Department of Physical Chemistry of the University of Sofia, Sofia (Bulgaria)

Thermodynamics of thin liquid films

I. Basic relations and conditions of equilibrium

B. V. Toshev and *I. B. Ivanov*

With 4 figures

The thermodynamic properties of a thin liquid film can be determined by measuring its disjoining pressure and/or surface tension. The surface tension of a polymolecular film, whose thickness is in the range of several hundreds of Ångström, differs very little from the surface tension of the meniscus surrounding the film. Hence for a long time the investigations on thin liquid films have been confined to establishing the dependence of the disjoining pressure on the film thickness (1). Recently, the interest to the so-called "black films" has increased. These films are only several tens of Ångström thick. The experimental measurement of such thicknesses is a difficult task and the very concept of "film thickness" can hardly be defined rigorously. Therefore, new methods of investigation of thin films have been developed (2, 3) which are based on the experimental observation that at equilibrium a contact angle arises between the film and the meniscus. This angle is a measure of the surface tension and, consequently, of the thermodynamic state of the film. In this way a number of investigations on the contact angles of black foams (4) and emulsion (5) films have been carried out.

The interpretation of the experimental data on the basis of the existing theories for the disjoining pressure (6) is only possible if a correct and complete thermodynamic theory of the thin liquid films is available. *Derjaguin* (7), *Frumkin* (8) and *Frenkel* (9) were the first to attack the problem. Recently *Derjaguin et al.* (10, 11, 12, 13) and *Rusanov* (14) have developed two different approaches of the thermodynamic theory of the thin films. Unfortunately, in these theories relatively few attention has been paid to the conditions of mechanical equilibrium between the film and the surrounding phases and to their application to the experimental data. In the literature concerning this subject there are quite a few unaccuracies and contradictions. For instance in most of the published works it is not clearly indicated whether the film tension or the film surface tension participates in the expression of the contact angle (see eq. [I. 43]). Recently we developed (15, 16, 17) a new approach of the thin films thermodynamics by giving greater consideration to the conditions of mechanical equilibrium. The purpose of the present series of papers is to describe briefly the formerly published results together with the recently obtained ones.

The thermodynamic approach we use is similar to the method developed by *Gibbs* (18)[1]. The derived expressions are in most of the cases generalizations of the respective equations in *Gibbs*' thermodynamics of the interfaces. In the present work the conditions of equilibrium between the film and its environment and the basic thermodynamic equations are derived.

1. Disjoining pressure

For the sake of simplicity we shall consider a particular system – a circular foam film, surrounded by a biconcaved meniscus, formed in a cylindrical tube (fig. 1). The results will

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[1]) An analogous method is also employed in (14) and (19).

be obviously valid for other systems, containing horizontal films[2]) as well for example two bubbles or two drops separated by a liquid film. In the case under consideration three phases are in equilibrium – the film, the liquid in the meniscus and the gas phase. These phases are denoted further by superscripts f, l and g respectively. The film is characterized by two geometrical parameters – the area A (or radius r) and the thickness h. The chemical potentials, the pressure and the other intensive parameters depend on the thickness of the film h. Since h can be defined correctly only on the basis of thermodynamic considerations, we postpone the discussion of this question for the next paper of these series (21).

Because of the intermolecular interactions the film is not homogeneous along the z – axis (see fig. 1). The pressure in the film must therefore be a tensor with two components – the normal component P_N and the tangential component P_T. In a system with plane interfaces P_N does not depend on z (14, 22). We shall call it film pressure P^f.

In the well known experiments of *Derjaguin* and *Kussakov* (7) the film is formed between two rigid plates. The fact that in these experiments it was necessary to apply an external force on the plates in order to keep the distance between them constant, means that the pressure in the film was different from the pressure P^l in the bulk liquid. This pressure difference[3])

$$\Pi = P^f - P^l \qquad [I.1]$$

has been called by *Derjaguin* (20) "disjoining pressure".

With a free film (with liquid-gas or liquid-liquid interfaces – see fig. 1), which is in equilibrium with a meniscus, the situation is more complicated since in this case the pressure jump can be localized in principle between either the film and the meniscus or the film and the gas phase (12). It is not difficult to show that the form of the thermodynamic
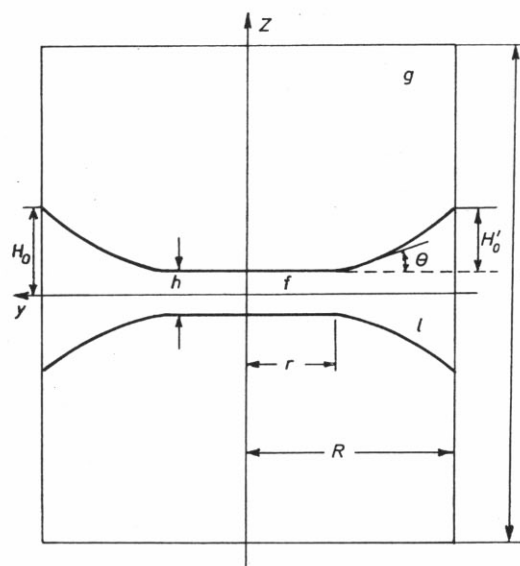

Fig. 1. Thin film formed in a biconcave meniscus

relations (e.g. the tangential condition of mechanical equilibrium – see eq. [I.43]) depends on the localization of the pressure jump. Therefore, this question deserves special attention.

We shall prove now that the disjoining pressure is the equilibrium pressure difference between the film and the meniscus. This result follows directly from the fact mentioned above that the normal component P_N of the pressure tensor does not depend on z and must have the same value in the film and in the gas phase, i.e.

$$P_N = P^f = P^g , \qquad [I.2]$$

P^g being the pressure in the gas phase. On the other hand we have

$$P^g - P^l = P_\sigma , \qquad [I.3]$$

where P_σ is the capillary pressure. From [I.1], [I.2] and [I.3] it follows that at equilibrium between the film and the meniscus exists a pressure jump

$$\Pi = P^f - P^l = P_\sigma \qquad [I.4]$$

It is useful to prove this statement in another way which is less rigorous but more illustrative (we shall not discuss in details the involved approximations). Suppose, the capillary with the film and the meniscus is at height H above

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[2]) The effect of gravity on the thermodynamic behaviour of the thin films is discussed in (19, 20).

[3]) The formulae in the present series of works are numbered with Roman numerals and ciphers. The Roman numeral is a number of the paper and the cipher is a number of the formula in the corresponding paper.
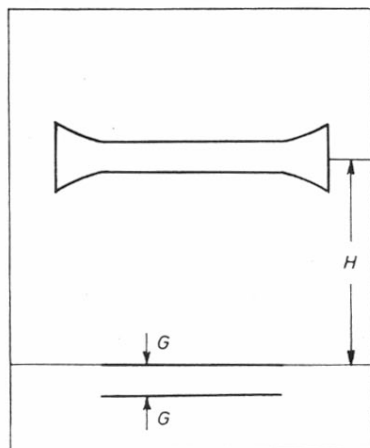
Fig. 2. Sketch of a thin film in equilibrium with a bulk liquid and a reference film

the level of the bulk liquid having the same composition as the liquid in the meniscus (Fig. 2). The height H is chosen in such a way that the vapour pressure at this level is equal to the equilibrium vapour pressure of the meniscus[4]. Let us imagine a reference film (of the same thickness and disjoining pressure as the film in the capillary), situated immediately under the surface of the bulk liquid. The reference film is formed between two rigid weightless plates. An external force G keeps the distance between the plates constant. According to [I.1] the disjoining pressure in the reference film is

$$\Pi = P_0^f - P_0^l = P_0^f - P_0^g \,, \qquad [I.5]$$

where we have used the fact that $P_0^l = P_0^g$ (subscript zero refers to the level $H = 0$). The conditions

a) $P^f = P_0^f - \varrho^l g H$

b) $P^l = P_0^l - \varrho^l g H$

c) $P^g = P_0^g - \varrho g H$ [I.6]

(g is gravity; ϱ^l and ϱ are densities of the liquid and gas phase respectively) must be satisfied in order the whole system to be in equilibrium. From [I.5] and [I.6] we obtain

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4) It is assumed that the gas phase contains only the solvent vapours.

a) $P^f - P^l = P_0^f - P_0^l = \Pi$

b) $P^g - P^l = P_\sigma = (\varrho^l - \varrho)gH$

c) $P^f - P^g = \Pi - P_\sigma$ [I.7]

Eq. [I.7a] show that the pressure jump Π is localized between the film and the meniscus. This means that $P^f = P^g$, so that from [I.7c] we obtain $\Pi = P_\sigma$. Eq. [I.7b] is the well known relation, used in the capillary method for surface tension measurements.

It should be noted that if the meniscus is assumed to be spherical, the pressure jump takes place at the film-gas interface ($\Pi = P^g - P^f$), and the pressure in the film is equal to the pressure in the meniscus, i.e. $P^f = P^l$ (see Appendix). Since this result is in contradiction with the equilibrium conditions [I.7], we must conclude that the meniscus cannot be spherical, which, as a matter of fact, is also proved by the equations for the form of the meniscus and for its capillary pressure [see (3, 23, 24)]. That is why, in some cases, essential errors could be made if the meniscus is regarded as spherical.

We shall express now the disjoining pressure through the difference in the chemical potentials of the solvent in the meniscus and in a film at the same pressure as the meniscus. The expression

$$\mu^f(P^f) = \mu^f(P^l) + \Pi v^l \qquad [I.8]$$

($v^l \approx v^f$ is partial molar volume) is a good approximation for the chemical potential of the solvent. Since at equilibrium

$$\mu^f(P^f) = \mu^l(P^l) \,,$$

from [I.8] we get

$$\Pi = \frac{\mu^l(P^l) - \mu^f(P^l)}{v^l} \qquad [I.9]$$

2. Film tension, film surface tension and basic thermodynamic equations

The work dw done for an infinitely small deformation of a plane-parallel liquid film of area A and volume

$$V^f = Ah \qquad [I.10]$$

can be written as (14)

$$dw = P_N dV^f - \Delta dA \,, \qquad [I.11]$$

where

$$\Delta = \int_{-h/2}^{h/2} (P_N - P_T)dz \qquad [I.12]$$

is the film tension[5]).

The equilibrium between the film, the gas phase and the liquid in the meniscus is determined by the conditions[6])

a) $P^g = P^f$

b) $P^g - P^l = P_\sigma$

c) $P^f - P^l = \Pi = P_\sigma$

d) $T^f = T^g = T^l = T$

e) $\mu_i^f = \mu_i^g = \mu_i^l = \mu_i$, $\qquad [I.14]$

where T denotes temperature and μ_i — the chemical potential of the $i-th$ component.

We shall now define the *Gibbs'* excess functions. Let us imagine the film and a part of the

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[5]) In the next paper (21) it will be shown that the limits of integration in [I.12] have to be expanded to $\pm \infty$:

$$\Delta = \int_{-\infty}^{\infty} (P_N - P_T)dz \qquad [I.13]$$

The last formula has been used in (25).

[6]) Eqs. [I.14a]–[I.14c] were derived above (see eqs. [I.2]–[I.4]). The other conditions are obvious.
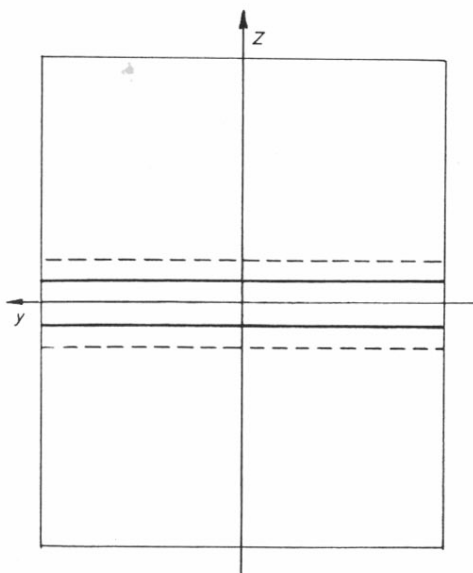
Fig. 3. Thin film and a part of the gas phase enclosed in a box of volume V.

gas phase enclosed in a box of volume V (see fig. 3). The dotted lines denote approximately the positions of the transition regions between the film and the gas phase. This will be our real system under investigation. According to the *Gibbs'* treatment we must construct an idealized system whose phases are homogeneous up to the *dividing* surfaces (shown with full lines in fig. 3) situated at $z = \pm \dfrac{h}{2}$ and have the same properties as the phases in the real system at great distance from the *dividing* surfaces. For the film this phase will be the bulk liquid from which the film has been built up, i. e. the liquid in the meniscus. Let E be the value of a given extensive property in the real system and E^g and E^l — its values for the respective homogeneous phases in the idealized system. In order E to have the same value both in the real and the idealized systems, we must attribute to the *dividing* surfaces an excess $\tilde{E}$ defined as follows:

$$\tilde{E} = E - E^g - E^l = E - e^g V - (e^l - e^g)Ah \qquad [I.15]$$

where e^g and e^l are respective molar values of E. Since $P^g = P^f$ and $V = V^g + V^f$ for the free energy we can then write[7])

$$dF = -Sdt - P^f dV + \Lambda dA + \sum \mu_i dN_i \qquad [I.16]$$

$$dF^l = -S^l dT - P^l dV^f + \sum \mu_i dN_i^l \qquad [I.17]$$

$$dF^g = -S^g dT - P^g dV^g + \sum \mu_i dN_i^g \qquad [I.18]$$

$$d\tilde{F} = -\tilde{S}dT - \Pi dV^f + \Delta dA + \sum \mu_i d\tilde{N}_i , \qquad [I.19]$$

where S is the entropy and N_i — the number of moles of the i-th component. After integration of [I.19] at constant intensive variables (T, Π, Δ and μ_i) we obtain

$$\tilde{F} = -\Pi V^f + \Delta A + \sum \mu_i \tilde{N}_i . \qquad [I.20]$$

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[7]) Depending on the definition of film thickness some terms of the kind $\mu_i d\tilde{N}$ or $\tilde{N}_i d\mu_i$ can vanish from the following equations. Since the question of the choice of the thickness is not considered in this paper [see (21)], we shall omit the summation limits. The subscript $\tilde{N}_i$ will mean that all $\tilde{N}_i$ are kept constant.

By introducing the specific quantities

$$\tilde{f} = \frac{\tilde{F}}{A} \; ; \; \tilde{F}_i = \frac{\tilde{N}_i}{A} \; ; \; \tilde{s} = \frac{\tilde{S}}{A} \qquad [I.21]$$

with [I.19] and [I.20] we get (see also [I.10])

$$d\tilde{f} = -\tilde{s}dT - \Pi dh + \sum \mu_i d\Gamma_i \qquad [I.22]$$

$$\tilde{f} = -\Pi h + \Delta + \sum \mu_i \Gamma_i \qquad [I.23]$$

After differentiating [I.23] and comparing the result to [I.22] we obtain the *Gibbs–Duhem's* equations for the film

$$d\Delta = -\tilde{s}dT + hd\Pi - \sum \Gamma_i d\mu_i \qquad [I.24]$$

By means of the usual thermodynamic transformations we can introduce, if necessary, other thermodynamic functions as well. For the *Gibbs'* free energy, for instance, we have

$$\tilde{G} = \tilde{F} + \Pi V^f - \Delta A = \sum \mu_i \tilde{N}_i \qquad [I.25]$$

and

$$d\tilde{G} = -\tilde{S}dT + V^f d\Pi - Ad\Delta + \sum \mu_i d\tilde{N}_i \qquad [I.26]$$

$$\tilde{g} = \frac{\tilde{G}}{A} = \sum \mu_i \Gamma_i \qquad [I.27]$$

$$d\tilde{g} = -\tilde{s}dT + hd\Pi - d\Delta + \sum \mu_i d\Gamma_i \qquad [I.28]$$

The above obtained equations differ from the respective *Gibbs'* equations by the terms containing the product Πh. Eq. [I.24], in particular, is a generalization of the *Gibbs'* adsorption isotherm. Nevertheless, it should be noted that the film tension Δ in not an exact analogue of the surface tension σ^l of the bulk phase. However we can introduce a new quantity

$$2\sigma^f = \Delta - \Pi h \qquad [I.29]$$

which better corresponds to the surface tension σ^l. Following to *Rusanov* (14) we shall call σ^f film surface tension. By using [I.29] we can write the above equations in terms of σ^f instead of Δ. For instance

$$d\tilde{F} = -\tilde{S}dT - \Pi Adh + 2\sigma^f dA + \sum \mu_i d\tilde{N}_i \qquad [I.30]$$

$$\tilde{F} = 2\sigma^f A + \sum \mu_i \tilde{N}_i \qquad [I.31]$$

$$\tilde{f} = 2\sigma^f + \sum \mu_i \Gamma_i \qquad [I.32]$$

$$2d\sigma^f = -\tilde{s}dT - \Pi dh - \sum \Gamma d\mu_i \qquad [I.33]$$

From eqs. [I.19] and [I.30] follow the thermodynamic definitions of Δ and σ^f

$$\Delta = \left(\frac{\partial \tilde{F}}{\partial A}\right)_{T, V^f, \tilde{N}_i} \qquad [I.34]$$

$$\sigma^f = \frac{1}{2}\left(\frac{\partial \tilde{F}}{\partial A}\right)_{T, h, \tilde{N}_i} \qquad [I.35]$$

From [I.34] and [I.35] follows that the tension Δ is defined at constant V^f, and the surface tension σ^f — at constant h. These expressions show that Δ is the total force (per unit length) acting upon the film perimeter and tending to decrease the film area while σ^f is a purely "surface" force. This is obvious from the following derivation of eq. [I.29] (see fig. 4). The total force Δ, acting upon a unit length of the perimeter of the film consists of the "surface" forces $2\sigma^f$ and the "volume" force $(P^f - P^l)h$. Thus, with [I.14c] we obtain [I.29]

$$\Delta = 2\sigma^f + (P^f - P^l)h = 2\sigma^f + \Pi h \qquad [I.36]$$

Finally we shall derive for σ^f an expression similar to [I.13]. Taking into account the symmetry of the film, by means of [I.13], [I.14c] (with $P^f = P_N$) and [I.29], we obtain

$$\sigma^f = \int_0^\infty (P_N - P_T)dz - \int_0^{h/2} (P_N - P^l)dz$$

$$= \int_0^{h/2} (P^l - P_T)dz + \int_{h/2}^\infty (P_N - P_T)dz \qquad [I.37]$$

If the position of the *dividing* surfaces is chosen in such a way that they lie in the homogeneous gas phase, where $P_N = P_T$, the second integral in [I.37] vanishes and we get a simpler expression for σ^f

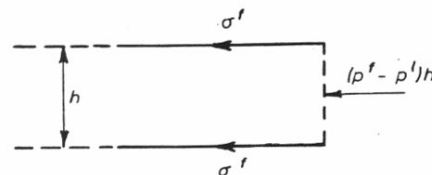$$\sigma^f = \int_0^{h/2} (P^l - P_T)dz \qquad [I.38]$$

Fig. 4. Balance of the forces acting upon the film perimeter

3. Contact angles

Since the thin film is a heterogeneous system whose thermodynamic state depends on two "geometrical" parameters (thickness and area), its mechanical equilibrium must be determined by two conditions — one for the normal component P_N of the pressure tensor and a second one for the tangential component P_T (normal and tangential conditions). The normal condition, is given by eq. [I.14c]. The tangential condition, relates σ^f, σ^l and the contact angle[8] θ. We shall derive this relation from the condition was the total free energy F_t of the system, shown in fig. 1, to be minimum. This system consist of a film, a biconcave meniscus and a gas phase, enclosed in a rigid cylindrical tube of radius R and height L. Omitting the terms of the kind SdT and $\sum \mu_i dN_i$, we can write

$$F_t = -P^f V^f - P^g V^g - P^l V^l$$
$$+ \Delta A + \sigma^l A^l + \sigma_1 A_1 + \sigma_2 A_2 , \qquad [I.39]$$

where A^l is the meniscus area, A_1 and A_2 are respectively the areas of the interfaces solid–liquid and solid–gas, and σ_1 and σ_2 are the corresponding surface tensions. On the basis of geometrical consideration we can write   •

$$A \quad = \pi r^2$$
$$V^f \quad = \pi r^2 h$$
$$V^g \quad = 2\pi \int_{h/2}^{H_0} y^2 dz + \pi (L - 2H_0) R^2$$
$$A^l \quad = 4\pi \int_{h/2}^{H_0} y \sqrt{1 + y'^2} \, dz$$
$$A_1 \quad = 4\pi R H_0$$
$$V^g + V^f + V^l = \text{const}$$
$$A_1 + A_2 = \text{const} , \qquad [I.40]$$

where $y(z)$ is the equation of the generatrix of the meniscus surface. The meaning of H_0 is clear from the figure. With the aid of [I.14a] and [I.14b] we thus obtain

$$F_t = \pi \int_{h/2}^{H_0} (-2P_\sigma y^2 + 4\sigma^l y \sqrt{1 + y'^2}) dz$$
$$+ \pi [2 P_\sigma R^2 H_0 - \Pi r^2 h + r^2 \Delta$$
$$+ 4(\sigma_1 - \sigma_2) R H_0] + \text{const} \qquad [I.41]$$

One of the conditions for extremum of functionals of the kind of eq. [I.41] has the form [see e.g. (24)]:

$$-\mathscr{F}_{y'} + \frac{\partial f_0}{\partial y} = 0 , \text{ at } y=r , \qquad [I.42]$$

where

$$\mathscr{F} = \pi(-P_\sigma y^2 + 4\sigma^l y \sqrt{1 + y'^2})$$

and

$$f_0 = \pi [2 P_\sigma R^2 H_0 - \Pi r^2 h + r^2 \Delta$$
$$+ 4(\sigma_1 - \sigma_2) R H_0] + \text{const}.$$

From [I.41] and [I.42] it is readily obtained

$$\Delta = 2\sigma^l \cos\theta + \Pi h \qquad [I.43]$$

or (see eq. [I.29])

$$\sigma^f = \sigma^l \cos\theta \qquad [I.44]$$

Eq. [I.44] has been used in (26). Eqs. [I.43] and [I.44] are the correct expressions relating the experimentally measured contact angles θ to the thermodynamic functions Δ and σ^f of the film. However, instead of them the equation

$$\Delta = 2\sigma^l \cos\theta \qquad [I.45]$$

is often employed. This equation is only valid for the special case when the film thickness is choused equal to zero [this is shown in the next paper of these series (21)]. It is also obtained in the hypothetical case of spherical bubbles, drops or menisci (see Appendix). It has to be noted that eq. [I.43] is closely related to eqs. [I.14a] and [I.14c]. If these conditions were of the form $P^f = P^l$ and $P^g - P^f = \Pi$, we would obtain [I.45] instead of [I.43].

Eqs. [I.43] and [I.45] differ by the term Πh. In many cases this difference is negligible but sometimes it can be important. For instance, if $\Pi = P_\sigma \simeq 5.10^2$ dyne/cm^2, $h = 2.10^{-6}$ cm, $\sigma^l = 50$ dyne/cm and $\theta \simeq 1°$, $\Pi h = 10^{-3}$ which is comparable to $\sigma^l - \sigma^f = \sigma^l(1 - \cos\theta) \simeq 7.10^{-3}$. The error introduced by neglecting Πh in [I.43] may become substantial when the

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[8]) The contact angle is defined as the angle between the extrapoled meniscus surface and the *Gibbs' dividing* surface of the film (3).

values of Δ are used in differential relations.

Eq. [I.44] allows a simple interpretation — it expressed the balance of the "surface" forces σ^f and σ^l and requires the surface of the film and the meniscus to be immobile. Eq. [I.44] and the condition $\Pi = P_\sigma$ (determining the equilibrium of the liquid in the bulk of the film and in the meniscus) have to be satisfied simultaneously in order the system film-meniscus to be in equilibrium.

We are indebted to Prof. *A. Scheludko* and to Dr. *P. Krugljakov* for valuable discussions.

Appendix

Conditions of mechanical equilibrium in a system with spherical menisci

We consider again the system, shown in fig. 1. For the free energy F_t of this system at equilibrium we can write

$$dF_t = - P^g dV^g - P^l dV^l - P^f dV^f + \Delta dA$$
$$+ \sigma^l dA^l + \sigma_1 dA_1 + \sigma_2 dA_2 = 0 \qquad [\text{I.A.1}]$$

We admit that the two surfaces of the meniscus represent parts of spheres. For the sake of simplicity the contact angle between the meniscus and the wall is assumed zero, so that

$$\sigma_2 - \sigma_1 = \sigma^l \qquad [\text{I.A.2}]$$

By means of simple geometrical considerations, [I.A.2] and the condition $A_1 + A_2 = 2\pi R L$, eq. [I.A.1] can be written as

$$- P^g dV^g - \pi[r^2 P^f + (R^2 - r^2)P^l + 2R\sigma^l]dh +$$
$$+ 2\pi[-rhP^f + r(H_0' + h)P^l + 2r\Delta]dr = 0 \quad [\text{I.A.3}]$$

For the total volume V_t of the system we have

$$dV_t = dV^g + dV^l + dV^f = dV^g$$
$$+ \pi R^2 dh - 2\pi R H_0' dr = 0 \qquad [\text{I.A.4}]$$

By applying to [I.A.3] and [I.A.4] the method of *Lagrange* for the undetermined multipliers and by using the equation $P^g - P^l = \dfrac{2\sigma^l}{R}$, we obtain

$$P^f = P^l \qquad [\text{I.A.5}]$$

and

$$\Delta = 2\sigma^l \frac{H_0'}{R} = 2\sigma^l \cos\theta \qquad [\text{I.A.6}]$$

The same results are obtained for a system containing a film formed by pressing together two *spherical* bubbles.

We see, therefore, that the assumption for the spherical form of the meniscus surface leads to wrong results for the conditions of mechanical equilibrium (compare [I.A.5] and [I.A.6] to [I.14c] and [I.43]). This means that this assumption has to be used with caution in the cases where films are present in the system under consideration.

However the situation is different when the equilibrium between a film and a spherical drop, *formed in it*, is studied[9]. The method, used above, leads in this case to the correct conditions [I.14c] and [I.43].

Summary

The conditions for equilibrium between a thin liquid film and its environment are investigated. It is shown that the pressure in the film and the gas phase are equal while between the film and the meniscus a pressure difference exists – the so-called disjoining pressure. Eq. [I.43] is a tangential condition for equilibrium between the film and the meniscus surface. Using the *Gibbs*' method, a general thermodynamical theory of thin films is derived.

Zusammenfassung

Die Bedingungen für Gleichgewicht zwischen einem dünnen flüssigen Film und seiner Umgebung wurden untersucht. Es wurde gezeigt, daß der Druck in dem Film und in der Gasphase gleich sind, während zwischen dem Film und dem Meniskus ein Druckunterschied besteht – der sogenannte Spaltdruck. Gleichung [I.43] ist die tangentiale Bedingung für Gleichgewicht zwischen dem Film und der Meniskusoberfläche. Mit der Hilfe der Methode von *Gibbs* wurde eine allgemeine thermodynamische Theorie des dünnen flüssigen Filmes aufgebaut.

References

1) *Derjaguin, B. V.* and *E. Obuchov*, Acta physicochim. URSS 5, 1 (1936); *Derjaguin, B. V.* and *S. A. Titijevskaja*, Kolloidn. Zhur. 15, 416 (1953); *Derjaguin, B. V.* and *Z. M. Zorin*, Zhur. Fiz. Khim. 29, 1755 (1955); *Scheludko, A.*, DAN SSSR 123, 1074 (1958); *van den Tempel, M.*, J. Colloid Sci. 13, 125 (1958); *Scheludko, A.* and *D. Exerova*, Kolloid-Z. 165, 148 (1959); Kolloid-Z. 168, 24 (1960); *Scheludko, A.* and *D. Platikanov*, Kolloid-Z. 175, 150 (1961); *Scheludko, A.*, Proc. Koninkl. Ned. Acad. Wet. B65, 76 (1962); *Duyvis, M. E.*, Thesis, Utrecht (1962); *Mysels, K. J.* and *C. M. Cox*, J. Colloid Sci. 17, 136 (1962); *Sonntag, H.*, Z. physik. Chem. 221, 365 (1962); *Zorin, Z. M.*, Kolloidn. Zhur. 25, 624 (1963); *Mysels, K. J.*, J. Phys. Chem. 68, 3441 (1964); *Vrij, A.*, J. Colloid Sci. 19, 1 (1964); *Sonntag, H.* and *H. Klare*, Kolloid-Z. u. Z. Polymere 195, 35 (1964); *Scheludko, A., D. Platikanov* and *E. Manev*, Discuss. Faraday Soc. 40, 253 (1965); *Lyklema, J.* and *K. J. Mysels*, J. Amer. Chem. Soc. 87, 2539 (1965); *Lyklema, J., P. C. Scholten* and *K. J. Mysels*, J. Phys. Chem. 69, 116 (1965).

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[9] Such systems have been investigated by *Haydon* and *Taylor* (2) and *Krugljakov, Rovin* and *Koretsky* (5).

2) *Mysels, K. J., H. F. Huisman* and *R. I. Razouk*, J. Phys. Chem. **70**, 1139 (1966); *Haydon, D. A.* and *J. L. Taylor*, Nature, **227**, 739 (1968); *Princen, H. M.*, J. Phys. Chem. **72**, 3342 (1968); *Prins, A.*, J. Colloid Interface Sci. **29**, 177 (1969); *Clint, J. H., J. S. Clunie, J. F. Goodman* and *J. R. Tate*, Nature, **223**, 291 (1969).

3) *Scheludko, A., B. Radoev* and *T. Kolarov*, Trans. Faraday Soc. **64**, 2213 (1968).

4) *Kolarov, T., A. Scheludko* and *D. Exerova*, Trans. Faraday Soc. **64**, 2864 (1968); Ann. Univ. Sofia, Fac. Chimie **62**, 75 (1967/1968); *Huisman, H. F.* and *K. J. Mysels*, J. Phys. Chem. **73**, 489 (1969); *Mysels, K. J.* and *J. W. Buchanan*, J. Electroanal. Chem. **37**, 23 (1972).

5) *Krugljakov, P. M., Y. G. Rovin* and *A. F. Koretsky*, Izv. Sib. otd. AN SSSR, ser. khim. nauk, No. 2, vyp. 1, 11 (1972); No. 4, vyp. 2, 14 (1972); *Krugljakov, P. M., Y. G. Rovin, I. A. Bagaveev* and *A. F. Koretsky*, Izv. Sib. otd. AN SSSR, ser. khim. nauk, No. 7, vyp. 3, 12 (1972).

6) *Kallman, H.* and *M. Willstaetter*, Naturwiss. **20**, 952 (1932); *de Boer, J. H.*, Trans. Faraday Soc. **32**, 21 (1936); *Hamaker, H. C.*, Physica **4**, 1058 (1937); *Dzyaloshinskii, I. E., E. M. Lifshitz* and *L. P. Pitaevskii*, JETP **37**, 229 (1959); *Derjaguin, B. V.*, Izv. AN SSSR, ser. khim. **5**, 1153 (1937); *Langmuir, I.*, J. Chem. Phys. **6**, 893 (1938); *Bergmann, P., P. Löw—Beer* and *H. Zocher*, Z. physik. Chem. **A181**, 301 (1938); *Derjaguin, B. V.* and *L. D. Landau*, JETP, **11** 802 (1941); *Vervey, E. J. W.* and *J. Th. G. Overbeek*, Theory of the Stability of Hydrophobic Colloid (Amsterdam 1948).

7) *Derjaguin, B. V.* and *M. M. Kussakov*, Izv. AN SSSR, ser. khim. **5**, 741 (1936); 1119 (1937).

8) *Frumkin, A.*, Zhur. Phys. Khim. **12**, 337 (1938).

9) *Frenkel, J.*, Kinetic Theory of Liquids (New York 1955).

10) *Martynov, G. A.* and *B. V. Derjaguin*, Kolloidn. zh. **24**, 480 (1962).

11) *Derjaguin, B. V., G. A. Martynov* and *Yu. V. Gutop*, Kolloidn. zh. **27**, 357 (1965).

12) *Derjaguin, B. V.* and *Yu. V. Gutop*, Kolloidn. Zhur. **27**, 674 (1965).

13) *Derjaguin, B. V.* and *Yu. V. Gutop*, Kolloidn. Zhur. **30**, 19 (1968).

14) *Rusanov, A. I.*, Fazovye ravnovesija i poverkhnostnye javlenija (Leningrad 1967).

15) *Toshev, B. V.* and *I. B. Ivanov*, Ann. Univ. Sofia, Fac. Chimie **66**, 147 (1971/1972).

16) *Toshev, B. V.* and *I. B. Ivanov*, Ann. Univ. Sofia, Fac. Chimie **66**, 157 (1971/1972).

17) *Toshev, B. V.* and *I. B. Ivanov*, Ann. Univ. Sofia, Fac. Chimie **66**, 171 (1971/1972).

18) *Gibbs, J. W.*, Collected Works, Vol. 1 (New York 1928).

19) *de Feijter, J. A., J. B. Rijnbout* and *A. Vrij* (private communication).

20) *Derjaguin, B. V.*, Kolloidn. Zhur. **17**, 207 (1955).

21) *Ivanov, I. B.* and *B. V. Toshev*, Colloid and Polymer Sci. (in press).

22) *Ono, S.* and *S. Kondo*, Molecular Theory of Surface Tension in Liquids (Berlin–Göttingen–Heidelberg 1960).

23) *Exerova, D., I. Ivanov,* and *A. Scheludko*, Ann. Univ. Sofia, Fac. Chimie **56**, 157 (1961/1962).

24) *Toshev, B. V.* and *I. B. Ivanov*, Ann. Univ. Sofia, Fac. Chimie **65**, 329 (1970/1971).

25) *Derjaguin, B. V.* and *Yu. V. Gutop*, DAN SSSR **171**, 652 (1966).

26) *de Feijter, J. A.* and *A. Vrij*, J. Electroanal. Chem. **37**, 9 (1972).

Authors' address:

Dr. *B. V. Toshev* and Dr. *I. B. Ivanov*
Department of Physical Chemistry, Faculty of Chemistry, University of Sofia,
1126 Sofia, 1, Anton Ivanov ave. (Bulgaria)