\partial \Pi} \right)_{T, r_2, \dots} = b + \left(\frac{\partial b}{\partial A} \right)_{T, \Pi, \tilde{N}_2, \dots} \quad \text{[II.53]}$$

The fact that eqs. [II.31] and [II.53] differ, emphasizes the importance of the clear definition of the thermodynamic parameters held constant in the experiment. Therefore it is more convenient to write [as in ref. (2)] the thermodynamic equations in terms of the experimental variables: pressure, concentrations etc. For the thermodynamic approach, used in the present paper, such equations have been derived in ref. (17). They will be used in a subsequent work to analyze some experimental cases.

We are indebted to Prof. A. Scheludko for his constant interest in this work and to Dr. Krugljakov (USSR) for the useful discussion.

Summary

The problem of the definition of the film thickness and its influence on the other thermodynamic quantities is discussed. It is shown that at given physical state of the system, the film thickness can have various values depending on the way it has been defined. A detailed analysis of the contact angle between the film and the meniscus is presented and is shown that the value of this angle depends on the definition of the film thickness. If the thickness is assumed zero, the contact angle proves to be directly related to the film tension. This yields a possibility for the film tension to be measured. Formulae relating the parameters of the generatrix of the meniscus surface and the capillary pressure have been obtained for the topographic method of Scheludko et al.

Zusammenfassung

Das Problem der Definition der Filmdicke und ihr Einfluß auf die anderen thermodynamischen Größen wurde erörtert. Es wurde gezeigt, daß bei einem gegebenen physikalischen Zustand die Filmdicke verschiedene Werte, abhängig von der Art auf der sie definiert worden war, haben kann. Eine ausführliche Analyse des Kontaktwinkels zwischen dem Film und dem Meniskus ist dargelegt. Es wurde gezeigt, daß der Wert des Kontaktwinkels abhängig von der Definition der Filmdicke ist. Wenn die Dicke Null angenommen ist, ist der Kontaktwinkel direkt mit der Filmspannung verbunden. Dies ergibt eine Möglichkeit für das Messen der Filmspannung. Die Gleichungen, die die Parameter der Meniskusoberfläche mit dem Kapillardruck verbinden, wurden abgeleitet für die topografische Methode von Scheludko et al.

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